

Synthesis, Crystal Structures, and Photophysical Properties of Electron-Accepting Diethynylindenofluorenediones

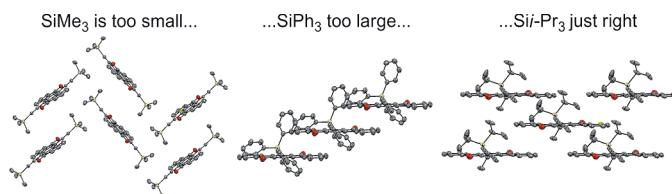
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ABSTRACT



A series of 6,12-bis[(trialkylsilyl)ethynyl]indeno[1,2-*b*]fluorene-5,11-diones has been synthesized. X-ray crystallographic analysis of these compounds reveals that triisopropylsilyl (TIPS) substitution on the alkyne terminus affords the largest number of intermolecular π – π interactions in the solid state. Conversely, use of trialkylsilyl groups smaller or larger than TIPS furnishes a variety of crystal-packing motifs that contain fewer π – π interactions. Electrochemical and photophysical data suggest that these molecules are excellent electron-accepting materials.

Conjugated hydrocarbons with extended polycyclic frameworks possess a rich history because of the fundamental, inherent properties (e.g., aromaticity, color, fluorescence) attributable to such structures.¹ More recently, these molecules as well as their heteroatom-containing analogues have been explored as organic materials² for applications in electronic devices such as photovoltaics, field-effect transistors, and light-emitting diodes.³ An important indicator of potential device performance when using organic molecules is the solid-state ordering of the material, which is

currently difficult to predict using theoretical modeling.^{3d} It is well-known that the mobilities of holes (for p-type) or electrons (for n-type) in solid-state organic materials are increased when both the intermolecular overlap of the π orbitals is maximized and those orbitals are in phase.^{3c}

In recent years, there has been considerable interest in the indenofluorene (IF) framework as an n-type material because of the planarity of the IF skeleton and its ability to reversibly accept electrons.⁴ Our laboratory has been examining alkynylated, fully conjugated indeno[1,2-*b*]fluorenes (e.g., **1**),⁵ which are derived from indenofluorene-5,11-diones (IF-diones) such as **2**.⁶ Prior work by

(1) (a) Balaban, A. T.; Banciu, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo- Derivatives and their Valence Isomers*; CRC Press: Boca Raton, 1987. (b) Hopf, H. *Classics in Hydrocarbon Chemistry*; Wiley-VCH: Weinheim, 2000.

(2) (a) *Functional Organic Materials*; Müller, T. J. J., Bunz, U. H. F., Eds.; Wiley-VCH: Weinheim, 2007. (b) *Organic Light Emitting Devices: Synthesis, Properties and Applications*; Müllen, K., Scherf, U., Eds.; Wiley-VCH: Weinheim, 2006. (c) *Carbon-Rich Compounds: From Molecules to Materials*; Haley, M. M., Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, 2006.

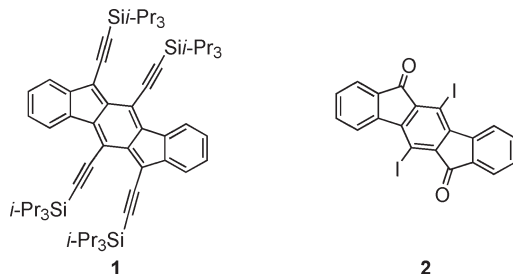
(3) (a) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365–377. (b) Dong, H.; Wang, C.; Hu, W. *Chem. Commun.* **2010**, 5211–5213. (c) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. *Adv. Mater.* **2010**, *22*, 3876–3892. (d) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L. *Chem. Rev.* **2007**, *107*, 926–952. (e) Facchetti, A. *Mater. Today* **2007**, *10*, 28–37.

(4) Inter alia: (a) Jacob, J.; Sax, S.; Piok, T.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 6987–6995. (b) Hadizad, T.; Zhang, J.; Wang, Z. Y.; Gorjanc, T. C.; Py, C. *Org. Lett.* **2005**, *7*, 795–797. (c) Miyata, Y.; Minari, T.; Nemoto, T.; Isoda, S.; Komatsu, K. *Org. Biomol. Chem.* **2007**, *5*, 2592–2598. (d) Nakagawa, T.; Kumaki, D.; Nishida, J.-i.; Tokito, S.; Yamashita, Y. *Chem. Mater.* **2008**, *20*, 2615–2617. (e) Usta, H.; Risko, C.; Wang, Z.; Huang, H.; Delimeroglu, M. K.; Zhukhovitskiy, A.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 5586–5608.

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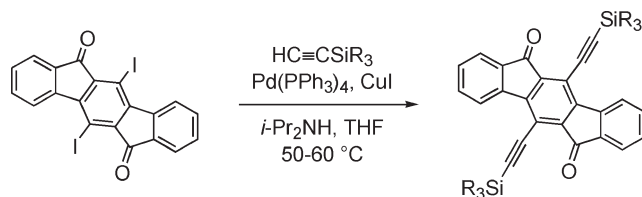
(6) Zhou, Q.; Carroll, P. J.; Swager, T. M. *J. Org. Chem.* **1994**, *59*, 1294–1301.

Anthony et al. has explored the relationship between alkylation and crystal packing for acene derivatives.⁷ We recognized that, starting from **2**, we could perform a similar detailed study on IF-diones. To this end, we report herein the synthesis and photophysical properties of alkynylated IF-diones **3–8** as well as solid-state structures of **3**, **6**, and **8**.



Compounds **3–8** were synthesized in low to moderate yields by Sonogashira cross-coupling of the appropriate (trialkylsilyl)acetylene with **2** (Scheme 1). One possible explanation for the low isolated yields is the lability of

Scheme 1. Synthesis of Alkynylated Indenofluorenediones



2	3–8		
compd	SiR ₃	SiR ₃ radius (Å) ^a	isolated yield (%)
3	SiMe ₃	2.38	40
4	SiEt ₃	3.75	8
5	Si <i>t</i> -BuMe ₂	2.42 ^b , 3.69 ^c	17
6	Si <i>i</i> -Pr ₃	3.78	61
7	Si <i>i</i> -Bu ₃	4.99	7
8	SiPh ₃	5.62	15

^a Measured using the internuclear distance from the silicon to the farthest atom of R. ^b Si–Me distance. ^c Si–*i*-Pr distance.

iodine atoms of **2**. Solutions of **2** at elevated temperatures turn pale violet, characteristic of iodine formation; however, the Sonogashira reaction proceeds sluggishly at temperatures less than 50 °C.

Orange single crystals of **3** and **6** suitable for X-ray diffraction were grown by slow cooling of hot hexanes solutions of the IF-diones, whereas **8** was recrystallized by slow evaporation from a binary combination of THF and hexanes. Similar to conjugated systems such as acenes, the IF-diones exhibit three types of packing in the solid state: (i) herringbone packing (e.g., **3**, Figure 1a), (ii) one-dimensional columns without π – π interactions (e.g., **8**, Figure 1b), and (iii) coplanar slip stacking (e.g., **6**,

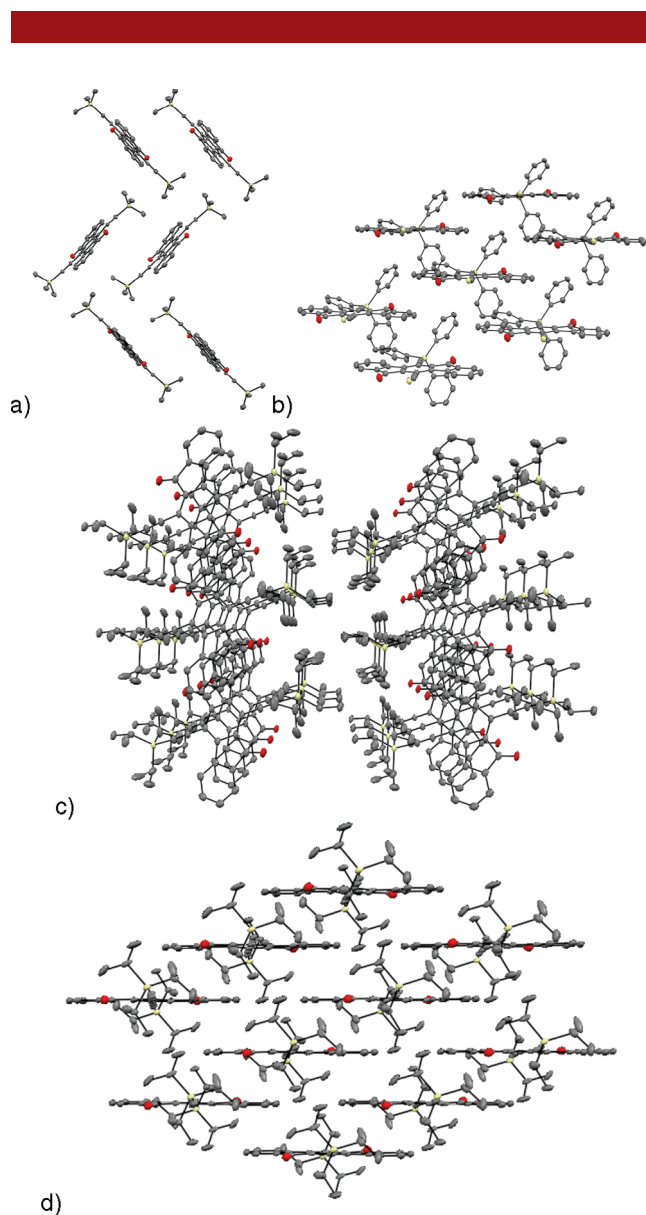


Figure 1. Crystal packing of IF-diones illustrating (a) herringbone (**3**), (b) 1-D columns without π – π interactions (**8**), and (c) coplanar slip stacking (**6**). (d) A side view of **6** shows the favorable brick and mortar packing. Thermal ellipsoids drawn at the 30% probability level.

Figure 1c and d). This last arrangement, also known as brick and mortar packing, was found only in **6** and maximizes the π – π interactions in two dimensions (Figure 1d) with an interplanar distance of 3.40 Å, in contrast to the interplanar distance of 3.77 Å in **8**. The situation for **6** is reminiscent of 6,13-bis[(triisopropylsilyl)ethynyl]pentacene, which showed coplanar slip stacking as well.⁷ Anthony attributed this phenomenon to the diameter of the triisopropylsilyl (TIPS) group being close to the stack spacing needed for intermolecular π – π interactions (3.4 Å).^{7b} Interestingly, previous crystal structures of IF-diones have also displayed herringbone packing with slip-stacked one-dimensional π – π interactions,^{4c} lamellar one-dimensional stacks,^{4d} or essentially no π – π interactions.^{4c}

(7) (a) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482–9483. (b) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15–18. (c) Purushothaman, B.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2010**, *12*, 2060–2063.

Another important consideration is the phase as well as the amount of orbital overlap in the crystal lattice (vide supra). As can be seen in Figure 2, the semiempirical single

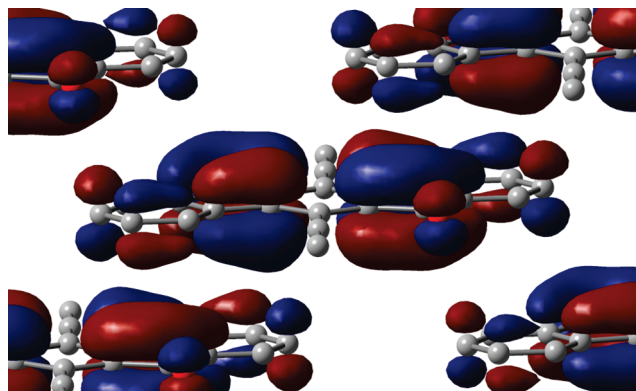


Figure 2. AM1-calculated (LUMO) interactions derived from the crystal packing in the X-ray structure of **6**.

point calculation based on the crystal structure of **6** shows that the orbitals are indeed in phase with orbital overlap between eight carbons between each molecule in one direction and four carbons in the other. Hence, the crystal packing of **6** possesses significant orbital interaction in one direction and less in the other.

The B3LYP/6-311+G(d,p)-minimized structure of **3** gives the energy levels of the HOMO at -6.28 eV and LUMO at -3.24 eV.⁸ Replacing the SiMe₃ groups with H atoms alters the calculated HOMO/LUMO values to -6.43 and -3.33 eV, respectively, illustrating the weak influence of the silyl substituent. These calculated numbers are in good agreement with the experimental cyclic voltammetry (CV) data, shown in Figure 3 and compiled in

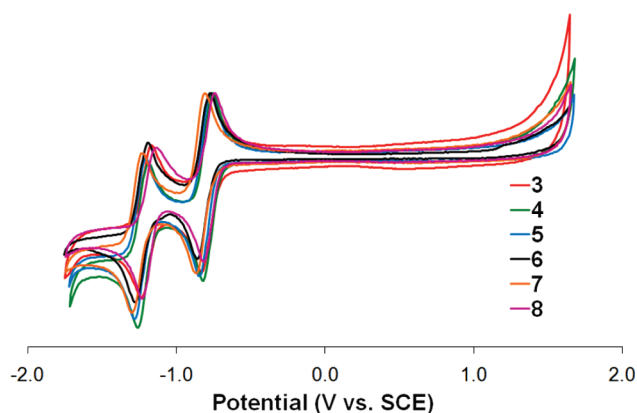


Figure 3. Cyclic voltammetry of IF-diones **3–8**; voltammogram currents are normalized to the to the E_{anodic}^1 peak.

Table 1. In solution, the IF-dione scaffold is capable of reversibly accepting up to two electrons, typically at low

potentials due to the low lying LUMO energy levels.^{4a,c,e,9} The first-reduction half-wave potential at ca. -0.81 V (vs SCE) for **3–8** is indeed less negative than the unsubstituted parent IF-dione (-1.19 V),^{4d} which can be attributed to the electron-withdrawing ethynyl moiety.¹⁰ In comparison to other known IF-diones, the first reduction half-wave potential of **3–8** is similar to 6,12-didodecyl-3,9-dibromo-IF-dione (-0.77 V)⁹ and more negative than 3,9-halogenated-IF-diones (-0.74 to -0.57 V)^{4d,11} and 1,2,3,4,7,8,9,10-octafluoro-6,12-diiodo-IF-dione (-0.45 V).^{4c,11} No oxidation process was observed, analogous to previous IF-diones.

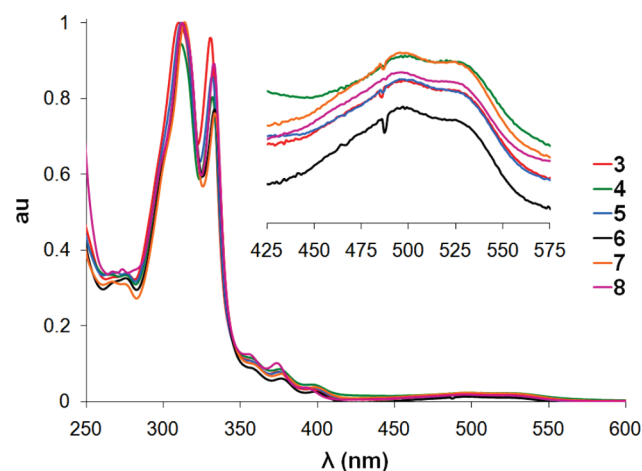


Figure 4. UV-vis data for IF-diones **3–8** in CHCl₃; inset magnified 12 times.

The UV-vis spectra of **3–8** (Figure 4) exhibit intense absorptions at approximately 312 and 330 nm due to the $\pi-\pi^*$ transitions. Very weak bands appear at ca. 500 and 525 nm and are attributed to the symmetry forbidden $n-\pi^*$ transition of the carbonyls.^{4c,12} The fluorescence spectra of **3–8** (Figure S1 in Supporting Information) show a single broad peak around 570 nm, with quantum yields in the range of 8–10%.¹³

In conclusion, a series of ethynylated IF-diones has been synthesized, and the packing motifs elucidated from X-ray diffraction of single crystals. The crystal packing and low LUMO levels indicate that **6** may be an ideal candidate as a solution processable n-type semiconductor. The device properties of **6** are the topic of current investigations.

(8) All calculations were performed using Gaussian 09, Revision A.02. Frisch, M. J. et al. Gaussian, Inc., Wallingford, CT, 2009. See the Supporting Information for the full citation.

(9) Usta, H.; Facchetti, A.; Marks, T. J. *Org. Lett.* **2008**, *10*, 1385–1388.

(10) Landgrebe, J. A.; Rynbrandt, R. H. *J. Org. Chem.* **1966**, *31*, 2585–2593.

(11) For comparison, the potential references were changed from Fc/Fc⁺ to SCE, as described in: Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877–910.

(12) Oldridge, L.; Kastler, M.; Müllen, K. *Chem. Commun.* **2006**, 885–887.

(13) Porrès, L.; Holland, A.; Palsson, L.; Monkman, A. P.; Kemp, C.; Beeby, A. J. *Fluoresc.* **2006**, *16*, 267–272.

Table 1. Experimental Optical and Electrochemical Data

compd	electrochemical				optical			
	E_{red}^1 (V) ^a	E_{red}^2 (V) ^a	E_{LUMO} (eV) ^b	E_{HOMO} (eV) ^c	λ_{abs} (nm)	E_{gap} (eV) ^d	λ_{em} (nm)	$\Phi_{\text{fluorescence}}$ ^e
3	−0.80	−1.21	−3.89	−6.26	310, 330, 498, 524	2.37	571	0.08
4	−0.79	−1.23	−3.90	−6.28	311, 332, 498, 522	2.38	569	0.08
5	−0.81	−1.25	−3.87	−6.23	312, 331, 498, 526	2.36	571	0.09
6	−0.82	−1.24	−3.87	−6.23	313, 333, 500, 525	2.36	568	0.10
7	−0.84	−1.26	−3.85	−6.22	314, 333, 498, 524	2.37	567	0.10
8	−0.78	−1.18	−3.90	−6.29	312, 333, 496, 520	2.39	570	0.09

^a CV recorded using 1–5 mM of analyte in 0.1 M tetrabutylammonium trifluoromethanesulfonate/CH₂Cl₂ using a scan rate of 50 mV/s. The working electrode was a glassy carbon electrode with a platinum coil counter electrode and silver 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 11. ^b Determined by $E_{\text{LUMO}} = -(4.44 + E_{\text{red}}^1)$; see ref 4e. ^c Estimated by subtracting the optical gap from the LUMO. ^d Determined using the wavelength at the maximum absorption of the lowest energy n → π^* transition from the UV–vis spectrum. ^e Determined via the integrating sphere method; see ref 13.

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Supporting Information Available. Experimental details and spectroscopic data for all new compounds; computational details for **3** and its desilylated analogue; X-ray data for **3**, **6**, and **8** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.