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Explorations of the Indenofluorenes and Expanded Quinoidal Analogues

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CONSPECTUS: Highly conjugated hydrocarbons have attracted interest for use as active materials in electronic devices such as organic field effect transistors (OFET) and organic photovoltaics (OPV). In this Account, we review our progress in synthesizing and studying a new class of small molecules for potential use as organic semiconductors. The idea originated from prior research on octadehydrodibenz[12]annulene, as the system can undergo double transannular cyclization to yield the indeno[1,2-*b*]fluorene skeleton. Subsequent functionalization afforded the first stable, well-characterized indeno[1,2-*b*]fluorene derivatives, albeit in minute quantities (tens of milligrams). The preparation of these formally antiaromatic compounds has since been optimized: the new synthetic routes utilize inexpensive starting materials, involve robust and high-yielding transformations, and are amenable to considerably larger scale reaction. We have since researched the chemical space of indeno[1,2-*b*]fluorenes and related quinoidal structures by substitution with a number of functional groups and by permutation of the indenofluorene scaffold. These modifications have allowed us to explore fundamental concepts such as biradical character and antiaromaticity, important considerations when tuning electronic properties to yield functional organic materials.

Altering the outer rings by exchange of carbocycles for heterocycles or by inclusion of additional rings as part of the fully conjugated skeleton is one strategy we have examined. Fusing these different aryl groups to *s*-indacene revealed a dependence of the antiaromaticity of the indacene core upon the outer group. Computational analysis of a series of indeno[1,2-*b*]fluorene derivatives uncovered an array of different levels of antiaromaticity in the core of the indeno[1,2-*b*]fluorene derivatives, with one of the benzothiophene derivatives calculated to be as antiaromatic as the parent *s*-indacene itself. Conversely, we have prepared compounds with expanded cores, starting with the naphthalene-based fluoreno[4,3-*c*]fluorene, which was produced through a similar route as the indeno[1,2-*b*]fluorene, using a dione as the key intermediate. Similar to indeno[1,2-*b*]fluorene, fluoreno[4,3-*c*]fluorene showed a closed shell ground state, with no evidence of open shell character even upon heating to 170 °C. Increasing the size of the quinoidal core to three rings afforded a diindeno[*b*,*i*]anthracene (DIAn) derivative, a compound with a much more complex electronic picture. To produce DIAn, a new synthetic route was devised involving a Friedel−Crafts alkylation to form the five-membered ring and a DDQ oxidation to produce the final compound. DIAn displayed NMR signals that were broadened at room temperature and disappeared when heated, indicative of a molecule with significant biradical character. Extensive computational and experimental investigation verified the controllable expression of its biradical character, with DIAn best described with a ground state that lies between a closed shell compound and a open-shell singlet biradical, with ready access to a thermally populated triplet state.

PROJECT ORIGINS

As an incoming graduate student in Fall 2009, one of the junior authors (B.D.R.) asked to work on a research project involving unusual hydrocarbons. The senior author (M.M.H.) had just the task for him, exploring an idea that had mulled around in the back of his mind for many years. Swager et al. had reported in 1994 that treatment of octadehydrodibenz[12]annulene (**1**, Scheme 1) with iodine resulted in "collapse" of the 12-membered ring to form three new rings, yielding a 6-5-6-5-6 fused-ring motif known as an indeno[1,2-*b*]fluorene.[1] We postulated the resultant tetraiodide **2** could then undergo a reaction our lab was very familiar with—Sonogashira cross-coupling—to install ethynyl units.[2] We chose (trialkylsilyl)ethynyl moieties since Anthony and many others have successfully utilized these in increasing solubility, improving solution stability, and altering the molecular packing of acenes and related structures.[3] Between our copious annulene studies[4] that utilized innumerable Sonogashira reactions, we were confident we could produce tetrayne **3**.

At the time, there were only three prior reports of fully conjugated indenofluorenes (IFs) in the literature.[1,5,6] Simple arguments could lead one to believe such systems may only be ephemeral compounds because of high reactivity. For example, aromatization of the center six-membered ring of the IF skeleton

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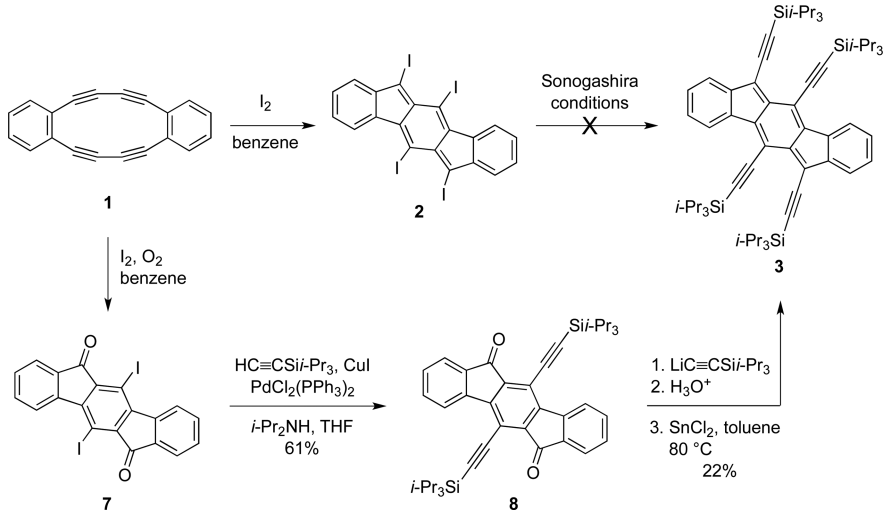
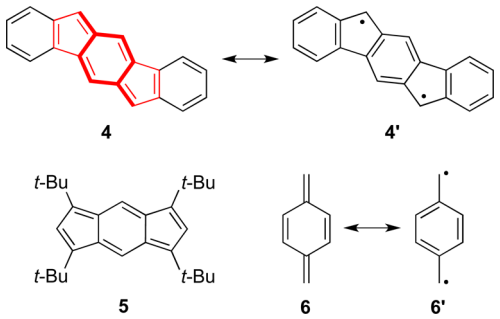
Scheme 1. Original Indeno[1,2-*b*]fluorene Synthetic Route



(**4**) might result in an unstable biradicaloid species (**4′**) as a major resonance contributor.[7] The tricyclic subunit of indeno[1,2-*b*]fluorene, *s*-indacene (red bonds in **4**), is exemplary of the difficulty in isolating molecules of this type. Due to its high reactivity, *s*-indacene required substitution with four bulky *tert*-butyl groups (e.g., **5**) to permit isolation and characterization.[8] An even simpler substructure of indeno[1,2-*b*]fluorene, *para*-xylylene (**6** (closed shell); bold bonds in **4**), is a well-known reactive intermediate with significant contribution from the biradical form **6′** (open shell) that readily undergoes dimer-/polymerization.[7] Despite a body of evidence suggesting potential high reactivity of [1,2-*b*]IF, we pushed forward.



Our confidence in generating **3** was shaken as multiple attempts to cross-couple to **2** afforded only uncharacterizable mixtures, likely due to the latter's reported instability.[1] As the end of BDR's fall rotation approached, we decided to pursue an alternate route. Swager also reported that transannular cyclization of **1** with iodine in the presence of oxygen formed diiododiketone **7**.[1] This molecule cleanly underwent Sonogashira cross-coupling to give diyne **8** (Scheme 1). Inspired by Anthony's acene studies,[3,9] we attempted nucleophilic attack of an acetylide on the carbonyls of **8** and then reductive dearomatization with $SnCl_2$ to ideally generate **3**. Most procedures reported fast color changes, indicating that acene formation occurred rapidly. On the other hand, similar treatment of our yellow dihydroxy intermediate produced no noticeable color change. After a couple hours at 40 °C, we decided to examine what, if anything, had become of the starting material. Fortunately, removal of the toluene solvent by rotary evaporation involved robust heating of the water bath, which induced a color change to deep blue originating from **3**; thus, purposeful treatment of the diol with $SnCl_2$ in toluene at 80 °C gave modest yields of **3** with the bulky (triisopropylsilyl)-ethynyl groups for protection. Though this route was less elegant than direct cross-coupling to **2**, it still afforded the desired product as the first well-characterized indeno[1,2-*b*]fluorene derivative.[10]

IMPROVED SYNTHESES OF INDENOFLUORENES

It was clear early on that if compounds like **3** were to become anything beyond laboratory curiosities, we needed short, scalable synthetic routes. The transannular cyclization methodology rendered it nearly impossible to prepare more than a hundred milligrams of compound 7, and as we discovered, annulene **1** is indeed prone to violent decomposition as previously reported.[11] To facilitate gram-scale production of material and allow for the exploration of a wide chemical space, we refined two routes to access the requisite indeno[1,2-*b*]fluorene-6,12-dione precursors and related derivatives.

These two general pathways (Scheme 2), dubbed "inside-out" and "outside-in", are based on the intramolecular Friedel−Crafts acylation of a terphenyl diacid, a route developed by Deuschel in 1951.[12] In the "inside-out" method, the carboxylic acids are appended to the central ring and cyclize onto the outer aromatic groups. This is preferential for simpler IF derivatives where there is no concern about regioselectivity of the acylation reaction. The "outside-in" route, where the acids/esters are already present on the outer rings and cyclize onto the central benzene, is used in cases where multiple regioisomers could arise from acylation onto the outer rings.

The biggest limitation with the original Deuschel route was the tedious, low-yield synthesis of the *para*-terphenyl intermediates; however, Wang and co-workers showed in 2002 that the terphenyls could be prepared easily by Suzuki cross-coupling.[13] This simple three-step pathway to the poorly soluble diones also permitted ready access to substitution on the peripheral benzene rings due to the myriad of known and/or commercially available arylboronic acids and arylboronate esters. This major development afforded greater quantities and varieties of indeno[1,2-*b*]fluorene-6,12-diones (e.g., **9**), synthesized in high yields from relatively inexpensive starting materials, thus opening the floodgates for our studies of this class of molecules (Scheme 3).

Our first foray using the Deuschel/Wang route led to derivatives with functional groups at the 2,8-positions (**10a−10i**). Unfortunately, we discovered that the electronic properties

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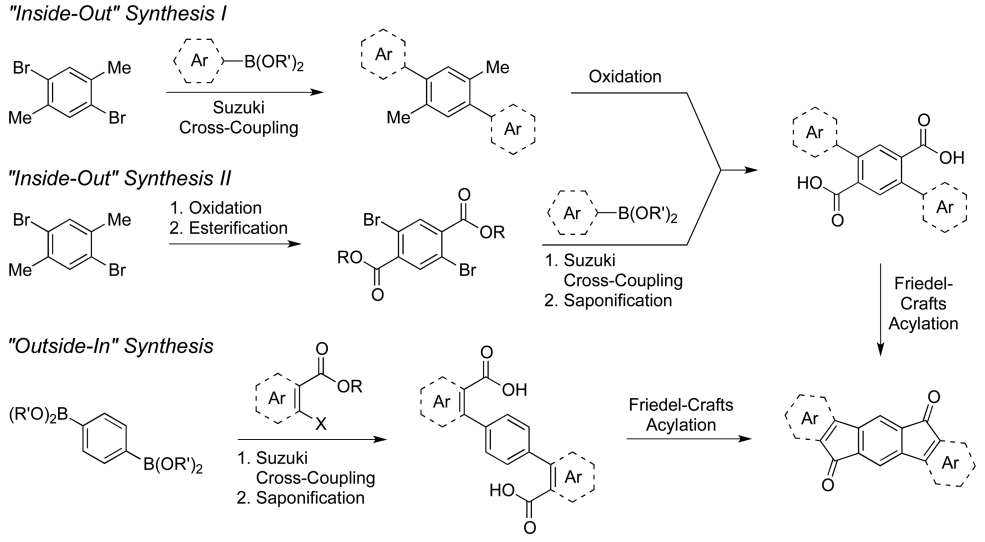
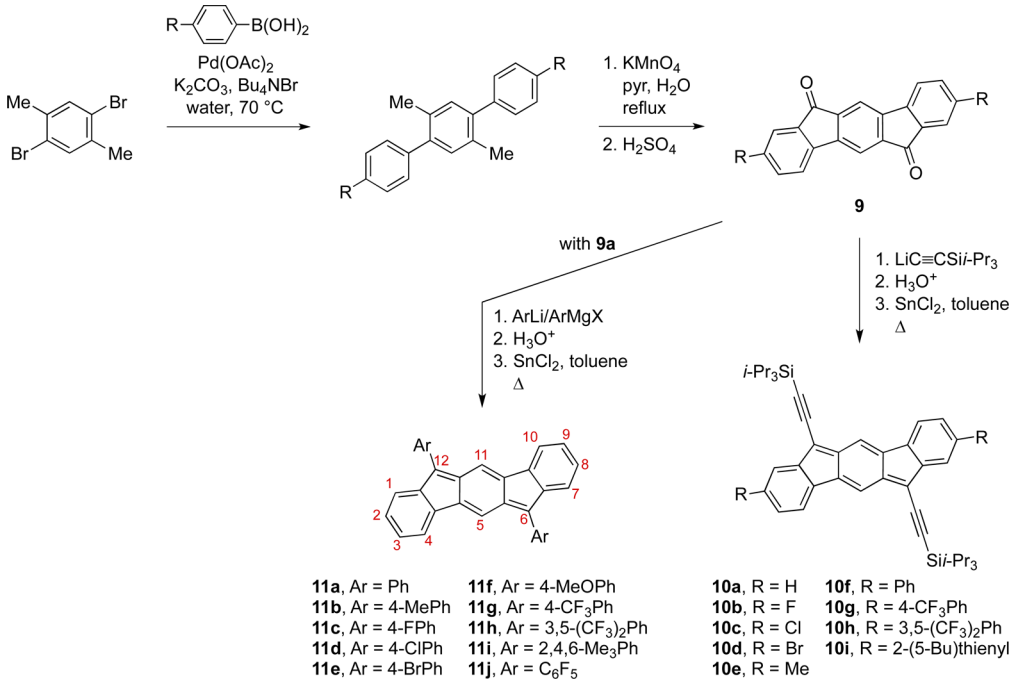
Scheme 2. General Routes to Indeno[1,2-*b*]fluorenediones and Analogues



Scheme 3. Improved Synthesis of Indeno[1,2-*b*]fluorenes



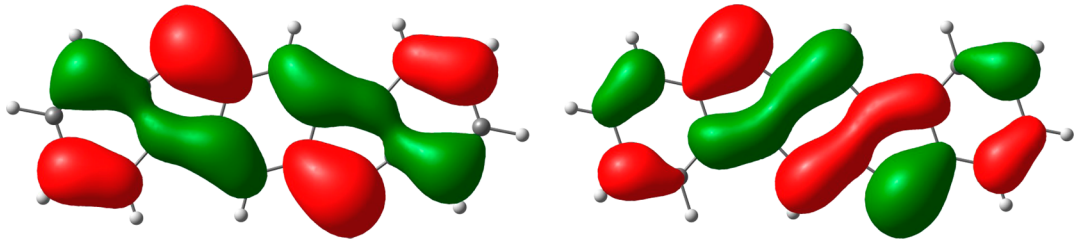


Figure 1. Calculated (B3LYP/6-311+G(d,p)) HOMO (left) and LUMO (right) wave function of the indeno[1,2-*b*]fluorene core; isovalue for orbitals is 0.02 electrons$^{1/2}$/bohr$^{3/2}$.

of **10a−10i** varied little.[14] Subsequent computations on the [1,2-*b*]IF core revealed that carbons 2/8 have minimal HOMO/LUMO density (Figure 1), relegating any influence to be through weaker inductive effects. Instead, the calculations suggested we should focus on functionalizing the 6,12-positions.

With access to multigram quantities of dione **9a**, we next explored the 6,12-diarylated indeno[1,2-*b*]fluorenes **11a−11j** (Scheme 3).[15] In principle, most nucleophiles will work, but the reactivity/instability of the core requires use of relatively bulky substituents and/or ones that are electron deficient. For example,

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the solution half-life of **11a** is roughly a few hours, whereas IFs **10a** or **11i** possessing bulkier substituents are on the order of several weeks.

Although a majority of our studies have focused on the [1,2-*b*]IF topology (**4**), the family of indenofluorenes is actually five regioisomers (Figure 2). The [1,2]-isomers have the apical

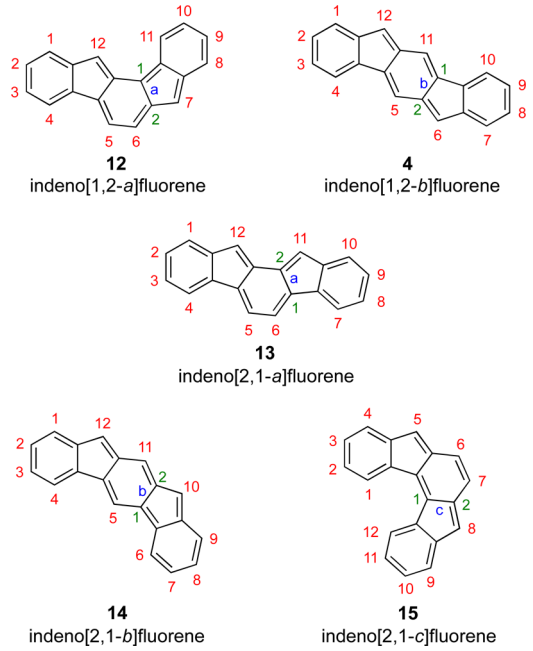

Figure 2. Nomenclature and numbering for indenofluorene isomers. Red numbers denote atom; green numbers denote numbering for apical carbon orientation; blue letter denotes the face of indene fusion.

carbons of the five-membered rings in an *anti* relationship, whereas the apical carbons of the [2,1]-isomers are *syn*. The letter corresponds to the edge of indene/fluorene ring fusion. Whereas molecules based on a fully conjugated [1,2-*a*]IF **12** are unknown, derivatives of the remaining four regioisomers have been reported in recent years. The Tobe group[16] has generated dimesityl derivatives of [2,1-*a*]IF **13**[17] and [2,1-*b*]IF **14**,[18] and we have disclosed a few derivatives of [2,1-*c*]IF **15**.[19]

INDENOFLUORENE FRAMEWORK ALTERATION

Optimization of the Deuschel/Wang path for dione synthesis was the watershed event for our studies given the countless cross-coupling partners in Suzuki reactions. One of the easiest ways to vary structure and thus properties is to alter the ring system fused to the indacene core (Figure 3). For example, inclusion of aromatic heterocycles affords the indacenodithiophenes (**16**, **17**, IDTs)[20] and indacenodibenzothiophenes (**18**, **19**, IDBTs).[21] Alternatively, introduction of other arenes furnishes the dinaphthoindacene regioisomers (**20**–**22**, DNIs) and diphenanthroindacenes (**23**, DPIs).[22]

We have investigated a number of derivatives in which the carbocyclic core has also been altered (Figure 4). One simple modification is to change ring fusion to generate the [2,1-*c*]IF regioisomer. Molecules **24a**–**c** retain the *para*-xylylene unit (highlighted in dark red) but are based on an *as*-indacene core (red) as opposed to the *s*-indacene core in **10**/**11**.[19] Other systems include core expansion, such as fluorenofluorene (**25**, FF)[23] and diindenoanthracene (**26**, DIAn),[24] and use of aromatic heterocycles, such as the diindeno[*n*]thiophenes series (**27**–**29**, DI*n*Ts).[25]

Admittedly, the Deuschel/Wang route is not "one size fits all", as the oxidation ($KMnO_4$) and Friedel–Crafts (conc. H_2SO_4) steps utilize harsh reagents and conditions. It is important to keep alternative reagents and procedures in mind. In some instances, we found that PPA or 10% PPA in $MeSO_3H$ is superior to H_2SO_4.[22] As another example, all thiophene-containing systems required "traditional" Friedel–Crafts acylation conditions (conversion of acid to acid chloride followed by $AlCl_3$) starting from already-installed ester groups so not to oxidize/destroy the thiophene rings.[20,21,25]

In a very few cases, we had to redesign the synthetic route altogether. Considering the linear topology of **26**, it was not immediately obvious how to construct the requisite dione, as preparation of anthracene derivatives with different substituents in the 2,6- and 3,7-positions is notoriously difficult; thus, we utilized Friedel–Crafts *alkylation* as the key step to form the five-membered rings (Scheme 4). By installing bulky mesityls, the steric clash between them and the triisopropylsilyl (TIPS) groups inhibited closure at the preferred 1,5-positions and instead directed the electrophilic carbons to close only at the 3,7-positions. Subsequent DDQ oxidation furnished **26** as deep blue crystals.[24] The only other systems to date requiring the

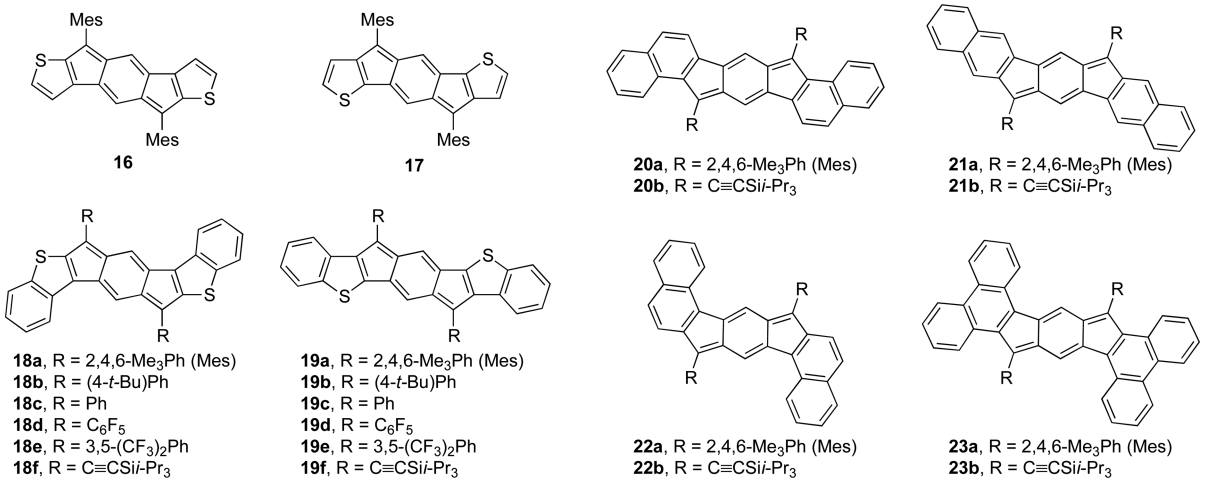

Figure 3. IDT, IDBT, DNI, and DPI derivatives prepared by the Haley group, where the outer benzene rings have been altered.

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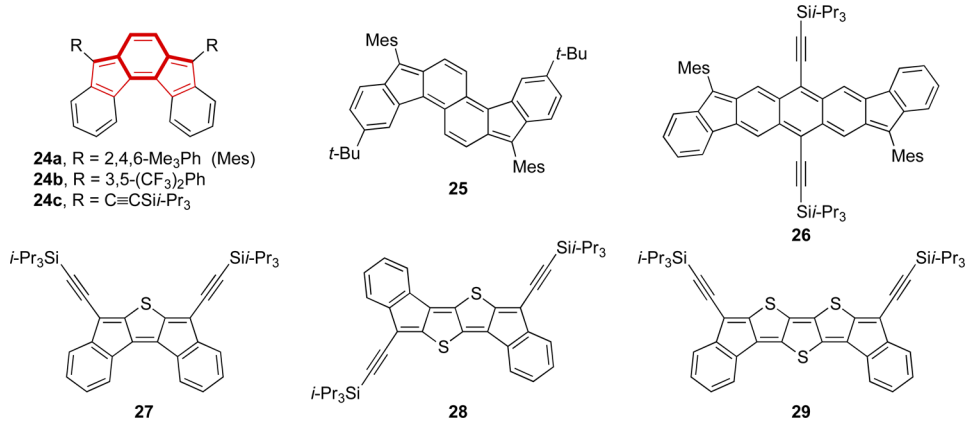
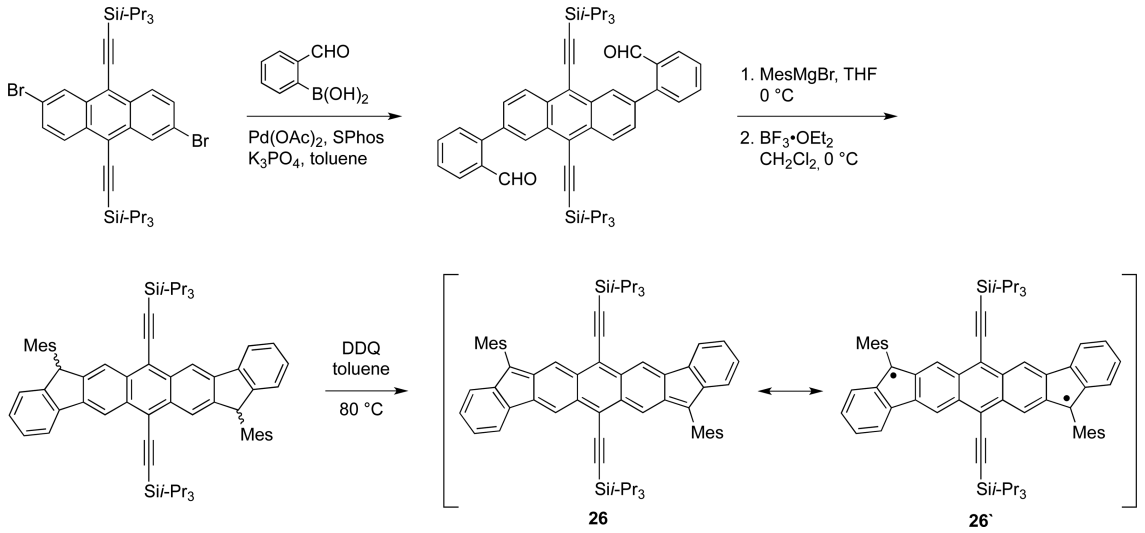


Figure 4. [2,1-*c*]IF, FF, DIAn, and DI*n*T derivatives prepared by the Haley group, where the inner six-membered ring has been altered.

Scheme 4. Friedel-Crafts Alkylation Route to Diindenoanthracene 26



Friedel–Crafts alkylation/DDQ route have been **20a** and **23a**.[22] In both cases the mesityl nucleophile failed to add to the corresponding diones, possibly because the carbonyls are situated in "bay"-like regions of the polycyclic ketones.

INTRINSIC PROPERTIES

Antiaromaticity

The indenofluorene regioisomers each contain 20 π-electrons and thus are formally antiaromatic according to Hückel's Rule. In fact, all quinoidal systems presented in this Account contain [4*n*] π-electrons as part of their fully conjugated framework. Since 1996 Nucleus Independent Chemical Shift (NICS) calculations[26] have been utilized to assess computationally the type and strength of ring currents in cyclic systems. Our initial NICS(1) calculations for the desilylated analogue of **3** (TIPS groups replaced by H) afforded values of 0.02, 1.84, and −7.12 ppm for rings A, B and C, respectively (see Figure 5 for ring labeling).[10] Considering the NICS(1) values of benzene and cyclobutadiene are −10.2 and 17.4 ppm, respectively, our results suggested slightly reduced aromaticity in the outer rings and essentially an atropic or very slightly paratropic indacene core. Experimentally, the weak paratropicity manifested itself in a slight upfield shift ($\Delta\delta \sim 0.05$–0.10 ppm) of the characteristic singlet for H5/H11 ($\delta \sim 7.2$–7.3 ppm) upon reductive dearomatization of the diol intermediate. For the DNI isomers, this same singlet appeared in the 6.6–7.0 ppm region,[22] and even further upfield in the 5.9–6.3 ppm range for IDTs **16**, **17** and IDBTs **18**, **19**.[20] The observed ∼1.4 ppm range for this one set of protons hinted at "tuning" of indacene paratropicity strength by variation of the fused rings.

To corroborate this hypothesis computationally, we turned to one of the more powerful NICS methodologies currently available—the NICS-XY scan using π-only models.[27] The NICS-XY scan explores local, semiglobal and global ring currents as well as the type of current(s) (diatropic vs paratropic) within a particular molecular skeleton. The π-only model removes the contribution of the σ electrons from the NICS values, affording ring current data produced solely from π-electrons.

As suspected, the nature of ring fusion to the indacene core has a pronounced effect on the molecule's antiaromaticity.[22] Unsubstituted *s*-indacene possesses $NICS_{\pi ZZ}$ values (Figure 5, black trace) of 23 and 26 ppm over rings A and B, respectively. Benzo-fusion as in [1,2-*b*]IF **4** significantly diminishes the paratropicity, with corresponding $NICS_{\pi ZZ}$ values (purple) of 4 and 7 ppm. For the DNI regioisomers, bond fusion and thus bond order tell a compelling story. Both *anti*- and *syn*-DNI are attached at the 1,2-bond, with a bond order of 1.66. The greater double bond character compared to benzo-fusion (bond order 1.5) translates to higher yet nearly identical $NICS_{\pi ZZ}$ values (green and red traces, respectively) of ca. 10 and 13–14 ppm for rings A and B.

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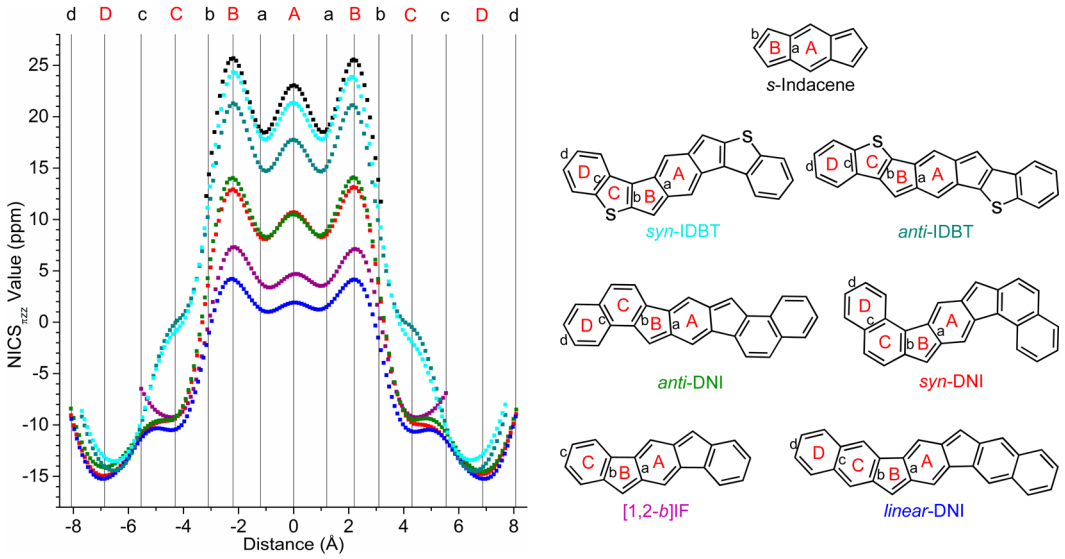

Figure 5. NICS(1.7)$_{\pi ZZ}$-XY scans (left) of the computed (B3LYP/6-311+G*) simplified structures (right) of select diareno-fused *s*-indacene derivatives, listed in order of decreasing paratropicity of the indacene core.

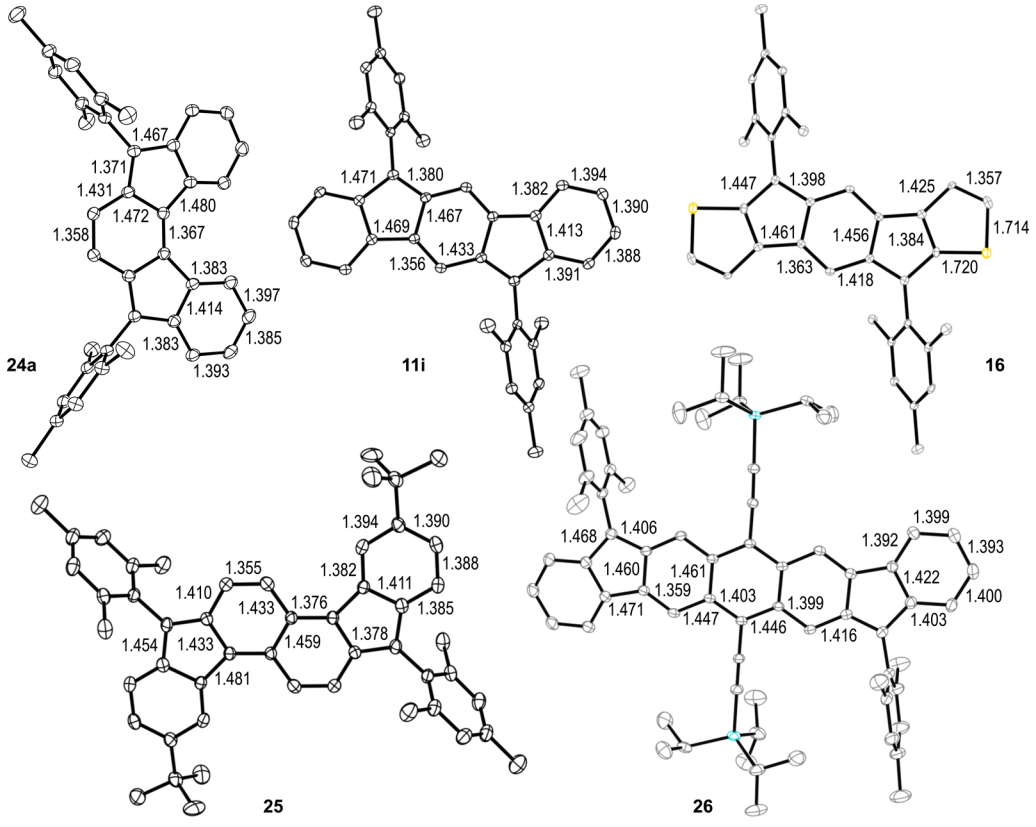

Figure 6. Molecular structures of and selected bond lengths for **11i**, **16**, **24a**, **25**, and **26**; hydrogen atoms omitted for clarity; ellipsoids set to 30% probability level.

Conversely, the NICS$_{\pi ZZ}$ values (blue) of *linear*-DNI (2,3-bond fusion; bond order 1.33) decrease to 2 and 4 ppm, respectively. If one significantly increases double bond character, as in fusion to a benzothiophene 1,2-bond (bond order >1.8), then the NICS$_{\pi ZZ}$ values (light blue and teal traces for *syn*- (ring A/B 21/24 ppm) and *anti*-IDBT (ring A/B 18/21 ppm), respectively) approach the values of *s*-indacene itself.

Despite this 20+ ppm variance in the NICS$_{\pi ZZ}$ 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 (IF, DNIs), the range of NICS$_{\pi ZZ}$ values for ring C is small (−9 to −11 ppm), and even smaller (−14 to −15 ppm) for ring D of the DNIs. Whereas the values of ring C show the "conflict" between opposing diatropic and paratropic ring currents, ring D is more isolated and thus the values are more typical of benzene/naphthalene. Exchanging carbocyclic ring C for a heterocyclic ring negates this "conflict", as the now-atropic thiophene (NICS$_{\pi ZZ}$ value of 0) acts as a spacer between the

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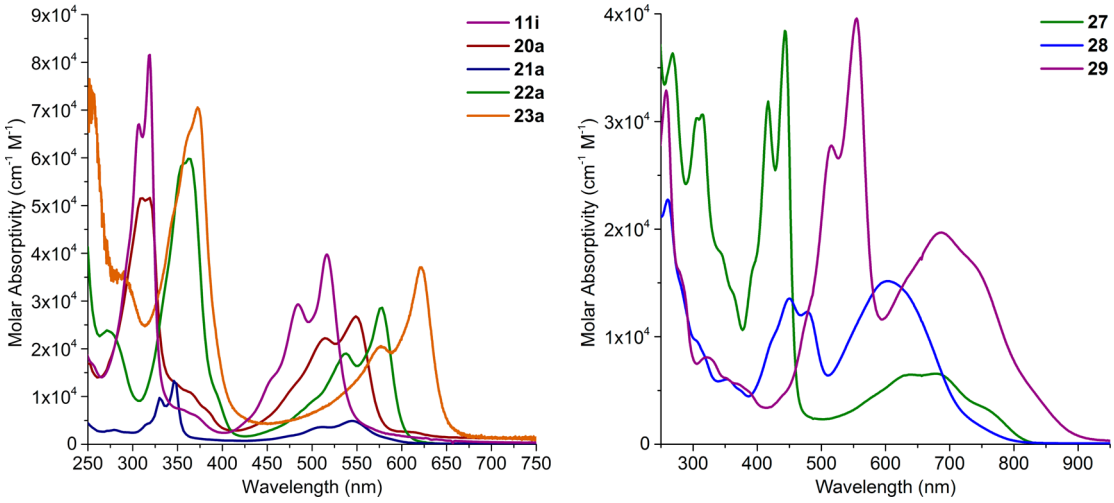

Figure 7. Representative electronic absorption spectra of **11i**, **20a**–**22a**, and **23a** (left) and **27**–**29** (right).

strongly diatropic outer benzenes and the highly paratropic indacene.

Quinoidal Structures

Gratifyingly, we have obtained X-ray crystal structures for over 40 of these fully conjugated molecules. A representative selection of dimesityl derivatives is given in Figure 6 along with key bond lengths. Without exception, all structures exhibit a quinoidal motif within the indacene core, with bonds possessing more double-bond character clearly evident. For example, the double bonds in the central six-membered rings of **11i**, **24a**, and **25** vary from 1.356 to 1.376 Å, and the bond between the cores and the apical carbons bearing the mesityl groups from 1.371 to 1.380 Å. The outer benzenes exhibit archetypical bond lengths of 1.382–1.397 Å, with the fused bond at 1.411–1.413 Å. A vast majority of the IF, FF, DNI, and DI*n*T structures are well-bracketed by these values, whether aryl- or alkynyl-substituted on the apical carbons. In addition, nearly all of the molecules are planar species, with root-mean-square deviations from the average molecular plane of 0.04 Å or less. Only the [2,1-*c*]IFs deviate modestly from planarity (RMS deviation up to 0.186 Å) due to helicene-like sterics.[19] Interestingly, either heterocycle fusion (**18**, **19**) or further expansion of the quinoidal moiety (**26**) affords structures where the bond between the core and the apical carbon bearing the mesityl lengthens to over 1.4 Å. While nowhere near the 1.437 Å distance in the dimesityl analogue of **14**,[18] the observed bond lengths of 1.399–1.416 Å begin to hint at the contribution of a biradical resonance form.

Biradical Character

Open-shell polycyclic hydrocarbons (PCHs), molecules that feature multiple unpaired electrons, are a class of compounds that have seen renewed interest due to predictions of materials applications in nonlinear optics, photovoltaic devices, and/or molecular spintronic devices.[28] The reactivity inherent in radical species can be controlled through delocalization of the spin over multiple rings (e.g., phenalenyl) and/or by kinetic stabilization with bulky groups (e.g., mesityls).[29] The contribution of a biradical resonance form to the overall ground state structure is described by the biradical character index, y. The index is a continuum that ranges from pure closed shell, $y = 0$, to pure open shell, $y = 1$. Most biradical PCHs have a spin-paired singlet ground state (S = 0) and low-lying, readily accessible spin-parallel triplet excited state (S = 1).

Admittedly, we did not set out to prepare biradical species, as a majority of the y values of our molecules are less than 0.3. Although we had not noted such reactivity in our previous works, Zhao and Fu reported that the trimethylsilyl analogue of **10a** afforded dimeric and trimeric structures that could only arise by invoking **4′**, where the radical had delocalized onto the alkyne.[30] In addition, Tobe showed that the dimesityl analogue of **14** possessed pronounced biradical character.[18]

Our perspective changed with the preparation of **26**,[24] with the initial clue being broadened proton NMR peaks at room temperature. Cooling to −20 °C furnished sharp peaks with well-defined coupling, whereas warming to 150 °C broadened the peaks into nondescript lumps that returned to their original shape upon cooling, importantly with no evidence of decomposition. In contrast, heating solutions of **18d** and **19e** over 100 °C or **25** to 150 °C resulted in no discernible line broadening, suggesting that only DIAn can easily populate an open shell, thermally accessible triplet state. Nonetheless, for an open-shell compound, **26** is remarkably stable to O_2 and heat (as noted above)—deep violet crystals can be stored for several months under ambient conditions and solutions have a half-life over 2 months. Our collaborative team of experimentalists and theorists from Spain, Japan and Sweden helped determine the important properties of **26**: (1) Calculations indicate that with a biradical character index of $y = 0.62$, the best description of DIAn in the ground state is a mixture between quinoidal resonance structure **26** and aromatic open-shell structure **26′** (Scheme 4). (2) SQUID measurements corroborate a thermally accessible triplet state for **26′**, with an experimental ΔE of 4.18 kcal mol^{-1} (versus a calculated value of 4.9 kcal mol^{-1}). (3) VT-Raman, NICS-XY scans, and ACID calculations all support the existence of the aromatic anthracene unit upon biradical formation. Unlike most biradical structures, DIAn exhibits no correlation between biradical character and chemical reactivity.

Optoelectronic Properties

The indenofluorene family of molecules is highly colored, covering a wide spectrum. Solution colors vary from orange (**11i**) to red (**11a**) to purple (**10a**) to light blue (**25**), deep blue (**26**, **29**) and dark green (**20f**, **27**). The intense colors are reflected in the electronic absorption spectra of the molecules. Unsurprisingly, as one lengthens the overall conjugation pathway, the λ_{max} of the low energy band(s) moves to longer wavelength and thus the optical gap decreases. Compared to **11i** (515 nm, Figure 7 left),

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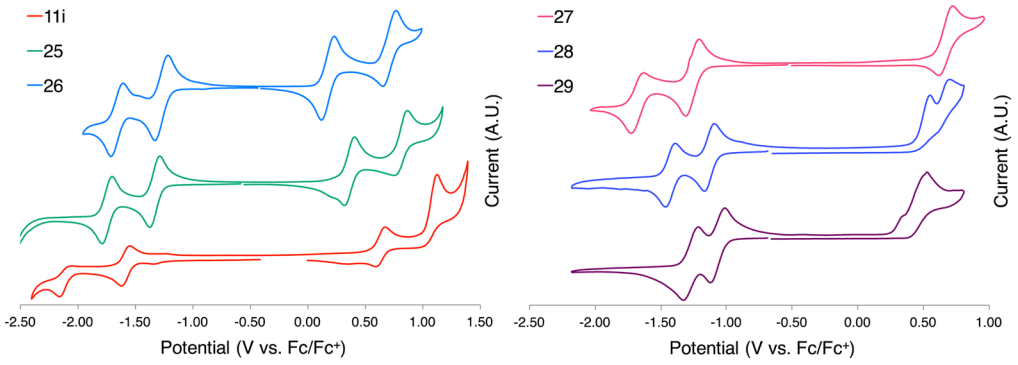

Figure 8. Representative CVs of [1,2-*b*]IF **11i**, FF **25**, and DIAn **26** (left) and of the DI*n*Ts **27**–**29** (right).

the λ_{max} of the DNI/DPI low energy band progressively shifts to the red: 543 (**21a**) 549 (**20a**), 578 (**22a**), and 622 nm (**23a**), decreasing the optical gap from ca. 2.3 to 1.9 eV.[22] Although not shown, replacement of the mesityls with TIPS-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 **10a** and **23b** 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° dihedral, Figure 6) to the indenofluorene backbone.

The DI*n*T series **27**–**29** illustrate the effects of lengthening the quinoidal core. All three exhibit strong, acene-like vibronic features from 350 to 600 nm and low energy absorptions reaching into the NIR (800–925 nm).[25] Interestingly, **27**–**29** exhibit similar absorbance profiles to their purely hydrocarbon analogues **15c**, **25**, and **26**. For the DI*n*Ts, the high energy optical bands red shift by ca. 50–100 nm and the low energy optical bands blue shift by ca. 15–35 nm.

Despite being highly colored and π-electron-rich systems, the indenofluorene family is completely nonfluorescent to the naked eye. In fact, residual fluorescence within a sample is indicative of impurities! Computationally we found that compounds with a symmetry inversion center (i.e., [1,2-*b*]IF framework) have a symmetry forbidden $S_0 \rightarrow S_1$ transition and for compounds possessing no symmetry inversion center (i.e., [2,1-*c*]IFs) the $S_0 \rightarrow S_1$ transition is allowed. This symmetry dependence can be seen experimentally in Figure 7 (right) as the DI*n*T absorption edges are staggered as a result of the family's alternating axo-/centrosymmetry.

The Wasielewski group at Northwestern helped provide the answer as to why our compounds are "dark".[31] Transient absorption spectroscopy of **10a**, **15c**, and **25** revealed that all three have extremely short S_1 lifetimes, on the order of 9–12 ps. Interestingly, studies on indacene **5**, the core substructure within indenofluorenes, showed it to have a lifetime of 18 ps for the S_1 to ground state relaxation.[32] Such extremely short lifetimes explain why these molecules are nonemissive, 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 nonemissiveness 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.[31−33] Similar to **5**, this process allows efficient internal conversion to the ground state, deactivating fluorescence and thus yielding "dark" molecules.

Electrochemistry

One aspect that drives our continued interest in this class of molecules is that all of these compounds have high electron affinities accompanied by low LUMO energy levels compared to typical PCHs, thus making IFs and their congeners potentially useful as n-type organic semiconductors.[34] Figure 8 shows representative cyclic voltammetry (CV) data for the two core-expanded series. As one increases the number of six-membered rings from **11i** to **25** and then **26**, the two oxidation and two reduction events become increasingly reversible, reflecting clean redox amphoterism in the latter two examples. While DI*n*Ts **27**–**29** reversibly accept two electrons, the reversible oxidation observed for **27** becomes an irreversible process in **28** and **29**, just the opposite of the hydrocarbon structures. In both series, enlarging the core unit from one to three rings not only makes the reduction potentials for both the first and second reduction less negative, but also decreases the separation between the two reductions by *ca.* 0.05 and 0.1 V for each benzene and thiophene unit added, respectively. This effect, known in related quinoidal thienoacene systems, is attributed to a decrease in Coulombic repulsion in the dianion as the two charges are capable of moving farther away from each other.[35]

Both the IDBTs **18**, **19** and DNIs/DPI **20**–**23** all show one reversible reduction along with a second reduction with its reversibility dependent on the substituent appended to the five-membered rings—aryl-substituted molecules in general show better reversibility than alkynyl ones. Consistent with computations showing the strong paratropic currents in their indacene core, the IDBTs display the least negative E^1_{red} potentials of the indeno[1,2-*b*]fluorene derivatives for each corresponding R group. In fact, a plot of the E^1_{red} of the available data for the TIPS-ethynyl- and mesityl-substituted compounds[14,15,22] versus the peak $NICS_{\pi ZZ}$ values (Figure 9) illustrates a trend of less negative reduction potentials correlating to higher $NICS_{\pi ZZ}$ values. This follows the hypothesis that part of the electron-accepting ability of indenofluorene derivatives is a result of removing the destabilization of the antiaromatic core; therefore, compounds with greater paratropicity are more easily reduced, which in turn imparts diatropic character (vide infra).[36,37]

Reflecting the high electron affinity of the indenofluorene family, we typically observe electron affinity energies in the range of −3.7 (e.g., **11a**, **11f**, **16**, and **17**) to −4.1 eV (e.g., **3**, **10b**, and **20b**), with electrochemically determined energy gaps from 2.2 eV (e.g., **11i**) down to 1.5 eV (**26**). These values are in stark contrast to acenes, which typically have much lower electron affinities unless heavily appended with electron-withdrawing groups. The pronounced electron affinity of the IF family can be rationalized in terms of the parent IF structure **4**: formation of

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Acc. Chem. Res. 2017, 50, 977–987

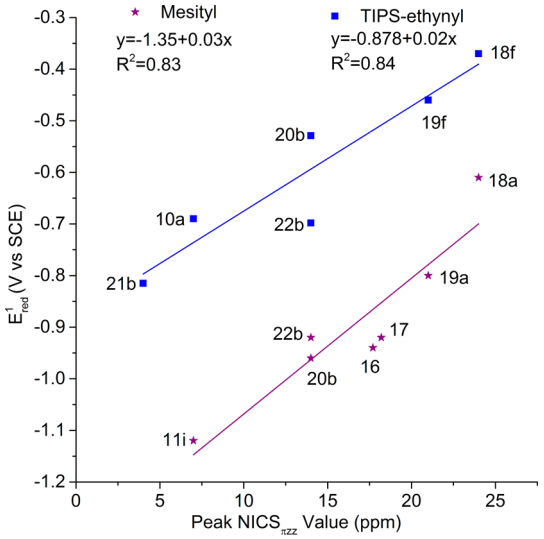

Figure 9. Relation between peak $NICS_{\pi ZZ}$ values and the measured E^1_{red} of mesityl- and TIPS-ethynyl-substituted compounds prepared in the Haley lab.

the dianion generates a fully aromatic, 22 π-electron system possessing two cyclopentadienyl anions and three benzene rings. Like the fullerenes, the presence of the five-membered rings containing all-sp^2 hybridized carbons makes these compounds inherently electron-accepting.

Isolation and characterization of the radical anion and dianion salts of DIAn **26** by X-ray analysis illustrates the effect on molecular structure upon successive reduction.[36] As expected, the bond distances within these noncontact ion pair products (Figure 10) reveal aromatization of the anthracene core. In the first reduction event, the "single" bonds within the anthracene-like core of show an average contraction of 0.017 Å compared to those in neutral **26**, whereas the "double" bonds in the core remain unchanged. The structure of $\mathbf{26}^{\bullet-}$ retains the bond distance alternation of the neutral ligand, but as a result of an electron in a previously nonbonding orbital, there is contraction of bond distances in the core. The next single-electron reduction to give $\mathbf{26}^{2-}$ shows the homogenization of the central bonds to 1.415−1.425 Å, values indicative of an anthracene-like structure. Based on the solid-state data, the first reduction results in contracted bond distances but overall retention of the quinoidal bonding pattern, and the second reduction completes the aromatization of the anthracene core. This drive to regain aromaticity by accepting electrons is also reflected in the molecular structure of the dianion of a modified **10a**, where cyclohexyl rings have replaced the isopropyl groups.[37] Although this structure is a contact-ion pair, it too suggests increased aromaticity—the nonfused C−C bonds homogenize from a 1.364−1.469 Å range in its quinoidal structure into a narrower window of 1.389−1.430 Å. Copious computations on the charged states of both of these molecular systems corroborate the experimental findings.[36,37]

MATERIALS APPLICATIONS

While predominantly focused on studying the fascinating structural and electronic properties inherent in the indenofluorene family of molecules, we have made very preliminary forays into their use as electron-transporting components in materials applications.[38,39] Our most interesting results involve the use of our quinoidal compounds as an active layer in organic field effect transistors (OFETs). While the accumulated electrochemical data suggest they might be useful as n-type or ambipolar organic semiconductors, a vast majority of the X-ray data we have obtained to date show herringbone or 1-D stacks in the solid-state, not the 2D "brick-and-mortar" packing commonly associated with planar structures that display good transport characteristics.[3,40] Of course, there are many parameters that must be optimized in devices, but good intermolecular overlap of the molecular orbitals is crucial for high charge mobilities.[41] While OFETs based on single-crystal of **11j** and **26** did indeed exhibit ambipolar behavior, the hole mobilities ($\mu_h = 7 \times 10^{-4}$ and 2×10^{-3} $cm^2\ V^{-1}\ s^{-1}$) and electron mobilities ($\mu_e = 3 \times 10^{-3}$ and 4×10^{-3} $cm^2\ V^{-1}\ s^{-1}$) were rather poor.[15,24]

The most promising OFET results to date use spin-coated IDBT **19f**, as the (triisopropylsilyl)ethynyl groups afford stability and solubility to aid in device processing. Compound **19f** packs in 1D slip-stacked columns with significant overlap between neighboring molecular planes and sub-van der Waals C−C contacts. Computations predict electronic orbital couplings of 50 meV for the HOMO−HOMO interaction (hole transport) and 100 meV for the LUMO−LUMO interaction (electron transport), levels similar to those of other high performance organic semiconductors.[21] Working with the Jurchescu group, top gate, bottom contact OFETs showed an average hole mobility of 0.14 $cm^2\ V^{-1}\ s^{-1}$ over 10 devices with a maximum mobility of 0.44 $cm^2\ V^{-1}\ s^{-1}$ and a threshold voltage of 1.33 V.[21]

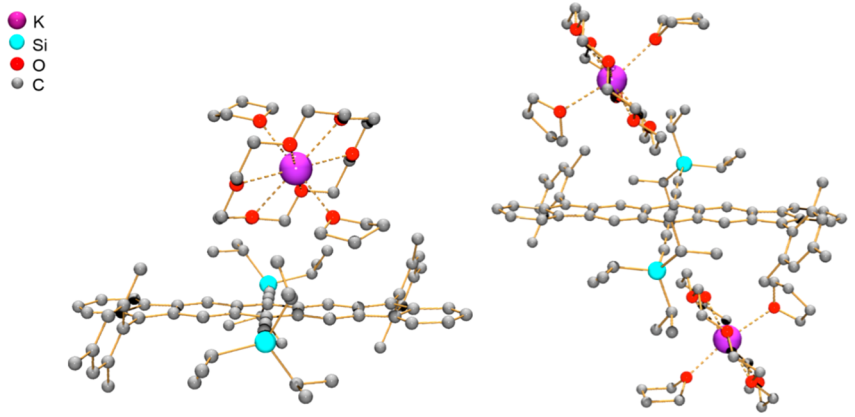

Figure 10. Molecular structure of the radical anion ({K(18-crown-6) $(THF)_2$}DIAn) and dianion ({K(18-crown-6) $(THF)_2$}$_2$DIAn) salts of **26**. All H atoms in the ball-and-stick X-ray structure models omitted for clarity.

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Acc. Chem. Res. 2017, 50, 977−987

A related study on single crystal FETs of **22f** found the system to exhibit hole mobilities as high as 0.64 $cm^2 V^{-1} s^{-1}$ and electron mobilities as high as 0.34 $cm^2 V^{-1} s^{-1}$,[42] which are the highest mobilities of an OFET produced from a fully conjugated indenofluorene derivative. While many more device studies need to be performed, this is clear proof of principle for use of members of the indenofluorene family as organic semiconductors.

CONCLUSIONS

This Account serves to highlight our recent work of bringing the fully conjugated indenofluorene scaffold out of the unknown and into the toolbox of organic materials available for study.[43] The improved accessibility of indenofluorenes and related molecules discussed above has opened the door to new polycyclic antiaromatic systems containing quinoidal motifs. Recent work has demonstrated that many indenofluorenes and related structures are synthetically feasible, in addition to actually being kinetically stable and capable of isolation, where not long ago this was not the case. New and modified synthetic strategies have expanded the availability of compounds with a vast array quinoidal cores and outer arene groups. Studies of these scaffolds have revealed the interesting structural, photophysical, and redox properties they inherently possess, which in turn have provided new insights into long-standing, fundamental concepts related to PCHs such as antiaromaticity and biradical character. Nonetheless, for indenofluorenes and their congeners to become useful materials in organic electronic devices, challenges such as optimizing their third-order nonlinear optical responses[44] and increasing charge mobilities to a regime that makes them useful as organic semiconductors must be addressed. As their development continues,[45,46] it is our hope that these molecules will become a useful class of organic semiconductors, akin to their acene counterparts.

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Notes

The authors declare no competing financial interest.

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Bradley D. Rose was awarded his Ph.D. in 2014 at the University of Oregon under the direction of Prof. Haley. After postdoctoral work with Prof. Jean-Luc Bredas at King Abdullah University of Science and Technology, he returned to the midwest U.S. where he is a lecturer at Illinois Central College. His research interests are in the theoretical and experimental components of conjugated organic compounds that have interesting electronic and optical properties.

Michael M. Haley received his B.A. (1987) and Ph.D. (1991) degrees from Rice University in Houston, Texas. After a postdoctoral stay at the University of California, Berkeley, he joined the faculty at the University of Oregon in 1993 where he currently is the Richard M. and Patricia H. Noyes Professor of Chemistry. His current research interests focus on the synthesis and properties of novel organic semiconductors and on phenylacetylene-based molecular scaffolds for anion sensing.

DEDICATION

Dedicated to Professor Klaus Hafner, the father of indacene chemistry.

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