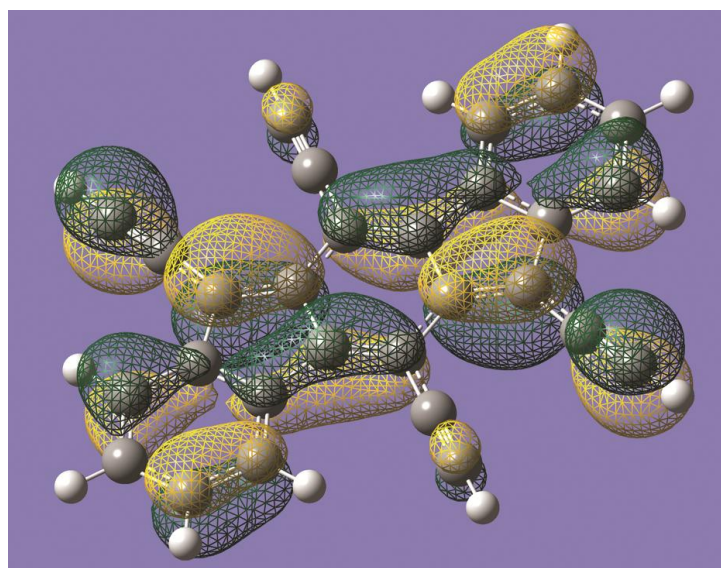# ChemComm

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Synthesis and charge transport studies of stable, soluble hexacenes†‡

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Acenes larger than pentacene are predicted to possess enticing electronic properties, but are insoluble and prone to rapid decomposition. Utilizing a combination of functionalization strategies, we present stable, solution-processable hexacenes and an evaluation of their hole and electron transport properties.

Recent interest in larger acenes is founded on pentacene's excellent device performance in a variety of electronic applications,[1] as well as theoretical predictions of enticing properties for fused aromatic systems with more than five rings.[2] This promise has generated a number of new functionalization strategies designed to yield reasonably stable versions of molecules such as hexacene and heptacene.[3] Although a number of quinoidal[4] or heteroaromatic[5] acenes with more than five fused rings have been studied in electronic devices, to-date soluble versions of hexacenes and larger acenes have not been prepared in a sufficiently stable form for film deposition and characterization of transport properties. Our recent study of the predominant decomposition pathways for silylethyne-substituted hexacenes provided guidelines for the preparation of suitably stable hexacenes,[6] and our earlier studies on pentacenes[7] and anthradithiophenes[8] further showed that partial fluorination yielded significant improvements in solution stability. Combining these functionalization and fluorination strategies, we report here the synthesis of tricyclo-hexylsilylethynyl-substituted derivatives of hexacene (**1**), tetra-fluorohexacene (**2**) and octafluorohexacene (**3**) (Fig. 1), and our initial study of the charge transport properties of solution-deposited films of these hexacenes.

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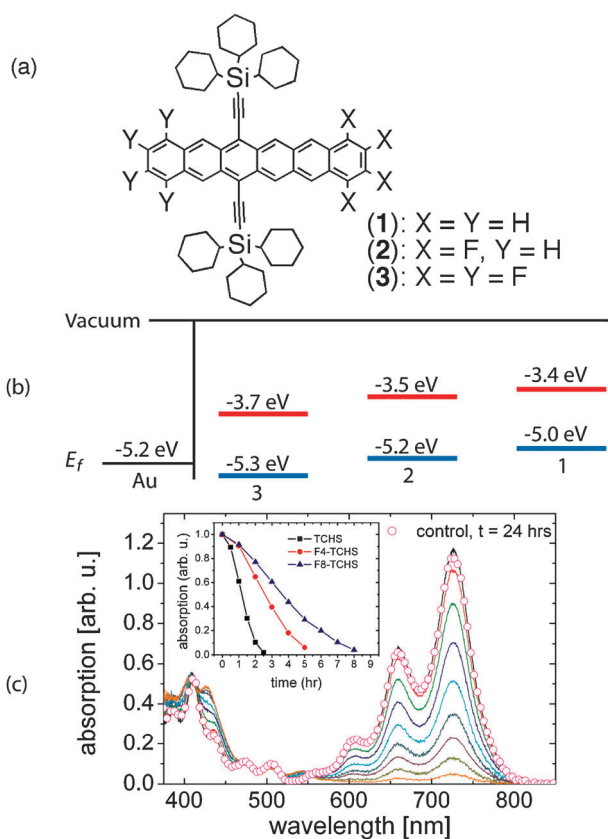
Silylethyne-substituted hexacenes are prepared from the corresponding hexacenequinones, and the requisite fluorinated quinones were formed by condensation of tetrafluoronaphthalene 2,3-dicarboxaldehyde with either 1,4-dihydroxyanthracene or tetrafluoro 1,4-dihydroxyanthracene, as described in the *supporting information*. Hexacenes **1–3** are green crystalline solids that did not decompose appreciably after several months' storage in the solid state in the dark (Fig. S1). Solutions of the hexacenes were characterized by absorption and emission spectroscopy, as well as by electrochemistry (Fig. 1). The disappearance of the long-wavelength absorptions upon exposure to bright laboratory lighting in air was used to gain initial insight into the solution stability of these materials (Fig. 1c and S2), and as expected the fluorine substituents led to a significant increase in solution half-life. Electrochemical analysis of **1–3**, performed by cyclic voltammetry and differential pulse voltammetry, provided estimates of the HOMO and LUMO energies[9] as presented in Fig. 1b. Crystallographic analysis of hexacene **1** was reported previously, and the structure consists of a strongly one-dimensional π-stacked array with significant distortion of the hexacene backbone.[6] Hexacenes **2** and **3** also formed crystals suitable for structural analysis. Unfortunately, disorder in the structure of **2** was extensive, and only a rough assessment of crystal packing order could be obtained; the molecules appear to adopt a two-dimensional π-stacked arrangement similar to functionalized pentacenes.[10] There was significantly less disorder in the structure of **3**, although it did incorporate recrystallization solvent into the structure, and the hexacene chromophores were again found to adopt a highly layered, strongly π-stacked arrangement as shown in Fig. S4. Thus, similar to prior-reported pentacene materials, both **2** and **3** are expected to show reasonable charge transport properties.[11]

For the initial electronic characterization of compounds **1–3**, drop-cast films were prepared on glass substrates with interdigitated Au electrode pairs. Current was measured as a function of voltage, both in the dark and under 765 nm continuous wave illumination, and photocurrent was calculated as the difference between the two. While films of all three hexacenes exhibited photoresponse (Fig. 2a), compounds **2** and **3** were considerably more photoconductive compared to **1**. In all films at higher voltage, the voltage (V) dependence of the dark currents (I_d) could be described as $I_d \sim V^\alpha$ with $\alpha \approx 2$.

Fig. 1 Structures (a) and energy levels (b) for hexacenes **1–3**, and (c) decomposition rate of **3** in solution measured every hour in air under laboratory lighting. The control trace consists of a similar sample kept in the dark. Inset: Integrated absorption spectra (640 nm to 824 nm) as a function of exposure time for **1–3**.

This suggests the space-charge limited current (SCLC) regime, enabled by efficient hole injection from Au electrodes (as expected from the estimated HOMO energies of **1–3**). From the SCLC measurements, we estimated effective charge carrier mobility (μ) values, which in our planar electrode experimental geometry depend upon the film thickness (see SI for details).[12] In the limiting case of infinitely thin film (infinite half-space), the mobility values yielded 1.7×10^{-4} cm^2 V^{-1} s^{-1} (3.8×10^{-4} cm^2 V^{-1} s^{-1}) for **1**, 8.4×10^{-3} cm^2 V^{-1} s^{-1} (1.9×10^{-2} cm^2 V^{-1} s^{-1}) for **2** and 6.9×10^{-4} cm^2 V^{-1} s^{-1} (1.6×10^{-3} cm^2 V^{-1} s^{-1}) for **3** (Fig. 2b). These values should be regarded as lower bounds of charge carrier mobility, as the SCLC trap-free limit was not achieved in our measurements.

The higher mobility and good stability of **2** led us to explore its use in bottom-gate field-effect transistors (FETs), which were fabricated on SiO$_2$ gate dielectric and chemically modified Au contacts (Fig. 3a). Heavily doped Si was used as gate electrode and 300 nm of thermally-grown SiO$_2$ at its surface served as gate dielectric. Ti/Au source and drain contacts were deposited by e-beam evaporation, and were treated with pentafluorobenzene thiol to enhance the crystallization of the fluorinated semi-conductor.[13] The organic semiconductor was drop-cast from a 0.2 wt% chlorobenzene solution, and the solvent was allowed to evaporate slowly in a covered petri dish in the dark for up to three days.[14] Fig. 3b shows an optical micrograph of the crystalline films obtained by this process – the large,
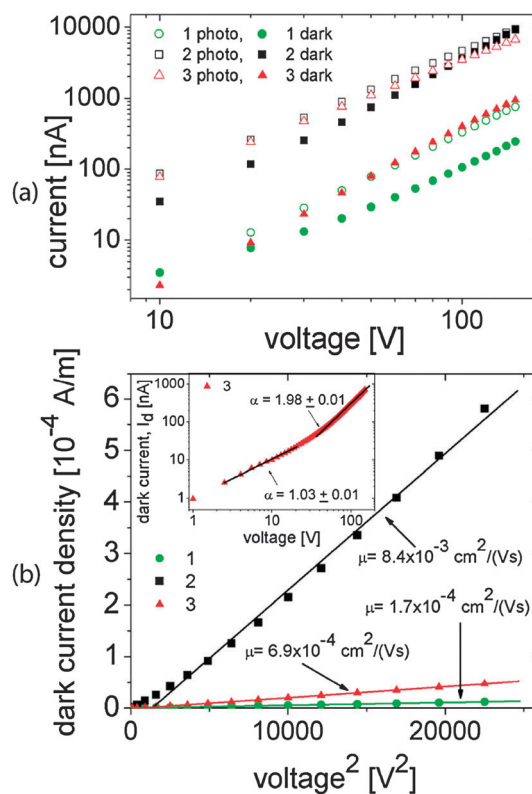

Fig. 2 (a) Dark and photocurrents for **1–3** as a function of applied voltage. (b) Dark current density of **1–3** as a function of voltage squared, along with the linear fits from which SCLC effective charge carrier mobilities were calculated. Inset: The current trace for **3**, showing the transition from Ohmic behavior.
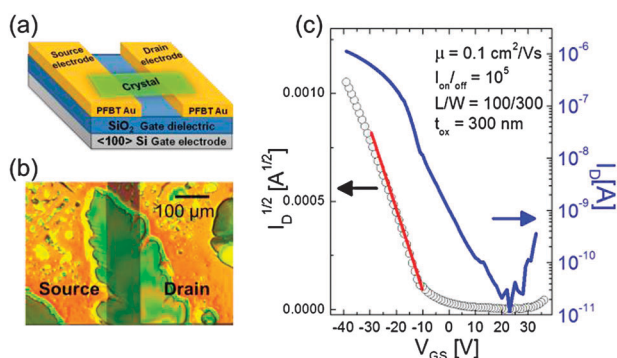

Fig. 3 Field-effect transistors fabricated from hexacene **2**. (a) Schematic representation of the FET geometry. (b) Top-view cross-polarized optical image of a device. (c) Evolution of the drain current I_D with the gate voltage V_{GS} for the same device.

leaf-shaped crystals appear single, and span the channel of the transistor, with crystal dimensions ranging from a few μm to hundreds of μm. The resulting FETs were measured under ambient conditions, and over 100 devices were sampled to yield hole mobility ranging from 0.01 to 0.10 cm^2 V^{-1} s^{-1}. The variability arises from different crystal quality along with the natural anisotropy present in these π-stacked systems.[15] Mobilities were calculated in the saturation regime (drain-to-source voltage $V_{DS} = -40$ V), and Fig. 3c shows the transfer characteristics for the device shown in Fig. 3b, demonstrating
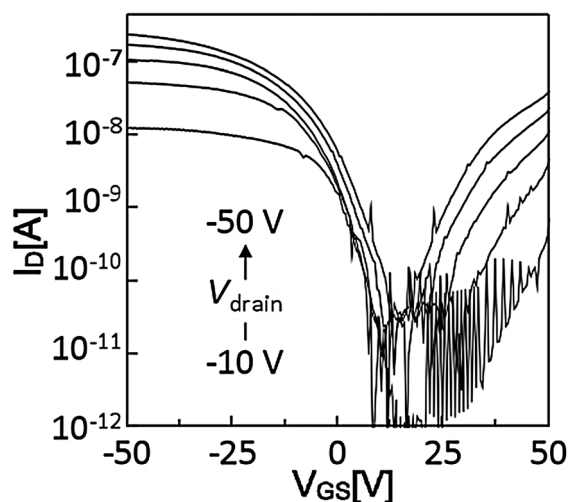
Fig. 4 Transfer characteristics of a typical FET fabricated with a binary blend of **3** and HDPE, 1 : 1 weight ratio. (Channel length L = 10 μm; channel width W = 10 mm).

a mobility of 0.1 cm^2 V^{-1} s^{-1} and current on/off ratio of 10^5. For mobility calculation, the channel width was defined as the portion of the channel covered by the crystals.

Recent reports of electron transport in vapour-deposited films of fluorinated pentacene derivatives[16] suggested that octafluoro hexacene **3** might be suitable for electron transport studies. Films of the semiconductor were formed by drop-casting xylene solutions of **3** onto pre-formed device substrates (Au electrodes) in an inert atmosphere glove box – devices were measured in the same glove box. While initial measurements on neat films of **3** were promising, poor film formation from solution, perhaps complicated by the incorporation of solvent in the crystals, led to numerous shorted or inoperative devices. Blending small molecules with insulating polymers has recently been shown an effective method to manipulate the solid-state microstructure and surface coverage of organic semiconductors.[17] Blends of **3** with high-density polyethylene (HDPE) in a 1 : 1 weight ratio were thus cast onto bottom-gate, bottom-contact transistor substrates. The resulting devices showed both electron *and* hole transport (μ_e = 0.003 cm^2 V^{-1} s^{-1}, μ_h = 0.0015 cm^2 V^{-1} s^{-1}) – a representative set of transfer characteristics are shown in Fig. 4. Thus, octafluoro hexacene **3** behaves as an ambipolar semiconductor with impressively balanced hole and electron mobilities.

We have demonstrated that hexacene can be made both sufficiently soluble and sufficiently stable for studies in solution-cast electronic devices. The fluorinated derivatives adopt π-stacked structures in the solid state amenable to good charge transport. Tetrafluoro derivative **2** formed large, plate-like crystals on transistor device substrates and yielded hole mobility as high as 0.1 cm^2 V^{-1} s^{-1}. Octafluoro derivative **3** required blending with an insulating polymer to give acceptable thin-film architectures, but rewarded this added complexity with ambipolar transistors exhibiting well-balanced hole and electron mobility. These promising results based on the first stable, soluble hexacene derivatives suggest that further tuning of the trialkylsilyl substituents to optimize crystal packing and enhance film morphology will yield materials with desirable electronic properties.

Notes and references

1 S. Lee, B. Koo, J. Shin, E. Lee, H. Park and H. Kim, *Appl. Phys. Lett.*, 2006, **88**, 162109; S. Yoo, B. Domercq and B. Kippelen, *Appl. Phys. Lett.*, 2004, **85**, 5427.
2 W.-Q. Deng and W. A. Goddard III, *J. Phys. Chem. B*, 2004, **108**, 8614; J.-L. Bredas, D. Beljonne, V. Coropceanu and J. Cornil, *Chem. Rev.*, 2004, **104**, 4971; F. Valiyev, W.-S. Hu, H.-Y. Chen, M.-Y. Kuo, I. Chao and Y.-T. Chao, *Chem. Mater.*, 2007, **19**, 3018.
3 M. M. Payne, S. R. Parkin and J. E. Anthony, *J. Am. Chem. Soc.*, 2005, **127**, 8028; D. Chun, Y. Cheng and F. Wudl, *Angew. Chem., Int. Ed.*, 2008, **47**, 8380; I. Kaur, N. N. Stein, R. P. Kopreski and G. P. Miller, *J. Am. Chem. Soc.*, 2009, **131**, 3424.
4 For example, Q. Miao, M. Lefenfeld, T.-Q. Nguyen, T. Siegrist, C. Kloc and C. Nuckolls, *Adv. Mater.*, 2005, **17**, 407.
5 X. Zhang, A. P. Côté and A. J. Matzger, *J. Am. Chem. Soc.*, 2005, **127**, 10502; T. Okamoto, K. Kudoh, A. Wakamiya and S. Yamaguchi, *Chem.–Eur. J.*, 2007, **13**, 548; P. Gao, X. Feng, X. Yang, V. Enkelmann, M. Baumgarten and K. Müllen, *J. Org. Chem.*, 2008, **73**, 9207; P. Gao, D. Cho, X. Yang, V. Enkelmann, M. Baumgarten and K. Müllen, *Chem.–Eur. J.*, 2010, **16**, 5119; T. Yamamoto and K. Takimiya, *J. Am. Chem. Soc.*, 2007, **129**, 2224; K. P. Goetz, Z. Li, J. W. Ward, C. Bougher, J. Rivnay, J. Smith, B. R. Conrad, S. R. Parkin, T. D. Anthopoulos, A. Salleo, J. E. Anthony and O. D. Jurchescu, *Adv. Mater.*, 2011, **23**, 3698.
6 B. Purushothaman, S. R. Parkin and J. E. Anthony, *Org. Lett.*, 2010, **12**, 2060.
7 C. R. Swartz, S. R. Parkin, J. E. Bullock, J. E. Anthony, A. C. Mayer and G. G. Malliaras, *Org. Lett.*, 2005, **7**, 3163.
8 S. Subramanian, S. K. Park, S. R. Parkin, V. Podzorov, T. N. Jackson and J. E. Anthony, *J. Am. Chem. Soc.*, 2008, **130**, 2706.
9 A. P. Kulkarni, C. J. Tonzola, A. Babel and S. A. Jenekhe, *Chem. Mater.*, 2004, **16**, 4556.
10 J. E. Anthony, J. S. Brooks, D. L. Eaton and S. R. Parkin, *J. Am. Chem. Soc.*, 2001, **123**, 9482.
11 S. K. Park, T. N. Jackson, J. E. Anthony and D. A. Mourey, *Appl. Phys. Lett.*, 2007, **91**, 063514.
12 J. Day, A. D. Platt, S. Subramanian, J. E. Anthony and O. Ostroverkhova, *J. Appl. Phys.*, 2009, **105**, 103703; A. D. Platt, J. Day, S. Subramanian, J. E. Anthony and O. Ostroverkhova, *J. Phys. Chem. C*, 2009, **113**, 14006; and supporting information.
13 D. J. Gundlach, J. E. Royer, B. H. Hamadani, L. C. Teague, A. J. Moad, O. D. Jurchescu, O. Kirillov, C. A. Richter, J. G. Kushmeric, L. J. Richter, S. K. Park, T. N. Jackson, S. Subramanian and J. E. Anthony, *Nat. Mater.*, 2008, **7**, 216.
14 J. Chen, C. K. Tee, J. Yang, C. Shaw, M. Shtein, J. Anthony and D. C. Martin, *J. Polym. Sci., Part B: Polym. Phys.*, 2006, **44**, 3631.
15 C. W. Sele, B. K. C. Kjellander, B. Niesen, M. J. Thornton, J. Bas, P. H. van der Putten, K. Myny, H. J. Wondergem, A. Moser, R. Resel, A. J. J. M. van Breemen, N. van Aerle, P. Heremans, J. E. Anthony and G. H. Gelinck, *Adv. Mater.*, 2009, **21**, 4926.
16 M. L. Tang, J. H. Oh, A. D. Reichardt and Z. Bao, *J. Am. Chem. Soc.*, 2009, **131**, 3733.
17 S. Goffri, C. Müller, N. Stingelin-Stutzmann, D. W. Breiby, C. P. Radano, J. Andreasen, R. Thompson, R. A. J. Janssen, M. Nielsen, P. Smith and H. Sirringhaus, *Nat. Mater.*, 2006, **5**, 950.