ORGANIC LETTERS

2013
Vol. 15, No. 6
1362–1365

Indeno[2,1-*c*]fluorene: A New Electron-Accepting Scaffold for Organic Electronics

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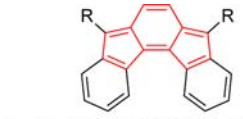
Received February 3, 2013

ABSTRACT



R = Mesityl, 3,5-$(CF_3)_2C_6H_3$, CCSi*i*-Pr_3

A new class of fully conjugated indenofluorenes has been synthesized and confirmed by solid-state structure analysis. These indeno[2,1-*c*]fluorene molecules, containing an antiaromatic *as*-indacene core (in red), possess high electron affinities and show a broad absorption that reaches into the near-IR region of the electromagnetic spectrum. All of the featured compounds reversibly accept up to two electrons. Their electronic properties make this class of compounds attractive for applications in organic electronic devices.

Organic electronic devices are becoming commonplace in many academic and industrial materials laboratories, and commercial application of these technologies is underway.[1] To maximize our understanding of organic electronics, a wide array of molecular frameworks is necessary, as it allows for a variety of optical and electronic properties to be systematically investigated.[2] With the ability to further tune each individual scaffold via derivatization, access to a broad spectrum of interesting materials is possible.[2,3]

Of particular interest in the search for organic electronic materials are the cyclopenta-fused polyaromatic hydrocarbons (CP-PAHs, e.g., fullerenes,[4] buckybowls[5]).[6] The cyclopentadiene rings within these compounds impart a higher electron affinity because of the driving force to aromatize the cyclopentadiene by accepting an electron. Another family of cyclopenta-fused molecules under investigation is based on the fully conjugated indenofluorene (IF) system,[7] which is comprised of five structural isomers (e.g., **1**–**5**, Figure 1).

To date nearly all reported studies have focused on derivatives of **2** (25+ examples),[8,9] as well as derivatives of **3** (2 examples).[10] Importantly, the [1,2-*b*]IF scaffold can serve as an electron-accepting or ambipolar material for organic electronics, with derivatives of **2** showing

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10.1021/ol400318z
Published on Web 03/05/2013

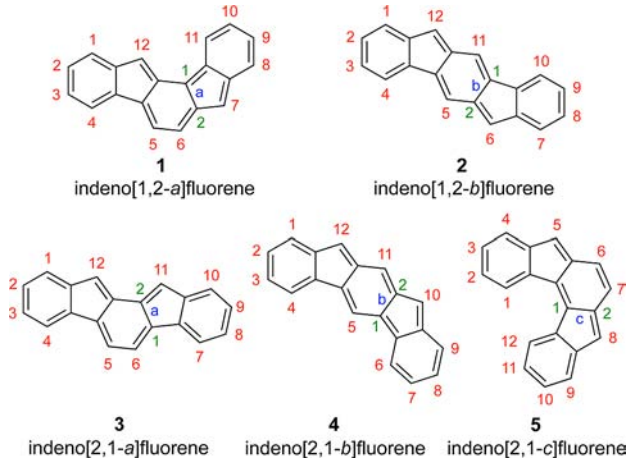


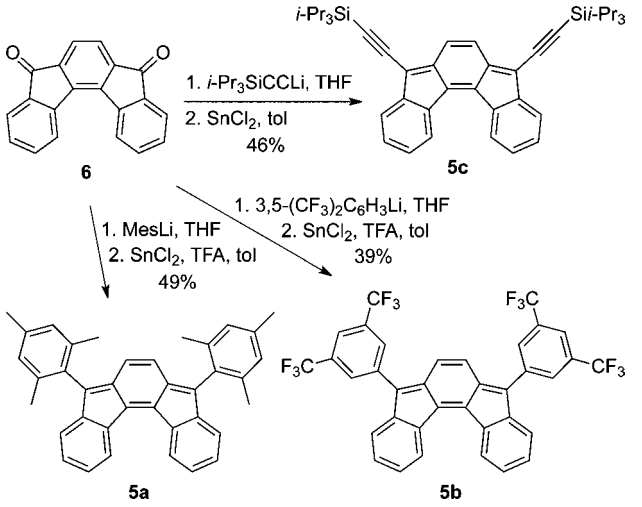
Figure 1. Five possible indenofluorene regioisomers **1**–**5**.

ambipolar transport in both a single crystal OFET[8c] and thin-film OFETs.[9c] Of the remaining unknown regioisomers, formation of IFs **1** and **4** will dearomatize an internal *and* a peripheral benzene to achieve closed-shell structures; thus, we anticipate the resultant molecules would be considerably less stable than **2**. Like **2**, the formation of **5** requires dearomatization of only one internal benzene ring, and the immediate IF-dione precursor is easily accessible in multigram quantities in four steps from cheap, commercially available precursors.[11] Reported herein are the synthesis and charcterization of three derivatives of the fully conjugated indeno[2,1-*c*]-fluorene scaffold ([2,1-*c*]IF, **5**).

Realization of target molecules **5a**–**c** occurs by nucleophilic attack on dione **6** with either an aryl or ethynyl lithiate and subsequent reductive dearomatization with anhydrous $SnCl_2$ (Scheme 1), producing the desired compounds in moderate yields after purification. Unlike the [1,2-*b*]IFs and [2,1-*a*]IFs, which are blue/purple in solution, [2,1-*c*]IFs **5a**–**c** are green in solution and green/black in the solid state.

The UV–vis spectra of **5a**–**c** (Figure 2) display strong absorbances in the higher energy range, with a broad, low energy absorbance that extends into the near-IR region. Interestingly, these broad low-energy bands (550–800 nm) are similarly observed in the spectrum of 11,12-dimesityl[2,1-*a*]IF (**3a**),[10b] which also possesses

Scheme 1. Synthesis of Indeno[2,1-*c*]fluorenes **5a**–**c**



the *as*-indacene core. This is in contrast to the spectra of [1,2-*b*]IFs, which are based on the *sym*-indacene skeleton, as the lowest energy peak of the derivatives of **2** to date has been less than 615 nm.[8,9] Similar to other fully conjugated IFs, **5a**–**c** are nonemissive.

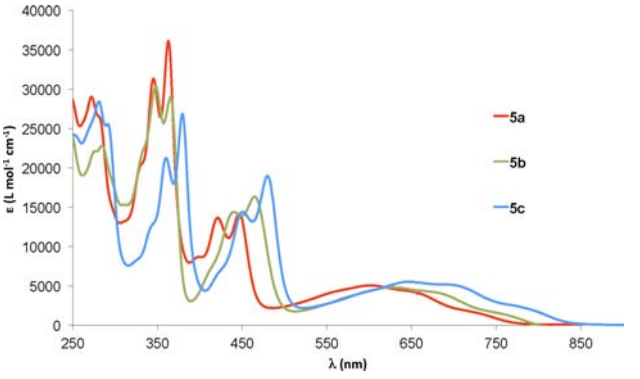


Figure 2. Electronic absorption spectra of [2,1-*c*]IFs **5a**–**c**.

Single crystals of **5a** suitable for X-ray diffraction were obtained via slow crystallization from toluene. The resultant structure solution (Figure 3) shows that the molecule packs in two symmetrically independent arrangements, with each molecule bent slightly out of plane. The two independent molecules possess helicene-like axial chirality, but the barrier to inversion is extremely small, calculated to be 0.02 kcal mol^{-1}.[12,13] Dihedral angles between the

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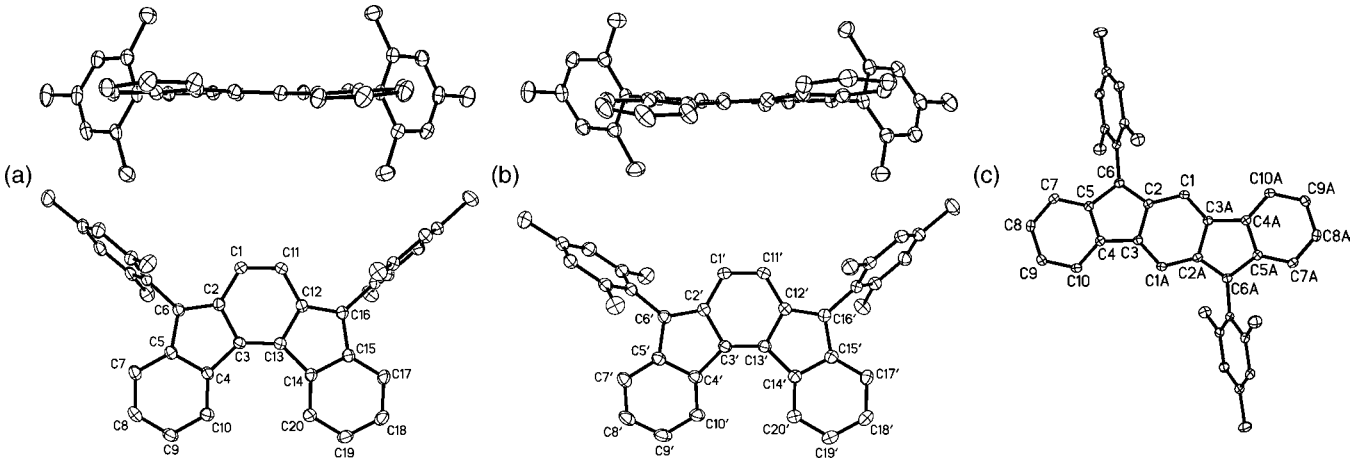

Figure 3. X-ray structure of **5a** (two crystallographically independent molecules); side and top view of the (a) P-helicene and (b) M-helicene. (c) X-ray structure of 6,12-dimesitylindeno[1,2-*b*]fluorene (**2a**) for comparison. Ellipsoids drawn at the 30% probability level, and H-atoms omitted for clarity.

average planes of the central six-membered ring, the bridging five-membered ring, and the terminal six-membered ring of the P-isomer of **5a** are 2.26(5)°, 4.32(5)° and 1.98(5)°, 2.40(6)°, respectively; the corresponding angles in the M-isomer are 4.78(7)°, 6.63(6)° and 4.67(8)°, 3.66(8)°. There is no cofacial packing within the crystal lattice, and the closest interplanar contact distance (C9′−C20) is 3.47 Å.

While both the [2,1-*a*]IFs and [2,1-*c*]IFs contain the *as*-indacene core, the [2,1-*a*]IF possesses the reactive *o*-quinodimethane motif. For structural comparison, we chose the two independent molecules of **5a** and 6,12-dimesityl[1,2-b]IF **2a**[8c] as both incorporate a central *p*-quinodimethane unit. As can be seen in Table 1, there

Table 1. Select Bond Lengths (Å) of IFs **2a** and **5a**

bond[a,b]	**5a**-*P* (left)	**5a**-*M* (center)	**2a** (right)[c]
C1−C2	1.428(2)	1.439(2)	1.433(3)
C1−C11	1.359(2)	1.355(2)	1.356(2)[d]
C2−C3	1.472(2)	1.468(2)	1.467(2)
C2−C6	1.371(2)	1.370(2)	1.380(2)
C3−C4	1.482(2)	1.474(2)	1.469(3)
C3−C13	1.367(2)	1.364(2)	1.356(2)[e]
C4−C5	1.414(2)	1.413(2)	1.413(2)
C5−C6	1.468(2)	1.464(2)	1.471(2)
C11−C12	1.434(2)	1.433(2)	1.433(3)
C12−C13	1.471(2)	1.469(2)	1.467(2)
C12−C16	1.371(2)	1.377(2)	1.380(2)
C13−C14	1.483(2)	1.475(2)	1.469(3)
C14−C15	1.415(2)	1.419(2)	1.413(2)
C15−C16	1.464(2)	1.461(2)	1.471(2)

[a] Numbering scheme shown in Figure 3. [b] Due to symmetry, atoms C1A to C10A in **5** correspond to atoms C11 to C20 in **2**. [c] See ref 8c. [d] C1−C3A in **2a**. [e] C3−C1A in **2a**.

is very little difference in the quinoidal bond lengths between molecules. For example, C1−C11 in **5a** (1.359/1.355 Å) is essentially identical to C1−C3A in **2a** (1.356 Å), whereas C3−C13 (1.367/1.364 Å) is marginally longer. The quinoidal "double bonds" in the five-membered ring of **5a** (C2−C6, avg 1.371 Å; C12−C16, avg 1.374 Å) are slightly shorter than those found in **2a** (C2−C6, 1.380 Å). The structural similarity of the two IF skeletons extends to the bonds in the peripheral arene rings, where the homogeneous bond lengths (avg 1.387 Å for **5a**, 1.389 Å for **2a**) clearly suggest retention of their aromatic character. Only the bond shared with the five-membered ring (C4−C5) shows a slight elongation from that of a typical aryl subunit. Despite the presence of the *p*-quinodimethane moiety, calculations reveal that the scaffold exists as a closed shell ground state and has little biradical character.[14]

Cyclic voltametry (CV) data indicate that **5a**−**c**, like the [1,2-*b*]IFs and [2,1-*a*]IFs, are electron deficient (Figure 4, Table 2). The molecules can reversibly accept up to two electrons and possess LUMO energies estimated at −3.6 to −4.0 eV, analogous to those found in derivatives of **2**;[8b,c] however, the HOMO energies of **5a**−**c** are roughly 0.15 eV higher, thus leading to reduced gap energies compared to their identically substituted analogs of **2** (e.g., 1.89 eV for **2c** vs 1.73 eV for **5c**).[8b,c] These results suggest that **5a**−**c** could be good candidates for use as *n*-type organic semiconducting materials with low threshold voltages.[3,15]

In conclusion, we have synthesized and characterized a short series of [2,1-*c*]IF derivatives. The ease of manufacture, high electron affinities, and small HOMO−LUMO energy gaps of these new molecules should make this class

(14) Broken symmetry UB3LYP/6-311+G(2df,2pd) was used to determine biradical character; see Supporting Information.

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Table 2. Optical and Electrochemical Data of Indeno[2,1-*c*]fluorenes **5a**–**c**

	electrochemical						optical		
compd	E_{red}^1 (V)[a]	E_{red}^2 (V)[a]	E_{ox} (V)[a]	E_{LUMO} (eV)[b]	E_{HOMO} (eV)[b]	E_{gap} (eV)	λ_{max} (nm)	ε ($\times 10^4$ L·M^{-1}·cm^{-1})	E_{gap} (eV)[c]
5a	−1.05	−1.51	1.02	−3.63	−5.70	2.08	345, 363, 421, 447, 603	3.13, 3.61, 1.37, 1.42, 0.51	1.60
5b	−0.71	−1.02	—[d]	−3.97	—[d]	—[d]	348, 365, 441, 465, 627	3.04, 2.90, 1.44, 1.64, 0.49	1.54
5c	−0.66	−1.11	1.07	−4.02	−5.75	1.73	360, 380, 451, 480, 647	2.12, 2.68, 1.44, 1.90, 0.55	1.48

[a] CV data recorded using 1–5 mM of analyte in 0.1 M Bu_4NOTf in 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 pseudoreference. Values reported as the half-wave potential (vs SCE) using the Fc/Fc^+ couple (0.46 V) as an internal standard; see ref 16. [b] HOMO and LUMO energy levels in eV were approximated using SCE = −4.68 eV vs vacuum; see ref 17. [c] Determined using the wavelength at the maximum absorption of the lowest energy $\pi \rightarrow \pi^*$ transition from the UV–vis spectrum. [d] Reversible oxidation of **5b** was not achieved.

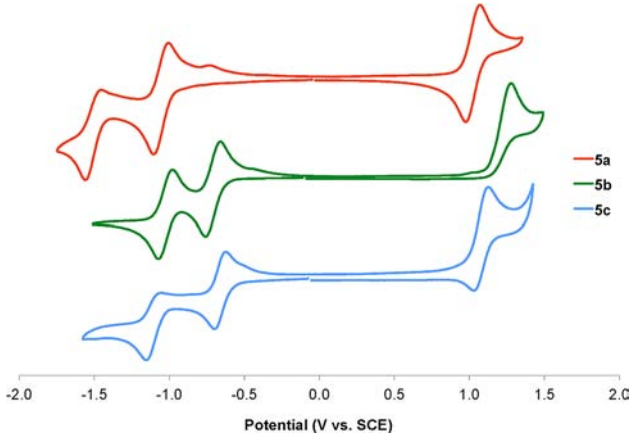

Figure 4. CV data of [2,1-*c*]IFs **5a**–**c**; voltammogram currents are normalized to the E_{pa} (A/A^-)peak.

of cyclopenta-fused hydrocarbons attractive candidates for application in a variety of organic electronic devices. We are currently exploring the preparation of additional fully conjugated indeno[2,1-*c*]fluorenes as well as device studies with these new electron-accepting materials.

Acknowledgment. We thank the National Science Foundation (CHE-1013032) for supporting this research as well as support in the form of instrumentation (CHE-0923589) and computer grants (OCI-0960354). B.D.R. acknowledges the ACS-DOC for the Emmanuil Troyansky Fellowship (2012-2013). We thank Prof. Mark Lonergan (University of Oregon) for use of his group's potentiostat.

Supporting Information Available. Experimental and computational details; NMR spectra of **5a**–**c**; X-ray cif file of **5a**; complete ref 12. This material is free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.