## Synthesis and characterization of 2,7-bis(pentafluorophenylethynyl)hexafluoroheterofluorenes: new materials with high electron affinities<sup>†</sup>

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The synthesis, optical, electrochemical and physical characterization of 2,7-bis(pentafluorophenylethynyl)hexafluoroheterofluorenes is described along with a preliminary evaluation of their performance in photovoltaic applications.

The use of organic semiconducting materials for applications in "plastic electronics" continues to attract considerable interest, as organic systems offer the possibility for economical raw materials and low processing costs, and are readily modified to access a wide range of physical, optical and electrical properties.<sup>1-4</sup> In contrast to the development of improved conjugated organic  $\pi$ -systems that demonstrate effective hole-transporting (p-type) properties,<sup>5</sup> the advancement of efficient electron-conducting (n-type) organic compounds has been slow. A number of devices are expected to exhibit improved performance with incorporation of n-type organic materials that exhibit a low barrier to electron injection and effective charge transport.<sup>4,6</sup> To achieve this, compounds with electron-deficient  $\pi$ -systems and close cofacial intermolecular packing in the solid state are desired.<sup>7–13</sup>

In general, many of the electron-deficient building blocks (i.e. pyridines, oxadiazoles, perylene diimides, metalloles, fluorinated aromatics) used to construct n-type materials are difficult to synthetically manipulate, as required for the tuning of important physical and electronic properties.<sup>7-12</sup> A new class of compounds, the perfluoroheterofluorenes (structures **2–4.** Scheme 1), includes a number of interesting structural units that are expected to exhibit good electron-accepting properties and cofacial  $\pi$ -stacking in the solid state (vide infra). While synthetic variation of the heteroatom (and its substituents) is relatively straightforward, substitutions on the fluorinated biaryl framework are more challenging since the typically employed nucleophilic aromatic substitution reactions are very sensitive to minor variations in substrate.<sup>9a,14</sup> In this communication, we describe a facile, general synthetic route to a variety of 2,7-substituted hexafluoroheterofluorenes, which utilizes a combination of nucleophilic aromatic substitution (S<sub>N</sub>Ar<sub>F</sub>) and Pd-catalyzed coupling reactions. The availability of the key 4,4'-bisethynyl-2, 2'-dibromo-3,3',5,5',6,6'-hexafluorobiphenyl intermediate (Scheme 1), which is readily coupled to aryl halides (*vide infra*), greatly facilitates incorporation of the hexafluorohetero-fluorene fragment into a variety of extended conjugated organic systems (*e.g.* compounds 1–4). Here we describe use of this method to obtain several molecular species with high electron affinities, and preliminary results on their behavior as n-type components in photovoltaic devices.

The synthesis of 2,7-bis(pentafluorophenylethynyl)hexafluoroheterofluorenes is described in Scheme 1. The alkynyl functionality was installed via a nucleophilic aromatic substitution reaction of triisoproylsilyl lithium acetylide with 2,2'-dibromooctafluorobiphenyl. Use of a 4 : 1 toluene : THF solvent mixture at  $\sim 2 \times 10^{-2}$  M concentration gave the 4,4'-bis-(triisopropylsilylethynyl)-2,2'-dibromo-3,3',5,5',6,6'-hexafluorobiphenyl product in moderate conversion ( $\sim 65\%$ as determined by <sup>19</sup>F NMR) after 3 days at room temperature. Longer reaction times increased the conversion to the disubstituted product; however, elevated temperatures led to a mixture of mono-, di- and trisubstituted material. The triisopropylsilyl groups were removed by the addition of Bu<sub>4</sub>NF to a dilute (0.0001 M) toluene–THF solution ( $\sim 2\%$ THF) of 4,4'-bis(triisopropylsilylethynyl)-2,2'-dibromo-3,3', 5,5',6,6'-hexafluo robiphenyl. Aqueous work-up and filtration through a silica plug gave a crude reaction mixture predominantly containing the key 4,4'-bisethynyl-2,2'dibromo-3,3',5,5',6,6'-hexafluorobiphenyl intermediate that was then capped with C<sub>6</sub>F<sub>5</sub> groups by a Pd catalyzed Sonogashira coupling reaction with  $C_6F_5I$  at 45 °C to give 1. No conversion to 1 was observed when  $C_6F_5Br$  was used as the aryl halide. Compound 1 was isolated via column chromatography in 55% yield based on the starting 2,2'-dibromooctafluorobiphenyl. Lithiation of 1 with BuLi in Et<sub>2</sub>O-THF at -78 °C, followed by addition of the appropriate



Scheme 1

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Compound	$E_{\rm g}^{\rm opt}/{ m eV}^a$	$\lambda_{ems}/nm^b$	${\Phi_{ t PL}}^c$	LUMO energy/eV <sup>a</sup>
2a	3.2	382	~1	$-3.2^{e}$
2b	3.3	378	$\sim 1$	$-3.2^{e}$
3a	3.3	378	$\sim 1$	$-3.2^{f}$
3b	3.3	376	$\sim 1$	$-3.2^{e}$
4a	3.1	385	$\sim 1$	$-3.5^{g}$
4b	3.2	391	$\sim 1$	$-3.4^{g}$

<sup>*a*</sup> HOMO-LUMO energy gaps  $(E_g^{opt})$  were calculated from the absorption onset wavelength, determined by the intersection of the leading edge tangent with the *X*-axis. <sup>*b*</sup> Emission energies were measured with 350 nm excitation. <sup>*c*</sup> Dilute solution state (optical density 0.1) photoluminescence quantum yields calculated with respect to 9,10-diphenylanthracene in THF = 0.9. <sup>*d*</sup> In CH<sub>3</sub>CN electrolyte solution (0.1 M solution of Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>3</sub>CN) and LUMO energy levels calculated with respect to ferrocenium–ferrocene (Fc<sup>+</sup>/Fc) reduction (Fc HOMO energy of -4.8 eV relative to vacuum).<sup>20 e</sup> Irreversible. <sup>*f*</sup> Quasireversible. <sup>*g*</sup> Reversible.

dichloroheteroatom reagent, produced the desired heterofluorene product in quantitative yield (as determined by <sup>19</sup>F NMR), and isolated yields are good in all cases except with dichlorodiphenylsilane. With the latter reagent, the reaction proceeds to 65% conversion resulting in low isolated yields (<10%).

The solution state UV-vis data collected for all compounds are summarized in Table 1. UV-visible absorption behavior of the disubstituted hexafluoroheterofluorenes exhibit very little dependence on the heteroatom, and possess HOMO-LUMO energy gaps of 3.1-3.3 eV. Furthermore, the energy gaps are rather insensitive to changes of substituents at the heteroatom (Ph vs. alkyl); thus modifications of these groups to tune physical properties should not greatly perturb the electronic properties of interest. Strong violet emission, with a Stokes shift of 25 to 30 nm, was observed for all compounds (Table 1). It has been observed that the photoluminescent quantum yield  $(\Phi_{\rm PL})$  may be increased or decreased upon fluorination, depending on both the molecular framework and the degree of fluorination.<sup>8,9</sup> The vibronic coupling observed in both the absorption and emission spectra (see ESI for details<sup>†</sup>) was independent of heteroatom. The specific origin of this coupling has not been explored but it is quite typical for many organic systems. Although optical properties for the non-fluorinated analogues of compounds 2-4 have not been reported, polymers and oligomers containing fluorene and heterofluorene units are highly emissive;<sup>15,16</sup> thus the near unity emission intensity of the reported 2,7-bis(pentafluorophenylethynyl)hexafluoroheterofluorenes indicates that fluorination of the terminal rings does not diminish the intensity of the emitted light.

The solution state redox behavior of all compounds was investigated *via* differential pulse voltammetry (reduction potentials) and cyclic voltammetry (reversibility) and the LUMO energy levels are reported in Table 1. The LUMO energies range from -3.2 eV to -3.5 eV and the reversibility of these reductions is highly dependent on heteroatom. These LUMO energy levels are significantly lower than those of related heterofluorene compounds previously reported in the literature (-2.1 to -2.6 eV),<sup>16–18</sup> and are in the range established for useful n-type conducting materials.<sup>4,11,17–19</sup> The oxidation behavior of these compounds was not observed within the solvent/electrolyte window (0.1 M solution of Bu<sub>4</sub>NPF<sub>6</sub> in



**Fig. 1** Crystal structures for germafluorene **3a** (Fig. 1a) and phosphafluorene **4a** (Fig. 1b). Hydrogen atoms have been removed for clarity. View (a) illustrates the unidirectional  $\pi$ -stacking of **3a** and view (b) illustrates the bidirectional interactions of **4a**.

CH<sub>3</sub>CN). It was observed that the reduction potentials of the disubstituted hexafluoroheterofluorenes exhibit a slight dependence on the heteroatom itself (Si, Ge vs. P), but as was observed for the  $E_g^{\text{opt}}$  values, they are rather insensitive to the nature of the substituents at the heteroatom (aryl vs. alkyl).

Single crystal X-ray analyses of 3a and 4a (Fig. 1) show that both molecules possess planar  $\pi$  systems that pack to give stacked columns with parallel heterofluorene fragments.<sup>21</sup> Germafluorene 3a packs in hexagonally arranged columns with close  $\pi$ -stacking interactions (3.2–3.4 Å; Fig. 1a) and significant interaction between adjacent heterofluorene cores. This motif is thought to be ideal for many electron transporting applications.<sup>7–13</sup> The packing of phosphafluorene 4a (Fig. 1b and Fig. S11<sup>+</sup>) illustrates how changes in the heteroatom substituent can lead to dramatically different packing characteristics. Although 4a maintains a heterofluorene-layered structure, the molecules stack in two nearly perpendicular directions throughout the crystal, unlike the unidirectional assembly of **3a**, with  $\pi$ -systems that do not exhibit direct interactions. The latter structural feature may be described by an interplane distance between the heterofluorenes of ca. 6 Å, and a tilting of the molecular stacks such that the molecules are offset laterally from one another to avoid a cofacial arrangement. It is also worth noting short O1...C24 and O1...C25 contacts ( $\sim 2.8$  Å) which suggest that an interaction between the electron-rich oxygen atom and the electron-deficient  $\pi$ -system influence the solid state assembly.

As a preliminary proof of concept that the compounds may work well as electron transporting materials, device studies were performed to evaluate germafluorene **3b** and phosphafluorene **4b** as electron transport materials in a basic photovoltaic (PV) configuration. Unoptimized PV cells were made from 1 : 1 wt% blends of **3b**-regioregular poly-3-hexylthiophene (P3HT) and **4b**-P3HT that were spin-coated onto an ITO surface from chloroform solution (10 mg mL<sup>-1</sup>, ~80 nm thick films) with



**Fig. 2** Photovoltaic performance of spin-coated devices with P3HT as the hole transport material and **3b** (blue) or **4b** (red) as the electron transport material (performance for **3b**:  $V_{\rm oc} = 0.905$  V,  $J_{\rm sc} = 0.211$  mA cm<sup>-2</sup>, fill factor = 0.184,  $\eta = 0.035\%$ ; **4b**:  $V_{\rm oc} = 0.743$  V,  $J_{\rm sc} = 0.064$  mA cm<sup>-2</sup>, fill factor = 0.255,  $\eta = 0.012\%$ ; P3HT-only:  $V_{\rm oc} = 0.04$  V,  $J_{\rm sc} = -0.044$  mA cm<sup>-2</sup>, fill factor = 0.253,  $\eta = 0.0004\%$ .)

a vapor deposited aluminium cathode. The devices were tested under an argon atmosphere with an Oriel xenon arc lamp with an AM 1.5G solar filter, and the resulting current density– voltage curves are illustrated in Fig. 2 (additional current–voltage data are available in the ESI†).

As illustrated in Fig. 2, the PV devices made with blends of 3b-P3HT and 4b-P3HT clearly exhibit improved performance over the P3HT-only devices. This can be attributed to a much higher open circuit voltages  $(V_{oc})$  in the blend systems (0.905 V and 0.743 V respectively for the devices containing 3b and 4b, vs. 0.040 V for pure P3HT), which result in greater charge separation than in the pure P3HT system. In fact, these  $V_{oc}$ values are greater than the typical values observed for the highest efficiency P3HT–PCBM devices ( $\sim 0.65$  V, PCBM = [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester).<sup>22</sup> Additionally, the short circuit current densities  $(J_{sc})$  of the blend devices are significantly larger than that of the pure P3HT system, which suggests that the incorporation of 3b and 4b improves overall charge transport in the devices. The efficiencies of these devices are rather low (0.035% for 3b and 0.012% for 4b) compared to those obtained for optimized devices based on P3HT-PCBM  $(4-5\%)^{21}$  and P3HT-pervlene diimide  $(0.5-1\%)^{23}$  Further modifications to the structures of such fluorinated, heterofluorene-based compounds should provide increased light absorption and more efficient charge transport.<sup>24</sup> Also, optimization of processing parameters (e.g. blend ratio, annealing conditions, etc.) and device assembly (e.g. cathode material, surface treatment, etc.) should enable better charge transport throughout the device and higher PV efficiencies.<sup>25</sup>

In summary, 2,7-bis(pentafluorophenylethynyl)hexafluoroheterofluorenes show great potential as electron transporting organic materials, in applications such as organic PV and LED devices. The availability of the 4,4'-bisethynyl-2,2'-dibromo-3,3',5,5',6,6'-hexafluorobiphenyl synthetic intermediate, and its ready conversion to heterofluorene derivatives, demonstrates the versatility of these compounds and enables the convenient incorporation of this fragment into a wide variety of extended organic systems.

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## Notes and references

- (a) S. R. Forrest, *Chem. Rev.*, 1997, 97, 1793; (b) S. Jenekhe, *Chem. Mater.*, 2004, 16, 4382 special issue on organic electronics; (c) S. R. Forrest and M. E. Thompson, *Chem. Rev.*, 2007, 107, 923 special issue on organic electronics.
- 2 D. H. Hwang, S. K. Kim, M. J. Park, B. W. Koo, I. N. Kang, S. H. Kim and T. Zyung, *Chem. Mater.*, 2004, **16**, 1298.
- 3 M. Schwartz, G. Srinivas, A. Yeates, R. Berry and D. Dudia, *Synth. Met.*, 2004, **143**, 229.
- 4 Y. Zhu, M. M. Alam and S. A. Jenekhe, *Macromolecules*, 2003, **36**, 8958.
- 5 M. L. Renak, G. P. Bartholomew, S. J. Wang, P. J. Ricatto, R. J. Lachicotte and G. C. Bazan, J. Am. Chem. Soc., 1999, 121, 7787.
- 6 C. J. Tonzola, M. M. Alam, W. Kaminsky and S. A. Jenekhe, J. Am. Chem. Soc., 2003, 125, 13548.
- 7 A. Kulkarni, C. Tonzola, A. Babel and S. A. Jenekhe, *Chem. Mater.*, 2004, 16, 4556.
- 8 F. Babudri, G. Farinola, F. Naso and R. Ragni, *Chem. Commun.*, 2007(10), 1003.
- 9 (a) K. Geramita, J. McBee, Y. Shen, N. Radu and T. D. Tilley, *Chem. Mater.*, 2006, **18**, 3261; (b) J. F. Tannaci, M. Noji, J. McBee and T. D. Tilley, *J. Org. Chem.*, 2007, **72**, 5567.
- 10 K. Tamao, M. Uchinda, T. Izumizawa, K. Furukawa and S. Yamaguchi, J. Am. Chem. Soc., 1996, 118, 11974.
- 11 A. Facchetti, M. H. Yoon, C. L. Stern, H. E. Katz and T. J. Marks, Angew. Chem., Int. Ed., 2003, 42, 3900.
- 12 S. B. Heidenhain, Y. Sakamoto, T. Suzuki, A. Miura, H. Fujikawa, T. Mori, S. Tokito and T. Taga, J. Am. Chem. Soc., 2000, 122, 10240.
- 13 G. Hutchison, M. Ratner and T. J. Marks, J. Am. Chem. Soc., 2005, 127, 16866.
- 14 (a) H. Zimmerman, Tetrahedron, 1961, 16, 169; (b) J. Burdon, Tetrahedron, 1965, 21, 3373; (c) J. Burdon and I. Parsons, J. Am. Chem. Soc., 1977, 99, 7445; (d) R. D. Chambers and D. J. Spring, Tetrahedron, 1971, 1, 669; (e) J. Burdon, B. L. Kane and J. C. Tatlow, J. Fluorine Chem., 1971/72, 1, 185; (f) J. Burdon, A. C. Childs, I. W. Parsons and J. C. Tatlow, J. Chem. Soc., Chem. Commun., 198210), 534; (g) R. Bolton and J. Sandall, J. Chem. Soc., Perkin Trans. 2, 1978, 746; (h) J. Burdon, H. Gill, J. Chem. Soc., Perkin Trans. 1, 1979, 1351; (i) J. Burdon, H. Gill, I. Parsons and J. Tatlow, J. Chem. Soc., Perkin Trans. 1, 1980, 1726.
- 15 T. Matsuda, S. Kadowaki and T. Goya, Org. Lett., 2007, 9, 133–136.
- 16 K. L. Chan, M. McKiernan, C. Towns and A. B. Holmes, J. Am. Chem. Soc., 2005, 127, 7662–3.
- 17 T.-H. Huang, W.-T. Whang, J. Y. Shen, Y.-S. Wen, J. T. Lin, T.-H. Ke, L.-Y. Chen and C.-C. Wu, *Adv. Funct. Mater.*, 2006, 16, 1449.
- 18 Y. Mo, R. Tian, W. Shi and Y. Cao, Chem. Commun., 2005, 4925.
- 19 B. L. Lee and T. Yamamoto, Macromolecules, 1999, 32, 1375.
- 20 H. M. Koepp, H. Wendt and H. Strehlow, Z. Elektrochem., 1960, 64, 483.
- 21 Crystal data for **3a**: C<sub>40</sub>H<sub>10</sub>F<sub>16</sub>Ge, M = 867.07, triclinic, a = 7.922(2), b = 15.049(3), c = 15.823(3) Å, U = 1626.1(8) Å<sup>3</sup>, T = 118 K, space group  $P\bar{1}$ , Z = 2, 9156 reflections measured, 3384 unique ( $R_{int} = 0.1023$ ) were used in all calculations. The final  $wR(F_2) = 5.45$ . CCDC 697514. **4a**: C<sub>34</sub>H<sub>3</sub>F<sub>16</sub>OP, M = 764.35, monoclinic, a = 13.798(13), b = 5.938(5), c = 35.27(3) Å, U = 2840(5) Å<sup>3</sup>, T = 140 K, space group  $P2_1/n$ , Z = 4, 9224 reflections measured, 2955 unique ( $R_{int} = 0.0857$ ) which were used all calculations. The final  $wR(F_2) = 4.20$ . CCDC 697515.
- 22 S. A. Backer, K. Sivula, D. F. Kavulak and J. F. J. Fréchet, *Chem. Mater.*, 2007, **19**, 2927.
- 23 X. Zhan, Z. Tan, B. Domercq, Z. An, X. Zhang, S. Barlow, Y. Li, D. Zhu, B. Kippelen and S. Marder, *J. Am. Chem. Soc.*, 2007, **129**, 7246.
- 24 Target difference between donor LUMO energy (LUMO<sub>D</sub>) and acceptor LUMO energy (LUMO<sub>A</sub>) is  $\sim 0.5$  eV. For **3b**-P3HT  $\Delta$ (LUMO<sub>D</sub> LUMO<sub>A</sub>) is 0.1 eV and for **4b**-P3HT  $\Delta$ (LUMO<sub>D</sub> LUMO<sub>A</sub>) is 0.2 eV; J. G. S. Ramon and E. R. Bittner, *J. Phys. Chem. B*, 2006, **110**, 15.
- 25 P. C. Chang, J. Lee, D. Huang, V. Subramanian, A. R. Murphy and J. M. J. Fréchet, *Chem. Mater.*, 2004, 16, 4783.