Angewandte Chemie International Edition

DOI: 10.1002/anie.201104797

Polycycles

Electron-Accepting 6,12-Diethynylindeno[1,2-*b*]fluorenes: Synthesis, Crystal Structures, and Photophysical Properties**

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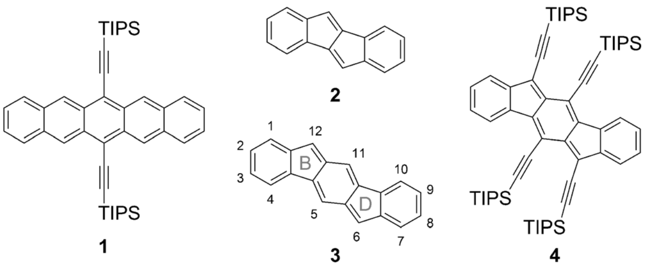
Polycyclic hydrocarbons that possess extended π conjugation are of significant interest because of their potential use in optical and electronic devices such as light emitting devices, field-effect transistors, and photovoltaics.[1] While a majority of studies have focused on acenes such as pentacene and its derivatives (e.g., **1**; Scheme 1),[2] these systems are susceptible to oxidative and photolytic degradation;[3] thus, there is a need for alternative, acene-like molecules. One avenue in this search has explored compounds containing five-membered rings, rather than the more traditional six-membered rings. Prime examples of such molecules are dibenzopentalene (**2**) and derivatives thereof, wherein the groups of Saito, Kawase, and Tilley have recently described improved methods for their construction.[4]

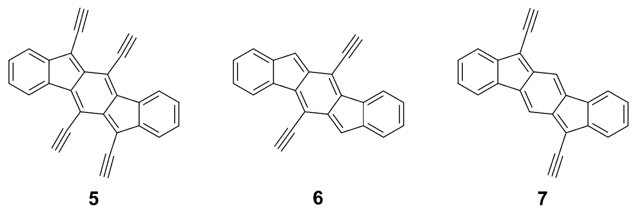


Scheme 1. Structures **1**–**4**. TIPS = triisopropylsilyl.

Another attractive topology is the indeno[1,2-*b*]fluorene (IF) skeleton (e.g., **3**), an acene analogue in which the B and D rings each contain one fewer carbon atom, thus making the 20-π-electron molecule formally antiaromatic. While the pentacyclic IF framework is common in the literature, nearly all examples bear substituents on the 6- and 12-positions, thus resulting in either cross-conjugation (e.g., ketones, exocyclic olefins)[5] or disrupted conjugation (e.g., disubstitution, spirofusion).[6] Of the four fully conjugated IFs known prior to 2011, three are rapidly oxidized by trace amounts of oxygen[7] and the other is poorly characterized.[8]

Very recently we reported the synthesis of tetraalkynylated indeno[1,2-*b*]fluorenes (e.g., **4**).[9] The compounds exhibited similar UV/Vis absorption profiles and slightly larger HOMO/LUMO energy gaps compared to those of **1** while maintaining potentially superior solution stabilities; however, the packing of **4** in the solid state resembled an expanded herringbone pattern, a motif often found in unsubstituted acenes. Since the steric bulk of the four interdigitated (triisopropylsilyl)ethynyl groups was the most likely cause for inhibiting a desirable "brick and mortar" π stacking, we sought to examine additional IF derivatives.[10]

As a guide for experimental studies, we performed DFT calculations (B3LYP/6-311 + G**[11] using Gaussian 09)[12] on substituted IFs to determine the effect ethynylogation of **3** has on the HOMO (−5.53 eV) and LUMO (−3.03 eV) energy levels, and the energy gap (2.50 eV) of the IF core (Scheme 2, Table 1). Inclusion of the four ethynyl units in **5** significantly lowers the LUMO by approximately 0.5 eV while the HOMO remains unchanged, thus affording a gap energy of 1.97 eV. Inclusion of only two acetylenes at positions 5 and 11 (e.g., **6**) slightly lowers the HOMO yet significantly raises the LUMO compared to **5**, thus affording a net gap increase of 0.41 eV. If the two alkynes are located at positions 6 and 12, as in **7**, the HOMO (−5.51 eV) is on par with that of **5** (−5.53 eV) and the LUMO is elevated slightly (−3.46 eV versus −3.56 eV), thus increasing the gap by only 0.08 eV. Similar to acenes,[2] these results illustrate that judicious positioning of the alkyne moieties will significantly affect the electronic and photophysical properties. Encouraged by these initial computational studies, we targeted a number of 6,12-diethynylindeno[1,2-*b*]fluorenes for synthesis and study. We disclose herein the preparation of IFs **8a**–**i** along with their respective optical, electrochemical, and computational data. We also report the X-ray structures of **8b** and **8h**, thereby highlighting the effects that substitution on the IF core has upon crystal packing.



Scheme 2. Calculated ethynylindenofluorene derivatives.

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[**] The authors gratefully acknowledge the National Science Foundation (CHE-1013032) for support of this research; see the Supporting Information for the full acknowledgement.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201104797.

Table 1: Computational, electrochemical, and optical data for indeno[1,2-*b*]fluorene derivatives.

Compd	Computational[a]			Electrochemical[b]					Optical	
	E_{HOMO}	E_{LUMO}	E_{Gap}	E (A^+/A)	E (A/A^-,A^-/A^{2-})	E_{HOMO}	E_{LUMO}	E_{Gap}	λ_{max}[c]	E_{Gap}[d]
3	−5.53	−3.03	2.50	–	–	–	–	–	–	–
4/**5**[e]	−5.53	−3.36	1.97	1.23	−0.62, −1.16	−5.92	−4.07	1.85	594	1.98
6	−5.62	−3.24	2.38	–	–	–	–	–	–	–
7	−5.51	−3.46	2.05	–	–	–	–	–	–	–
8a	−5.51	−3.46	2.05	1.20	−0.69, −1.20	−5.88	−4.00	1.89	568	2.12
8b	−5.79	−3.70	2.09	1.33	−0.60, −1.07	−6.01	−4.08	1.93	561	2.15
8c	−5.82	−3.74	2.08	1.35	−0.59, −1.07	−6.03	−4.09	1.94	567	2.13
8d	−5.83	−3.75	2.08	1.32	−0.60, −1.10	−6.01	−4.09	1.92	567	2.13
8e	−5.43	−3.36	2.07	1.16	−0.69, −1.27[f]	−5.84	−3.99	1.85	569	2.11
8f	−5.53	−3.47	2.06	1.21	−0.66, −1.20[f]	−5.90	−4.03	1.87	570	2.10
8g	−5.81	−3.75	2.06	1.25	−0.62, −1.11	−5.93	−4.06	1.87	572	2.11
8h	−5.97	−3.91	2.06	1.35	−0.52, −1.00	−6.03	−4.16	1.87	570	2.11
8i	−5.89[g]	−3.83[g]	2.06[g]	–[h]	–[h]	–[h]	–[h]	–[h]	577	2.08
PCBM[i]	–	–	–	1.54	−0.71, −1.12	−6.2	−3.95	2.25	–	–

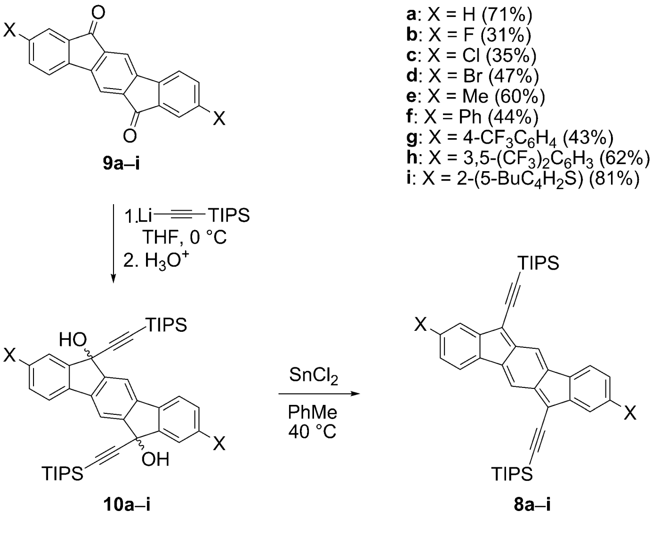
[a] Calculations performed at the B3LYP/6-311 + G** level of theory; energies in eV. For computational efficiency, the TIPS groups of **8a-i** were replaced by H atoms. [b] CV recorded using 1–5 mM of analyte in 0.1 M Bu_4NOTf/CH_2Cl_2 using a scan rate of 50 $mV s^{-1}$. The working electrode was a glassy carbon electrode with a Pt coil counter electrode and Ag wire pseudo reference. Values reported as the half-wave potential (vs. SCE) using the Fc^+/Fc couple (0.46 V) as an internal standard. HOMO and LUMO energy levels were approximated using SCE = −4.2 eV vs. vacuum; see Ref. [5b]. Reduction potentials in V; energies in eV. [c] Spectra obtained in $CHCl_3$; wavelength in nm. [d] The optical HOMO–LUMO gap was determined as the intersection of the x-axis and a tangent line that passes through the inflection point of the lowest energy absorption; energies in eV. [e] Experimental data for **4**; computational data for **5**. [f] The second reduction wave was irreversible; the potential of the peak anodic current is reported. [g] Me group in place of Bu to simplify calculations. [h] Unable to obtain. [i] Converted from Ref. [17].

Because the transannular cyclization route previously used to synthesize the IF skeleton was low yielding, intolerant of facile substitution, and difficult to scale up,[7,9,13] we sought a more efficient pathway. Fortunately, dione **9a** can be synthesized on a multigram scale by a three-step Suzuki/Friedel–Crafts route devised by Merlet et al.[14] Addition of lithiated (triisopropylsilyl)acetylene afforded the crude diol **10a** (Scheme 3). Subsequent reduction using $SnCl_2$ in toluene at 40 °C provided a deep magenta solution, from which the purple IF **8a** was isolated in very good yield and in up to gram quantities. This methodology could be extended to a variety of 2,8-disubstituted IFs starting from the respective diones, either known (**9b**–**d**[15]) or easily synthesized (**9e**–**i**; see the Supporting Information). The IFs **8b**–**i** were prepared by the same two-step process and isolated in moderate to very good yields after recrystallization.

The absorption spectra of the IFs **4** and **8a**,**b**,**i** are shown in Figure 1 (see the Supporting Information for the spectra of **8c**–**h**). Similar to **4**, **8a** exhibits three low-energy absorptions (λ_{max} = 567 nm), but these are blue-shifted by approximately 25–30 nm compared to those of **4**. This can be attributed to removal of the two acetylenes at the 5 and 11 positions, as in **8a**.

Interestingly, variation of the substituents bound to the IF core at the 2 and 8 positions has only a modest effect on the absorption profiles: the fluoro IF **8b** has the lowest λ_{max} value of 561 nm, whereas the λ_{max} value of the thienyl IF **8i** is at 577 nm. The optical data correspond to a relatively narrow 2.08–2.15 eV range for the HOMO–LUMO energy gaps of **8a**–**i**. As observed with **4**, **8a**–**i** are non-emissive, which is usually the case with [4*n*]-π-electron systems.

Figure 2 depicts the experimental cyclic voltammetry (CV) data for **4** and **8a**,**b**,**h** (see the Supporting Information for the CV data for **8c**–**g**). In solution, the IF diyne scaffold shows quasireversible behavior, that is, accepting up to two electrons. The first reduction half-wave potential at approximately −0.5 to −0.7 V (vs. SCE) for **8a**–**h** is 0.2–0.3 V less negative than that of the recently reported diynyl IF diones.[13] These data suggest that IFs might have comparable or greater electron affinities to that of the ubiquitous electron-acceptor



Scheme 3. Synthesis of the diethynyl IFs **8a**–**i**. THF = tetrahydrofuran.

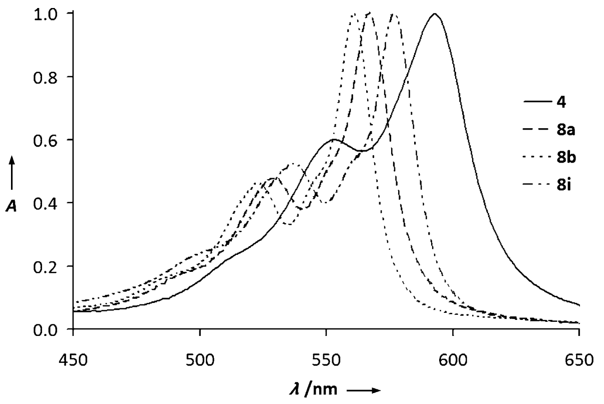


Figure 1. Electronic absorption spectra for the IFs **4** and **8a**,**b**,**i**.

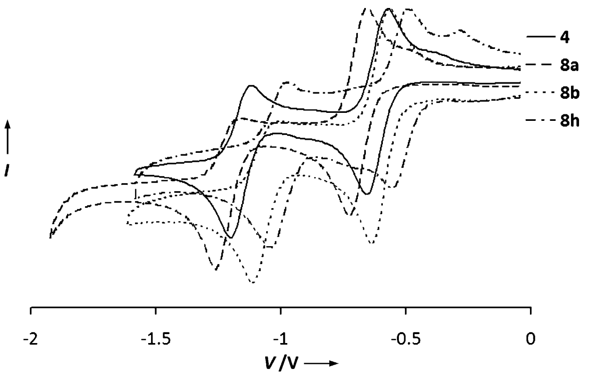


Figure 2. Cyclic voltammetry of the IFs **4** and **8a,b,h**; voltammogram currents are normalized to the E_{pa} (A/A$^-$) peak.

[6,6]-phenyl C61 butyric acid methyl ester (PCBM).[16,17] Substitution of electron-withdrawing groups on the IF core shifts the reduction half-wave potentials to less-negative values. This is chiefly observed with the parent **8a**, fluoro **8b**, and 3,5-$(CF_3)_2C_6H_3$ **8h**, which possess first reduction half-wave potentials of −0.69, −0.60, and −0.52 V, respectively. This trend is also seen for the second reduction half-wave potentials of −1.20, −1.07, and −1.00 V for **8a**, **8b**, and **8h**, respectively. Unlike the IF diones,[13] **8a–h** also exhibit an irreversible oxidation around 1.2–1.3 V (see the Supporting Information). In addition, the above-mentioned trend holds true for the oxidation half-wave potentials of the IF scaffold: substitution of increasingly electron-withdrawing groups shifts the half-wave potentials to the more positive values of 1.20, 1.33, and 1.35 V for **8a**, **8b**, and **8h**, respectively. This behavior is justified by examining the products of reduction or oxidation: a two-electron reduction of the IF core results in a 22-π-electron species wherein every ring is aromatic, that is, three benzenes and two Cp anions. Hence, increasing substituent electron affinity better stabilizes the dianion. Conversely, the formation of the oxidative products, especially the 18-π-electron dication, is destabilized by electron-withdrawing groups. The sole exception to the above-mentioned general behavior is **8i**, which exhibits an irreversible reduction and polymerizes under oxidative conditions.

Interestingly, while the electrochemically determined energy gaps are somewhat lower (1.85–1.94 eV) than the optical and computational values, all three data sets exhibit a less-than 0.1 eV range of values, whether substituted with electron-rich or electron-poor groups. Examination of the calculated HOMO/LUMO plots for **8a** (see the Supporting Information) reveals that the 2- and 8-positions possess little orbital density, and hence exhibit virtually no overlap; thus, perturbing the electronic nature of the IF scaffold from these positions can be performed only through weak inductive effects.

Single crystals of **8b** and **8h** suitable for X-ray diffraction were obtained from CH_2Cl_2/CH_3CN (1:1) and $CHCl_3$, respectively (Figure 3).[18] Similar to **4**, the molecular structures of **8b** and **8h** show that the fused ring system is essentially planar (within 0.017 and 0.042 Å, respectively); however, unlike **4**, the TIPS-capped acetylenes in both species are nearly linear (179°) and planar (0.5° deviation) with the 20-carbon-atom core, which is due to the fact that these lack the steric congestion that **4** possesses. Molecules **8b** and **8h** still retain the distinct *p*-xylylene unit within the IF core, but the C−C bonds in the central six-membered ring are slightly compressed (ca. 0.02 Å) compared to those of **4**.[9] In the crystal lattice **8b** and **8h** are arranged as one-dimesional (1D) π stacks with close C···C contacts of 3.43 and 3.40 Å, respectively. The 1D π stacks in **8b** form a layer with a shift between two nearest π stacks. Such an arrangement avoids strong π interactions between the π stacks in the layers, but some of C···C contacts between the 1D π stacks are in the range of 3.41–3.50 Å, thus indicating that weak interactions between the 1D π stacks in **8b** are possible. In contrast, the 1D π stacks in the crystal of **8h** are isolated without specific interstack interactions between them. Additionally, the peripheral 3,5-$(CF_3)_2C_6H_3$ groups for **8h** are nearly coplanar with the IF core, thus exhibiting a slight 5.5° twist, which is much less than the 35–45° torsion angle typically seen in biphenyls.[19] This unexpected co-planarity is likely due to the enhanced overlap the phenyl rings provide as they lay directly above and below the central arene of the neighboring molecules as well as the interdigitation of two electron-deficient CF_3 groups with electron-rich alkynes (3.50 Å intermolecular distance).

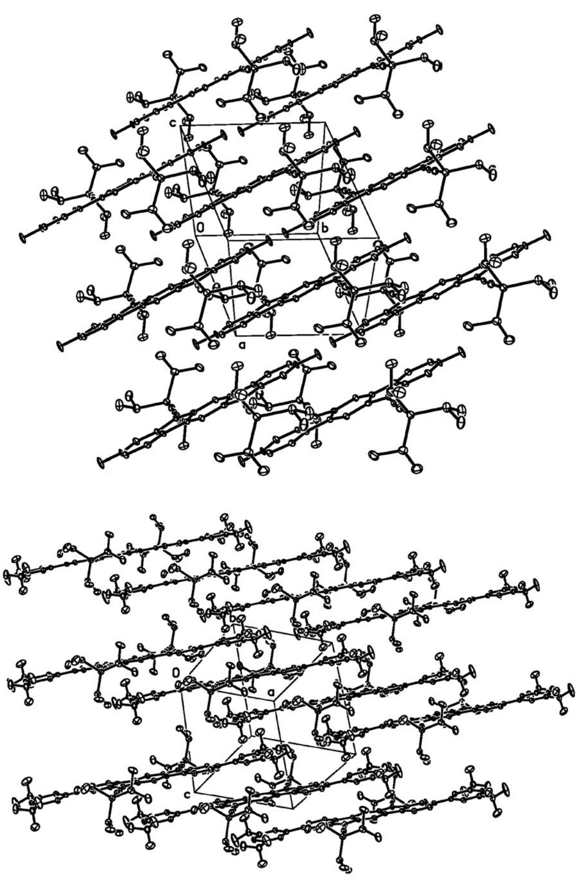


Figure 3. Crystal packing of the diethynyl IFs **8b** (top) and **8h** (bottom). Thermal ellipsoids drawn at the 30% probability level.

In summary, we have demonstrated a facile synthetic approach to a family of fully conjugated indeno[1,2-*b*]fluorenes. The optical and electrochemical data support the computational findings of low-lying HOMO and LUMO energy levels for **8a–i**, which are attributable to the formally antiaromatic [4*n*]-π-electron core IF structure. These values are similar to those of other small-molecule n-type semiconductors,[20] which unlike the IFs generally require inclusion of multiple strong electron-withdrawing groups. Through X-ray crystallography, **8b** and **8h** were shown to pack in 1D π stacks in the solid state. Together these results suggest that IFs could be potential complements to the usually p-type acenes. Future work will consist of employing **8a–i** in devices to test their performance as n-type organic semiconductors, as well as exploring additional derivatization of the indeno[1,2-*b*]fluorene scaffold.

Received: July 10, 2011

Keywords: aromaticity · electron acceptors · hydrocarbons · polycycles

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[18] X-ray data for **8b**: $C_{42}H_{50}F_2Si_2$, $M_r = 649.00$, $0.23 \times 0.19 \times 0.03$ mm, triclinic, $P\bar{1}$ (N 2), $a = 7.585(3)$, $b = 7.910(3)$, $c = 16.802(6)$ Å, $\alpha = 86.918(5)$, $\beta = 84.113(6)$, $\gamma = 68.699(5)°$, $V = 934.2(5)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.154$ g cm^{-1}, $\mu = 0.132$ mm^{-1}, $2\theta_{max} = 50.00°$, $T = 173(2)$ K, 8788 measured reflections, 3278 independent reflections [$R_{int} = 0.0669$], 208 independent refined parameters, $R1 = 0.0714$, $wR2 = 0.1545$ (with $I > 2\sigma(I)$), $R1 = 0.1165$, $wR2 = 0.1818$ (all data), GOF = 1.067, max/min residual electron density $+0.539/-0.319$ e Å^{-3}. X-ray data for **8h**: $C_{58}H_{56}F_{12}Si_2$, $M_r = 1037.21$, $0.37 \times 0.05 \times 0.02$ mm, triclinic, $P\bar{1}$ (N 2), $a = 9.268(2)$, $b = 11.807(3)$, $c = 12.531(3)$ Å, $\alpha = 80.996(4)$, $\beta = 79.842(4)$, $\gamma = 76.792(4)°$, $V = 1304.4(5)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.320$ g cm^{-1}, $\mu = 0.149$ mm^{-1}, $2\theta_{max} = 50.00°$, $T = 173(2)$ K, 12578 measured reflections, 4559 independent reflections [$R_{int} = 0.0558$], 437 independent refined parameters, $R1 = 0.0591$, $wR2 = 0.1127$ (with $I > 2\sigma(I)$), $R1 = 0.1017$, $wR2 = 0.1311$ (all data), GOF = 1.053, max/min residual electron density $+0.330/-0.263$ e Å^{-3}. CCDC 833037 and 833038 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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