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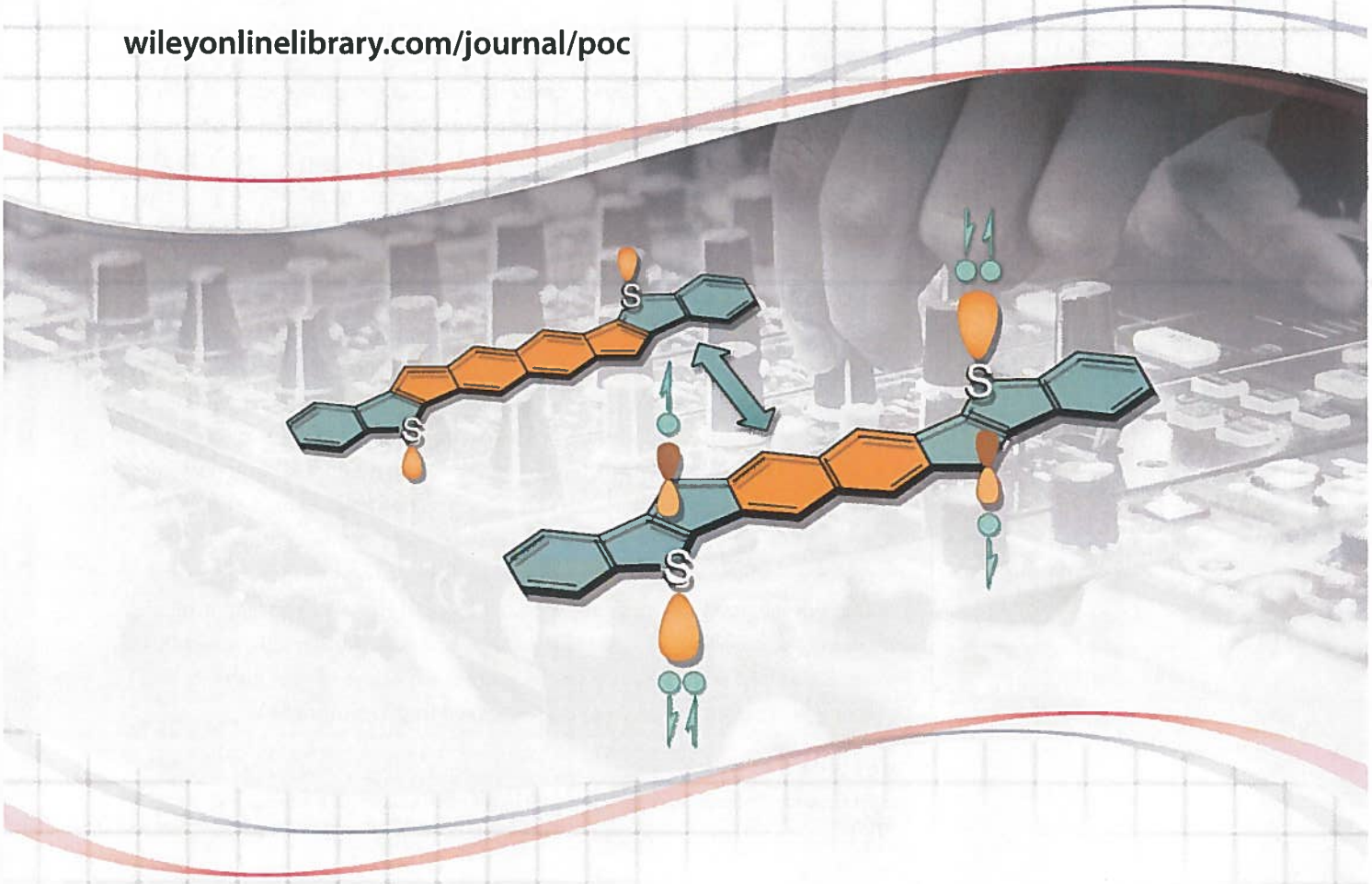

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by Justin J. Dressler and Michael M. Haley

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MINI REVIEW

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Learning how to fine-tune diradical properties by structure refinement

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Abstract

The literature has seen a large increase in the number of new carbon-based organic diradicals/diradicaloids in recent years. While a plethora of new and exciting structures have been created, there seemingly is a gap in knowledge of what fundamental electronic parameters are in play and thus how to rationally manipulate said parameters to "fine tune" the resultant diradical properties. Since 2014, the Haley group has been exploring methods to systematically alter the diradical character and the singlet-triplet energy gap in said class of molecules. Our entrance into organic diradicals began with the π-expansion of the benzene core of indeno[1,2-*b*]fluorene up to the anthracene core of diindenoanthracene (DIAn). DIAn possessed moderate diradical character ($y = 0.62$) with a surprising level of stability (more than 2 months in solution). From this molecular blueprint for producing stable diradicals, the Haley lab has investigated how to fine tune diradical properties via structural changes in two key positions: (a) the length of the acene core and (b) thoughtful exchange of the outer arenes. With this strategy at our disposal, we can make large scale changes to the diradical character index and singlet-triplet energy gap through changing the core length, and these properties can be further fine-tuned in a series of closely related diradicals by careful exchange of the outer arenes utilizing the straightforward methods described in this mini-review.

KEYWORDS

antiaromaticity, diradicals, open-shell, polycyclic hydrocarbons, singlet-triplet energy gap, SQUID

1 | INTRODUCTION

Graduate students and weathered professors alike lament that there is a great deal of luck and serendipity involved in the success and direction of their research. This cliché, while trite to some, is still very much true and can shape the directionality of many scientists' careers. Unsurprisingly, serendipity has played a large role in the Haley lab's entrance into and now detailed involvement in the field of stable organic diradicals. In 2016, when we reported the first stable organic diradical from our lab based on the diindenoanthracene (DIAn) scaffold,[1] searching for novel ways to make durable diradicals was not the motivation behind preparing DIAn. In fact, when the ultimately successful synthetic route was conceived in late 2014, there was no real intention of becoming a player in the challenging and intellectually stimulating field of organic diradicals. In reality, the motivation behind the project stemmed from a simple question that would further the research interests of the lab at the time:

In memoriam François Diederich

"What would happen to a molecule's optoelectronic properties if the benzene core of indeno[1,2-*b*]fluorene was π-expanded to naphthalene and/or anthracene?". Having explored a substantial degree of chemical space around the indenofluorene family,[2] this question seemed to provide an interesting and potentially productive avenue of research to investigate. But before beginning a discussion on the Haley lab's entry into the field of diradicals, we must first define and understand the unique properties of diradicals.

2 | WHAT IS A DIRADICAL?

While there is some disagreement in the literature on the exact definition of a diradical molecule, we define a diradical using the criteria put forth by Abe, which in turn were based on the IUPAC Compendium of Chemical Terminology, that is, the "Gold Book": a molecule in which there are two unpaired electrons (radicals), in which these radicals have a dipole-dipole interaction large enough to produce two spin states, namely, singlet and triplet states (spin states), due to the small interaction distance between the radicals.[3] If the electron exchange interaction between the two unpaired electrons is negligible because of a large distance between the two electrons, then the compound is instead defined as a biradical.[3] The unique nature of diradical compounds comes as a function of the uncommon open-shell and closed-shell resonance structures that these molecules possess in their ground state.[3,4] This concept can be better understood by examining one of the first reported diradicals, a molecule commonly known as Tschitschibabin's hydrocarbon[5] (**1**, Figure 1). Hydrocarbon **1** can exist either in the closed-shell resonance form **1a** or in the open-shell resonance form **1b**, where both resonance forms contribute to the overall nature and properties of the ground state. The switching between resonance structures results in breaking of the exocyclic π-bonds and leads to the formation of two aromatic benzene rings. This process is commonly described as a recovery of aromatic Clar sextets[6] and is often used to rationalize the drive for diradical compounds to exist in the open-shell form.[7] To describe the contribution of the open-shell resonance form to the overall ground state of the diradical, the diradical character index (y) is used. This term, simply put, expresses how diradical a compound is. The diradical character index is a computational value based on the natural orbital occupation number (NOON) analysis of the lowest unoccupied natural orbital.[8] The index y can range in value between 0 and 1, where a value of $y = 1$ is a purely open-shell/diradical compound and a value of $y = 0$ is completely closed-shell. In practice, most reported diradicals have a y value somewhere between 0.5 and 0.99, and molecules that have y indices below 0.4 often display few if any properties associated with diradical character. That said, the value of y can vary greatly depending upon basis set and/or the level of theory used to perform the calculations.

To add to the complexity, when a compound displays diradical character, the two electrons can exist either in a spin paired singlet state (**1b**) or a spin parallel triplet state (**1c**), and the energy it takes to go from the singlet to triplet state is known as the singlet-triplet energy gap (ΔE_{ST}). Due to the double-spin polarization effect,[9] the vast majority of diradicals possess a ground state singlet with a thermally accessible triplet state[3]; however, there is a only small number of ground state triplet diradicaloids.[10] Furthermore, there is a qualitative relationship that exists between diradical character and the singlet-triplet energy gap, in that as the diradical character of a compound increases the ΔE_{ST} decreases. While this rule of thumb applies for most diradicals, this relationship is only strictly quantitative in the case of a molecule with a y value equal to 1, where the ΔE_{ST} gap is equal to zero.[11] Like y, the calculated ΔE_{ST} values can vary greatly depending upon basis set and/or the level of theory.

Fueled by a fundamental interest in their unique ground and magnetic states and a desire to better understand these fickle compounds, there have been many classes of carbon-based diradicaloids (Figure 2) developed/explored in the last 12–15 years, including but not limited to zethrenes (**2**),[7a,12] anthenes (**3**),[13] bisphenalenyls (**4**),[14] extended quinodimethanes (**5**),[15] higher-order acenes (**6**),[16] indenofluorenes (**7**),[10a,17] and related diindenoacenes (**8–10**),[1,11,18] the last of

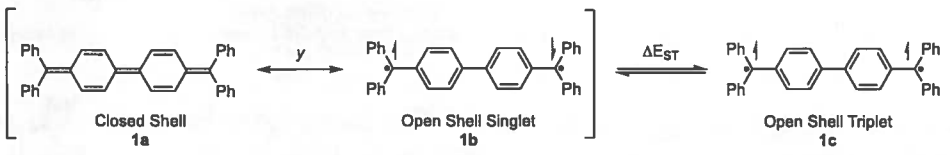


FIGURE 1 The electronic structure of Tschitschibabin's hydrocarbon where the ground state is composed of a mixture of the closed-shell (**1a**) and open-shell resonance structures (**1b**). The contribution of the open-shell form is described by the diradical character index y. The energy difference between the singlet ground (**1b**) and triplet excited state (**1c**) is defined as ΔE_{ST}

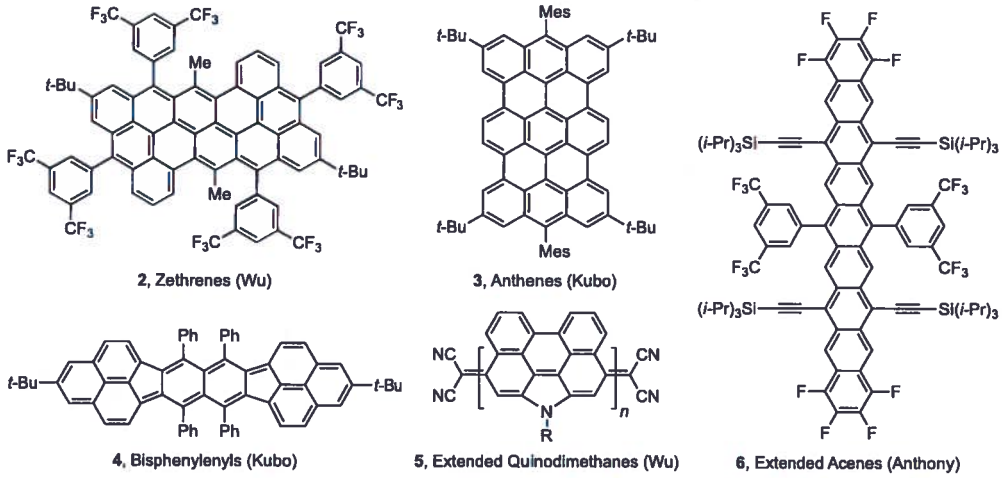


FIGURE 2 Prototypical examples (**2**–**6**) of recently reported diradicaloids, drawn in the closed-shell resonance form

which are the focus of this mini-review (see Figure 3). The diagnostic properties of diradicals, which arise from the unique combination of closed- and open-shell resonance forms, can include narrow HOMO-LUMO energy gaps,[7c,19] low-energy electronic absorptions due a low-lying doubly excited electronic configuration,[20] redox amphoterism,[14c,19a] electron spin resonance (ESR) signals and/or a magnetic response in a superconducting quantum interference device (SQUID) magnetometer,[18d] multicenter bonding,[14a,21] substantial two-photon absorption cross-sections,[22] and peak broadening or sharpening in the proton NMR spectrum due to the thermal equilibrium of the spin states. Because of these unusual properties, the diradical hydrocarbons listed above have been earmarked for various applications such as molecular electronics[3] and spintronics,[23] lithium-ion batteries,[24] nonlinear optics,[25] and singlet fission.[26] Plagued by the high reactivity and low modularity of currently available diradicals, their full potential in materials applications has yet to be realized, despite the many posited breakthrough uses. Nonetheless, there have been some preliminary device applications of diradicals[25d] in areas such as organic field effect transistors (OFETs),[27] near-infrared absorption dyes,[28] and singlet fission applications.[29] These latter examples provide a beacon of hope for the eventual implementation of diradicals into materials.

3 | PROJECT MOTIVATIONS

When we entered the field of organic diradicals, there was a clear abundance of interest in discovering new examples of open-shell species; however, we realized that, while there was this booming increase in the number of reported carbon-based diradicals, there were very few cases in which subsequent structural modification was made to the originally reported scaffold aimed at altering its optical and magnetic properties. This seeming lack of systematic modification of the diradical character and singlet-triplet energy gap set the stage for our group's mentality and efforts in the area of diradical research. We

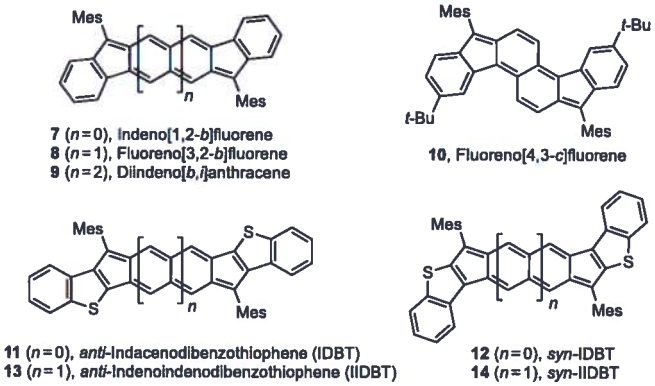


FIGURE 3 Molecules synthesized in the Haley lab based on the indeno[1,2-*b*]fluorene scaffold. Compounds **7**, **8**, **10**, **11**, and **12** do not display appreciable diradical character, whereas compounds **9**, **13**, and **14** have been tuned to display pronounced diradical character

wanted to gain a fundamental understanding of the inherit electronic and magnetic properties of open-shell compounds. We felt that in order to harness the potential of diradicals in meaningful application, specifically those applications wishing to exploit the unique spin-states that diradicals possess, the ability to the control and manipulate the diradical character and the related ΔE_{ST} gap with precision would be paramount. This key guiding principle of learning to fine-tune molecule properties in a systematic way has been the unifying theme of the Haley lab's research on diradicals for the last 5 years.

4 | FIRST STEPS AT Π-EXPANSION

In our initial attempts at answering the question, "What would happen to the optoelectronic properties if the core of indeno[1,2-*b*]fluorene ([1,2-*b*]IF, **7**) was π-expanded?", we prepared our first fluorenofluorene (FF) derivative, which is based on a central naphthalene core.[30] Starting from a known dione, addition of mesityllithium followed by a $SnCl_2$-mediated reductive dearomatization afforded deep blue fluoreno[4,3-*c*]fluorene **10**. Importantly, this result showed that we could successfully synthesize π-expanded systems in a manner analogous to the [1,2-*b*]IFs.[31] Despite its S-shaped geometry, the absorption spectrum of [4,3-*c*]FF was strikingly similar to the "parent" [1,2-*b*]IF, albeit with the expected red-shift of the low energy absorptions (515 nm in **7** to 649 nm in **10**) due to the expanded nature of the π-system. The CV data showed that **10** displayed redox amphoterism like **7**,[31] with a narrow electrochemical energy gap of 1.69 eV (vs. 2.22 eV for **7**).[30] As we noted at the time, despite its structural similarity to compounds displaying open-shell character, a lack of line broadening in the variable temperature (VT) proton NMR spectrum (up to 160°C) and the lack of an EPR signal of the powder and solution sample established the closed-shell nature of fluoreno[4,3-*c*]fluorene.

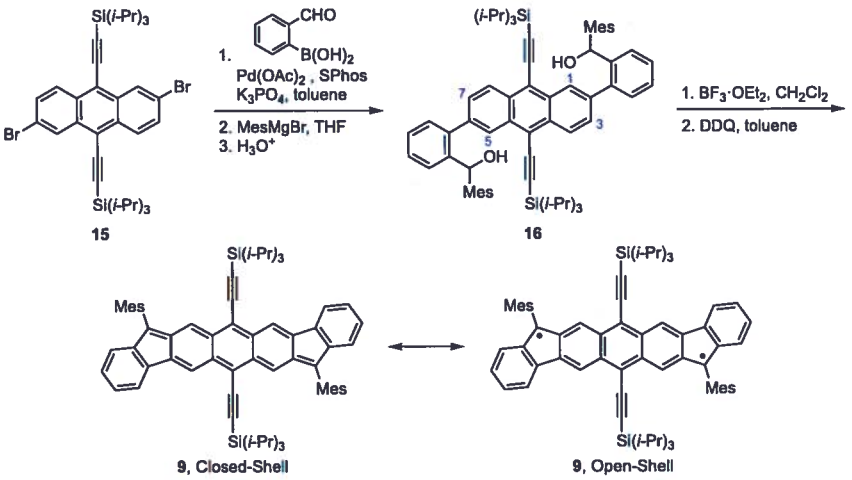
Recently, aided by the disclosure of a key bistriflate intermediate by the McCulloch group,[32] graduate student Josh Barker recently returned to the FF arena and successfully prepared the linearly fused, π-expanded [1,2-*b*]IF analogue, fluoreno[3,2-*b*]fluorene **8**.[33] Despite the different mode of fusion of the indene units to the central naphthalene, this work led to the same conclusions experimentally and computationally as the [4,3-*c*]FF study, more specifically, the observed structural and optical properties of [3,2-*b*]FF **8** were consistent with a quinoidal core, that is, a closed-shell molecule. Given that the changes to molecule properties were relatively modest for **8** and **10**, we were curious whether further expansion to an anthracene as the core motif would have a greater effect on the overall properties. Fortuitously, we unearthed profound changes to the properties of the anthracene-cored analogue of [1,2-*b*]IF and along with it a new research direction of stable diradical hydrocarbons.

5 | INAUGURAL DIRADICAL STUDIES

The breakthrough result was the isolation and characterization of a diindeno[*b*,*i*]anthracene (DIAn) derivative, as the open-shell molecule combined moderate diradical character ($y = 0.62$) with high chemical stability (half-life ~2 months in solution and indefinitely stable in the solid state).[1] Admittedly, we had started work on the molecule in late 2012, but it took until 2016 to bring this to fruition. As was the problem with linear [3,2-*b*]FF **8**, creating an anthracene derivative with the requisite 2,3,6,7-substitution pattern is nontrivial. To add to the complexity, for a successful synthesis, the 2,6-substituents (e.g., halogens/triflates for cross-coupling) must be different from those on the 3,7-positions (e.g., aldehydes/esters/acids for subsequent Friedel-Crafts reactions). Graduate student Gabe Rudebusch took on this challenge in fall 2014 and devised the synthetic route in Scheme 1. He identified the need for kinetic stabilization at the areas of high spin density (primarily the apical carbons in the five-membered rings) by using bulky mesityl(2,4,6-trimethylphenyl) groups orthogonally oriented to the conjugated scaffold and bulky triisopropylsilylethynyl (TIPS) groups on carbons 9 and 10 to enhance the solubility of the large polycyclic hydrocarbon (PCH) as well as to inhibit endoperoxide formation across the anthracene core (a common acene decomposition pathway).

Starting from known dibromide **15** (Scheme 1), Suzuki cross-coupling gave an intermediate dialdehyde that was then treated with mesitylmagnesium bromide to furnish diol **16**. To his credit, Rudebusch recognized that the steric bulk of the TIPS and mesityl groups was paramount in the directionality of the Friedel-Crafts alkylation reaction, as the steric clash blocked the undesired ring closure at the electronically favored 1/5-positions of the anthracene core and instead led to closure at electronically disfavored carbons 3 and 7 (blue numbers in Scheme 1). Steric interaction is key in this step as replacement of the mesityl group with a smaller phenyl ring does give 1,5-ring closure (determined by X-ray), whereas use of the electron-poor pentafluorophenyl motif shuts down Friedel-Crafts reactivity altogether.[34] Lastly, oxidation with DDQ furnished DIAn **9** as deep violet

SCHEME 1 Synthetic route used to prepare diindenoanthracene (DIAn) **9** on the gram scale



crystals. Notably, these reactions could be performed on the gram scale with no need for column chromatography.

With an ample supply of **9** in hand, we performed a variety of spectroscopic measurements and experiments that can suggest the presence of an open-shell resonance contribution to the molecule. The low energy absorption in the UV-Vis spectrum was significantly red shifted (λ_{max} ~700 nm) due to the π-extended nature of the core. Additionally, a weak shoulder appeared 775 nm that extends to the near-IR region, which is indicative of the symmetry-forbidden transition typical of diradical compounds. Cyclic voltammetry (CV) displayed two reversible, one-electron oxidation and two reversible, one-electron reduction peaks, indicative of the amphoteric redox character that DIAn possess. Moreover, the CV data gave rise to a narrow HOMO-LUMO energy gap of 1.45 eV, which is very small for a PCH with no pendant electron withdrawing units. Examination of the X-ray crystal structure of DIAn revealed that the bond length from the apical carbon (sp^2 center) of the five-membered ring to the central anthracene core was 1.406 Å, which is roughly the mean value of the analogous bond lengths in closed-shell [1,2-*b*]IF (1.381 Å) and open-shell [2,1-*b*]IF (1.437 Å).[17] This bond length suggests that the open-shell resonance structure is contributing to the overall ground state of DIAn, as the open-shell form has single bond character in this key position, elongating the bond length.

To cement the diradical nature of DIAn, we turned to experiments that would confirm its accessible paramagnetic properties. The room temperature proton NMR spectrum of **9** showed relatively well resolved aromatic signals that further sharpened upon cooling to −25°C due to depopulation of the triplet state. On the other hand, heating the sample broadened the aromatic proton resonances, which by 150°C had essentially disappeared into the base line. Importantly, the aromatic resonances return upon cooling back to room temperature, with no evidence of decomposition. To experimentally measure the singlet-triplet energy gap, we utilized SQUID magnetometry, where a powder sample of DIAn was heated from 4 to 400 K while monitoring the magnetic response of the sample. SQUID allowed us to experimentally track the small change in magnetism that arises from switching from the singlet to triplet state. Fitting the raw data using the Bleaney-Bowers equation[35] gave an experimentally determined ΔE_{ST} of −4.2 kcal mol^{-1}, which was in good agreement with the calculated value of −4.9 kcal mol^{-1}.[36]

6 | BLUEPRINT FOR STABLE AND TUNABLE DIRADICALS

After reporting DIAn in summer 2016, we realized we had a unique opportunity to push the boundaries of organic diradicals in a systematic way. Looking at its construction, the DIAn scaffold provided both a relatively easy to modify system and, just as importantly, a blueprint for stable diradicals with two customizable positions: (i) the size of the acene core and (ii) exchange of the outer benzenes with other fused arenes (Figure 4).

Fortuitously, in our original pursuit of π-expanding the [1,2-*b*]IF core, we had already inadvertently performed a study on how changing the conjugation pathway between the radical centers affected the diradical character index and the singlet-triplet energy gap. What we observed were overall large-scale changes in y and ΔE_{ST} as we altered core size. As you increase the size of the acene core (point (i) above; computational numbers shown here) from benzene (**7**, y = 0.24, ΔE_{ST} = −19.4 kcal mol^{-1}) to naphthalene (**8**, y = 0.49, ΔE_{ST} = −10.3 kcal mol^{-1}) up to anthracene (**9**, y = 0.62, ΔE_{ST} = −4.9 kcal mol^{-1}), the diradical character of the

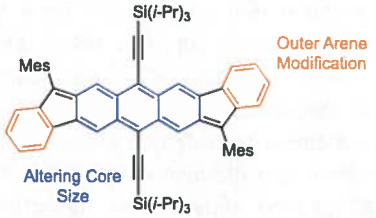


FIGURE 4 The blueprint for stable organic diradicals base on the diindenoanthracene scaffold. There are two areas of potential modification (a) altering the core length (shown in blue) and/or (b) outer arene exchange (shown in orange)

molecule increases to the point of being experimentally observable and the singlet-triplet energy gap decreases to where it can be determined by SQUID. Notably, these results match other groups studies on altering the conjugation distance between the two distinct radical centers in other PCH diradicals such as zethrenes,[12a] bisphenalenyls,[4a] and the indeno[2,1-*b*] fluorene analogues.[17,18b] While this trend of increased core size leads to enhanced diradical character is a fundamentally important steppingstone, it only provides the ability to perform a "course shim" on the overall properties of the diradicals. With both the FF and DIAn scaffolds, we also have the ability to alter potential diradical properties through outer arene exchange, as judicious choice of these external arenes should enable a systematic study where we can perform a "fine shim" in adjusting y and ΔE_{ST}.

7 | DIRADICAL DERIVATIVES WITH NAPHTHALENE CORES

When pondering the question of how to add to our library of stable diradicals, coauthor Justin Dressler next wondered if we could unlock diradical behavior in systems with naphthalene cores. Both FFs **8** and **10** had nonnegligible calculated diradical character indices yet displayed only closed-shell behavior experimentally. To perform a "fine shim" of the yet to be actualized diradical properties of the FF analogues, we turned to outer arene exchange. We had already explored this concept the previous few years on the benzene core structures, that is, [1,2-b]IF **7**, finding that replacement of the external benzenes with benzothiophenes resulted in a significant increase in the antiaromaticity of the *s*-indacene motif within the indacenodibenzothiophenes (IDBTs) **11** and **12**.[37] We attributed this increase in paratropicity to the increase in bond order (BO) of the fusion bond of the outer rings to the five-membered ring of the indacene unit, whereas decreasing fusion bond order decreased antiaromaticity,[38] increasing bond order to roughly double-bond character (BO = 2) afforded molecules like **11** and **12** whose antiaromaticity was almost as great as that of *s*-indacene itself.[37,38a] Applying this same logic to the naphthalene analogues **13** and **14**, known as indenoindenodibenzothiophenes (IIDBTs), and given the known connection between diradical character and antiaromaticity,[7b,39] Dressler hypothesized that increasing the paratropicity of the π-expanded *s*-indacene might favor the open-shell resonance structures in the IIDBTs.

Our initial IIDBT studies focused on anti-isomer **13** (as by our naming convention the sulfur and apical carbon of the five-membered rings were on opposite sides of the molecule).[11] Computationally, our hypothesis was reaffirmed, as the diradical character index for **13** was calculated by collaborator Masayoshi Nakano and his coworkers to be 0.61, surprisingly close to the y value for DIAn of 0.62; however, there was a large difference between the calculated singlet-triplet energy gaps of **9** and **13**, −4.9 kcal mol^{-1} and −8.8 kcal mol^{-1}, respectively. To rationalize why IIDBT **13** possesses such a large singlet-triplet energy gap for a molecule with moderate diradical character, we turn to the two-electron/two-site diradical model.[25b,c,40] Equation 1 provides the dependence of the singlet-triplet energy gap (ΔE_{ST}) on y (defined in Equation 2), illustrating their interconnection:

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

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

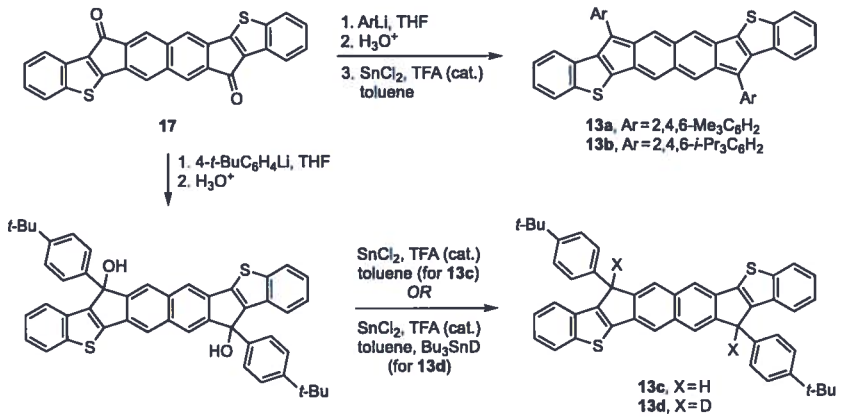
In this model, U is defined as the electron repulsion term, t_{ab} is the energy resonance term or the transfer integral, and finally K_{ab} is the direct exchange integral. Importantly, for our given systems, the direct exchange integral is negligibly small and can be removed from consideration, leaving U and t_{ab} as the electronic factors that govern the singlet-triplet energy gap. Analysis of these two electronic parameters reveals that the large ΔE_{ST} of **13** compared with **8** or **9** is in large part due to the electron-rich sulfur atom, with lone pairs, leading to a stronger repulsion environment near the radical centers. This leads to an increase in U and thus results in an overall greater ΔE_{ST}. Put another way by collaborator Juan Casado, changing the outer benzene for a benzothiophene resulted in electronic repulsion between the radical center and sulfur lone pair, thus leading to the usually high predicted ΔE_{ST} value for IIDBT all the

while maintaining moderate diradical character. Regardless of the electronic reasons, we knew proving the diradical nature of **13** would be considerably more difficult should this large value for ΔE_{ST} be correct (*vide infra*).

The synthesis of the IIDBT derivatives was fortunately a straightforward process (Scheme 2). Starting from dione **17**, itself prepared from the same bistriflate[32] that ultimately afforded [3,2-*b*]FF **8**,[33] addition of bulky aryllithiates followed by $SnCl_2$-mediated reductive dearomatization gave IIDBTs **13a-b**. At this same time, it occurred to us that if the IIDBTs were truly open-shell molecules with distinct radical centers, reducing the steric protection about the apical carbon atoms should allow the radical centers to behave like true radicals and thus scavenge hydrogen atoms. Installation instead of less bulky 4-*t*-butylphenyl units followed by the Sn(II) reaction furnished the dihydro species **13c**, confirmed by mass spectrometry and by the appearance of a new singlet in the proton NMR spectrum. To prove that this product was a result of radical reactivity, we performed the Sn-mediated reduction again but in the presence of Bu_3SnD, a known radical deuterium source. Much to our delight, the dideuterated species **13d** was the sole isolable product of this reaction, thus providing important chemical evidence of radical reactivity.

Spectroscopic evidence also hinted at appreciable diradical character: (a) comparison of the absorption profile of **13** with anti-IDBT **11** showed a clear red shift in the low-energy λ_{max}, in line with the increased π-conjugation of the naphthalene core.[11] Additionally, as was the case with DIAn, there was a weak absorption shoulder extending out to 800 nm indicative of the two-photon absorption band arising from the diradical nature of IIDBT. The optical energy gap of **13** was 1.55 eV, which is on par with the energy gap seen in DIAn, and also agrees well with TD-DFT calculations. (b) The X-ray crystal data revealed that bond length from the apical carbon to the naphthalene core is 1.424 Å, longer than the analogous bond in DIAn (1.406 Å) and much longer than found at this position in IF derivatives (1.38 and 1.39 Å). This extended bond length pointed towards significant contribution of the open-shell singlet form of **13** to the overall ground state of the molecule. (c) VT proton NMR spectroscopy of a solution of **13a** in 1,1,2,2-tetrachloroethane-d_2 showed modest broadening of the aromatic resonances when heated up to 125°C. While we had amassed a strong body of circumstantial evidence to support the diradical nature of **13** as strongly persistent in the singlet ground state, some doubts remained that we did not have an open-shell system because it was believed that one cannot have a diradical without the ability to access the triplet state.

To finally prove that the IIDBT framework had a triplet state with a prohibitively large singlet-triplet energy gap, we renewed our collaboration with Prof. Carlos Gómez-García. In the intervening 2 years between the DIAn and IIDBT studies, he had purchased/adapted a SQUID magnetometer with a heated sample chamber such that one could measure magnetic susceptibilities at temperatures well above 400 K, something that was not common practice in the SQUID field, but a necessity in the case of IIDBT. With the appropriate experimental set up available, he performed SQUID measurements of **13a** up to 800 K. Fitting the raw magnetic susceptibility response data to the Bleaney-Bowers equation furnished an experimental ΔE_{ST} value of −8.0 kcal mol^{-1}, within 10% of the calculated value of −8.8 kcal mol^{-1}.[11] This experiment provided the key proof that we could access a thermally excited triplet state, thus putting the nail in the coffin that IIDBT scaffold was indeed an unusual diradicaloid molecule, one that exhibited pronounced diradical character yet persisted in the singlet ground state.



SCHEME 2 Synthetic route used to prepare anti-indenoindenodibenzothiophenes (IIDBTs) **13**

8 | FINE-TUNING ΔE_{ST} IN PERSISTENT SINGLET DIRADICALOIDS USING MOLECULE ISOMERISM

Near the end of the original IIDBT studies, graduate student Barker began to wonder if it was possible to fine-tune the singlet-triplet energy gap of our persistent diradical simply by anti → syn isomerism of the benzothiophene units (**13** → **14**). As shown by the bolded bonds in Figure 5, the two constitutional isomers have an identical 2,6-naphtho orientation of the apical carbons, which results in the same conjugation pathway for the radical center; thus, any changes in properties can be attributed solely to the flipping of the benzothiophene units. Noted above, the unusually large singlet-triplet energy gap of **13** comes from the interaction of the sulfur lone pair with the radical center (U term). We then rationalized that moving the location of the sulfur lone pair would effectively change the electronic repulsion factor and thus alter ΔE_{ST}. We posited that using a "structure refinement approach", based on small alteration of the molecular geometry yet with retention of the same radical conjugation pathway, would permit a more rational modulation of ΔE_{ST}.[18c]

Computationally, our hypothesis of switching the benzothiophene unit from an anti to syn relationship was confirmed as the calculations predicted that syn-IIDBT (**14**, y = 0.66, ΔE_{ST} = −8.1 kcal mol^{-1}) would have a larger diradical character and a smaller singlet-triplet energy gap that anti-IIDBT (**13**, y = 0.61, ΔE_{ST} = −8.8 kcal mol^{-1}). The predicted increase in diradical character can be rationalized by a drawing out the complete possible resonance structures for radical delocalization of the two IIDBTs. In the case of syn-IIDBT, there exists a benzylic radical resonance structure that would enable the radical to delocalize on to the external benzene units stabilizing the open-shell resonance form through further delocalization. To rationalize the decrease in ΔE_{ST}, we must examine the conjugation between the sulfur and the radical center as seen in Figure 5. In the case of the anti-IIDBT, there is linear conjugation, and in the case of the syn-IIDBT, there is a cross conjugation pattern. Linear conjugation enables stronger electronic communication of the sulfur lone pair and radical centers compared with the syn-IIDBT case. Additionally, through these resonance structures, one can note that in the case of **13**, the radical center can be delocalized to only one carbon center away from the sulfur atom and its lone pair, whereas in **14**, the radical can only be within two carbon centers of the sulfur atom, minimizing the electronic repulsion interaction in the case of **14**.

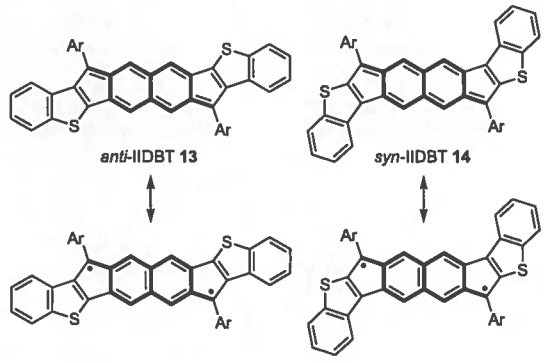


FIGURE 5 Comparison of the anti-(**13**) and syn-indenoindenodibenzothiophene (IIDBT) (**14**) structures, highlighting the 2,6-naphtho conjugation orientation of the diradical centers in both molecules

Synthetically, **14** was prepared in an analogous fashion to **13** with the key exchange from benzothiophene 2-boronpinacolate to benzothiophene 3-boronpinacolate ester in the Suzuki-cross-coupling step to afford the syn orientation.[18c] Comparison of the absorption spectra of **13** and **14** unsurprisingly reveals very similar absorption profiles between the compounds with a redshift of 25 nm in the case of syn-IIDBT, matching the expectations of TD-DFT predict spectra. As could be expected, there was a tailing low energy absorption shoulder in the newly synthesized IIDBT, which is a signature feature for diradical compounds. The X-ray structure showed that **14** also possessed a long C–C bond length (1.419 Å) from the apical carbon to the pro-aromatic naphthalene core. In the VT proton NMR experiment thermal broadening of the aromatic resonances of **14** begin at 75°C, whereas **13** showed very little peak broadening even at 125°C. This result hinted at an experimentally smaller ΔE_{ST} for syn-IIDBT, and SQUID measurements up to 675 K corroborated this suspicion. Fitting the raw magnetic susceptibility data to the Bleaney-Bowers equation yielded an experimental singlet-triplet energy gap of −6.9 kcal mol^{-1} for **14**, agreeing quite well with the predicted value. This ~1 kcal mol^{-1} modulation in ΔE_{ST} by anti → syn isomerism of the benzothiophene units demonstrates a finer adjustment of the energy gap than previously reported from most groups, and importantly, we understand the electronic rationale (modification of the U term) behind this change. Furthermore, to bolster our confidence in the thermal resilience of our compounds, heating and cooling runs were performed where the magnetic susceptibility was measured in both directions. Gratifyingly, the resultant ΔE_{ST} values for the heating and cooling scans were within 2% and 3% of one another, corroborating the thermal stability of the IIDBT series.

9 | FINE-TUNING DIRADICAL CHARACTER AND ΔE_{ST} IN DIAN DERIVATIVES

If the mode of benzothiophene fusion allowed us to modulate the electron repulsion term U in the two-electron/two-sites model, we sought to determine what structural factors would permit us to rationally alter the transfer integral term t_{ab}. Similar to the related IDBT/IIDBT series, we had unknowingly performed a closely related study that would provide the answer. Once again, it came down to the bond order of the ring system fused to the antiaromatic core. While changing from benzene (BO = 1.5) to benzothiophene (BO = 2) significantly enhanced the paratropicity of the *s*-indacene core of the IDBTs,[37] a subsequent study showed that naphtho fusion along either the 1,2-bond (BO = 1.66) or the 2,3-bond (BO = 1.33) allowed us to "tune" the paratropicity of the indacene motif to an even finer degree.[38a] Understanding that there is a strong connection between antiaromaticity and diradical character as noted earlier,[7b,39] graduate student Dressler hypothesized that if we altered the fusion bond order (red in Figure 6) on both sides of the 2,6-anthraceno core (bolded in Figure 6) found in the 5-6-6-6-5 fused ring system of DIAn **9**, we could construct a series of closely related molecules that would permit a systematic study on how to change the diradical character and ΔE_{ST} incrementally via the "structure refinement approach". To this end, Dressler set out to prepare and study DIAn derivatives **18–21** (Figure 6).

Based on the calculated y and ΔE_{ST} values presented in Figure 6, computationally, our hypothesis holds true across the series of molecules: As we increase the bond order, this leads to a corresponding increase in diradical character (y). As the fusion bond order increases (highlighted in red), the antiaromaticity of the π-expanded *s*-indacene core also increases. This buildup of antiaromatic character provides the driving force for the molecule to exist in the open-shell resonance form, thus regaining anthracene aromaticity. The increase in conjugation length in **18–20** leads to enhanced delocalization over the terminal parts of the ring system, which is synonymous with a decrease in t_{ab} (yet with minimal change to U). This decrease in t_{ab} in turn leads to increased diradical character and decreased ΔE_{ST} gaps (see Equations 1 and 2). Furthermore, as we had seen previously in the IIDBT case, the electronic repulsion factor plays a large role in the increased diradical character of the BT-DIAn **21** due the interaction between the sulfur lone pair and the radical center, as **20** and **21** have nearly identical t_{ab} values yet U is considerably larger for the latter molecule.[18d]

All five molecules were successfully prepared using the two synthetic pathways described previously. Compounds **20** and **21** (as well as a new synthesis of **9**) were made through a route that relied on a Friedel-Crafts acylation to form the five membered rings followed

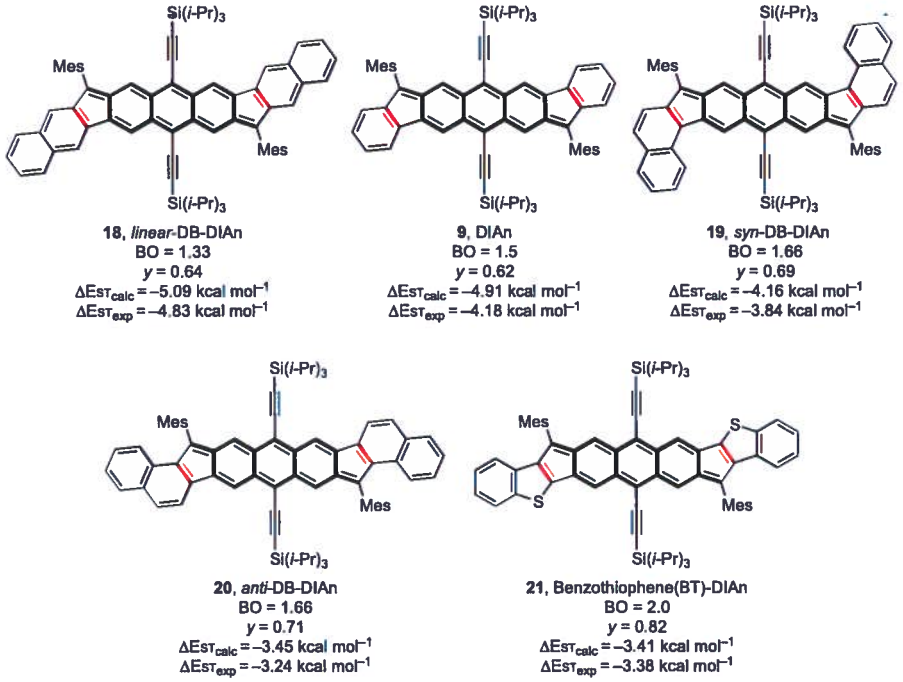


FIGURE 6 Comparison of diindenoanthracene (DIAn) **9** with new derivatives **18–21**, highlighting the 2,6-anthraceno conjugation orientation of the diradical centers. The bond order (BO) of the fused bond (highlighted in red) is given, along with the calculated y and ΔE_{ST} values as well as the experimentally determined (superconducting quantum interference device [SQUID]) ΔE_{ST} values

by nucleophile addition/$SnCl_2$-mediated reduction (analogous to Scheme 2), whereas **18** and **19** were prepared via a route more akin to the original DIAn synthesis (Scheme 1), relying upon a Friedel-Crafts alkylation for ring closure and then DDQ oxidation, to afford the fully conjugated backbones.[18d] Fortuitously, we obtained crystals suitable for X-ray diffraction of all four new DIAn derivatives, thus confirming the structures of **18–21**. As with parent DIAn **9**, the bond length from the apical carbon to anthracene core is a good indicator of diradical character. For hydrocarbons **9** and **18–20**, this value ranges between 1.391 and 1.412 Å, with **21** the largest at 1.434 Å, again suggesting contributions from both the open-shell and the closed-shell resonance structures. The electronic absorption spectra of **18–21** are similar to parent DIAn **9**, displaying the characteristic anthracene absorptions around 350 nm extending out to 475 nm, while also displaying a low energy absorption that is red-shifted in **19–21** and slightly blue-shifted for **18**, compared with **9**. All of the compounds have a well-defined shoulder on the low-energy absorption due to a low-lying doubly excited electronic configuration,[20] again a trademark of diradical compounds. Unsurprisingly, with their lower calculated ΔE_{ST} values, **19–21** require substantial cooling (−55°C) in order to depopulate the triplet state and thus observe their proton NMR spectra, as at room temperature the spectra showed either broad/unresolved aromatic resonances or completely flat baselines. On the other hand, with its larger calculated ΔE_{ST} value, compound **18** displayed well resolved aromatic resonances at room temperature and upon heating to 140°C did these proton resonances only begin to broaden.

To quantitatively determine the singlet-triplet energy gap we again turned to SQUID measurements. Unfortunately, the reduced stability of **18–21** compared with **9** and **13** and **14** proved problematic, as the first two sets of samples we sent decomposed while awaiting clearance through Spanish customs. The answer was to send Dressler to Valencia, Spain in May 2019 and have him make the molecules on-site so that Gómez-García could perform the SQUID measurements with freshly prepared samples. As shown in Figure 7, the magnetic behavior (magnetic susceptibility) of all the DIAns were measured up to 400 K and then the raw data subjected to a Bleaney-Bowers analysis. Importantly, as demonstrated in the case of the IIDBTs, the magnetic measurements are fully reversible, as the changes between the heating and cooling direction were smaller than 5% of the total magnetic susceptibility. Gratifyingly, the experimentally determined ΔE_{ST} values of **18–21** were within 10% variance of the calculated singlet-triplet energy gaps shown in Figure 6. The very narrow range (1.6 kcal mol^{-1}) of ΔE_{ST} values clearly illustrates our ability to incrementally

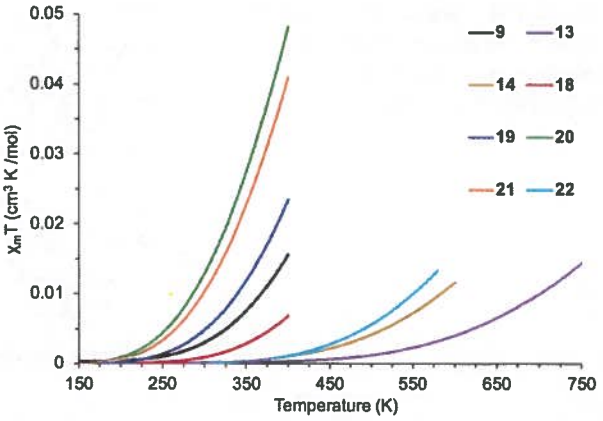


FIGURE 7 Bleaney-Bowers fits of the superconducting quantum interference device (SQUID) data for the series of molecules based on anthracene (**9**, **18–21**) and naphthalene (**13**, **14**, **22**) pro-aromatic cores, illustrating our ability to tune ΔE_{ST} values by discrete structural modification

fine tune the magnetic properties of diradicals using a "structure refinement approach" by making a change as minor as altering the fusion bond order.[18d] Figure 7 also depicts another method for manipulating the singlet-triplet energy gap, namely, late-stage oxidation of the sulfur atoms of **14** with mCPBA to give the corresponding bis-sulfone **22** (structure not shown). In this case oxidation not only lowers the HOMO and LUMO energy levels but also narrows the experimentally determined ΔE_{ST} gap from −6.9 to −6.5 kcal mol^{-1}.[41]

10 | DIINDENOACENES FROM OTHER GROUPS

It is important to point out that the purposeful choice of using indene (or "indeno") units as the fused groups on DIAn has led to the discovery of another design principle for stable organic diradicals. While we were one of the first research groups to do so, diindeno-fusion on either side of a pro-aromatic core (in our case a naphthalene and anthracene) has become a popular strategy towards producing diradical PCHs that are robust enough to be isolated and further studied (Figure 8). In the last 3 years, there have been reports of diindenopicenes (**23**),[42] fluoreno[2,3-*b*]fluorene ("diindenonaphthalene," **24**),[18b] diindenophenanthrene (DIPh, **25**),[43] diindenocorannulenes (DIC, **26** and **27**),[44] and diindenobischrysene (**28**),[45] all of which possess diradical character once the central π-system has been capped with two indeno units. Interestingly enough, recently reported DIPh **25** is actually a constitutional isomer of DIAn **9**, where the fusion pattern of the three

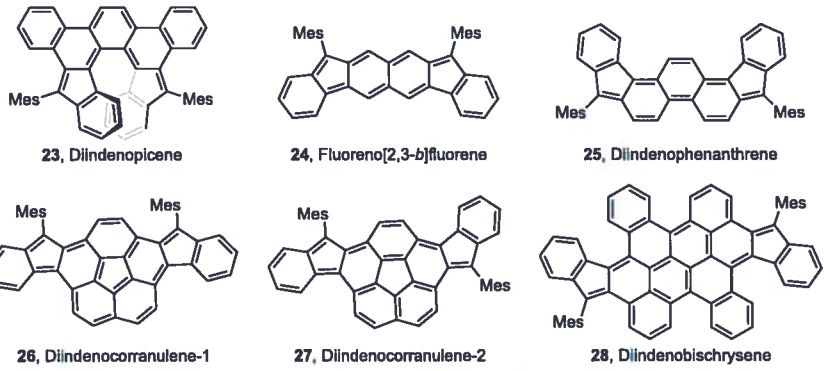


FIGURE 8 Representative examples that have used diindeno fusion as a method for the production of diradical/diradicaloid molecules

central benzenes is the main structural difference between the two compounds. While the change in the way that the benzenes are linked through the core does not lead to a significant difference in diradical character *y*, the experimental (ESR) singlet-triplet energy gap substantially narrows from −4.18 kcal mol^{-1} for **9** to −1.43 kcal mol^{-1} for **25**. Furthermore, in the recent disclosure of diindenocorannulene (DIC), the Cao group reported two different DIC isomers with which they were able to tune the diradical character and ΔE_{ST} through molecule isomerism; however, unlike the anti/syn-IIDBTs **13** and. **14**, the DIC isomers had different orientations of the radical centers, similar to comparing indeno [1,2-*b*]fluorene to its [1,2-*a*]IF congener. We should also note that diindeno-fusion does not always ensure formation of an open-shell molecule, as diindenopyrene[46] and diindenoperylene[47] were found to be closed-shell species; however, in both these cases, the closed-shell resonance forms still maintained considerable aromaticity and thus the drive to "rearomatize" as the open-shell form was negated.

11 | CONCLUSIONS

Over the last 5 years, the Haley lab has had a strong run of publishing insightful work in the field of organic carbon-based diradicals that we anticipate will have impact on the further development of the field. As demonstrated by the studies above, we aim to produce open-shell compounds with moderate to good stability, exploiting the key electronic structure concepts such as *U* and t_{ab} that control diradical properties (*y* and ΔE_{ST}) according to the two-electron two-site model. Structure-property connections and a deep understanding of these studies are mandatory for the rational design of diradicals with tailored singlet-triplet energy gaps. A fundamental understanding of the inherit electronic and magnetic properties of open-shell diradicals is essential so that these properties can be modified to match the future needs of researchers. Simply put, tuning of the singlet-triple energy gap to match application is key for these compounds to realize the many posited uses of diradicals in electronic and magnetic applications. Above all else, the development of practical diradicals—those with intermediate *y* values, where the singlet-triplet energy gap can be tailored to be operational at room temperature or slightly above—will be paramount for their use in common place organic electronics.

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