

Efforts Toward Diindenoarene Radicaloids: A Reach for Mixed Electronic Configurations

and The Properties They Manifest

by

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DISSERTATION ABSTRACT

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Doctor of Philosophy in Chemistry

Title: Efforts Toward Diindenoarene Radicaloids: A Reach for Mixed Electronic Configurations and The Properties They Manifest

Semiconductors are ubiquitous in modern electronic devices, and their market serves an important role in the global economy. Recent advancements have increasingly incorporated organic materials, such as polycyclic conjugated molecules, due to the tunability of their optoelectronic properties. Antiaromatic molecules are a class of organic compounds that inherently have narrow HOMO/LUMO energy gaps, strong low energy absorption and often exhibit ambipolar charge transport behavior. Radicaloids have also garnered attention as promising organic materials because they have those same desirable properties and offer an additional degree of freedom with magnetic susceptibility. This dissertation will highlight key strategies to tune antiaromaticity and diradical character in polycyclic molecules, in addition to discussing refinement of diradicaloid structures and preparation for use in single-molecule junctions. The design of elongated radicaloids and novel photoactive molecules will cap this exposition to inspire continued pursuit of polycyclic conjugated molecules.

Chapter I provides perspective on the research accomplished in the Haley lab towards tuning antiaromaticity via arene annulation onto *s*-indacene and elucidating the electronic parameters dictating the diradical character of indenofluorene analogues. Chapter II explores the differences in molecular properties between alkyne-substituted and alkyne-free diindeno[1,2-*b*;1',2'-*i*]anthracenes. Simplified diindenoanthracene from Chapter II allows for fair comparison between π -expanded indenofluorene derivatives validating the single-molecule conductance

studies detailed in Chapter III. The ideas and synthetic efforts contained in Chapter IV capitalize on indenofluorene design principles to establish a few directions for the development of polyradicaloids and novel molecular motors.

This dissertation includes previously published and unpublished co-authored material.

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Lawson, B.; Vidal Jr., E.; Haley, M. M.; Kamenetska, M. Extreme Anomalous Conductance Enhancement in Neutral Diradical Acene-like Molecular Junctions. *ACS Nano* **2024**, *18*, 29059–29066.

Vidal Jr., E.; Zakharov, L. N.; Gómez-García, C. J.; Haley, M. M. Probing the Influence of Alkyne Substitution on the Electronic and Magnetic Properties of Diindeno[1,2-*b*;1',2'-*i*]anthracenes. *J. Org. Chem.* **2024**, *89*, 14515–14519.

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CHAPTER I

THE INTERPLAY OF ANTIAROMATICITY AND DIRADICAL CHARACTER IN DIARENOINDACENES AND DIINDENOARENES

This chapter includes unpublished and co-authored material intended to be submitted as a Perspective article in *Chemical Science* by Dr. Gabrielle I. Warren, Dr. Joshua E. Barker, Efrain Vidal Jr., and Prof. Michael M. Haley. This manuscript titled The Interplay of Antiaromaticity and Diradical Character in Diarenoindacenes and Diindenoarenes was written by Dr. Gabrielle I. Warren with help from Dr. Joshua E. Barker, Efrain Vidal Jr., and Prof. Michael M. Haley

1.1 Introduction

Aromaticity and antiaromaticity are fundamental concepts in organic chemistry that still sustain considerable discussion and research within the community.¹ The $[4n+2]$ π -electron rule, proposed by Hückel in 1931,² continues to be taught and permits quick identification of aromatic species. Breslow and Dewar later postulated the $[4n]$ π -electron rule for systems which they coined the term “antiaromatic”.³ Antiaromaticity is the “opposite” of aromaticity, in that the ring current (in the presence of a magnetic field) is diatropic (stabilizing) for aromatic molecules and paratropic (destabilizing) for antiaromatic molecules. Antiaromatic molecules are of fundamental interest due to their extremely reactive nature, making them nearly impossible to isolate in their unsubstituted form.⁴ As a result, antiaromatic molecules find pathways to relieve this destabilization. For example, cyclooctatetraene (COT) adopts its well-known, nonplanar tub shape, and cyclobutadiene undergoes rapid dimerization.

Polycyclic antiaromatic hydrocarbons (PAAHs), compounds that contain one or more antiaromatic motifs as part of the overall hydrocarbon backbone, tend to be the black sheep of π -conjugated molecules and materials. Unlike the well-studied polycyclic aromatic hydrocarbons (PAHs) that often feature multiple stabilizing, aromatic $[4n+2]$ π -electron pathways,⁵ inclusion of the antiaromatic $[4n]$ π -electron unit(s) very often results in significant destabilization of the resultant molecule. Nonetheless, interest in PAAHs has seen a strong resurgence over the last 15 years because of the promising optoelectronic properties that are inherent to these compounds, such as small HOMO/LUMO energy gaps, low HOMO and LUMO energy levels, redox amphoterism, and increased conductance; thus, such molecules could potentially find use in device applications such as organic field-effect transistors (OFETs) or organic solar cells (OSCs).⁶

Fortunately, chemists have devised ways to tame highly reactive antiaromatic molecules. For example, when Hafner attempted in the early 1970s to prepare the parent pentalene **1** (Figure 1.1), an 8 π -electron analogue of COT, the molecule rapidly dimerized into **2** even at $-80\text{ }^{\circ}\text{C}$ to alleviate the destabilizing paratropic ring current.⁷ Bally *et al.* showed that this process, which is thought to occur via diradical intermediates and thus indicative of the presence of a low-lying triplet state, is reversible upon photolysis of **2** in an Ar matrix, with the photocleavage occurring in two distinct steps—formation first of a diradical then regeneration of **1**.⁸ To obtain an isolable hydrocarbon, Hafner subsequently installed three *t*-butyl groups onto the pentalene skeleton, e.g., **3**, thus kinetically stabilizing the molecule.⁹ Kinetic stabilization with bulky substituents was a very popular method in the 1970s and 1980s to generate a variety of stable, isolable antiaromatic compounds, including those with cyclobutadiene and indacene cores.⁴

Another widely-used strategy to tame paratropic compounds is to fuse one or more aromatic rings, such as in dibenzopentalene **4**, a PAAH first reported in 1912, as such fusion results in a thermodynamically more stable hydrocarbon.¹⁰ This stabilization comes with a cost, however, as arene fusion weakens the paratropic ring current significantly, which results in an increased HOMO/LUMO energy gap and higher HOMO and LUMO energy levels compared to the parent antiaromatic hydrocarbon. Nonetheless, Kawase and Takimiya showed in 2010 that derivatized dibenzopentalenes could be used as an active layer in OFETs that showed modest hole mobilities ($1.8 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) as well as be the electron-donor layer in OSCs (PCE = 0.94%), clearly demonstrating the materials potential of PAAHs.¹¹ Very recently, a combination of steric blocking and extended conjugation with pendant aryl groups led to the isolation and thorough characterization of the 1,3,4,6-tetraphenyl derivative of **1**.¹²

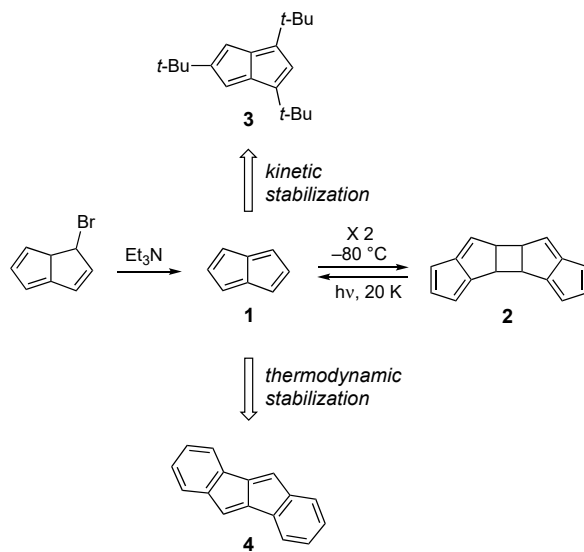


Figure 1.1. Two popular methods to tame antiaromatic molecules.

Properties associated with antiaromaticity drive motivation to study these systems in their own right, but there is a unique relationship between the antiaromatic nature of a molecule and

irregular electronic configurations that bolsters the merit of investigating such species. A recent theoretical survey of antiaromatic $[4n]$ annulenes conducted by Quintero *et al.* examined the role of frontier orbitals in a balancing act of stabilization from disjoint orbital character and inter- vs. intra-orbital electron-electron repulsions that favor unpaired electrons to varying degrees.¹³ For example, computationally forcing COT into a planar conformation permits investigation of this interplay between paired and unpaired configurations. The electronic structure of planar D_{8h} COT featured unpaired spins residing in two degenerate singly occupied molecular orbitals (SOMOs), which was stabilized by the non-bonding and disjoint character of the frontier orbitals. The authors describe D_{8h} COT as having an open-shell (OS) electronic configuration as opposed to one that is closed-shell (CS) based on these results. As this type of electronic stabilization can be extrapolated to other $[4n]$ annulenes and their congeners via perturbation, antiaromatic molecules can be thought of as having some inherent diradical character on account of their frontier orbitals and configurational mixings.¹³

It is crucial to be clear and consistent regarding the description of diradical-like species. We will use the definition found in the IUPAC “Gold Book” for diradicals, which states that diradicals are “Molecular species having two unpaired electrons, in which at least two different electronic states with different multiplicities [electron-paired (singlet state) or electron-unpaired (triplet state)] can be identified”.¹⁴ Pure diradicals are described as molecules in which two electrons occupy two degenerate non-bonding molecular orbitals (e.g., *m*-xylylene/*m*-quinodimethane **5**, Figure 1.2), while the term *diradicaloids* is used to identify diradical-like molecules in which the two molecular orbitals are nearly degenerate (e.g., *p*-xylylene/*p*-quinodimethane **6**). Quantum chemical calculations are indispensable to any study of diradicaloids for determining the effects responsible for changes in diradical character. Standard

diradical calculations involve determination of the diradical index value (y_0), which represents the occupation of the lowest unoccupied natural orbital (LUNO) according to natural orbital occupation number (NOON) analysis. In this scheme, $y_0 = 1$ represents pure OS character while $y_0 = 0$ represents a pure CS system.¹⁵ The magnitude of the value is used as an indicator for the likelihood that a molecule will exhibit diradical-like properties, and compounds with intermediate y_0 values are predicted to be diradicaloids. It is important to note that y_0 value calculations depend heavily on functional selection and as a result they are only reliably compared when the functional and basis set are the same. This theoretical understanding of novel π -systems provides an additional handle for the organic electronic materials as they share similar properties as CS antiaromatics (e.g., narrow HOMO/LUMO energy gaps and amphoteric redox behavior). Such amphoteric redox behavior is exemplified in bisphenalenyl diradicaloids that display both hole and electron mobilities up to $3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹⁶

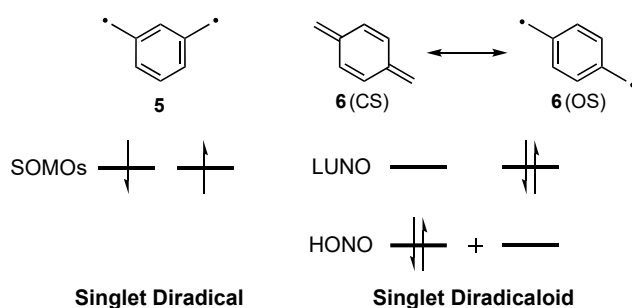


Figure 1.2. Depiction of frontier molecular orbitals for diradical **5** (two degenerate orbitals) and diradicaloid **6** (two nearly degenerate orbitals).

Installing one six-membered ring between the two five-membered rings of pentalene, a process long-ago called “benzinterposition”,¹⁷ affords the tricyclic hydrocarbon known as indacene. Depending upon the symmetric or asymmetric fusion of the five-membered rings on the six-membered ring leads to *s*-indacene **7** and *as*-indacene **8** (Figure 1.3a).^{4,18} As one might

expect, Hafner and co-workers investigated antiaromatic **7** as well, finding that inclusion of four *t*-butyl groups kinetically stabilized¹⁹ the otherwise highly reactive molecule.²⁰ A number of similarly stabilized *s*-indacenes have been disclosed over the subsequent ~40 years.²¹ Very recent work by Tobe and co-workers showed that a series of stable hexaaryl-substituted derivatives of **7** could be readily prepared and their properties modulated by the aryl substituents.²² Interestingly, studies on **8**, or simple derivatives thereof, have not been reported in the literature.

In fall 2009, the Haley group initiated studies into *s*-indacene derivatives. Similar to Kawase and others, we elected to include benzo-fusion to help stabilize the paratropic core. Rather than “dibenzoindacene” or “diindenobenzene”, IUPAC nomenclature calls such structures *indenofluorenes* (IFs), of which there are five possible regioisomers (**9-13**) depending upon whether the structure contains an *s*- or *as*-indacene core, shown in red in Figure 3b. When we started our studies, only two of the five IF isomers had been described: LeBerre reported in 1957 the attempted synthesis of 11,12-diphenyl derivative of **11**, which proved to be extremely unstable.²³ In 1994 the Swager group disclosed the 5,6,11,12-tetraiodo analogue of **10** that also was prone to rapid decomposition.²⁴ Two years later, Scherf and co-workers claimed the synthesis of 6,12-diphenyl analogue of **10** as a model system for an indenofluorene polymer;²⁵ however, there were no experimental or characterization data in the paper aside from an absorption spectrum λ_{max} of 543 nm to corroborate this structure.[§] As of late 2009, there was no definitive evidence of stable, well-characterized indenofluorenes in the literature.

The calculated y_0 values of the IF regioisomers (Figure 1.3b) offer some insight as to why LeBerre and Swager had difficulty with their systems, as all IF isomers are predicted to possess modest (**10**, **11**, **13**) to pronounced (**9**, **12**) diradicaloid character.²⁶ This is especially easy to

understand for molecules **9** and **12**, as in the open shell form there are three aromatic Clar sextets versus only one sextet in the closed shell form (shown in blue in Figure 1.3c), in addition to the

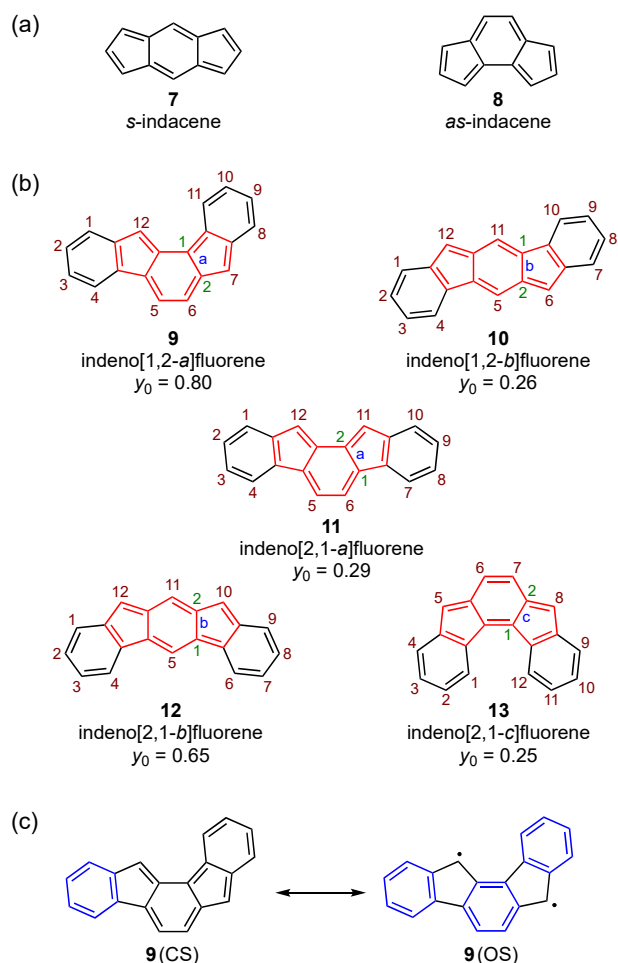


Figure 1.3. Isomeric (a) indacenes **7-8** and (b) indenofluorenes **9-13**; the indacene core is highlighted in red in the latter examples. The computed values of y_0 for the parent hydrocarbons are taken from reference 26. (c) Closed-shell (CS) and open shell (OS) resonance forms of IF **9**.

contribution of **5** in the open-shell form of **9** and **12**. For compounds **10**, **11**, and **13**, the closed shell form possesses two Clar sextets as well as the presence of an *o*- or *p*-quinodimethane core, which results in an appreciable drop in diradical character. Unfortunately, any regain of aromatic stabilization is offset by the introduction of radical reactivity at the apical carbons of the five-

membered rings. These positions too can be kinetically stabilized by the introduction of bulky aryl groups (e.g., mesityl) on the apical carbon atoms. Tobe and co-workers prepared 10,12-dimesitylindeno[2,1-*b*]fluorene in 2013 and confirmed via multiple techniques that the molecule, while possessing a singlet diradicaloid ground state, exhibited significant triplet character at room temperature.²⁷ Haley and co-workers found in 2017 that the 7,12-dimesityl analogue of **9**, predicted to be a ground state triplet, was so reactive that the molecule had to be analyzed as a dilute, degassed solution. While the spectral data implicated formation of the [1,2-*a*]IF, confirmation of its successful synthesis came about with the x-ray crystal structure of the dianion reduction product, confirming the correct skeletal connectivity.²⁶

Until 2024 (*vide infra*), these were the only examples of the [1,2-*a*]IF and [2,1-*b*]IF isomers, so they will not be discussed further. The Tobe and Haley groups reported the syntheses of stable, isolable derivatives of the [2,1-*a*]IF²⁸ and [2,1-*c*]IF²⁹ regioisomers in 2011 and 2013, respectively, of which the spectral (NMR, UV-Vis) and structural (x-ray) data support the dominance of the closed-shell structure. Both isomers have been revisited by the Haley³⁰ and Das³¹ groups in recent years; still, the number of [2,1-*a*] and [2,1-*c*]IFs is rather limited, so these too will not be discussed further. By far, the [1,2-*b*]IF scaffold, and its structurally-related, heterocycle-fused *s*-indacene congeners (*vide infra*), will be the main focus of the antiaromaticity studies described in this article. We refer the reader to several reviews with more information on the other IF regioisomers.^{18,32}

1.1.1 Synthetic strategies

Our studies of PAAHs began in fall 2009 as a rotation project for a first-year graduate student. We repeated the synthesis of the 5,6,11,12-tetraido analogue of **10** via double

transannular cyclization of octadehydrodibenzo[12]annulene;²⁴ however, all attempts at Sonogashira cross-coupling degraded the IF starting material. Rather, we introduced the (triisopropylsilyl)ethynyl (TIPSethynyl) groups as two independent steps. Gratifyingly, this revised strategy worked, leading to the first well-characterized and stable indeno[1,2-*b*]fluorene derivatives (**14**);³³ however, this route suffered from three major pitfalls: (1) the transannular cyclization afforded no more than a hundred milligrams of tetraiodo material per run, and often much less; (2) the yields for preparing the octadehydrodibenzo[12]annulene were also low;²⁴ and (3) the [12]annulene was prone to violent decomposition, as we (re)discovered.³⁴ An improved synthetic route for IF synthesis was developed based on work of Deuschel³⁵ and Wang.³⁶ This modular and scalable strategy has been and continues to be our main method for preparing a wide variety of IFs and related quinoidal analogues from strongly

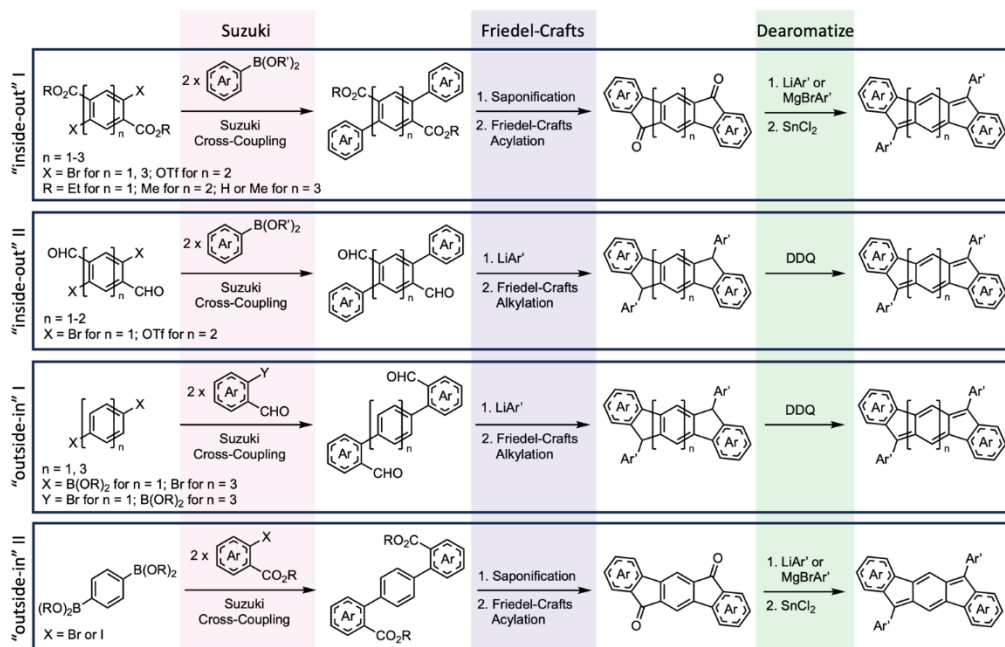


Figure 1.4. General synthetic strategy for the preparation of indenofluorenes and quinoidal analogues.

diradical to strongly antiaromatic and spanning a variety of carbocycle- and heterocycle-fused rings. The variations of the current syntheses, termed “inside-out” and outside-in”, share three key steps: a Suzuki cross-coupling, Friedel-Crafts acylation or alkylation, and finally an oxidative or reductive dearomatization of the central arene. The “inside-out” route starts with the desired core, which possesses two halides (or pseudohalides) and either two esters or two aldehydes. The core is then Suzuki cross-coupled to outer arenes, which are typically functionalized with a boronic acid or boronate ester. If the resultant *para*-substituted core has two ester groups, saponification followed by Friedel-Crafts acylation yields the poorly soluble diketone precursor to the desired IF derivative (route I). Nucleophilic addition of bulky aryl or ethynyl groups, either by lithiate addition or Grignard addition, gives the penultimate diol precursor. Subsequent reductive dearomatization using SnCl_2 yields the desired IF (Figure 1.4, top entry). If the Suzuki cross-coupling furnished a *para*-substituted core with two aldehydes (route II), nucleophilic addition of the bulky aryl groups (by lithiate addition or Grignard addition) followed by Friedel-Crafts alkylation via the resultant secondary alcohol gives the dihydro precursor. Finally, oxidative dearomatization with DDQ yields the desired IF (Figure 1.4, second entry).

The “outside-in” method follows the same steps as the “inside-out” but starts with the functional handles in reversed positions. This method only requires the core to have *para*-substituted boronic esters/acids or while the outer arene cross-coupling partner bears the carbonyl functionality. After the Suzuki cross-coupling, the two “outside-in” routes parallel the “inside-out” methods – nucleophilic addition of bulky aryl groups, Friedel-Crafts alkylation, and oxidative dearomatization with DDQ (Figure 1.4, third entry) or Friedel-Crafts acylation, nucleophilic addition of the aryl groups, and reductive dearomatization using SnCl_2 (Figure 1.4,

last entry). While the “outside-in” route does lead predominantly to the formation of the [1,2-*b*]IF core, the Friedel-Crafts reaction can “close” the wrong way to produce a very small amount of the [2,1-*a*]IF isomer.^{30b} Given the proper functionalization on the core and corresponding coupling partners, these two general methods provide ready access to a wide range of indenofluorene and related quinoidal topologies, allowing us to explore both core π -extension and outer arene modification.

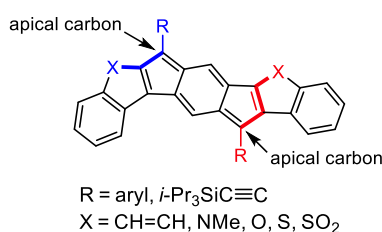


Figure 1.5. Generic carbocycle- or heterocycle-fused *s*-indacene with labelled apical carbons; *syn*-fusion is highlighted in blue and *anti*-fusion is highlighted in red.

As the new synthetic strategies were employed for increasingly complex systems, new naming practices became important to adopt. When fusing a simple benzene to *s*-indacene (as in the parent IFs), there are only two possible isomers (e.g., [1,2-*b*]IF vs. [2,1-*b*]IF). Extending the parent [1,2-*b*]IF by one benzene on each side introduces three possible isomers, which were named *linear*-, *syn*-, and *anti*-, according to the direction of the angular naphthalene fusion.³⁷ In the case of fusing heterocycles to an *s*-indacene core, there are two symmetric orientations possible. In one case, the heteroatom is on the same side as the apical carbon of the 5-membered core ring (*syn*-) and the other case the heteroatom is on the opposite side as the apical carbon (*anti*-) (Figure 1.5).³⁸ This naming convention is utilized throughout the remainder of this article.

1.2 Initial studies

Admittedly, when we first started working on the 20 π -electron indenofluorenes, we assumed their high degree of conjugation might mean their electronic properties could be similar to the well-known 22 π -electron pentacenes,³⁹ yet the IFs did not possess the Achilles' heel that leads to acene degradation, namely the reactive *s-cis* diene orientation of the double bonds. In many ways, our naïveté proved to be a blessing in disguise. Aside from this one (wrong) assumption of an indenofluorene/pentacene correlation, the slate was completely blank given the dearth of known indenofluorenes.

After our initial work on **14** showed that the [12]annulene transannular cyclization route was not scalable as well as potentially hazardous,^{33,34} we switched to a variation of “inside-out” route I reported by Wang³⁶ where the central piece was commercially available 2,5-dibromo-*p*-xylene. After the Suzuki cross-coupling, we oxidized the benzylic methyl groups with basic KMnO₄ and then completed IF synthesis as outlined at the top of Figure 4. While this route did provide a small library of stable donor- or acceptor-substituted [1,2-*b*]IFs **15** (Figure 1.6),⁴⁰ it too had drawbacks as some of the R substituents were not tolerant of the harsh KMnO₄ oxidation. In addition, this study illustrated the need to examine the potential targets computationally *before* attempting their syntheses. Had we done so, we would have found that substitution on the 2- and 8-positions is undesirable as these carbons have minimal HOMO/LUMO electron density, relegating any influence to be through weaker inductive effects. Instead, the calculations suggested we should functionalize the 6- and 12-positions, which led to the series of [1,2-*b*]IFs **16**.⁴¹ This proved much more successful, as we could vary the UV-Vis λ_{max} by ~50 nm, whereas for **15** this variation of λ_{max} was a very modest 16 nm. Importantly, this latter study also demonstrated that we could prepare single-crystal OFETs with a [1,2-*b*]IF as the active layer that

showed ambipolar transport, our first demonstration of the materials chemistry potential of the IFs,⁴¹ but more on that below.

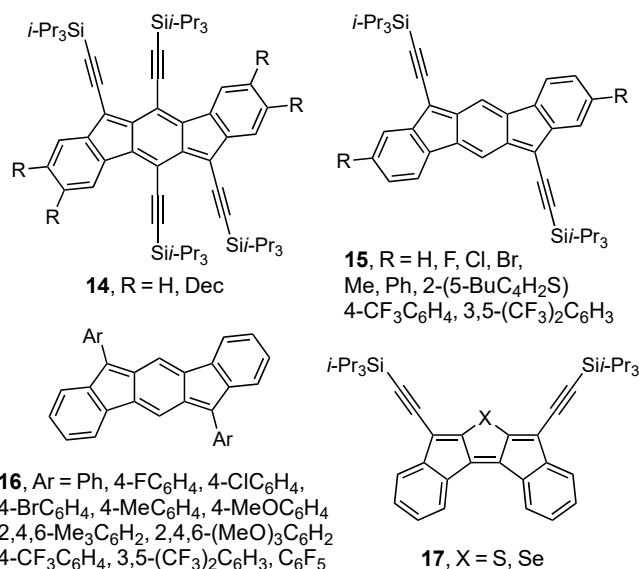


Figure 1.6. Early attempts to alter IF optoelectronic properties.

One other area we examined briefly was to exchange the central benzene ring with either a thiophene or selenophene, leading to [2,1-*c*]IF analogues **17**.⁴² While this structural variation altered the optoelectronic properties by ~25 nm compared to the [2,1-*c*]IF, the λ_{max} were *hypsochromically* shifted much to our surprise. Furthermore, the difference between S and Se was minimal (1 nm), so further efforts on this pathway were abandoned. Rather than inclusion of the heterocycle within the antiaromatic core, we soon discovered that that fusion of heterocycles to the core was the trick to generate highly antiaromatic structures (*vide infra*).

As noted earlier, the indenofluorenes sit at a unique intersection of antiaromaticity and diradical character. Modification of the indenofluorene scaffold has followed two main directions: core π -extension and outer π -extension (Figure 1.7). Consistent with earlier comput-

ational studies on a series of dicyclopenta-fused acenes,⁴³ we will show that expanding the quinoidal indenofluorene core by successive “benzinterposition”¹⁷ from one benzenoid ring ([1,2-*b*]IF **10**) to two or three benzenoid rings (diindenoacenes), while significantly weakening core paratropicity, leads to strong diradical character in the latter systems.⁴⁴ [1,2-*b*]IFs that possess an *s*-indacene core generally do not have strong diradical character; however, they do

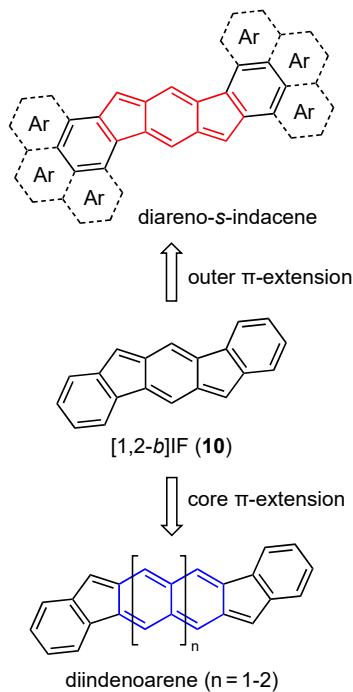


Figure 1.7. Modification of the [1,2-*b*]IF scaffold follows two main lines of investigation—outer π -extension/ alteration with aromatic carbocycles or heterocycles (diareno-*s*-indacenes, top) and core π -extension from benzenoid to naphthoquinoid and anthraquinoid (diindenoacenes, bottom).

maintain a higher degree of antiaromaticity in the core. Concurrent exploration of the antiaromaticity and diradical character of these quinoidal systems has led to modification of the outer π -system to modulate the antiaromaticity within the *s*-indacene motif and thus translation of these findings about the outer arenes to π -expanded cores furnishes systems with tunable diradical character, thus highlighting the antiaromaticity/diradical character interrelationship.¹³ Modifications to rationally alter antiaromaticity will be presented first, followed by methods

used to assess antiaromaticity and other inherent properties of these molecules. The use of different outer arenes to increase diradical character will be discussed next, and finally some device applications that take advantage of the antiaromaticity/diradical interrelationship will be described.

1.3 Tuning the paratropicity strength of the *s*-indacene core by outer arene modification

While antiaromatic *s*-indacene derivatives have a potential role in the future of organic electronics, for this potential to be realized, we needed to better understand how to alter the strength of the antiaromatic *s*-indacene ring current in a rational manner, especially through fusion of different arenes to the outside. Our first test of this hypothesis in 2014 fused thiophene (indacenodithiophene, IDT) and benzothiophene (indacenodibenzothiophene, IDBT) to **7**.³⁸

While the initial idea was more curiosity driven and not motivated originally by increasing the

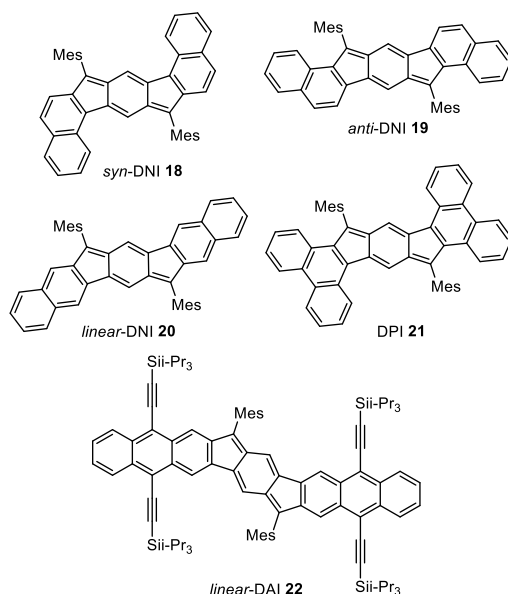


Figure 1.8. Aromatic carbocycle-fused *s*-indacene derivatives—DNIs **18-20**, DPI **21**, and DAI **22**.

antiaromaticity from the parent [1,2-*b*]IF, we found via NICS calculations that these heterocycle-fused systems restored the paratropic ring current of the *s*-indacene motif close to that calculated for the parent hydrocarbon **7**. This initially surprising result suggested that we needed to do a much deeper dive to elucidate the effects of outer arene alteration. Of course, this begs the question—what exactly are we “tuning”? The main effect is varying the HOMO/LUMO energy gap, with a secondary effect of altering the exact HOMO and LUMO energy levels (*vide infra*). Our first intentional foray into tuning the paratropicity of the *s*-indacene core was achieved by creating a series of molecules with fused aromatic carbocycles such as naphthalene (dinaphthoindacenes (DNI) **18-20**, Figure 1.8), phenanthrene (diphenanthroindacene (DPI) **21**), and anthracene (dianthracenoindacene (DAI) **22**).^{37,45} While **18**, **19**, and **21** showed core paratropcities between those of [1,2-*b*]IF and the IDTs/IDBTs, both **20** and **22** indicated weaker core paratropicity than [1,2-*b*]IF.³⁷ From these studies, a simple “bond order” rationalization suggested that greater double bond character of the fused bond (e.g., the bond order of the fused bond in **21** is 1.8) resulted in increased antiaromaticity of the *s*-indacene core, whereas less double bond character of the fused bond (e.g., bond order of fused bond in **22** is 1.2) resulted in decreased antiaromaticity. Interestingly, DAI **22** is the only fluorescent indacene derivative to date.⁴⁵ The linear 2,3-anthracene fusion severely diminished the paratropicity of the core of **22**, resulting in an increase of the $S_0 \rightarrow S_1$ energy gap and thus deactivating the low-barrier conical intersection observed in all other *s*-indacene derivatives.⁴⁶ Nonetheless, this rudimentary “bond order” rationalization only works for hydrocarbon-fused *s*-indacenes. In the realm of heterocycle-fused *s*-indacenes, the heteroatom plays an important role in affecting the antiaromaticity of the core, and this nuance is not captured simply by the bond order of the fused ring.

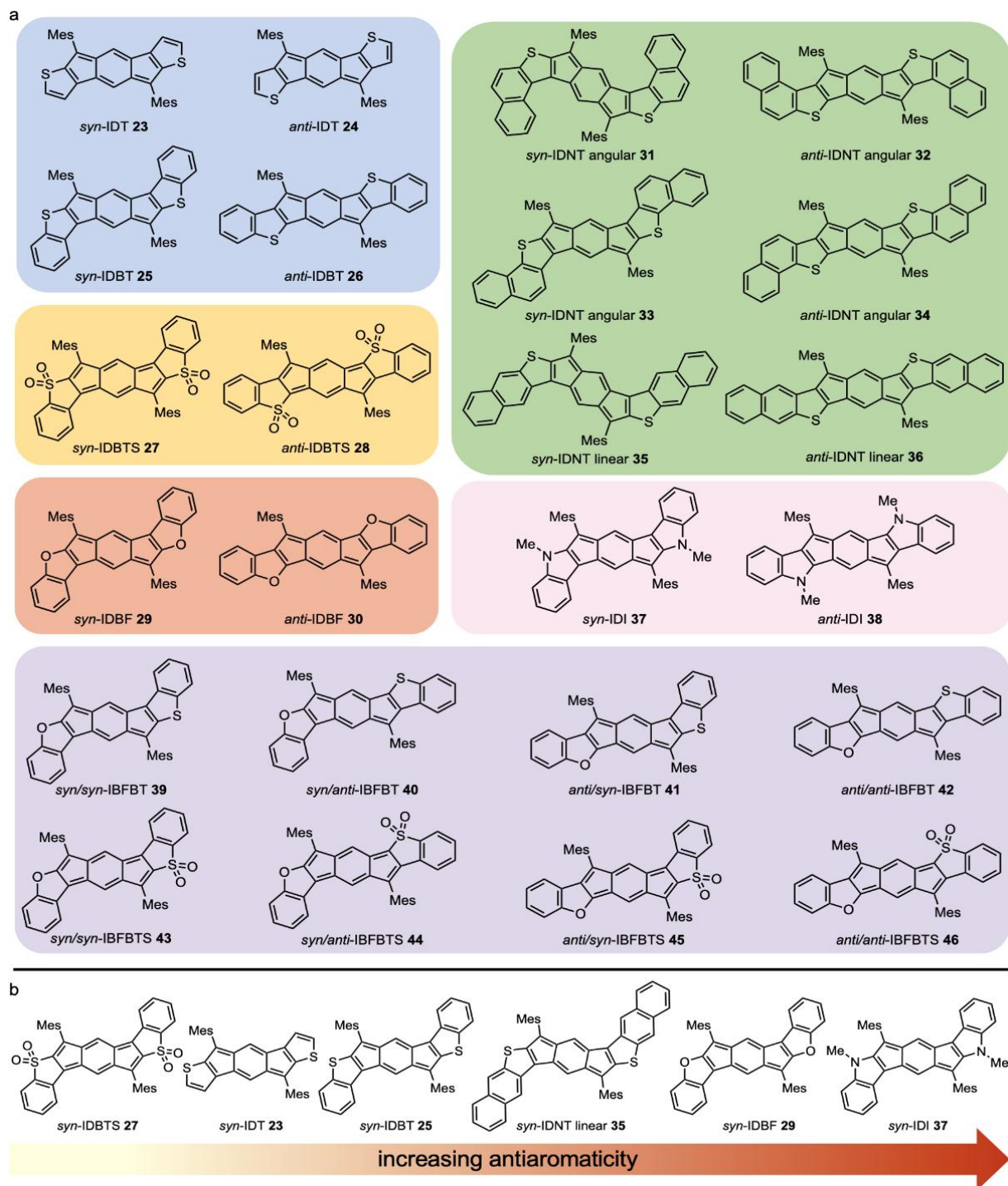


Figure 1.9. (a) Heterocycle-fused *s*-indacene core antiaromatics grouped by family of heterocycle: thiophenes/ benzothiophenes **23-26** (blue), benzothiophene sulfones **27-28** (yellow), benzofurans **29-30** (orange), naphthothiophenes **31-36** (green), indoles **37-38** (pink), and mixed benzofurans/benzothiophenes **39-42** and their corresponding sulfones **43-46** (purple). (b) *syn*-Heterocycle-fused *s*-indacenes in order of increasing antiaromaticity.

After initially fusing thiophene (**23-24**) and benzothiophene (**25-26**) rings to *s*-indacene and observing an increase in antiaromaticity from the parent [1,2-*b*]IF,^{38,47} we became interested in further manipulating the antiaromaticity of the *s*-indacene core. Whereas fusion of arenes to **7** affects the degree of decreased paratropicity, fusion of heterocycles restores the antiaromaticity of **7** and has the potential to increase beyond the level of unsubstituted *s*-indacene itself. To further explore the effect of heterocycle fusion, we examined three different directions: oxidation of the benzothiophene-fused *s*-indacenes to sulfones (indacenodibenzothiophenesulfone (IDBTS) **27-28**),⁴⁸ further π -extending the outer arenes from thiophenes and benzothiophenes to naphthothiophenes (indacenodinaphthothiophene (IDNT) **31-36**),⁴⁹ and changing the heteroatom from sulfur to oxygen (indacenodibenzofuran (IDBF) **29-30**)⁵⁰ or nitrogen (indacenodiindole (IDI) **37-38**).⁵¹ With the modular synthetic routes available (Figure 1.4), if the desired outer arene cross-coupling partner could be accessed, the “inside-out” method yielded the desired isomers.

The ultimate examples of this precision synthetic method were showcased in the preparation of unsymmetrical, regioisomeric indacenobenzofuranbenzothiophenes (IBFBTs) **39-42** and their corresponding oxidized donor/acceptor IBFBTS counterparts **43-46** via selective Suzuki cross-coupling to dimethyl 2-chloro-5-iodoterephthalate,⁵² whereas such specific, highly defined molecular geometries in acenes and related structures would be difficult to produce given current preparative methods (e.g., regio-random Aldol condensation).³⁹ While a majority of these *s*-indacenes were stable and could be thoroughly characterized, a few either were short-lived (**30**, **46**) or afforded something other than the desired product (**38**).

1.4 Computational techniques

When evaluating the antiaromaticity of *s*-indacene derivatives, we employ a variety of experimental *and* computational techniques. Our most powerful and useful computational tool is NICS-XY scans.⁵³ This convenient and information-rich method plots the NICS values of dummy atoms placed in a set path across the compound of interest (Figure 1.10a), making it visually simple to identify trends in aromaticity and antiaromaticity across a series of molecules (Figures 1.10b-10d). Using NICS-XY scans, students in the Haley lab identified several new substituted *s*-indacene targets with pronounced paratropicity (e.g., **29-38**), as they were predicted to be more antiaromatic than our benchmark, unsubstituted C_{2h} *s*-indacene **7**.⁴⁹⁻⁵¹

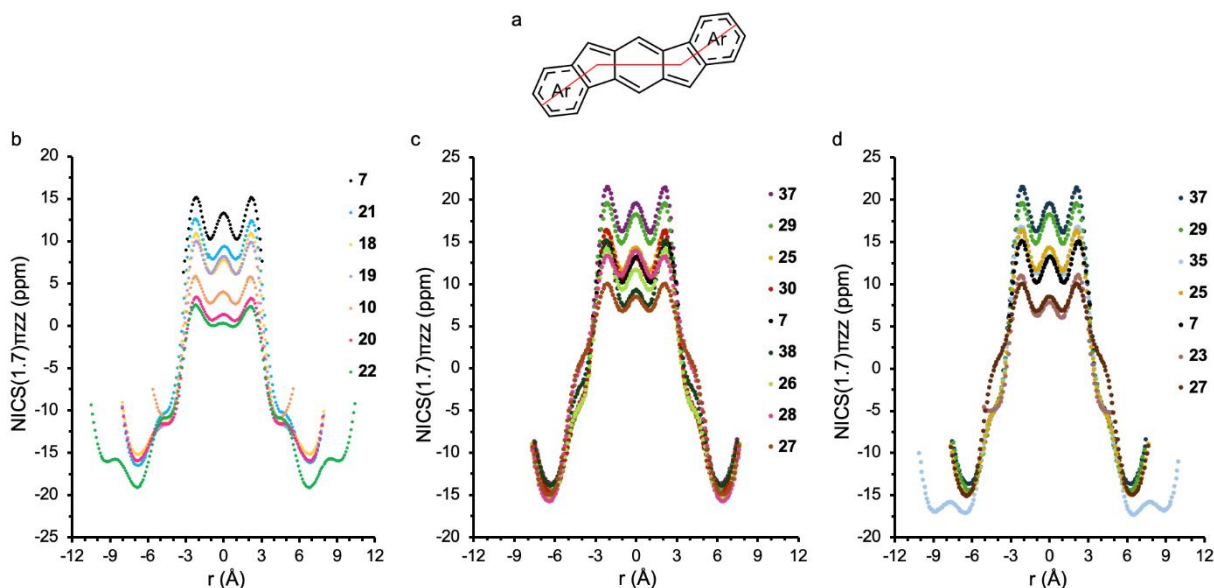


Figure 1.10. (a) Example path of the dummy atoms in NICS-XY(1.7) π_{ZZ} scan calculations. NICS-XY scans of (b) carbocycle-fused systems (**10** and **18-22**) and (c) heterocycle-fused systems (**25-30** and **37-38**) versus that of *s*-indacene reference molecule **7**. (d) NICS-XY scans of only the *syn*-fused heterocycles in Fig. 9b. All NICS scan plots are ordered from most to least antiaromatic. NICS-XY scans performed at 1.7 Å above the ring system using the M11/6-311+G** level of theory.

Figure 1.10 includes NICS-XY scans for selected carbocycle- (**10** and **18-22**) and

heterocycle-fused compounds (**25-30** and **37-38**) with benchmark **7**. It should be noted that these are recently recalculated/newly published NICS scans based on M11-optimized geometries,⁵⁴ as Wu and co-workers showed that NICS scans based on B3LYP-optimized geometries, as we originally published, can often provide values that overestimate delocalization in the *s*-indacene core.⁵⁵ It is also important to note that one should not focus solely on the absolute NICS values but rather on the trends in data that are all calculated with the same parameters. For the carbocycle series (Figure 1.10b), *s*-indacene **7** is the most antiaromatic followed by phenanthro-fused **21**, the *syn/anti*-DNI isomers (**18/19**), the parent [1,2-*b*]IF (**10**), and then the *linear*-analogues (**20/22**), supporting the simple “bond order” rationalization for paratropicity strength.

Whereas the differences between *syn*- and *anti*-fusion are minimal in the carbocycles, the differences are much more pronounced in the heterocycle series (Figure 1.10c). In general, *syn*-fused aromatic heterocycle isomers are more antiaromatic than the *anti*-fused isomers, with the *syn*-indole (**37**), -benzofuran (**29**) and -benzothiophene (**25**) all more paratropic than benchmark **7** and *anti*-indole (**38**), -benzofuran (**30**) and -benzothiophene (**26**) possessing roughly comparable paratropicity to **7**. Interestingly, the nonaromatic benzothiophene sulfone-fused derivatives **27** and **28** are calculated to be less antiaromatic than **7** and are the only heterocycle-fused *s*-indacenes that reverse the trend of increased antiaromaticity for *syn*-fusion, i.e., *anti*-IDBTS **28** is more paratropic than *syn*-IDBTS **27**.

While Figures 1.10b-10d show an appreciable ~20 ppm variance in the NICS_{πZZ} values of the *s*-indacene core, the corresponding values of the external rings are essentially insensitive to bond fusion/bond order. In the carbocyclic series, the range of NICS_{πZZ} values for the ring directly fused to *s*-indacene is small (–10 to –12 ppm), and even smaller (–15 to –16 ppm) for the terminal ring of the DNIs. Whereas the values of the inner ring show the ‘conflict’ between

opposing diatropic and paratropic ring currents, the outer ring is more isolated and thus the values are more typical of benzene/naphthalene. Exchanging the fused carbocyclic ring for a heterocyclic ring significantly negates this ‘conflict’, as the now-weakly diatropic heterocycles (NICS π_{ZZ} values of -2 to -4 ppm) or atropic sulfone **27** (+1 ppm) act as a spacer separating the strongly diatropic outer benzenes and the highly paratropic *s*-indacene.

While our studies had shown that extending the π -system of *s*-indacene through heterocycle or benzoheterocycle annelation leads to modification of the antiaromatic character of the core, we did not know whether this was a result extension of the π -system or the presence/location of the heteroatom. To understand these differences, we examined a series of test molecules to elucidate the specific effects of the heteroatom and its substitution position, the heterocycle, and the further extension of π -conjugation.⁵⁶ Computationally this was accomplished using NICS calculations,⁵⁷ current density maps,⁵⁸ and NICS2BC,⁵⁹ all of which painted a consistent picture. Firstly, we found that the heteroatom itself can have a dramatic effect on the antiaromaticity of the core: placing uncyclized heteroatoms at the 1,5-positions (i.e., the *anti*-isomers) affords the greatest extent of antiaromaticity alleviation, leading in the case of the NH₂-substituted *s*-indacene to almost complete loss of antiaromatic character. Second, we established that this effect is highly site-specific. Using resonance structures, we rationalized this site-sensitivity by showing that the *anti*-position enables the substituent to interact with the core via resonance while the *syn*-position does not. Third, by comparing the two types of isomers we found that the extension of the π -system by heterocycle annelation does indeed alleviate the antiaromaticity of the core, although it is a weaker effect than the resonative heteroatom effect. Finally, we demonstrated that this effect is dampened by the addition of another ring, i.e., benzannelation. Overall, this study showed that the reduction in antiaromaticity in the *anti*-isomers is

primarily a heteroatom effect, which is weakened by cyclization and further benzannelation. In contrast, for the *syn*-isomers (Figure 1.9b) the heteroatom effect is weak and the majority of antiaromaticity alleviation is achieved by the neighboring ring effect; however, further benzannelation cancels this, allowing the *s*-indacene to regain (and even surpass) its full antiaromaticity, as illustrated in Figure 1.10d.^{56a}

1.5 NMR spectroscopy

¹H NMR spectroscopy is a routine part of characterizing new *s*-indacene derivatives and provides an additional way to compare the paratropicity of similar systems. The protons on the six-membered ring of the *s*-indacene core are shifted upfield relative to the degree of paratropicity—the more antiaromatic molecules show a greater upfield shift of the core protons. When the bulky aryl groups are consistent, e.g., the mesityls in Figures 8 and 9a, comparisons between different systems become possible. This is a powerful tool for several reasons: NMR spectroscopy is a magnetic-based method, making it easy to compare with magnetic criteria based computational methods such as NICS, and it can be compared across a wider range of systems than cyclic voltammetry (CV) or UV-Vis spectroscopy, for example.

In most cases, comparison of the chemical shift of the core protons matches the order predicted by the NICS-XY scans. Table 1 shows the collected values for *s*-indacene core IF analogues. NICS-XY scans predict *syn*-fusion of the sulfur heteroatom to increase antiaromaticity through π -extension (IDT **23**→IDBT **25**→IDNT **35**), and this matches with the further upfield chemical shift of the core proton: IDT **23** (6.06 ppm) > IDBT **25** (6.02 ppm) > IDNT **35** (5.99 ppm). While the ordering within the six IDNT regioisomers does not follow the NICS-XY scans perfectly, the differences are small and other effects sometimes dominate.^{49b}

The oxidized IDBTSs reverse in trend and the *anti*-fusion has the more upfield chemical shift (**28**, 6.03 ppm) than the *syn*-fusion (**27**, 6.91 ppm).⁴⁸ Through various modifications to the sulfur-based heterocycle-fused IFs, we notice a significant upfield shift from the parent IF and smaller changes within the family. Consistent with the computational studies,^{56a} changing the heteroatom from sulfur to oxygen or nitrogen leads to a dramatic upfield shift of the core proton to 5.60 ppm for *syn*-IDBF **29**⁵⁰ and 5.39 ppm for *syn*-IDI **37**.⁵¹ From these trends we can conclude that large changes to antiaromaticity can be made through heteroatom alteration, and fine tuning antiaromaticity is done through fusion orientation (*syn*-/*anti*-), π -extension (IDT, IDBT, IDNT), and electronics (thiophene vs. thiophene sulfone). Finally, the core proton shifts of the unsymmetric IBFBT systems can be thought of as an “average” of their two constituent pieces, e.g., the core protons of *syn,syn*-IBFBT (5.90, 5.80 ppm) are roughly the average of those in *syn*-IDBT **25** (6.02 ppm) and *syn*-IDBF **29** (5.60 ppm).

Table 1.1. ¹H NMR chemical shift of the core protons of select *s*-indacene derivatives

cmpd	δ (ppm), (solvent)	cmpd	δ (ppm), (solvent)
7 (Ar = Mes) ^a	6.51 (CDCl ₃)	16 (Ar = Mes)	6.86 (CDCl ₃)
18	6.68 (CD ₂ Cl ₂)	19	6.62 (CD ₂ Cl ₂)
20	7.14 (CDCl ₃)	21	6.95 (CDCl ₃)
22	7.19 (CDCl ₃)	—	—
23	6.06 (CDCl ₃)	24	6.05 (CDCl ₃)
25	6.02 (CDCl ₃)	26	6.07 (CDCl ₃)
27	6.91 (CDCl ₃)	28	6.03 (CDCl ₃)
29	5.60 (CD ₂ Cl ₂)	30	6.14 (CD ₂ Cl ₂)
35	5.99 (CDCl ₃)	36	6.09 (CDCl ₃)
37	5.39 (CD ₂ Cl ₂)	—	—
39	5.85 (CD ₂ Cl ₂) ^b	40	5.87 (CD ₂ Cl ₂) ^b
41	6.05 (CD ₂ Cl ₂) ^b	42	6.10 (CD ₂ Cl ₂) ^b
43	6.17 (CD ₂ Cl ₂) ^b	44	5.64 (CD ₂ Cl ₂)
45	6.50 (CD ₂ Cl ₂) ^b	46	5.99 (CD ₂ Cl ₂)

^aReference 22. ^bAverage of two peaks.

1.6 Electrochemical and photophysical properties

The electrochemical and photophysical properties of the diarenoindacenes are also indicative of their antiaromaticity. While they possess HOMO-LUMO energy gaps and thus low energy absorptions similar to acenes, the diarenoindacenes are characterized by considerably lower HOMO and LUMO energy levels, typical of antiaromatic molecules. Additionally, these systems are redox active and usually have two reduction and one or two oxidation events. Unlike NMR spectroscopy, it is more difficult to draw meaningful comparisons of the photophysical and electrochemical properties across a wide range of derivatives. The HOMO-LUMO gap is affected by both antiaromaticity and π -extension, making it difficult to deconvolute their combined impact. Similarly, direct comparison of photophysical properties across families of diarenoindacenes is complicated by the same factors, resulting in red-shifted absorptions; however, both CV and UV-Vis provide important information about the system and its antiaromaticity, especially the ability to tune the HOMO-LUMO energy gap.

Table 1.2 contains the HOMO and LUMO energy levels, HOMO-LUMO energy gaps, and λ_{max} of the low energy absorption of a variety of diarenoindacenes. In general, we see that the more antiaromatic systems (**25**, **29**, and **35**) have a smaller HOMO-LUMO energy gap and more red-shifted absorption, especially when comparing the *syn*- and *anti*-isomers of a particular heterocycle. The broad class of diarenoindacenes typically has HOMO and LUMO energy levels in the range of -5.5 to -5.8 and -3.7 to -4.1 eV, respectively, with HOMO-LUMO energy gaps in the range of 1.4 - 2.0 eV. Interestingly, oxidation of the benzothiophenes to their corresponding sulfones (**27/28/43**) further drops the LUMO energy level (-4.4 to -4.5 eV). The low LUMO energy levels reflect the high electron affinity of the diarenoindacene family, which stand in

Table 1.2. Electrochemical and photophysical values of select *s*-indacene derivatives

cmpd	E _{HOMO} (eV)	E _{LUMO} (eV)	E _{gap} (eV)	λ _{max} (nm)
16 (Ar = Mes)	−5.34	−2.92	2.42	516
18	−5.73	−3.72	2.01	578
19	−5.59	−3.68	1.91	549
20	—	—	—	543
21	−5.73	−3.87	1.86	622
22	—	—	—	615 (em 664)
25	−5.54	−3.93	1.61	626
26	−5.52	−3.81	1.71	618
27	−6.28	−4.51	1.77	624
28	−6.12	−4.46	1.67	587
29	−5.55	−3.97	1.58	642
30	—	—	—	584
35	−5.49	−4.08	1.41	697
36	−5.43	−3.83	1.60	665
39	−5.67	−4.08	1.59	630
43	−5.84	−4.44	1.40	670

contrast to acenes, which typically have much lower electron affinities unless heavily appended with electron-withdrawing groups. These molecules' pronounced electron affinities make intuitive sense—as they are successively reduced, the compounds regain an aromatic configuration and thus aromatic stabilization. Much like fullerenes, the presence of the five-membered rings containing all-*sp*² hybridized carbons makes this class compounds inherently electron-accepting.

The diarenoindacenes are highly colored, covering a broad spectrum with colors varying from orange (**23**) to red-orange (**16a**) to purple (**27**) to blue (**36**), which are reflected in the electronic absorption spectra of the molecules. Compared to **16** (516 nm, Table 1.2), the λ_{max} of the low energy band of the carbocycle-fused indacenes progressively shifts to the red—543 (**20**), 549 (**19**), 578 (**18**), and 622 nm (**21**), decreasing the optical gap from ca. 2.3 to 1.9 eV.³⁷

Although not shown in Table 1.2, replacement of the mesityls with (triisopropylsilyl)ethynyl

groups typically shifts the low-energy λ_{max} further into the red by roughly 50-75 nm (e.g., low-energy λ_{max} for TIPSethynyl-substituted **16** and **21** are 568 and 692 nm, respectively). This difference is attributable to the degree of the conjugation of the quinoidal core with apical substituents: whereas the alkynes are fully conjugated to the π -electron-rich cores, the mesityls are in partial π -electronic communication only due to their near orthogonality ($>75^\circ$ dihedral) to the diarenoindacene backbone.

Despite being highly colored and π -electron-rich systems, the diarenoindacenes are surprisingly non-fluorescent due to a non-radiative decay pathway,⁴⁶ as was also observed in earlier studies of *s*-indacene derivatives.⁶⁰ Transient absorption spectroscopy of derivatives of **10** and **13** were shown to possess extremely short S_1 lifetimes of ~ 10 -15 ps.⁴⁶ Interestingly, studies on tetrakis(*t*-butyl) analogue of core structure **7** showed it to have a lifetime of 18 ps for the S_1 to ground state relaxation.^{60a} Such extremely short lifetimes explain why these molecules are non-emissive, since fluorescence (typically occurring with lifetimes of greater than 10^{-9} s) is not a competitive process at this time scale. Quantum chemical calculations indicate this non-emissiveness to be the result of an easily accessible potential energy surface crossing between the first excited singlet state (S_1) and ground electronic state (S_0), i.e., a conical intersection.^{46,60} Similar to **7**, this process allows efficient internal conversion to the ground state, deactivating fluorescence and thus yielding ‘dark’ molecules. As noted earlier, the only exception to this case is DAI **19**—with its antiaromaticity turned ‘off’ by 2,3-anthraceno-fusion, the S_0 and S_1 states in **19** separate enough in energy that fluorescence, albeit weak, is restored.⁴⁵

1.7 X-ray crystallography

X-ray crystallography and its use in determining bond lengths has been an important

factor in understanding our *s*-indacene derivatives. We find that when fusing arenes or heteroarenes to an *s*-indacene core, we observe a bond localized structure similar to C_{2h} symmetric *s*-indacene **7**. Applying X-ray crystallography to understand the change in antiaromaticity in the IF scaffold focuses on the bond length alternation in the *s*-indacene core. Generally, we observe that the structures with a greater degree of antiaromaticity have more bond length alternation, e.g., the short bonds are shorter and the long bonds are longer as antiaromaticity increases. While this metric provides support for ranking the antiaromaticity of IF derivatives, it also has some pitfalls.

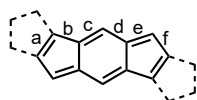


Table 1.3. Core C–C bond lengths (Å) of select *s*-indacene derivatives

cmpd	a	b	c	d	e	f
16 (Ar =	1.413	1.469	1.356	1.433	1.380	1.471
18	1.401	1.470	1.367	1.431	1.377	1.461
22^a	1.450	1.447	1.368	1.418	1.378	1.452
23	1.384	1.461	1.363	1.418	1.398	1.447
24	1.389	1.452	1.360	1.431	1.388	1.460
25	1.391	1.457	1.371	1.421	1.407	1.441
26	1.393	1.437	1.377	1.412	1.409	1.435
27^a	1.442	1.397	1.415	1.371	1.467	1.376
28	1.437	1.384	1.420	1.370	1.464	1.375
29	1.374	1.451	1.371	1.418	1.418	1.432
30	1.390	1.412	1.386	1.394	1.435	1.419
35	1.373	1.468	1.368	1.422	1.389	1.438
36^a	1.397	1.433	1.376	1.406	1.413	1.429
37^a	1.382	1.458	1.363	1.429	1.394	1.448

^a Average of two independent molecules in the crystal lattice.

In addition to the complex relationship between antiaromaticity and bond lengths, crystal packing forces are known to affect bond lengths and make bond length analysis difficult,²²

however, as well as some antiaromatic compounds can also be delocalized.⁶¹ Table 1.3 lists the core bond lengths of mesityl-substituted **16**, **18**, **22-30**, and **35-37**. All the structures exhibit the *para*-quinoidal motif of closed shell **6** within the indacene core, with bonds c and e possessing more double-bond character clearly evident, e.g., *syn*-IDI **37** in Figure 1.11 (left). For example, double bond c in the central six-membered ring varies from 1.356 to 1.386 Å.

Bond e between the core and the apical carbon bearing the mesityl groups varies from 1.371 to 1.380 Å in the hydrocarbon structures, yet lengthens to 1.389–1.435 Å in the hetero-cycle-fused systems, which begins to hint at the contribution of a biradical resonance form such as open-shell **6**. The outer benzenes exhibit archetypical bond lengths of 1.38–1.40 Å, with the fused bond at ~1.41 Å. A large majority of the diarenoindacene structures are well-bracketed by these values, whether aryl- or alkynyl-substituted on the apical carbons. In addition, nearly all the molecules are planar species, with root-mean-square deviations from the average molecular plane of 0.04 Å or less. Interestingly, we find that sulfone-fused *s*-indacenes **27** and **28** exhibit a “flipped” core in which the double bonds are exocyclic to the heterocycle.

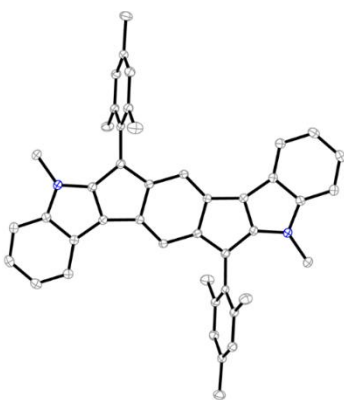


Figure 1.11. Molecular structure of *syn*-IDI **37** (CCDC 2416146; ellipsoids drawn at the 50% probability level and hydrogen atoms are omitted for clarity).

1.8 Dicyclopenta[*b,i*]anthracene: the core to achieve strong OS Character

After establishing a large body of work on indenofluorenes with multiple strategies for external acene and heterocycle fusion on *s*-indacene to tune optoelectronic properties and paratropicity, the next logical progression was internal π -expansion featuring dicyclopenta-[*b,g*]naphthalene (DCN) and dicyclopenta[*b,i*]anthracene (DCA) cores, e.g. sequential benzinterposition, to investigate further changes in optoelectronic properties. However, the relationship between antiaromaticity and diradical character discussed above sees a greater shift towards OS character proportional to size and can be thought of as a continuum from antiaromaticity to diradical character (Figure 1.12).^{13,43c,62} While unintended at the time, the Haley lab would find itself entering the arena of stable diradicaloids on account of the elongated quinoidal conjugation within the pro-aromatic DCN and DCA cores. Admittedly, core expansion did begin with fluoreno[4,3-*c*]fluorene ([4,3-*c*]FF)⁶³, but discussion of the FF homologues will be described later as they uniquely straddle CS and OS behavior. The focus here will instead be on DCA-based diindeno[1,2-*b*/1',2'-*i*]anthracene (DIAn) homologues as we now know they are strong diradicaloids and serve as our upper limit to OS character in our lab so far.

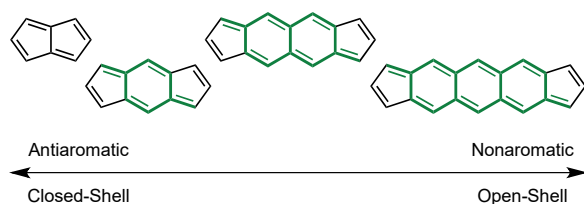


Figure 1.12. Continuum of core PAAHs from antiaromatic to diradicaloid featuring sequential insertion of 6-membered rings, i.e., benzinterposition. Pro-aromatic *p*-QDM, 2,6-naphthoquinodimethane (NQD) and 2,6-anthroquinodimethane (AQD) fragments are highlighted.

Pursuit of DIAn **47** (Figure 1.13) had begun in 2012 motivated by anticipation of enhanced optoelectronic properties, but the project remained slow going until then graduate student, Gabriel Rudebusch, completed the synthesis in 2015 following our “outside-in” I strategy.⁶⁴ To his credit he rationalized that inclusion of both the bulky mesityl and TIPSethynyl groups in the starting material would impede the Friedel-Crafts alkylation at the favored 1/5-positions of the anthracene core because of steric clash, but rather close onto to the less favored 3/7-positions, which worked brilliantly. Treatment with DDQ afforded deep blue crystals of **47**. Interestingly, the peaks in the proton NMR spectrum at room temperature were slightly broadened, so Rudebusch performed variable-temperature ¹H NMR (VT-NMR) experiments up to 150 °C to qualitatively probe a singlet to triplet state transition. Upon warming, the aromatic peaks in the series of spectra gradually broadened as the paramagnetic triplet state is populated. By 150 °C, all the peaks were in the baseline save those of the nondeuterated NMR solvent, and all the peaks returned to their former shape and height upon cooling to room temperature, offering the first evidence of having a genuine diradicaloid. In the electronic absorption of **47**, a major low energy

absorbance at 690 nm was recorded with a peculiar shoulder starting near 725 nm and tailing to 900 nm. This peculiar profile hints towards OS character as shoulders extending into the near-infrared (NIR) region have been attributed to the doubly-excited configuration in diradicaloids.⁶⁵ The system also exhibited textbook redox amphoterism via cyclic voltammetry as two quasi-reversible single-electron oxidations and reductions were recorded, affording a particularly narrow E_{gap} of 1.45 eV, which is a much smaller value compared to its relative [1,2-*b*]IF cousin (2.22 eV). A single crystal of DIAn suitable for X-ray diffraction was then grown and analyzed. Of particular importance was the 1.406 Å bond length between the apical carbon

and the anthracene core, suggesting this bond was displaying some single bond character reflecting the OS resonance structure. Other elongated double bond lengths in the crystal structure suggested there was substantial contribution from the OS form in the ground state canonical structure. These findings frame DIAn as a stable singlet diradicaloid, especially when paired with its y_0 value of 0.623.

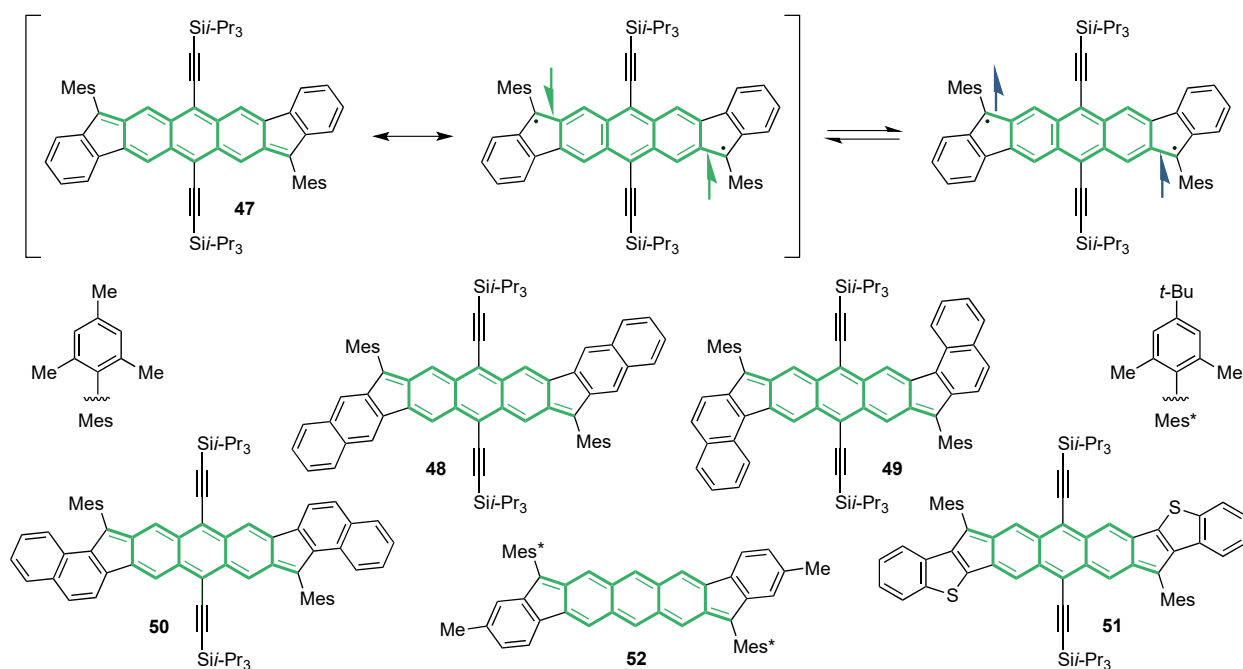


Figure 1.13. CS and OS resonance structures of DIAn **47** depicting transition from singlet to triplet states alongside DIAn homologues **48-52**. Pro-aromatic AQR fragments are highlighted.

Inspired by our work with IFs, naphthalene fusion to the periphery of the DIAn scaffold affords three dibenzodiindenoanthracene (DBDIAns) isomers **48-51** that mirror the *linear*-, *syn*- and *anti*-fusions seen in IFs **18-20**. With such π -extension, the diradicaloid character sequentially strengthens from **48-50** covering a y_0 range of 0.623-0.711 for the hydrocarbon DIAns (Table 1.4).⁶⁶ Benzothiophene fusion in **51** pushes OS character even further ($y_0 = 0.812$) and effectively caps our suite of diradicaloids as the upper bound. Each analogue exhibited

prominent diradicaloid signatures in VT ^1H NMR and electronic absorption experiments with spin-state transitions qualitatively observed in NMR signal broadening along with double-excitonic features in the NIR region. Elongated double bonds between the apical carbon and anthracene in crystal structures (1.391-1.434 Å) also supported substantial OS character.

Further structural adjustment resulted in DIAn **52**. The structural design of **47** included TIPSethynyl groups pendant to the DCA backbone on account of directing the correct closure during the Friedel-Crafts alkylation step of “outside-in” I, additional solubility, and thermodynamic stabilization along the core. It was suspected that the ethynyl groups were electronically non-innocent due to a y_0 value shifting to 0.615.⁶⁶ Investigation of **52** revealed a very similar UV/Vis profile and X-ray structure to **47**, so optoelectronic properties were minimally impacted by loss of alkyne substitution.⁶⁷ Even so, the new y_0 suggests there is a change to the diradicaloid character. This computational and experimental evidence begins to paint a detailed image of our diradicaloids; however, the finer details regarding changes in spin-state transitions between DIAn derivatives were still unclear. To probe deeper into the OS nature of our DIAns, it was necessary for our collaborators to dig computationally into the details.

1.8.1 Calculated singlet-triplet energy gaps and electronic parameters

The energy gap between the singlet state and triplet state (ΔE_{ST}) in diradicaloids is an important property that can be calculated and then unambiguously measured experimentally to quantify diradical character. Calculations using the two-electron/two-state model were carried out by our collaborators in the Nakano group to probe the parameters contributing to ΔE_{ST} . Equations 1 and 2 describe the model’s determination of ΔE_{ST} and its relationship to y , where a and b represent the two electrons in localized natural orbitals, with several key terms: U is

defined as the difference between onsite and intersite Coulomb repulsions, t_{ab} is the transfer integral, and K_{ab} as the direct exchange integral. Within this framework, the balance between U and t_{ab} is detailed and rationalizes underlying structure-property relationships in this series of diradicaloids.

$$(1) \Delta E_{ST} = \frac{U}{2} \left[1 - \frac{1}{\sqrt{y(2-y)}} \right] + 2K_{ab}$$

$$(2) y = 1 - \frac{1}{\sqrt{1 + \left(\frac{U}{4t_{ab}} \right)^2}}$$

Analysis of DIAn **47** provided a calculated ΔE_{ST} value of $-4.7 \text{ kcal mol}^{-1}$ and serves as a reference point for the remaining derivatives (Table 1.4). In the case of **48-50**, t_{ab} appreciably decreases corresponding to an increase in OS character in accordance with Eq 2. U only slightly changes between these three isomers highlighting the major contribution of external delocalization to t_{ab} . DIAn **51** has the smallest t_{ab} of this set and a larger U attributed to the electron rich S-atom enhancing diradical character with both parameters. Despite the trend in increasing y_0 , predicted ΔE_{ST} values hold **48** and **50** as the largest and smallest gaps, respectively, in this set of diradicaloids. DIAn **52** increases in its calculated ΔE_{ST} to $-5.4 \text{ kcal mol}^{-1}$ with slightly higher Coulombic repulsions and transfer integral values relative to **47**. TIPSethynyl substitution there-fore assists in stabilizing the triplet state in all DIAns to some degree. This computational analysis illustrates the balance between U and t_{ab} on both diradical character and ΔE_{ST} , where they trend proportionally together. However, careful consideration of heterocycle fusion is needed as in the case of **51**.

Table 1.4. Electronic Parameters and Singlet-Triplet Energy Gap for DIAn derivatives **47-52**

cmpd	$U/2$ (eV) ^{a,b}	t_{ab} (eV) ^{a,b}	y_0 ^{a,c}	ΔE_{STcalc} (kcal mol ⁻¹) ^{a,d}	ΔE_{STexpt} (kcal mol ⁻¹)
DIAn 47	1.435	0.916	0.623	-4.71	-4.2
<i>linear</i> -DBDIAn	1.348	0.905	0.638	-5.09	-4.8
<i>syn</i> -DBDIAn 49	1.378	0.818	0.686	-4.16	-3.8
<i>anti</i> -DBDIAn 50	1.377	0.781	0.711	-3.45	-3.2
DBTDIAn 51	1.572	0.774	0.815	-3.41	-3.4
DIAn 52	1.463	0.957	0.615	-5.42	-4.6

^aGeometries optimized at R- and UB3LYP/6-311G* levels. ^bEstimated at CASCI(2,2)/6-311G* level using (tuned-)LC-RBLYP MOs (denoted as tuned-LC-RBLYP-CASCI(2,2)/6-311G*). ^cCalculated at the PUHF/6-311G* level. ^dAdiabatic ΔE_{ST} value calculated at the spin-flip noncollinear (SF-NC)-TDDFT PBE5050/6-311G* level along with R- or UB3LYP/6-311G* zero-point vibrational energy correction for each spin state.

1.8.2 SQUID magnetometry

A crucial part of the puzzle is experimental determination of ΔE_{ST} by superconducting quantum interference device (SQUID) magnetometry. This technique was initially employed on **47** by the Gómez-García group from the University of Valencia for experimental measure of ΔE_{ST} where small magnetic responses were recorded while heating powder samples to 400 K. Having fit the collected data to the Bleaney-Bowers equation (Figure 1.14),⁶⁸ the experimental ΔE_{ST} for **47** was -4.2 kcal mol⁻¹, in reasonable agreement with its predicted value. Similar examination of **52** shows a change of +0.4 kcal mol⁻¹, agreeing with the predicted increase of the ΔE_{ST} compared to **47**. SQUID magnetometry performed on **48-51** revealed ΔE_{ST} values (Table 1.4) that are in reasonable agreement with calculated estimates when fit to the Bleaney-Bowers equation and confirm the ordering of ΔE_{ST} in DIAns **47-52** where **48** features the largest spin-state energy gap and **50** has the smallest gap. Our diradicaloids exhibit the power of logical structural alterations in fine tuning magnetic behavior (Figure 1.14) with greater radical delocalization (smaller t_{ab}) and minimal

Coulombic repulsions (smaller U) favoring small ΔE_{ST} values. This level of control over spin-paired and spin-unpaired states is desirable for magnetic material applications for on-demand transitions.

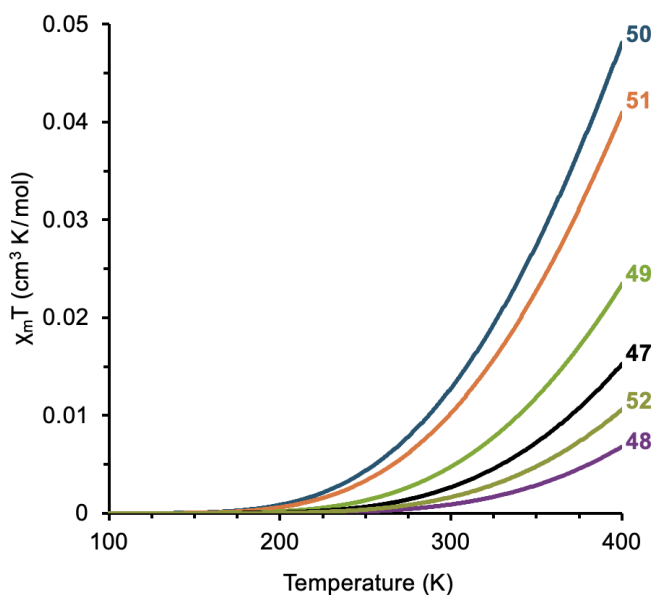
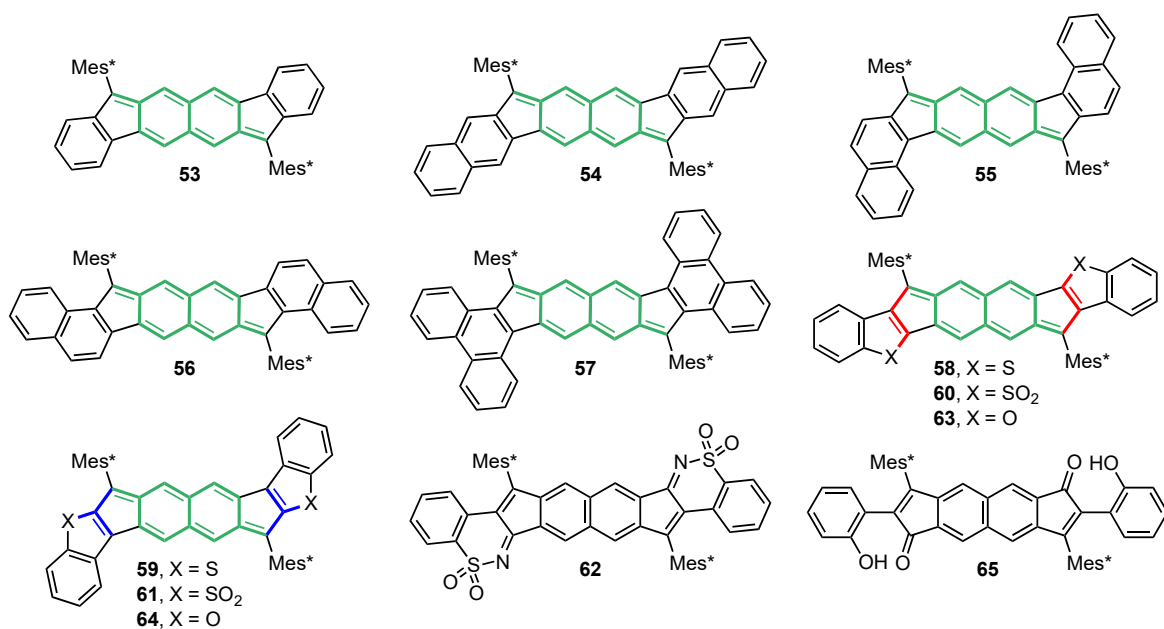


Figure 1.14. Bleaney-Bowers fits of heating cycle SQUID data for the DIAn series **48-52**; traces are shown only up to 400 K for consistency.

1.9 Caught in the middle: DCN-based molecules straddle closed- and open-shell structures

Recalling the continuum from antiaromaticity to diradical character, the sections in this perspective have so far illustrated our group's mastery over the two extreme ends where IFs only exhibit CS behavior and DIAns exhibit prominent OS behavior. As suggested by its placement in the continuum, the NQD unit within the DCN core provides the basis for moderate diradicaloids and would help elucidate the cross-over from CS to OS characteristics. The aforementioned [4,3-*c*]FF had a y_0 value of 0.377 and no observable indication of an OS electronic structure.^{63,69} Efforts for in depth investigations were then placed on [3,2-*b*]FF **53** (Figure 1.15) as it was predicted to have

greater OS character ($\gamma_0 = 0.434$).^{69,70} Optoelectronic properties were indeed enhanced due to longer conjugation with a redshifted low energy absorption and a very weak low energy shoulder teasing a doubly-excited configuration; however, the lack of peak broadening in the proton NMR spectrum and distinct bond alternation within the quinoidal core led us to erroneously believe that **53** was CS when first reported in 2017.



1.9.1 Breaking open diradical character in fluorenofluorenes

Strategies for developing diradical character in FFs ultimately followed our theme of external arene modification to push its homologues into the intermediate diradicaloid regime. Angular dibenzo-fusion was adapted to the FF scaffold since π -extension influenced paratropicity and OS character in previous studies. It was hypothesized that large changes to t_{ab} in FFs would boost diradical character as it did in the DIAn series. Computational analysis

supported this hypothesis as increasing y_0 values evolved over *linear*-, *syn*-, and *anti*-fusion as t_{ab} decreased (Table 1.5).⁷⁰ Further π -extension in **57** by way of phenanthrene fusion pushed the extent of FF OS character even further within the hydrocarbon series ($y_0 = 0.629$).

Table 1.5. Electronic Parameters and Singlet-Triplet Energy Gap for FF derivatives **53-63**

cmpd	$U/2$ (eV) ^{a,b}	t_{ab} (eV) ^{a,b}	y_0 ^{a,c}	ΔE_{STcalc} (kcal mol ⁻¹) ^{a,d}	ΔE_{STexpt} (kcal mol ⁻¹)
FF 53	1.446	1.163	0.49	-10.25	-9.3
<i>linear</i> -DBFF 54	1.315	1.143	0.51	-10.03	-9.6
<i>syn</i> -DBFF 55	1.352	1.055	0.56	-9.63	-8.7
<i>anti</i> -DBFF 56	1.336	1.012	0.60	-8.61	-7.8
TBFF 57	1.349	0.96	0.63	-7.90	-7.6
<i>anti</i> -IIDBT 58	1.563	1.031	0.613	-8.77	-8.2
<i>syn</i> -IIDBT 59	1.404	0.905	0.658	-8.06	-7.2
<i>anti</i> -IIDBTS 60 ^d	—	—	0.601	-9.65	—
<i>syn</i> -IIDBTS 61 ^d	—	—	0.652	-8.29	-6.5
<i>anti</i> -IIDBF 63	1.677	1.058	0.623	-9.10	—
<i>syn</i> -IIDBF 64	1.38	0.865	0.682	-7.68	-6.0

^aGeometries optimized at the R- and UB3LYP/6-311G* levels. ^bEstimated at the CASCI(2,2)/6-311G* level using the (tuned-)LC-RBLYP MOs (denoted as tuned-LC-RBLYP-CASCI(2,2)/6-311G*).

^cCalculated at the PUHF/6-311G* level. ^dAdiabatic ΔE_{ST} value calculated at the spin-flip noncollinear (SF-NC)-TDDFT PBE5050/6-311G* level along with R- or UB3LYP/6-311G* zero-point vibrational energy correction for each spin state. ^eElectronic parameters were not calculated for these entries.

In collaboration with the Kato group at the University of Shiga Prefecture, FFs **54-57** were synthesized following the “inside-out” II strategy. Characterization of this new set of dibenzofluorenofluorenes (DBFFs) confirmed appreciable diradical character in **56** and **57** with peak broadening in the ¹H NMR spectra at elevated temperatures (~90 °C) and double exciton state signatures in the NIR region. *syn*-DBFF **55** showed weak indications of OS character requiring ~150 °C to see minimal ¹H signal broadening and **54** exhibited a CS structure like **53**.

Fortunately, the SQUID magnetometer had been recently upgraded to support temperatures up to 800 K; thus, experimental data for the weaker diradicaloids could be obtained.^{§§} The spin-state dynamics of these FFs illustrate stepwise decrease in ΔE_{ST} from **54**→**53**→**55-57** (Figure 1.16). Like in the DIAn series, *linear* **54** has a larger ΔE_{ST} compared to parent **53** due to the slight increase in U corresponding to a greater electronic screening between the peripheral arene moiety and the core.

It is known that heterocycle fusion in **51** dramatically affects the electronic parameter U contributing to elevated diradical character while widening ΔE_{ST} relative to **50** on account of Pauli repulsions disfavoring the unpaired spin-state. Fusion of DCN with benzothiophene, like in **51**, can result in an *anti*-relationship between the S-atom and apical carbon of the core's five-membered ring. The *syn*-relationship can also be attained when reversing the fusion mode of benzothiophene onto DCN. As such, electron-rich indenoindenodibenzothiophenes (IIDBTs) **58** and **59** were prepared by Justin Dressler and Joshua Barker, respectively.⁷¹ These isomers feature different conjugation patterns between the radical center and S-atom where the *anti*-isomer has a linear pattern, and the *syn*-isomer has a cross pattern (Figure 1.5). Following these conjugation patterns, there is less interaction between the unpaired electrons and S-atoms in **59** as they come within two atoms from each other while they can neighbor each other in **58**. Applying the same late-stage modification used to prepare sulfones **27** and **28** should give the IIDBTs analogues, yielding changes to their OS characteristics as we know the S-atom influences both y_0 and ΔE_{ST} . Oxidation of **59** furnished sulfone **61**, whose calculated y_0 and ΔE_{ST} values show that it retains the diradical character of **59** yet exhibits an earlier spin-state transition than **60**.⁴⁸ Unfortunately, oxidation of **58** did not yielded sulfone **60** but rather the nitrogen-insertion product **62** (X-ray).⁴⁸

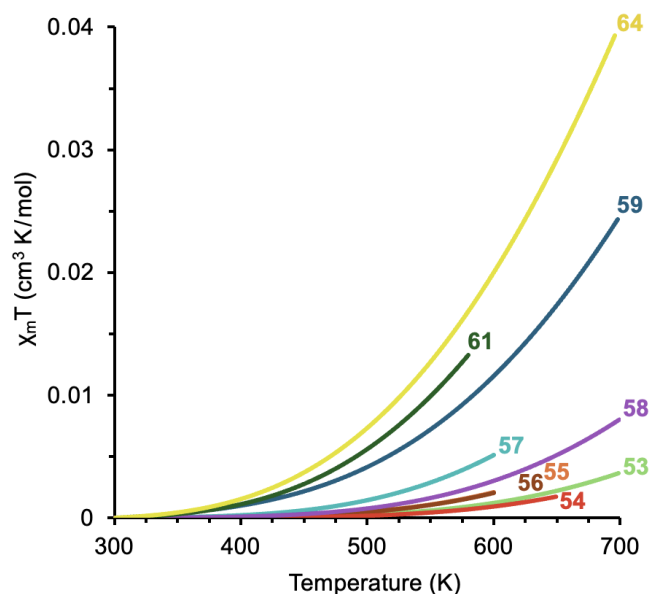


Figure 1.16. Bleaney-Bowers fits of recorded SQUID data for FF homologues **53-59**, **61**, and **64**.

Relating these structural considerations to U and t_{ab} , both parameters are greater in **58** than they are in **59**, as listed in Table 1.5, leading to increased OS character and a slightly narrower singlet-triplet gap for the *syn*-isomer. This is supported by elongation of the bond between the apical carbon and the core (1.419 and 1.421 Å, respectively) and red shifting of low energy absorption features from *anti*- to *syn*-fusion. The key evidence lies in SQUID results confirming the narrowed ΔE_{ST} in **59**, relative to **58**. When comparing these heterocycle-fused isomers to the hydrocarbon series, **56** and **57** sit between **58** and **59** in the range of ΔE_{ST} values for FF derivatives. Ordering of these FFs mirrors the ordering of DIAns **49-51** highlighting the consistent effect of electron repulsions with linear conjugation between the radical carbon and S-atom across multiple analogues. **59** capitalizes on the balance between π delocalization and coulombic repulsions and offers a design strategy to enhance y_0 and ΔE_{ST} through *syn*-fusion. The experimentally determined ΔE_{ST} of **61** unexpectedly subverts that of **53** despite the calculated value being greater by 0.13 kcal mol⁻¹. This was a sensible discovery since oxidation

of these S-atoms imparts electron deficiency further decreasing electronic repulsions near the cross-conjugated pathway.

Exploration of heteroatom effects on diradical character in the FF scaffold continued with the inclusion of benzofurans as the O-atoms would provide even greater electronegativity which we know enhanced molecular properties in the IF congeners **29-30**.⁵⁰ Quantum chemical calculations on indenoindenodibenzofurans (IIDBFs) **63-64** painted these regioisomers as worthwhile targets on account of increased OS character compared to their benzothiophene counterparts. Calculated ΔE_{ST} values suggested *syn*-IIDBF **64** to be more magnetically interesting between the two, as we would now expect given the behavior of **59** compared to **58**. Unfortunately, all attempts to prepare **63** instead afforded ring-opened product **65**, analogous to the case of **30**, where ring-opened material predominated.⁵⁰ *syn*-IIDBF **64** was remarkably stable and its high diradical character with SQUID data revealed that **64** has the smallest ΔE_{ST} of the FF homologues at $-6.0 \text{ kcal mol}^{-1}$. Such results exemplify the profound effect electronegativity has on optoelectronic *and* magnetic properties in these highly conjugated systems. Taking a look at the ground covered by our forays into diradicaloids shows a wide window of the ΔE_{ST} landscape filled by our lab comprising a total range of $6.4 \text{ kcal mol}^{-1}$ across the DIAn and FF families, from as low as -3.2 to as high as $-9.6 \text{ kcal mol}^{-1}$. Such efforts effectively demonstrate our mastery of tuning OS character and ΔE_{ST} through our judicious molecular designs.

1.10 What IF we turned to devices?

Having produced such a large library of diarenoindacenes and diindenoarenes, we have covered a wide range of frontier orbital energy levels, low energy absorptions, and redox potentials through precise structural modification. The CS nature of IF derivatives allows

(trialkylsilyl)ethynyl groups to installed on their apical carbons providing favorable solid-state packing and solution processability compared to Mes and Mes* groups. These properties are desirable for semiconductor applications, as was mentioned several times throughout this perspective, so how *do* these molecules perform in device active layers?

1. Single crystals of **16** (R = C₆F₅) Weak and unbalanced ambipolar transport in an OFET constructed using single crystals of perfluorophenyl substituted [1,2-*b*]IF had been reported by our group with hole and electron mobilities of 7×10^{-4} and $3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.⁴¹
2. Another instance of ambipolar behavior was observed in an OFET containing **47** having a hole mobility of $2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an electron mobility of $4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (for additional fabrication and experimental details, we direct readers to appropriate references for each OFET example).⁶⁴ The balanced transport seen here is ideal for effective ambipolar transport, but performance is limited due to 1D stacking of **47**.
3. TIPS *anti*-IDBT also exhibited hole-carrier transport in an OFET ($0.44 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).⁴⁷ Shortly after our work, a group in China showed that TIPS *anti*-IDBT was also ambipolar, with hole mobilities up to of $0.64 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an electron mobilities up to $0.34 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.⁷²
4. Best OFETs were TIPSethynyl substituted *linear*- and *anti*-DNI regioisomers were successfully spin-coated and annealed while retaining bricklayer packing.⁷³ Evaluation of charge-carrier transport revealed average hole mobilities of $1.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $4.72 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for TIPS *linear*-DNI and TIPS *anti*-DNI, respectively. Engineering the solid-state packing of OS molecules with simpler groups remains limited by the reactivity at the radical centers as was demonstrated during hydrogen/deuterium abstraction experiments with **12**.²⁴

Another method to probe transport properties that circumvents poor packing is scanning tunneling microscope break junction (STM-BJ) technique.⁷⁴ Key molecular handles needed to bind to Au electrodes in this technique are Lewis bases, such as thioethers in our case, which were incorporated into a select group of our molecules (Figure 1.17b) to undergo room temperature single molecule conductance experiments. In collaboration with the Kamanetska group at Boston University, hydrocarbons **67-68** were found to have moderate to high conductance ($G_0 = 10^{-4}$ – 10^{-2}) as molecular length increased following anti-ohmic decay.⁷⁵

Similar behavior was observed in **69** and **70**. Notably, **70** behaved similarly to **68** rather than **67** despite its DCN core indicating greater constructive quantum interference (CQI) with diradicaloids having persistent singlet spin-states. Enhanced CQI is possible due to the electronic configurations in these strong open-shell molecules bringing their frontier orbitals closer to the

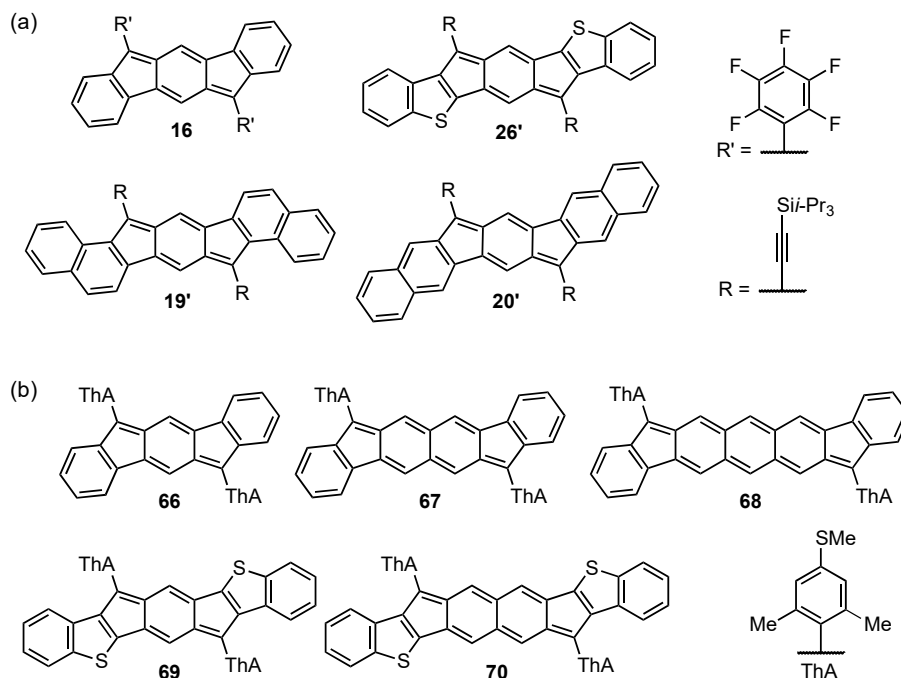


Figure 1.17. Chemical structures of quinoidal derivatives used in (a) OFET evaluation and (b) single molecule conductance measurements.

Fermi energy of the gold electrodes in the single-molecule junctions. See Chapter III for an in-depth theoretical discussion on quantum interference effects.

1.11 Conclusions

Over the last 13 years, the Haley lab has contributed quite the library of molecules to antiaromaticity and diradicaloid literature. There have been several synthetic routes presented in our work and their modularity provides a powerful tool to logically extend conjugation in the core and periphery. Heterocycle fusion adds additional possibilities synthetic targets as we have shown with benzothiophene, benzofuran, and indole. While we have certainly made our mark with these achievements, it is no secret that there are many others in the antiaromatic/diradicaloid arena. This field remains highly active with major contenders such as the Tobe group producing fluoreno[2,3-*b*]fluorene⁷⁶ and indeno[2,1-*b*]fluorene,²⁷ the Stepien group presenting diindeno[1,2-*a*:2',1'-*i*]phenanthrene⁷⁷ and twisted alkene oligoradicaloids,⁷⁸ the Wu group with periacenes⁷⁹ and zethrenes,⁸⁰ the Chi group reporting nanographene fragments⁸¹ and heteroacenes,⁸² and many others.⁸³ New minds are also making impacts with even larger conjugated systems incorporating multiple *s*- and *as*-indacene moieties like those from the Das group.^{84,85} We hope that our contributions offer inspiration to emerging groups and motivation to continue research in antiaromatic, OS molecules, and their device performance as the desire for novel organic electronic materials persists.

CHAPTER II

PROBING THE INFLUENCE OF ALKYNE SUBSTITUTION ON THE ELECTRONIC AND MAGNETIC PROPERTIES OF DIINDENO[1,2-B;1',2'-I]ANTHRACENES

This chapter includes previously published and co-authored material from Vidal Jr., E.; Zakharov, L. N.; Gómez-García, C.; and Haley, M. M. Probing the Influence of Alkyne Substitution on the Electronic And Magnetic Properties of Diindeno[1,2-*b*;1',2'-*i*]Anthracenes. *J. Org. Chem.* **2024**, 89, 14515-14519. This manuscript was written by Efrain Vidal Jr. with assistance from Prof. Michael M. Haley. The project in this chapter was conceived by Prof. Michael M. Haley. The experimental work in this chapter was performed by Efrain Vidal Jr with help from Dr. Lev N. Zakharov (X-ray crystallography) and Prof. Carlos Gómez-García (SQUID).

2.1 Introduction

Open-shell polycyclic conjugated hydrocarbons are molecules that have unpaired π -electrons in their ground-state electron configurations, and in the case of diradicaloids, there are two unpaired electrons available for through-space and through-bond communication. These molecules are important for an intimate understanding of π -bonding and spin-spin interactions.¹⁻⁷ Narrow highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) energy gaps,^{8,9} amphoteric redox behavior,^{10,11} strong low energy absorption in the UV-vis region,^{8,12} and usually strong magnetic coupling^{13,14} are associated properties of this unique class of molecules, which contribute to the deep interest in developing these systems. Due to

their properties, organic diradicaloids are thought to be suitable in nanoscale electronics,^{15,16} spintronics,^{17,18} nonlinear optics,^{19,20} and singlet fission.^{21,22} The first of these diradicaloids was Thiele's hydrocarbon,²³ followed quickly by Tschitschibabin's hydrocarbon²⁴ as an extension to the quinoidal conjugation, lending a proaromatic nature to these systems. Many diradicaloids have been synthesized and studied since, such as zethrenes,^{25,26} bisphenalenyls,^{27,28} anthenes,^{29,30} extended quinodimethanes,^{31,32} and diindenoacenes.^{33–36} Stability in these systems is accomplished by the inclusion of bulky groups on the high-spin density carbon centers to slow decomposition, thus allowing for thorough study of stable, novel, open-shell scaffolds.

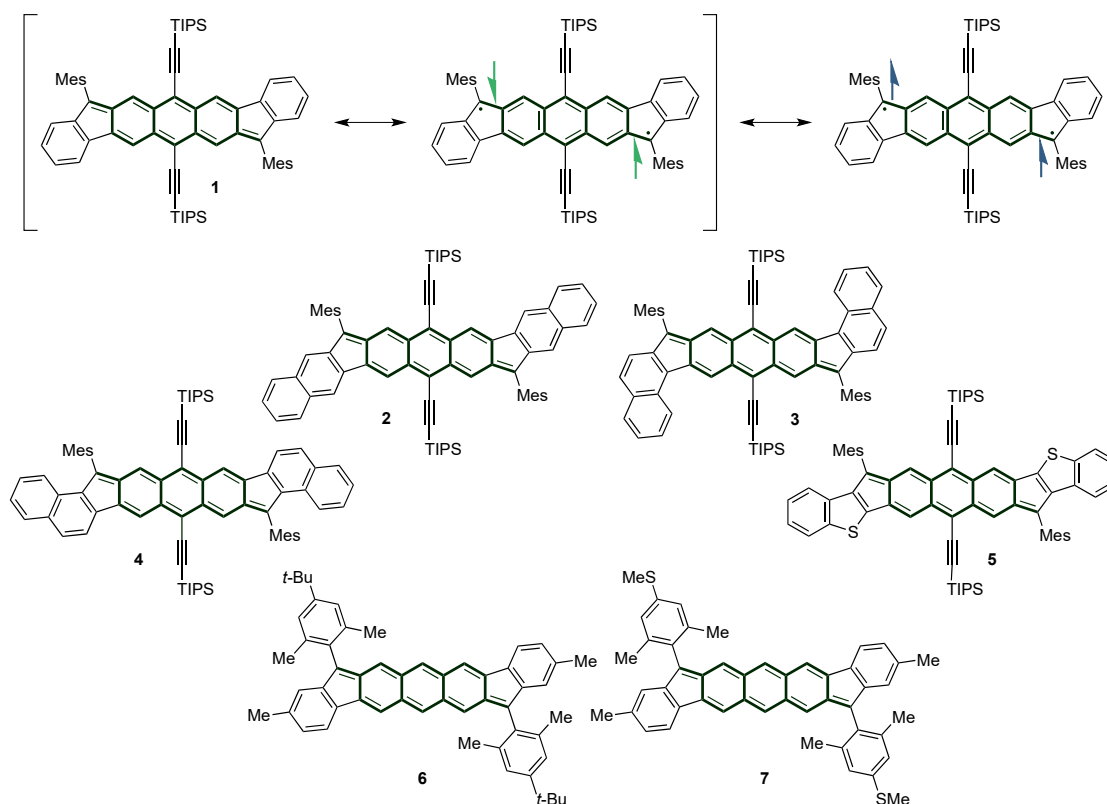


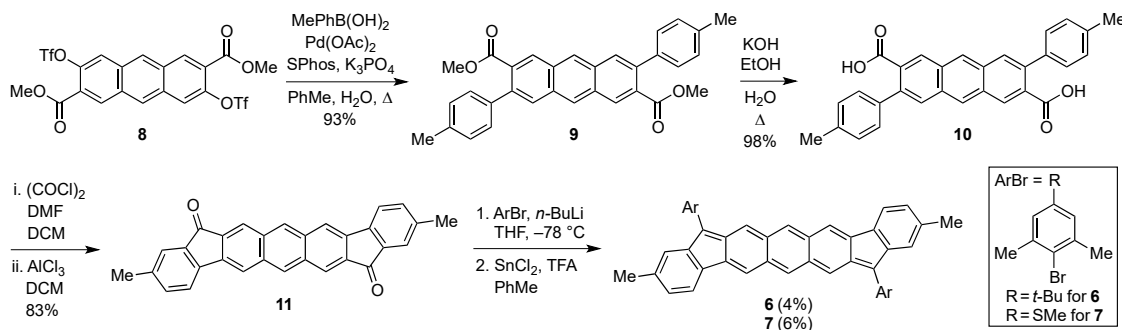
Figure 2.1. Structures of the known DIAn family 1–5 and new DIAn derivatives 6 and 7 lacking the alkyne groups. The common 2,6-anthroquinoidal/diyl relationship in all molecules is denoted by the bolded bonds.

In 2016 we reported the synthesis and properties of diindenoanthracene **1** (DIAn, Figure 2.1), a diradical with excellent stability, a narrow HOMO/LUMO energy gap (E_{gap}), strong absorption within the red region of visible light and weak absorption into the near-infrared region due to a doubly-excited state, and a singlet-triplet energy gap (ΔE_{ST}) that allows for a thermally accessible triplet excited state above room temperature.³⁵ From design principles learned with **1** and a desire to rationally tune ΔE_{ST} , a library of DIAn derivatives (**2–5**) was prepared featuring varied arene fusion to the anthracene core while maintaining the same 2,6-diradical orientation (Figure 2.1).³⁶ Through judicious adjustments of the electronic parameters dictating the diradical character (γ_0) and ΔE_{ST} , a rational, stepwise fine-tuning of ΔE_{ST} resulted in an overall range of 1.6 kcal mol⁻¹ for **1–5**. Despite this success, their syntheses required the presence of bulky (triisopropylsilyl)ethynyl (TIPSEthynyl) groups to ensure correct Friedel-Crafts ring closure to complete the requisite core, as well as to impart added solubility. Fortuitously, a recent publication described the synthesis of an anthracene core without diethynyl substitution,³⁷ providing the means of simplifying the electronic structure of the quinoidal backbone of DIAn. The current study of “alkyne-free” DIAns **6** and **7** aims to answer the influence alkyne substitution has on molecule properties and whether there are significant consequences in omitting the alkynes.

The ability to study an electronically “pure” DIAn core requires an anthracene-based building block with advantageous substitution on the 2,3/6,7 positions. Granhøj et al. recently reported a synthetic route to bis-triflate **8**,³⁷ which can be subjected to Suzuki-Miyaura cross-coupling conditions with 4-methylphenylboronic acid to reach diester **9** (Scheme 2.1). The 2,3/6,7 substitution pattern of the esters and pendant tolyl groups negates the need of the directing effect from the TIPSEthynyl groups present on the 9 and 10 positions in the original

DIAn synthesis to avoid unproductive ring closure at the 1 and 5 positions.³⁵ Saponification of the diester to **10** followed by Friedel-Crafts acylation gave dione **11**. This ketone functionality permits the final two transformations—nucleophilic addition of the lithiate of 2-bromo-4-*t*-butyl-

Scheme 2.1. Synthesis of diindeno[1,2-*b*:1',2'-*i*]anthracenes **6** and **7**.



1,3-methylbenzene followed by trifluoroacetic acid-catalyzed SnCl_2 reduction of the diol intermediate to afford diradicaloid **6**. Similarly, use of 4-bromo-3,5-dimethylthioanisole³⁸ in the lithiate reaction results in the formation of DIAn derivative **7**. The low yields of **6** and **7** are due to material loss during the removal of residual Sn salts during purification, which we attribute to the significantly reduced solubility caused by the absence of the two TIPSethynyl groups.

The structural differences between **1**, **6**, and **7** allow us to rationalize changes in optoelectronic properties as a consequence of TIPSethynyl substitution, or lack thereof. As expected, the absorbance profiles in the UV-vis region for **6** and **7** resemble other acene based quinoids and is very similar to that of **1** (Figure 2.2a). The λ_{max} in the red region of the UV-vis spectra are at 658 and 661 nm for **6** and **7**, respectively, followed by second absorption deeper into the red (~ 720 nm), compared to a single broad absorption for **1** (690 nm). It is reasonable to attribute both the broader absorption and the ~ 30 nm red-shift to the two ethynyl groups in **1**

seeing as the spectra of both **6** and **7** illustrate multiple defined absorbance features in the same lower energy region. In addition, common to diradicaloids is the weak shoulder band (~ 760 nm), indicative of a double-excitonic state.^{12,36,39–41} This low-energy shoulder is present regardless of substitution and has a strikingly similar shape between all three DIAn derivatives, suggesting a nearly identical doubly-excited electronic configuration within the polycyclic core.

2.2 Results and Discussion

Cyclic voltammetry (CV) of DIAns **6** and **7** exhibit two one-electron oxidations and reductions with symmetry between both processes that match parent DIAn **1** (Figure 2.2b). Notable differences between CV traces of **1** and **6** are their redox potentials. Quasi-reversible reductions occur at -0.93 and -1.31 V (vs. SCE) without ethynyl substitution; however, analogous reductions are shifted upwards to -0.81 and -1.20 V (vs. SCE) with ethynyl substitution (see Appendix A for additional CV details). The oxidations of these systems also are shifted from 0.51 and 0.99 V in **6** to 0.63 and 1.17 V in **1**. HOMO energy levels are estimated as -5.19 and -5.32 eV for **6** and **1**, respectively, whereas LUMO energy levels are estimated as -3.72 and -3.87 eV. The electrochemically derived E_{gap} for DIAn **6** is 1.47 eV, which is very close to the reported E_{gap} of 1.45 eV for the bis-ethynyl substituted analogue **1**.

In the case of **7**, the potentials for all four possible redox events are shifted slightly up from both **1** and **6**, making it more susceptible to electrochemical reduction, but also more resistant to oxidation (see Table A1 for full electrochemical data of **7**), yet it too has an E_{gap} of 1.47 eV. The equivalent energy gap between **6** and **7** can be rationalized by poor overlap between the orthogonal, bulky pendent aryl groups and the quinoidal core, rendering any electronic influence of the electron-rich sulfur atom in **7** on the gap itself negligible. There is

very little change to the E_{gap} of DIAn diradicaloids despite substitution on the apical carbon of the five-membered rings and substitution on the central six-membered ring, analogous to related indeno[1,2-*b*]fluorenes featuring bulky substituents.⁴²

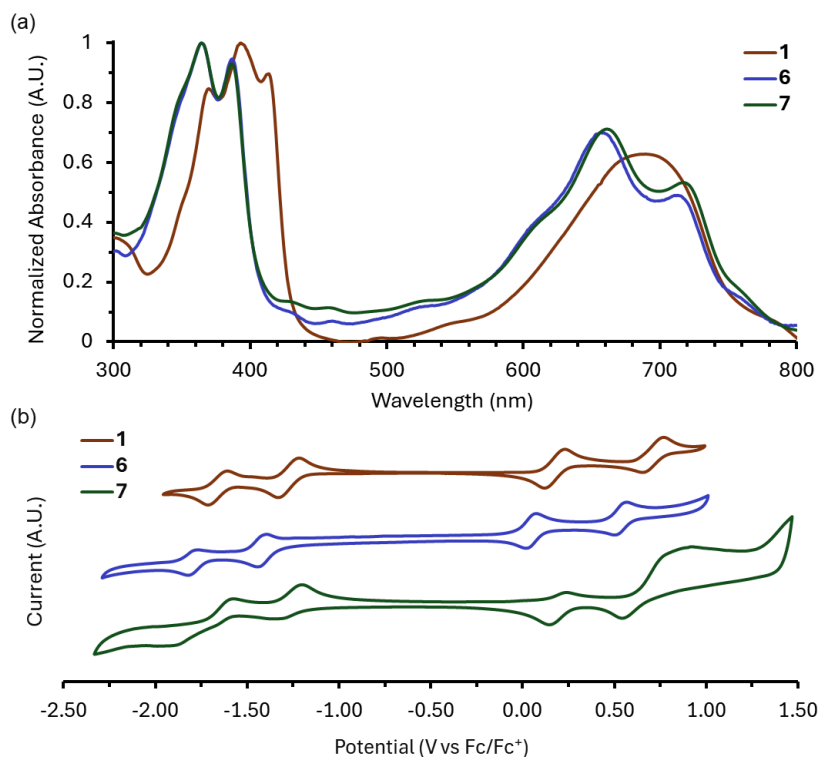


Figure 2.2. (a) Electronic absorption spectra for **1**, **6**, and **7** in CH_2Cl_2 at room temperature. (b) CV of **1**, **6** and **7** in CH_2Cl_2 showing two quasi-reversible one-electron reductions and two quasi-reversible one-electron oxidations. Voltammograms are generated according to IUPAC plotting convention; the starting point for each voltammogram is 0.0 V and scans proceed from oxidizing to reducing potentials.

Single-crystal X-ray diffraction (XRD) of crystals of **6** grown by vapor diffusion of heptane into a CH_2Cl_2 solution at room temperature successfully afforded its molecular structure (Figure 2.3a). Similar to **1**, analogue **6** is centrosymmetric, planar, and retains roughly 1D stacking with overlapping peripheral six-membered rings (Figure A3). Bond lengths within the

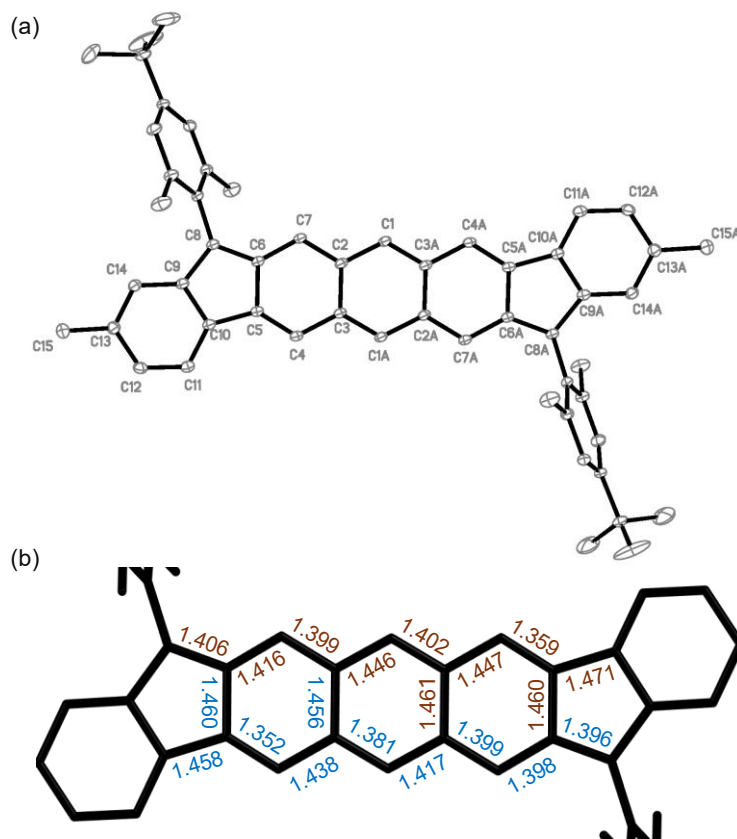


Figure 2.3. (a) Crystal structure of DIAn **6** drawn with 50% thermal ellipsoids, hydrogen atoms are omitted for clarity. (b) Comparison of selected bond lengths (Å) of **1** (brown)³⁵ and **6** (blue).

quinoidal core of **6** alternate as was observed for **1**, which reflect the closed-shell structure well (Figure 2.3b). Within **6**, the bond distances vary between 1.352–1.460 Å and tend to be slightly shorter than those of DIAn **1**, indicating minimal changes in the ground-state structure between alkyne substituted and unsubstituted quinoidal cores. The bond distance between the apical carbon and the anthracene core (C6–C8), which can indicate contributions from both an open-shell and closed-shell structure, is roughly the same (1.396 Å) as the values found in DIAn derivatives **1-4** (1.391–1.406 Å).³⁸ A discussion of the differences in the molecular packing of **1** and **6** (Figure A9) can be found in the Supporting Information.

Prior computational studies on simplified models of **1** and **6/7** have suggested that omission of the alkynyl substituents will have minimal effect on the diradical character index, y_0 (0.623 vs. 0.615, respectively (PUHF/6-311G*)), yet will have an appreciable impact on ΔE_{ST} ((SF-NC)-TDDFT PBE50/6-311G*), raising it from -4.71 kcal mol $^{-1}$ in **1** to -5.42 kcal mol $^{-1}$ in **6/7**.³⁶ To this end, the magnetic properties of **6** and **7** were studied using superconducting quantum interference device (SQUID) magnetometry. While **6** and **7** do contain two additional methyl groups in the core, their presence should have very little influence on magnetic properties based on the computed odd-electron density map of **1**.³⁶ As expected, the two analogues have very similar SQUID magnetic responses (Figure 2.4) since the only difference is *t*-butyl- versus thiomethyl-substitution on the pendant phenyl rings. When fit to the Bleaney-Bowers equation,⁴³ the data better fit to a dimer model from which ΔE_{ST} values of -4.6 and -4.5 kcal mol $^{-1}$ are obtained for **6** and **7**, respectively, numbers that are in fairly good agreement with the previously calculated ΔE_{ST} of -5.4 kcal mol $^{-1}$.³⁵ DIAns **6** and **7** exhibit a thermally accessible triplet excited state from a singlet ground-state, which is consistent with the larger library of DIAn derivatives

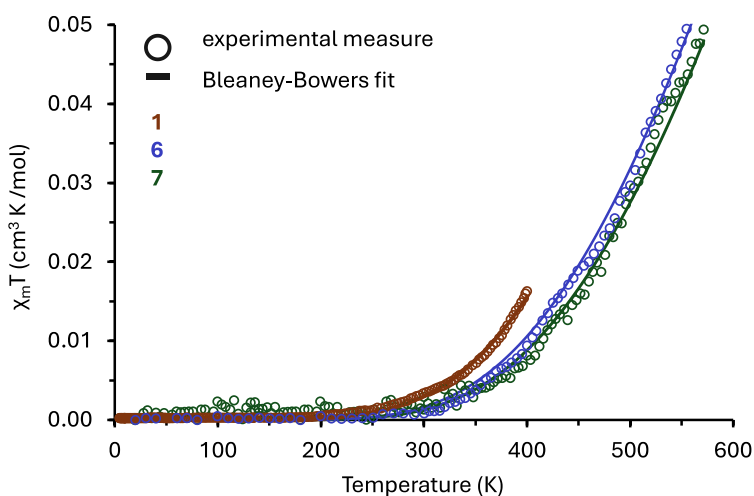


Figure 2.4. SQUID data of **1**, **6**, and **7** (empty circles) and the corresponding Bleaney-Bowers fit (solid lines).

from our lab.³⁶ Comparing the ΔE_{ST} of **6** and **7** to that of **1** ($-4.2 \text{ kcal mol}^{-1}$),³⁵ there is a difference of less than $0.4 \text{ kcal mol}^{-1}$, indicating a fine tuning of the ΔE_{ST} in these anthracene-based diradicaloids.

2.3 Conclusions

In summary, we report the facile synthesis and study of DIAns **6** and **7** without ethynyl substitution. In depth characterization was completed with single-crystal XRD, UV-Vis spectroscopy, CV, and magnetic measurements with computational support from previously reported theoretical values providing experimental corroboration to a long standing curiosity towards the influence of bis-ethynyl substitution. Further fine-tuning of ΔE_{ST} extends the intrigue of this family of diradicaloids and parallels widespread interest of open-shell molecules in the realm of spintronics.

CHAPTER III

EXTREME ANOMALOUS CONDUCTANCE ENHANCEMENT IN NEUTRAL DIRADICAL ACENE-LIKE MOLECULAR JUNCTIONS

This chapter includes previously published and co-authored material from Lawson, B.; Vidal Jr., E.; Luna, S.; Haley, M. M.; and Kamenetska, M. Extreme Anomalous Conductance Enhancement in Neutral Diradical Acene-like Molecular Junctions. *ACS Nano* **2024**, *18*, 29059-29066. This manuscript was written by Brent Lawson and Prof. Maria Kamenetska with assistance from Prof. Michael M. Haley and Efrain Vidal Jr. The project in this chapter was conceived by Prof. Maria Kamenetska and Prof. Michael M. Haley. The experimental work in this chapter was performed by Efrain Vidal Jr. and Brent Lawson. The computational work in this chapter was performed by Brent Lawson with help from Sigifredo Luna.

3. 1 Introduction

With increasing drive for miniaturization, the properties of nanoscale materials such as individual particles or molecules take on added significance for the development of future technologies. For example, passing electronic current across single molecules attached to metal electrodes has been shown to result in switching or diode-like behavior, raising the prospect of molecules as active components in next generation electronic devices.¹⁻⁵ Appealingly, the properties of such molecular circuits can be tuned using synthetic control of the molecular atomic structure. A challenge in the field is that electronic states of an organic molecular bridge are typically off-resonance with the Fermi energy of the conducting electrons in the metal.⁶⁻⁹ As a result, typical molecular junctions behave as quantum tunnel barriers and tend to be highly

insulating, with an electronic conductance that decreases exponentially with molecule length. Thus, with few exceptions, molecules longer than ~ 2 nm in length have vanishing conductance and therefore possess limited usefulness as candidates for nanoscale electronics. Developing molecular materials that overcome this limitation, known as *ohmic* decay, is an important challenge for the field.

Recent work has identified radical molecules with open-shell electronic structures containing unpaired electrons, as molecular wires with topologically non-trivial electronic states that can sustain higher conductance over longer lengths.^{10–15} At room temperature and ambient conditions, charged diradicals generated through chemical oxidation were shown to exhibit *anti-ohmic* behavior, with conductance increasing modestly with molecular length up to ~ 2 nm and then decreasing again.¹¹ This reversal to typical conductance decay in longer charged organic diradicals was attributed to decreased coupling of edge topological states across the extended molecular backbone due to their localized character and the rotational degrees of freedom of phenyl constituents in the molecules.^{11,16} Incorporating a chain of charged radicals in series in a single molecule restored anti-ohmic trends at longer molecular lengths, but required challenging experimental protocols to maintain the high oxidation charged state of a single organic wire.¹³ Here, we report extreme anti-ohmic behavior at room temperature in neutral diradicaloid molecules composed of cyclic benzoquinoidal units linearly fused together as in acenes, which we term the **BQ_n** series (Figure 3.1a). Unlike the aforementioned unstable, charged radical series, the neutral, stable **BQ_n** molecules are inherently diradicaloid. Critically, we observe that conductance is enhanced over two orders of magnitude for a molecular backbone length increase of ~ 5 Å from **BQ₁** to **BQ₃** even at low bias voltage, suggesting that neutral polycyclic diradicals can serve as highly efficient electron transport nanowires. These neutral systems are robust to

oxidation and display increased anti-ohmic character at higher bias voltage. We measure the I-V characteristics to reveal that the HOMO-LUMO energy gap of the **BQ_n** series shrinks as expected with extended molecule length but, critically, that transmission does *not* decay in the HOMO-LUMO gap as it does in most other quasi-1D nanowires. We adapt and extend the 1D

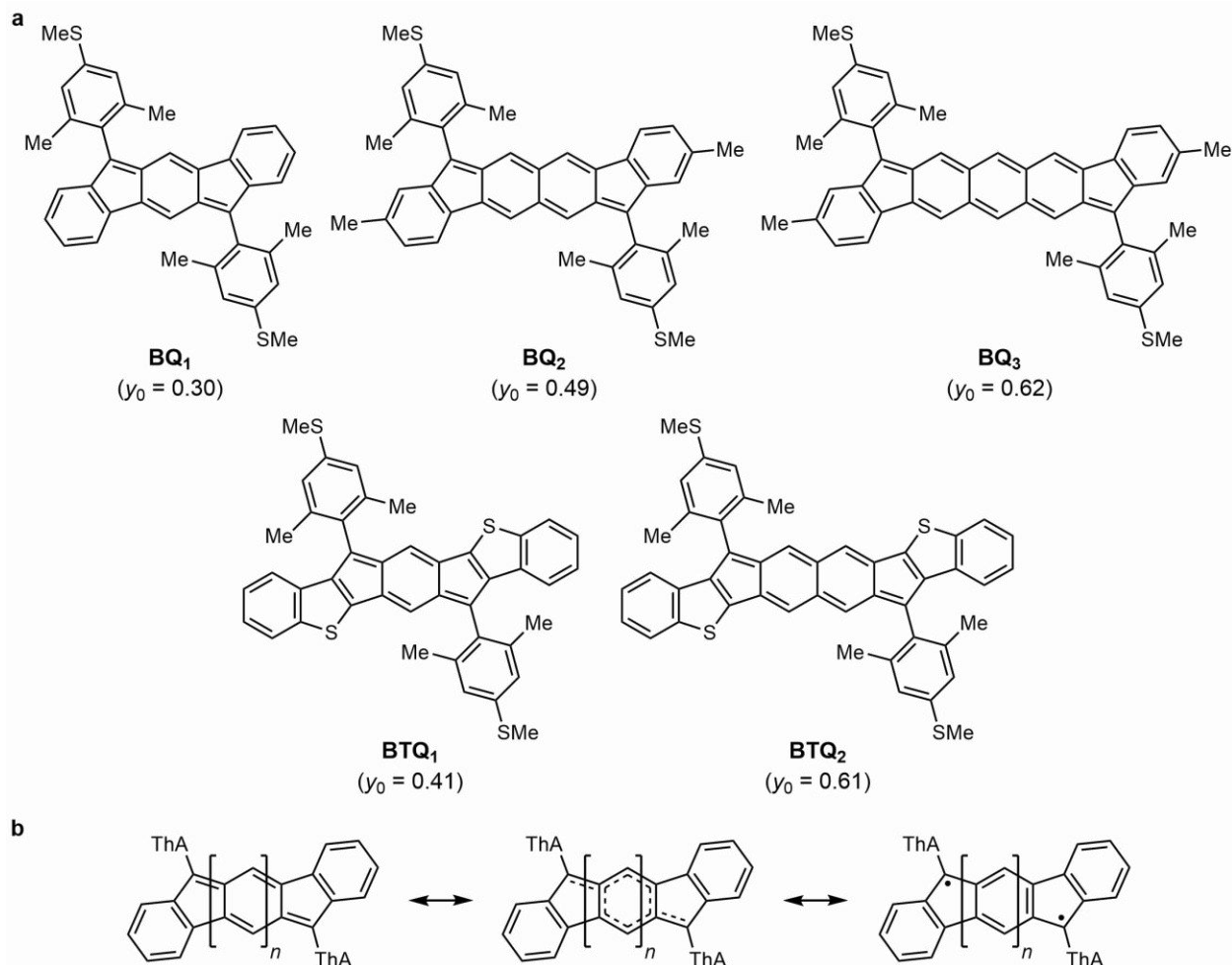


Figure 3.1. (a) Molecular structures of the **BQ** and **BTQ** molecules; calculated y_0 values (PUHF) are from ref. 21. (b) Resonance structures converting between the quinone, delocalized, and diradical form of the family of benzo-fused quinoids (**BQ_n**) where $n = 1-3$. Thioanisole linkers (ThA = 2,6-dimethyl-4-(methylthio)phenyl) serve to anchor the molecule to gold electrodes in the junction.

Su-Schrieffer-Heeger (1D-SSH) formalism to model the topological phases in cyclic planar aromatic compounds studied here and combine it with the non-equilibrium Green's function method to predict conductance trends. We demonstrate that the anti-ohmic behavior observed experimentally is intrinsic in this family of molecules when realistic bond-order parameters are incorporated into the 1D-SSH parametrization. Our analysis reveals that the conductance enhancement we observe is due to growing constructive quantum interference (CQI) between the frontier orbitals in fused cyclic systems, which we demonstrate to be a distinctive feature of our polycyclic system. Finally, we leverage the tunability of the molecular system to demonstrate further enhancement of anti-ohmic behavior in a related set of benzothiophene-fused quinoidal molecules (**BTQ_n**, Figure 1a) with higher diradical character than the **BQ_n** series. Overall, our study identifies a class of 1D molecular materials as superior nanowires and provides an analytical framework and mechanistic insights needed to guide the development of highly conducting molecular circuits.

3. 2 Results and Discussion

We perform room temperature single molecule conductance measurements of the **BQ_n** series using a scanning tunneling microscope break junction (STM-BJ) technique.^{17–19} The **BQ_n** series shown in Figure 3.1a are characterized by modest to intermediate diradical character, y_0 , in their uncharged state.^{20,21} Generally, as the number of fused six-membered rings increases, the diradical character of the molecule also increases, reflecting a higher residence of the molecules in the diradical structure (Figure 3.1b, right) over the quinone (Figure 3.1b, left)). Overall, these molecules have been shown to be air-stable open-shell diradical singlets in the ground state, with long term stability at room temperature.^{20,22–26} Importantly, the diradical character y_0 , which can

be tuned rationally via judicious structural modification, is inherent to the molecule and independent of solvent conditions.²³

The **BQ_n** and **BTQ_n** were prepared analogously to their previously reported mesityl analogues via the reaction of the lithiate prepared from 4-bromo-3,5-dimethylthioanisole (ThA) with the corresponding **BQ** and **BTQ** diones. Subsequent reductive dearomatization with SnCl₂ afforded the target molecules; see Appendix B for the synthetic and spectroscopic details. Inclusion of the thioanisole functionality is critical to ensure binding to the Au electrodes. All measurements in the STMBJ were performed in 1 mM solution of 1-bromonaphthalene (BNP), a nonpolar organic solvent.

The 1D and 2D conductance histograms constructed from more than 5000 traces recorded in the presence of molecules **BQ₁₋₃** are shown in Figures 3.2a,b. We compare conductance of the molecules measured at low bias (100 mV) and high bias (> 250 mV) on the top and bottom of the figures, respectively. In both conditions, we observe distinct conductance peaks, attributable to the formation of stable single molecule junctions with each molecule. Importantly, we observe a conductance increase with increasing molecule length from 1 to 3 repeating quinoidal units. The most likely conductance of each molecule, determined from gaussian fits to the histograms, increases over two orders of magnitude upon a molecular backbone increase of ~5 Å (Figure 3.2c). To estimate the average rate of increase of conductance with length, we fit an exponential model to the experimental data in Figure 3.2c of the form:²⁷

$$G = G_c e^{-\beta L}$$

where G_c is the contact conductance, β is the conductance decay constant, and L is the length of the molecules. We obtain a negative beta value of -1.1 Å^{-1} for the low bias measurements. We note that the data deviate slightly from pure exponential growth as has been found previously for

cationic radicals.¹³ Nevertheless, the negative value of the extrapolated decay constant, $\beta < 0$, indicates a reverse conductance decay and anti-ohmic transport trends in these molecules in the absence of chemical or electric oxidation.

Measurements at high bias, 833 mV for **BQ**₁₋₂ and 250 mV for **BQ**₃, show a further enhancement in single molecule junction conductance compared with measurements at 100 mV, especially for $n = 2$ and $n = 3$ (Figures 3.2a,b bottom). The high bias voltages correspond to the conditions that can be sustained reliably by each molecular junction over several hours of data acquisition (see Appendix B for more details). We also observe that the distribution of measured conductance values for **BQ**₃ narrows at higher bias, which has been previously identified as a signature of near-resonant transport.²⁸ Increases in the conductance of **BQ**₂₋₃ at higher bias enhance the anti-ohmic characteristics, with a fit to the most likely conductance values yielding

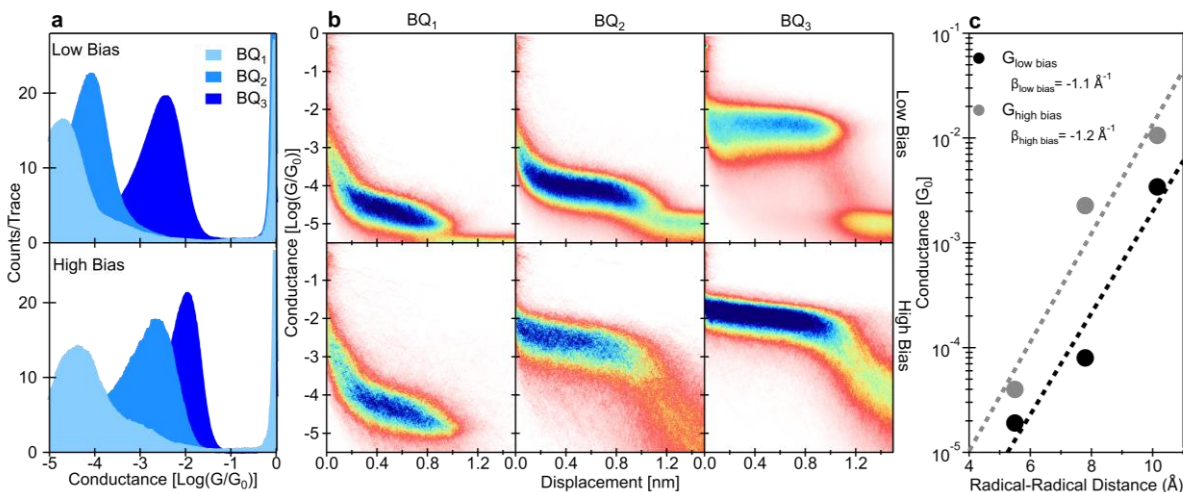


Figure 3.2. (a) Single-molecule conductance histograms of **BQ**₁₋₃ in BNP at low bias, −100 mV, in the top panel and high bias, −833 mV for **BQ**₁₋₂ and −250 mV for **BQ**₃, in the bottom panel. (b) Single-molecule 2D conductance vs displacement histograms of **BQ**₁₋₃ at low bias in the top three panels and high bias in the bottom three panels. (c) Calculated conductance from Gaussian fits to the peaks in Figure 2a for both low bias (black) and high bias (gray) with exponential fits given by the dashed lines.

a β of $-1.2 \text{ \AA}^{-1}$ (Figure 3.2c). This corresponds to a dramatic increase of nearly *three orders of magnitude* in conductance from $n = 1$ to $n = 3$.

To understand the voltage dependent conductance behavior of each molecule and estimate the position of the frontier electron orbitals relative to E_F , we perform single molecule current-voltage (IV) measurements by sweeping the voltage between the two electrodes while the molecule is held in the junction and recording the current using previously published protocols; additional details are provided in Appendix B.²⁹ IV histograms for **BQ**₁₋₃ (Figure 3.3a) are constructed from at least 5000 traces with the average IV curve, shown in white, calculated from gaussian fits to vertical slices at each voltage. The dashed black lines are linear curves shown for references. We observe that in all three cases, the molecular IV characteristics are non-linear at a range of biases probed here. For the shortest molecule, a linear current-voltage relationship is observed below $\sim 500 \text{ mV}$, but the current starts to increase exponentially above $\sim 600 \text{ mV}$, suggesting that at this higher bias, the probed voltage range of $\pm 300 \text{ mV}$ around E_F approaches a resonance feature associated with a frontier electronic state in the transmission spectrum of **BQ**₁. In the longer molecules, **BQ**₂ and **BQ**₃, the exponential increase sets in above 100 and 0 mV, respectively, indicating the presence of molecular resonances within narrower voltage ranges for the longer molecules. Overall, the IV curves for the three molecules indicate a decreasing distance to one of the frontier orbitals as the number of repeating fused benzene units increases, suggesting a smaller HOMO-LUMO energy gap, E_{gap} , in longer molecules.

We replot the averaged IV curves from Figure 3.3a as conductance and group them for direct comparison in Figure 3.3b. The sharp upturns in these conductance spectra correspond to the supra-linear regions of the IV curves noted above. Importantly, we observe that the conductance at low bias, which probes transport in the vicinity of the E_{gap} midpoint, follows anti-ohmic

behavior. This reverse, anti-ohmic conductance decay at all bias regimes is anomalous compared to transport trends through most single molecule junctions observed to date. The data confirms that the neutral acene-like materials display anti-ohmic behavior in their neutral state, even in mild and accessible experimental conditions.

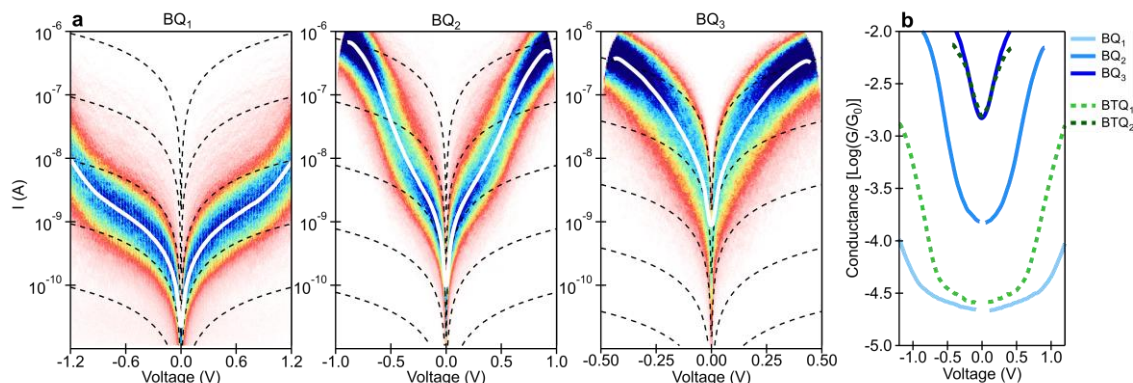


Figure 3.3. (a) Current-Voltage histograms for **BQ₁₋₃** from thousands of IV curves taken while holding each molecule between two Au electrodes. Dotted lines correspond to the linear grid lines and the white lines are calculated from the average of gaussian fits of vertical slices of each histogram IV histogram. (b) Fits of the conductance-voltage histograms derived from the current-voltage histograms for **BQ₁₋₃** and **BTQ₁₋₂**.

We develop a 1D-SSH model appropriate for describing the contribution of the diradical character to the electron transport properties of quinonic molecular systems, such as **BQ_n** studied here in order to probe the mechanism behind anti-ohmic transport. In prior studies, the 1D-SSH, or tight-binding, Hamiltonian was used to describe electronic phases in linear chains such as polyenes or polymethine, which are molecules composed of a series of alternating single and double bonds, as shown in the purple path through **BQ₁** (Figure 3.4a).^{16,30} In a Hamiltonian formalism, the double and single bonds correspond to a large and small coupling energy respectively.⁷ For linear molecules, a single parameter δ was used to parameterize the transition between resonance structures, with $1 > \delta > -1$, spanning the range from zero diradical character $y_0 = 0$, to full diradical, $y_0 = 1$, respectively. For this parameterization, the coupling energy terms t_1

and t_2 are set to scale as $t_0 e^{\pm a\delta}$, with t_0 and a set to 1, resulting in the purple bonds alternating between double (high coupling) and single (low coupling) as δ goes between -1 ($t_1 < t_2 \rightarrow$ diradical) and 1 ($t_1 > t_2 \rightarrow$

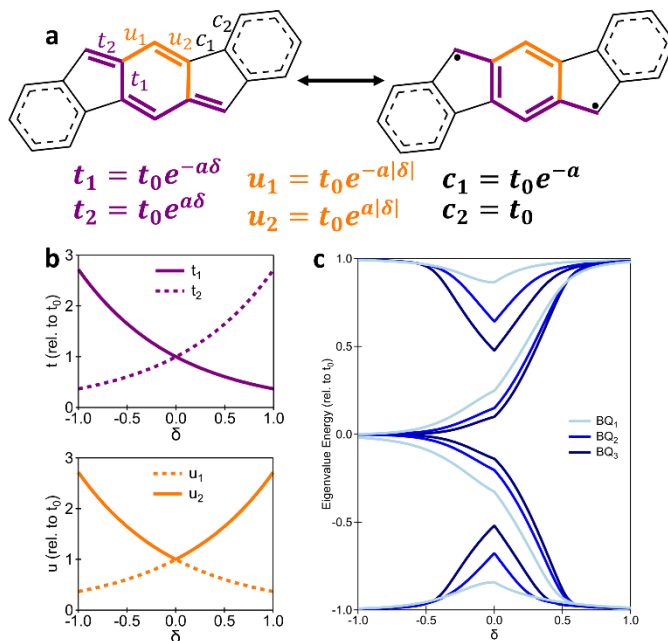


Figure 3.4. Modification to the 1D-SSH Model for polycyclic molecular systems like **BQ_n**. (a) Description of the coupling energies ($t_0, t_1, t_2, u_1, u_2, c_1, c_2$) describe by diradical parameter (δ) and scaling parameter (a) used in the modified 1D SSH Hamiltonian. (b) Graphical representation of the energies t_1, t_2, u_1, u_2 . (c) The calculated band structure for **BQ₁₋₃** as a function of δ .

polyene).^{7,16} Intermediate values of δ describe intermediate scenarios, with $\delta = 0$ corresponding to a delocalized electronic state with 50% diradical character. As fully diradical polyenes ($\delta = -1$) are not stable and thus experimentally inaccessible, this earlier model can instead be applied to cumulenes or polymethines, which are linear carbon chains with a fully delocalized state well approximated by the $\delta = 0$. In cumulenes and other molecular chains, conductance was found to remain nearly constant as the molecular length increased.^{16,31–33}

Here, we implement a modified 1D-SSH Hamiltonian for polycyclic systems. We include an additional set of hopping parameters, u_1 and u_2 , shown in orange (Figure 3.4a), which are not entirely independent from t_1 and t_2 . For example, unlike the purple bonds, the orange bonds do not flip from double to single in the transition from $\delta = -1$ (diradical aromatic) to $\delta = 1$ (closed-shell quinone). Instead, these bonds are described by alternative coupling terms (u_1, u_2) given by $t_0 e^{\pm a|\delta|}$ and they retain the same bond order value at $\delta = -1$ as at $\delta = 1$ (Figure 3.4b). Critically, using this parameterization, all bonds t_1, t_2, u_1 and u_2 are equivalent when $\delta = 0$ and the molecule is in a fully delocalized state. The delocalized benzene ring at the extrema of the molecules are described as constants (c_1, c_2) independent of δ , in agreement with previous experimental characterization of these systems.^{20,23,25}

Using this model, we calculated the eigenvalues near E_F as a function of δ (Figure 3.4c). As expected, the electronic structure transitions between the quinone ($\delta = 1$) and diradical ($\delta = -1$) states as the range of δ is scanned. As in the polyene system, here we observe a wide bandgap in the quinone structure, which closes as the molecule become a diradical.³⁴ These results confirm that our modification to the 1D-SSH model preserves the characteristic of the 1D topological insulators state at $\delta = -1$, with $E_{\text{gap}} \rightarrow 0$ in this limit.

To model transport in the **BQ_n** series, we convert the unitless 1D-SSH model above to a realistic energy scale characteristic of sp^2 systems containing alternating double bonds. We use established double-bond coupling energy parameters for conjugated systems and the observed bond-orders in such systems to fit t_0 and a .^{7,35,36} We obtain $t_0 = 2.7\text{eV}$ and $a = 0.08$ (Appendix B). Establishing this realistic 1D-SSH parameterization allows for the conversion of the reported diradical character y_0 to δ as $\delta = -2y_0 + 1$. We note that the previously measured diradical character of BQ_{1,2,3} correspond to $\delta = 0.4, 0$ and -0.2 , respectively (Figure 3.5a).

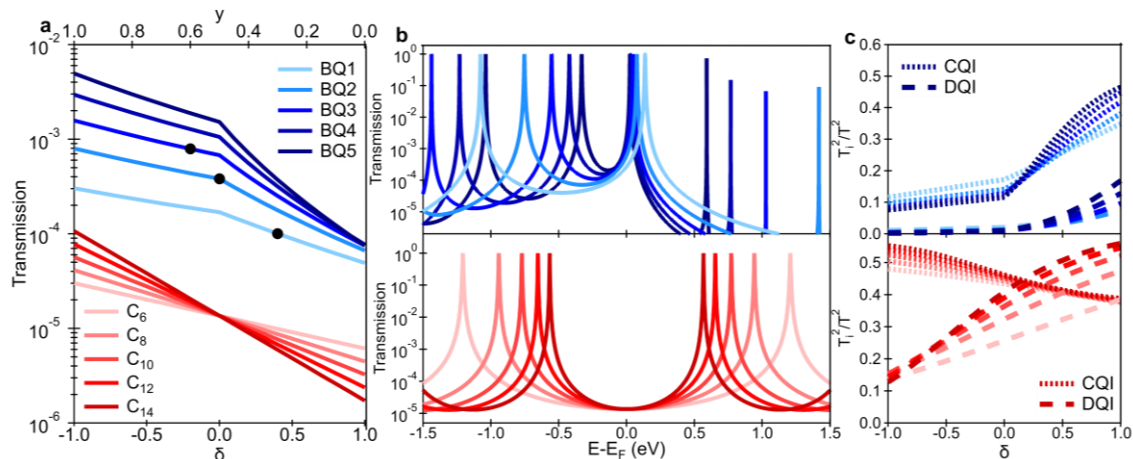


Figure 3.5. Extreme anti-ohmic behavior of acene-like systems is due to quantum interference effects. (a) Calculated transmission at $E-E_F = 0$ eV of **BQ_n** and **C_n** series as a function of diradical character. (b) Transmission curves for **BQ_n** (top) and **C_n** series (bottom) for the case $\delta = 0$. (c) Contribution of constructive quantum interference (CQI, dotted) and destructive quantum interference (DQI, dashed) to the total transmission for **BQ_n** and **C_n** series as a function of δ .

We use the wideband limit within the non-equilibrium Green's function (NEGF) approach described previously and in the Appendix B to calculate the transmission of molecules **BQ_n** as a function of δ and compare them to the standard polyene (polyacetylene) case, **C_n** (Figure 3.5a).^{16,37,38} We calculate the polyene transmission using the standard 1D-SSH model with the realistic parameterization described above. In both cases, we observe that predicted conductance depends both on the diradical character δ and on the length of the molecular wire (Figure 3.5a). Importantly, however, we observe that in the case of the polycyclic quinoidal systems studied here and plotted in blue, transport is predicted to be anti-ohmic at *all* values of δ . Our model predicts that even in the closed-shell $\delta = 1$ case, molecules of different length will follow modest reversed conductance decay. We note that this expectation for closed-shell polycyclic molecules is consistent with recent observations of non-decaying conductance trends

in porphyrin wires.^{39,40} This prediction for polycyclic molecules is in direct contrast to the linear polyene chains, C_n , plotted in red, where transport is predicted to decay exponentially with molecule length for $\delta > 0$ and becomes anti-ohmic only in the experimentally inaccessible regime of $\delta < 0$. These predictions are consistent with prior work. For example, for polyenes, at $\delta = 0$, transmission in Figure 3.5 (bottom) is independent of length, in agreement with experimental measurements of cumulene and polymethine wires.^{32,33,41,42}

In contrast, for the BQ_n series, characterized by an n and δ value marked by black points in Figure 3.5a, the qualitative predictions of conductance enhancement match well to our experimental measurements. At the Fermi energy, the enhancement of BQ3 over BQ1 conductance predicted by the model is a factor of ~ 8 , but at ~ 50 mV of bias voltage, it grows to a factor of ~ 100 , which is in agreement with measurements at low bias in Figure 3.2. We note that the model does not account for electrostatic changes due to electrode shape or solvent environment, so the predicted energy alignment cannot be expected to match the experiment exactly. As the intermediate diradicals BQ_n have a small energy gap due to the edge state contributions, these slight variations will result in large deviations of measured conductance from predicted values. However, we note that the essential features and trends in the transmission calculated using the 1D-SSH agree well with the more computationally expensive density functional theory (DFT)-based transmission calculations of relaxed junction geometries (Figure B23), in agreement with previous theoretical calculations.^{43,44} Our results suggest that the 1D-SSH one-electron model of the π system captures the experimentally observed anomalous conductance enhancement in the BQ_n series.⁴¹

Unlike many-body correlations, quantum interference (QI) among the frontier orbitals is included in the one-electron 1D-SSH formalism and is thus a candidate mechanism for the

distinct conductance phenomena observed here in the **BQ_n** molecules. Previous work shows that QI effects can be explained by symmetry considerations of frontier MOs. To investigate the contribution of QI to transport trends in diradicals, we first compare the transmission spectra of polyenes and polycyclic systems at $\delta = 0$ calculated using the 1D-SSH (Figure 3.5b). We observe that in both series, the E_{gap} shrinks as the molecules grow longer, as expected from basic considerations of energy spacing with system size. However, for polyenes, the zero-bias conductance at E_F , remains constant, even as the band-gap closes, as was discussed above. This feature is a signature of destructive quantum interference (DQI) between the frontier orbitals.⁹ In fact, ohmic conductance decay observed in the majority of polymeric molecular wires can be attributed to DQI, which counteracts the decrease in E_{gap} at longer lengths to cause dips in transmission at E_F . In contrast, the predicted zero-bias transmission in **BQ_n** grows with molecule length concomitantly with the closing of the band-gap, suggesting that DQI is a less significant factor in the polycyclic diradical system.

We calculate the CQI and DQI contributions explicitly using methods reported previously using the output of the 1D-SSH model developed here (Figure 3.5c).⁹ We observe very distinct QI trends in the linear polyene and polycyclic molecular systems. In polyenes **C_n**, the transition from anti-ohmic to ohmic conductance coincides with an increase in DQI and a decrease in CQI as δ goes from -1 to 1 .⁴⁵ Specifically, DQI (CQI) increases (decreases) in magnitude from $\sim 20\%$ ($\sim 45\%$) to $\sim 40\%$ ($\sim 35\%$) of the total transmission. At $\delta=0$, CQI and DQI approximately cancel. In contrast, for the **BQ_n** series, the CQI contribution dominates at all regimes and grows from $\sim 20\%$ to $\sim 40\%$ with increasing δ , while the DQI fraction increases slightly but remains below $\sim 20\%$. These trends corroborate and explain the origin of the extreme anti-ohmic behavior observed in **BQ_n** compared to other polymers with diradical character.

Critically, we see that in the case of polycyclic systems, increasing diradical character coincides with increasing CQI, providing mechanistic insight into engineering conducting molecular wires.

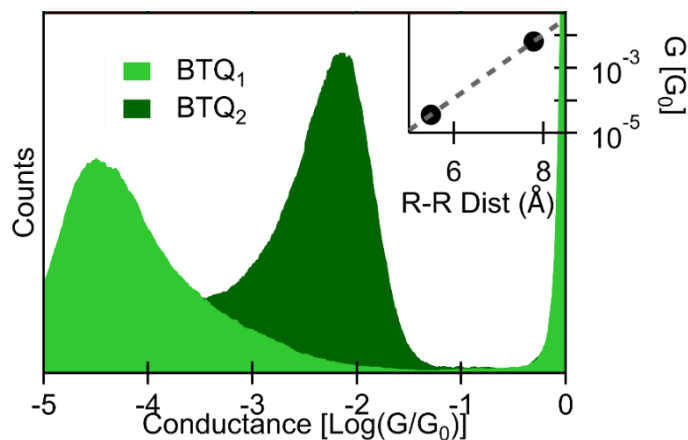


Figure 3.6. Engineering enhancement in anti-ohmic conductance through synthetic control. Single-molecule conductance histograms of **BTQ**₁₋₂ (structures shown in Figure 1a) in BNP at –500 mV. Inset: most likely conductance of **BTQ**₁₋₂ determined from the histograms plotted against radical-radical (R-R) distance results shows inverse decay and a β value of $-2.3/\text{\AA}$.

To demonstrate the power of this experimental system, we measure the conductance of a derivative of the **BQ** series with benzothiophene elements fused to the benzoquinodal core with the thiophene S atoms in an *anti*- orientation to the diradical site (Figure 3.1a).⁴⁶ We term these the **BTQ**_n and note that the backbone length of the quinoidal cores and structure of these molecules is identical to the **BQ**_n. **BTQ**_n have been previously shown to have higher diradical character than **BQ**_n for the same number of fused benzoquinone units n (Figure 3.1a).²³ We measure the conductance of **BTQ**_n for n = 1, 2 at a bias V = 500 mV (Figures 3.6 and B25). We observe that conductance of this series is higher than in **BQ**_n of identical length, particularly for the longer **BTQ**₂ molecule. The IV curves for the **BTQ**_n series are plotted in Figure 3.3b for direct comparison to **BQ**_n. Significantly, the conductance of **BTQ**₂ is enhanced compared to **BQ**₂ by at least one order of magnitude at all bias regimes, despite their identical radical-radical and

overall lengths. We also note the inferred smaller E_{gap} for **BTQ₂** compared to **BQ₂** as a result of increasing diradical character. Overall, we achieve a striking reverse conductance decay in the **BTQ_n** series, with a β value of $-2.3 \text{ \AA}^{-1}$ (Figure 3.6 inset).

3.3 Experimental Methods

STM-BJ measurements are performed by repeatedly crashing and pulling out an Au tip from an Au substrate in the presence of molecules in solution, with a fixed bias across the two electrodes while recording the current, voltage, as well as the electrode displacement. Conductance is calculated at every displacement point during pull out by dividing current by voltage to generate a conductance trace. Plateaus in the conductance trace indicate formation of persistent junction configurations with a well-defined conductance. We statistically analyze the measurements by constructing 1D conductance histograms and 2D conductance vs displacement histograms from thousands of individually recorded raw data traces as detailed previously.^{19,47,48} Reproducible molecular conductance plateaus result in peaks in the histograms in the conductance range below $1 G_0$.

3.4 Conclusions

We have identified a class of molecular organic diradicals with a fused polycyclic core, where the equilibrium electronic structure is optimal for conductance enhancement at longer molecular lengths. We develop a 1D-SSH model which provides mechanistic insight into the source of conductance enhancement and identify quantum interference effects as key to anti-ohmic transport inherent to these systems. Crucially, we apply this understanding to demonstrate how molecular acene-like system can be synthetically altered and designed to further tune the

diradical character, bandgap and QI to engineer molecular junctions with higher conductance and increasing anti-ohmic trends. These results set the stage for future engineering of conductance enhancement and other functional behaviors in cyclic diradicals based on an acene core.

CHAPTER IV

A QUEST FOR EXTENDED SCAFFOLDS AND NEW DIRECTIONS

This chapter includes unpublished and co-authored material. The synthetic procedures detailed in this chapter were developed by Efrain Vidal Jr. and Dr. Joshua E. Barker. Michael P. Miller contributed substantially to the development of standard synthetic protocols concerning *n*-alkylbenzene intermediates and stepwise Suzuki cross-coupling. Computational work was done by Prof. Ryohei Kishi at Osaka University. Transformations on alkoxy-substituted diones will be completed by the Kaleta group at the Institute of Organic Chemistry and Biochemistry of the CAS. The text in this chapter was written by Efrain Vidal Jr. with assistance from Prof. Michael M. Haley.

4.1 Introduction

Logical molecular design and precise synthetic control are vital for synthetic chemists to explore a wide range of molecular properties. Polycyclic conjugated hydrocarbons (PCHs) have received great attention in this regard and are desired for electronic applications due to their tunable HOMO/LUMO energy gaps, redox potentials, and optical absorption profiles. Commonly employed structural features to achieve these optoelectronic properties include high degrees of conjugation¹⁻⁴, donor and acceptor groups⁵⁻⁷, angular ring fusion⁸⁻¹⁰, and non-alternant ring fusion¹⁰⁻¹⁵. Chapter I of this dissertation demonstrates the strategic use of these motifs across a large library of molecules; the latter feature in particular causes a $4n$ π -electron count and pro-aromatic unit giving rise to antiaromatic electronic configurations that cross over into the radicaloid domain. As discussed in Sections 1.2 and 1.3, magnetic properties begin to

develop due to the open-shell character afforded by these pro-aromatic quinoidal units. The molecules studied so far in this dissertation have only included one quinoidal unit within their backbone; however, this chapter primarily aims to blueprint extended scaffolds that contain two pro-aromatic moieties along with one additional case of a potential molecular motor.

Mixing of doubly excited electronic configurations allows antiaromatic molecules to adopt open-shell character to different degrees and is aided by pro-aromatic quinoidal motifs (see Section 1.1). This configurational mixing has been largely explored in diradical systems, but great interest has grown in accessing polyradical character with the hope of expanding on magnetic behavior and spin properties of small molecules.^{16–19} Tetraradicaloids have become

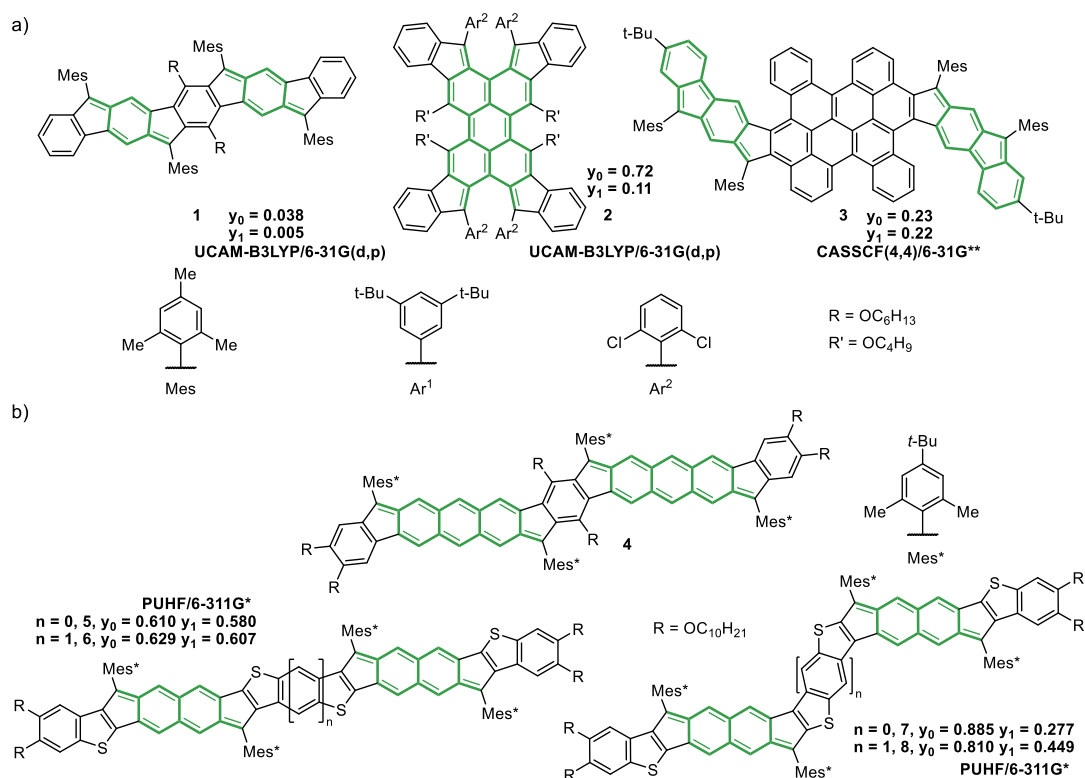


Figure 4.1. Molecular structures of a) reported tetraradicaloid examples with corresponding y_0 and y_1 values and b) proposed tetraradicaloids based on AQD and NQD with NOON analysis for 5–9. Functional and basis sets are included as these vary among research groups which could invalidate comparisons. Pro-aromatic units are highlighted in green.

new targets to access quintet spin states in addition to the commonly observed singlet and triplet spin-states.^{20–26} Several examples have been reported where two diradicaloids are fused about an aromatic spacer to make non-macrocyclic dimers, of which a small selection (**1–3**) is shown in Figure 4.1a.^{27–29} Inspired by this approach, we designed π -ladder type tetraradicaloids **4–9** utilizing 2,6-anthroquinodimethane (AQD) and 2,6-naphthoquinodimethane (NQD) scaffolds seen in previous chapters (Figure 4.1b).

Similar to evaluating diradical character with DFT calculations, tetraradical character can be theoretically probed by natural orbital occupation number (NOON) analysis. NOON estimates occupation of the lowest unoccupied natural orbital LUNO and the unoccupied natural orbital LUNO+1 as y_0 and y_1 values corresponding to diradical and tetraradical character, respectively.^{30–32} The open-shell character in **1–2** is largely dominated by diradical contributions with weak tetraradical contribution according to NOON values, but **3** showcases modest contribution from both values. Calculating y_0 and y_1 values for **4** has proven non-trivial; however, it is expected to exhibit open-shell characteristics due to the strong diradical character of the monomeric diindenoanthracene DIAn ($y_0 = 0.623$)³³. Successful calculation of diradical and tetraradical character for indenoindenodibenzothiophene (IIDBT) containing π -ladders **5–8** indicate strong tetraradical character for internal *anti*-isomers **5** and **6** whereas **7** and **8** are dominated by diradical character on account of their overwhelming y_0 values. Despite the different levels of theory to obtain these NOON values, the high tetraradical character predicted here has motivated our synthesis of π -ladders **4** and **5** whose progress is detailed in Section 4.2.

Another approach to dimerization is tethering both monomers to a central spacer, often an aromatic unit, instead of fusing the entire backbone (Figure 4.2). This strategy establishes

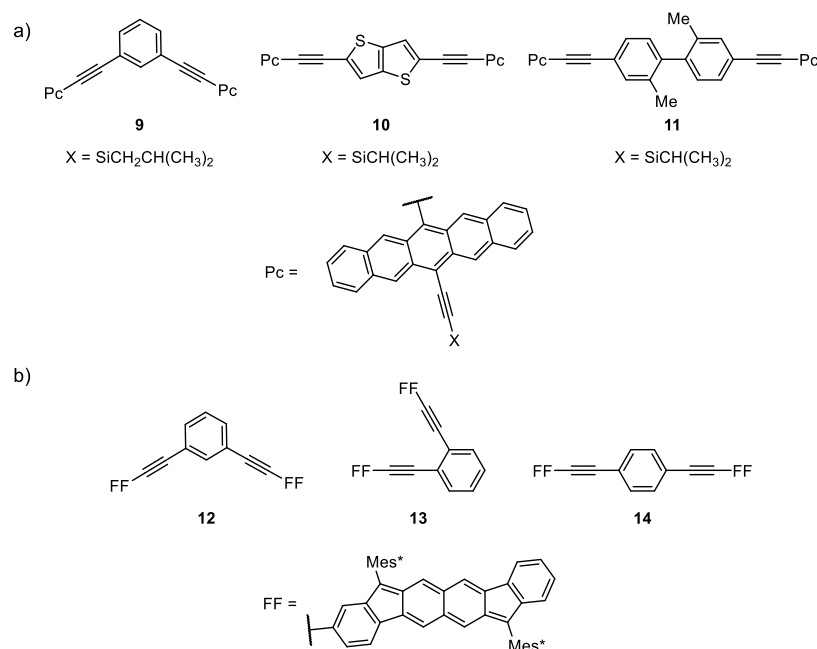


Figure 4.2. Selection of a) reported TIBS-(ref. 39) and TIPS (ref. 40)-pentacene dimers featuring varying π -spacers and b) target fluorenofluorene (FF) dimers isomers.

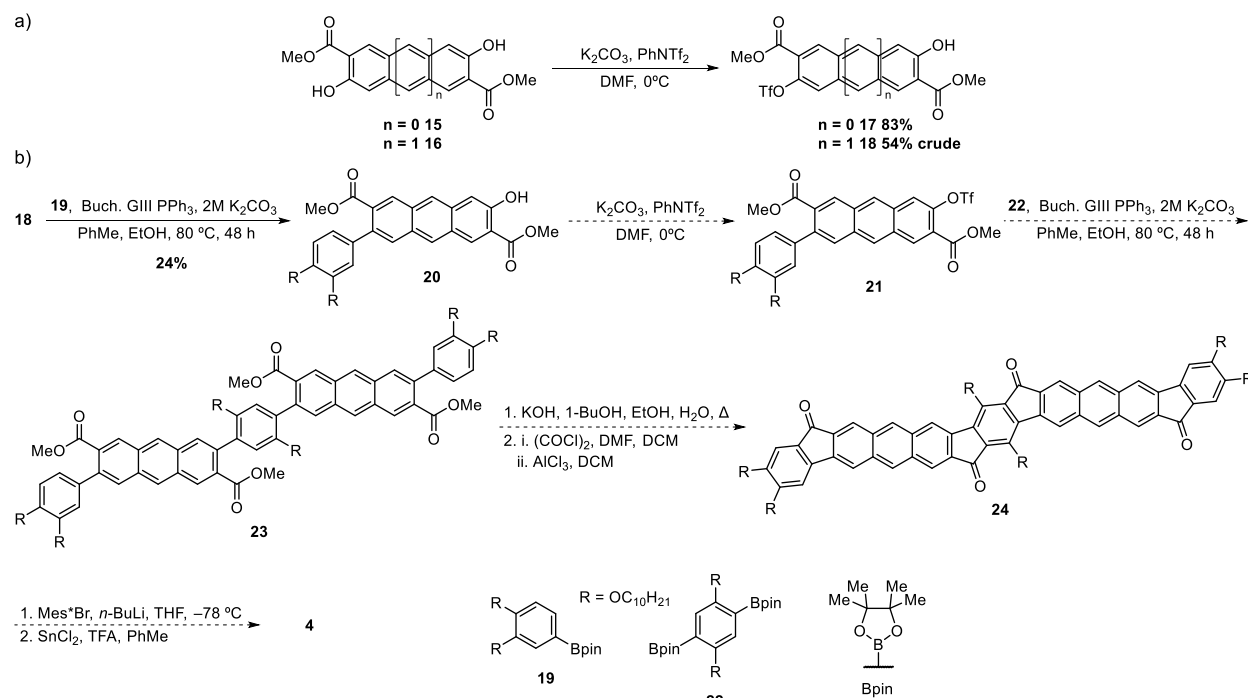
rotational degrees of freedom about the tethering bonds between PCHs and the spacer which provides an opportunity to probe the balance between through-bond electronic coupling and through-space electronic coupling.^{34,35} These coupling modes are influential in spin-dynamic processes such as intramolecular singlet fission (iSF) where a photoexcited singlet-state converts into two triplet-states across two chromophores when energy is conserved according to $0 \leq E_{S1} - 2E_{T1}$.^{36–38} Such energy conservation has been observed in tethered acene dimers with pentacene being the most popular chromophore studied (Figure 4.2a). Theoretical studies of non-alternant structures such as indenofluorene homologues and open-shell species estimate singlet- and triplet-state energies that satisfy $0 \leq E_{S1} - 2E_{T1}$ motivating our efforts toward synthesizing dimers **9–11** to assess the potential of iSF between antiaromatic chromophores (Figure 4.2b).^{41–46} The extent of these efforts is outlined in Section 4.3.

Lastly, a very early collaboration has emerged between the Haley and Kaleta groups with the goal of constructing molecular motors featuring non-alternant PCH backbones. Section 4.4 discusses the synthesis of key intermediates diketone **46** and **49** (Scheme 4.5). The syntheses described herein have not been completed, so only the progress toward target molecules will be detailed.

4.2 Synthesis Toward π -Ladder Type Tetraradicaloids

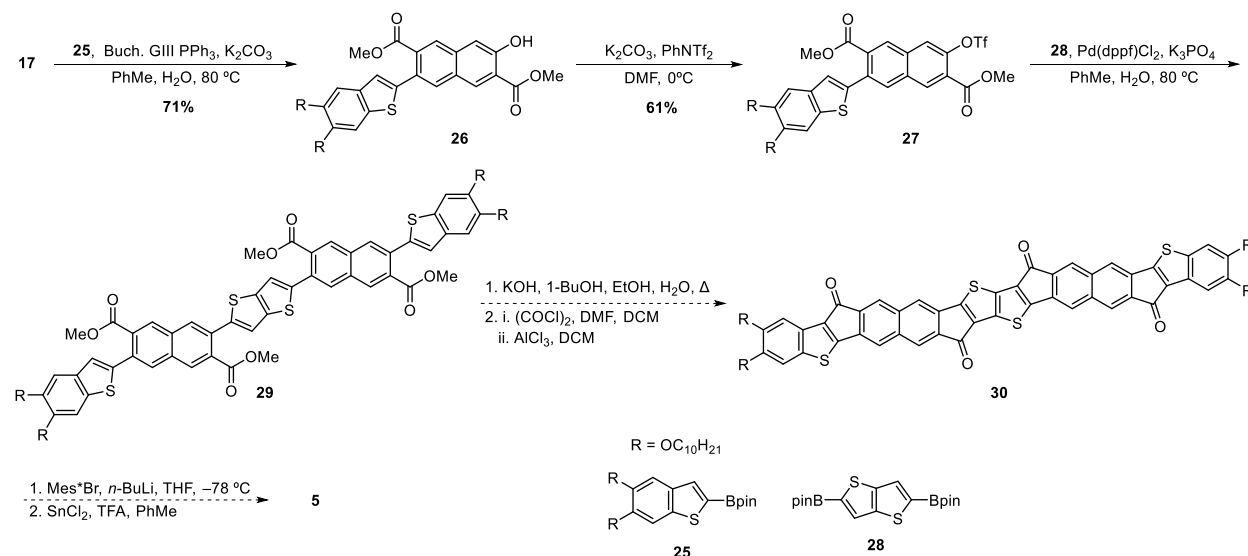
π -Ladders **4** and **5** were chosen as the initial extended radicaloids to prepare. Tetra-radicaloid **4** would establish a hydrocarbon-based reference like DIAn in the series of AQD based diradicaloids, and **5** would provide a benchmark for molecules containing NQD moieties. The synthetic routes for both ladders follow a modular synthesis adapted from the Haley lab

Scheme 4.1 Synthesis of a) common asymmetric mono-triflate intermediates and b) π -ladder **4**.



strategy “inside-out” I illustrated in Figure 1.4. A key distinction here is the use of asymmetric mono-triflates accessed through controlled triflation of dihydroxy starting materials where monotriflate **17** and **18** were employed for ladders **5** and **4**, respectively (Scheme 4.1a).

Scheme 4.2 Synthesis of bis-IIDBT **5**.

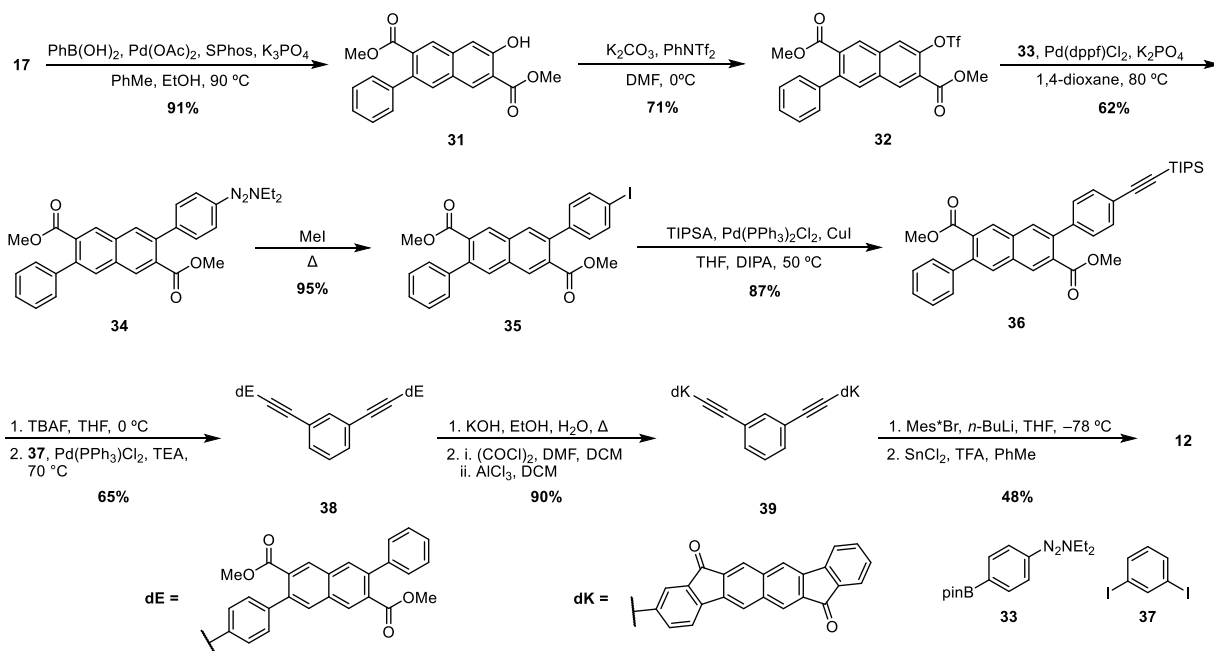


The initial step towards **4** was a Suzuki cross-coupling between **18** and phenyl boronic acid ester **19** to provide diester **20** (Scheme 4.1b). Subsequent triflation sets up what would be a two-fold Suzuki cross-coupling resulting in tetra-ester **23**. The following saponification and Freidel-Crafts acylation would then yield tetra-ketone **24**. After a four-fold nucleophilic addition of bulky Mes* groups, reduction with SnCl₂ would afford bis-DIAN ladder **4**. A similar sequence of transformations was drafted to construct bis-IIDBT ladder **5** where stepwise Suzuki reactions onto triflates **17** and **27** yields tetra-ester **29** (Scheme 4.2). Following the saponification and Friedel-Crafts reaction on **29**, tetra-ketone **30** would then be subjected to nucleophilic attack and permit the final reduction.

4.3 Synthesis Toward Covalent Dimers

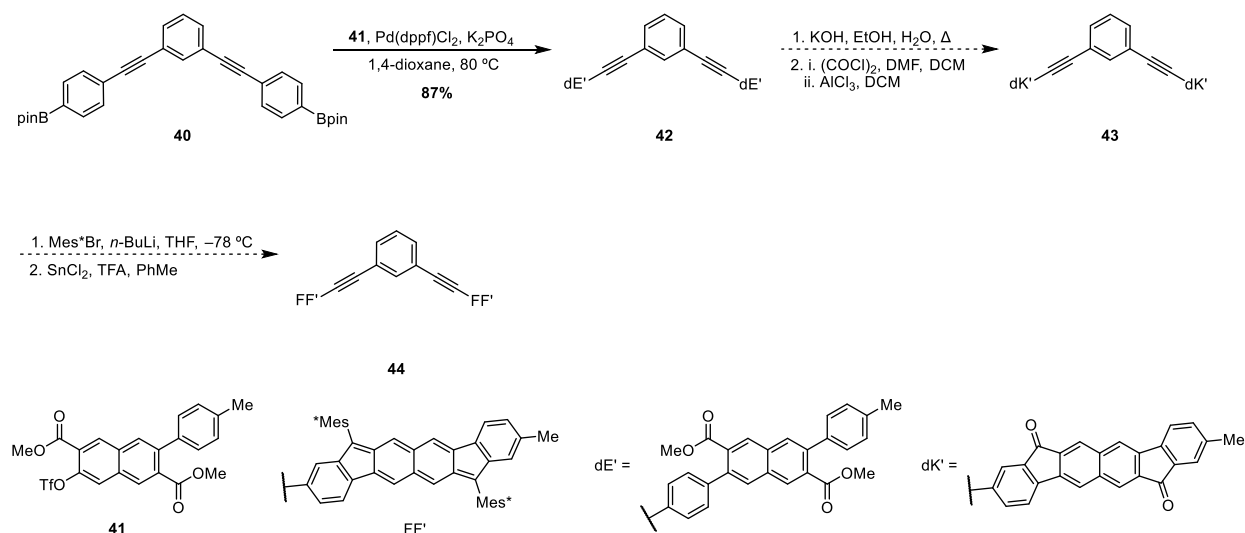
The synthesis of *m*-isomer **12** was investigated first due to an expected strong through-space coupling between the tethered π -systems. Stepwise cross-coupling from monotriflate **17** leads to diester **34** where phenyl and *p*-phenyl triazene substituents occupy the 3 and 7 positions (Scheme 4.3). Treatment of **34** with methyl iodide produces aryl iodide **35**, which is then cross-coupled with (trimethylsilyl)acetylene under Sonogashira conditions to install the ethynyl tethering group. Subsequent deprotection of ethyne **36** and Sonogashira cross-coupling with diiodobenzene afforded tetra-ester **38**. Traditional strategies can then be employed where saponification and Friedel Crafts acylation provide tetra-ketone **39**. Finally, nucleophilic addition of kinetic stabilizing groups and Sn(II) reduction yield *m*-dimer **12**.

Scheme 4.3 Synthesis of *m*-dimer **12**.



Optimization of reaction conditions for the two-fold Sonogashira cross-coupling in Scheme 4.3 proved difficult as incomplete conversion was encountered numerous times. Reassessment of synthetic strategies resulted in an approach involving diboronic acid ester substituted aryl ethynyl cores. Initial work on this route was done with the *m*-substituted core since ^1H NMR spectra could be compared to those obtained from the original synthesis (Scheme 4.4). Starting from a two-fold Suzuki cross-coupling of **40** with **41**, the resulting adduct would have been subjected to saponification and Friedel-Crafts acylation to obtain **43**. This route was ultimately left incomplete as the synthesis of target molecules in Section 4.2 took priority.

Scheme 4.4 Alternate synthesis of *m*-dimer **44**.

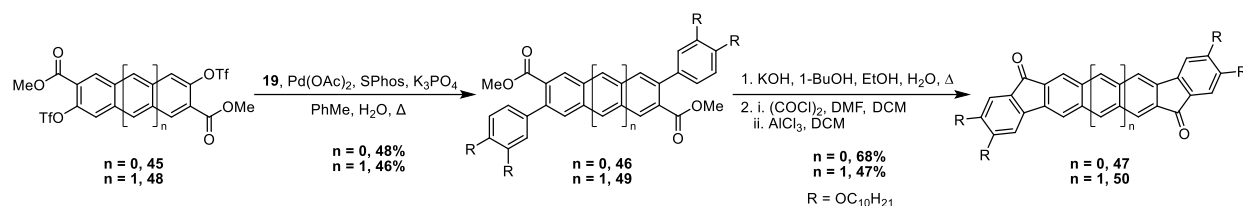


4.4 Synthesis Toward Indenofluorenone Based Motors

Molecular motors based on indenofluorenone analogues were synthesized from bistriflates **45** and **48** (Scheme 4.5). Suzuki cross-coupling with **19** resulted in diesters **46** and **49** which were then saponified and subjected to Friedel-Crafts conditions yielding diones **47** and **50**.

From these dione intermediates, the Kaleta at the Institute of Organic Chemistry and Biochemistry of the CAS will carry the synthesis forward to a set of molecular motors.

Scheme 4.5 Synthesis of key intermediates **47** and **50**.



4.5 Final Remarks

The works discussed in Chapters I–III demonstrate our thorough investigation into indeno[1,2-*b*]fluorene and its congeners. From initial forays to revitalized purpose in molecular devices, the work done in the Haley lab has provided remarkably refined synthetic strategies toward stabilized antiaromatic and open-shell molecules. Such strategies gave way to the work presented here in Chapter IV where the approach is altered to include sequential cross-coupling to reach for extended structures that are expected to show unique behavior. Evidently, progress toward the target molecules proposed has come to a halt; however, the blueprints have been drafted. These molecules now patiently wait for their creation to be fully realized.

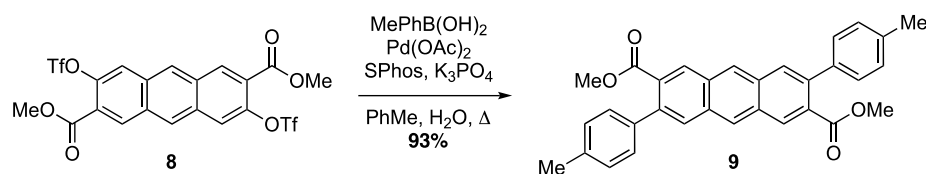
APPENDIX A

SUPPLEMENTARY INFORMATION FOR CHAPTER II

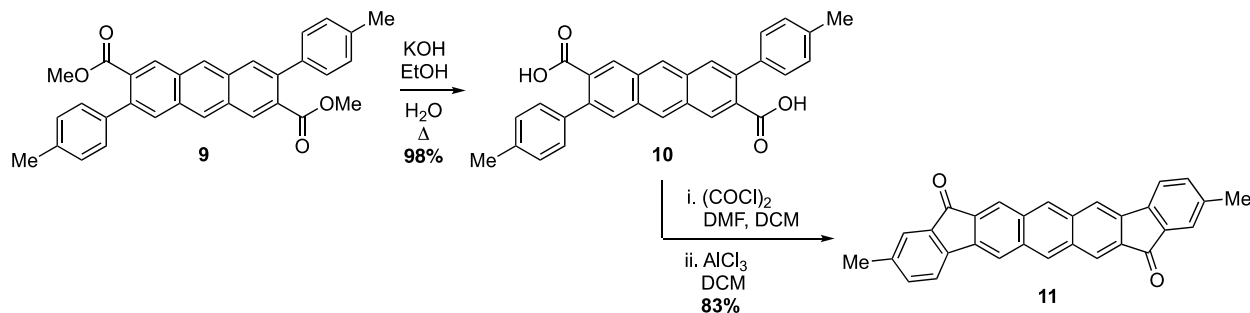
Appendix A is the supplementary information for Chapter II. Experimental details, experimental data, spectra and additional references relevant to the content of Chapter II are provided here.

Experimental Details

General. All air-sensitive reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk technique. Silica gel (240-300 mesh) was used for chromatography. All other reagents were purchased and used as received. NMR spectra were recorded on a Bruker Avance III HD 500 equipped with a Prodigy multinuclear cryoprobe (^1H : 500 MHz, ^{13}C : 126 MHz) or Bruker Avance III HD 600 equipped with a Prodigy multinuclear broadband cryoprobe (^1H : 600 MHz, ^{13}C : 151 MHz) NMR spectrometer at room temperature unless otherwise noted. ^1H and ^{13}C NMR chemical shifts (δ) are expressed in ppm relative to the residual non-deuterated solvent reference (CD_2Cl_2 : ^1H 5.32 ppm, ^{13}C 53.84 ppm; $\text{DMSO}-d_6$: ^1H 2.54 ppm, ^{13}C 40.45 ppm). UV-Vis spectrum was recorded on an Agilent Technologies Cary 60 UV-Vis spectrometer in HPLC grade CH_2Cl_2 . HRMS was recorded on a Waters GCT Premier orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer. Unless stated otherwise, all solvents and reagents were used as received. Diester **8**¹ and 4-bromo-3,5-dimethylthioanisole² were prepared as previously described in the literature.



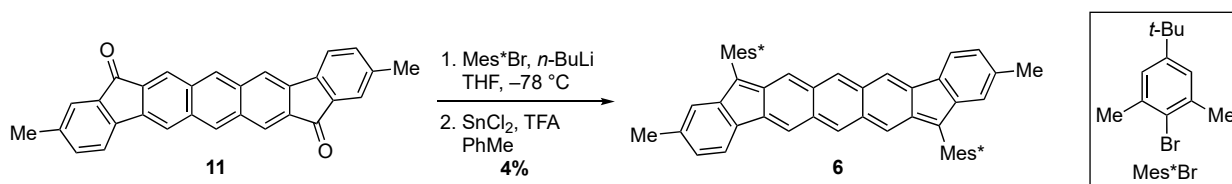
Diester 9. A three-neck round bottom flask fitted with a condenser containing bistriflate **8**¹ (165 mg, 0.279 mmol, 1 equiv.), 4-methylphenyl boronic acid (153 mg, 0.587 mmol, 2.1 equiv.), Pd(OAc)₂ (2.5 mg, 0.0112 mmol, 0.04 equiv.), SPhos (9 mg, 0.0224 mmol, 0.08 equiv.), and K₃PO₄ (178 mg, 0.838 mmol, 3 equiv.) was placed under a N₂ atmosphere. The solids were suspended in degassed PhMe (9 mL) and H₂O (1 mL) and then stirred at reflux (heating mantle) overnight. After cooling to room temperature, the mixture was quenched with H₂O to precipitate a gray solid. The resulting precipitate was filtered, washed with H₂O, and dried in an oven for 15 min. The solids were suspended in CH₂Cl₂ and filtered through a celite/silica plug then concentrated to yield the desired product **9** (123 mg, 93%) as a yellow solid. ¹H NMR (500 MHz, CD₂Cl₂) δ (ppm) 8.56 (s, 2H), 8.53 (s, 2H), 7.99 (s, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 3.76 (s, 6H), 2.44 (s, 6H). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂) δ 169.1, 138.6, 138.4, 137.6, 132.7, 131.9, 131.4, 130.9, 130.2, 129.3, 128.7, 128.6, 128.0, 52.5, 21.3. HRMS (TOF) *m/z*: [M⁺] Calcd for C₃₂H₂₆O₄ 474.1831; Found 474.1841.



Dione 11. EtOH (200 mL) and H₂O (50 mL) were added to a 500 mL round bottom flask containing **9** (1.62 g, 3.41 mmol, 1 equiv.) and KOH (3.06 g, 54.6 mmol, 15 equiv.). The flask was

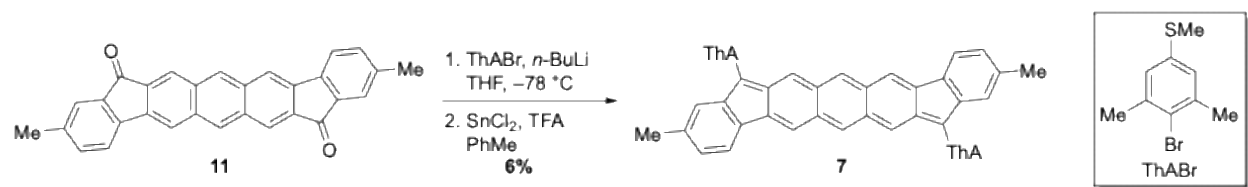
fitted with a condenser and stirred at reflux (heating mantle) open to air for 6 h. Once cooled, the volume of the reaction was reduced to approx. 15% and then acidified with a 3M HCl solution to form a precipitate. The solids were filtered, washed with water, and then dried in an oven to yield the crude diacid **10** (1.50 g, 98%) as a yellow solid. ^1H NMR (600 MHz, DMSO- d_6) δ (ppm) 8.82 (s, 2H), 8.54 (s, 2H), 8.09 (s, 2H), 7.39 (d, J = 8.0 Hz, 4H), 7.28 (d, J = 7.8 Hz, 4H), 2.38 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO- d_6) δ 183.7, 152.1, 151.5, 150.7, 145.93, 145.90, 144.7, 144.6, 143.6, 143.1, 142.5, 141.8, 35.1. HRMS (TOF) m/z : [M^+] Calcd for $\text{C}_{30}\text{H}_{22}\text{O}_4$ 446.1440; Found 446.1447.

To a suspension of diacid **10** (1.497 g, 3.35 mmol, 1 equiv.) in dry CH_2Cl_2 (135 mL) was added DMF (0.517 mL, 6.70 mmol, 2 equiv.) and oxalyl chloride (1.14 mL, 13.41 mmol, 4 equiv.). The reaction was stirred at room temperature overnight and the volatiles were then removed under reduced pressure. AlCl_3 (2.23 g, 16.76 mmol, 5 equiv.) was added to the flask and the solids were dissolved in dry CH_2Cl_2 (135 mL) then stirred at room temperature overnight. The reaction mixture was poured into an HCl-ice mixture to precipitate the crude dione. The solids were filtered and washed successively with H_2O , acetone, CH_2Cl_2 , and hexanes to yield dione **11** (1.37 g, 83%) as a pale orange solid. Similar to previously studied diones,³ the extremely poor solubility of **11** precluded acquisition of NMR spectra. HRMS (TOF) m/z : [M^+] Calcd for $\text{C}_{30}\text{H}_{18}\text{O}_2$ 410.1307; Found 410.1317.



Diindenoanthracene 6. Dry THF (11 mL) was added to an oven-dried 100 mL round-bottom flask containing 2-bromo-5-*t*-butyl-1,3-dimethylbenzene (Mes*Br, 0.531 g, 2.20 mmol, 8 equiv.) under a N₂ atmosphere. The mixture was cooled to −78 °C for 25 min and *n*-BuLi (0.826 mL, 2.5 M, 2.06 mmol, 7.5 equiv.) was added dropwise. After stirring at −78 °C for 30 min, the lithiated species was transferred by cannula to a suspension of dione **11** (0.113 g, 0.275 mmol, 1 equiv.) in dry THF (7 mL) at −78 °C. The reaction was stirred, warmed to room temperature overnight, and then quenched with sat. aqueous NH₄Cl. The mixture was extracted with CH₂Cl₂ (3x) and the combined organics were washed with brine, dried (MgSO₄), and concentrated *in vacuo*. The resulting crude oil was diluted with hexanes to precipitate the crude diol, which was used with no further purification.

The diol (~34 mg, 0.046 mmol, 1 equiv.) and SnCl₂ (35 mg, 0.185 mmol, 4 equiv.) were dissolved in dry degassed PhMe (10 mL) and catalytic trifluoroacetic acid (4 drops) was added. After stirring for 4 h, the mixture was filtered through a silica plug, eluted first with hexanes to remove toluene and then with CH₂Cl₂ to collect crude product. Organics were removed *in vacuo* and the resulting residue was precipitated with CH₂Cl₂/CH₃CN/EtOH to yield **6** (7.1 mg, 4%) as a poorly soluble deep blue solid. ¹H NMR (600 MHz, CD₂Cl₂) δ (ppm) 7.66–7.61 (m, 4H), 7.48 (s, 2H), 7.23 (s, 4H), 7.03–6.98 (m, 4H), 6.72 (s, 2H), 2.30 (s, 6H), 2.13 (s, 12H), 1.40 (s, 18H). The poor solubility of **6** precluded acquisition of ¹³C NMR data. UV-Vis (CH₂Cl₂) I_{max} (ε) 367 (91680), 389 (85940), 659 (65220), 715 (45600), 760 (sh, 13500) nm. HRMS (TOF) m/z: [M⁺] Calcd for C₅₄H₅₂ 700.4069; Found 700.4064.



Diindenoanthracene 7. Dry THF (40 mL) was added to an oven-dried 100 mL round-bottom flask containing 4-bromo-3,5-dimethylthioanisole (ThABr, 3.39 mL, 19.49 mmol, 8 equiv.) under a N_2 atmosphere and the mixture was cooled to $-78\text{ }^{\circ}\text{C}$ for 25 min. *n*-BuLi (7.55 mL, 2.5 M, 18.88 mmol, 6.8 equiv.) was added dropwise and the reaction was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. The lithiated species was added to a suspension of dione **11** (1.0 g, 2.43 mmol, 1 equiv.) in dry THF (60 mL) at $-78\text{ }^{\circ}\text{C}$. The reaction was stirred, warmed to room-temperature overnight, and then quenched with sat. aqueous NH_4Cl and extracted with CH_2Cl_2 (3x). The organics were washed with brine, dried over MgSO_4 , and concentrated *in vacuo*. The resulting crude oil was diluted with hexanes to precipitate the crude diol, which was used with no further purification.

The diol (approx. 770 mg, 1.07 mmol, 1 equiv.) and SnCl_2 (1.80 g, 9.51 mmol, 4 equiv.) were dissolved in dry degassed PhMe (80 mL) and stirred at $80\text{ }^{\circ}\text{C}$ for 3h. The reaction was cooled to room temperature and filtered through a silica plug, eluting with hexanes then CH_2Cl_2 to collect crude product. Organics were removed *in vacuo* and the resulting residue was precipitated with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}/\text{EtOH}$ to yield **7** (100 mg, 6%) as a poorly soluble deep blue solid. ^1H NMR (500 MHz, CD_2Cl_2) δ (ppm) 7.65–7.61 (m, 4H) 7.47 (s, 2H), 7.10 (s, 4H), 7.02–6.98 (m, 4H), 6.72 (s, 2H), 2.56 (s, 6H), 2.29 (s, 6H), 2.11 (s, 12H). The poor solubility of **7** precluded acquisition of ^{13}C NMR data. UV-Vis (CHCl_3) λ_{max} (e) 366 (80610), 388 (74530), 661 (58100), 716 (43940), 766 (sh, 12230) nm. HRMS (TOF) m/z : $[\text{M} + \text{H}^+]$ Calcd for $\text{C}_{48}\text{H}_{40}\text{S}_2$ 680.2571; Found 680.2566.

Copies of NMR Spectra



Figure A1. ¹H NMR spectrum (500 MHz) of **9** in CD₂Cl₂.

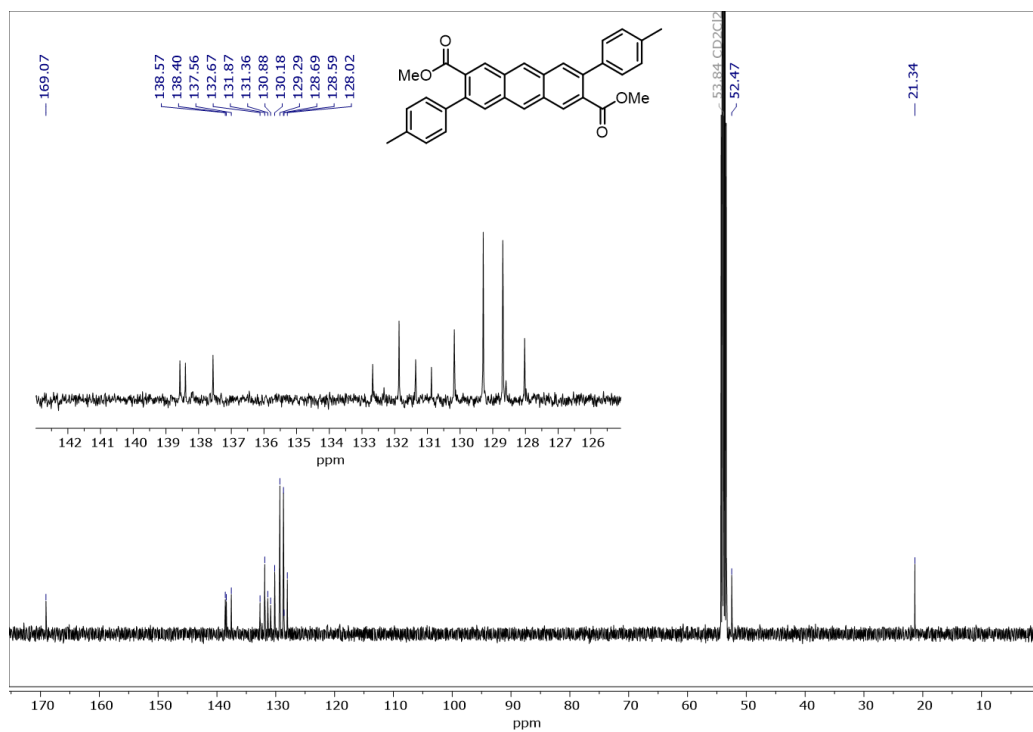


Figure A2. ¹³C{¹H} NMR spectrum (126 MHz) of **9** in CD₂Cl₂.

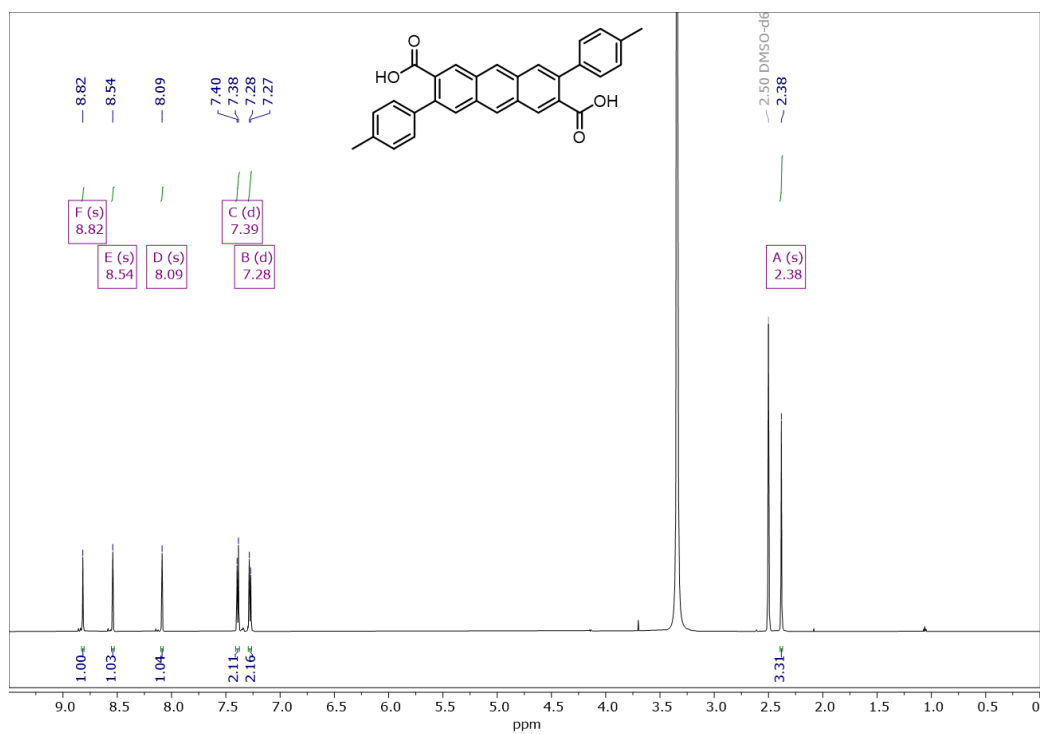


Figure A3. ¹H NMR spectrum (500 MHz) of **10** in DMSO-*d*₆.

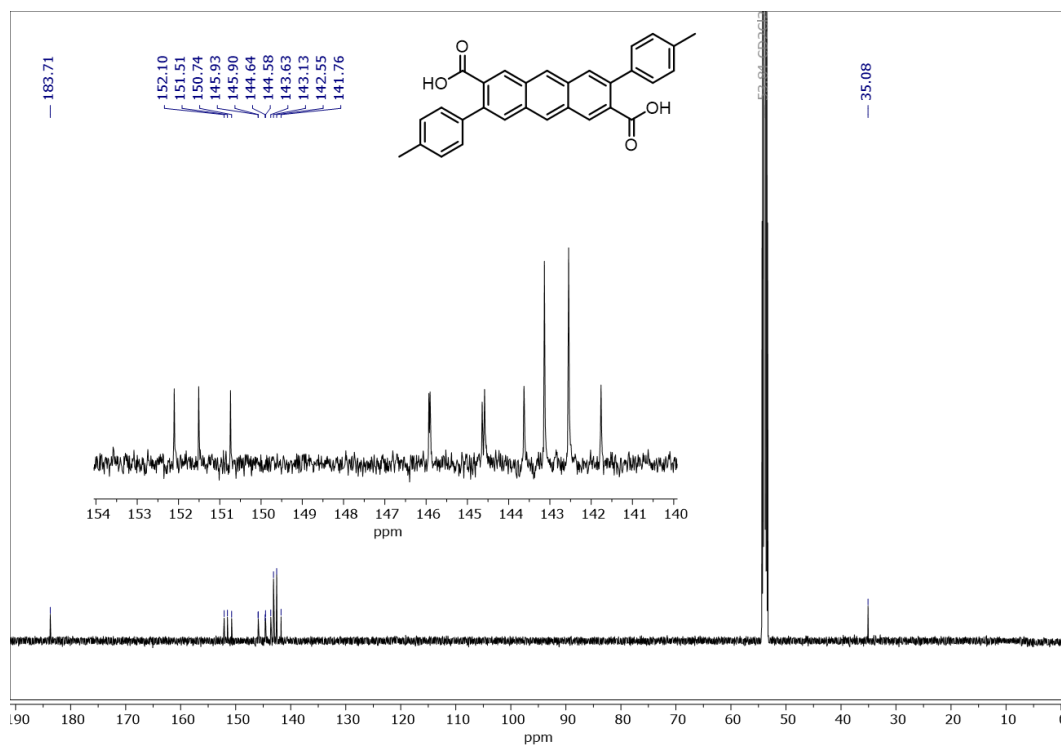
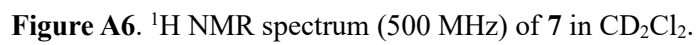
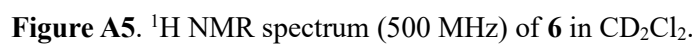


Figure A4. ¹³C{¹H} NMR spectrum (126 MHz) of **10** in DMSO-*d*₆.



Electronic Absorption Spectroscopy

UV-Vis spectra of **6** and **7** were recorded on an Agilent Technologies Cary 60 UV-Vis spectrometer in HPLC grade CH₂Cl₂. Spectrum for **1** has been previously reported.³

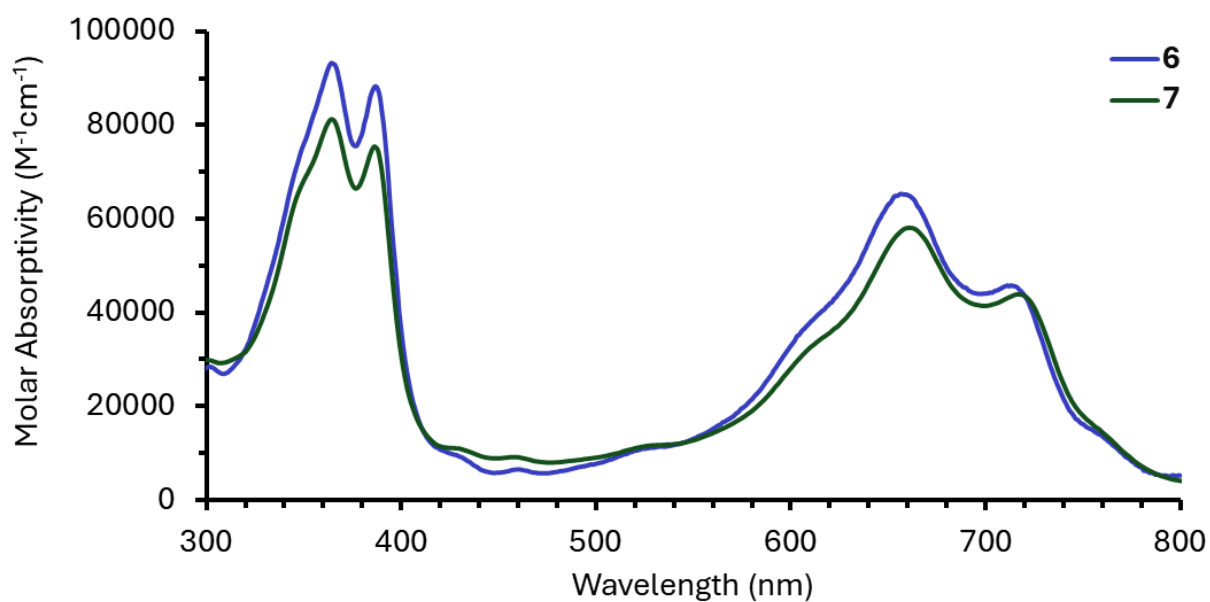


Figure A7. Molar absorptivity of DIAn **6** and **7** plotted against wavelength (nm) in CH₂Cl₂ (1.2×10^{-5} M and 1.1×10^{-5} M, respectively).

Cyclic Voltammetry

All electrochemical experiments were conducted with a 3-electrode geometry using a Biologic SP-50 potentiostat. Cyclic voltammetry (CV) for **6** and **7** was carried out in a degassed three-compartment electrochemical cell in CH₂Cl₂ with 0.1 M TBAPF₆ solutions using a glassy carbon (3-mm diameter) working electrode, a Pt counter-electrode, and a Ag wire as pseudo-reference electrode. The glassy carbon electrode was polished with a figure eight motion using Whatman Nuclepore Tack-Etch Membrane media from 1 μm, 0.25 μm, 0.1 μm and a fine alumina membrane. All other electrodes were treated with concentrated nitric acid to remove surface impurities. Potential was swept within 1.30 V to –2.00 V at 20 mV s^{–1} in the case of **6** and 1.70 V to –2.30 V at 50 mVs^{–1} for **7**. Ferrocene was used as an internal standard. Potentials were re-referenced to SCE using a value of 0.46 (V vs SCE) for the Fc/Fc⁺ couple in CH₂Cl₂. SCE = –4.68 eV vs. vacuum was used to approximate HOMO and LUMO levels.⁴ All CV experiments were done in a dry, three-neck round bottom flask under N₂ atmosphere. E_{1/2} values were calculated assuming $E_{1/2} \approx E_o' = (E_{\text{anodic}} + E_{\text{cathodic}})/2$ based on these observations for reversible couples. The approximate concentrations of the samples are ca. 2×10^{-3} M and 1×10^{-3} M for **6** and **7**, respectively.

Table A1. Reduction and oxidation half-wave potentials (V vs. SCE) and the corresponding electrochemically derived HOMO/LUMO energy gaps for **1**, **6**, and **7** obtained from cyclic voltammetry.

compound	E _{red1}	E _{red2}	E _{ox1}	E _{ox2}	E _{HOMO}	E _{LUMO}	E _{gap}
1 ^a	–0.81	–1.20	0.63	1.17	–5.32	–3.87	1.45
6	–0.96	–1.33	0.51	0.99	–5.19	–3.72	1.47
7	–0.89	–1.53	0.60	1.37	–5.33	–3.86	1.47

^aReference 3.

X-ray Crystallography

General. Diffraction intensities for **6** were collected at 173 K on a Bruker Apex2 single crystal diffractometer using MoK α radiation, 0.71073 Å. Space group was determined based on intensity statistics. Absorption correction was applied by SADABS.⁵ Structure was solved by direct methods and Fourier techniques and refined on F² using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. H atoms were refined in calculated positions in a rigid group model. All calculations were performed by the Bruker SHELXL-2014/7 package.⁶

Crystallographic Data for 6: C₅₆H₅₆Cl₄, M = 870.80, 0.19 x 0.18 x 0.13 mm, T = 173(2) K, Triclinic, space group P-1, a = 9.1807(13) Å, b = 9.3548(13) Å, c = 13.998(2) Å, α = 101.716(3)°, β = 96.684(2)°, γ = 99.004(3)°, V = 1148.9(3) Å³, Z = 1, D_c = 1.259 Mg/m³, μ (Mo) = 0.295 mm⁻¹, F(000) = 460, 2 θ _{max} = 60.78°, 19106 reflections, 6865 independent reflections [R_{int} = 0.0416], R₁ = 0.0667, wR₂ = 0.1818 and GOF = 1.020 for 6865 reflections (299 parameters) with I > 2 σ (I), R₁ = 0.1042, wR₂ = 0.2080 and GOF = 1.020 for all reflections, max/min residual electron density +0.538/−0.509 eÅ⁻³. CCDC-2361007.

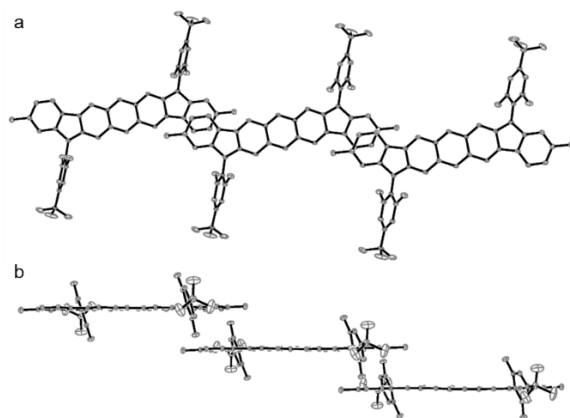


Figure A8. Depiction of terminal six-membered ring overlaps between molecules of **6** within solid-state packing from the (a) pi-face and (b) edge viewpoints. Hydrogens are omitted for clarity.

Removal of the two (triisopropylsilyl)ethynyl groups results in a change in the molecular packing of **6** versus that previously observed in **1**.^{3,9} The views in Figure S9 are along a normal to the average planes of the central part of the molecules. DIAn **6** forms a 1-D chain with π - π overlapping at the ends of the molecule core (mean plane distance of 3.36 Å). The nearest molecules of **1** are shifted and exhibit much less overlap, though the mean plane distance is slightly smaller (3.31 Å). The “voids” in the packing of **6** are “filled” by CH₂Cl₂ solvent molecules, whereas **1** has no voids/contains no solvent molecules.

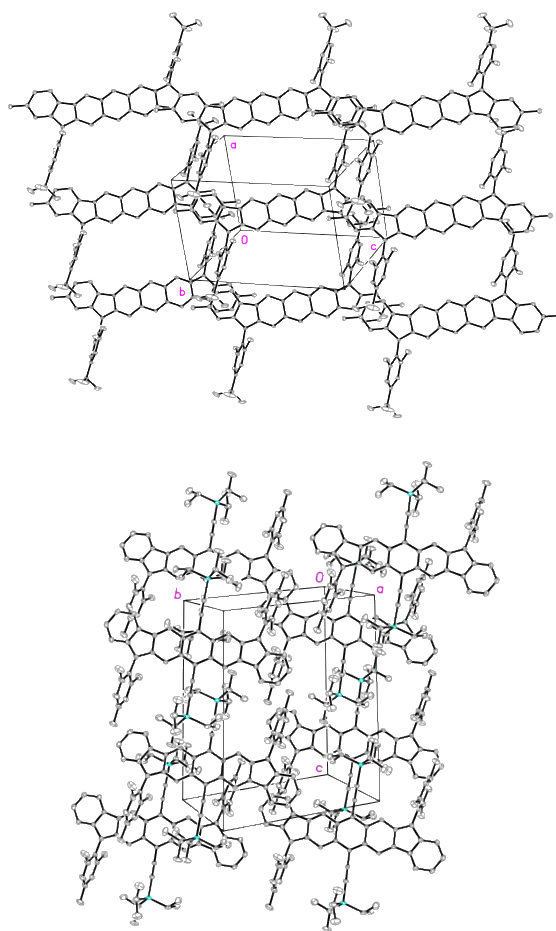


Figure A9. Comparison of the molecular packing of **6** (top) with that previously reported for **1** (bottom);^{3,9} the view is along the normal to the average plane of the central part of the molecules.

SQUID Magnetometry

Magnetic susceptibility measurements for **6** and **7** were performed with a Quantum Design MPMS-XL7 SQUID susceptometer. The magnetic measurements were performed in the 20-600 K temperature range with an applied field of 1 T using a sample space oven with the samples inserted in a 1.5 mm diameter aluminum foil cylinder. The susceptibility data were corrected for the same sample holder previously measured using the same conditions and for the diamagnetic contributions of the compound as deduced by using Pascal's constant tables.⁷ The magnetic measurements were fitted using the classical Bleaney-Bowers model for an antiferromagnetic $S = \frac{1}{2}$ dimer plus a monomeric $S = \frac{1}{2}$ impurity.⁸ This model reproduces satisfactorily the magnetic properties with $g = 2.0$ (fixed) with $J = -2242$ and -2313 K for **6** and **7**, respectively. These J values correspond to experimental ΔE_{ST} of -4.5 and -4.6 kcal mol⁻¹ for **6** and **7**, respectively, which is in good agreement with the previously calculated ΔE_{ST} of -5.4 kcal mol⁻¹ and within 15-17% variance.⁹

References

1. Granhøj, J.; Zalibera, M.; Malček, M.; Pedersen, V. B. R.; Hillers-Bendtsen, A. E.; Mikkelsen, K. V.; Rapta, P.; Nielsen, M. B. *Chem. Eur. J.* **2024**, *30*, e202302688.
2. Zysman-Colman, E.; Arias, K.; Siegel, J. S. *Can. J. Chem.* **2009**, *87*, 440–447.
3. Rudebusch, G. E.; Zafra, J. L.; Jorner, K.; Fukuda, K.; Marshall, J. L.; Arrechea-Marcos, I.; Espejo, G. L.; Ortiz, R. P.; Gomez-Garcia, C. J.; Zakharov, L. N.; Nakano, M.; Ottoson, H.; Casado, J.; Haley, M. M. *Nat. Chem.* **2016**, *8*, 753–759.
4. Reiss, H.; Heller, A. *J. Phys. Chem.* **1985**, *89*, 4207–4213.
5. G. M. Sheldrick, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, WI, 1998.
6. Sheldrick, G. M. *Acta Cryst. C* **2015**, *71*, 3–8.
7. Bain, G. A.; Berry, J. F. *J. Chem. Ed.* **2008**, *85*, 532–536.
8. Bleaney, B.; Bowers, K. D. *Proc. R. Soc. Lond. A* **1952**, *214*, 451–465.
9. Dressler, J. J.; Cárdenas Valdivia, A.; Kishi, R.; Rudebusch, G. E.; Ventura, A. M.; Chastain, B. E.; Gómez-García, C. J.; Zakharov, L. N.; Nakano, M.; Casado, J.; Haley, M. M. *Chem* **2020**, *6*, 1353–1368.

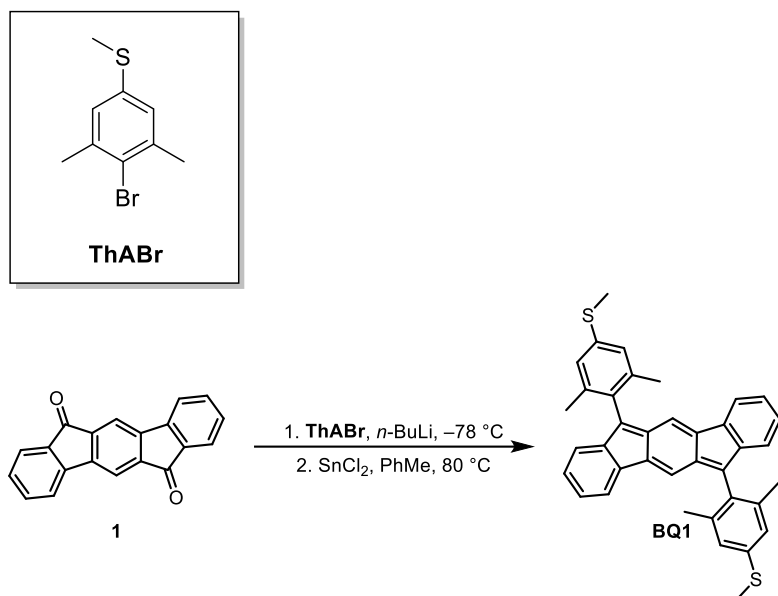
APPENDIX B

SUPPLEMENTARY INFORMATION FOR CHAPTER III

Appendix B is the supplementary information for Chapter III. Experimental details, experimental data, spectra and additional references relevant to the content of Chapter III are provided here.

Experimental Details

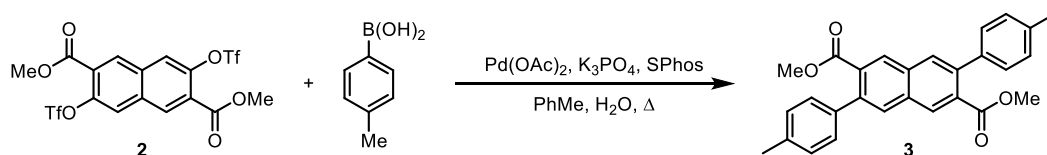
General Procedures. All air-sensitive reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk technique. Silica gel (240-300 mesh) was used for chromatography. All other reagents were purchased and used as received. NMR spectra were recorded on a Bruker Avance III HD 500 equipped with a Prodigy multinuclear cryoprobe (^1H : 500 MHz, ^{13}C : 126 MHz) or Bruker Avance III HD 600 equipped with a Prodigy multinuclear broadband cryoprobe (^1H : 600 MHz, ^{13}C : 151 MHz) NMR spectrometer at room temperature unless otherwise noted. ^1H and ^{13}C NMR chemical shifts (δ) are expressed in ppm relative to the residual non-deuterated solvent reference (CDCl_3 : ^1H 7.26 ppm, ^{13}C 77.16 ppm; CD_2Cl_2 : ^1H 5.32 ppm, ^{13}C 53.84 ppm); $\text{C}_2\text{D}_2\text{Cl}_4$: ^1H 6.00 ppm). UV-Vis spectra were recorded on an Agilent Technologies Cary 60 UV-Vis spectrometer in HPLC grade CH_2Cl_2 . HRMS were recorded on a Waters GCT Premier EI/CI/FD/FI mass spectrometer. Unless stated otherwise, all solvents and reagents were used as received. 4-Bromo-3,5-dimethylthioanisole (**ThABr**)^{1,2}, diones **1**,³ **10**,⁴ and **11**,⁵ bistriflate **2**,⁶ and **BQ3**⁷ were prepared according to previously described methods.



Thioanisole Indenofluorene BQ1. Dry THF (21 mL) was added to an oven-dried round-bottom flask (50 mL) containing **ThABr** (1.80 mL, 10.34 mmol, 6 equiv.) under a N_2 atmosphere and the mixture was cooled to $-78\text{ }^{\circ}\text{C}$ for 25 min. *n*-BuLi (3.85 mL, 2.5 M, 9.64 mmol, 5.6 equiv.) was added dropwise and the reaction was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. The lithiated species was added via cannula to a solution of dione **1**³ (486 mg, 1.72 mmol, 1 equiv.) in dry THF (40 mL) at $-78\text{ }^{\circ}\text{C}$. The reaction was stirred, slowly warming to room-temperature overnight. The mixture was then quenched with sat. aqueous NH_4Cl and extracted with CH_2Cl_2 3x. The combined organics were washed with brine, dried over MgSO_4 , filtered, and concentrated in vacuo. The resulting crude oil was diluted with hexanes to precipitate the crude diol, which was used with no further purification.

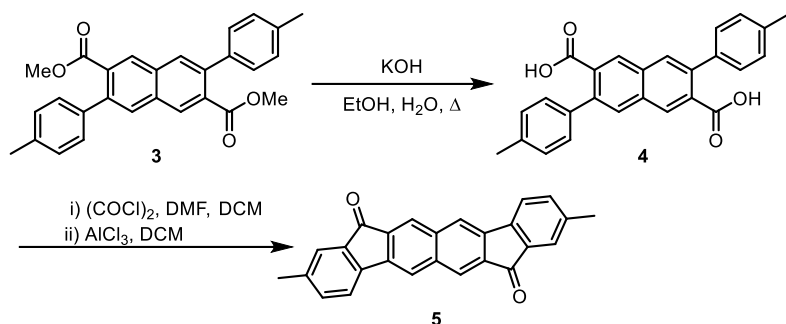
The diol (approx. 385 mg, 0.656 mmol, 1 equiv.) and SnCl_2 (497 mg, 2.62 mmol, 4 equiv.) were dissolved in dry degassed PhMe (40 mL) and stirred at $80\text{ }^{\circ}\text{C}$ overnight. The reaction was cooled to room temperature and filtered through a silica plug, eluting with hexanes then CH_2Cl_2

to collect crude product. The volatiles were removed *in vacuo* and the resulting residue was precipitated with CH₂Cl₂/CH₃CN/EtOH to yield **BQ₁** (104 mg, 29%) as a deep red solid. ¹H NMR (500 MHz, CD₂Cl₂) δ (ppm) 7.32 (d, *J* = 7.5 Hz, 2H), 7.08 (s, 2H), 7.01 (td, *J* = 7.4, 1.3 Hz, 2H), 6.96 (td, *J* = 7.3, 1.2 Hz, 2H), 6.85 (s, 4H), 6.67 (d, *J* = 6.9 Hz, 2H), 2.54 (s, 6H), 2.17 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 145.37, 144.40, 139.48, 138.45, 138.22, 138.02, 135.27, 130.02, 128.31, 127.62, 125.30, 122.22, 120.78, 119.30, 20.55, 15.60. UV-Vis (CHCl₃) λ_{max} (ε) 518 (35570) nm. HRMS (ASAP) for C₃₈H₃₂S₂ [M⁺]: calc'd 552.1945, found 552.1940.



Diester 3. A three-neck round bottom flask fitted with a condenser containing bistriflate **2**⁶ (900 mg, 1.66 mmol, 1 equiv.), 4-methylphenyl boronic acid (475 mg, 3.49 mmol, 2.1 equiv.), Pd(OAc)₂ (15 mg, 0.067 mmol, 0.04 equiv.), SPhos (55 mg, 0.133 mmol, 0.08 equiv.), and K₃PO₄ (1.06 g, 4.99 mmol, 3 equiv.) was placed under a N₂ atmosphere. The solids were suspended in degassed PhMe (31.5 mL) and H₂O (3.5 mL) and then stirred at reflux overnight. The reaction was cooled to room temperature and quenched with H₂O to precipitate a gray solid. The resulting precipitate was filtered, washed with H₂O, and dried in an oven for 15 min. The solids were suspended in CH₂Cl₂ and filtered through a celite/silica plug and then concentrated to yield the desired product (696 mg, 98%) as an off-white solid. ¹H NMR (500 MHz, CD₂Cl₂) δ (ppm) 8.33 (s, 2H), 7.91 (s, 2H), 7.32 (d, *J* = 7.9 Hz, 4H), 7.27 (d, *J* = 7.8 Hz, 4H), 3.73 (s, 6H), 2.43 (s, 6H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 169.08, 139.69, 138.28, 137.70, 132.79, 132.12, 130.57, 130.39,

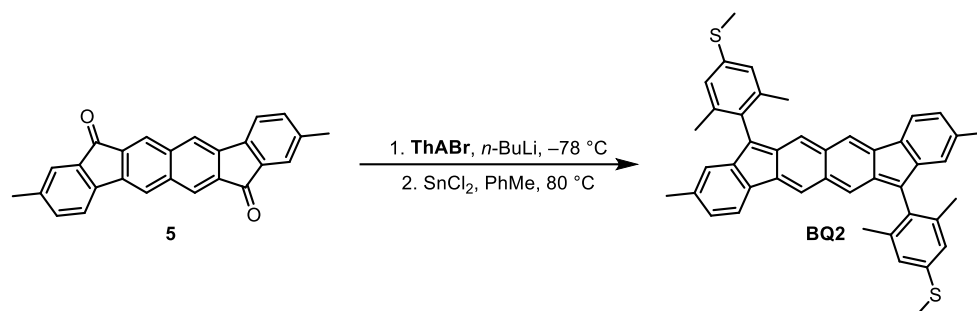
129.33, 128.76, 52.51, 21.33. HRMS (ASAP) for $C_{28}H_{24}O_4$ $[M-H]$: calcd 395.1283, found 395.1279.



Dione 5. EtOH (91 mL) and H₂O (23 mL) were added to a 250 mL round bottom flask containing **3** (696 mg, 1.64 mmol, 1 equiv.) and KOH (1.380 g, 24.6 mmol, 15 equiv.). The flask was fitted with a condenser and stirred at reflux open to air for 6 h. Once cooled, the volume of the reaction was reduced to approx. 15% and then acidified with a 3M HCl solution to form a precipitate. The solids were filtered and washed with water and dried in an oven to yield the crude diacid **4** (572 mg, 88%) as a pale yellow solid. ¹H NMR (600 MHz, DMSO-*d*₆) δ (ppm) 13.00 (s, 2H), 8.39 (s, 2H), 8.06 (s, 2H), 7.35 (d, J = 8.0 Hz, 4H), 7.27 (d, J = 7.8 Hz, 4H), 2.37 (s, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 169.52, 138.20, 137.59, 136.52, 132.73, 131.70, 129.47, 129.16, 128.82, 128.33, 20.75.

To a suspension of diacid **4** (572 mg, 1.44 mmol, 1 equiv.) in dry CH₂Cl₂ (84 mL) was added DMF (0.222 mL, 2.88 mmol, 2 equiv.) and oxalyl chloride (0.492 mL, 5.77 mmol, 4 equiv.). The reaction was stirred at room temperature overnight and the volatiles were then removed under reduced pressure. AlCl₃ (962 mg, 7.21 mmol, 5 equiv.) was added to the flask and the solids were dissolved in dry CH₂Cl₂ (87 mL) and then stirred at room temperature overnight. The reaction mixture was poured into an HCl-ice mixture to precipitate the crude dione. The solids were filtered

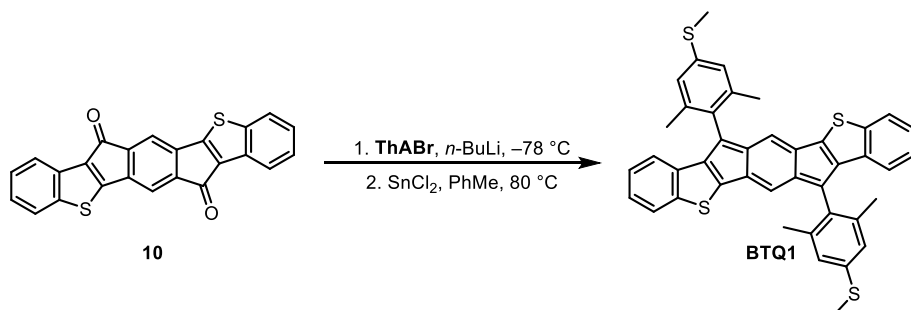
and washed successively with H₂O, acetone, CH₂Cl₂, and hexanes to yield dione **5** (415 mg, 80%) as a very poorly soluble salmon solid. HRMS (ASAP) for C₂₆H₁₆O₂ [M⁺]: calcd 360.1150, found 360.1159.



Thioanisole Fluorenofluorene BQ₂. Dry THF (20 mL) was added to an oven-dried 100 mL round-bottom flask containing **ThABr** (1.40 mL, 8.06 mmol, 7 equiv.) under a N₂ atmosphere. The mixture was cooled to −78 °C for 25 min, after which *n*-BuLi (3.13 mL, 2.5 M, 7.83 mmol, 6.8 equiv.) was added dropwise and the reaction was stirred at −78 °C for 30 min. The lithiated species was added to a suspension of dione **5** (415 mg, 1.15 mmol, 1 equiv.) in dry THF (30 mL) at −78 °C. The reaction was stirred while warming to room-temperature overnight. The mixture was quenched with sat. aqueous NH₄Cl and extracted with CH₂Cl₂ 3x. The organics were washed with brine, dried over MgSO₄, filtered, and concentrated *in vacuo*. The resulting crude oil was diluted with hexanes to precipitate the crude diol, which was used with no further purification.

Diol (approx. 710 mg, 1.07 mmol, 1 equiv.) and SnCl₂ (810 mg, 4.27 mmol, 4 equiv.) were dissolved in dry degassed PhMe (50 mL) and stirred at 80 °C overnight. The reaction was cooled to room temperature and filtered through a silica plug, eluting with hexanes then CH₂Cl₂ to collect the crude product. Organics were removed *in vacuo* and the resulting residue was precipitated with CH₂Cl₂/CH₃CN/EtOH to yield **BQ₂** (213 mg, 29%) as a deep blue solid. ¹H NMR (500 MHz,

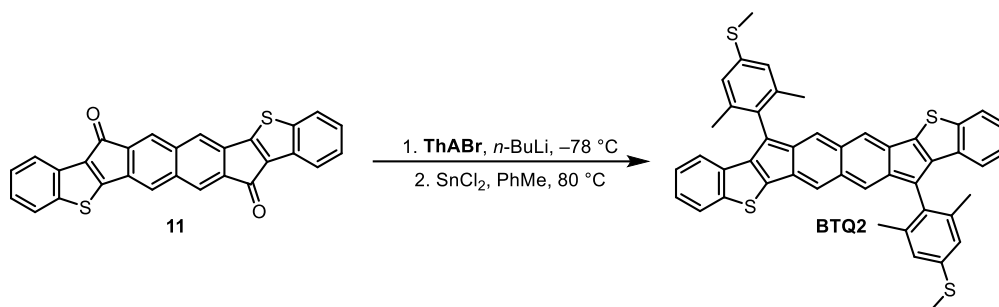
CD₂Cl₂) δ (ppm) 7.46 (d, J = 7.7. Hz, 2H) 7.31 (s, 2H), 7.09 (s, 4H), 6.84 (d, J = 7.7 Hz, 2H), 6.87 (s, 2H), 6.64 (s, 2H), 2.55 (s, 6H), 2.25 (s, 6H), 2.12 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 144.37, 141.32, 138.63, 138.41, 138.30, 137.81, 135.49, 134.74, 131.97, 130.54, 128.05, 127.60, 125.35, 124.59, 122.73, 120.91, 21.67, 20.53, 15.67. UV-Vis (CHCl₃) λ_{max} (ϵ) 606 (44590) nm. HRMS (ASAP) for C₄₄H₃₈S₂ [M⁺]: calcd 630.2415, found 630.2409.



Thioanisole *anti*-Indacenodibenzothiophene (BTQ₁). Dry THF (30 mL) was added to an oven-dried 100 mL round-bottom flask containing **ThABr** (1.27 mL, 7.29 mmol, 7 equiv.) under a N₂ atmosphere and the mixture was cooled to −78 °C for 25 min. *n*-BuLi (2.83 mL, 2.5 M, 7.08 mmol, 6.8 equiv.) was added dropwise and the reaction was stirred at −78 °C for 30 min. The lithiated species was added via cannula to a suspension of dione **10**⁴ (411 mg, 1.04 mmol, 1 equiv.) in dry THF (26 mL) at −78 °C. The reaction was stirred, warmed to room-temperature overnight, and then quenched with sat. aqueous NH₄Cl and extracted with CH₂Cl₂ 3x. The organics were washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The resulting crude oil was diluted with hexanes to precipitate the crude diol, which was used without further purification.

The crude diol (579 mg, 0.828 mmol, 1 equiv.) and SnCl₂ (628 mg, 3.31 mmol, 4 equiv.) were dissolved in dry degassed PhMe (41 mL) and stirred at 80 °C for 3 h. The reaction was cooled

to room temperature and filtered through a silica plug, eluting with hexanes then CH₂Cl₂ to collect the crude product. Organics were removed *in vacuo* and the resulting residue was precipitated with CH₂Cl₂/CH₃CN/EtOH to yield **BTQ₁** (102 mg, 18%) as a blue solid. ¹H NMR (500 MHz, CD₂Cl₂) δ (ppm) 7.49 (d, *J* = 8.0 Hz, 2H), 7.05 (s, 4H), 7.05-7.01 (m, 2H), 6.98 (t, *J* = 7.5 Hz, 2H), 6.63 (d, *J* = 7.9 Hz, 2H), 6.10 (s, 2H), 2.54 (s, 6H), 2.33 (s, 12H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 148.40, 147.88, 144.26, 143.37, 138.88, 137.71, 137.33, 133.26, 132.06, 129.86, 126.26, 125.99, 125.17, 124.55, 124.07, 120.93, 20.72, 15.49. UV-Vis (CHCl₃) λ_{max} (ε) 624 (37920) nm. HRMS (ASAP) for C₄₂H₃₂S₄ [M⁺]: calcd 664.1387, found 664.1381.



Thioanisole *anti*-Indenoindenodibenzothiophene (BTQ₂). Dry THF (16 mL) was added to an oven-dried 100 mL round-bottom flask containing **ThABr** (0.900 mL, 5.16 mmol, 8 equiv.) under a N₂ atmosphere and the mixture was cooled to −78 °C for 25 min. *n*-BuLi (1.93 mL, 2.5 M, 4.82 mmol, 7.5 equiv.) was added dropwise and the reaction was allowed to stir at −78 °C for 30 min. The lithiated species was added to a suspension of dione **11**⁵ (286 mg, 0.645 mmol, 1 equiv.) in dry THF (16 mL) at −78 °C. The reaction was stirred while warming to room-temperature overnight, and was then quenched with sat. aqueous NH₄Cl and extracted with CH₂Cl₂ 3x. The organics were washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The resulting

crude oil was diluted with hexanes to precipitate the crude diol, which was used with no further purification.

The diol (approx. 57 mg, 0.0761 mmol, 1 equiv.) and SnCl₂ (58 mg, 0.304 mmol, 4 equiv.) were dissolved in dry degassed PhMe (12 mL) and stirred at 80 °C for 3 h. The reaction was cooled to room temperature and filtered through a silica plug, eluting with hexanes then CH₂Cl₂ to collect crude product. Organics were removed *in vacuo* and the resulting residue was precipitated with CH₂Cl₂/CH₃CN/EtOH to yield **BTQ₂** (22 mg, 13%) as a deep purple solid. ¹H NMR (500 MHz, CD₂Cl₂) δ (ppm) 7.65 (d, *J* = 7.9 Hz, 2H) 7.22–7.15 (m, 4H), 7.10 (br s, 6H), 6.93 (d, *J* = 7.9 Hz, 2H), 6.85 (s, 2H), 2.57 (s, 6H), 2.21 (s, 12H). ¹³C NMR (151 MHz, CD₂Cl₂) δ 145.10, 144.65, 142.61, 138.22, 138.07, 137.83, 132.62, 131.61, 130.79, 130.18, 130.13, 127.56, 125.53, 125.28, 124.93 (2C), 123.81, 121.75, 20.23, 15.17. UV-Vis (CHCl₃) λ_{max} (ε) 730 (30690) nm. HRMS (ASAP) for C₄₆H₃₄S₄ [M⁺]: calcd 714.1543, found 714.1538.

UV-Vis Electronic Absorption Spectroscopy

UV-Vis spectra of **BQ**₁₋₃ (Figure B1) and **BTQ**₁₋₂ (Figure B2) were recorded on an Agilent Technologies Cary 60 UV-Vis spectrometer in HPLC grade CHCl₃. As might be expected, the spectra are nearly identical to the previously reported mesityl analogues.^{3-5,8,9}

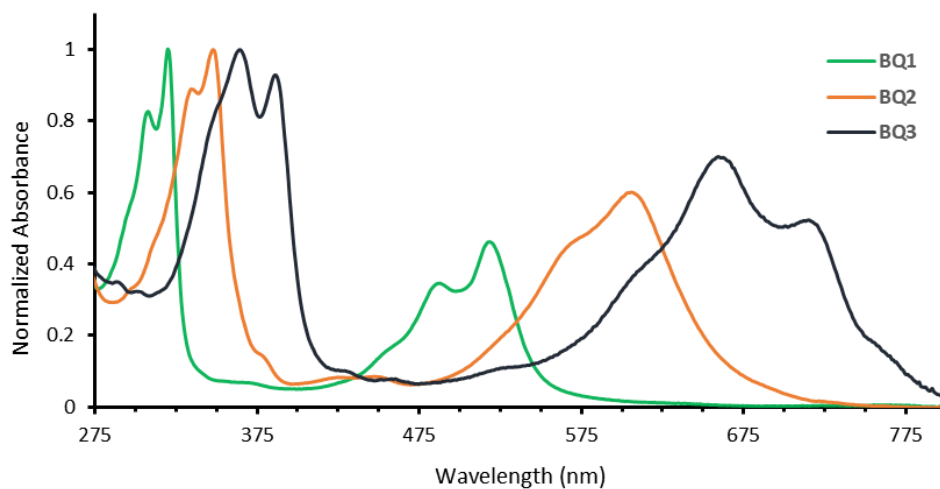


Figure B1. Plot of wavelength vs. normalized absorbances for **BQ**₁₋₃ in CHCl₃ solutions (10^{-5} M).

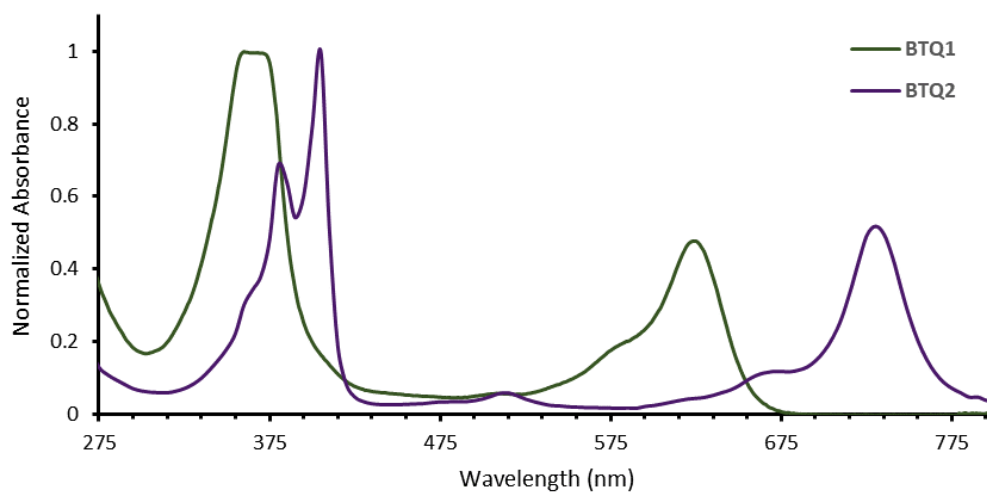


Figure B2. Plot of wavelength vs normalized absorbances for **BTQ**₁₋₂ in CHCl₃ solutions (10^{-5} M).

NMR Spectra

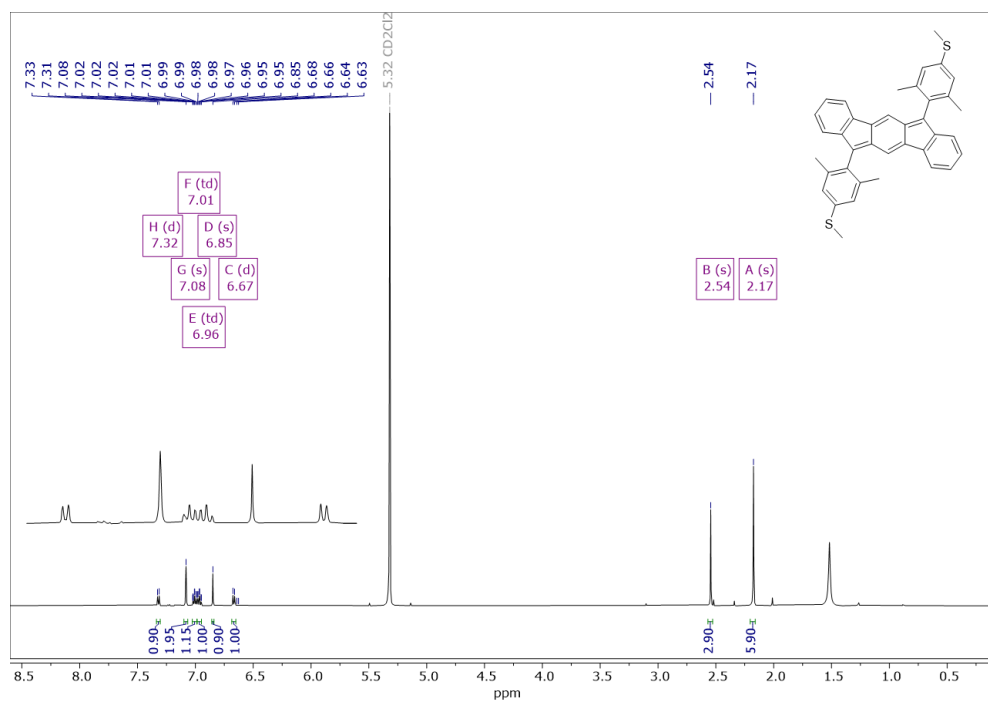


Figure B3. ¹H NMR spectra of BQ₁.

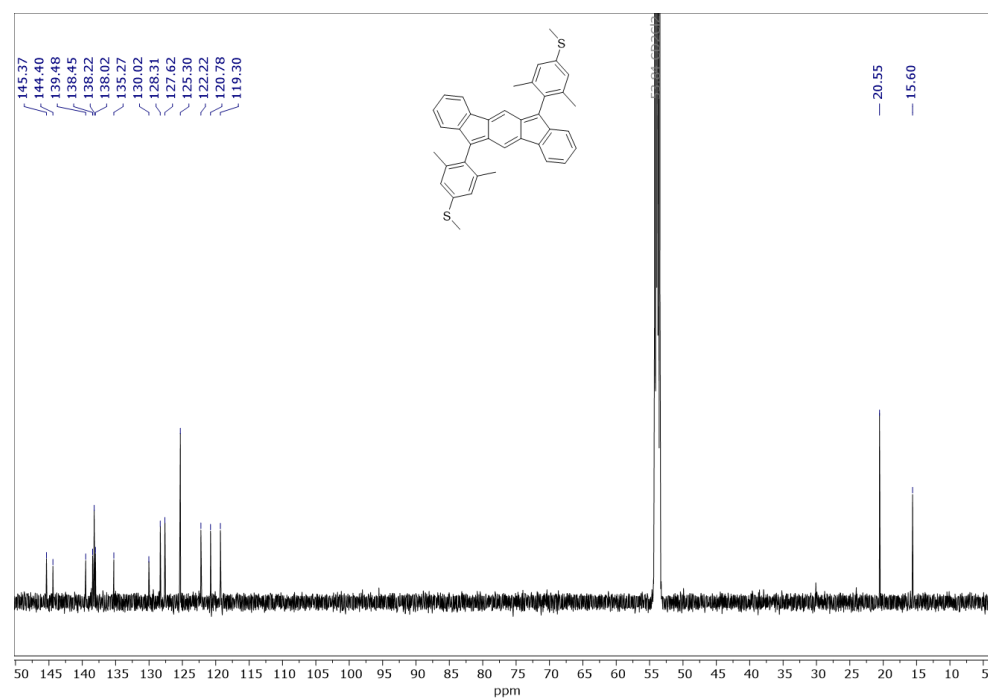


Figure B4. ¹³C NMR spectra of BQ₁.

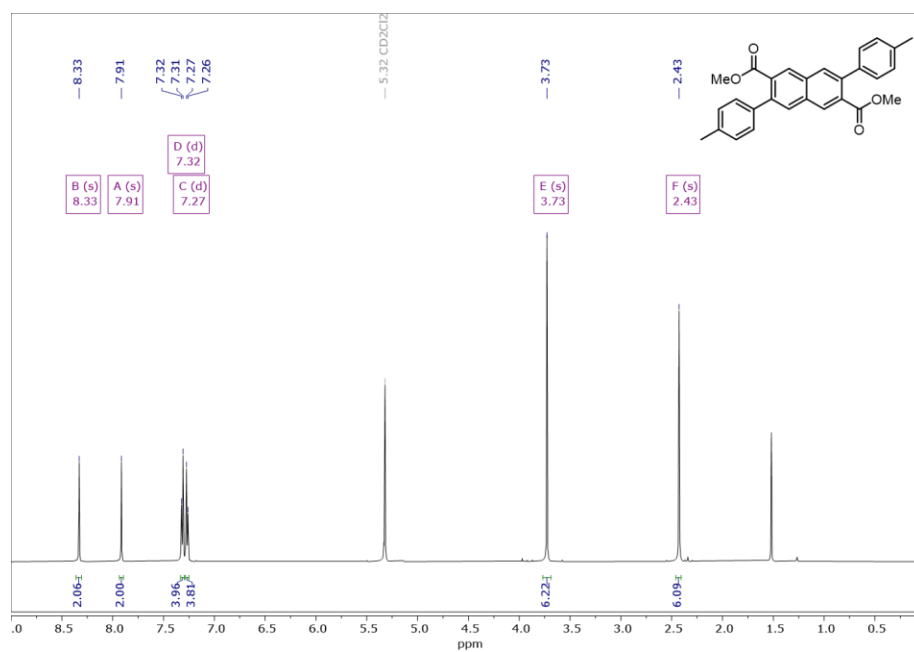


Figure B5. ¹H NMR spectra of **3**.

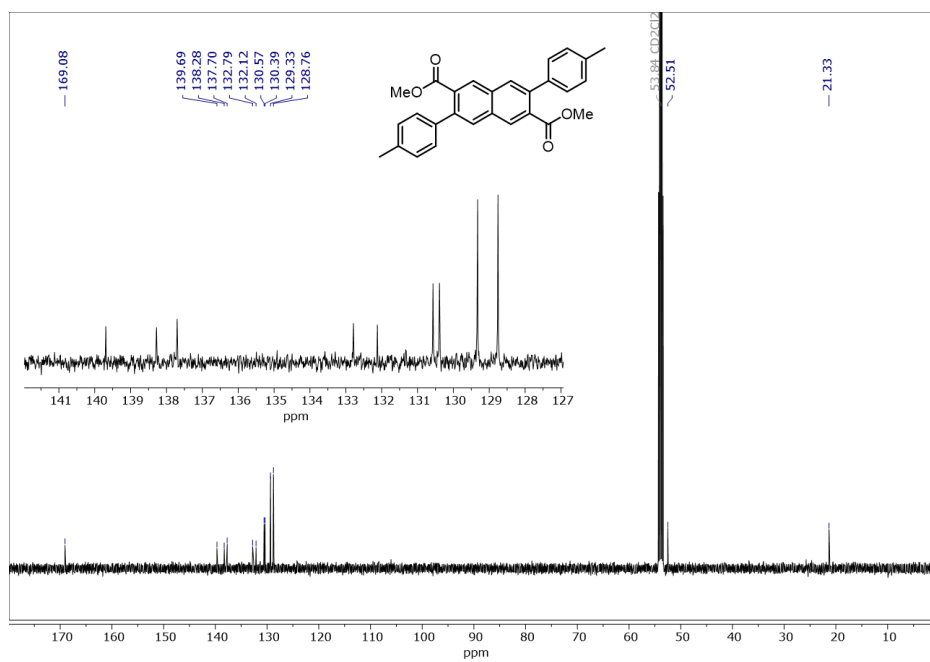


Figure B6. ¹³C NMR spectra of **3**.

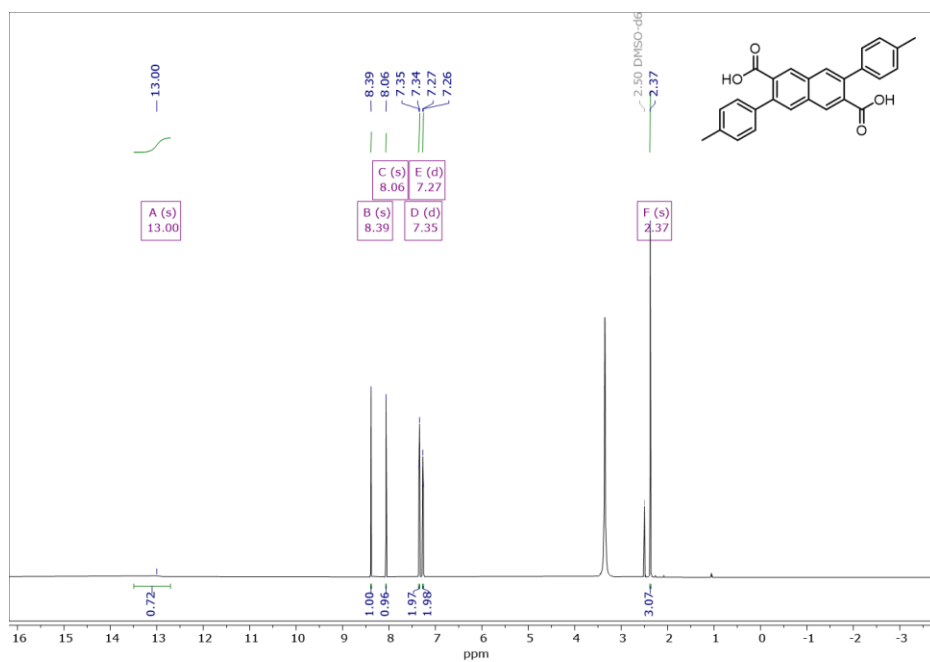


Figure B7. ¹H NMR spectra of **4**.

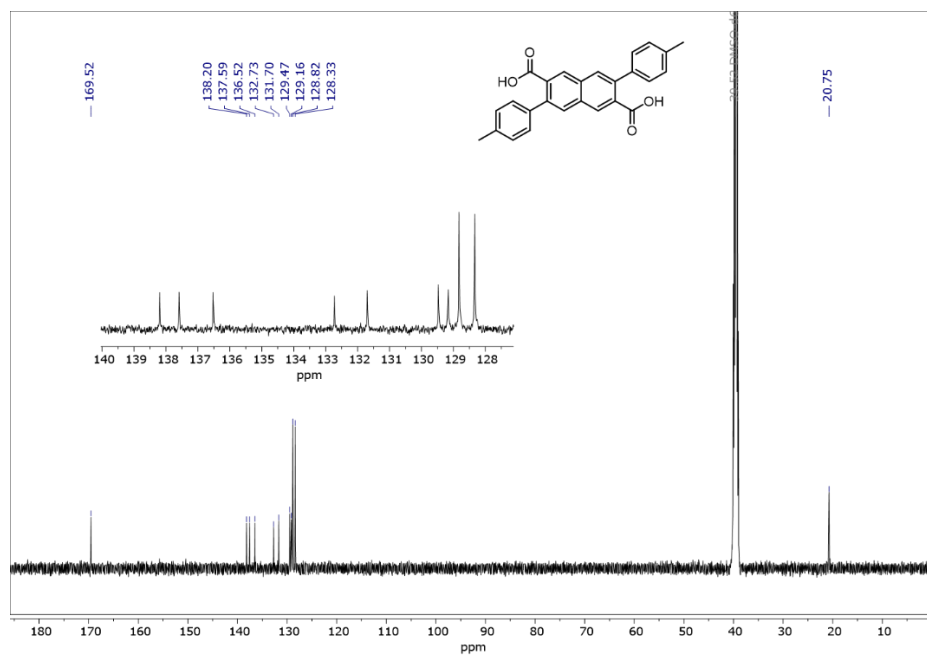


Figure B8. ¹³C NMR spectra of **4**.

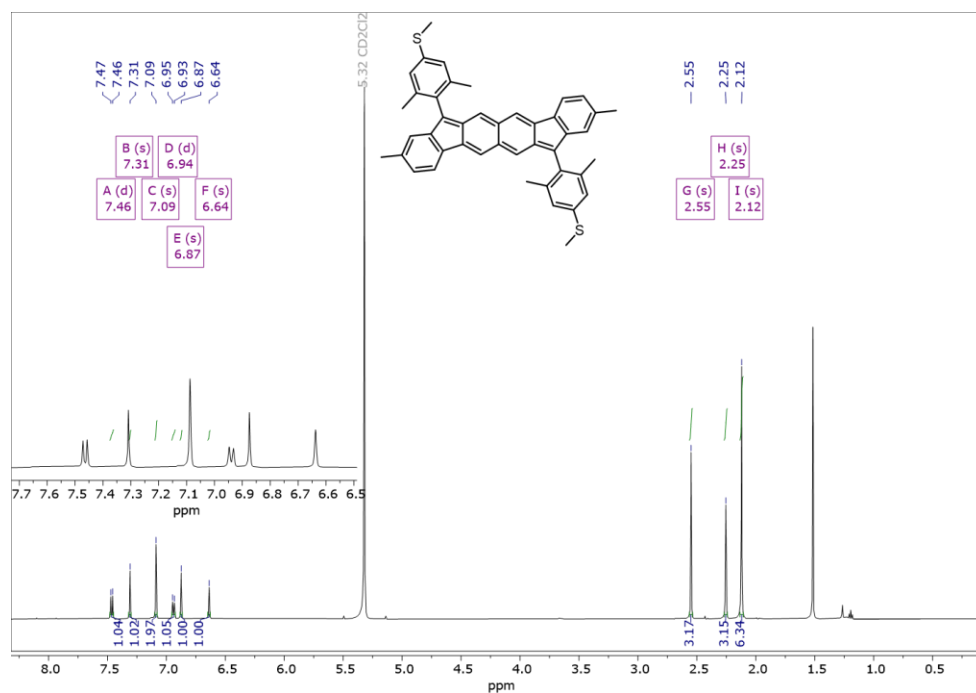


Figure B9. ¹H NMR spectra of BQ₂.

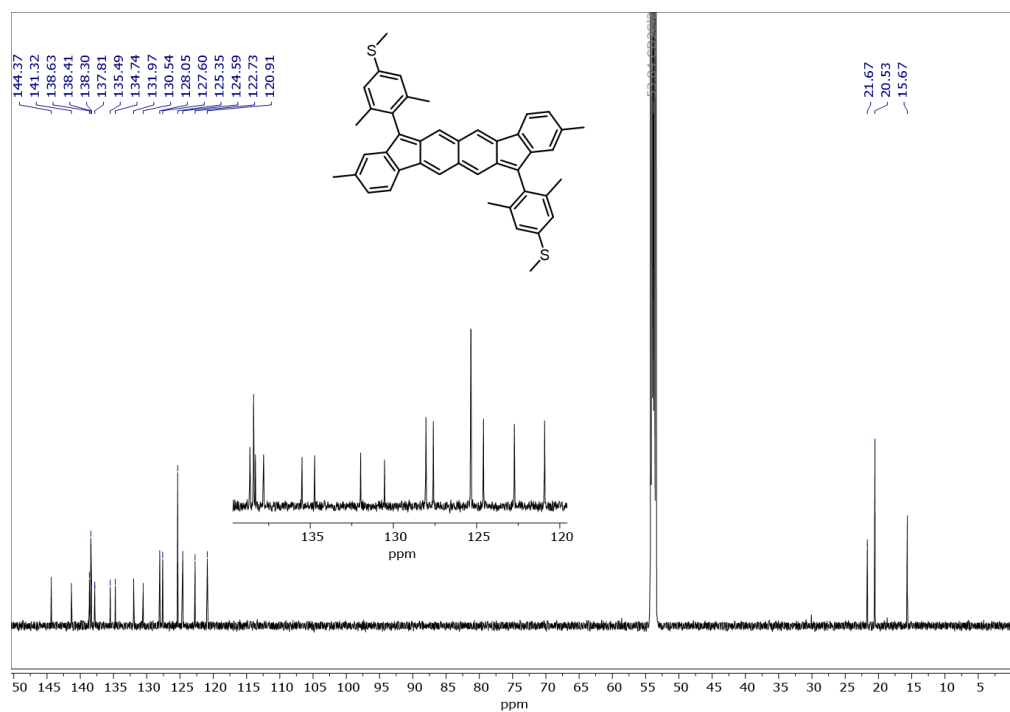


Figure B10. ¹³C NMR spectra of BQ₂.

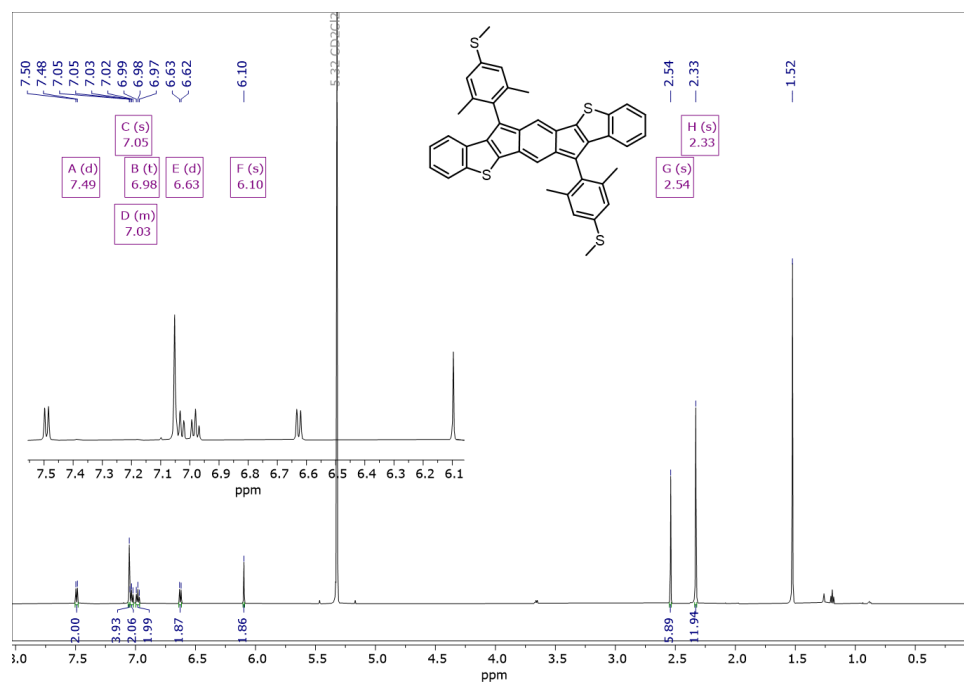


Figure B11. ¹H NMR spectra of BTQ₁.

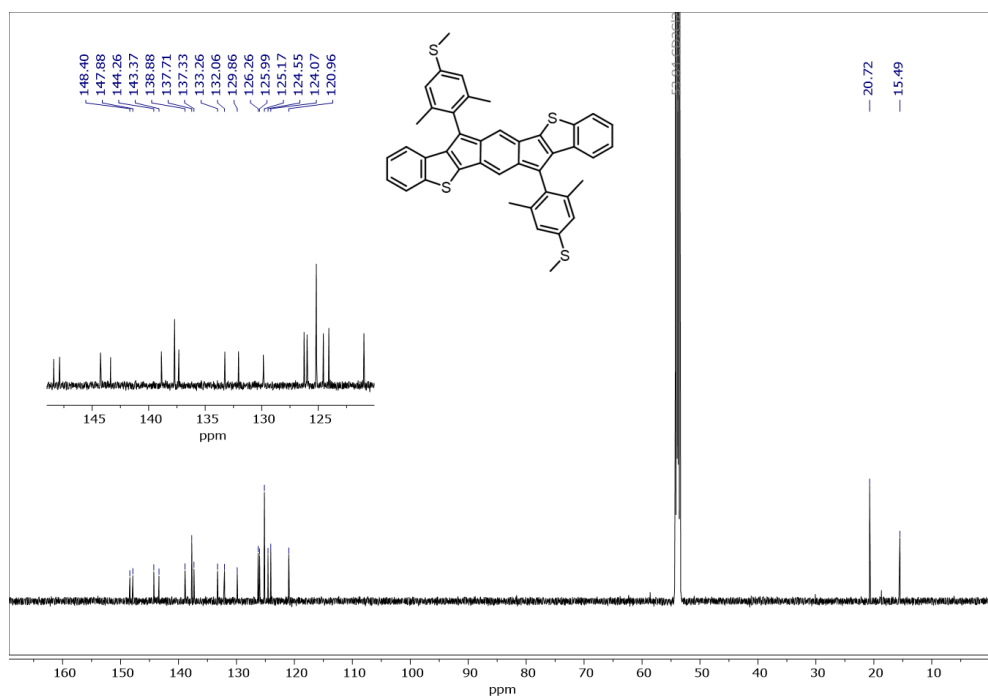


Figure B12. ¹³C NMR spectra of BTQ₁.

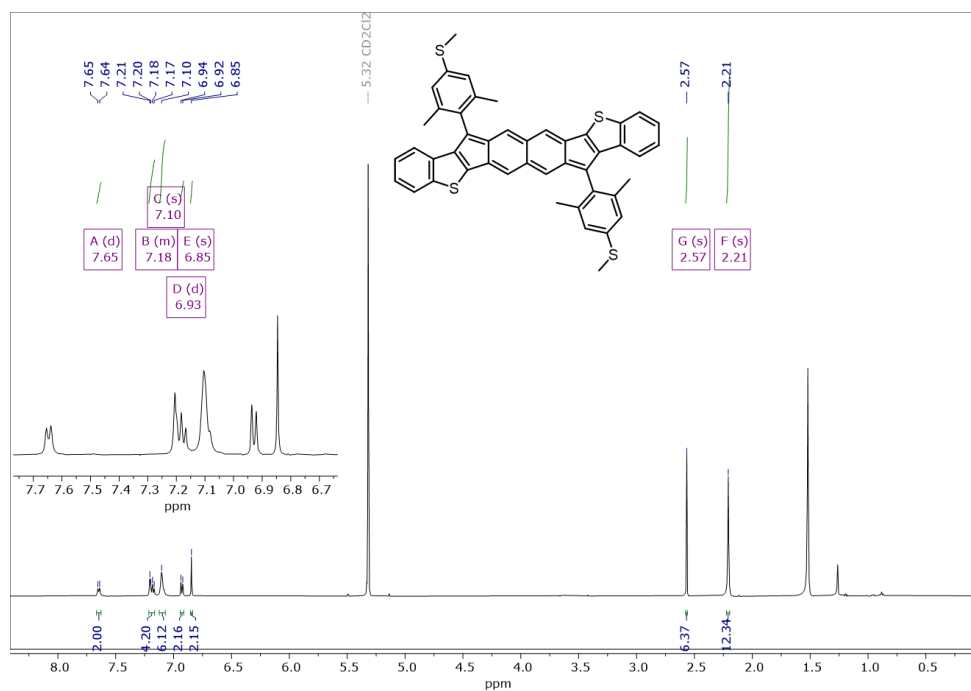


Figure B13. ¹H NMR spectra of BTQ₂.

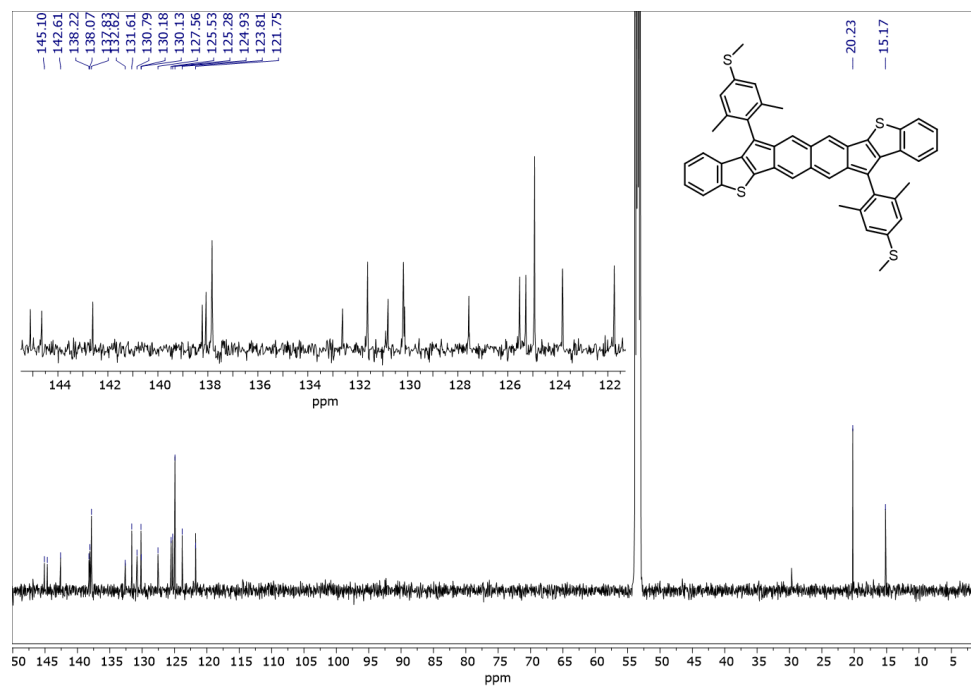


Figure B14. ¹³C NMR spectra of BTQ₂.

IV Measurement Procedure and Analysis

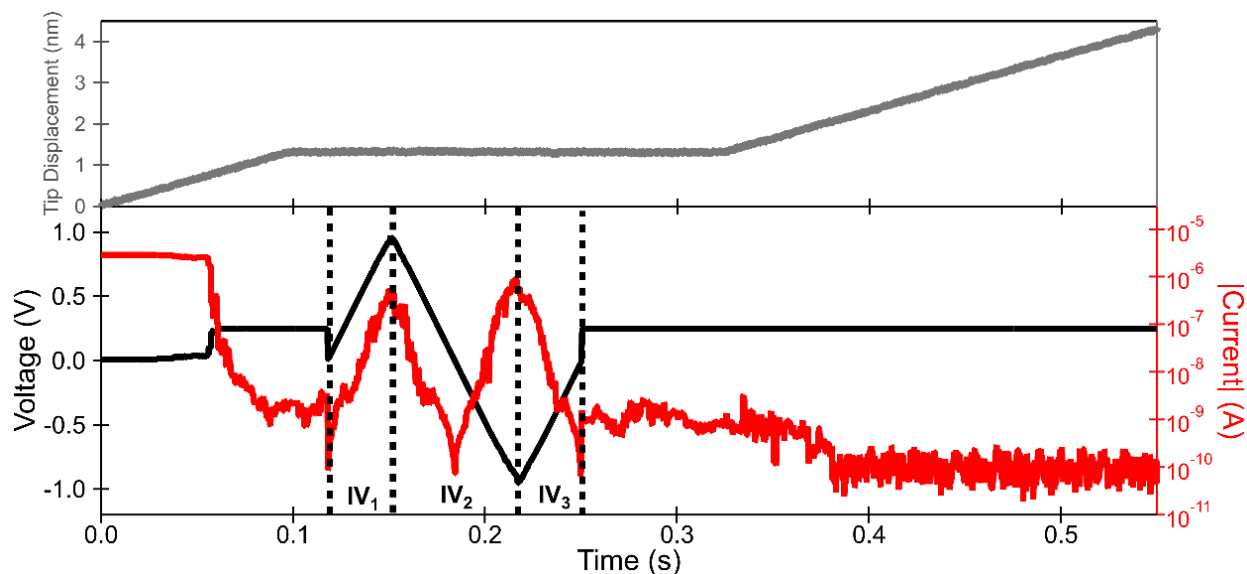


Figure B15. Single tip displacement, voltage and current traces during the IV scan procedure.

Current-voltage measurements were obtained by scanning the junction voltage, while Holding the junction distance constant, as described previously.¹⁰ An example displacement, voltage and current traces are shown in Figure B15. The Au sample and tip are initially pulled apart, at a fixed junction bias, and then held at a fixed position. No feedback is used so the conductance during the hold varies from trace to trace. During the hold, the junction bias is initially set to 0 V, and then swept between a positive maximum voltage, $+V_{\text{max}}$, (IV_1) and a negative maximum voltage, $-V_{\text{max}}$, (IV_2), before returning to 0 V and then back to the initial junction bias as shown in the figure in black. At the end of the bias sweep, the tip and sample resume pulling apart until the molecular junction fully ruptures.

The collected data is post-processed to select traces with a hold conductance which corresponds to a molecule bridging the gap. This is accomplished by examining the conductance immediately before and after the IV ramps to ensure it is consistent with the molecular signature in

a previously collected 1D histogram. These selected traces are then binned into a 2D heat map, binning bias voltage on the x-axis and current on the y-axis. For the data shown in the manuscript Figure 3, only IV_2 data is included.

Additional IV Data

It has been previously observed that a molecule can undergo chemical or redox changes in the junction under a large bias.¹¹ This effect can show up as an asymmetric or inconsistent IV curve, where the current changes irreversibly as the voltage is repeated swept between $\pm V_{\text{max}}$. In this work, we examine the distinct regions IV_1 , IV_2 and IV_3 shown in the figure above, to ensure current signatures remain repeatable. The 2D IV heat maps for **BQ**₁₋₃ including all regions IV_1 , IV_2 and IV_3 are shown in Figures B16-S20. We observe that **BQ**₁ IV curves remain consistent and symmetric until voltages up to ± 1.2 V. In contrast, the signatures of **BQ**₂ and **BQ**₃ undergo irreversible changes at a molecule-dependent threshold bias, indicating chemical or redox changes in the junction. All data shown in the manuscript include measurements of the **BQ**_n series collected below these threshold bias conditions.

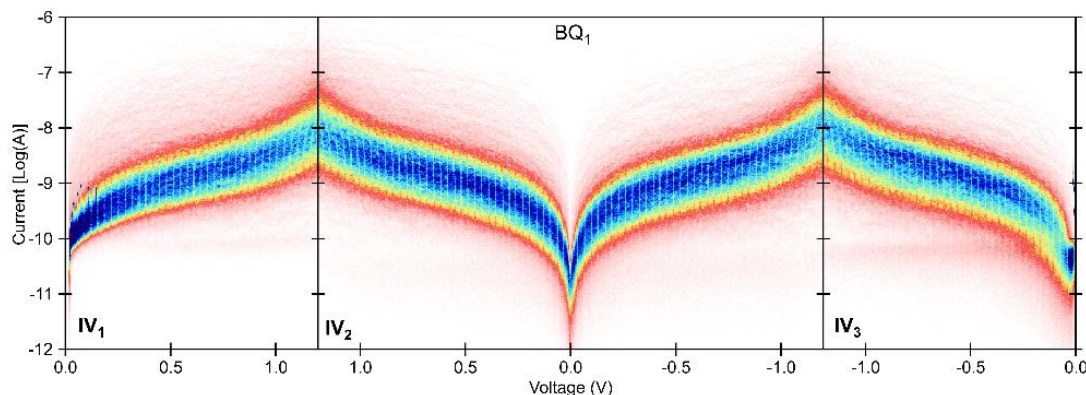


Figure B16. Consecutive IV spectra of **BQ**₁ with $V_{\text{max}} = 1.2$ V.

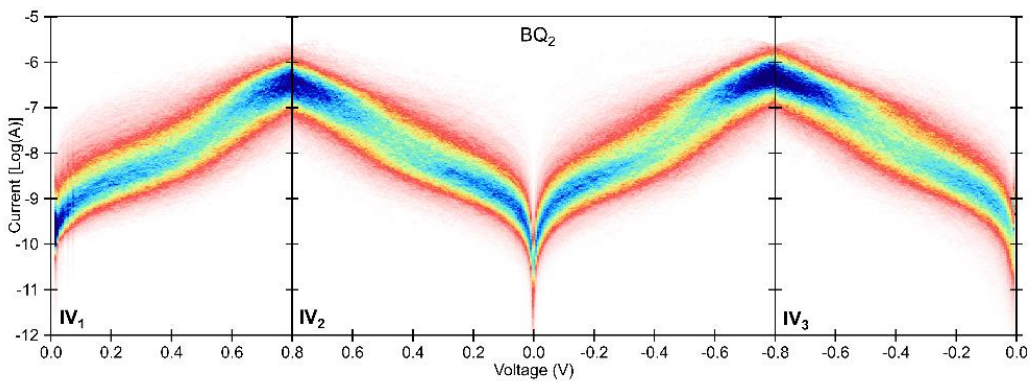


Figure B17. Consecutive IV spectra of **BQ₂** with $V_{\text{max}} = 0.8$ V.

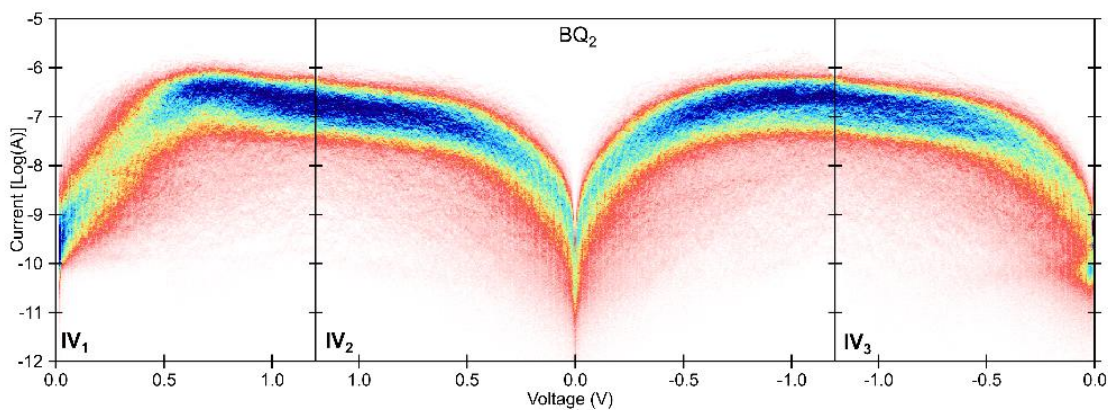


Figure B18. Consecutive IV spectra of **BQ₂** with $V_{\text{max}} = 1.2$ V.

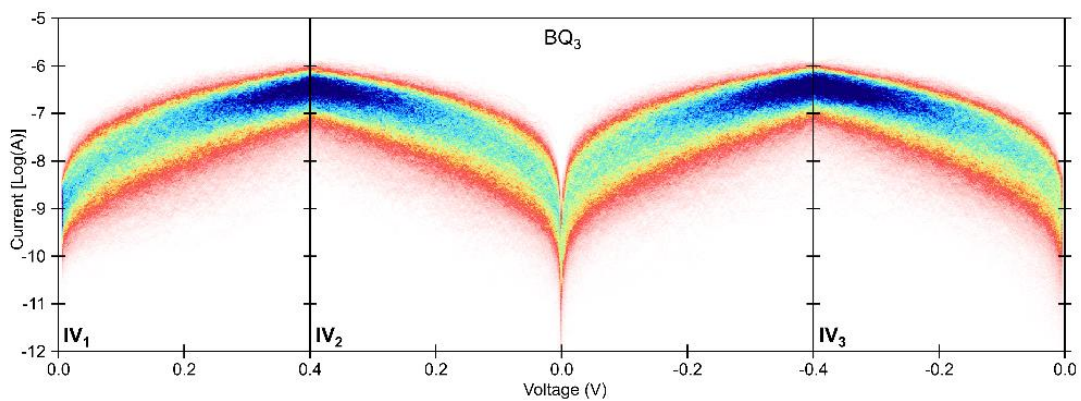


Figure B19. Consecutive IV spectra of **BQ₃** with $V_{\text{max}} = 0.4$ V.

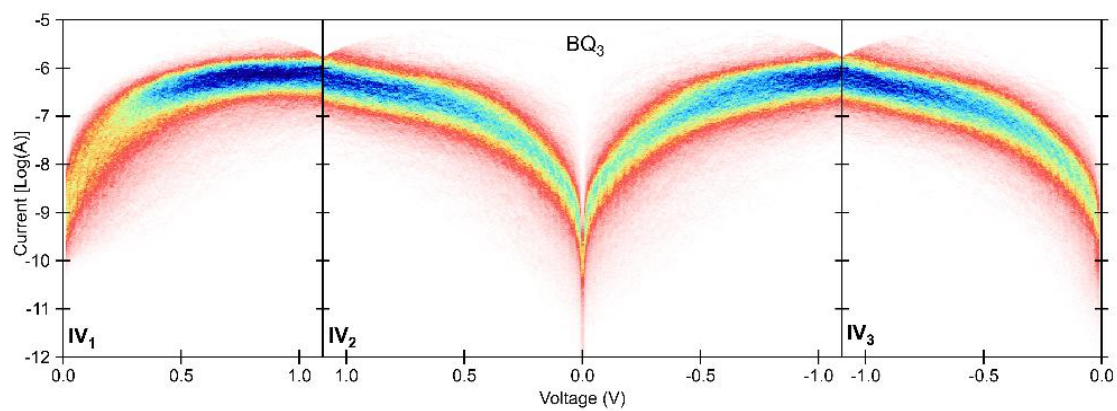
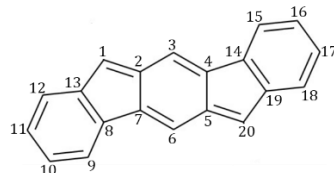


Figure B20. Consecutive IV spectra of **BQ₃** with $V_{\text{max}} = 1.1$ V.

Modified 1D SSH Model

Comparison of the bond order alternation behavior for the **BQ_n** resonance structures (diradical $\rightarrow$ delocalized $\rightarrow$ quinone), as shown in Figure 4, indicates that not all bonds have the same dependence on δ . The bonds described by the traditional 1D-SSH model, given by t_1 and t_2 scale between 0.37 and 2.72 eV over the full range of δ . In contrast, for these cyclic molecules, there are additionally bonds which start at one of the extrema (0.37 or 2.72 eV) and become delocalized at $\delta = 0$, but then revert back to their starting value over the full range of δ . These bonds are given by u_1 and u_2 . Bonds outside the benzoquinone core are not impacted by the shift between diradical and quinone resonance structures and are described by constants c_1 and c_2 with corresponding values based on their bond order.^{12–14} With those parameters, a modified 1D-SSH Hamiltonian for the **BQ_n** series can be constructed as shown for **BQ₁** in Figure B28.



	Atom Number																			
Atom Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	ϵ	t_2	0	0	0	0	0	0	0	0	0	0	c_1	0	0	0	0	0	0	0
2	t_2	ϵ	u_1	0	0	0	t_1	0	0	0	0	0	0	0	0	0	0	0	0	0
3	0	u_1	ϵ	u_2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4	0	0	u_2	ϵ	u_1	0	0	0	0	0	0	0	0	c_1	0	0	0	0	0	0
5	0	0	0	u_1	ϵ	t_1	0	0	0	0	0	0	0	0	0	0	0	0	0	t_2
6	0	0	0	0	t_1	ϵ	t_2	0	0	0	0	0	0	0	0	0	0	0	0	0
7	0	t_1	0	0	0	t_2	ϵ	c_1	0	0	0	0	0	0	0	0	0	0	0	0
8	0	0	0	0	0	0	c_1	ϵ	c_2	0	0	0	c_2	0	0	0	0	0	0	0
9	0	0	0	0	0	0	0	c_2	ϵ	c_2	0	0	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0	c_2	ϵ	c_2	0	0	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0	0	0	c_2	ϵ	c_2	0	0	0	0	0	0	0	0
12	0	0	0	0	0	0	0	0	0	0	c_2	ϵ	c_2	0	0	0	0	0	0	0
13	c_1	0	0	0	0	0	0	c_2	0	0	0	c_2	ϵ	0	0	0	0	0	0	0
14	0	0	0	c_1	0	0	0	0	0	0	0	0	0	ϵ	c_2	0	0	0	c_2	0
15	0	0	0	0	0	0	0	0	0	0	0	0	0	c_2	ϵ	c_2	0	0	0	0
16	0	0	0	0	0	0	0	0	0	0	0	0	0	0	c_2	ϵ	c_2	0	0	0
17	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	c_2	ϵ	c_2	0
18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	c_2	ϵ	c_2
19	0	0	0	0	0	0	0	0	0	0	0	0	0	c_2	0	0	0	c_2	ϵ	c_1
20	0	0	0	0	t_2	0	0	0	0	0	0	0	0	0	0	0	0	0	c_1	ϵ

Figure B21. Atom numbering and the modified 1D-SSH matrix for **BQ₁**.

The parameterization used in Figure 4, that was used in prior work, overestimates the range of t in order to achieve the zero band-gap edge state by reaching the dimerization limit.¹⁵ In order to obtain a range of t and u that represent realistic bond alternation parameters, we reference the experimentally and theoretically determined range of nearest neighbor couplings for acene-like systems and then fit those values to $t = t_0 e^{a\delta}$ to extract the values of t_0 and a . This is accomplished based on prior work as follows:

1. In the delocalized state, the bonds are all equivalent and have a hopping parameter of $t = t_0$. This hopping parameter for benzene and graphene is known to be equal to 2.7 eV. To remain consistent with this empirical result, we take $t_0 = 2.7$.^{16,17}
2. The known range of t for conjugated molecules, determined as an overlap integral for known bond alternation lengths (BLA), is given by $0.93t_0 < t < 1.09t_0$.^{18,19} This corresponds to BLA of 1.35 to 1.44 Å. Thus, we determine the physically relevant range of t and u as: $2.51 \text{ eV} < t, u < 2.94 \text{ eV}$.
3. Using the empirical limits above and $t = t_0 e^{a\delta}$, we determined $a = 0.08$.

We also check our parameterization against our DFT results (see DFT procedures in Density Function Theory section). We calculate the gas-phase structure of the molecules and extract the bond lengths for the closed-shell, $\delta=1$ case. An example result for **BQ₃** with labeled bond lengths is shown in Figure B22. These lengths vary from 1.369 to 1.461 Å. This result is within the range of previously observed BLAs for conjugated molecules and is consistent with the overlap integrals from the literature in our procedure above.¹⁸

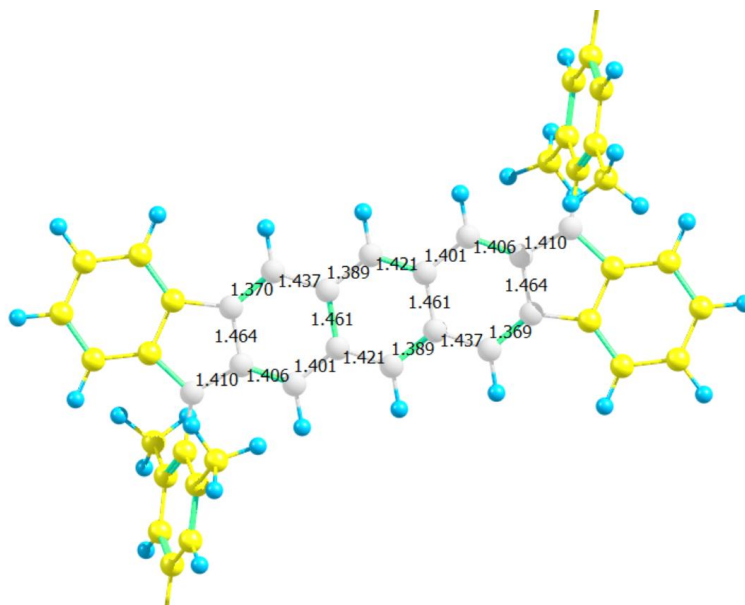


Figure B22. The result of a gas phase DFT calculations and the predicted bond lengths of the acene core of BQ₃.

Quantum Interference Calculations

The procedure to calculate the transmission contributions from both constructive (CQI) and destructive quantum interference (DQI) between different conducting molecular orbitals was established in prior work.^{20–24} Using the method of calculating the transmission from nonequilibrium greens function within the basis of the conducting molecular orbitals, yields a transmission matrix calculated at $E - E_F = 0$ eV, with the diagonal transmission terms, T_{jj} , corresponding to the transmission contribution from conducting molecular orbital j , termed T_{res} . The off-diagonal terms, T_{jk} , are the interference contributions to the transmission between orbitals j and k . The CQI terms are associated with the positive off-diagonal terms while the DQI are negative.

The overall transmission is defined as:

$$T_{tot} = T_{res} + T_{cqi} + T_{dqi}$$

where,

$$T_{res} = \sum_j T_{jj}$$

$$T_{cqi} = \sum_{jk} T_{jk} \text{ for } T_{jk} > 0$$

$$T_{dqi} = \sum_{jk} T_{jk} \text{ for } T_{jk} < 0$$

We note that the sign of T_{dqi} is negative, so this term decreases the overall conductance.

To quantify the fractional contributions of cqi and dqi to the overall transmission, we establish the following protocol. We define a distinct quantity, T_{tot}' , as:

$$T_{tot}' = T_{res} + T_{cqi} + |T_{dqi}|$$

In this case, the destructive interference term adds positively to T_{tot}' . The relative individual contributions of the three mechanisms plotted in Figure 5c are then calculated from the magnitude of each transmission term relative to the sum:

$$\frac{|T_i|}{T_{tot}'}, \text{ where } i = res, cqi, \text{ or } dqi$$

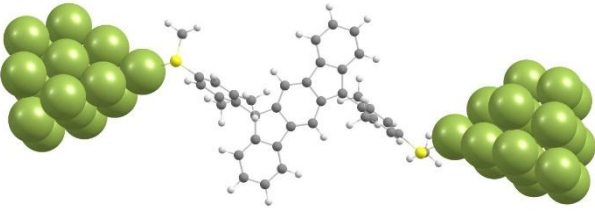
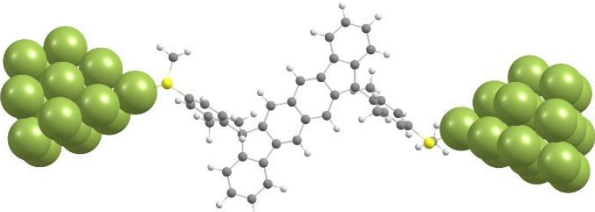
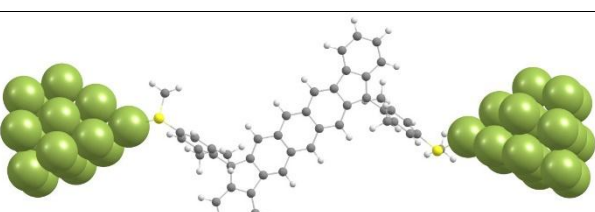
The resulting fractions are always less than unity. By comparing the fraction for the cqi and dqi terms using this definition, we can assess the degree to which the negative contributions of the dqi terms cancel out the positive contributions from cqi.

Density Functional Theory Calculations

The Kohn-Sham states are computed with an all-electron, atom-centered basis set. The FHI-aims suite supplies several options for optimized, numerical basis sets. Final results were computed with the PBE functional using the “tight” level basis set (similar to double zeta plus polarization) for the atoms in the molecule and the “loose” level (double zeta) for the Au atoms in the electrodes.^{25–27} The size of the gold structures used to model gold electrodes was converged with increasing number of gold atoms. The final calculations are performed with 18 atoms per electrode. Relaxation was considered complete when all force components/atom were less than 10^{-2} eV/Å.

Each molecule, **BQ**₁₋₃ was first relaxed in the gas-phase and then bound to the apex Au atoms of two Au₁₈ clusters. The relaxed junction geometry was found by moving the Au₁₈ electrodes in and out in steps of 0.05 Å and finding the lowest energy geometry. At each step, all atoms associated with the molecule as well as the four apex Au atoms in the Au₁₈ electrode were allowed to relax while the other Au atoms were frozen in place. Previous work has found that singly occupied molecular orbitals of the **BQ**_n series (SOMOs) are degenerate.^{8,12,28} Here we use the restricted DFT calculations which do not distinguish between spins to estimate transmission. We note that we do not use DFT here for quantitative comparisons, but only for qualitative checks. Importantly, our results agree qualitatively with previous DFT reports for these molecules as cited above. NEGF transport calculations were performed on the lowest energy geometry for each molecule using AITRANSS.^{29,30} The calculated transmission spectra for **BQ**₁₋₃ using DFT were then compared to the transmission spectra calculated using the modified 1D-SSH model with realistic parameters.

Table B1. Calculated molecular junction geometries for **BQ₁₋₃** using DFT.

Molecule	DFT Geometry
BQ₁	
BQ₂	
BQ₃	

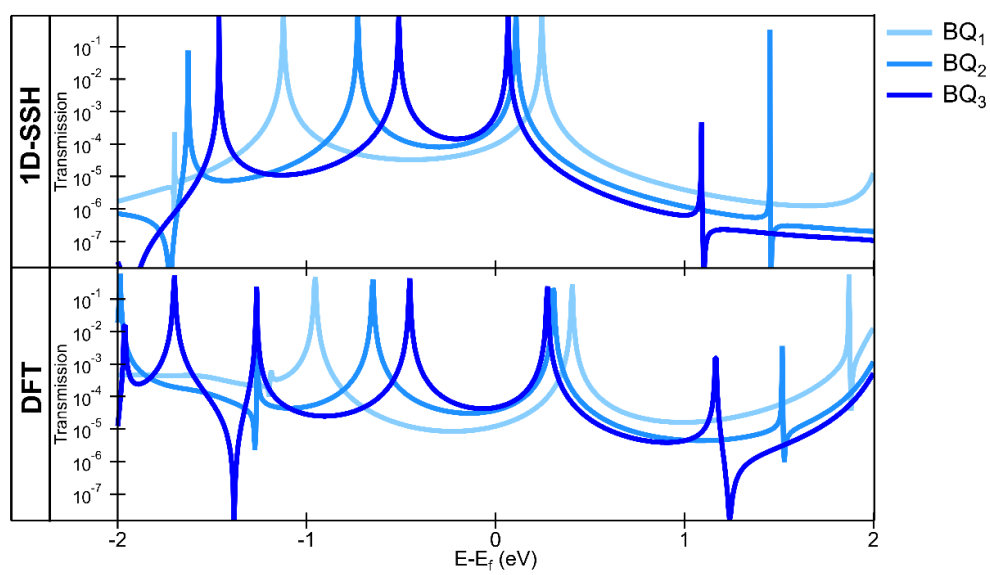


Figure B23. Comparison of NEGF transmission spectra for **BQ₁₋₃** from the modified 1D-SSH model and DFT.

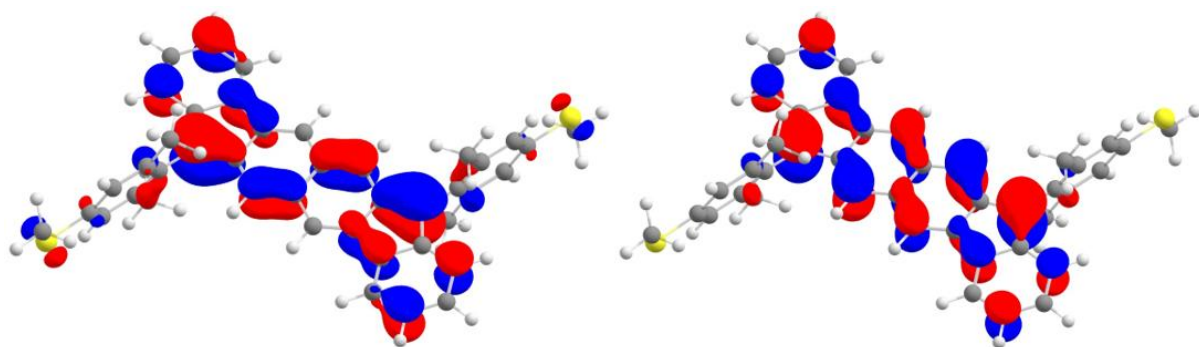


Figure B24. DFT-calculated closed-shell HOMO (left) and LUMO (right) of the **BQ₂**, which shows consistency with prior results.¹²

Additional 2D Histograms of BTQ_n Molecules

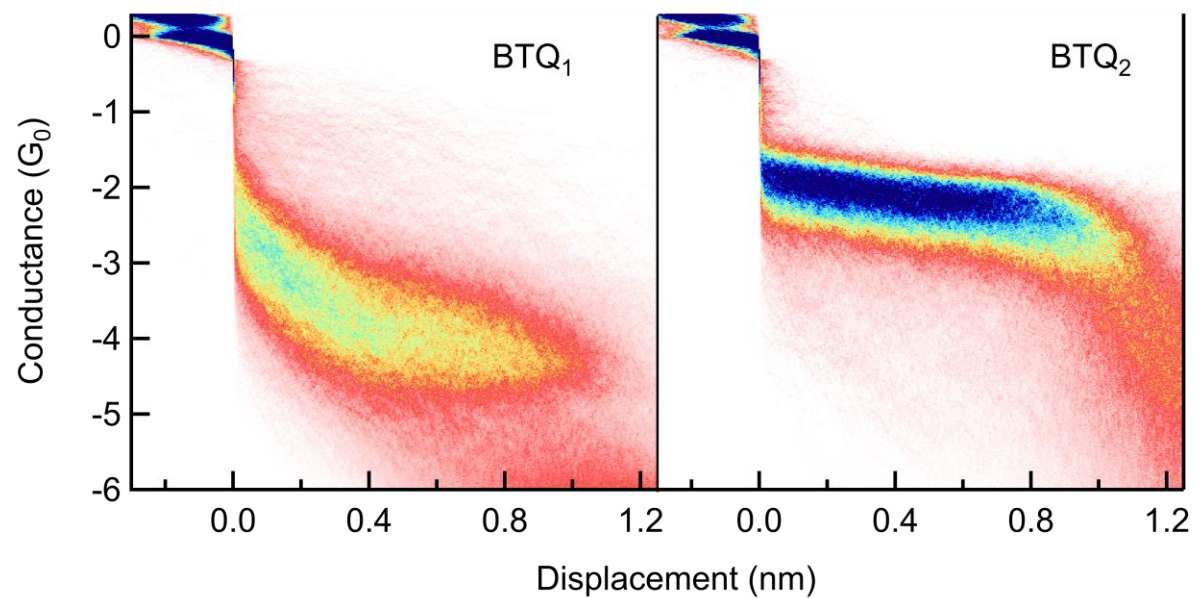


Figure B25. 2D Conductance histograms of BTQ₁ (left) and BTQ₂ (right) measured in BNP at -500 mV.

XYZ Coordinates of Lowest Energy Junctions

BQ₁ (top row of Table B1)

6	0.152101000	0.699961150	19.687418460
6	-0.684232360	1.520744140	18.812645670
6	0.122122650	1.229422190	20.980006810
6	-0.733850420	2.410495790	20.966209830
6	-1.232352150	2.598692690	19.639303870
6	-0.838996180	1.204428790	17.486087640
6	0.849015320	-0.438728050	19.175460640
6	0.695269320	-0.754601490	17.848926700
6	-0.161005650	0.051653430	16.979131800
6	-0.158407320	-0.501360050	15.696451080
6	1.236467910	-1.838679410	17.026649110
6	0.705753440	-1.676437840	15.709110080
1	-1.461463020	1.806559880	16.819165510
1	1.482809610	-1.032127010	19.839441940
6	-0.921209170	-0.019391030	14.521226850
6	-2.294788800	-0.341834240	14.405691860
6	-0.266992120	0.736627710	13.515279070
6	-3.003458880	0.108787020	13.283371650
6	-1.001192400	1.167005690	12.402657790
6	-2.360898830	0.862493710	12.298513700
1	-4.061441720	-0.136358930	13.174678400
1	-0.506262580	1.731088580	11.608956420
6	0.821859050	0.684104900	22.165742840
6	2.011312920	1.295250090	22.626589000
6	0.300091790	-0.456787120	22.827621800
6	2.682107370	0.748671930	23.730700610
6	0.990287840	-0.981839440	23.923989980
6	2.178661060	-0.387697750	24.365850470
1	3.602613370	1.223046930	24.069597920

1	0.593224580	-1.859862860	24.438152680
6	-2.999447000	-1.164582250	15.455919290
1	-2.441531180	-2.084285600	15.681511790
1	-3.094689990	-0.611752600	16.402095400
1	-4.006746570	-1.443192040	15.122183720
6	1.194974980	1.087978830	13.636741500
1	1.520644370	1.714758860	12.797623670
1	1.393854040	1.629666790	14.572839780
1	1.824061520	0.186064190	13.654635970
16	-3.355998660	1.393422070	10.892933030
6	2.586061960	2.504582580	21.930761420
1	1.908802450	3.368230640	22.000496690
1	3.550133180	2.790967590	22.369260340
1	2.737899090	2.308382230	20.859567290
6	-0.983231640	-1.106883400	22.372300980
1	-1.324934140	-1.851763030	23.101546620
1	-1.779946180	-0.361969340	22.237405700
1	-0.855326090	-1.612870200	21.403919730
16	3.005367570	-1.219182480	25.724511170
6	4.535091900	-0.256618900	25.966558780
1	4.315017030	0.784618670	26.223076670
1	5.039954020	-0.740416330	26.810662840
1	5.157174130	-0.331145440	25.066870720
6	-3.585347390	3.176534190	11.268547880
1	-4.167485490	3.262185950	12.193098030
1	-2.617299800	3.677866140	11.361741980
1	-4.144918770	3.593785740	10.423140020
6	2.091202170	-2.902313420	17.309790780
6	1.028125650	-2.586024690	14.693862800
6	1.889165240	-3.649857050	14.992602780
6	2.415309300	-3.805007230	16.283945690

1	2.504503110	-3.041533880	18.310805190
1	0.614921810	-2.470695190	13.689678730
1	2.152557000	-4.366857320	14.213921040
1	3.083429270	-4.641075180	16.495373590
6	-1.105632940	3.282325890	21.997419390
6	-2.086505110	3.663136020	19.357750350
6	-1.962993440	4.349465870	21.699362280
6	-2.445263370	4.538883720	20.395558480
1	-2.476534750	3.821069780	18.350170670
1	-0.738758170	3.130435650	23.014664160
1	-2.261764560	5.039605120	22.489507380
1	-3.112033170	5.376397430	20.185545160
79	-2.041178160	1.443387220	8.865968770
79	0.041825050	1.093690420	7.178944590
79	-2.656911810	0.162560440	6.484110720
79	-2.143949490	3.062017420	6.671750780
79	2.121564310	0.842006760	5.338511260
79	-0.526732890	-0.109963820	4.709121190
79	-3.175030060	-1.061934420	4.079731100
79	-0.013999610	2.723079960	4.872905890
79	-2.662296790	1.771109370	4.243515830
79	-2.149563510	4.604153130	4.407300530
79	1.599877560	-0.383360630	2.780743590
79	-1.048419630	-1.335331230	2.151353510
79	2.112610810	2.449683130	2.944528310
79	-0.535686350	1.497712550	2.315138970
79	-3.183983540	0.545741950	1.685748140
79	-0.022953080	4.330756330	2.478922950
79	-2.671250270	3.378785710	1.849532870
79	2.634297570	3.675050540	5.502295980
79	1.786456540	-0.840486160	27.787974050

79	0.299442980	-2.346282690	29.529580670
79	3.045165640	-1.415850000	30.178389040
79	0.860813300	0.549673190	29.895642690
79	-1.189431780	-3.744026570	31.415454620
79	1.496104930	-2.874316890	32.004823440
79	4.181641620	-2.004607240	32.594192280
79	-0.627992870	-0.937951920	31.771248680
79	2.057543830	-0.068242280	32.360617500
79	-0.066553960	1.868122700	32.127042750
79	-0.025752570	-4.303787180	33.993899220
79	2.659784130	-3.434077530	34.583268050
79	-2.149850330	-2.367422220	33.760324450
79	0.535686350	-1.497712550	34.349692530
79	3.221223050	-0.628002910	34.939062120
79	-1.588411430	0.438652410	34.116118510
79	1.097125280	1.308362070	34.705487340
79	-3.313529550	-1.807661580	31.181879860

BQ₂ (middle row of Table B1)

6	0.555938100	0.311265340	20.123198300
6	-0.121703880	1.435436280	20.643376790
6	-0.949170830	2.257731760	19.766533940
6	-1.090436090	1.927897580	18.444762900
6	-0.422931420	0.774613410	17.903952680
6	0.425034990	-0.034835900	18.778887630
6	-0.142763000	1.975747700	21.941604430
6	-0.982308160	3.157548080	21.915337440
6	-1.485226720	3.342554080	20.585239550
1	1.192491600	-0.292308590	20.775989940
1	-1.709374660	2.528288580	17.772578750
6	-0.567699650	0.417336400	16.563672940

6	1.111492140	-1.174332500	18.233924610
6	0.963478790	-1.510245840	16.914697660
6	0.097853460	-0.716444110	16.047313600
6	0.103249640	-1.273558120	14.756381170
6	1.513403590	-2.587045250	16.095755890
6	0.977793780	-2.429913920	14.775227980
1	-1.200126140	1.023950100	15.909618190
1	1.748564840	-1.760848770	18.901324070
6	-0.664380670	-0.793224830	13.584626820
6	-2.043322550	-1.099711830	13.481744020
6	-0.012137880	-0.047559150	12.569336130
6	-2.758235210	-0.643775130	12.364968630
6	-0.752568420	0.389778410	11.463873890
6	-2.116417220	0.100991330	11.372153110
1	-3.819630190	-0.878990320	12.267007200
1	-0.259796860	0.948564050	10.665133800
6	0.561626320	1.426882430	23.121608860
6	1.749671150	2.039813540	23.585236010
6	0.051364280	0.274120610	23.772995530
6	2.429896650	1.483544880	24.678798800
6	0.751379020	-0.261203960	24.857882810
6	1.937052940	0.336162370	25.302560730
1	3.348957930	1.959845630	25.019053620
1	0.361948700	-1.147921290	25.362930180
6	-2.744283630	-1.919113410	14.537631790
1	-2.194885900	-2.847565230	14.748392600
1	-2.817290790	-1.372801290	15.489529840
1	-3.760185950	-2.182555650	14.217777000
6	1.455727930	0.284566710	12.670749680
1	1.770257380	0.933061190	11.843933920
1	1.681311630	0.793374540	13.618942760

1	2.074372030	-0.624465670	12.645917620
16	-3.110488580	0.641555370	9.968896000
6	2.311005810	3.265214510	22.906289960
1	1.641198020	4.129926960	23.021643090
1	3.289021830	3.534713790	23.324310760
1	2.428793260	3.100037680	21.825744470
6	-1.236818280	-0.371458520	23.325004270
1	-1.567160460	-1.128371690	24.047090250
1	-2.035495300	0.375481530	23.214851120
1	-1.124377390	-0.860570680	22.346154920
16	2.765400830	-0.497976010	26.658582730
6	4.299090080	0.460134850	26.893399900
1	4.083284320	1.500279540	27.157387750
1	4.811286780	-0.029419770	27.729704120
1	4.912623780	0.389891630	25.987453290
6	-3.337603460	2.422978870	10.355912980
1	-3.920433770	2.503544500	11.280536080
1	-2.368933080	2.922318390	10.453908100
1	-3.895971150	2.847165840	9.513127340
6	2.383110500	-3.640757810	16.378180490
6	1.315080090	-3.340387110	13.759819970
6	2.188555890	-4.388965420	14.060074780
6	2.718612720	-4.537547050	15.354026750
1	2.798676580	-3.774015220	17.379030000
1	0.899893160	-3.232036930	12.755735070
1	2.462409400	-5.103322970	13.282405820
1	3.398377840	-5.364496230	15.563911230
6	-1.345142870	4.046256810	22.941069020
6	-2.329824350	4.415232580	20.298488590
6	-2.189577580	5.116901710	22.635280990
6	-2.675047380	5.301710020	21.328614190

1	-2.721390220	4.569140000	19.290945260
1	-0.978377270	3.898581650	23.958915600
1	-2.479696650	5.817394080	23.419684310
1	-3.333632280	6.144748190	21.115171420
79	-1.796577300	0.703549280	7.934570410
79	0.295557390	0.353399700	6.245657270
79	-2.400175130	-0.577867470	5.550974210
79	-1.886621100	2.319642240	5.739165170
79	2.381746930	0.100565340	4.403670720
79	-0.266550270	-0.851405240	3.774280650
79	-2.914847440	-1.803375840	3.144890560
79	0.246183010	1.981638540	3.938065350
79	-2.402114170	1.029667950	3.308675290
79	-1.889380890	3.862711710	3.472459990
79	1.860060180	-1.124802050	1.845903050
79	-0.788237010	-2.076772650	1.216512970
79	2.372793430	1.708241710	2.009687770
79	-0.275503730	0.756271130	1.380298430
79	-2.923800920	-0.195699470	0.750907600
79	0.237229540	3.589314910	1.544082410
79	-2.411067650	2.637344290	0.914692330
79	2.894480190	2.933609120	4.567455440
79	1.543009460	-0.108391250	28.722749560
79	0.042558680	-1.607604350	30.463531600
79	2.790489470	-0.676812660	31.115374630
79	0.604888590	1.287252700	30.827293160
79	-1.449614400	-3.002585150	32.350295160
79	1.235922310	-2.132875470	32.939663980
79	3.921459000	-1.263165820	33.529032820
79	-0.888175490	-0.196510500	32.706089220
79	1.797361210	0.673199140	33.295458040

79	-0.326736580	2.609564120	33.061883290
79	-0.285935190	-3.562345760	34.928739760
79	2.399601510	-2.692636110	35.518108590
79	-2.410032950	-1.625980800	34.695164990
79	0.275503730	-0.756271130	35.284533070
79	2.961040430	0.113438510	35.873902660
79	-1.848594050	1.180093830	35.050959050
79	0.836942660	2.049803490	35.640327880
79	-3.573712170	-1.066220160	32.116720400

BQ₃ (bottom row of Table B1)

6	0.297985110	1.047269400	21.073691830
6	-0.370236620	2.171888470	21.590607220
6	-1.197565810	2.998608620	20.710427300
6	-1.344900700	2.672204030	19.388534110
6	-0.165438920	0.015784550	16.960301710
6	0.688836440	-0.787717200	17.831023430
6	-0.387914380	2.719220080	22.889567990
6	-1.221044420	3.901893810	22.858168000
6	-1.726562880	4.085427320	21.527451350
1	0.933762410	0.438678830	21.722193330
1	-1.961497670	3.277349490	18.718782130
6	-0.319997400	-0.342359360	15.614105280
6	1.372644730	-1.928760390	17.287121650
6	1.215056220	-2.264871160	15.969139660
6	0.343382820	-1.471700090	15.099497740
6	0.350609050	-2.033415660	13.806871920
6	1.763588000	-3.340397180	15.151338090
6	1.225650030	-3.185823140	13.830045130
1	-0.957430920	0.264288410	14.965369570
1	2.015408990	-2.513600210	17.950214990

6	-0.412186430	-1.554323010	12.631023100
6	-1.791547040	-1.857871060	12.520851650
6	0.245795270	-0.813646920	11.615543050
6	-2.499671780	-1.405459850	11.398118860
6	-0.487615990	-0.378908700	10.504063250
6	-1.851216990	-0.665767630	10.405638980
1	-3.560436450	-1.641359800	11.295018840
1	0.010432940	0.176824110	9.706506700
6	0.312189500	2.170484310	24.072210600
6	1.498512020	2.782216350	24.542680710
6	-0.203684970	1.020369070	24.724676500
6	2.169427460	2.229828240	25.644353670
6	0.486389140	0.489032120	25.817839170
6	1.669166090	1.086515510	26.269819960
1	3.086671130	2.706164830	25.989712730
1	0.092305200	-0.395323570	26.323485040
6	-2.499871930	-2.672992990	13.574972410
1	-1.956084350	-3.604541790	13.786672130
1	-2.571634960	-2.126658530	14.527001300
1	-3.516586990	-2.930583300	13.252685360
6	1.713654360	-0.483104610	11.722379400
1	2.030956110	0.168120020	10.898721610
1	1.936859160	0.021721570	12.673207920
1	2.331621030	-1.392592420	11.695870480
16	-2.837934640	-0.125432880	8.995852990
6	2.068188490	4.002920990	23.862108810
1	1.404466610	4.872558870	23.976659430
1	3.048342090	4.266335550	24.279175670
1	2.183770500	3.835540320	22.781657460
6	-1.487400080	0.371969510	24.268601240
1	-1.817753220	-0.389449770	24.985924410

1	-2.288417040	1.116272380	24.157542680
1	-1.368414140	-0.112282890	23.288093760
16	2.484902770	0.253645840	27.634830910
6	4.031097480	1.193192160	27.863506660
1	3.829991530	2.238372260	28.119748650
1	4.536445710	0.703039270	28.703684530
1	4.643387590	1.107649830	26.957844670
6	-3.077565310	1.652939480	9.391463090
1	-3.666119620	1.724196790	10.313423680
1	-2.112115990	2.156559660	9.499091080
1	-3.633723530	2.079720760	8.548591940
6	2.635856550	-4.391869440	15.437008070
6	1.566087580	-4.100805420	12.817603460
6	2.440802720	-5.145905050	13.121964670
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1	2.715721890	-5.862351010	12.346458100
1	3.654003790	-6.116188430	14.628328930
6	-1.582995650	4.796723520	23.881160400
6	-2.570881870	5.158421480	21.238030310
6	-2.426468720	5.865791710	23.572009040
6	-2.914492370	6.048020010	22.264653000
1	-2.963495770	5.308400940	20.230279490
1	-1.216596850	4.651956540	24.899502920
1	-2.716390630	6.568426070	24.354717750
1	-3.573988320	6.890014370	22.050307970
6	-0.817635130	1.150471840	17.515365600
6	-0.682795290	1.515812770	18.848891260
6	0.820028620	-0.425332380	19.165457230
6	0.158939360	0.702498640	19.722709560

1	-1.449888710	1.756316930	16.860118410
1	1.455718170	-1.028522120	19.819817070
79	-1.523165230	-0.050340090	6.960231080
79	0.568897680	-0.401472830	5.269083660
79	-2.125341730	-1.333284030	4.573166490
79	-1.611622980	1.564573950	4.761591140
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79	0.008953460	-1.607676370	2.796397970
79	-2.639343710	-2.559646970	2.167007880
79	0.521686740	1.225367410	2.960182670
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79	0.000000000	0.000000000	0.402415750
79	-2.648297190	-0.951970600	-0.226975080
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References

- (1) Zysman-Colman, E.; Arias, K.; Siegel, J. S. Synthesis of Arylbromides from Arenes and N-bromosuccinimide (NBS) in Acetonitrile - A Convenient Method for Aromatic Bromination. *Can. J. Chem.* **2009**, *87* (2), 440–447. <https://doi.org/10.1139/V08-176>.
- (2) Su, T. A.; Widawsky, J. R.; Li, H.; Klausen, R. S.; Leighton, J. L.; Steigerwald, M. L.; Venkataraman, L.; Nuckolls, C. Silicon Ring Strain Creates High-Conductance Pathways in Single-Molecule Circuits. *J. Am. Chem. Soc.* **2013**, *135* (49), 18331–18334. <https://doi.org/10.1021/ja410656a>.
- (3) Chase, D. T.; Fix, A. G.; Kang, S. J.; Rose, B. D.; Weber, C. D.; Zhong, Y.; Zakharov, L. N.; Lonergan, M. C.; Nuckolls, C.; Haley, M. M. 6,12-Diarylindeno[1,2-b]Fluorenes: Syntheses, Photophysics, and Ambipolar OFETs. *J. Am. Chem. Soc.* **2012**, *134* (25), 10349–10352. <https://doi.org/10.1021/ja303402p>.
- (4) Young, B. S.; Chase, D. T.; Marshall, J. L.; Vonnegut, C. L.; Zakharov, L. N.; Haley, M. M. Synthesis and Properties of Fully-Conjugated Indacenedithiophenes. *Chem. Sci.* **2014**, *5* (3), 1008–1014. <https://doi.org/10.1039/c3sc53181c>.
- (5) Dressler, J. J.; Teraoka, M.; Espejo, G. L.; Kishi, R.; Takamuku, S.; Gómez-García, C. J.; Zakharov, L. N.; Nakano, M.; Casado, J.; Haley, M. M. Thiophene and Its Sulfur Inhibit Indenoindenodibenzothiophene Diradicals from Low-Energy Lying Thermal Triplets. *Nat. Chem.* **2018**, *10* (11), 1134–1140. <https://doi.org/10.1038/s41557-018-0133-5>.
- (6) Knall, A. C.; Ashraf, R. S.; Nikolka, M.; Nielsen, C. B.; Purushothaman, B.; Sadhanala, A.; Hurhangee, M.; Broch, K.; Harkin, D. J.; Novák, J.; et al. Naphthacenodithiophene Based Polymers—New Members of the Acenodithiophene Family Exhibiting High Mobility and Power Conversion Efficiency. *Adv. Funct. Mater.* **2016**, *26* (38), 6961–6969. <https://doi.org/10.1002/adfm.201602285>.
- (7) Vidal Jr., E.; Zakharov, L. N.; Gómez-García, C. J.; Haley, M. M. Probing the Influence of Alkyne Substitution on the Electronic and Magnetic Properties of Diindeno[1,2-b;1',2'-i]anthracenes. *J. Org. Chem.* **2024**, *89*, accepted. <https://doi.org/10.1021/acs.joc.4c01500>.
- (8) Rudebusch, G. E.; Zafra, J. L.; Jorner, K.; Fukuda, K.; Marshall, J. L.; Arrechea-Marcos, I.; Espejo, G. L.; Ponce Ortiz, R.; Gómez-García, C. J.; Zakharov, L. N.; et al. Diindeno-Fusion of an Anthracene as a Design Strategy for Stable Organic Biradicals. *Nat. Chem.* **2016**, *8* (8), 753–759. <https://doi.org/10.1038/nchem.2518>.
- (9) Barker, J. E.; Frederickson, C. K.; Jones, M. H.; Zakharov, L. N.; Haley, M. M. Synthesis and Properties of Quinoidal Fluorenofluorenes. *Org. Lett.* **2017**, *19* (19), 5312–5315. <https://doi.org/10.1021/acs.orglett.7b02605>.
- (10) Capozzi, B.; Xia, J.; Adak, O.; Dell, E. J.; Liu, Z. F.; Taylor, J. C.; Neaton, J. B.; Campos, L. M.; Venkataraman, L. Single-Molecule Diodes with High Rectification Ratios through Environmental Control. *Nat. Nanotechnol.* **2015**, *10* (6), 522–527. <https://doi.org/10.1038/nnano.2015.97>.
- (11) Li, L.; Louie, S.; Evans, A. M.; Meirzadeh, E.; Nuckolls, C. Topological Radical Pairs Produce Ultrahigh Conductance in Long Molecular Wires. *J. Am. Chem. Soc.* **2023**, *145* (4), 2492–2498. <https://doi.org/10.1021/jacs.2c12059>.
- (12) Frederickson, C. K.; Rose, B. D.; Haley, M. M. Explorations of the Indenofluorenes and Expanded Quinoidal Analogues. *Acc. Chem. Res.* **2017**, *50* (4), 977–987. <https://doi.org/10.1021/acs.accounts.7b00004>.

- (13) Hayashi, H.; Barker, J. E.; Cárdenas Valdivia, A.; Kishi, R.; Macmillan, S. N.; Gómez-García, C. J.; Miyauchi, H.; Nakamura, Y.; Nakano, M.; Kato, S. I.; et al. Monoradicals and Diradicals of Dibenzofluoreno[3,2- b]Fluorene Isomers: Mechanisms of Electronic Delocalization. *J. Am. Chem. Soc.* **2020**, *142* (48), 20444–20455. <https://doi.org/10.1021/jacs.0c09588>.
- (14) Dressler, J. J.; Cárdenas Valdivia, A.; Kishi, R.; Rudebusch, G. E.; Ventura, A. M.; Chastain, B. E.; Gómez-García, C. J.; Zakharov, L. N.; Nakano, M.; Casado, J.; et al. Diindenoanthracene Diradicaloids Enable Rational, Incremental Tuning of Their Singlet-Triplet Energy Gaps. *Chem* **2020**, *6* (6), 1353–1368. <https://doi.org/10.1016/j.chempr.2020.02.010>.
- (15) Li, L.; Gunasekaran, S.; Wei, Y.; Nuckolls, C.; Venkataraman, L. Reversed Conductance Decay of 1D Topological Insulators by Tight-Binding Analysis. *J. Phys. Chem. Lett.* **2022**, *13* (41), 9703–9710. <https://doi.org/10.1021/acs.jpcllett.2c02812>.
- (16) Stauber, T.; Beltrán, J. I.; Schliemann, J. Tight-Binding Approach to Pentagraphene. *Sci. Rep.* **2016**, *6*, 4–11. <https://doi.org/10.1038/srep22672>.
- (17) Castro Neto, A. H.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. The Electronic Properties of Graphene. *Rev. Mod. Phys.* **2009**, *81* (1), 109–162. <https://doi.org/10.1103/RevModPhys.81.109>.
- (18) Tsuji, Y.; Movassagh, R.; Datta, S.; Hoffmann, R. Exponential Attenuation of Through-Bond Transmission in a Polyene: Theory and Potential Realizations. *ACS Nano* **2015**, *9* (11), 11109–11120. <https://doi.org/10.1021/acs.nano.5b04615>.
- (19) Mulliken, R. S.; Rieke, C. A.; Orloff, D.; Orloff, H. Formulas and Numerical Tables for Overlap Integrals. *J. Chem. Phys.* **1949**, *17* (12), 1248–1267. <https://doi.org/10.1063/1.1747150>.
- (20) Gunasekaran, S.; Greenwald, J. E.; Venkataraman, L. Visualizing Quantum Interference in Molecular Junctions. *Nano Lett.* **2020**, *20* (4), 2843–2848. <https://doi.org/10.1021/acs.nanolett.0c00605>.
- (21) Géranton, G.; Seiler, C.; Bagrets, A.; Venkataraman, L.; Evers, F. Transport Properties of Individual C60-Molecules. *J. Chem. Phys.* **2013**, *139* (23), 234701. <https://doi.org/10.1063/1.4840535>.
- (22) Camarasa-Gómez, M.; Hernangómez-Pérez, D.; Inkpen, M. S.; Lovat, G.; Fung, E. D.; Roy, X.; Venkataraman, L.; Evers, F. Mechanically Tunable Quantum Interference in Ferrocene-Based Single-Molecule Junctions. *Nano Lett.* **2020**, *20* (9), 6381–6386. <https://doi.org/10.1021/acs.nanolett.0c01956>.
- (23) Datta, S.; Melloch, M. R.; Bandyopadhyay, S.; Noren, R.; Vaziri, M.; Miller, M.; Reifenger, R. Novel Interference Effects between Parallel Quantum Wells. *Phys. Rev. Lett.* **1985**, *55* (21), 2344–2347. <https://doi.org/10.1103/PhysRevLett.55.2344>.
- (24) Evers, F.; Korytár, R.; Tewari, S.; Van Ruitenbeek, J. M. Advances and Challenges in Single-Molecule Electron Transport. *Rev. Mod. Phys.* **2020**, *92* (3), 35001. <https://doi.org/10.1103/RevModPhys.92.035001>.
- (25) Blum, V.; Gehrke, R.; Hanke, F.; Havu, P.; Havu, V.; Ren, X.; Reuter, K.; Scheffler, M. Ab Initio Molecular Simulations with Numeric Atom-Centered Orbitals. *Comput. Phys. Commun.* **2009**, *180* (11), 2175–2196. <https://doi.org/10.1016/j.cpc.2009.06.022>.
- (26) Ren, X.; Rinke, P.; Blum, V.; Wieferink, J.; Tkatchenko, A.; Sanfilippo, A.; Reuter, K.; Scheffler, M. Resolution-of-Identity Approach to Hartree-Fock, Hybrid Density Functionals, RPA, MP2 and GW with Numeric Atom-Centered Orbital Basis Functions.

- New J. Phys.* **2012**, *14* (053020), 053020. <https://doi.org/10.1088/1367-2630/14/5/053020>.
- (27) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>.
- (28) Nieman, R.; Silva, N. J.; Aquino, A. J. A.; Haley, M. M.; Lischka, H. Interplay of Biradicaloid Character and Singlet/Triplet Energy Splitting for Cis-/Trans-Diindenoacenes and Related Benzo[thiophene]-Capped Oligomers as Revealed by Extended Multireference Calculations. *J. Org. Chem.* **2020**, *85* (5), 3664–3675. <https://doi.org/10.1021/acs.joc.9b03308>.
- (29) Arnold, A.; Weigend, F.; Evers, F. Quantum Chemistry Calculations for Molecules Coupled to Reservoirs: Formalism, Implementation, and Application to Benzenedithiol. *J. Chem. Phys.* **2007**, *126* (17), 174101. <https://doi.org/10.1063/1.2716664>.
- (30) Bagrets, A. Spin-Polarized Electron Transport across Metal-Organic Molecules: A Density Functional Theory Approach. *J. Chem. Theory Comput.* **2013**, *9* (6), 2801–2815. <https://doi.org/10.1021/ct4000263>.

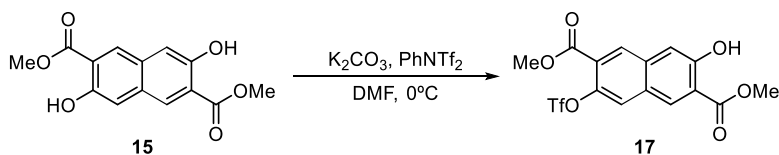
APPENDIX C

SUPPLEMENTARY INFORMATION FOR CHAPTER IV

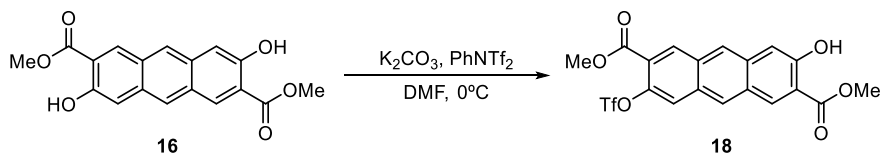
Appendix C is the supplementary information for Chapter IV. Experimental details, experimental data, spectra, and additional references relevant to the content of Chapter IV are provided here.

Experimental Details

General. All air-sensitive reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk technique. Silica gel (240-300 mesh) was used for chromatography. All other solvents and reagents were purchased and used as received unless stated otherwise. NMR spectra were recorded on a Bruker Avance III HD 500 equipped with a Prodigy multinuclear cryoprobe (^1H : 500 MHz, ^{13}C : 126 MHz) or Bruker Avance III HD 600 equipped with a Prodigy multinuclear broadband cryoprobe (^1H : 600 MHz, ^{13}C : 151 MHz) NMR spectrometer at room temperature unless otherwise noted. ^1H and ^{13}C NMR chemical shifts (δ) are expressed in ppm relative to the residual non-deuterated solvent reference (CDCl_3 : ^1H 7.26 ppm, ^{13}C 77.16 ppm; CD_2Cl_2 : ^1H 5.32 ppm, ^{13}C 53.84 ppm). UV-Vis spectrum was recorded on an Agilent Technologies Cary 60 UV-Vis spectrometer in HPLC grade CH_2Cl_2 . HRMS was recorded on a Waters GCT Premier orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer at the UIUC Mass Spectrometry Lab. Boronic acid esters **19**¹, **22**², **28**³, and **33**⁴; alkoxy aryl iodide **AC1**⁵, bis-aryl ethynyl dibromide **AC6**⁶; dihydroxy-diesters **15**⁷ and **16**⁸; and bistriflates **44**⁷ and **47**⁸ were prepared as previously described in the literature.

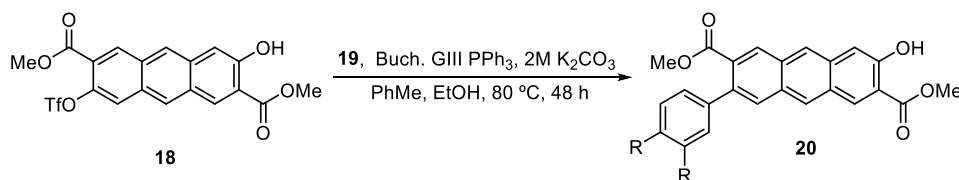


Monotriflate 17. A round bottom flask containing **15** (2.07 g, 7.24 mmol, 1 equiv.) and K_2CO_3 (2.07 g, 14.48 mmol, 2 equiv.) was placed under a N_2 atmosphere. The solids were suspended in anhydrous DMF (100 mL) and cooled to 0°C while stirring for 40 min. A solution of PhNTf_2 (2.68 g, 7.24 mmol, 1 equiv.) in DMF (20 mL) was prepared under N_2 in a round bottom flask. After 40 min, the PhNTf_2 solution was slowly added at 0°C and the reaction was allowed to warm to room temperature while stirring overnight. The reaction was re-cooled to 0°C and quenched with a 3M HCl solution. The resulting precipitate was filtered, washed with H_2O , and dried in an oven for 15 min. The solids were triturated in CH_2Cl_2 against Hexanes to yield the desired product **17** (2.51 g, 85%) as a yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 10.61 (s, 1H), 8.55 (s, 1H), 8.47 (s, 1H), 7.73 (s, 1H), 7.47 (s, 1H), 4.07 (s, 3H), 4.02 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 169.63, 164.28, 158.15, 143.23, 135.82, 133.15, 132.17, 127.83, 125.14, 122.33, 117.56, 113.55, 53.26, 53.04. ^{19}F NMR (471 MHz, CDCl_3) δ -73.20.



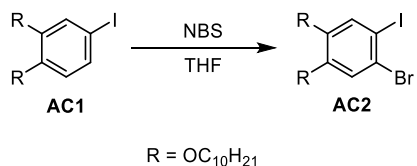
Monotriflate 18. A round bottom flask containing **16** (1.02 g, 3.12 mmol, 1 equiv.) and K_2CO_3 (0.864 g, 6.25 mmol, 2 equiv.) was placed under a N_2 atmosphere. The solids were suspended in anhydrous DMF (47 mL) and cooled to 0°C while stirring for 40 min. A solution of PhNTf_2 (1.12 g, 3.12 mmol, 1 equiv.) in DMF (13 mL) was prepared under N_2 in a round bottom flask. After 40 min, the PhNTf_2 solution was slowly added at 0°C and the reaction was

allowed to warm to room temperature while stirring overnight. The reaction was re-cooled to 0 °C and quenched with a 3M HCl solution. The resulting precipitate was filtered, washed with H₂O, and dried in an oven for 15 min. The solids were triturated in THF against Hexanes to yield the desired product **18** (1.01 g, crude 54%) as an orange solid. Bistriflate byproduct (¹³C δ 8.88 (s, 2H), 8.67 (s, 2H), 7.98 (s, 2H), 4.07 (s, 6H); ¹⁹F δ -73.04) was inseparable due to poor solubility incompatible with chromatography. ¹H NMR (500 MHz, CDCl₃) δ 10.43 (s, 1H), 8.79 (s, 1H), 8.76 (s, 1H), 8.49 (s, 1H), 8.41 (s, 1H), 7.84 (s, 1H), 7.50 (s, 1H), 4.09 (s, 3H), 4.04 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 169.80, 164.41, 155.72, 143.56, 136.00, 135.87, 134.12, 131.06, 129.88, 129.41, 128.13, 126.56, 123.23, 121.64, 117.71, 110.59, 53.19, 52.95. ¹⁹F NMR (471 MHz, CDCl₃) δ -73.16.



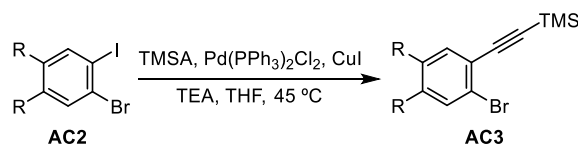
Diester 20. Conditions were adapted from ref 9. A three-neck round bottom flask containing **18** (712 mg, 4.55 mmol, 1 equiv.), **19** (.963 mg, 1.86 mmol, 1.2 equiv.), and Buchwald GIII PPh₃ precatalyst (49.1 mg, 0.077 mmol, 0.05 equiv.) was placed under a N₂ atmosphere. PhMe (18 mL), MeOH (4.5 mL), and 2M K₂CO₃ (4.5 mL) were added, and the reaction mixture was sparged for 40 min. The reaction was then stirred at 80 °C for 48h. Once cooled to room temperature, the reaction mixture was concentrated and redissolved in EtOAc and washed with DI H₂O twice and brine once. The combined organic fractions were dried over MgSO₄, which was then filtered and concentrated. The crude residue was then triturated in Hexanes against MeOH to yield **20** (257 mg, 24%) as a dark orange solid. Over integrated

aliphatic proton signals (*) are attributed to peak widening caused by asymmetric chemical environments of decyloxy-groups and inseparable aliphatic impurities. ^1H NMR (500 MHz, CDCl_3) δ 10.33 (s, 1H), 8.77 (s, 1H), 8.45 (s, 1H), 8.40 (s, 1H), 8.32 (s, 1H), 7.91 (s, 1H), 7.47 (s, 1H), 6.99 – 6.93 (m, 3H), 4.09 – 4.00 (m, 8H)*, 3.73 (s, 3H), 1.89 – 1.80 (m, 6H)*, 1.54 – 1.45 (m, 6H)*, 1.40 – 1.24 (m, 39H)*, 0.91 – 0.85 (m, 9H)*. ^{13}C NMR (126 MHz, CDCl_3) δ 170.07, 169.46, 154.88, 149.00, 148.80, 136.84, 135.19, 134.39, 134.08, 131.90, 131.35, 131.02, 130.67, 129.74, 128.98, 127.69, 125.20, 120.98, 116.64, 114.49, 113.67, 110.27, 69.57, 69.48, 52.98, 52.41, 32.08, 32.07, 29.82, 29.80, 29.76, 29.75, 29.64, 29.61, 29.54, 29.52, 29.51, 26.25, 26.23, 22.85, 22.83, 14.27, 14.25.

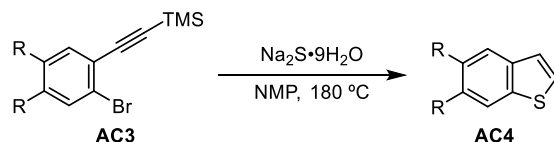


6-Bromo-3,4-didecyloxy-1-iodobenzene AC2. A round bottom flask containing **AC1** (8.82 g, 17.1 mmol, 1 equiv.) was charged with THF (150 mL) and covered in foil to block ambient light. NBS (3.65 g, 20.5 mmol, 1.2 equiv.) was then added and the reaction mixture was stirred in the dark overnight. DI H_2O was added to the flask (300 mL) and the organic layer was separated. The aqueous layer was further extracted with EtOAc (75 mL) thrice. Combined organic fractions were washed with 1M K_2CO_3 (200 mL), DI H_2O (200 mL), and brine (200 mL) then dried over MgSO_4 . The organics were then filtered and concentrated in vacuo. The crude residue was then recrystallized in EtOH to yield **AC2** (9.51 g, 94%) as a white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.23 (s, 1H), 7.07 (s, 1H), 3.97 – 3.90 (m, 4H), 1.83 – 1.75 (m, 4H), 1.49 – 1.40 (m, 4H), 1.37 – 1.24 (m, 24H), 0.88 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ

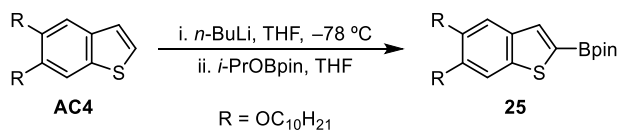
150.23, 149.04, 124.48, 120.21, 117.52, 88.95, 69.82, 69.64, 32.06, 29.74, 29.71, 29.49, 29.24, 29.17, 26.07, 22.83, 14.26. HRMS (TOF) m/z : $[M^+]$ Calcd for $C_{26}H_{44}BrIO_2$ 594.1564; Found 594.1559.



1-Bromo-3,4-didecyloxy-6-(trimethylsilyl)ethynylbenzene AC3. A round bottom flask containing **AC2** (9.51 g, 16.0 mmol, 1 equiv.), bis(triphenylphosphine)palladium(II) dichloride (5 mol%), and copper(I) iodide (5 mol%) placed under a N_2 atmosphere and charged with degassed THF (10.6 mL) and TEA (21.1 mL). The mixture was stirred at 50 $^\circ\text{C}$ for 45 min then cooled to 30 $^\circ\text{C}$ while TMSA was added dropwise. The reaction was sparged with N_2 for 10 min then stirred at 48 $^\circ\text{C}$ until the reaction was complete according to TLC analysis. Volatile organics were removed in vacuo and the residue was redissolved in CH_2Cl_2 (100 mL), washed with DI H_2O (200 mL) and brine (200 mL). The organics were dried over MgSO_4 then filtered through a 2 cm celite pad and concentrated. The crude residue was subjected to column chromatography on silica (eluted with a gradient from 0–20% CH_2Cl_2 in Hexanes) to yield **AC3** (7.59 g, 84%) as an auburn oil. ^1H NMR (500 MHz, CDCl_3) δ 7.00 (s, 1H), 6.96 (s, 1H), 4.01 – 3.91 (m, 4H), 1.85 – 1.76 (m, 4H), 1.49 – 1.40 (m, 4H), 1.36 – 1.25 (m, 24H), 0.88 (t, J = 6.8 Hz, 6H), 0.26 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 150.13, 147.81, 117.52, 116.97, 116.72, 103.43, 97.16, 69.34, 69.25, 31.81, 29.50, 29.48, 29.46, 29.26, 29.24, 29.01, 28.91, 25.85, 25.81, 22.58, 14.00, -0.15. HRMS (TOF) m/z : $[M^+]$ Calcd for $C_{26}H_{44}BrO_2\text{Si}$ 564.2993; Found 564.2988.



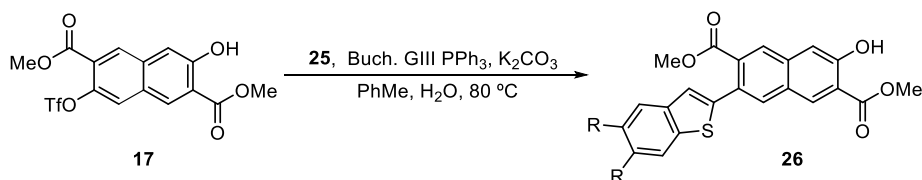
5,6-didecyloxybenzo[b]thiophene AC4. A round bottom flask containing $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (4.25 g, 17.7 mmol, 2.5 equiv.) was placed under a N_2 atmosphere. The salt was suspended in distilled anhydrous NMP (75 mL) and stirred until the solution turned light blue. **AC3** was then dissolved with NMP (25 mL) and transferred to the sulfide solution under N_2 . The reaction was stirred overnight at $180\text{ }^{\circ}\text{C}$. Once cooled to room temperature, the reaction was quenched with saturated aqueous NH_4Cl (200 mL). The precipitate was filtered and washed with DI H_2O . The Buchner funnel was transferred to a separate side-arm flask and the crude precipitate was dissolved with CH_2Cl_2 then concentrated. The crude product was subjected to column chromatography on silica (eluting with a gradient from 0–14% CH_2Cl_2 in Hexanes) to yield **AC4** (801 mg, 25%) as a tan solid. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.31 (s, 1H), 7.27 (d, $J = 5.3$ Hz, 1H), 7.26 (s, 1H), 7.19 (d, $J = 5.3$ Hz, 1H), 4.02 (t, $J = 6.6$ Hz, 4H), 1.83 (p, $J = 6.8$ Hz, 5H), 1.49 (q, $J = 7.6$ Hz, 5H), 1.41 – 1.26 (m, 28H), 0.89 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 148.86, 148.69, 133.80, 132.81, 124.47, 123.81, 107.56, 106.55, 69.91, 69.84, 32.36, 30.08, 30.03, 29.89, 29.87, 29.79, 29.75, 26.53, 26.51, 23.13, 14.30.



5,6-didecyloxy-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[3]thiophene 25.

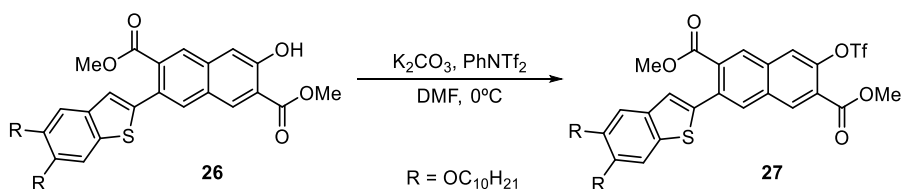
Anhydrous THF (11 mL) was added to an oven dried round bottom flask containing **AC4** (664 mg, 1.48 mmol, 1 equiv.). The stirring solution was cooled to $-78\text{ }^{\circ}\text{C}$. Once the solution had

firmed, *n*-BuLi (2.67 mL, 2.5 M, 6.69 mmol, 4.5 equiv.) was added dropwise. The flask was then transferred to an ice bath and stirred for 10 min at 0 °C then returned to –78 °C to stir for another 45 min. *i*-PrOBpin (1.46 mL, 7.13 mmol, 4.8 equiv) was then added and the reaction warmed to room temperature overnight. The reaction was quenched with saturated aqueous ammonium chloride and extracted with EtOAc thrice. The combined organics were washed with brine, dried over MgSO₄, filtered, and concentrated. The crude residue was subjected to column chromatography on silica (eluting with 5% EtOAc in Hexanes) to yield **25** (365 mg, 43%) as a white solid. ¹H NMR (500 MHz, CD₂Cl₂) δ 7.67 (s, 1H), 7.31 (s, 1H), 7.26 (s, 1H), 4.07 – 3.99 (m, 4H), 1.89 – 1.78 (m, 4H), 1.52 – 1.46 (m, 4H), 1.41 – 1.25 (m, 36H), 0.89 (t, *J* = 6.8 Hz, 6H). ¹³C NMR (126 MHz, CD₂Cl₂) δ 150.06, 148.70, 137.45, 134.61, 134.34, 107.55, 105.65, 84.64, 69.79, 69.67, 32.35, 30.07, 30.02, 29.87, 29.84, 29.78, 29.73, 29.66, 26.51, 26.49, 25.01, 23.12, 14.29. ¹¹B NMR (160 MHz, CD₂Cl₂) δ 27.93.



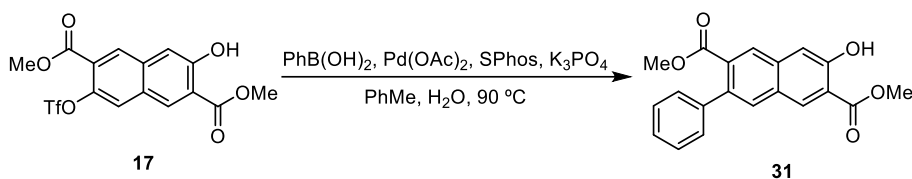
Diester 26. A three-neck round bottom flask was charged with **17** (331 mg, 0.812 mmol, 1 equiv.), **25** (558 mg, 0.974 mmol, 1.2 equiv.), Buchwald GIII PPh₃ precatalyst (5 mol%), K₂CO₃ (168 mg, 1.22 mmol, 1.5 equiv.) and placed under a N₂ atmosphere. A degassed mixture of PhMe (13.5 mL) and H₂O (1.5 mL) was cannulated into the flask and the reaction was stirred at 80 °C overnight. The reaction was then cooled to room temperature, quenched with DI H₂O, extracted with CH₂Cl₂ thrice, dried organics over MgSO₄, filtered through a silica/celite pad (1.5 cm, eluting with CH₂Cl₂), and concentrated. The crude residue was subjected to column

chromatography on silica (eluted with a gradient from 0–30% EtOAc in Hexanes) to yield **26** (407 mg, 71%) as a yellow solid. ^1H NMR (500 MHz, CD_2Cl_2) δ 10.55 (s, 1H), 8.57 (s, 1H), 8.07 (s, 1H), 8.00 (s, 1H), 7.39 (s, 1H), 7.30 (s, 1H), 7.24 (s, 1H), 7.14 (s, 1H), 4.07 – 4.01 (m, 7H), 3.80 (s, 3H), 1.89 – 1.80 (m, 4H), 1.54 – 1.47 (m, 4H), 1.43 – 1.36 (m, 4H), 1.37 – 1.26 (m, 20H), 0.91 – 0.86 (m, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.41, 169.03, 157.79, 148.97, 148.90, 140.20, 136.60, 134.39, 133.43, 133.37, 132.85, 131.80, 129.06, 128.60, 127.79, 122.79, 116.80, 112.67, 107.71, 106.32, 69.96, 69.88, 53.28, 52.86, 32.36, 30.09, 30.03, 29.89, 29.87, 29.79, 29.74, 26.53, 26.51, 23.12, 14.30.

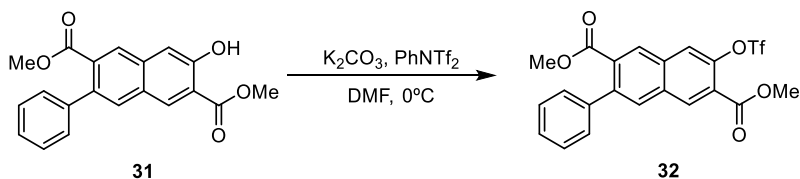


Triflate 27. A round bottom flask containing **26** (407 mg, 0.577 mmol, 1 equiv.) and K_2CO_3 (160 mg, 1.15 mmol, 2 equiv.) was placed under a N_2 atmosphere. The solids were suspended in anhydrous DMF (13 mL) and cooled to 0 °C while stirring for 40 min. A solution of PhNTf_2 (206 mg, 0.577 mmol, 1 equiv.) in DMF (8 mL) was prepared under N_2 in a round bottom flask. After 40 min, the PhNTf_2 solution was slowly added at 0 °C and the reaction was allowed to warm to room temperature while stirring overnight. The reaction was re-cooled to 0 °C and quenched with a 3M HCl solution. The resulting precipitate was filtered, washed with H_2O , and dried over vacuum. The solids were triturated in CH_2Cl_2 against Hexanes to yield the desired product **17** (2.51 g, 85%) as a light yellow-green solid. ^1H NMR (600 MHz, CD_2Cl_2) δ 8.69 (s, 1H), 8.28 (s, 1H), 8.18 (s, 1H), 7.86 (s, 1H), 7.31 (s, 1H), 7.26 (s, 1H), 7.22 (s, 1H), 4.08 – 4.01 (m, 4H), 4.01 (s, 3H), 3.83 (s, 3H), 1.89 – 1.81 (m, 4H), 1.50 (d, $J = 7.8$ Hz, 4H), 1.39 (p,

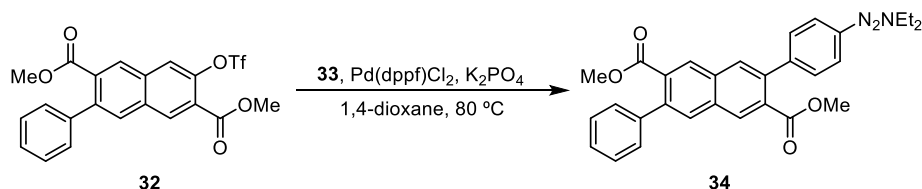
$J = 6.7$ Hz, 4H), 1.34 – 1.27 (m, 20H), 0.91 – 0.86 (m, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 168.49, 164.30, 149.32, 149.02, 145.86, 138.94, 134.91, 134.26, 134.05, 133.77, 133.72, 133.57, 132.43, 131.42, 129.88, 124.66, 123.77, 122.05, 107.77, 106.14, 69.93, 69.87, 53.22, 53.12, 32.35, 30.08, 30.03, 29.88, 29.86, 29.78, 29.76, 29.71, 26.53, 26.50, 23.12, 14.29. ^{19}F NMR (471 MHz, CD_2Cl_2) δ -73.48.



Diester 31. A three-neck round bottom flask fitted with a reflux condenser was charged with **17** (2.66 g, 6.50 mmol, 1 equiv.), PhB(OH)_2 (874 mg, 7.17 mmol, 1.1 equiv.), Pd(OAc)_2 (4 mol%), SPhos (8 mol%), K_3PO_4 (168 mg, 1.22 mmol, 1.5 equiv.) and placed under a N_2 atmosphere. A degassed mixture of PhMe (36 mL) and H_2O (4 mL) was cannulated into the flask and the reaction was stirred at 90 °C overnight. The reaction was then cooled to room temperature, quenched with DI H_2O , extracted with CH_2Cl_2 thrice, dried organics over MgSO_4 , filtered through a silica/celite pad (2 cm, eluting with CH_2Cl_2), and concentrated to yield **31** (2.00 g, 90%) as a light yellow solid. ^1H NMR (500 MHz, CDCl_3) δ 10.51 (s, 1H), 8.53 (s, 1H), 8.18 (s, 1H), 7.80 (s, 1H), 7.43 – 7.37 (m, 6H), 4.05 (s, 3H), 3.69 (s, 3H).

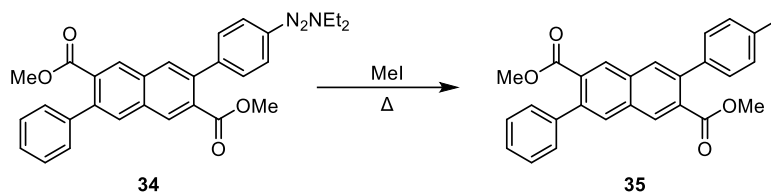


Triflate 32. A round bottom flask containing **31** (2.00 g, 5.95 mmol, 1 equiv.) and K₂CO₃ (1.64 g, 11.9 mmol, 2 equiv.) was placed under a N₂ atmosphere. The solids were suspended in anhydrous DMF (100 mL) and cooled to 0 °C while stirring for 40 min. A solution of PhNTf₂ (3.72 g, 10.4 mmol, 1.75 equiv.) in DMF (20 mL) was prepared under N₂ in a round bottom flask. After 40 min, the PhNTf₂ solution was slowly added at 0 °C and the reaction was allowed to warm to room temperature while stirring overnight. The reaction was re-cooled to 0 °C and quenched with a 3M HCl solution. The resulting precipitate was filtered, washed with H₂O, and dried over vacuum. The solids were triturated in CH₂Cl₂ against Hexanes to yield the desired product **32** (2.00 g, 71%) as a yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 8.68 (s, 1H), 8.39 (s, 1H), 7.98 (s, 1H), 7.85 (s, 1H), 7.49 – 7.36 (m, 5H), 4.04 (s, 3H), 3.71 (s, 3H).

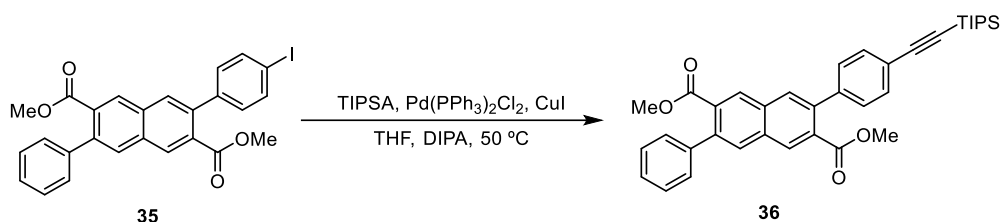


Triazene 34. A three-neck round bottom flask fitted with a reflux condenser was charged with **32** (2.00 g, 4.27 mmol, 1 equiv.), **33** (1.94 g, 6.40 mmol, 1.5 equiv.), Pd(dppf)Cl₂ (3 mol%), K₃PO₄ (4.53 g, 21.3 mmol, 5 equiv.) and placed under a N₂ atmosphere. Degassed 1,4-dioxane (100 mL) was cannulated into the flask and the reaction was stirred at 80 °C overnight. The reaction was then cooled to room temperature, quenched with DI H₂O, and the precipitate was filtered and dried in an oven for 15 min. The crude solid was dissolved in CH₂Cl₂ and filtered through a silica/alumina pad (2 cm, eluting with CH₂Cl₂), and concentrated to yield **34** (2.12 g, quant) as a dark yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 8.38 (s, 1H), 8.33 (s, 1H), 7.94 (s,

1H), 7.90 (s, 1H), 7.51 (d, $J = 8.3$ Hz, 2H), 7.45 – 7.36 (m, 7H), 3.80 (q, $J = 7.2$ Hz, 4H), 3.72 (s, 3H), 3.70 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 6H).

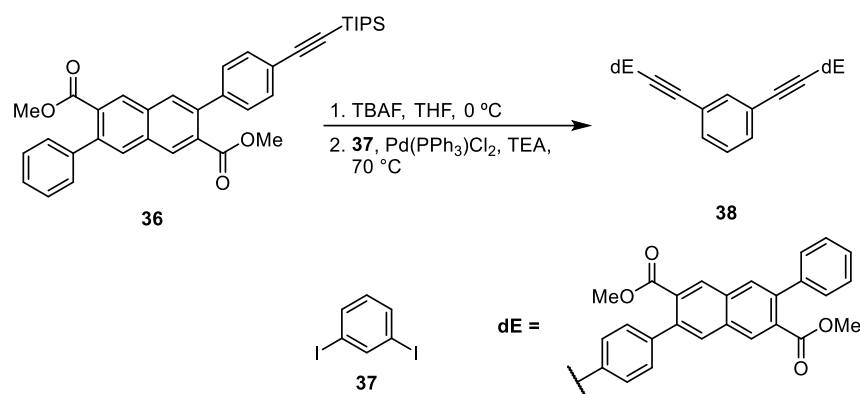


Aryl Iodide 35. Distilled MeI (15 mL) was added to an oven dried heavy walled round bottom pressure flask containing **34** (2.12 g, 4.27 mmol, 1 equiv) under a N₂ atmosphere. After sealing the flask with a Teflon screw cap, the reaction was stirred for 22 h in a heating mantle set to 120 °C. The reaction was then cooled to room temperature, filtered through a silica pad (eluting with CH₂Cl₂), and the filtrate was concentrated in vacuo via a secondary cold trap. The crude residue was triturated in CH₂Cl₂ against Hexanes to yield **35** as a beige solid. ¹H NMR (500 MHz, CDCl₃) δ 8.41 (s, 1H), 8.37 (s, 1H), 7.92 (s, 1H), 7.86 (s, 1H), 7.78 (d, $J = 7.2$ Hz, 2H), 7.49 – 7.37 (m, 5H), 7.15 (d, $J = 7.1$ Hz, 2H), 3.75 (s, 3H), 3.70 (s, 4H).



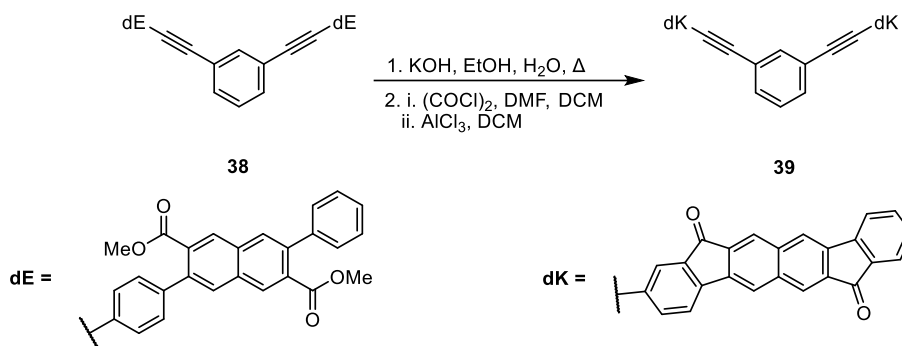
Aryl (TIPS)Ethyne 36. A degassed mixture of THF (21 mL) and TEA (21 mL) was cannulated into a round bottom flask containing **35** (1.45 g, 2.77 mmol, 1 equiv.), TIPSA (0.778 mL, 3.47 mmol, 1.25 equiv.), Pd(PPh₃)₂Cl₂ (3 mol%) , and CuI (6 mol%) under a N₂ atmosphere. The reaction was stirred overnight at 45 °C. Once cooled to room temperature, the reaction was concentrated, suspended in DI H₂O, extracted with CH₂Cl₂ thrice, washed with brine, dried over

MgSO₄, filtered through a celite/silica pad (2 cm), and concentrated. The crude residue was suspended in Hexanes and sonicated for 20 min then filtered and dried over vacuum to yield **36** (1.40 g, 87%) as a beige solid ¹H NMR (500 MHz, CDCl₃) δ 8.40 (s, 1H), 8.38 (s, 1H), 7.92 (s, 1H), 7.88 (s, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.47 – 7.39 (m, 5H), 7.35 (d, *J* = 7.8 Hz, 2H), 3.74 (s, 3H), 3.70 (s, 3H), 1.16 (s, 21H).



Tetraester 38. A round bottom flask containing **36** (600 mg, 1.04 mmol, 1 equiv.) under a N₂ atmosphere was charged with THF (53 mL) and cooled to 0 °C while stirring. TBAF (4.16 mL, 1M) was then added, and the reaction was stirred for 4 h. The reaction quenched with DI H₂O and the precipitate was filtered, washed with water and minimal Hexanes. The crude deprotected ethyne was added to a round bottom flask containing **37** (152 mg, 0.462 mmol, .44 equiv.) and Pd(PPh₃)₂Cl₂ (8 mol%), placed under a N₂ atmosphere and dissolved in degassed TEA (38 mL). The reaction was stirred overnight at 70 °C then cooled to room temperature and concentrated. The residue was then suspended in DI H₂O, extracted with CH₂Cl₂, washed with brine, dried over MgSO₄ and filtered. The organics were concentrated in vacuo and the residue was sonicated in a mixture of Et₂O and EtOAc. The solids were filtered to yield **38** (275 mg, 65%) as a dark yellow solid. An inseparable impurity inflates the integration for the multiplet

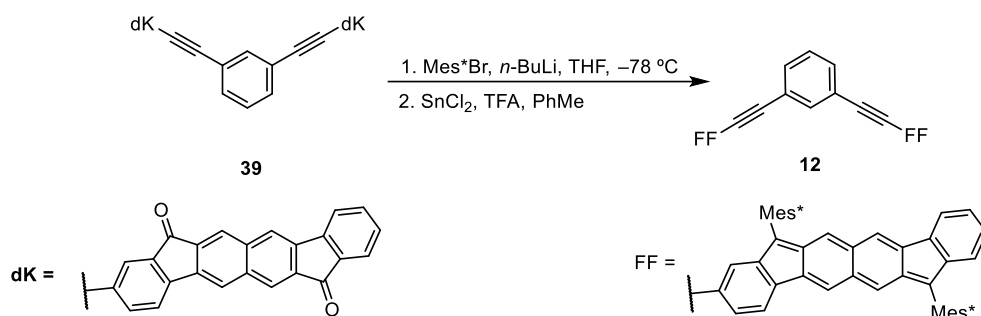
from 7.48–7.39 ppm in the ^1H . ^1H NMR (500 MHz, CDCl_3) δ 8.42 (s, 2H), 8.40 (s, 2H), 7.94 (s, 4H), 7.78 (t, $J = 1.3$ Hz, 1H), 7.64 (s, 2H), 7.63 (s, 2H), 7.54 (dd, $J = 7.7, 1.7$ Hz, 2H), 7.48 – 7.39 (m, 18H), 3.74 (s, 6H), 3.71 (s, 6H).



Tetraketone 39. EtOH (39 mL) and H_2O (13 mL) were added to a round bottom flask containing **38** (275 mg, 0.300 mmol, 1 equiv.) and KOH (337 mg, 6.01 mmol, 20 equiv.). The flask was fitted with a condenser and stirred at reflux (heating mantle) open to air overnight. Once cooled, the volume of the reaction was reduced to approx. 15% and then acidified with a 3M HCl solution to form a precipitate. The solids were filtered, washed with water, and then dried in an oven to yield the crude tetraacid and was used without further purification.

To a suspension of the crude tetraacid in anhydrous CH_2Cl_2 (25 mL) was added anhydrous DMF (0.100 mL, 1.19 mmol, 4 equiv.) and oxalyl chloride (0.203 mL, 2.38 mmol, 8 equiv.). The reaction was stirred at room temperature overnight and the volatiles were then removed under reduced pressure. AlCl_3 (397 mg, 2.98 mmol, 10 equiv.) was added to the flask and the solids were dissolved in anhydrous CH_2Cl_2 (25 mL) then stirred at room temperature overnight. The reaction mixture was poured into an HCl-ice mixture to precipitate the crude tetraketone. The solids were filtered and washed successively with H_2O , acetone, CH_2Cl_2 , and Hexanes. The solids were sonicated in acetone and filtered once more to yield tetraketone **39**

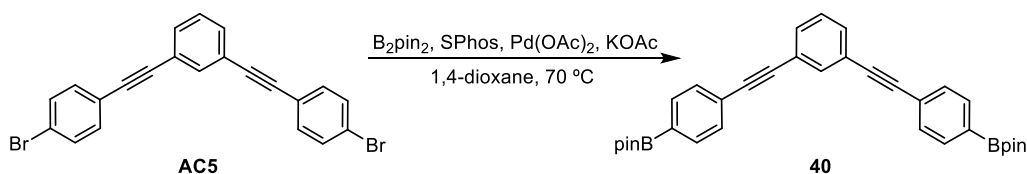
(213 mg, 90%) as a dark orange solid. The extremely poor solubility of **39** precluded acquisition of NMR spectra.



***m*-FF Dimer 12.** Anhydrous THF (15 mL) was added to an oven-dried round-bottom flask containing 2-bromo-5-*t*-butyl-1,3-dimethylbenzene (Mes*Br, 644 mg, 2.67 mmol, 21 equiv.) under a N₂ atmosphere. The mixture was cooled to $-78\text{ }^\circ\text{C}$ for 25 min and *n*-BuLi (1.04 mL, 2.5 M, 2.60 mmol, 20.5 equiv.) was added dropwise. After stirring at $-78\text{ }^\circ\text{C}$ for 30 min, the lithiated species was transferred by cannula to a suspension of **39** (100 mg, 0.127 mmol, 1 equiv.) in anhydrous THF (20 mL) at $-78\text{ }^\circ\text{C}$. The reaction was stirred, warmed to room temperature overnight, and then quenched with sat. aqueous NH₄Cl. The mixture was extracted with CH₂Cl₂ thrice, and the combined organics were washed with brine, dried over MgSO₄, and concentrated in vacuo. The resulting crude oil was diluted with hexanes to precipitate the crude tetrahydroxyl intermediate, which was used with no further purification.

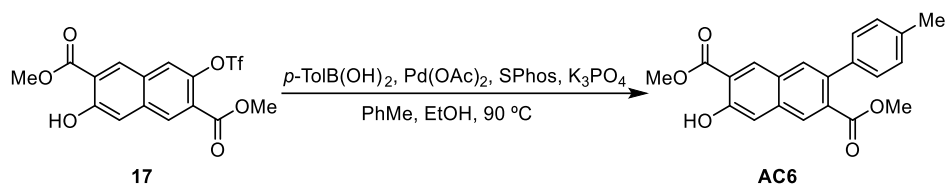
The tetrahydroxyl intermediate (~110 mg, 0.0766 mmol, 1 equiv.) and SnCl₂ (116 mg, 0.613 mmol, 8 equiv.) were dissolved in anhydrous degassed PhMe (20 mL) and stirred at 80 °C for 4 h. The mixture was cooled to room temperature and the reaction was poured into cold MeOH and swirled vigorously. The precipitate was filtered and triturated in CH₂Cl₂ against CH₃CN and allowed to cool in a freezer overnight. The solids were filtered to yield an impure

sample of **12** (85.0 mg, crude 48%) as a poorly soluble deep blue solid. ^1H NMR experiments returned ambiguous signals in the aromatic region and aliphatic region while the ^{13}C NMR spectrum reveals diagnostic alkyne signals and is only missing two signals that may belong to quaternary carbons in the Mes* groups. ^{13}C NMR (151 MHz, CD_2Cl_2) δ 151.31, 151.25, 151.21, 144.22, 143.14, 141.31, 138.06, 137.30, 137.24, 137.13, 137.03, 135.77, 135.15, 135.13, 134.60, 132.24, 131.93, 131.47, 130.45, 130.17, 130.05, 128.65, 128.51, 127.94, 127.89, 127.84, 127.25, 126.06, 125.20, 125.14, 124.98, 124.05, 122.50, 121.14, 121.04, 91.05, 88.90, 34.74, 31.55, 31.01, 30.08, 20.78.

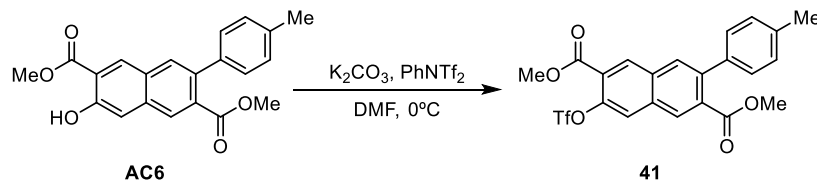


Diethynyl DiBpin 40. A three-neck round bottom flask was charged with **AC5** (280 mg, 0.642 mmol, 1 equiv.), B_2pin_2 (366 mg, 1.44 mmol, 2.25 equiv.), SPhos (12 mol%), $\text{Pd}(\text{OAc})_2$ (5 mol%), and KOAc (378 mg, 3.85 mmol, 6 equiv.) and then placed under a N_2 atmosphere. Degassed anhydrous 1,4-dioxane (18 mL) was cannulated into the flask and the reaction was stirred at $70\text{ }^\circ\text{C}$ overnight. The reaction was then cooled to room temperature, quenched with DI H_2O , extracted with CH_2Cl_2 thrice, washed with DI H_2O , washed with brine, dried over MgSO_4 , filtered through a celite/silica pad (1.5 cm), and concentrated. The crude solid was washed with EtOH and filtered to remove insoluble impurities. The filtrate was concentrated to yield **40** (255 mg, crude 75%) as an off white solid. Small amounts of impurities remained in the sample and was not purified further. ^1H NMR (500 MHz, CDCl_3) δ 7.80 (d, $J = 8.0$ Hz, 4H), 7.73 (d, $J = 1.6$

Hz, 1H), 7.54 (d, $J = 8.0$ Hz, 4H), 7.50 (dd, $J = 7.7, 1.7$ Hz, 2H), 7.33 (t, $J = 6.8$ Hz, 1H), 1.36 (s, 24H).

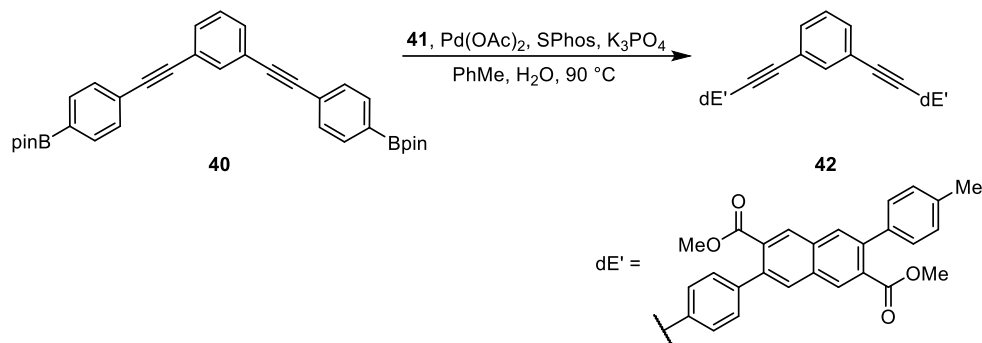


Diester AC6. A three-neck round bottom flask fitted with a reflux condenser was charged with **17** (820 mg, 2.01 mmol, 1 equiv.), *p*-TolB(OH)₂ (357 mg, 2.41 mmol, 1.2 equiv.), Pd(OAc)₂ (4 mol%), SPhos (8 mol%), K₃PO₄ (640 mg, 3.01 mmol, 1.5 equiv.) and placed under a N₂ atmosphere. A degassed mixture of PhMe (12 mL) and H₂O (1 mL) was cannulated into the flask and the reaction was stirred at 90 °C overnight. The reaction was then cooled to room temperature, quenched with DI H₂O, extracted with CH₂Cl₂ thrice, dried organics over MgSO₄, filtered through a silica/celite pad (2 cm, eluting with CH₂Cl₂), and concentrated to yield **AC6** (610 mg, 87%) as a light yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 10.51 (s, 1H), 8.44 (s, 1H), 8.12 (s, 1H), 7.74 (s, 1H), 7.36 (s, 1H), 7.29 (d, $J = 7.9$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 4.01 (s, 3H), 3.74 (s, 3H), 2.43 (s, 3H).



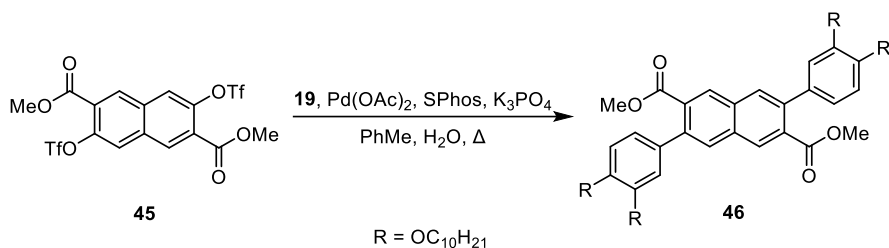
Triflate 41. A round bottom flask containing **AC6** (610 mg, 1.74 mmol, 1 equiv.) and K₂CO₃ (482 mg, 3.49 mmol, 2 equiv.) was placed under a N₂ atmosphere. The solids were suspended in anhydrous DMF (29 mL) and cooled to 0 °C while stirring for 40 min. A solution

of PhNTf₂ (685 mg, 1.92 mmol, 1.1 equiv.) in DMF (9 mL) was prepared under N₂ in a round bottom flask. After 40 min, the PhNTf₂ solution was slowly added at 0 °C and the reaction was allowed to warm to room temperature while stirring overnight. The reaction was re-cooled to 0 °C and quenched with a 3M HCl solution. The resulting precipitate was filtered, washed with H₂O, and dried over vacuum. The solids were triturated in CH₂Cl₂ against Hexanes to yield the desired product **41** (815 mg, quant.) as a pale yellow solid. The aromatic signals of the pendant tolyl group* are eclipsed by the CDCl₃ peak and are under integrated by 1. ¹H NMR (500 MHz, CDCl₃) δ 8.67 (s, 1H), 8.36 (s, 1H), 7.96 (s, 1H), 7.83 (s, 1H), 7.27 (d, *J* = 4.4 Hz, 3H), 4.03 (s, 3H), 3.74 (s, 3H), 2.43 (s, 3H)*.

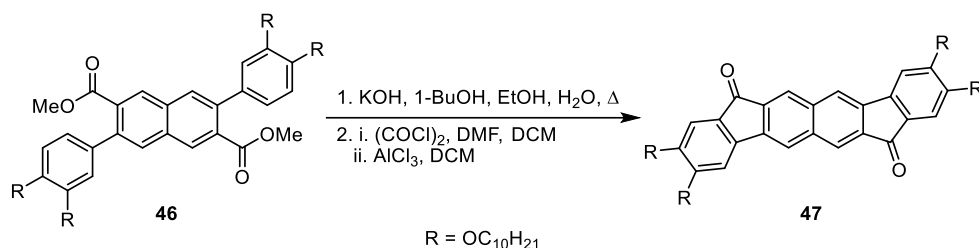


Tetraester 42. A three-neck round bottom flask fitted with a reflux condenser was charged with **40** (255 mg, 0.482 mmol, 1 equiv.), **41** (483 mg, 1.04 mmol, 2.15 equiv.), Pd(OAc)₂ (5 mol%), SPhos (12 mol%), K₃PO₄ (614 mg, 2.89 mmol, 6 equiv.) and placed under a N₂ atmosphere. A degassed mixture of PhMe (18 mL) and H₂O (2 mL) was cannulated into the flask and the reaction was stirred at 90 °C overnight. The reaction was then cooled to room temperature, quenched with DI H₂O, extracted with CH₂Cl₂ thrice, dried organics over MgSO₄, filtered through a silica/celite pad (2 cm, eluting with CH₂Cl₂), and concentrated to yield **AC6** (610 mg, 87%) as a light yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 10.51 (s, 1H), 8.44 (s, 1H),

8.12 (s, 1H), 7.74 (s, 1H), 7.36 (s, 1H), 7.29 (d, $J = 7.9$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 4.01 (s, 3H), 3.74 (s, 3H), 2.43 (s, 3H).



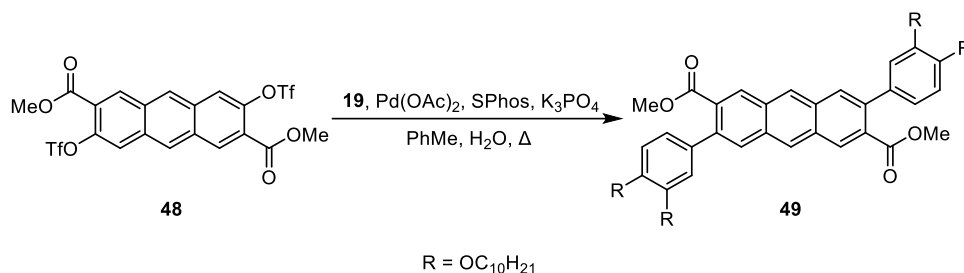
Diester 46. A three-neck round bottom flask fitted with a reflux condenser was charged with **45** (177 mg, 0.327 mmol, 1 equiv.), **19** (372 mg, 0.721 mmol, 2.2 equiv.), Pd(OAc)₂ (4 mol%), SPhos (8 mol%), K₃PO₄ (206 mg, 0.982 mmol, 3 equiv.) and placed under a N₂ atmosphere. A degassed mixture of PhMe (4.50 mL) and H₂O (0.500 mL) was cannulated into the flask and the reaction was stirred at reflux overnight. The reaction was then cooled to room temperature, filtered through a celite/silica pad (1 cm, eluting with CH₂Cl₂) and concentrated. The crude residue was triturated in CH₂Cl₂ against Hexanes to yield **46** (244 mg, 48%) as a pale yellow solid. ¹H NMR (500 MHz, CDCl₃) δ 8.28 (s, 2H), 7.89 (s, 2H), 6.96 – 6.92 (m, 6H), 4.07 – 4.01 (m, 8H), 3.71 (s, 6H), 1.89 – 1.81 (m, 8H), 1.51 – 1.45 (m, 8H), 1.41 – 1.35 (m, 8H), 1.32 – 1.25 (m, 40H), 0.91 – 0.86 (m, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 169.49, 149.04, 148.96, 139.12, 133.70, 132.40, 132.02, 130.17, 129.86, 121.12, 114.51, 113.65, 69.57, 69.47, 52.45, 32.09, 32.07, 29.81, 29.80, 29.76, 29.75, 29.63, 29.61, 29.52, 29.51, 26.25, 26.23, 22.85, 22.84, 14.27, 14.26.



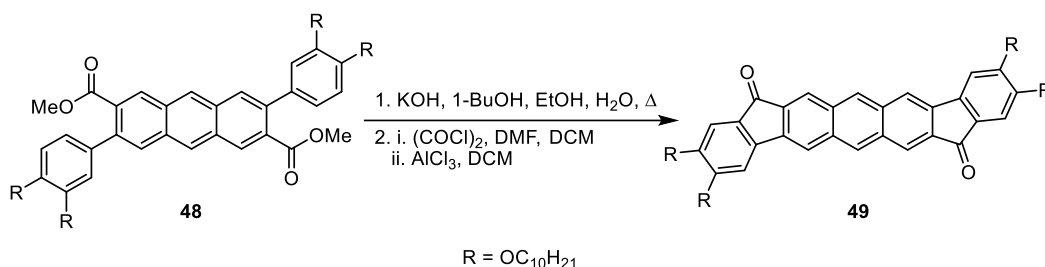
Dione 47. EtOH (12 mL) and H₂O (2.4 mL) were added to a round bottom flask containing **46** (244 mg, 0.240 mmol, 1 equiv.) and KOH (134 mg, 2.39 mmol, 10 equiv.). The flask was fitted with a condenser and stirred at reflux (heating mantle) open to air overnight. Once cooled, the volume of the reaction was reduced to approx. 15% and then acidified with a 3M HCl solution to form a precipitate. The solids were filtered, washed with water, and then dried in an oven to yield the crude diacid and was used without further purification.

To a suspension of the crude diacid in anhydrous CH₂Cl₂ (12 mL) was added anhydrous DMF (0.0245 mL, 0.318 mmol, 2 equiv.) and oxalyl chloride (0.0542 mL, 0.636 mmol, 4 equiv.). The reaction was stirred at room temperature overnight and the volatiles were then removed under reduced pressure. AlCl₃ (106 mg, 0.795 mmol, 5 equiv.) was added to the flask and the solids were dissolved in anhydrous CH₂Cl₂ (12 mL) then stirred at room temperature overnight. The reaction mixture was poured into an HCl-ice mixture to precipitate the crude tetraketone. The solids were filtered and washed successively with H₂O, acetone, CH₂Cl₂, and Hexanes. The solids were recrystallized from CH₂Cl₂ to yield **47** (103 mg, 68%) as a pink solid. ¹H NMR (500 MHz, CDCl₃) δ 7.87 (s, 2H), 7.57 (s, 2H), 7.17 (s, 2H), 7.07 (s, 2H), 4.17 (t, *J* = 6.6 Hz, 4H), 4.03 (t, *J* = 6.7 Hz, 4H), 1.91 (p, *J* = 6.8 Hz, 4H), 1.85 (p, *J* = 6.9 Hz, 4H), 1.58 – 1.51 (m, 4H), 1.48 (q, *J* = 7.8 Hz, 4H), 1.44 – 1.37 (m, 4H), 1.35 – 1.25 (m, 40H), 0.89 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 192.11, 155.70, 150.42, 139.65, 139.60, 137.31, 136.07, 128.79,

124.43, 119.76, 108.36, 104.78, 69.61, 69.48, 32.08, 29.79, 29.75, 29.57, 29.52, 29.26, 26.18, 26.15, 22.85, 14.27. HRMS (TOF) m/z : $[M^+]$ Calcd for $C_{64}H_{92}O_6$ 956.6894; Found 956.6888.



Diester 49. A three-neck round bottom flask fitted with a reflux condenser was charged with **48** (419 mg, 0.709 mmol, 1 equiv.), **19** (769 mg, 1.49 mmol, 2.1 equiv.), $Pd(OAc)_2$ (4 mol%), SPhos (8 mol%), K_3PO_4 (452 mg, 2.13 mmol, 3 equiv.) and placed under a N_2 atmosphere. A degassed mixture of PhMe (10 mL) and H_2O (1 mL) was cannulated into the flask and the reaction was stirred at reflux overnight. The reaction was then cooled to room temperature, filtered through a celite/silica pad (1 cm, eluting with CH_2Cl_2) and concentrated. The crude residue was triturated in CH_2Cl_2 against Hexanes to yield **49** (352 mg, 46%) as a pale orange solid. ^1H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 2H), 8.49 (s, 2H), 8.00 (s, 2H), 7.01 – 6.93 (m, 6H), 4.09 – 4.00 (m, 8H), 3.73 (s, 6H), 1.91 – 1.82 (m, 8H), 1.52 – 1.45 (m, 8H), 1.42 – 1.35 (m, 8H), 1.35 – 1.23 (m, 40H), 0.91 – 0.86 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.51, 149.04, 148.87, 137.89, 134.04, 132.34, 131.46, 131.01, 130.88, 129.61, 127.66, 121.04, 114.47, 113.68, 69.57, 69.49, 52.43, 32.09, 32.07, 29.82, 29.81, 29.77, 29.75, 29.64, 29.61, 29.55, 29.53, 29.51, 26.26, 26.24, 22.86, 22.84, 14.27, 14.26. HRMS (TOF) m/z : $[M^+]$ Calcd for $C_{70}H_{102}O_6$ 1070.7575; Found 1070.7569.



Dione 50. EtOH (18 mL) and H₂O (3.6 mL) were added to a round bottom flask containing **49** (352 mg, 0.330 mmol, 1 equiv.) and KOH (184 mg, 3.30 mmol, 10 equiv.). The flask was fitted with a condenser and stirred at reflux (heating mantle) open to air overnight. Once cooled, the volume of the reaction was reduced to approx. 15% and then acidified with a 3M HCl solution to form a precipitate. The solids were filtered, washed with water, and then dried in an oven to yield the crude diacid and was used without further purification.

To a suspension of the crude diacid in anhydrous CH₂Cl₂ (20 mL) was added anhydrous DMF (0.0530 mL, 0.686 mmol, 2 equiv.) and oxalyl chloride (0.117 mL, 1.37 mmol, 4 equiv.). The reaction was stirred at room temperature overnight and the volatiles were then removed under reduced pressure. AlCl₃ (229 mg, 1.72 mmol, 5 equiv.) was added to the flask and the solids were dissolved in anhydrous CH₂Cl₂ (20 mL) then stirred at room temperature overnight. The reaction mixture was poured into an HCl-ice mixture to precipitate the crude tetraketone. The solids were filtered and washed successively with H₂O, acetone, CH₂Cl₂, and Hexanes. The solids were recrystallized from EtOH to yield **50** (157 mg, 68%) as a red-orange solid. Trace impurities are present in the ¹H NMR despite repeated purification attempts. ¹H NMR (500 MHz, CDCl₃) 7.94 (s, 2H), 7.89 (s, 2H), 7.39 (s, 2H), 7.04 (s, 2H), 6.95 (s, 2H), 4.14 (t, *J* = 6.6 Hz, 4H), 3.98 (t, *J* = 6.8 Hz, 4H), 1.92 (p, *J* = 6.9 Hz, 4H), 1.84 (p, *J* = 7.0 Hz, 4H), 1.59 – 1.53 (m, 6H), 1.52 – 1.40 (m, 4H), 1.40 – 1.34 (m, 4H), 1.34 – 1.28 (m, 20H), 0.93 – 0.87 (m, 12H). ¹³C NMR (126 MHz, CDCl₃) δ 191.58, 155.62, 150.54, 139.77, 137.39, 134.99, 134.25, 132.90,

130.21, 129.87, 124.79, 117.12, 107.40, 104.32, 69.44, 69.27, 32.11, 29.85, 29.80, 29.65, 29.64, 29.56, 29.55, 29.32, 29.27, 26.24, 26.17, 22.87, 14.28. HRMS (TOF) m/z: [M⁺] Calcd for C₆₈H₉₄O₆ 1006.7050; Found 1006.7045.

NMR Spectra

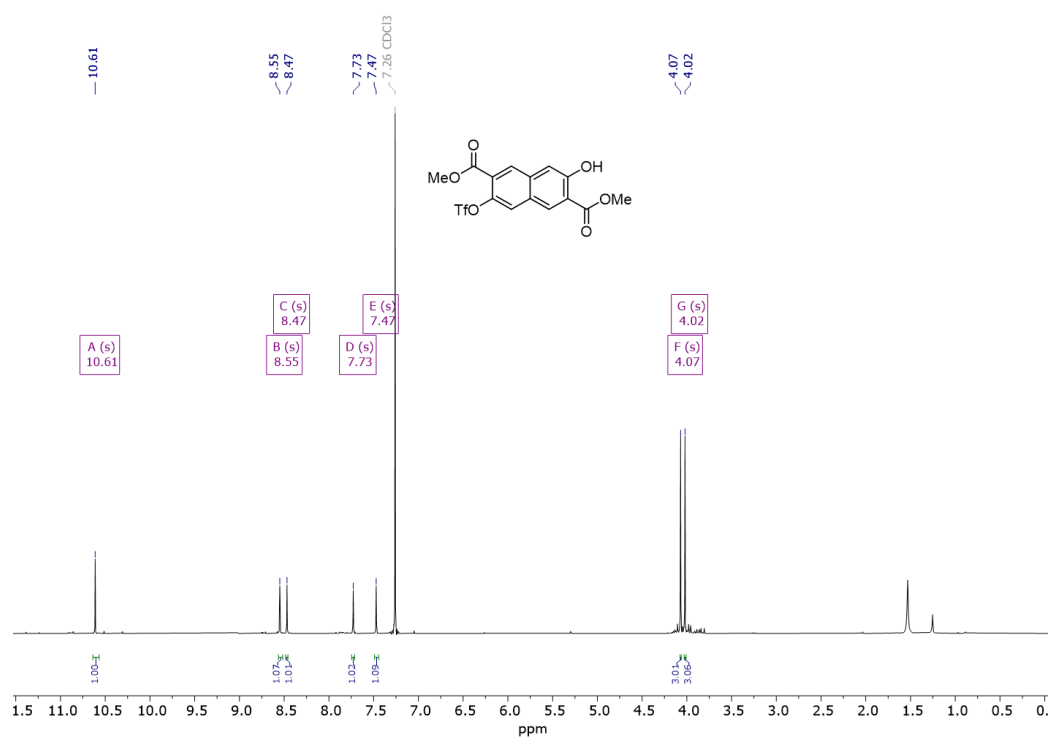


Figure C1. ^1H NMR spectrum (500 MHz) of **17** in CDCl_3 .

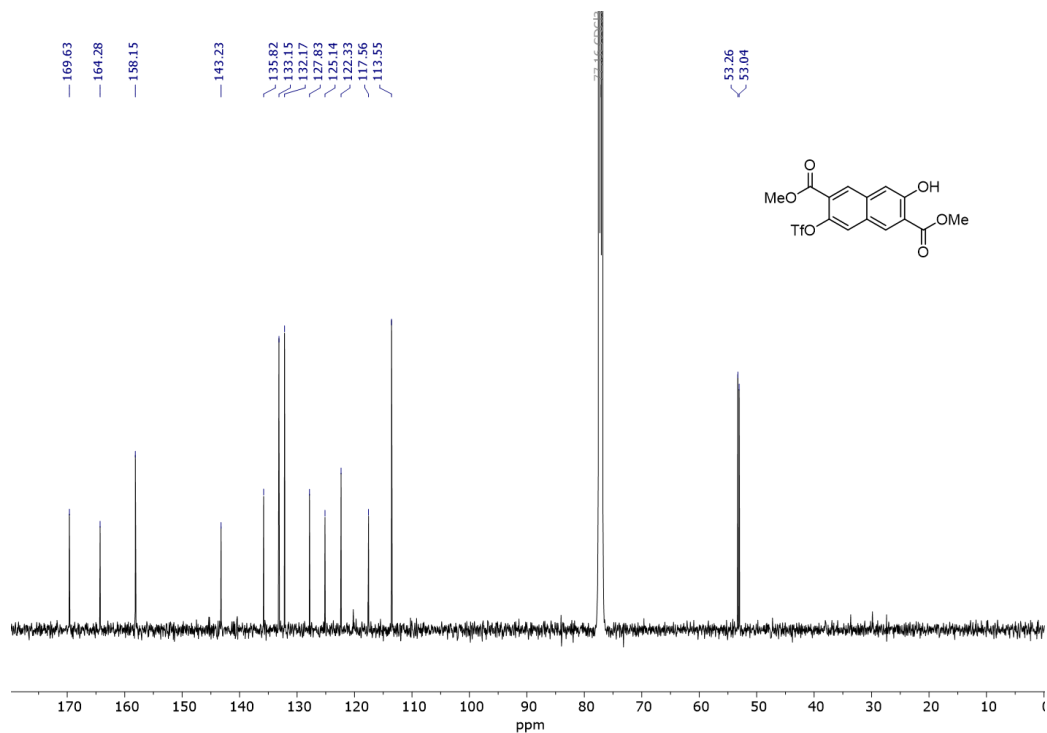


Figure C2. ^{13}C NMR spectrum (126 MHz) of **17** in CDCl_3 .

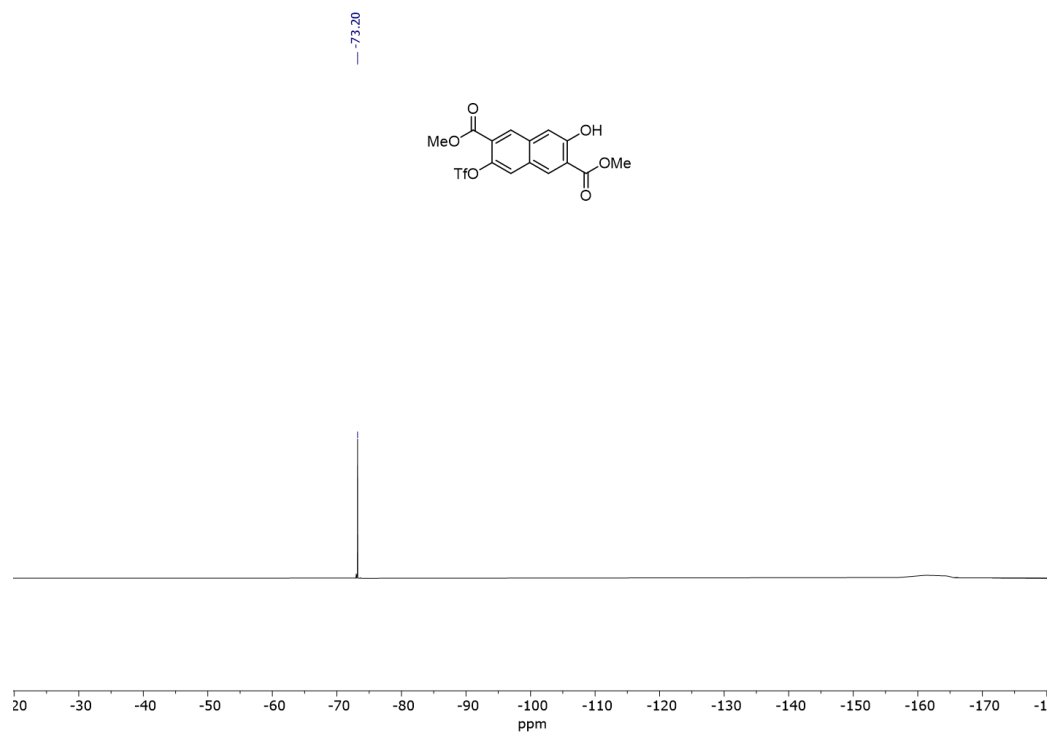


Figure C3. ^{19}F NMR spectrum (471 MHz) of 17 in CDCl_3 .

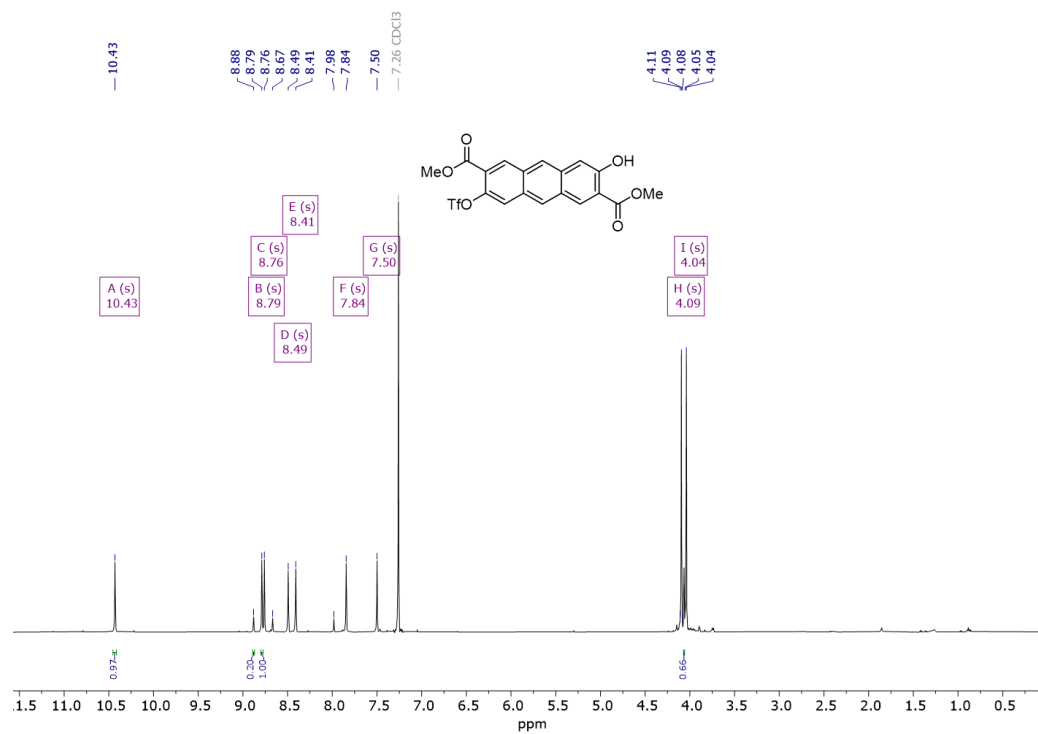


Figure C4. ^1H NMR spectrum (500 MHz) of 18 in CDCl_3 .

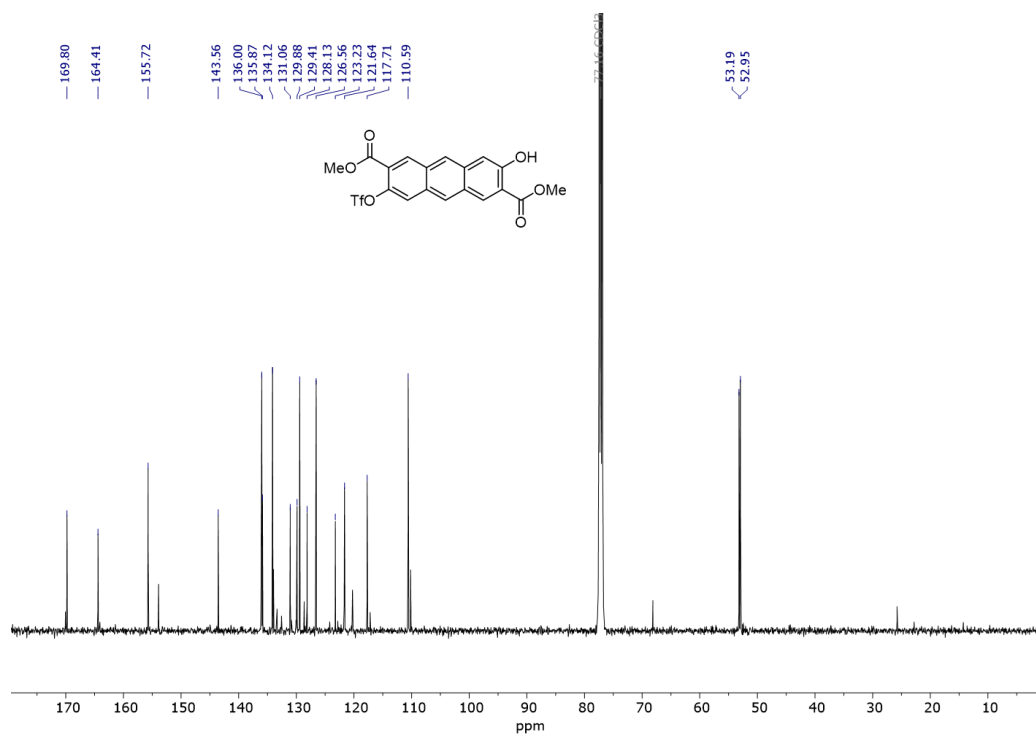


Figure C5. ¹³C NMR spectrum (126 MHz) of **18** in CDCl₃.

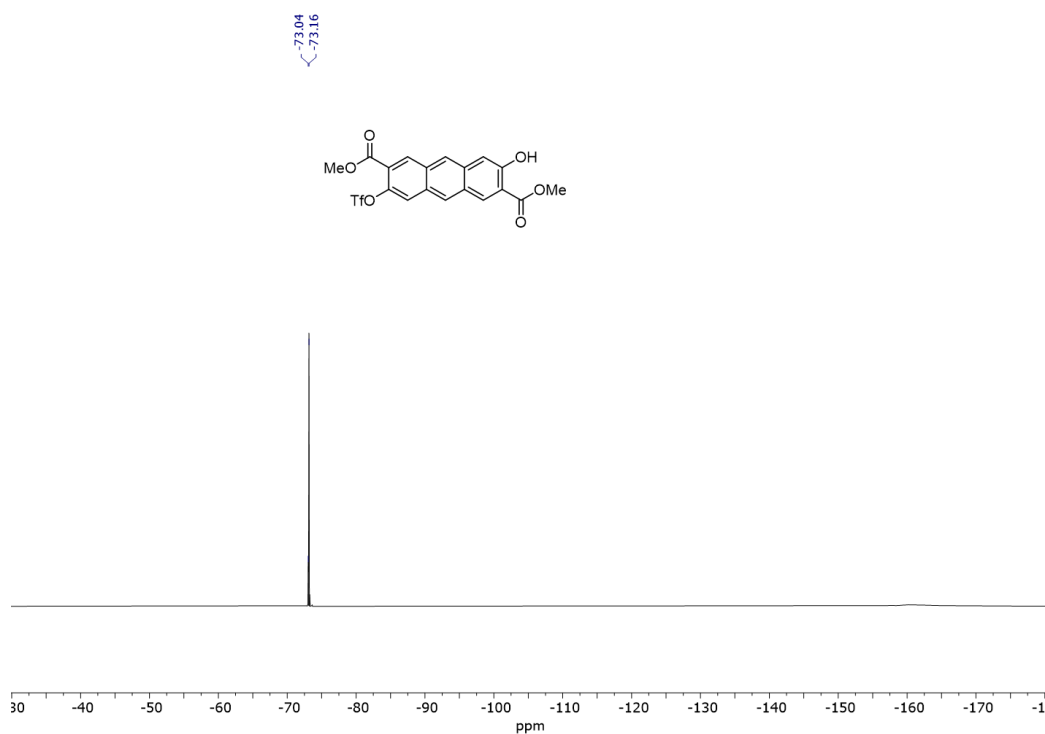


Figure C6. ¹⁹F NMR spectrum (471 MHz) of **18** in CDCl₃.

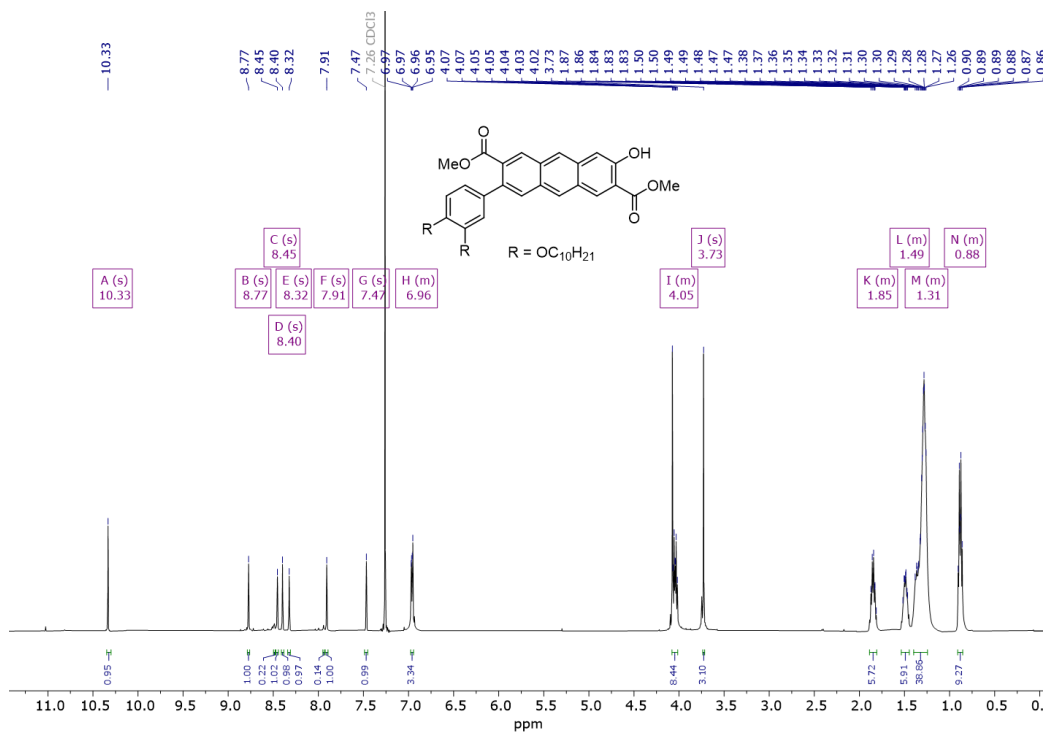


Figure C7. ^1H NMR spectrum (500 MHz) of **20** in CDCl_3 .

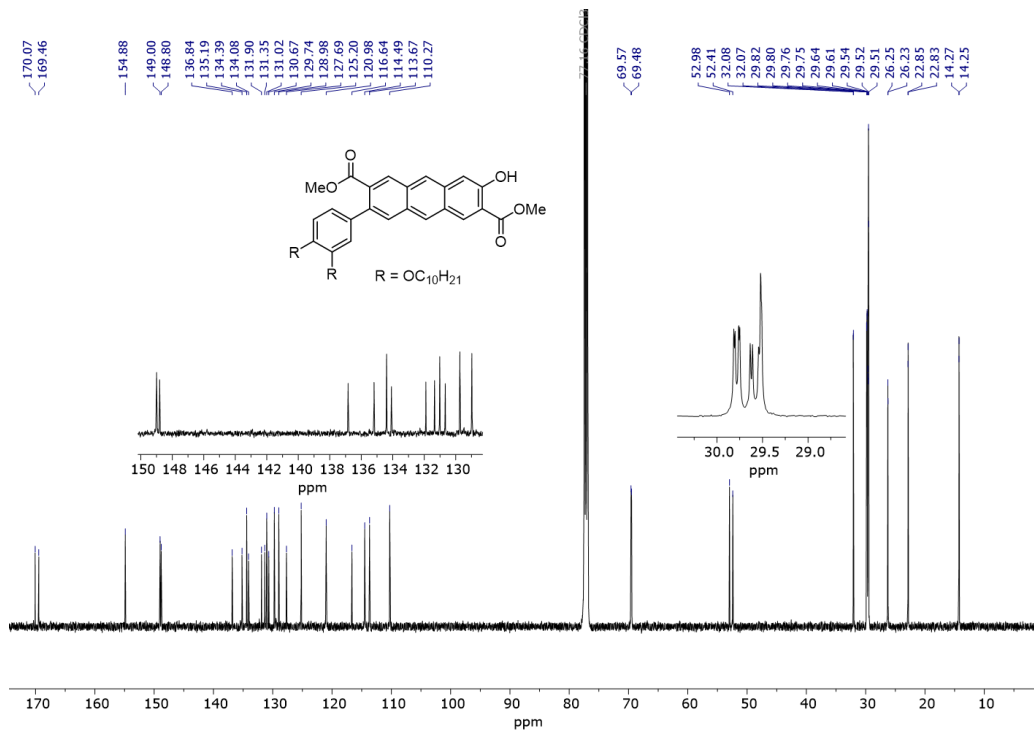


Figure C8. ^{13}C NMR spectrum (126 MHz) of **20** in CDCl_3 .

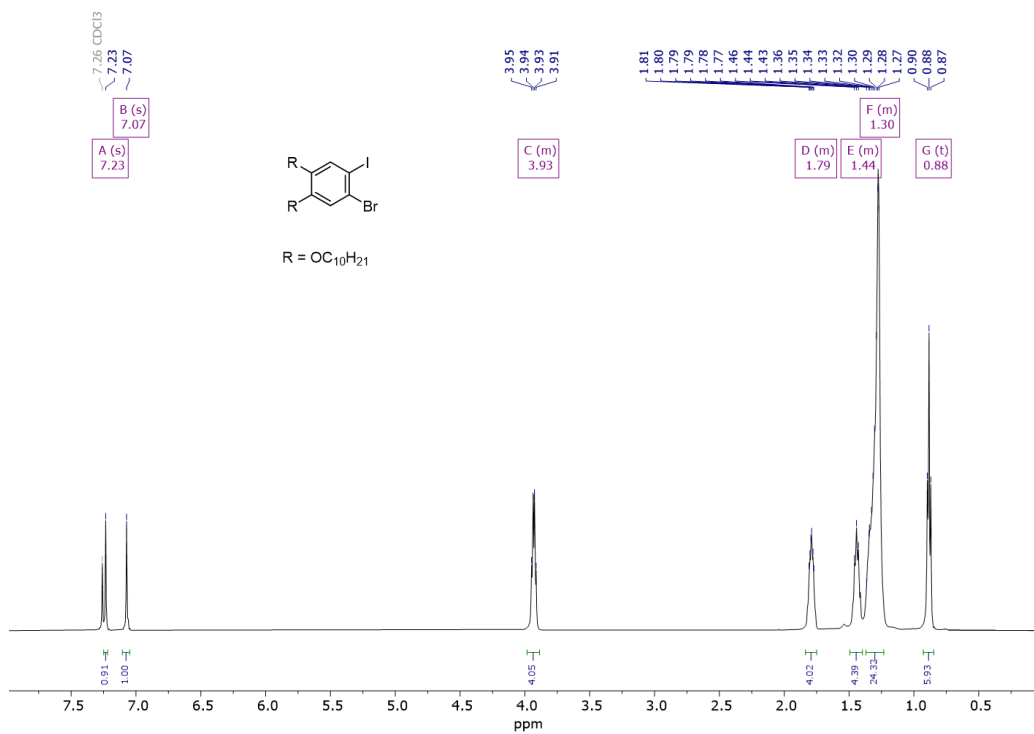


Figure C9. ¹H NMR spectrum (500 MHz) of AC2 in CDCl₃.

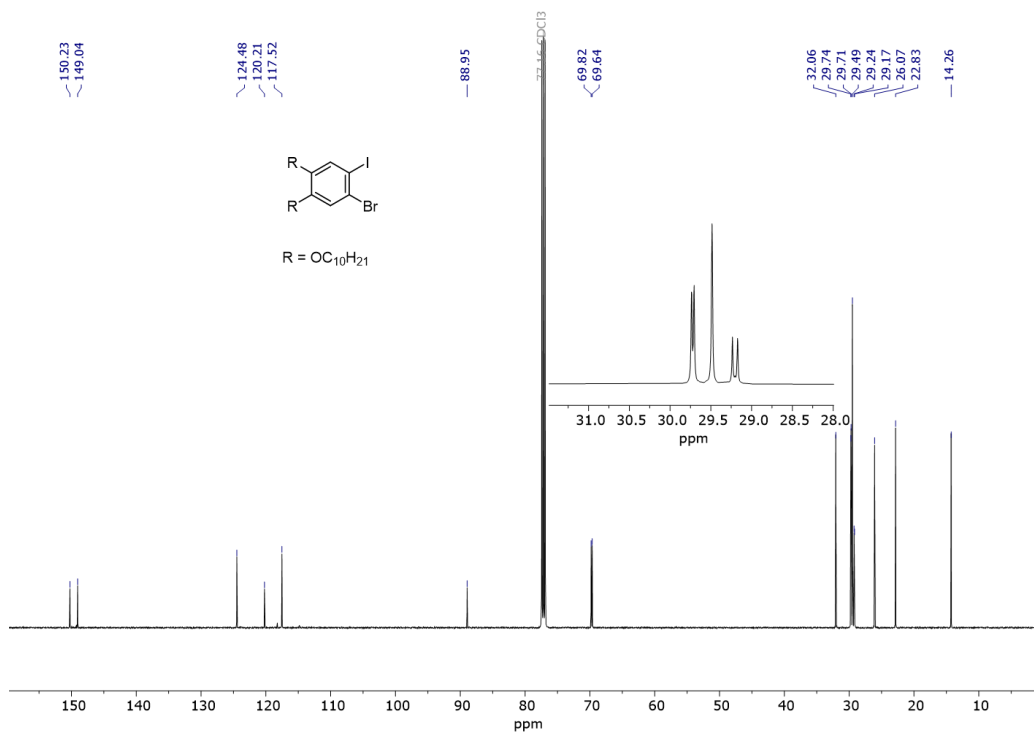


Figure C10. ¹³C NMR spectrum (126 MHz) of AC2 in CDCl₃.

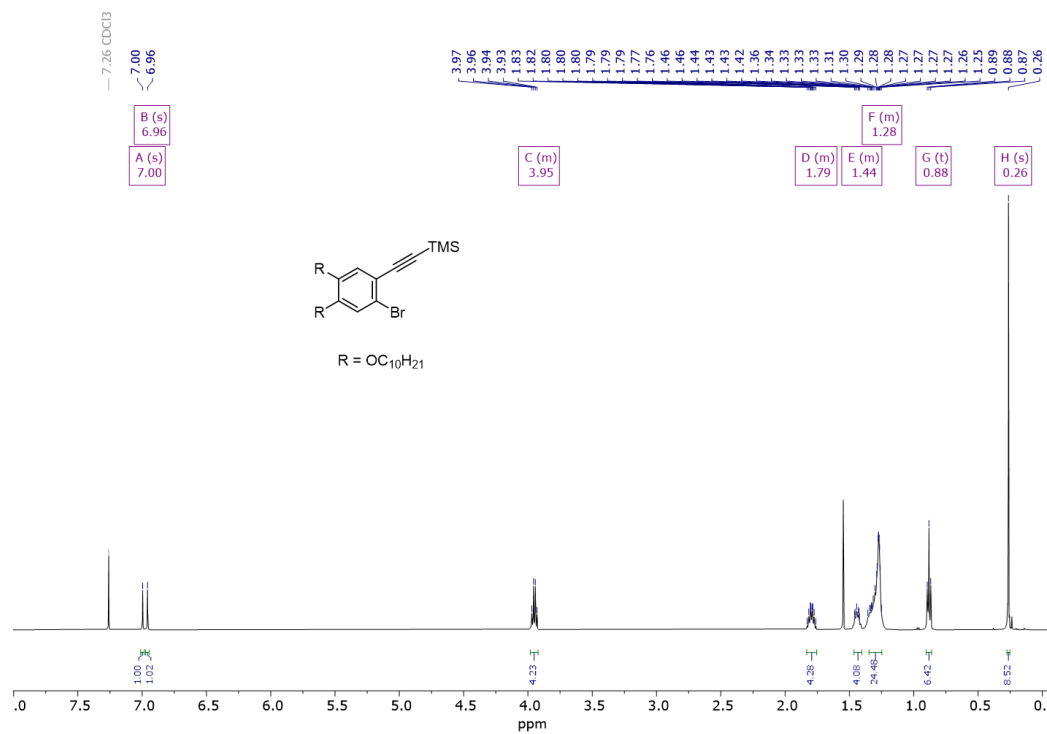


Figure C11. ¹H NMR spectrum (500 MHz) of AC3 in CDCl₃.

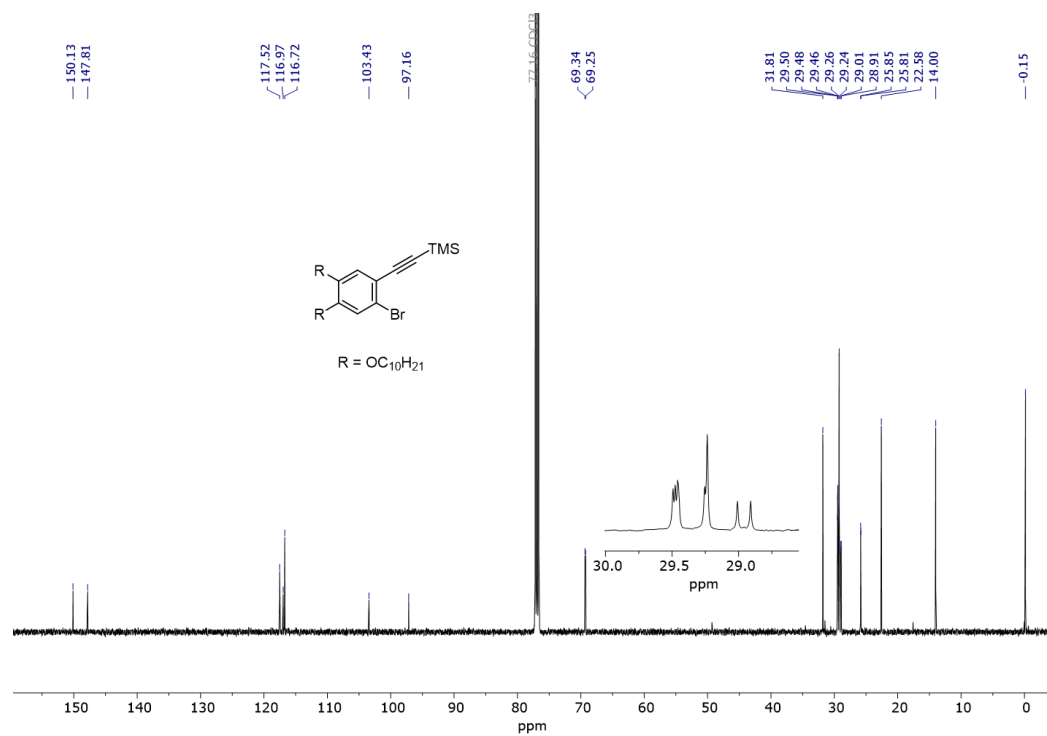


Figure C12. ¹³C NMR spectrum (126 MHz) of AC3 in CDCl₃.

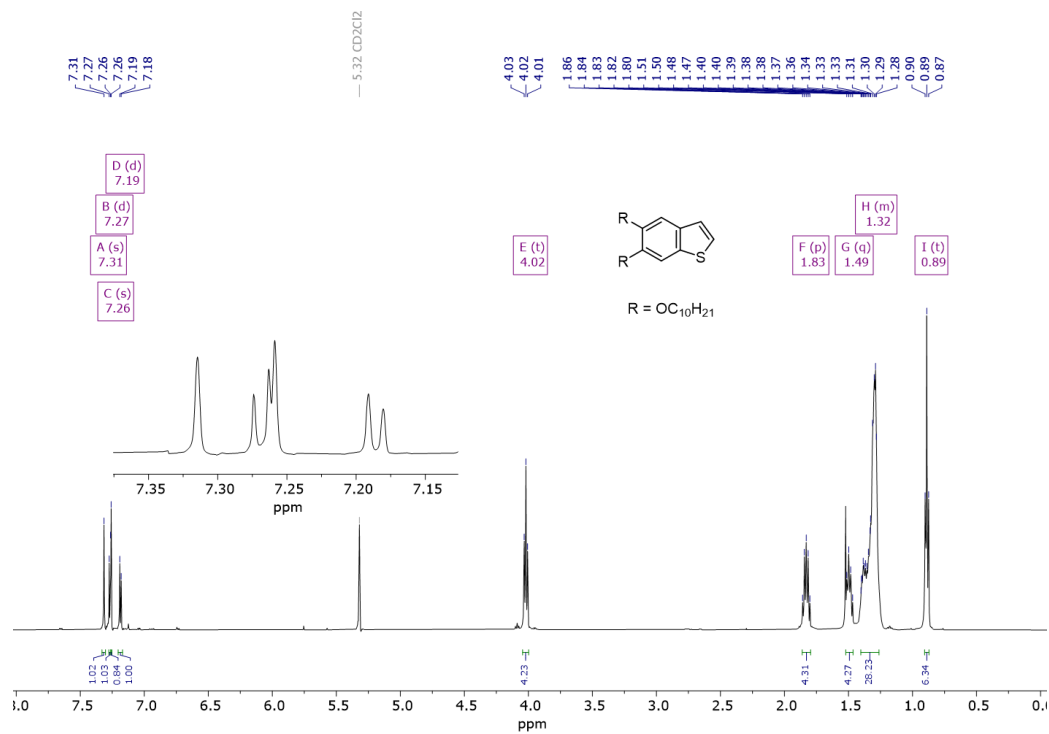


Figure C13. ¹H NMR spectrum (500 MHz) of AC4 in CD₂Cl₂.

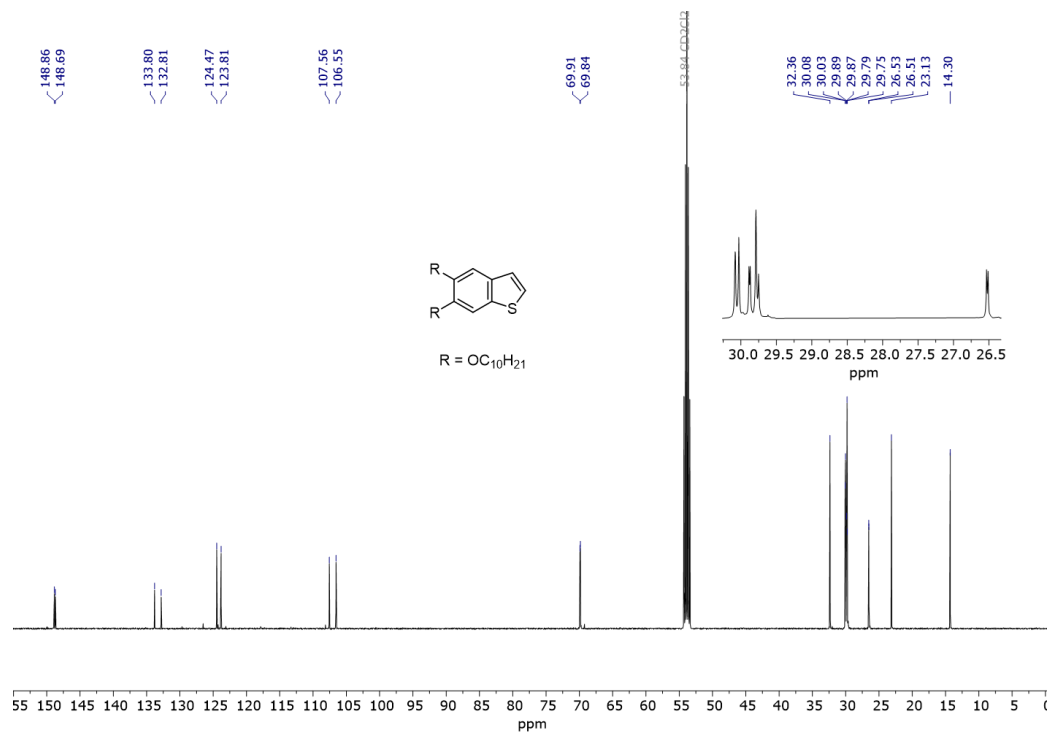


Figure C14. ¹³C NMR spectrum (126 MHz) of AC4 in CD₂Cl₂.

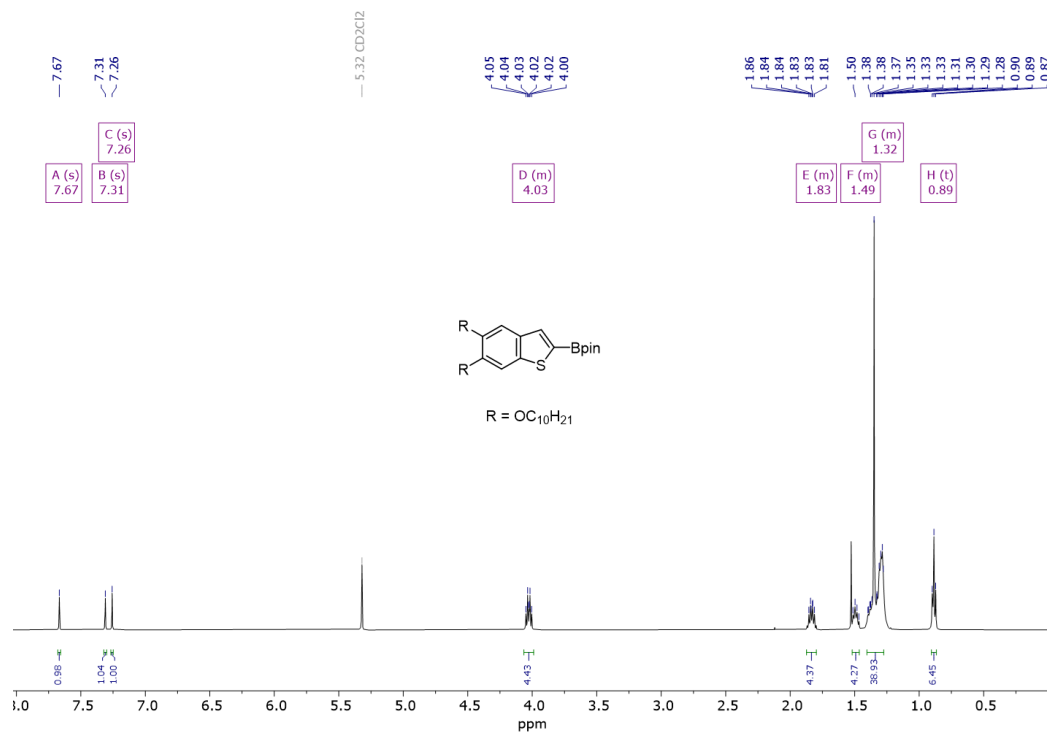


Figure C15. ¹H NMR spectrum (500 MHz) of **25** in CD₂Cl₂.

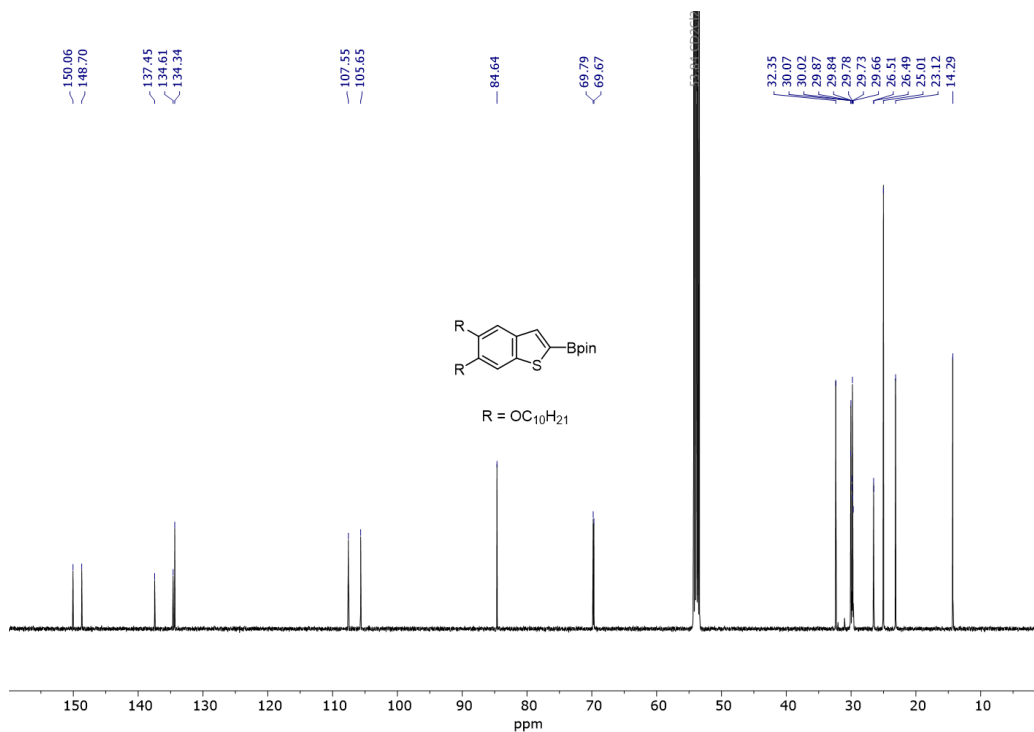


Figure C16. ¹³C NMR spectrum (126 MHz) of **25** in CD₂Cl₂.

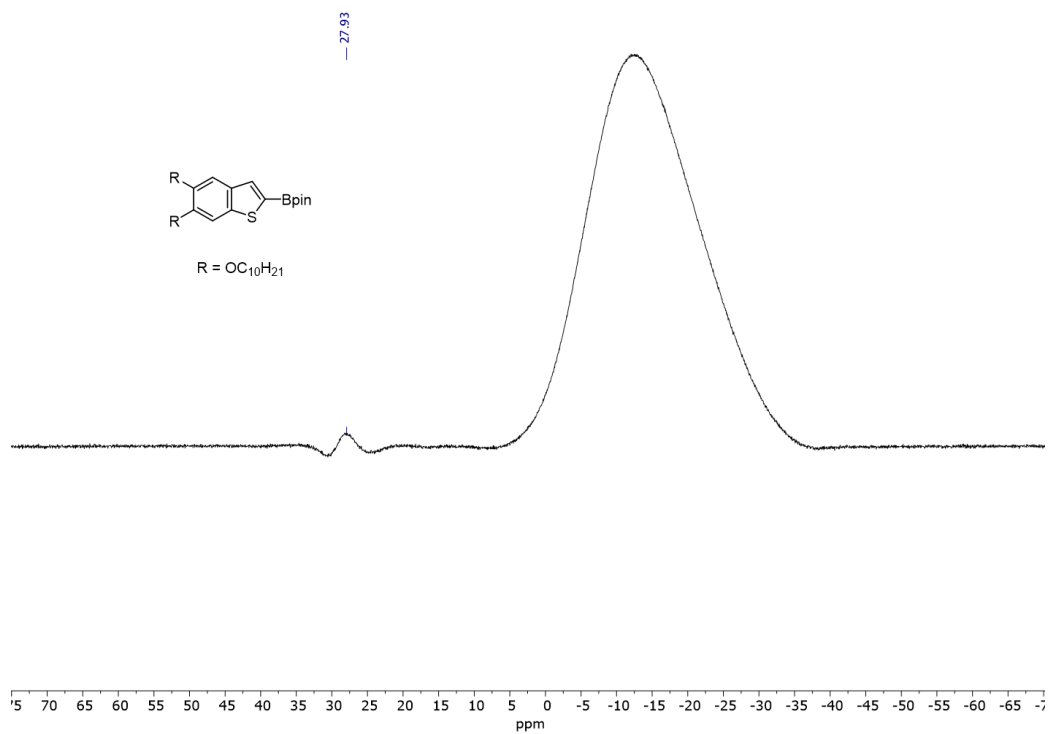


Figure C15. ¹¹B NMR spectrum (160 MHz) of **25** in CD₂Cl₂.

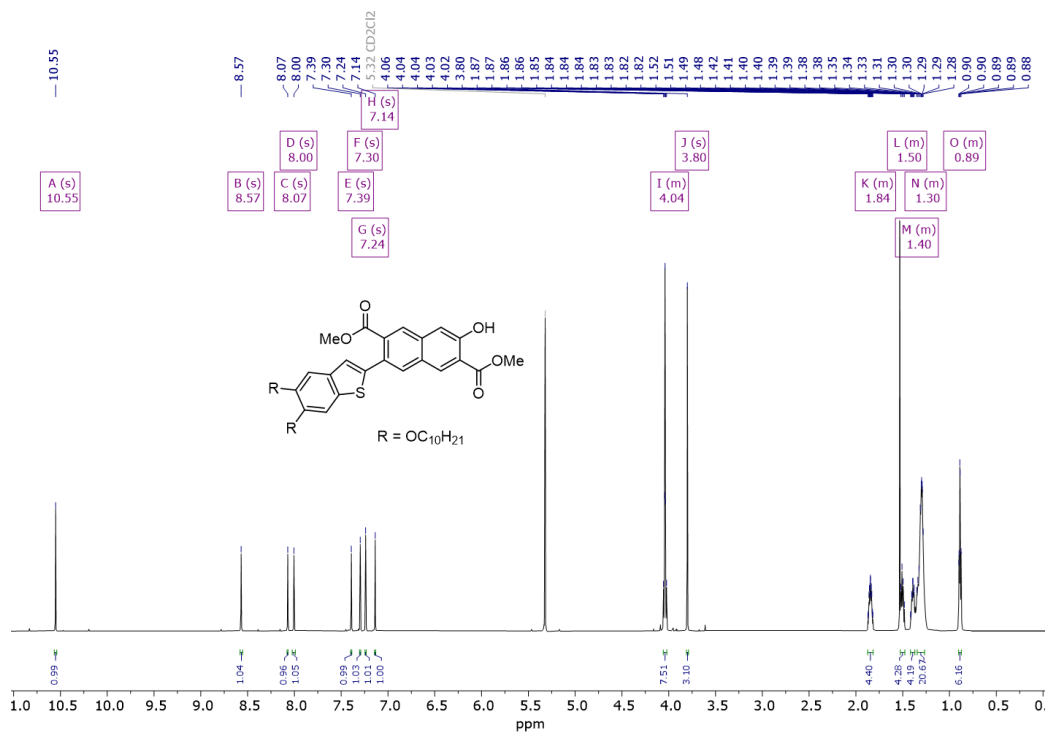


Figure C16. ¹H NMR spectrum (500 MHz) of **26** in CD₂Cl₂.

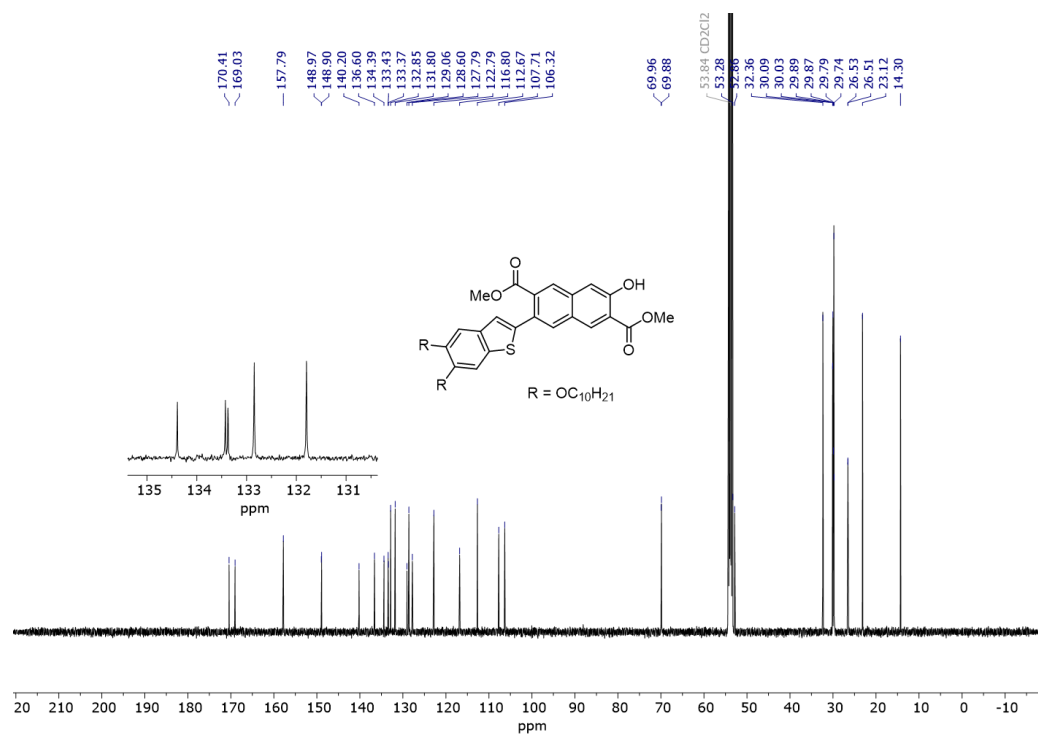


Figure C17. ^{13}C NMR spectrum (126 MHz) of **26** in CD_2Cl_2 .

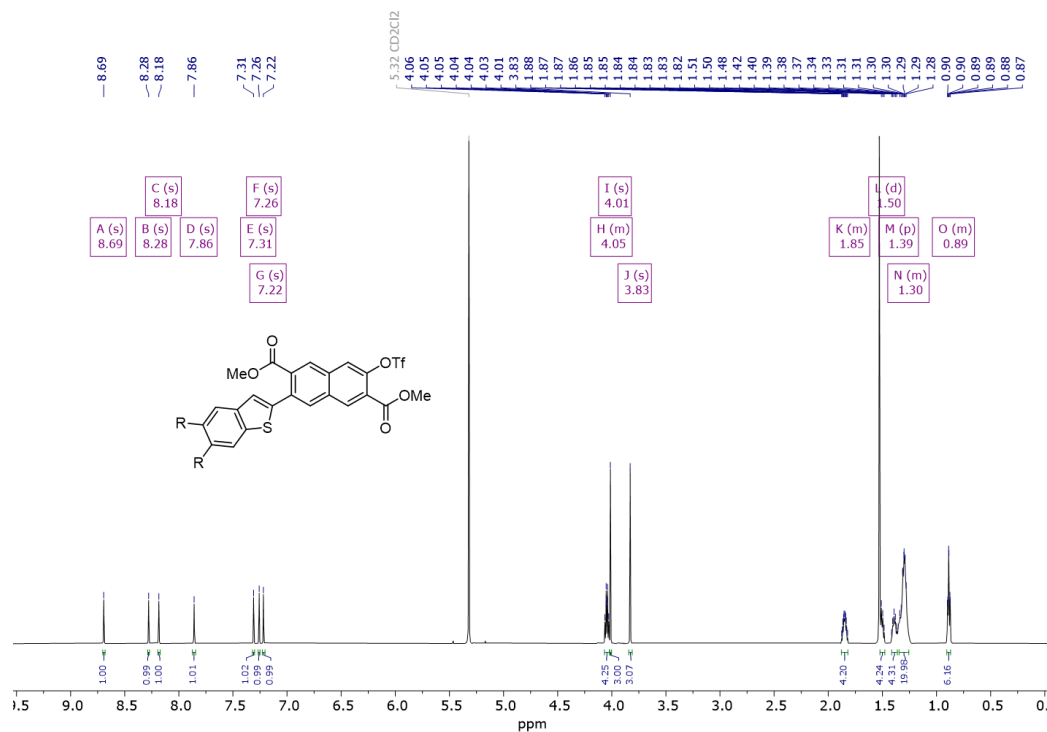


Figure C18. ^1H NMR spectrum (600 MHz) of **27** in CD_2Cl_2 .

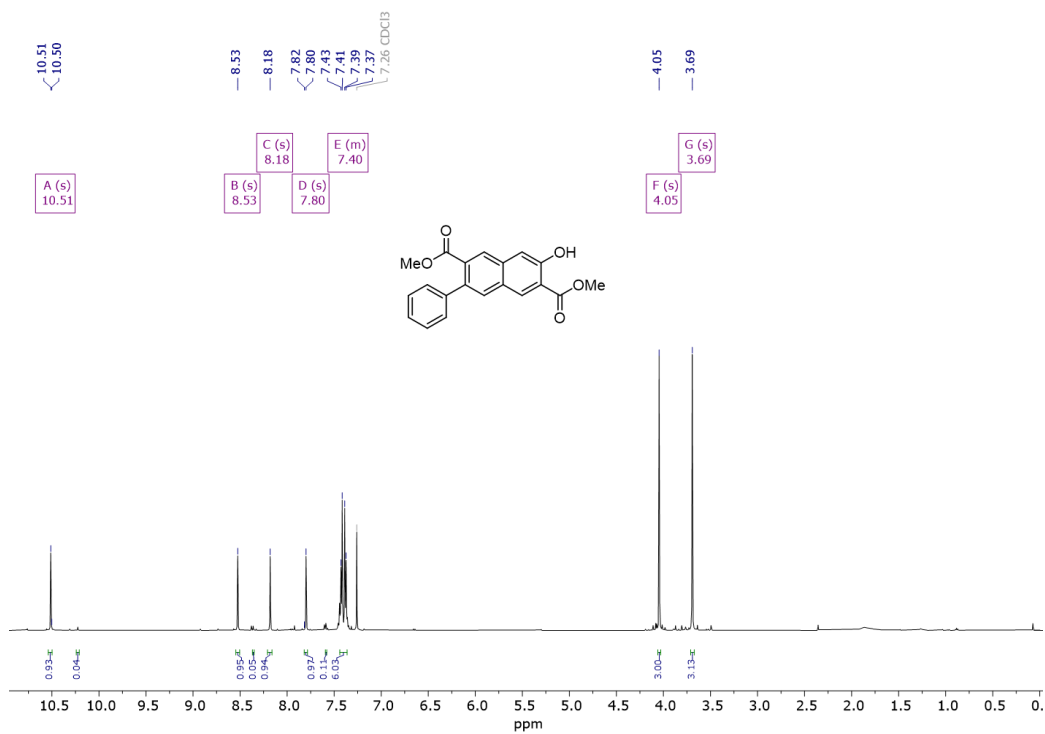


Figure C21. ¹H NMR spectrum (500 MHz) of **31** in CDCl₃.

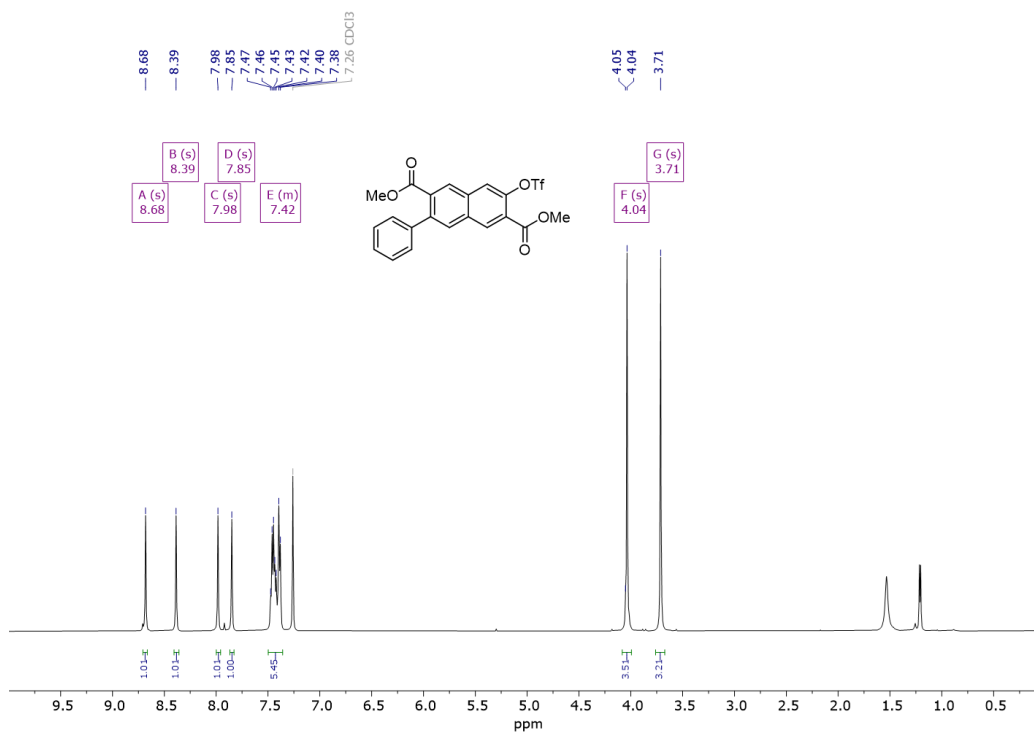


Figure C22. ¹H NMR spectrum (500 MHz) of **32** in CDCl₃.

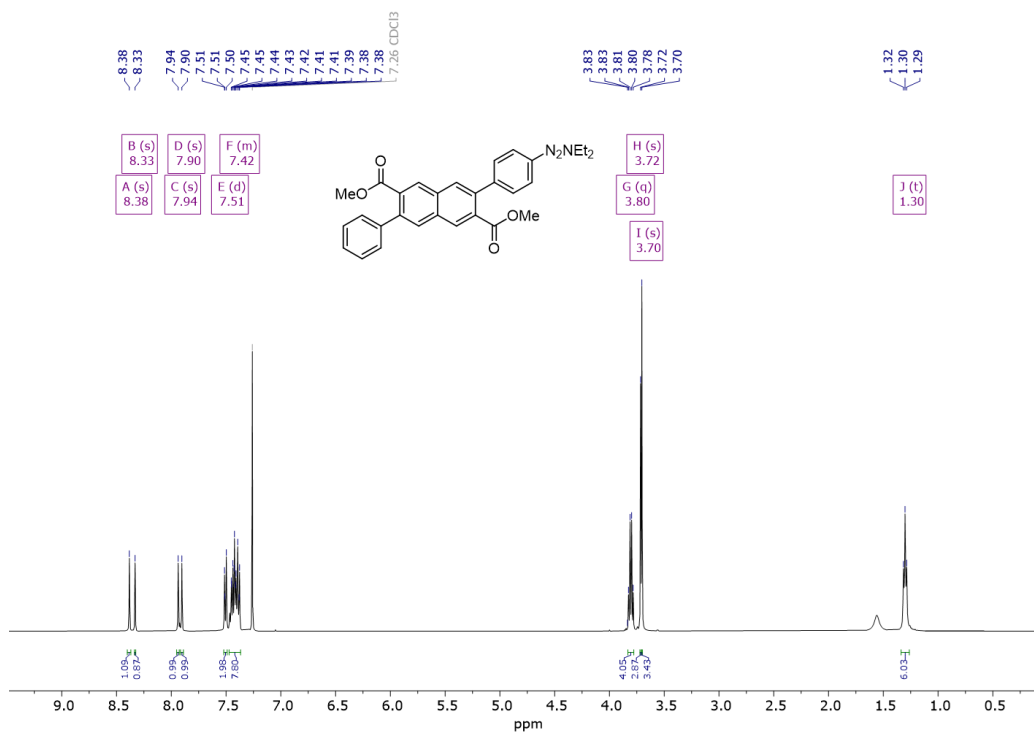


Figure C23. ^1H NMR spectrum (500 MHz) of **34** in CDCl_3 .

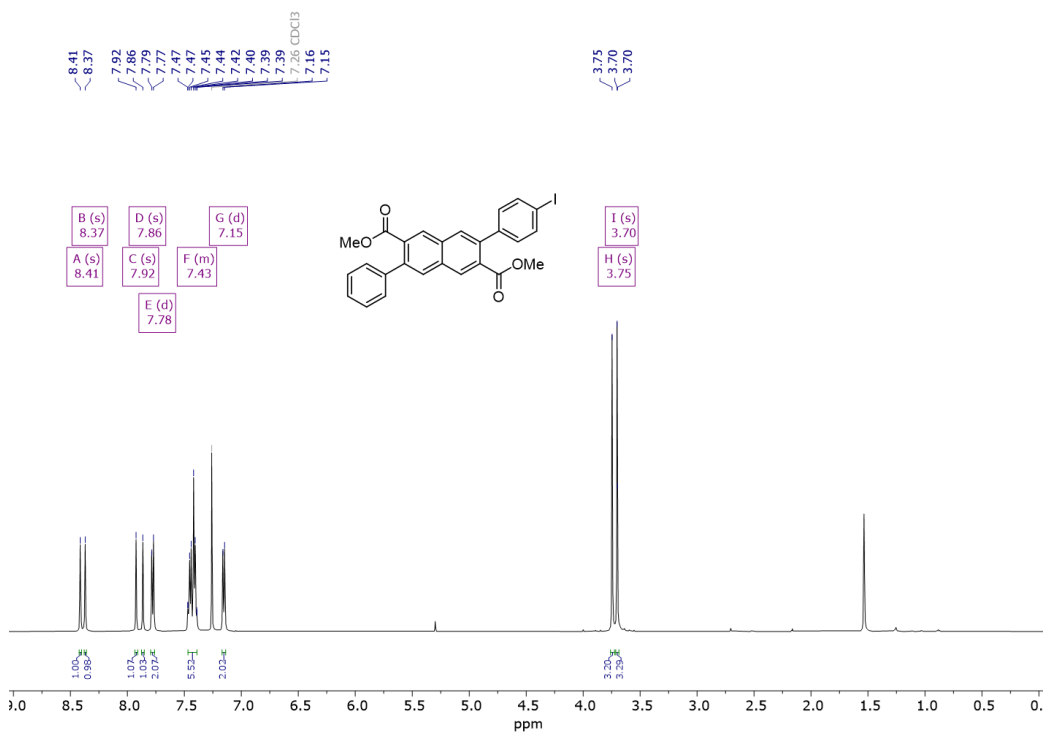
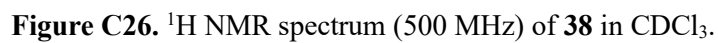
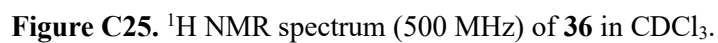


Figure C24. ^1H NMR spectrum (500 MHz) of **35** in CDCl_3 .



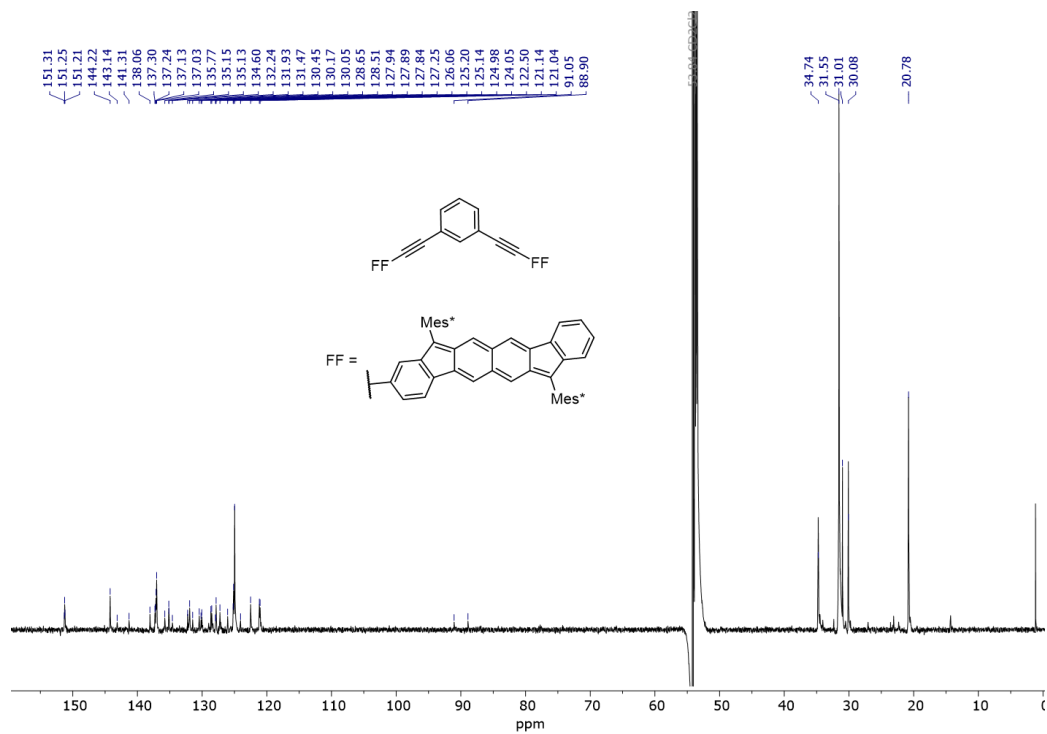


Figure C27. ^{13}C NMR spectrum (151 MHz) of **12** in CD_2Cl_2 .

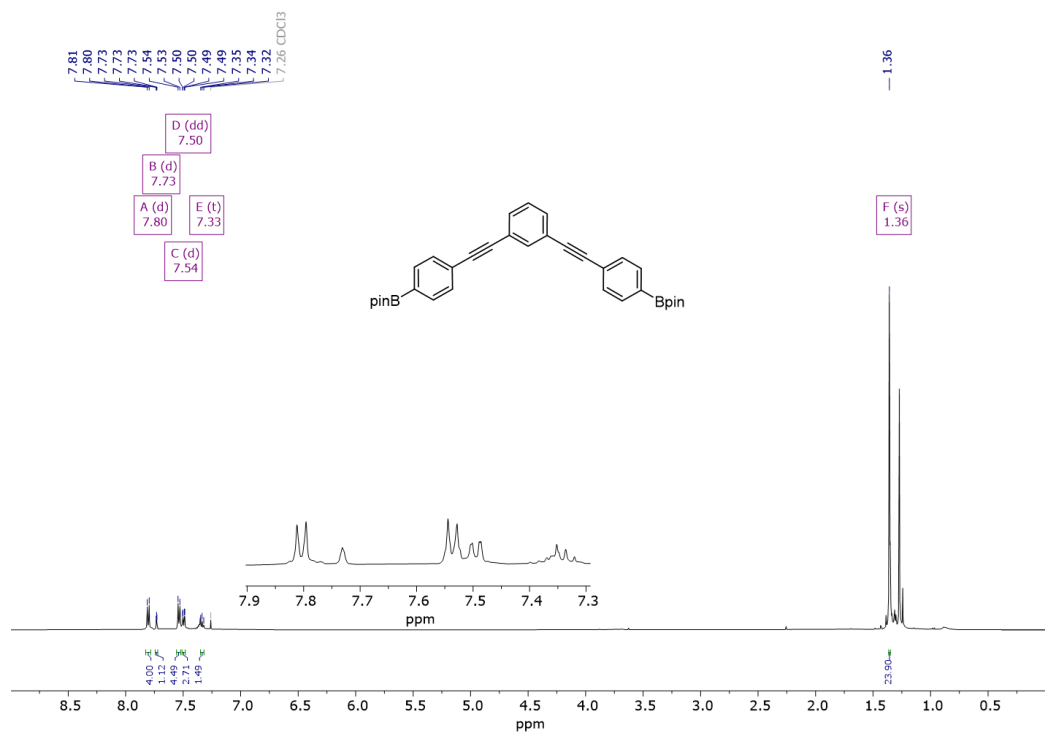


Figure C28. ^1H NMR spectrum (500 MHz) of **40** in CDCl_3 .

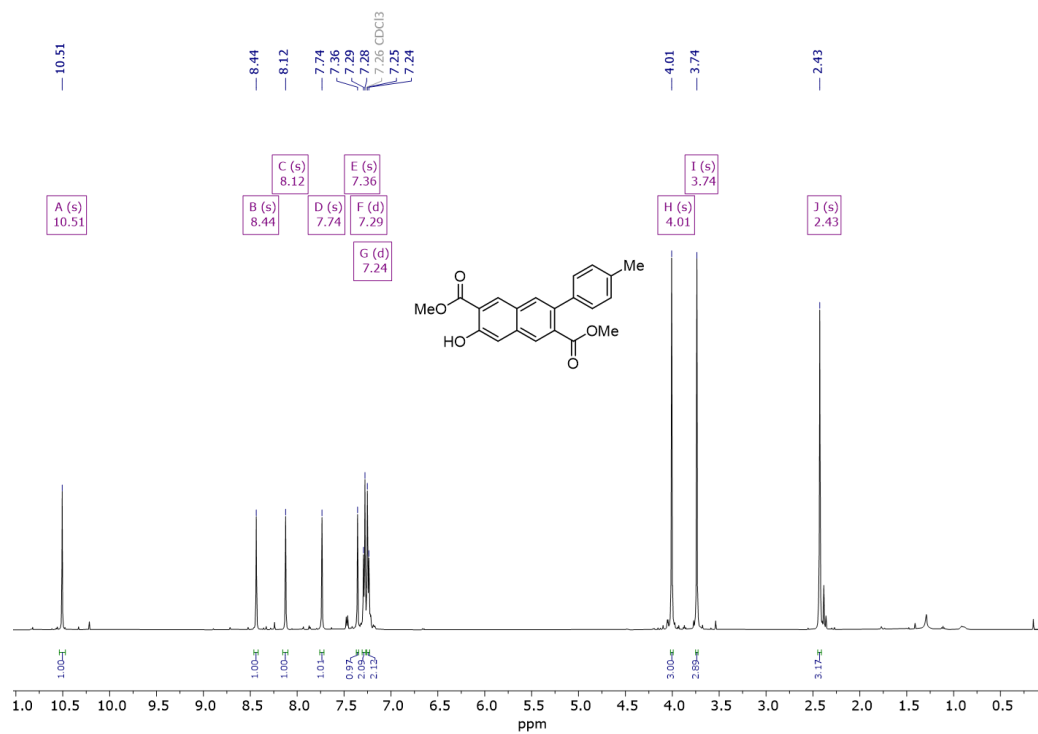


Figure C29. ¹H NMR spectrum (500 MHz) of AC6 in CDCl₃.

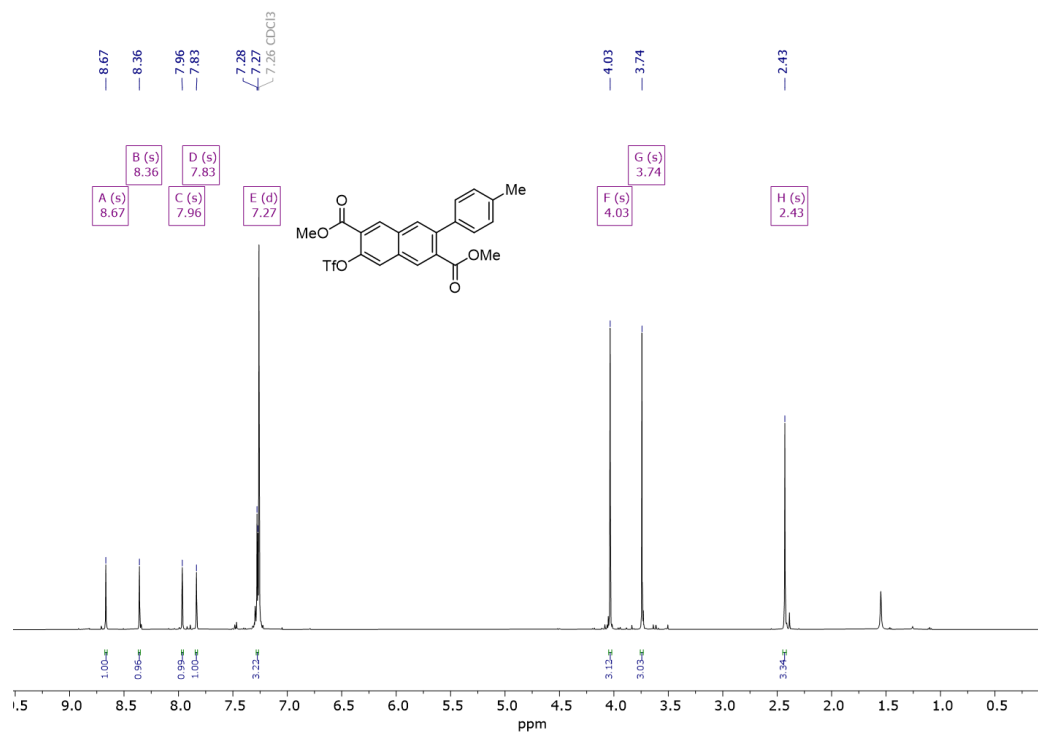


Figure C30. ¹H NMR spectrum (500 MHz) of 41 in CDCl₃.

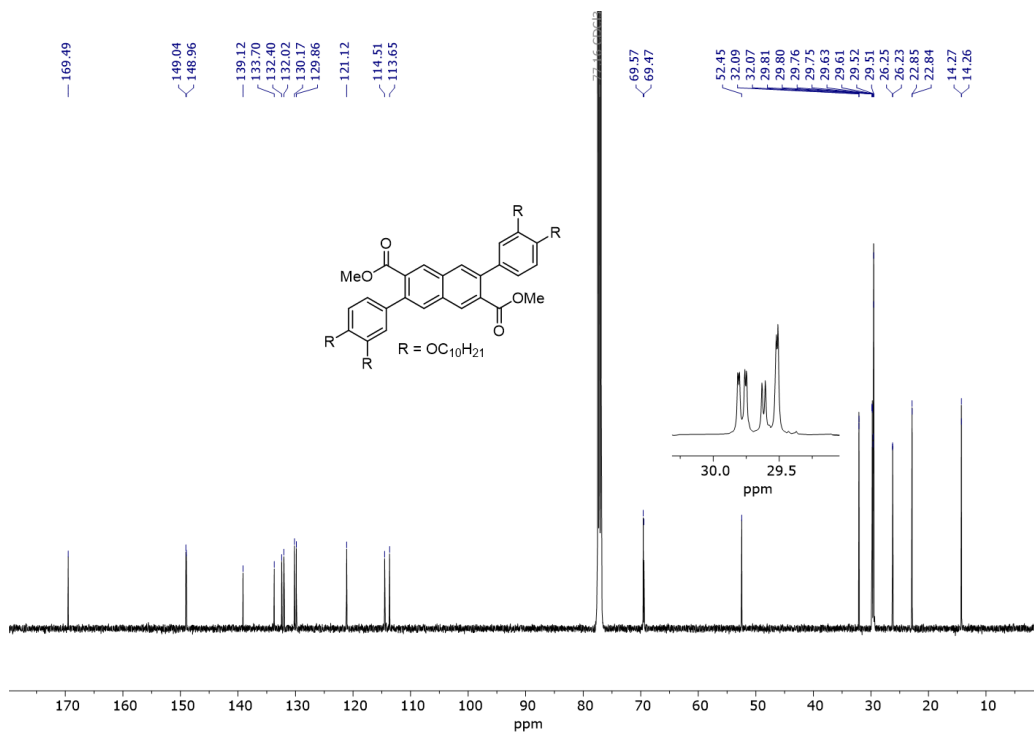


Figure C33. ¹³C NMR spectrum (126 MHz) of **46** in CDCl₃.

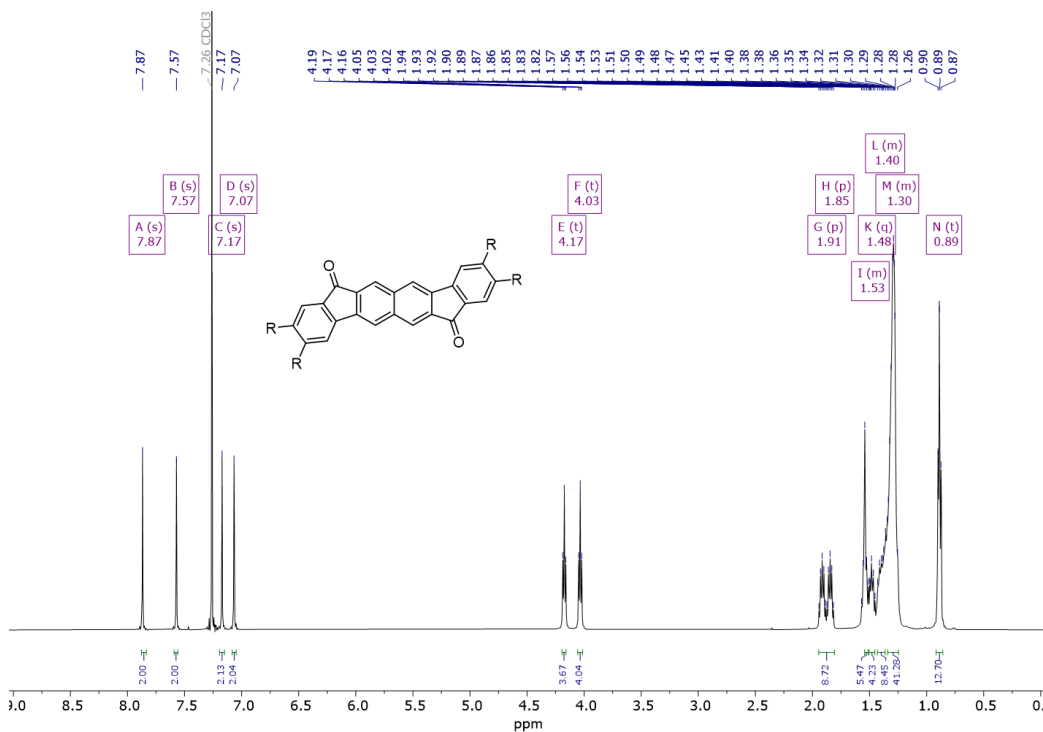


Figure C34. ¹H NMR spectrum (500 MHz) of **47** in CDCl₃.

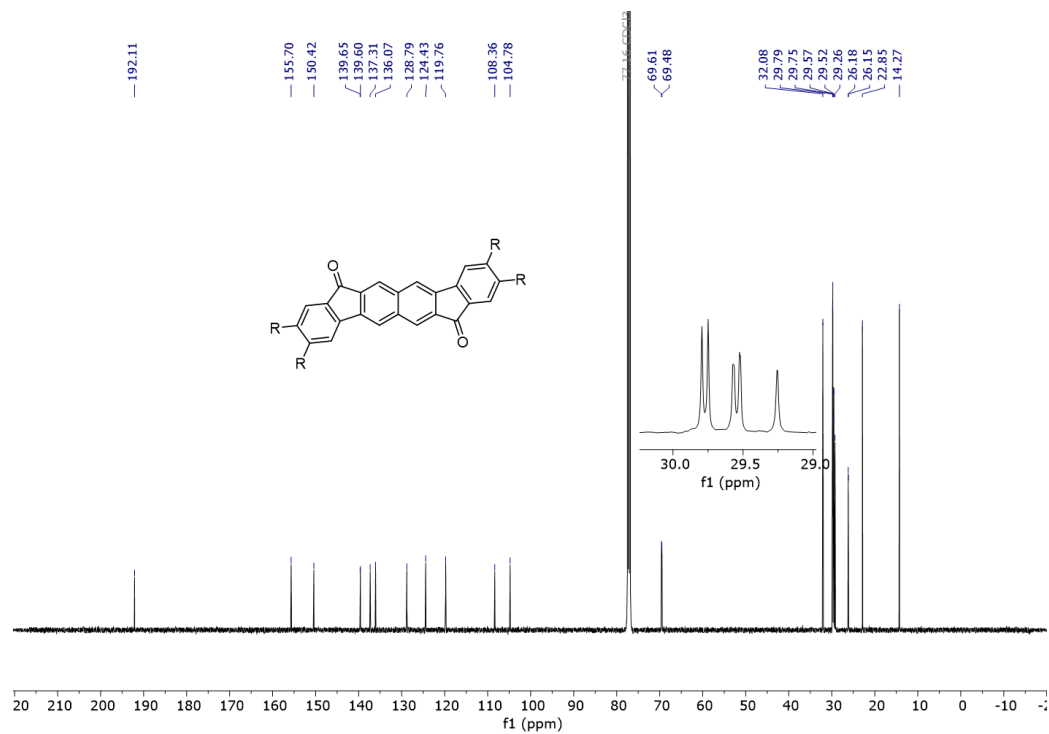


Figure C35. ¹³C NMR spectrum (126 MHz) of **47** in CDCl₃.

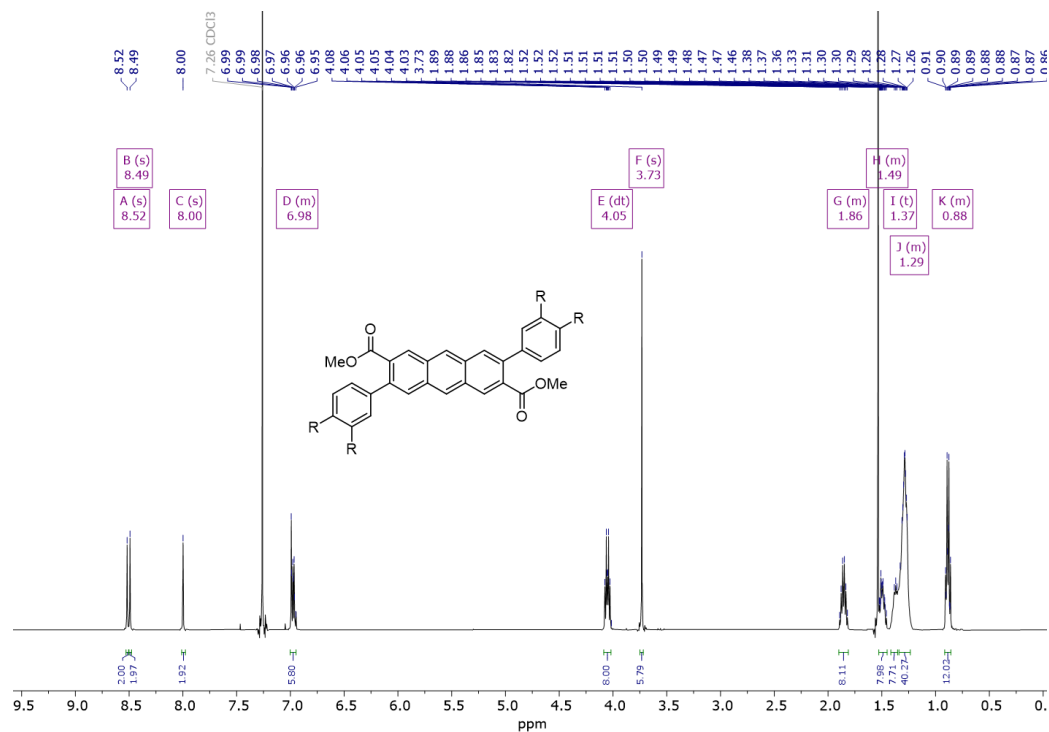


Figure C36. ¹H NMR spectrum (500 MHz) of **49** in CDCl₃.

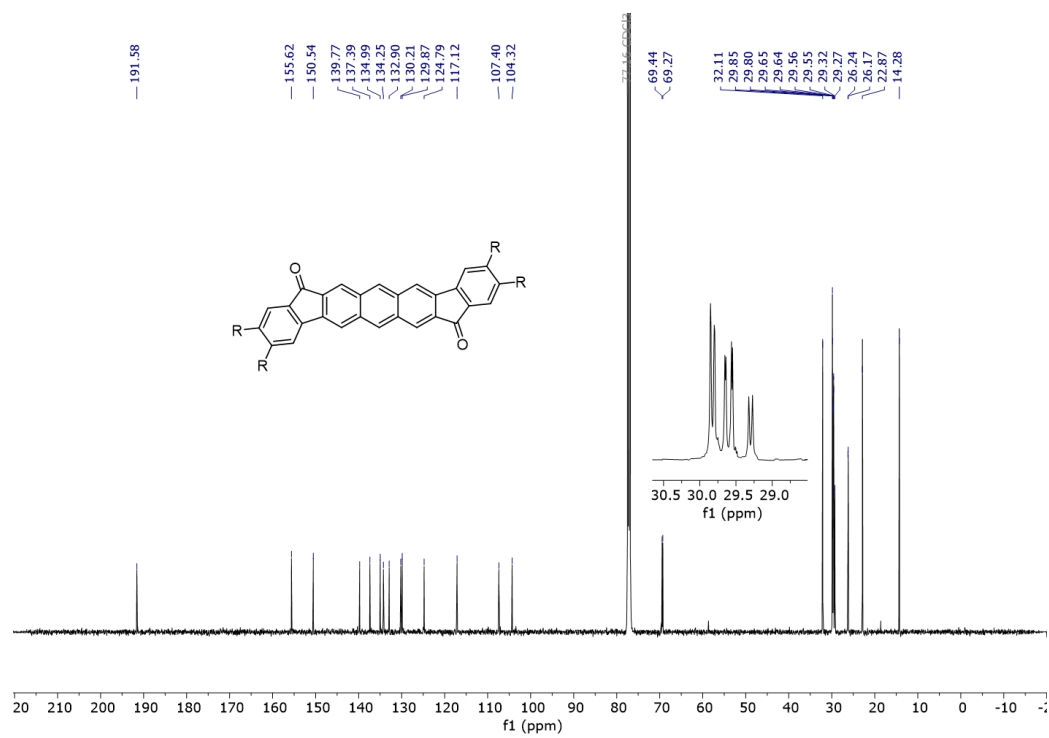


Figure C39. ¹³C NMR spectrum (126 MHz) of **50** in CDCl₃.

References

1. Yeh, M.-C.; Su, Y.-L.; Tzeng, M.-C.; Ong, C.W.; Kajitani, T.; Enozawa, H.; Takata, M.; Koizumi, Y.; Saeki, A.; Seki, S.; Fukushima, T. *Angew. Chem.- Int. Ed.* **2013**, *52*, 1031–1034.
2. Zhu, Y.; Champion, R.D.; Jenekhe, S.A. *Macromolecules* **2006**, *39*, 8712–8719.
3. Wang, P.; Cai, N.; Zhang, M. CN102863812B, September 01, 2013.
4. Korich, A.L.; McBee, I.A.; Bennion, J.C.; Gifford, J.I.; Hughes, T.S. *J. Org. Chem.* **2014**, *79*, 1594–1610.
5. McKenna, M.D.; Baerbera, J.; Marcos, M.; Serrano, J.L. *J. Am. Chem. Soc.* **2005**, *127*, 619–625.
6. Johnson, A.M.; Moshe, O.; Gamboa, A.S.; Langloss, B.W.; Limitiaco, J.F.K.; Larive, C.K.; Hooley, R.J. *Inorg. Chem.* **2011**, *50*, 9430–9442.
7. Knall, A.C.; Ashraf, R.S.; Nikolka, M.; Nielsen, C.B.; Purushothaman, B.; Sadhanala, A.; Hurhangee, M.; Broch, K.; Harkin, D.J.; Novák, J.; Neophytou, M.; Hayoz, P.; Sirringhaus, H.; McCulloch, I. *Adv. Funct. Mater.* **2016**, *26*, 6961–6969.
8. Granhøj, J.; Zalibera, M.; Malček, M.; Pedersen, V. B. R.; Hillers-Bendtsen, A.E.; Mikkelsen, K.V.; Rapta, P.; Nielsen, M.B. *Chem. Eur. J.* **2024**, *30*, e202302688.

REFERENCES CITED

Chapter I

- § Before modern journal requirements, Supporting Information documents as part of a publication were a rarity; thus, reference 25 had no SI file describing the properties or spectral data of 6,12-diphenylindeno[1,2-*b*]fluorene. Prof. Scherf kindly sent the corresponding author Haley the pages from the student's Ph.D. thesis. The data in the thesis matched identically to those reported in reference 41.
- §§ The maximum SQUID temperature initially was 400 K when **47** was studied. The instrument was upgraded in 2017 and can achieve temperatures upwards of 800 K. Since then, the standard protocol has been to acquire both DSC and TGA data on our samples and then stopped SQUID data acquisition 25 K before the onset of decomposition. In addition, a SQUID cooling curve is also acquired to corroborate the heating data and that no covalent modification of the framework has occurred.
1. *Inter alia*: (a) *Aromaticity: Modern Computational Methods and Applications* (Ed.: I. Fernández), Elsevier, Amsterdam, Netherlands, 2021. (b) K. Cocq, C. Lepetit, V. Maraval and R. Chauvin, *Chem. Soc. Rev.*, 2015, **44**, 6535–6559. (c) D. Chen, Y. Hua and H. Xia, *Chem. Rev.*, 2020, **120**, 12994–13086. (d) M. Rosenberg, C. Dahlstrand, K. Kilså and H. Ottosson, *Chem. Rev.*, 2014, **114**, 5379–5425. (e) P. v. R. Schleyer, *Chem. Rev.*, 2001, **101**, 1115–1118. (f) R. Gleiter and G. Haberhauer, *Aromaticity and Other Conjugation Effects*, Wiley-VCH: Weinheim, Germany, 2012.
 2. E. Huckel, *Z. Phys.*, 1931, **70**, 204–286.
 3. (a) R. Breslow, *Chem. Eng. News Archive*, 1965, **43**, 90–100. (b) R. Breslow, J. Brown and J. J. Gajewski, *J. Am. Chem. Soc.*, 1967, **89**, 4383–4390. (c) M. J. S. Dewar, in *Advances in Chemical Physics* (Ed.: R. Doudel), John Wiley & Sons, Inc., Hoboken, New Jersey, 2007, pp. 64–131.
 4. H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH: Weinheim, Germany, 2000.
 5. (a) Randić, M. *Chemical Reviews* **2003**, *103*, 3449–3606. (b) Belloli, R.C. *J. Chem. Educ.* **1983**, *60*, 190–191. (c) Baird, N.C. *J. Chem. Educ.* **1971**, *48*, 509–513. (d) Balaban, A.T.; Oniciu, D.C.; Katritzky, A.R. *Chem. Rev.* **2004**, *104*, 2777–2812. (e) Anthony, J.E. *Angew. Chem.- Int. Ed.* **2008**, *47*, 452–483
 6. *Inter alia*: (a) J. Usuba, M. Hayakawa, S. Yamaguchi and A. Fukazawa, *Chem. Eur. J.*, 2021, **27**, 1638–1647. (b) J. S. Wössner, J. Kohn, D. Wassy, M. Hermann, S. Grimme and B. Esser, *Org. Lett.*, 2022, **24**, 983–988. (c) P. J. Mayer, O. El Bakouri, T. Holczbauer, G. F. Samu, C. Janáky, H. Ottosson and G. London, *J. Org. Chem.*, 2020, **85**, 5158–5172. (d) Y. C. Teo, Z. Jin and Y. Xia, *Org. Lett.*, 2018, **20**, 3300–3304. (e) M. Schmidt, D. Wassy, M. Hermann, M. T. González, N. Agrait, L. A. Zotti, B. Esser and E. Leary, *Chem. Commun.*, 2021, **57**, 745–748. (f) C. Liu, S. Xu, W. Zhu, X. Zhu, W. Hu, Z. Li and Z. Wang, *Chem. Eur. J.*, 2015, **21**, 17016–17022. (g) J. Wang, M. Chu, J.-X. Fan, T.-K. Lau, A.-M. Ren, X. Lu and Q. Miao, *J. Am. Chem. Soc.*, 2019, **141**, 3589–3596.
 7. (a) K. Hafner, R. Dönges, E. Goedecke and R. Kaiser, *Angew. Chem. Int. Ed. Engl.*, 1973, **12**, 337–339. (b) R. Dönges, K. Hafner and H. J. Lindner, *Tetrahedron Lett.*, 1976, **17**, 1345–1348.
 8. T. Bally, S. Chai, M. Neuenschwander and Z. Zhu, *J. Am. Chem. Soc.*, 1997, **119**, 1869–1875.
 9. K. Hafner and H. U. Süss, *Angew. Chem. Int. Ed. Engl.*, 1973, **12**, 575–577.

10. *Inter alia*: (a) K. Brand, *Ber. Deutsch. Chem. Ges.*, 1912, **45**, 3071–3077. (b) J. Blum, W. Baidossi, Y. Badrieck and R. E. Hoffman, *J. Org. Chem.*, 1995, **60**, 4738–4742. (c) J. Yang, M. V. Lakshmikantham and M. P. Cava, *J. Org. Chem.*, 2000, **65**, 6739–6742. (d) M. Saito, M. Nakamura, T. Tazima and M. Yoshioka, *Angew. Chem. Int. Ed.*, 2007, **46**, 1504–1507. (e) G. Babu, A. Orita and J. Otera, *Chem. Lett.*, 2008, **37**, 1296–1297. (f) T. Kawase, A. Konishi, K. Hirao, K. Matsumoto, H. Kurata and T. Kubo, *Chem. Eur. J.*, 2009, **15**, 2653–2661. (g) Z. U. Levi and T. D. Tilley, *J. Am. Chem. Soc.*, 2009, **131**, 2796–2797. (h) J. Zhao, K. Oniwa, N. Asao, Y. Yamamoto and T. Jin, *J. Am. Chem. Soc.*, 2013, **135**, 10222–10225.
11. T. Kawase, T. Fujiwara, C. Kitamura, A. Konishi, Y. Hirao, K. Matsumoto, H. Kurata, T. Kubo, S. Shinamura, H. Mori, E. Miyazaki and K. Takimiya, *Angew. Chem. Int. Ed.*, 2010, **49**, 7728–7732.
12. H. J. Sanderson, A. Helbig, G. Kociok-Köhn, H. Helten and U. Hintermair, *Chem. Sci.*, 2025, **16**, 952–961.
13. S. M. Quintero, M. M. Haley, M. Kertesz and J. Casado, *Angew. Chem. Int. Ed.*, 2022, **61**, e202209138.
14. V. Gold, *The IUPAC Compendium of Chemical Terminology: The Gold Book*, International Union of Pure and Applied Chemistry (IUPAC), Research Triangle Park, NC, 2019.
15. M. Nakano, R. Kishi, T. Nitta, T. Kubo, K. Nakasuji, K. Kamada, K. Ohta, B. Champagne, E. Botek and K. Yamaguchi, *J. Phys. Chem. A*, 2005, **109**, 885–891.
16. (a) M. Chikamatsu, T. Mikami, J. Chisaka, Y. Yoshida, R. Azumi, K. Yase, A. Shimizu, T. Kubo, Y. Morita and K. Nakasuji, *Appl. Phys. Lett.*, 2007, **91**, 043506. (b) K. Kanai, Y. Noda, K. Kato, T. Kubo, K. Iketaki, A. Shimizu, Y. Ouchi, K. Nakasuji, and K. Seki, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12570–12577.
17. (a) D. Peters, *J. Chem. Soc.*, 1958, 1028–1038. (b) D. Peters, *J. Chem. Soc.*, 1958, 1039–1043.
18. Y. Tobe, *Top. Curr. Chem. (Z)*, 2018, **376**, 12.
19. (a) K. Hafner, B. Stowasser, H.-P. Krimmer, S. Fischer, M. C. Böhm and H. J. Lindner, *Angew. Chem. Int. Ed. Engl.*, 1986, **25**, 630–632. (b) K. Hafner, *Pure Appl. Chem.*, 1982, **54**, 939–956.
20. (a) K. Hafner, K. H. Häfner, C. König, M. Kreuder, G. Ploss, G. Schulz, E. Sturm and K. H. Vöpel, *Angew. Chem. Int. Ed. Engl.*, 1963, **2**, 123–134. (b) K. Hafner, *Angew. Chem. Int. Ed. Engl.*, 1964, **3**, 165–173.
21. (a) K. Hafner and H.-P. Krimmer, *Angew. Chem. Int. Ed. Engl.*, 1980, **19**, 199–201. (b) S. Schardt, K. Hafner, T. S. Balaban and V. Sturm, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 330–332. (c) S. Schardt and K. Hafner, *Tetrahedron Lett.*, 1996, **37**, 3829–3832. (d) K. Hanida, J. Kim, N. Fukui, Y. Tsutsui, S. Seki, D. Kim and H. Shinokubo, *Angew. Chem. Int. Ed.*, 2021, **60**, 20765–20770.
22. S.-J. Jhang, J. Pandidurai, C.-P. Chu, H. Miyoshi, Y. Takahara, M. Miki, H. Sotome, H. Miyasaka, S. Chatterjee, R. Ozawa, Y. Ie, I. Hisaki, C.-L. Tsai, Y.-J. Cheng and Y. Tobe, *J. Am. Chem. Soc.*, 2023, **145**, 4716–4729.
23. A. LeBerre, *Ann. Chim.*, 1957, **2**, 371–423.
24. Q. Zhou, P. J. Carroll and T. M. Swager, *J. Org. Chem.*, 1994, **59**, 1294–1301.
25. H. Reisch, U. Wiesler, U. Scherf and N. Tsytyl'kov, *Macromolecules*, 1996, **29**, 8204–8210.
26. J. J. Dressler, Z. Zhou, J. L. Marshall, R. Kishi, S. Takamuku, Z. Wei, S. N. Spisak, M. Nakano, M. A. Petrukhina and M. M. Haley, *Angew. Chem. Int. Ed.*, 2017, **56**, 15363–15367.
27. A. Shimizu, R. Kishi, M. Nakano, D. Shiomi, K. Sato, T. Takui, I. Hisaki, M. Miyata and Y. Tobe, *Angew. Chem. Int. Ed.*, 2013, **52**, 6076–6079.

28. A. Shimizu and Y. Tobe, *Angew. Chem. Int. Ed.*, 2011, **50**, 6906–6910.
29. A. G. Fix, P. E. Deal, C. L. Vonnegut, B. D. Rose, L. N. Zakharov and M. M. Haley, *Org. Lett.*, 2013, **15**, 1362–1365.
30. (a) T. Jousselin-Oba, P. E. Deal, A. G. Fix, C. K. Frederickson, C. L. Vonnegut, A. Yassar, L. N. Zakharov, M. Frigoli and M. M. Haley, *Chem. Asian J.*, 2019, **14**, 1737–1744. (b) J. E. Barker, T. Kodama, M. K. Song, C. K. Frederickson, T. Jousselin-Oba, L. N. Zakharov, J. Marrot, M. Frigoli, R. P. Johnson and M. M. Haley, *ChemPlusChem*, 2019, **84**, 665–672.
31. *Inter alia*: (a) H. Sharma, P. K. Sharma and S. Das, *Chem. Commun.*, 2020, **56**, 11319–11322. (b) H. Sharma, N. Bhardwaj and S. Das, *Org. Biomol. Chem.*, 2022, **20**, 8071–8077. (c) H. Sharma, A. Ankita, P. Bhardwaj, U. K. Pandey and S. Das, *Org. Mater.*, 2023, **5**, 72–83. (d) P. K. Sharma, P. Jana, S. Bandyopadhyay and S. Das, *Chem. Commun.*, 2024, **60**, 7319–7322. (e) H. Sharma, Ankita, V. Mittal, U. K. Pandey and S. Das, *Org. Lett.*, 2024, **26**, 2617–2622.
32. (a) A. G. Fix, D. T. Chase and M. M. Haley, *Top. Curr. Chem.*, 2012, **349**, 159–195. (b) G. E. Rudebusch and M. M. Haley, In *Polycyclic Arenes and Heteroarenes*; Q. Miao, Ed.; Wiley, 2015, pp. 37–60. (c) J. L. Marshall and M. M. Haley, In *Organic Redox Systems*, T. Nishinaga, Ed.; Wiley, 2016, pp. 311–358. (d) C. K. Frederickson, B. D. Rose and M. M. Haley, *Acc. Chem. Res.*, 2017, **50**, 977–987. (e) A. Can, A. Facchetti and H. Usta, *J. Mater. Chem. C*, 2022, **10**, 8496–8535.
33. D. T. Chase, B. D. Rose, S. P. McClintock, L. N. Zakharov and M. M. Haley, *Angew. Chem. Int. Ed.*, 2011, **50**, 1127–1130.
34. (a) U. H. F. Bunz and V. Enkelmann, *Chem. Eur. J.*, 1999, **5**, 263–266. (b) O. M. Behr, G. Eglinton, A. R. Galbraith and R. A. Raphael, *J. Chem. Soc.*, 1960, 3614–3625.
35. (a) W. Deuschel, *Helv. Chim. Acta*, 1951, **34**, 2403–2416. (b) F. Ebel and W. Deuschel, *Chem. Ber.*, 1956, **89**, 2794–2799.
36. S. Merlet, M. Birau and Z. Y. Wang, *Org. Lett.*, 2002, **4**, 2157–2159.
37. C. K. Frederickson, L. N. Zakharov and M. M. Haley, *J. Am. Chem. Soc.*, 2016, **138**, 16827–16838.
38. B. S. Young, D. T. Chase, J. L. Marshall, C. L. Vonnegut, L. N. Zakharov and M. M. Haley, *Chem. Sci.*, 2014, **5**, 1008–1014.
39. (a) J. E. Anthony, *Chem. Rev.*, 2006, **106**, 5028–5048. (b) J. E. Anthony, *Angew. Chem. Int. Ed.*, 2008, **47**, 452–483.
40. D. T. Chase, A. G. Fix, B. D. Rose, C. D. Weber, S. Nobusue, C. E. Stockwell, L. N. Zakharov, M. C. Lonergan and M. M. Haley, *Angew. Chem. Int. Ed.*, 2011, **50**, 11103–11106.
41. D. T. Chase, A. G. Fix, S. J. Kang, B. D. Rose, C. D. Weber, Y. Zhong, L. N. Zakharov, M. C. Lonergan, C. Nuckolls and M. M. Haley, *J. Am. Chem. Soc.*, 2012, **134**, 10349–10352.
42. (a) G. E. Rudebusch, A. G. Fix, H. A. Henthorn, C. L. Vonnegut, L. N. Zakharov and M. M. Haley, *Chem. Sci.*, 2014, **5**, 3627–3633. (b) J. L. Marshall, G. E. Rudebusch, L. N. Zakharov and M. M. Haley, *Tetrahedron Lett.*, 2015, **56**, 3235–3239.
43. (a) I. García Cuesta, S. Coriani, P. Lazzeretti and A. M. J. Sánchez De Merás, *ChemPhysChem*, 2006, **7**, 240–244. (b) M. Makino and J. Aihara, *Phys. Chem. Chem. Phys.*, 2008, **10**, 591–599. (c) S. Motomura, M. Nakano, H. Fukui, K. Yoneda, T. Kubo, R. Carion and B. Champagne, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20575–20583. (d) T. Nagami, J. Fujiyoshi, T. Tonami, K. Watanabe, M. Yamane, K. Okada, R. Kishi, M. Nakano, B. Champagne and V. Liégeois, *Chem. Eur. J.*, 2018, **24**, 13457–13466.
44. J. J. Dressler and M. M. Haley, *J. Phys. Org. Chem.*, 2020, **33**, e4114.

45. C. K. Frederickson, J. E. Barker, J. J. Dressler, Z. Zhou, E. R. Hanks, J. M. Bard, L. N. Zakharov, M. A. Petrukhina and M. M. Haley, *Synlett*, 2018, **29**, 2562–2566.
46. B. D. Rose, L. E. Shoer, M. R. Wasielewski and M. M. Haley, *Chem. Phys. Lett.*, 2014, **616–617**, 137–141.
47. J. L. Marshall, K. Uchida, C. K. Frederickson, C. Schütt, A. M. Zeidell, K. P. Goetz, T. W. Finn, K. Jarolimek, L. N. Zakharov, C. Risko, R. Herges, O. D. Jurchescu and M. M. Haley, *Chem. Sci.*, 2016, **7**, 5547–5558.
48. J. J. Dressler, J. E. Barker, L. J. Karas, H. E. Hashimoto, R. Kishi, L. N. Zakharov, S. N. MacMillan, C. J. Gomez-Garcia, M. Nakano, J. I. Wu and M. M. Haley, *J. Org. Chem.*, 2020, **85**, 10846–10857.
49. (a) G. I. Warren, J. E. Barker, L. N. Zakharov and M. M. Haley, *Org. Lett.*, 2021, **23**, 5012–5017. (b) G. I. Warren, L. J. Zocchi, L. N. Zakharov and M. M. Haley, *Chem. Eur. J.*, 2023, **29**, e202301153.
50. J. E. Barker, T. W. Price, L. J. Karas, R. Kishi, S. N. MacMillan, L. N. Zakharov, C. J. Gómez-García, J. I. Wu, M. Nakano and M. M. Haley, *Angew. Chem. Int. Ed.*, 2021, **60**, 22385–22392.
51. J. E. Barker, G. I. Warren, L. N. Zakharov and M. M. Haley, unpublished results.
52. I. S. Demachkie, M. P. Miller, G. I. Warren, J. E. Barker, E. T. Strand, L. N. Zakharov and M. M. Haley, *Angew. Chem. Int. Ed.*, 2025, **64**, e202420989.
53. (a) A. Rahalkar and A. Stanger, *Aroma*. http://schulich.technion.ac.il/Amnon_Stanger.htm. (b) A. Stanger, *J. Org. Chem.*, 2006, **71**, 883–893. (c) A. Stanger, *J. Org. Chem.*, 2010, **75**, 2281–2288. (d) R. Gershoni-Poranne and A. Stanger, *Chem. Eur. J.*, 2014, **20**, 5673–5688.
54. (a) M. P. Miller and M. M. Haley, *J. Phys. Org. Chem.*, 2025, **38**, e4648. (b) S. Jalife, personal communication.
55. L. J. Karas, S. Jalife, R. V. Viesser, J. V. Soares, M. M. Haley and J. I. Wu, *Angew. Chem. Int. Ed.*, 2023, **62**, e202307379.
56. (a) G. I. Warren, K. Młodzikowska-Pieńko, S. Jalife, I. S. Demachkie, J. I. Wu, M. M. Haley and R. Gershoni-Poranne, *Chem. Sci.*, 2025, **16**, 575–583. (b) See also: S. Jalife and J. I. Wu, *J. Org. Chem.*, 2025, **90**, 4012–4017.
57. P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao and N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* 1996, **118**, 6317–6318. (b) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. von Schleyer, *Chem. Rev.*, 2005, **105**, 3842–3888.
58. G. Monaco, F. F. Summa and R. Zanasi, *J. Chem. Inf. Model.*, 2021, **61**, 270–283.
59. E. Paenurk and R. Gershoni-Poranne, *Phys. Chem. Chem. Phys.*, 2022, **24**, 8631–8644.
60. (a) R. Klann, R. J. Bäuerle, F. Laermer, T. Elsaesser, M. Niemeyer and W. Lüttke, *Chem. Phys. Lett.*, 1990, **169**, 172–178. (b) M. J. Bearpark, P. Celani, F. Jolibois, M. Olivucci, M. A. Robb and F. Bernardi, *Mol. Phys.*, 1999, **96**, 645–652.
61. J. Conradie, C. Foroutan-Nejad and A. Ghosh, *Sci. Rep.*, 2019, **9**, 4852.
62. R. Santiago, M. A. Carvajal, J. Poater, I. de P. R. Moreira, S. T. Bromley, M. Deumal and J. Ribas-Arino, *Chem. Sci.*, 2025, **16**, 430–447.
63. B. D. Rose, C. L. Vonnegut, L. N. Zakharov and M. M. Haley, *Org. Lett.*, 2012, **14**, 2426–2429.
64. G. E. Rudebusch, J. L. Zafra, K. Jorner, K. Fukuda, J. L. Marshall, I. Arrechea-Marcos, G. L. Espejo, R. P. Ortiz, C. J. Gómez-García, L. N. Zakharov, M. Nakano, H. Ottosson, J. Casado and M. M. Haley, *Nat. Chem.*, 2016, **8**, 753–759.

65. (a) J. Kolc, J. W. Downing, A. P. Manzara and J. Michl, *J. Am. Chem. Soc.*, 1976, **98**, 930–937. (b) S. Di Motta, F. Negri, D. Fazzi, C. Castiglioni and E. V. Canesi, *J. Phys. Chem. Lett.*, 2010, **1**, 3334–3339.
66. J. J. Dressler, A. C. Valdivia, R. Kishi, G. E. Rudebusch, A. M. Ventura, B. E. Chastain, C. J. Gómez-García, L. N. Zakharov, M. Nakano, J. Casado and M. M. Haley, *Chem*, 2020, **6**, 1353–1368.
67. E. Vidal Jr., L. N. Zakharov, C. J. Gómez-García and M. M. Haley, *J. Org. Chem.*, 2024, **89**, 14515–14519.
68. B. Bleaney and K. D. Bowers, *Proc. R. Soc. London A*, 1952, **214**, 451–465.
69. J. E. Barker, C. K. Frederickson, M. H. Jones, L. N. Zakharov and M. M. Haley, *Org. Lett.*, 2017, **19**, 5312–5315.
70. H. Hayashi, J. E. Barker, A. C. Valdivia, R. Kishi, S. N. MacMillan, C. J. Gómez-García, H. Miyauchi, Y. Nakamura, M. Nakano, S. -I. Kato, M. M. Haley and J. Casado, *J. Am. Chem. Soc.*, 2020, **142**, 20444–20455.
71. (a) J. J. Dressler, M. Teraoka, G.L. Espejo, R. Kishi, S. Takamaku, C. J. Gómez-García, L. N. Zakharov, M. Nakano, J. Casado and M. M. Haley, *Nat. Chem.*, 2018, **10**, 1134–1140. (b) J. E. Barker, J. J. Dressler, A. C. Valdivia, R. Kishi, E. T. Strand, L. N. Zakharov, S. N. MacMillan, C. J. Gómez-García, M. Nakano, J. Casado and M. M. Haley, *J. Am. Chem. Soc.*, 2020, **142**, 1548–1555.
72. L. Ren, C. Liu, Z. Wang and X. Zhu, *J. Mater. Chem. C*, 2016, **4**, 5202–5206
73. A. M. Zeidell, L. Jennings, C. K. Frederickson, Q. Ai, J. J. Dressler, L. N. Zakharov, C. Risko, M. M. Haley and O. D. Jurchescu, *Chem. Mater.*, 2019, **31**, 6962–6970.
74. B. Xu and N. J. Tao, *Science*, 2003, **301**, 1221–1223.
75. B. Lawson, E. Vidal Jr., S. Luna, M. M. Haley and M. Kamanetska, *ACS Nano*, 2024, **18**, 29059–29066.
76. H. Miyoshi, M. Miki, S. Hirano, A. Shimizu, R. Kishi, K. Fukuda, D. Shiomi, K. Sato, T. Takui, I. Hisaki, M. Nakano and Y. Tobe, *J. Org. Chem.*, 2017, **82**, 1380–1388.
77. M. A. Majewski, P. J. Chmielewski, A. Chien, Y. Hong, T. Lis, M. Witwicki, D. Kim, P. M. Zimmerman and M. Stępień, *Chem. Sci.*, 2019, **10**, 3413–3420.
78. B. Prajapati, M. D. Ambhore, D.-K. Dang, P. J. Chmielewski, T. Lis, C. J. Gómez-García, P. M. Zimmerman and M. Stępień, *Nat. Chem.*, 2023, **15**, 1541–1548.
79. Y. Zou, L. Jiao, Y. Han, L. Ren, Q. Zhou and J. Wu, *J. Am. Chem. Soc.*, 2024, **146**, 27293–27298.
80. Z. Sun, S. Lee, K. Park, X. Zhu, W. Zhang, B. Zheng, P. Hu, Z. Zeng, S. Das, Y. Li, C. Chi, R. Li, K. Huang, J. Ding, D. Kim and J. Wu, *J. Am. Chem. Soc.*, 2013, **135**, 18229–18236.
81. Q. Jiang, Y. Han, X. Hou, S. Wu, T. Xu, M. Orozco-Ic, G. Merino and C. Chi, *Angew Chem. Int. Ed.*, 2024, **63**, e202416833.
82. Q. Jiang, H. Wei, X. Hou and C. Chi, *Angew. Chem. Int. Ed.*, 2023, **62**, e202306938.
83. S. Dong, T. Y. Gopalakrishna, Y. Han, H. Phan, T. Tao, Y. Ni, G. Liu and C. Chi, *J. Am. Chem. Soc.*, 2019, **141**, 62–66.
84. P. K. Sharma, P. Jana, S. Bandyopadhyay and S. Das, *Chem. Commun.*, 2024, **60**, 7319–7322.
85. H. Sharma, P. Jana, D. Mallick, S. Bandyopadhyay and S. Das, *Chem. Sci.*, 2024, **15**, 20215–20222.

Chapter II.

1. Stuyver, T.; Chen, B.; Zeng, T.; Geerlings, P.; Proft, F. D.; Hoffmann, R. Do Diradicals Behave Like Radicals? *Chem. Rev.* **2019**, *119*, 11291–11351.
2. Wang, T.; Angulo-Portugal, P.; Berdonces-Layunta, A.; Jancarik, A.; Gourdon, A.; Holec, J.; Kumar, M.; Soler, D.; Jelinek, P.; Casanova, D.; Corso, M. Tuning the Diradical Character of Pentacene Derivatives via Non-Benzenoid Coupling Motifs. *J. Am. Chem. Soc.* **2023**, *145*, 10333–10341.
3. Horbatenko, Y.; Sadiq, S.; Lee, S.; Filatov, M.; Choi, C. H. Mixed-Reference Spin-Flip Time-Dependent Density Functional Theory (MRSF-TDDFT) as a Simple yet Accurate Method for Diradicals and Diradicaloids. *J. Chem. Theory. Comput.* **2021**, *17*, 848–859.
4. Sun, Z.; Wu, J. Open-Shell Polycyclic Aromatic Hydrocarbons. *J. Mater. Chem.* **2012**, *22*, 4151–4160.
5. *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds*; Hicks, R. G., Ed.; Wiley: Chichester, UK, **2010**.
6. Manabu, Abe. Diradicals. *Chem. Rev.* **2013**, *113*, 7011–7088.
7. Ortiz, Ricardo; Boto, Roberto A.; García-Martínez, Noel; Sancho-García, Juan C.; Melle-Franco, Manuel; Fernán dez-Rossier, Joaquín. Exchange Rules for Diradical π -Conjugated Hydrocarbons. *Nano Lett.* **2019**, *19*, 5991–5997.
8. Muthike, A. K.; Awais, M. A.; Wang, C.; Orr, M. E.; Almeida, N. M. S.; North, S. C.; Yu, L.; Wilson, A. K.; Goodson III, T. G. Effect of Long-Lived Ground-State Diradicaloids on the Photophysics of Semiladder Thiophene-Based Polymer Aggregates for Organic Light-Emitting Transistor Applications. *ACS Appl. Energy Mater.* **2024**, *7*, 4904–4918.
9. Kim, Y.; Kim, Y.-J.; Kim, Y.-A.; Jung, E.; Mok, Y.; Kim, K.; Hwang, H.; Park, J.-J.; Kim, M.-G.; Mathur, S.; Kim, D.-Y. Open-Shell and Closed-Shell Quinoid–Aromatic Conjugated Polymers: Unusual Spin Magnetic and High Charge Transport Properties. *ACS Appl. Mater. Interfaces* **2021**, *13*, 2887–2898.
10. Higashino, T.; Mori, Takehiko. Small-Molecule Ambipolar Transistors. *Phys. Chem. Chem. Phys.* **2022**, *24*, 9770–9806.
11. Dai, Y.; Zerbini, A.; Casado, J.; Negri, F. Ambipolar Charge Transport in Organic Semiconductors: How Intramolecular Reorganization Energy Is Controlled by Diradical Character. *Molecules* **2023**, *28*, 4642, 1–16.
12. Li, Z.; Bu, Y.; Xie, S.; Ni, Y.; Yang, K.; Zeng, Z. Pyridinic Nitrogen Doping: A Versatile Approach for Precise Structure–Property Manipulations of Nanographenes. *Chem. Mater.* **2024**, *36*, 3058–3080.
13. de Oteyza, D. G.; Frederiksen, T. Carbon-Based Nanostructures as a Versatile Platform for Tunable π -Magnetism. *J. Phys. Condens. Matter* **2022**, *34*, 443001 (41pp).
14. Baranac-Stojanovic, M.; Stojanovic, M. The Effect of Two Types of Dibenzoannulation of Pentalene on Molecular Energies and Magnetically Induced Currents. *Phys. Chem. Chem. Phys.* **2019**, *21*, 3250–3263.
15. Tsuji, Y.; Hoffmann, R.; Strange, M.; Solomon, G. C. Close Relation between Quantum Interference in Molecular Conductance and Diradical Existence. *Proc. Natl. Acad. Sci. U.S.A.* **2016**, *113*, E413–E419.
16. Stuyver, T.; Zeng, T.; Tsuji, Y.; Fias, S.; Geerlings, P.; Proft, F. D. Captodative Substitution: A Strategy for Enhancing the Conductivity of Molecular Electronic Devices. *J. Phys. Chem. C* **2018**, *122*, 3194–3200.

17. Moodera, J. S.; Koopmans, B.; Oppeneer, P. M. On the Path toward Organic Spintronics. *MRS Bull.* **2014**, *39*, 578–581.
18. Tan, Y.; Hsu, S.-N.; Tahir, H.; Dou, L.; Savoie, B. M.; Boudouris, B. W. Electronic and Spintronic Open-Shell Macromolecules, Quo Vadis? *J. Am. Chem. Soc.* **2022**, *144*, 626–647.
19. Yoshida, W.; Matsui, H.; Miyamoto, H.; Tonami, T.; Sugimori, R.; Yoneda, K.; Kishi, R.; Nakano, M. Theoretical Study on Third-Order Nonlinear Optical Properties for One-Hole-Doped Diradicaloids. *ACS Omega* **2021**, *6*, 3046–3059.
20. Yoneda, K.; Nakano, M.; Fukuda, K.; Matsui, H.; Takamuku, S.; Hirotsaki, Y.; Kubo, T.; Kamada, K.; Champagne, B. Third-Order Nonlinear Optical Properties of One-Dimensional Open-Shell Molecular Aggregates Composed of Phenalenyl Radicals. *Chem. Eur. J.* **2014**, *20*, 11129–11136.
21. Tonami, T.; Nagami, T.; Okada, K.; Yoshida, W.; Nakano, M. Singlet-Fission-Induced Enhancement of Third-Order Nonlinear Optical Properties of Pentacene Dimers. *ACS Omega* **2019**, *4*, 16181–16190.
22. Nagami, T.; Okada, K.; Miyamoto, H.; Yoshida, W.; Tonami, T.; Nakano, M. Molecular Design Principle for Efficient Singlet Fission Based on Diradical Characters and Exchange Integrals: Multiple Heteroatom Substitution Effect on Anthracenes. *J. Phys. Chem. C* **2020**, *124*, 11800–11809.
23. Thiele, J.; Balhorn, H. Ueber Einen Chinoiden Kohlenwasserstoff. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 1463–1470.
24. Tschitschibabin, A. E. Über einige phenylierte Derivate des p,p-Ditolyls. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 1810–1819.
25. Lukman, S.; Richter, J. M.; Yang, L.; Hu, P.; Wu, J.; Greenham, N. C.; Musser, A. J. Efficient Singlet Fission and Triplet-Pair Emission in a Family of Zethrene Diradicaloids. *J. Am. Chem. Soc.* **2017**, *139*, 18376–18385.
26. Zeng, W.; Sun, Z.; Herng, T. S.; Goncalves, T. P.; Gopalakrishna, T. Y.; Huang, K.-W.; Ding, J.; Wu, J. Super-Heptazethrene. *Angew. Chem. Int. Ed.* **2016**, *55*, 8615–8619.
27. Kubo, T.; Shimizu, A.; Uruichi, M.; Yakushi, K.; Nakano, M.; Shiomi, D.; Sato, K.; Takui, T.; Morita, Y.; Nakasuji, K. Singlet Biradical Character of Phenalenyl-Based Kekule' Hydrocarbon with Naphthoquinoid Structure. *Org. Lett.* **2007**, *9*, 81–84.
28. Kubo, T. Syntheses and Properties of Open-Shell π -Conjugated Molecules. *Bull. Chem. Soc. Jpn.* **2021**, *94*, 2235–2244.
29. Konishi, A.; Hirao, Y.; Nakano, M.; Shimizu, A.; Botek, E.; Champagne, B.; Shiomi, D.; Sato, K.; Takui, T.; Matsumoto, K.; Kurata, H.; Kubo, T. Synthesis and Characterization of Teranthene: A Singlet Biradical Polycyclic Aromatic Hydrocarbon Having Kekule' Structures. *J. Am. Chem. Soc.* **2010**, *132*, 11021–11023.
30. Konishi, A.; Horii, K.; Shiomi, D.; Sato, K.; Takui, T.; Yasuda, M. Open-Shell and Antiaromatic Character Induced by the Highly Symmetric Geometry of the Planar Heptalene Structure: Synthesis and Characterization of a Nonalternant Isomer of Bisanthene. *J. Am. Chem. Soc.* **2019**, *141*, 10165–10170.
31. Zeng, Z.; Lee, S.; Zafra, J. L.; Ishida, M.; Zhu, X.; Sun, Z.; Ni, Y.; Webster, R. D.; Li, R.-W.; Navarrete, J. T. L.; Chi, C.; Ding, J.; Casado, J.; Kim, D.; Wu, J. Tetracyanoquaterylene and Tetracyanohexarylenequinodimethanes with Tunable Ground States and Strong Near-Infrared Absorption. *Angew. Chem. Int. Ed.* **2013**, *52*, 8561–8565.

32. Hayashi, Y.; Suzuki, S.; Suzuki, T.; Ishigaki, Y. Dibenzotropylium-Capped Orthogonal Geometry Enabling Isolation and Examination of a Series of Hydrocarbons with Multiple 14π -Aromatic Units. *J. Am. Chem. Soc.* **2023**, *145*, 2596–2608.
33. Dressler, J. J.; Teraoka, M.; Espejo, G. L.; Kishi, R.; Takamuku, S.; Gómez-García, C. J.; Zakharov, L. N.; Nakano, M.; Casado, J.; Haley, M. M. Thiophene and Its Sulfur Inhibit Indenoindenodibenzothiophene Diradicals from Low-Energy Lying Thermal Triplets. *Nat. Chem.* **2018**, *10*, 1134–1140.
34. Barker, J. E.; Dressler, J. J.; Valdivia, A. C.; Kishi, R.; Strand, E. T.; Zakharov, L. N.; MacMillan, S. N.; Gómez-García, C. J.; Nakano, M.; Casado, J.; Haley, M. M. Molecule Isomerism Modulates the Diradical Properties of Stable Singlet Diradicaloids. *J. Am. Chem. Soc.* **2020**, *142*, 1548–1555.
35. Rudebusch, G. E.; Zafra, J. L.; Jorner, K.; Fukuda, K.; Marshall, J. L.; Arrechea-Marcos, I.; Espejo, G. L.; Ponce Ortiz, R.; Gómez-García, C. J.; Zakharov, L. N.; Nakano, M.; Ottosson, H.; Casado, J.; Haley, M. M. Diindeno-Fusion of an Anthracene as a Design Strategy for Stable Organic Biradicals. *Nat. Chem.* **2016**, *8*, 753–759.
36. Dressler, J. J.; Cárdenas Valdivia, A.; Kishi, R.; Rudebusch, G. E.; Ventura, A. M.; Chastain, B. E.; Gómez-García, C. J.; Zakharov, L. N.; Nakano, M.; Casado, J.; Haley, M. M. Diindenoanthracene Diradicaloids Enable Rational, Incremental Tuning of Their Singlet-Triplet Energy Gaps. *Chem* **2020**, *6*, 1353–1368.
37. Granhøj, J.; Zalibera, M.; Malček, M.; Pedersen, V. B. R.; Hillers-Bendtsen, A. E.; Mikkelsen, K. V.; Rapta, P.; Nielsen, M. B. Extended Tetrathiafulvalenes with Fluoreno[3,2-*b*]Fluorene and Diindeno[1,2-*b*:1',2'-*i*]Anthracene Cores. *Chem. Eur. J.* **2024**, *30*, e202302688.
38. Zysman-Colman, E.; Arias, K.; Siegel, J. S. Synthesis of arylbromides from arenes and Nbromosuccinimide bromosuccinimide (NBS) in acetonitrile – A convenient method for aromatic bromination. *Can. J. Chem.* **2009**, *87*, 440–447.
39. Kolc, J.; Downing, J. W.; Manzara, A. P.; Michl, J. π,π -Biradicaloid Hydrocarbons. The Pleiadene Family. II. A Doubly Excited State of Pleiadene. *J. Am. Chem. Soc.* **1976**, *98*, 930–937.
40. Kamada, K.; Ohta, K.; Kubo, T.; Shimizu, A.; Morita, Y.; Nakasuji, K.; Kishi, R.; Ohta, S.; Furukawa, S.; Takahashi, H.; Nakano, M. Strong Two-Photon Absorption of Singlet Diradical Hydrocarbons. *Angew. Chem. Int. Ed.* **2007**, *46*, 3544–3546.
41. Di Motta, S.; Negri, F.; Fazzi, D.; Castiglioni, C.; Canesi, E. V. Biradicaloid and Polyenic Character of Quinoidal Oligothiophenes Revealed by the Presence of a Low-Lying Double-Exciton State. *J. Phys. Chem. Lett.* **2010**, *1*, 3334–3339.
42. Chase, D. T.; Fix, A. G.; Kang, S. J.; Rose, B. D.; Weber, C. D.; Zhong, Y.; Zakharov, L. N.; Lonergan, M. C.; Nuckolls, C.; Haley, M. M. 6,12-Diaryllindeno[1,2-*b*]fluorenes: Syntheses, Photophysics, and Ambipolar OFETs. *J. Am. Chem. Soc.* **2012**, *134*, 10349–10352.
43. Bleaney, B.; Bowers, K. D. Anomalous Paramagnetism of Copper Acetate. *Proc. R. Soc. Lond. A* **1952**, *214*, 451–465.

Chapter III.

1. Aviram, A.; Ratner, M. A. Molecular Rectifiers. *Chem. Phys. Lett.* **1974**, *29*, 277–283.
[https://doi.org/10.1016/0009-2614\(74\)85031-1](https://doi.org/10.1016/0009-2614(74)85031-1).

2. Quek, S. Y.; Kamenetska, M.; Steigerwald, M. L.; Choi, H. J.; Louie, S. G.; Hybertsen, M. S.; Neaton, J. B.; Venkataraman, L. Mechanically Controlled Binary Conductance Switching of a Single-Molecule Junction. *Nat. Nanotechnol.* **2009**, *4*, 230–234. <https://doi.org/10.1038/nnano.2009.10>.
3. Yuan, L.; Nerngchamnong, N.; Cao, L.; Hamoudi, H.; Del Barco, E.; Roemer, M.; Sriramula, R. K.; Thompson, D.; Nijhuis, C. A. Controlling the Direction of Rectification in a Molecular Diode. *Nat. Commun.* **2015**, *6*, 6324. <https://doi.org/10.1038/ncomms7324>.
4. Zhou, P.; Fu, Y.; Wang, M.; Qiu, R.; Wang, Y.; Stoddart, J. F.; Wang, Y.; Chen, H. Robust Single-Supramolecule Switches Operating in Response to Two Different Noncovalent Interactions. *J. Am. Chem. Soc.* **2023**, *145*, 18800–18811. <https://doi.org/10.1021/jacs.3c03282>.
5. Skipper, H.; Lawson, B.; Pan, X.; Degtiareva, V.; Kamenetska, M. Manipulating Quantum Interference between σ and π Orbitals in Single-Molecule Junctions via Chemical Substitution and Environmental Control. *ACS Nano* **2023**, *17*, 16107–16114. <https://doi.org/10.1021/acsnano.3c04963>.
6. Datta, S. *Electronic Transport in Mesoscopic Systems*; Cambridge University Press: Cambridge, UK, 1995.
7. Tsuji, Y.; Movassagh, R.; Datta, S.; Hoffmann, R. Exponential Attenuation of Through-Bond Transmission in a Polyene: Theory and Potential Realizations. *ACS Nano* **2015**, *9*, 11109–11120. <https://doi.org/10.1021/acsnano.5b04615>.
8. Perrin, M. L.; Perrin, M. L.; Eelkema, R.; Thijssen, J.; Grozema, F. C.; Van Der Zant, H. S. J. Single-Molecule Functionality in Electronic Components Based on Orbital Resonances. *Phys. Chem. Chem. Phys.* **2020**, *22*, 12849–12866. <https://doi.org/10.1039/D0CP01448F>.
9. Gunasekaran, S.; Greenwald, J. E.; Venkataraman, L. Visualizing Quantum Interference in Molecular Junctions. *Nano Lett.* **2020**, *20*, 2843–2848. <https://doi.org/10.1021/acs.nanolett.0c00605>.
10. González-Herrero, H.; Mendieta-Moreno, J. I.; Edalatmanesh, S.; Santos, J.; Martín, N.; Écija, D.; de la Torre, B.; Jelinek, P.; González-Herrero, H.; Edalatmanesh, S.; et al. Atomic Scale Control and Visualization of Topological Quantum Phase Transition in π -Conjugated Polymers Driven by Their Length. *Adv. Mater.* **2021**, *33*, 2104495. <https://doi.org/10.1002/ADMA.202104495>.
11. Li, L.; Low, J. Z.; Wilhelm, J.; Liao, G.; Gunasekaran, S.; Prindle, C. R.; Starr, R. L.; Golze, D.; Nuckolls, C.; Steigerwald, M. L.; et al. Highly Conducting Single-Molecule Topological Insulators Based on Mono- and Di-Radical Cations. *Nat. Chem.* **2022**, *14*, 1061–1067. <https://doi.org/10.1038/s41557-022-00978-1>.
12. Naghibi, S.; Sangtarash, S.; Kumar, V. J.; Wu, J. Z.; Judd, M. M.; Qiao, X.; Gorenskaia, E.; Higgins, S. J.; Cox, N.; Nichols, R. J.; et al. Redox-Addressable Single-Molecule Junctions Incorporating a Persistent Organic Radical. *Angew. Chemie - Int. Ed.* **2022**, *61*, e202116985. <https://doi.org/10.1002/anie.202116985>.

13. Li, L.; Louie, S.; Evans, A. M.; Meirzadeh, E.; Nuckolls, C. Topological Radical Pairs Produce Ultrahigh Conductance in Long Molecular Wires. *J. Am. Chem. Soc.* **2023**, *145*, 2492–2498. <https://doi.org/10.1021/jacs.2c12059>.
14. Henson, J. D.; Reddel, R. R. Assaying and Investigating Alternative Lengthening of Telomeres Activity in Human Cells and Cancers. *FEBS Lett.* **2010**, *584*, 3800–3811. <https://doi.org/10.1016/j.febslet.2010.06.009>.
15. Stuyver, T.; Zeng, T.; Tsuji, Y.; Geerlings, P.; De Proft, F. Diradical Character as a Guiding Principle for the Insightful Design of Molecular Nanowires with an Increasing Conductance with Length. *Nano Lett.* **2018**, *18*, 7298–7304. https://doi.org/10.1021/ACS.NANOLETT.8B03503/ASSET/IMAGES/LARGE/NL-2018-035039_0005.JPEG.
16. Li, L.; Gunasekaran, S.; Wei, Y.; Nuckolls, C.; Venkataraman, L. Reversed Conductance Decay of 1D Topological Insulators by Tight-Binding Analysis. *J. Phys. Chem. Lett.* **2022**, *13*, 9703–9710. <https://doi.org/10.1021/acs.jpcclett.2c02812>.
17. Xu, B.; Tao, N. J. Measurement of Single-Molecule Resistance by Repeated Formation of Molecular Junctions. *Science*. **2003**, *301*, 1221–1223. <https://doi.org/10.1126/science.1087481>.
18. Venkataraman, L.; Klare, J. E.; Tam, I. W.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. Single-Molecule Circuits with Well-Defined Molecular Conductance. *Nano Lett.* **2006**, *6*, 458–462. <https://doi.org/10.1021/nl052373+>.
19. (19) McNeely, J.; Miller, N.; Pan, X.; Lawson, B.; Kamenetska, M. Angstrom-Scale Ruler Using Single Molecule Conductance Signatures. *J. Phys. Chem. C* **2020**, *124*, 13427–13433. <https://doi.org/10.1021/acs.jpcc.0c02063>.
20. Hayashi, H.; Barker, J. E.; Cárdenas Valdivia, A.; Kishi, R.; Macmillan, S. N.; Gómez-García, C. J.; Miyauchi, H.; Nakamura, Y.; Nakano, M.; Kato, S. I.; et al. Monoradicals and Diradicals of Dibenzofluoreno[3,2- b]Fluorene Isomers: Mechanisms of Electronic Delocalization. *J. Am. Chem. Soc.* **2020**, *142*, 20444–20455. <https://doi.org/10.1021/jacs.0c09588>.
21. Dressler, J. J.; Cárdenas Valdivia, A.; Kishi, R.; Rudebusch, G. E.; Ventura, A. M.; Chastain, B. E.; Gómez-García, C. J.; Zakharov, L. N.; Nakano, M.; Casado, J.; et al. Diindenoanthracene Diradicaloids Enable Rational, Incremental Tuning of Their Singlet-Triplet Energy Gaps. *Chem* **2020**, *6*, 1353–1368. <https://doi.org/10.1016/j.chempr.2020.02.010>.
22. Dressler, J. J.; Teraoka, M.; Espejo, G. L.; Kishi, R.; Takamuku, S.; Gómez-García, C. J.; Zakharov, L. N.; Nakano, M.; Casado, J.; Haley, M. M. Thiophene and Its Sulfur Inhibit Indenoindenodibenzothiophene Diradicals from Low-Energy Lying Thermal Triplets. *Nat. Chem.* **2018**, *10*, 1134–1140. <https://doi.org/10.1038/s41557-018-0133-5>.
23. Choppella, S.; Paramasivam, G.; Sambasivam, S.; Ravva, M. K. Understanding the Stability of π -Conjugated Diradicaloid Organic Molecules. *J. Electron. Mater.* **2023**, *52*, 1681–1690. <https://doi.org/10.1007/s11664-022-10082-2>.

24. Dressler, J. J.; Haley, M. M. Learning How to Fine-Tune Diradical Properties by Structure Refinement. *J. Phys. Org. Chem.* **2020**, *33*, 1–13.
<https://doi.org/10.1002/poc.4114>.
25. Frederickson, C. K.; Rose, B. D.; Haley, M. M. Explorations of the Indenofluorenes and Expanded Quinoidal Analogues. *Acc. Chem. Res.* **2017**, *50*, 977–987.
<https://doi.org/10.1021/acs.accounts.7b00004>.
26. Rudebusch, G. E.; Zafra, J. L.; Jorner, K.; Fukuda, K.; Marshall, J. L.; Arrechea-Marcos, I.; Espejo, G. L.; Ponce Ortiz, R.; Gómez-García, C. J.; Zakharov, L. N.; et al. Diindeno-Fusion of an Anthracene as a Design Strategy for Stable Organic Biradicals. *Nat. Chem.* **2016**, *8*, 753–759. <https://doi.org/10.1038/nchem.2518>.
27. Reznikova, K.; Hsu, C.; Schosser, W. M.; Gallego, A.; Beltako, K.; Pauly, F.; Van Der Zant, H. S. J.; Mayor, M. Substitution Pattern Controlled Quantum Interference in [2.2]Paracyclophane-Based Single-Molecule Junctions. *J. Am. Chem. Soc.* **2021**, *143*, 13944–13951.
https://doi.org/10.1021/JACS.1C06966/ASSET/IMAGES/LARGE/JA1C06966_0006.JPEG.
28. Li, S.; Yu, H.; Li, J.; Angello, N.; Jira, E. R.; Li, B.; Burke, M. D.; Moore, J. S.; Schroeder, C. M. Transition between Nonresonant and Resonant Charge Transport in Molecular Junctions. *Nano Lett.* **2021**, *21*, 8340–8347.
<https://doi.org/10.1021/acs.nanolett.1c02915>.
29. Widawsky, J. R.; Kamenetska, M.; Klare, J.; Nuckolls, C.; Steigerwald, M. L.; Hybertsen, M. S.; Venkataraman, L. Measurement of Voltage-Dependent Electronic Transport across Amine-Linked Single-Molecular-Wire Junctions. *Nanotechnology* **2009**, *20*, 434009.
30. Gu, J.; Wu, W.; Danovich, D.; Hoffmann, R.; Tsuji, Y.; Shaik, S. Valence Bond Theory Reveals Hidden Delocalized Diradical Character of Polyenes. *J. Am. Chem. Soc.* **2017**, *139*, 9302–9316. <https://doi.org/10.1021/jacs.7b04410>.
31. Li, L.; Nuckolls, C.; Venkataraman, L. Designing Long and Highly Conducting Molecular Wires with Multiple Nontrivial Topological States. *J. Phys. Chem. Lett.* **2023**, *14*, 5141–5147. <https://doi.org/10.1021/acs.jpcllett.3c01081>.
32. Xu, W.; Leary, E.; Sangtarash, S.; Jirasek, M.; González, M. T.; Christensen, K. E.; Abellán Vicente, L.; Agraït, N.; Higgins, S. J.; Nichols, R. J.; et al. A Peierls Transition in Long Polymethine Molecular Wires: Evolution of Molecular Geometry and Single-Molecule Conductance. *J. Am. Chem. Soc.* **2021**, *143*, 20472–20481.
<https://doi.org/10.1021/jacs.1c10747>.
33. Gunasekaran, S.; Hernangómez-Pérez, D.; Davydenko, I.; Marder, S.; Evers, F.; Venkataraman, L. Near Length-Independent Conductance in Polymethine Molecular Wires. *Nano Lett.* **2018**, *18*, 6387–6391.
https://doi.org/10.1021/ACS.NANOLETT.8B02743/SUPPL_FILE/NL8B02743_SI_001.PDF.
34. Kiess, H. G. *Conjugated Conducting Polymers*; Springer-Verlag, 1992.
<https://doi.org/10.1007/978-3-642-46729-5>.

35. Castro Neto, A. H.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. The Electronic Properties of Graphene. *Rev. Mod. Phys.* **2009**, *81*, 109–162. <https://doi.org/10.1103/RevModPhys.81.109>.
36. Stauber, T.; Beltrán, J. I.; Schliemann, J. Tight-Binding Approach to Pentagraphene. *Sci. Rep.* **2016**, *6*, 4–11. <https://doi.org/10.1038/srep22672>.
37. Verzijl, C. J. O.; Seldenthuis, J. S.; Thijssen, J. M. Applicability of the Wide-Band Limit in DFT-Based Molecular Transport Calculations. *J. Chem. Phys.* **2013**, *138*, 094102. <https://doi.org/10.1063/1.4793259>.
38. Hernangómez-Pérez, D.; Gunasekaran, S.; Venkataraman, L.; Evers, F. Solitonics with Polyacetylenes. *ACS Appl. Mater. Interfaces* **2020**, *20*, 2615–2619. <https://doi.org/10.1021/acs.nanolett.0c00136>.
39. Leary, E.; Limburg, B.; Alanazy, A.; Sangtarash, S.; Grace, I.; Swada, K.; Esdaile, L. J.; Noori, M.; González, M. T.; Rubio-Bollinger, G.; et al. Bias-Driven Conductance Increase with Length in Porphyrin Tapes. *J. Am. Chem. Soc.* **2018**, *140*, 12877–12883. <https://doi.org/10.1021/jacs.8b06338>.
40. Deng, J.-R.; González, M. T.; Zhu, H.; Anderson, H. L.; Leary, E. Ballistic Conductance through Porphyrin Nanoribbons. *J. Am. Chem. Soc.* **2024**, *146*, 3651–3659. <https://doi.org/10.1021/jacs.3c07734>.
41. Zang, Y.; Fu, T.; Zou, Q.; Ng, F.; Li, H.; Steigerwald, M. L.; Nuckolls, C.; Venkataraman, L. Cumulene Wires Display Increasing Conductance with Increasing Length. *Nano Lett.* **2020**, *20*, 8415–8419. <https://doi.org/10.1021/acs.nanolett.0c03794>.
42. Xu, W.; Leary, E.; Hou, S.; Sangtarash, S.; González, M. T.; Rubio-Bollinger, G.; Wu, Q.; Sadeghi, H.; Tejerina, L.; Christensen, K. E.; et al. Unusual Length Dependence of the Conductance in Cumulene Molecular Wires. *Angew. Chemie - Int. Ed.* **2019**, *5*, 8378–8382. <https://doi.org/10.1002/anie.201901228>.
43. Leary, E.; Roldán-Piñero, C.; Rico-Sánchez-Mateos, R.; Zotti, L. A. Antiaromatic Non-Alternant Heterocyclic Compounds as Molecular Wires. *J. Mater. Chem. C* **2024**, *12*, 4306–4315. <https://doi.org/10.1039/d3tc04266a>.
44. Nieman, R.; Silva, N. J.; Aquino, A. J. A.; Haley, M. M.; Lischka, H. Interplay of Biradicaloid Character and Singlet/Triplet Energy Splitting for Cis-/ Trans-Diindenoacenes and Related Benzothiophene-Capped Oligomers as Revealed by Extended Multireference Calculations. *J. Org. Chem.* **2020**, *85*, 3664–3675. <https://doi.org/10.1021/acs.joc.9b03308>.
45. Tsuji, Y.; Hoffmann, R.; Strange, M.; Solomon, G. C. Close Relation between Quantum Interference in Molecular Conductance and Diradical Existence. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, E413–E419. <https://doi.org/10.1073/PNAS.1518206113/-/DCSUPPLEMENTAL>.
46. Barker, J. E.; Dressler, J. J.; Cárdenas Valdivia, A.; Kishi, R.; Strand, E. T.; Zakharov, L. N.; Macmillan, S. N.; Gómez-García, C. J.; Nakano, M.; Casado, J.; et al. Molecule Isomerism Modulates the Diradical Properties of Stable Singlet Diradicaloids. *J. Am. Chem. Soc.* **2020**, *142*, 1548–1555. <https://doi.org/10.1021/jacs.9b11898>.

47. Kamenetska, M.; Koentopp, M.; Whalley, A. C.; Park, Y. S.; Steigerwald, M. L.; Nuckolls, C.; Hybertsen, M. S.; Venkataraman, L. Formation and Evolution of Single-Molecule Junctions. *Phys. Rev. Lett.* **2009**, *102*, 126803. <https://doi.org/10.1103/PhysRevLett.102.126803>.
48. Lawson, B.; Zahl, P.; Hybertsen, M. S.; Kamenetska, M. Formation and Evolution of Metallocene Single-Molecule Circuits with Direct Gold-ITLlinks. *J. Am. Chem. Soc.* **2022**, *144*, 6504–6515. <https://doi.org/10.1021/jacs.2c01322>.

Chapter IV.

1. Tönshoff, C.; Bettinger, H.F. Photogeneration of octacene and nonacene *Angew. Chem., Int. Ed.* **2010**, *49*, 4125–4128.
2. Watanabe, M.; Su, W.-T.; Chen, K.-Y.; Chien, C.-T.; Chao, T.-H.; Chang, Y.J.; Liu, S.-W.; Chow, T.J. A soluble precursor of hexacene and its application in thin film transistors *Chem. Commun.* **2013**, *49*, 2240–2242.
3. Ye, Q.; Chi, C. Recent highlights and perspectives on acene based molecules and materials *Chem. Mater.* **2014**, *26*, 4046–4056.
4. Tönshoff, C.; Bettinger, H.F. Pushing the limits of acene chemistry: the recent surge of large acenes *Chem. Eur. J.* **2021**, *27*, 3193–3212.
5. Saha, H.K.; Mallick, D.; Das, S. Dibenzoheterole-fused *s*-indacenes *J. Org. Chem.* **2023**, *88*, 16248–16258.
6. Kamebuchi, H.; Makino, R.; Hiruma, K.; Tomura, K.; Tadokoro, M. Covalently linked 5,6,11,12-tetraazaphthalene dimer and its triptycene-capped derivatives as electron acceptors *Chem. Eur. J.* **2024**, *30*, e202400632.
7. Belova, V.; Hinderhofer, A.; Zeiser, C.; Storzer, T.; Rozboril, J.; Hagenlcoher, J.; Novak, J.; Gerlach, A.; Scholz, R.; Schreiber, F. Structure-dependent charge transfer in molecular perylene-based donor/acceptor systems and role of side chains *J. Phys. Chem. C* **2020**, *124*, 11639–11651.
8. Gupta, A.; Flynn, B.L. Linear and angular heteroacenes from double-electrophilic cyclization (DEC) and DEC-reductive elimination of diynes *Org. Lett.* **2017**, *19*, 1939–1941.
9. Saha, H.K.; Mallick, D.; Das, S. Unveiling two antiaromatic *s*-indacenodicarbazole isomers with tunable paratropicity *Chem. Commun.* **2022**, *58*, 8492–8495.
10. Sharma, P.K.; Mallick, D.; Sharma, H.; Das, S. Dominating antiaromatic character of *as*-indacene decides overall properties of a formally aromatic dicyclopenta[*c*]fluorenothiophene *Org. Lett.* **2023**, *25*, 2201–2206.
11. Tobe, Y. Non-alternant non-benzenoid aromatic compounds: past present, and future *Chem. Rec.* **2015**, *15*, 86–96.
12. Frederickson, C.K.; Rose, B.D.; Haley, M.M. Explorations of the indenofluorenes and expanded quinoidal analogues *Acc. Chem. Res.* **2017**, *50*, 977–987.
13. Jiang, Q.; Han, Y.; Zou, Y.; Phan, H.; Yuan, L.; Herng, T.S.; Ding, J.; Chi, C. S-shaped *para*-quinodimethane-embedded double [6]helicene and its charged species showing open-shell diradical character *Chem. Eur. J.* **2020**, *26*, 15613–15622.
14. Wang, J.; Gamez, F.G.; Marin-Beloqui, J.; Diaz-Andre, A.; Miao, X.; Casanova, D.; Casado, J.; Liu, J. Synthesis of a dicyclohepta[*a,g*]heptalene-containing polycyclic, conjugated

- hydrocarbon and the impact of non-alternant topologies *Angew. Chem., Int. Ed.* **2023**, *62*, e202217124.
15. Can, A.; Facchetti, A.; Usta, H. Indenofluorenes for organic optoelectronics: the dance of fused five- and six-membered rings enabling structural versatility *J. Mater. Chem. C* **2022**, *10*, 8496–8538.
 16. Zeng, Z.; Shi, X.; Chi, C.; Lopez Navarrete, J.T.; Casado, J.; Wu, J. Pro-aromatic and anti-aromatic π -conjugated molecules: an irresistible wish to be diradicals *Chem. Soc. Rev.* **2015**, *44*, 6578–6596.
 17. Hu, X.; Wang, W.; Wang, D.; Zheng, Y. The electronic applications of stable diradicaloids: present and future *J. Mater. Chem. C* **2018**, *6*, 11232–11242.
 18. Dressler, J.J.; Haley, M.M. Learning how to fine-tune diradical properties by structure refinement *J. Phys. Org. Chem.* **2020**, *33*, e4114.
 19. Gopalakrishna, T.Y.; Zeng, W.; Lu, X.; Wu, J. From open-shell singlet diradicaloids to polyradicaloids *Chem Commun.* **2018**, *54*, 2186–2199.
 20. Rajca, A.; Olankitwanit, A.; Wang, Y.; Boratynski, P.J.; Pink, M.; Rajca, S. High spin $S = 2$ ground state aminyl tetradicaloids *J. Am. Chem. Soc.* **2013**, *135*, 18205–18215.
 21. Rajca, A.; Boratynski, P.J.; Olankitwanit, A.; Shiraishi, K.; Pink, M.; Rajca, S. Ladder oligo(*m*-aniline)s: derivatives of azaacenes with cross-conjugated π -systems *J. Org. Chem.* **2012**, *77*, 2107–2120.
 22. Nobusue, S.; Miyoshi, H.; Shimizu, A.; Hisaki, I.; Fukuda, K.; Nakano, M.; Tobe, Y. Tetracyclopenta[*def,jkl,pqr,vwx*]tetraphenylene: a potential tetradicaloid hydrocarbon *Angew. Chem., Int. Ed.* **2015**, *54*, 2090–2094.
 23. Lu, X.; Lee, S.; Kim, J.O.; Gopalakrishna, T.Y.; Phan, H.; Herng, T.S.; Lim, Z.; Zeng, Z.; Ding, J.; Kim, D.; Wu, J. Stable 3,6-linked fluorenyl radical oligomers with intramolecular antiferromagnetic coupling and polyradical characters *J. Am. Chem. Soc.* **2016**, *138*, 13048–13058.
 24. Lu, X.; Lee, S.; Hong, Y.; Phan, H.; Gopalakrishna, T.Y.; Herng, T.S.; Tanaka, T.; Sandoval-Salinas, M.E.; Zeng, W.; Ding, J.; Casanova, D.; Osuka, A.; Kim, D.; Wu, J. Fluorenyl based macrocyclic polyradicaloids *J. Am. Chem. Soc.* **2017**, *139*, 13173–13183.
 25. Sabuj, M.A.; Saha, C.; Huda, M.M.; Rai, N. Designing molecules with a high spin (quintet, $S = 2$) ground state for magnetic and spintronic applications *Mol. Syst. Des. Eng.* **2023**, *8*, 874–886.
 26. Prajapati, B.; Ambhore, M.D.; Dang, D.-K.; Chmielewski, P.J.; Lis, T.; Gomez-Garcia, C.J.; Zimmerman, P.M.; Stepień, M. Tetrafluorenofulvalene as a sterically frustrated open-shell alkene *Nat. Chem.* **2023**, *15*, 1541–1548.
 27. Hu, P.; Lee, S.; Herng, T.S.; Aratani, N.; Goncalves, T.P.; Qi, Q.; Shi, X.; Yamada, H.; Huang, K.-W.; Ding, J.; Kim, D.; Wu, J. Toward tetradicaloid: the effect of fusion mode on radical character and chemical reactivity *J. Am. Chem. Soc.* **2016**, *138*, 1065–1077.
 28. Guo, J.; Li, Z.; Zhang, J.; Li, B.; Liang, Y.; Wang, Y.; Xie, S.; Phan, H.; Herng, T.S.; Ding, J.; Wu, J.; Tang, B.Z.; Zeng, Z. Stable quadruple helical tetradicaloid with thermally induced intramolecular magnetic switching. *CCS Chem.* **2022**, *4*, 95–103.
 29. Ma, J.; Zhang, K.; Schellhammer, K.S.; Fu, Y.; Komber, H.; Xu, C.; Popov, A.A.; Hennersdorf, F.; Weigand, J.J.; Zhou, S.; Pisula, W.; Ortmann, F.; Berger, R.; Liue, J.; Feng, X. Wave-shaped polycyclic hydrocarbons with controlled aromaticity *Chem. Sci.* **2019**, *10*, 4025–4031.

30. Yamanaka, S.; Okumura, M.; Nakano, M.; Yamaguchi, K. EHF theory of chemical reactions Part 4. UNO CASSCF, UNO CASPT2, and R(U)HF coupled-cluster (CC) wavefunctions *J. Mol. Struct.* **1994**, *310*, 205–218.
31. Head-Gordon, M. Characterizing unpaired electrons from the one-particle density matrix *Chem. Phys. Lett.* **2003**, 508–511.
32. Minkin, V.I.; Starikov, A.G.; Starikova, A.A. Acene-linked zethrenes and bisphenalenyls: a DFT search for organic tetradiradicals *J. Phys. Chem. A* **2021**, *125*, 6562–6570.
33. Dressler, J. J.; Cárdenas Valdivia, A.; Kishi, R.; Rudebusch, G. E.; Ventura, A. M.; Chastain, B. E.; Gómez-García, C. J.; Zakharov, L. N.; Nakano, M.; Casado, J.; Haley, M. M. Diindenoanthracene Diradicaloids Enable Rational, Incremental Tuning of Their Singlet-Triplet Energy Gaps. *Chem* **2020**, *6*, 1353–1368.
34. Ulrich, T.; Munz, D.; Guldi, D.M. Unconventional singlet fission materials *Chem. Soc. Rev.* **2021**, *50*, 3485–3518.
35. Bo, Y.; Hou, Y.; Lavergne, D.A.X.; Clark, T.; Ferguson, M.J.; Tykwinski, R.R.; Guldi, D.M. Reversible gating of singlet fission by tuning the role of a charge-transfer state *Nat. Commun.* **2025**, *16*, 2968.
36. Merrifield, R.E.; Avakian, P.; Groff, R.P. Fission of singlet excitons into pairs of triplet excitons in tetracene crystals *Chem. Phys. Lett.* **1969**, *3*, 386–388.
37. Smith, M.B.; Michl, J. Singlet Fission *Chem. Rev.* **2010**, *110*, 6891–6936.
38. Piland, G.B.; Burdett, J.J.; Dillon, R.J.; Bardeen, C.J. Singlet fission: from coherences to kinetics *J. Phys. Chem. Lett.* **2014**, *5*, 2312–2319.
39. Zirzmeier, J.; Lehnher, D.; Coto, P.B.; Chernick, E.T.; Casillas, R.; Basel, B.S.; Thoss, M.; Tykwinski, R.R.; Guldi, D.M. Singlet fission in pentacene dimers *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112*, 5325–5330.
40. Majumder, K.; Mukherjee, S.; Panjwani, N.A.; Lee, J.; Bittl, R.; Kim, W.; Patil, S.; Musser, A.J. Controlling intramolecular singlet fission dynamics via torsional modulation of through-bond versus through-space couplings *J. Am. Chem. Soc.* **2023**, *145*, 20883–20896.
41. Paci, I.; Johnson, J.C.; Chen, X.; Rana, G.; Popovic, D.; David, D.E.; Nozik, A.J.; Ratner, M.A.; Michl, J. Singlet fission for dye-sensitized solar cells: can a suitable sensitizer be found? *J. Am. Chem. Soc.* **2006**, *128*, 16546–16553.
42. Ito, S.; Minami, T.; Nakano, M. Diradical character based design for singlet fission of condensed-ring systems with $4n\pi$ electrons *J. Phys. Chem. C* **2012**, *116*, 19729–19736.
43. Naskar, S.; Das, M. Energy ordering of singlet and triplet excited states in indenodithiophene and indenofluorenes molecules in singlet fission: a model exact and density matrix renormalization group study *Chem. Phys. Lett.* **2020**, *749*, 137368.
44. Minami, T.; Nakano, M. Diradical character view of singlet fission *J. Phys. Chem. Lett.* **2012**, *3*, 145–150.
45. Lopez-Carballeria, D.; Casanova, D.; Ruiperez, F. Theoretical design of conjugated diradicaloids as singlet fission sensitizers: quinones and methylene derivatives *Phys. Chem. Chem. Phys.* **2017**, *19*, 30227–30238.
46. Lukman, S.; Richter, J.M.; Yang, L.; Hu, P.; Wu, J.; Greenham, N.C.; Musser, A.J. Efficient singlet fission and triplet-pair emission in a family of zethrene diradicaloids *J. Am. Chem. Soc.* **2017**, *139*, 18376–18385.