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1,3,6,8-Tetrasubstituted Pyrenes: Solution-Processable Materials for Application in Organic Electronics

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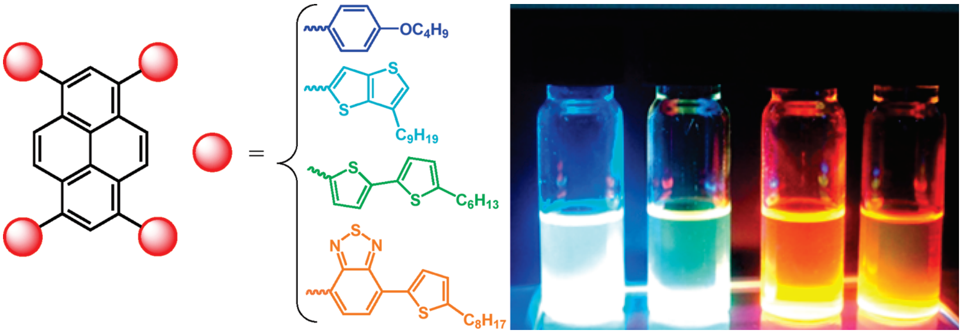
ABSTRACT



A series of star-shaped organic semiconductors have been synthesized from 1,3,6,8-tetrabromopyrene. The materials are soluble in common organic solvents allowing for solution processing of devices such as light-emitting diodes (OLEDs). One of the materials, 1,3,6,8-tetrakis(4-butoxyphenyl)pyrene, has been used as the active emitting layer in simple solution-processed OLEDs with deep blue emission (CIE = 0.15, 0.18) and maximum efficiencies and brightness levels of 2.56 cd/A and >5000 cd/m^2, respectively.

The quest for new and improved organic semiconductors continues with emphasis on optimizing key properties such as luminescence, absorption, energy band gaps, charge transport, and stability.[1,2] With regard to device fabrication, organic semiconductors can be classified into two general families: those that can be processed into devices by vacuum deposition (small molecules) or by solution processing (polymers). Small molecules are advantageous because they can be (1) purified by common techniques such as recrystallization, chromatography, and sublimation and (2) vacuum deposited in multilayer stacks, both important for device lifetime and efficiency.[3] However, vacuum-deposition techniques require costly processes that are limited to practical substrate size and relatively low yields in the manufacture of high volume products using masking technologies.[4] On the other hand, polymers are generally of lower purity than small molecules but can be used to achieve larger display

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(1) (a) Shirota, Y.; Kageyama, H. *Chem. Rev.* **2007**, *107*, 953. (b) Lloyd, M. T.; Anthony, J. E.; Malliaras, G. G. *Mater. Today* **2007**, *10*, 34. (c) Garnier, F. *Acc. Chem. Res.* **1999**, *32*, 209. (d) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.

(2) (a) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1. (b) Mitschke, U.; Bäuerle, P. *J. Mater. Chem* **2000**, *10*, 1471.

(3) Anthony, J. E.; Heeney, M.; Ong, B. S. *MRS Bull.* **2008**, *33*, 698.

(4) Shtein, M.; Peumans, P.; Benziger, J. B.; Forrest, S. R. *Adv. Mater.* **2004**, *16*, 1615.

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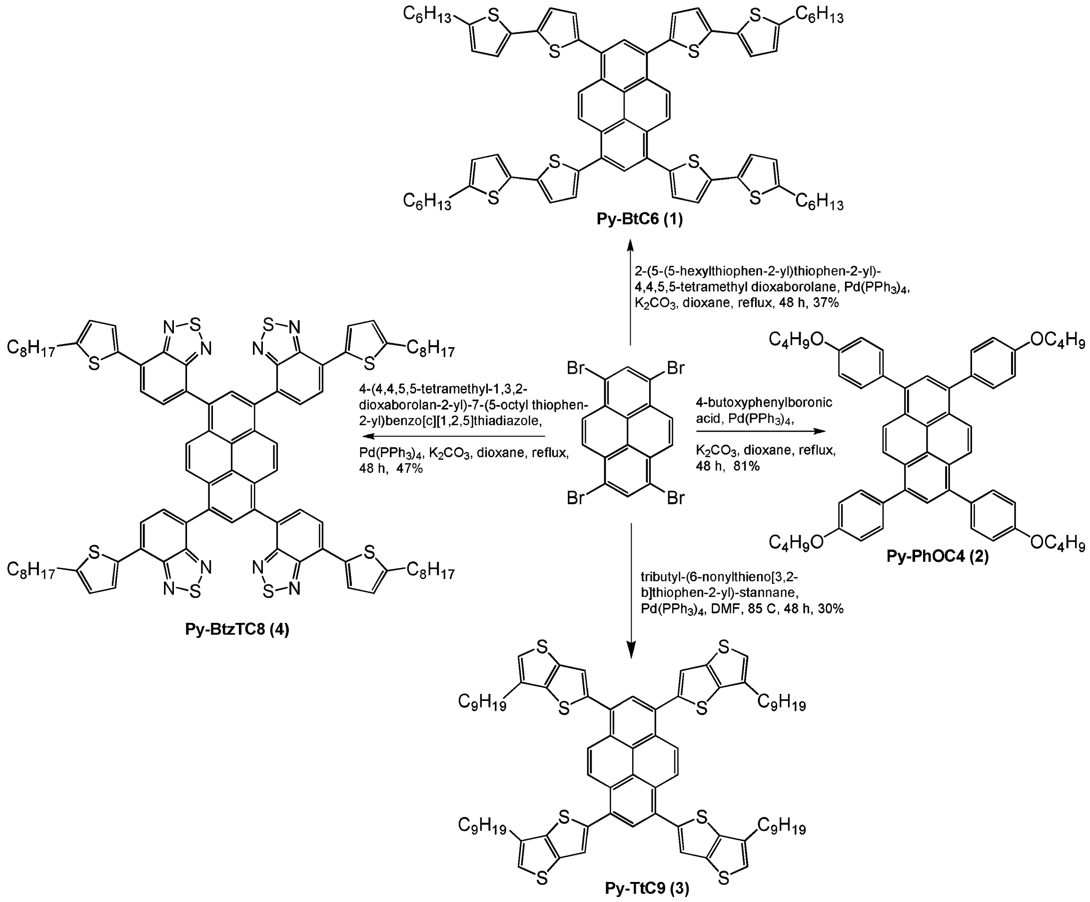
Scheme 1. Synthesis of Compounds **1**−**4**



sizes at much lower costs using technologies such as ink jet and screen printing.[5] Our interest lies in materials that combine the advantages of both small molecules and polymers, specifically monodisperse star-shaped materials with high purity and solution processability as will be explained in this paper. Previous reports from our group describe the use of multifunctionalized *insulating* inorganic cores, such as octavinylsilsesquioxane and cyclic triphosphazenes, as platforms from which organic chromophores were attached for application in solution processable OLEDs.[6] In this method, the conjugated component is electronically isolated, with the core serving as an inert rigid platform to impart amorphous behavior and enhanced thermal properties.

Here, we report the straightforward synthesis, characterization, photophysical, and thermal properties of multifunctionalized solution processable materials using a *conjugated* core, 1,3,6,8-tetrabromopyrene, from which to attach the conjugated organic chromophores. In this approach, the active components are electronically connected through the conjugated planar pyrene core. Tetrafunctional pyrene-based materials, with their extended delocalized π-electrons,

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(5) (a) Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 394. (b) Loo, Y. L.; McCulloch, I. *MRS Bull.* **2008**, *33*, 653. (c) Brabec, C. J.; Durrant, J. R. *MRS Bull.* **2008**, *33*, 670. (d) Sirringhaus, H.; Ando, M. *MRS Bull.* **2008**, *33*, 676.

(6) (a) Lo, M. Y.; Sellinger, A. *Synlett* **2006**, *18*, 3009. (b) Lo, M. Y.; Ueno, K.; Tanabe, H.; Sellinger, A. *Chem. Rec.* **2006**, *6*, 157. (c) Lo, M. Y.; Zhen, C. G.; Lauters, M.; Jabbour, G. E.; Sellinger, A. *J. Am. Chem. Soc.* **2007**, *129*, 5808. (d) Sudhakar, S.; Sellinger, A. *Macromol. Rapid Commun.* **2006**, *27*, 247.

(7) (a) Sagara, Y.; Mutai, T.; Yoshikawa, I.; Araki, K. J. *Am. Chem. Soc.* **2007**, *129*, 1520. (b) Lackowicz, J. R. In *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum Publishers: New York, 1999; pp 595−614. (c) Birks, J. B. In *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970.

(8) (a) Moorthy, J. N.; Natarajan, P.; Venkatkrishnan, P.; Huang, D. F.; Chow, T. J. *Org. Lett.* **2007**, *9*, 5215. (b) Mikroyannidis, J. A. *Synth. Met.* **2005**, *155*, 125. (c) Venkataramana, G.; Sankararaman, S. *Org. Lett.* **2006**, *8*, 2739. (d) Zhang, H. J.; Wang, Y.; Shao, K. Z.; Liu, Y. Q.; Chen, S. Y.; Qiu, W. F.; Sun, X. B.; Qi, T.; Ma, Y. Q.; Yu, G.; Su, Z. M.; Zhu, D. B. *Chem. Commun.* **2006**, *7*, 755. (e) Sienkowska, M. J.; Farrar, J. M.; Zhang, F.; Kusuma, S.; Heiney, P. A.; Kaszynski, P. *J. Mater. Chem.* **2007**, *17*, 1399. (f) Liu, F.; Lai, W. Y.; Tang, C.; Wu, H. B.; Chen, Q. Q.; Peng, B.; Wei, W.; Huang, W.; Cao, Y. *Macromol. Rapid Commun.* **2008**, *29*, 659. (g) Gingras, M.; Placide, V.; Raimundo, J. M.; Bergamini, G.; Ceroni, P.; Balzani, V. *Chem.*—*Eur. J.* **2008**, *14*, 10357. (h) Xia, R. D.; Lai, W. Y.; Levermore, P. A.; Huang, W.; Bradley, D. D. C. *Adv. Funct. Mater.* **2009**, *19*, 2844. (i) Zhao, Z. J.; Li, J. H.; Chen, X. P.; Wang, X. M.; Lu, P.; Yang, Y. *J. Org. Chem.* **2009**, *74*, 383. (j) Halleux, V. de.; Calbert, J. P.; Brocorens, P.; Cornil, J.; Declercq, J. P.; Bredas, J. L.; Geerts, Y. *Adv. Funct. Mater.* **2004**, *14*, 649. (k) Faulkner, L. R.; Bard, A. J.; Tachikaw, H. *J. Am. Chem. Soc.* **1972**, *94*, 691. (l) Tang, C.; Liu, F.; Xia, Y. J.; Xie, L. H.; Wei, A.; Li, S. B.; Fan, Q. L.; Huang, W. *Org. Electron.* **2006**, *7*, 155. (m) Hayer, A.; Halleux, V. de.; Kohler, A.; El-Garoughy, A.; Meijer, E. W.; Barbera, J.; Tant, J.; Levin, J.; Lehmann, M.; Gierschner, J.; Cornil, J.; Geerts, Y. H. *J. Phys. Chem. B* **2006**, *110*, 7653. (n) Oh, H. Y.; Lee, C.; Lee, S. *Org. Electron.* **2009**, *10*, 163. (o) Kim, H. M.; Lee, Y. O.; Lim, S.; Kim, J. S.; Cho, B. R. *J. Org. Chem.* **2008**, *73*, 5127.

Table 1. Optical, Electrochemical, and Thermal Properties of Compounds **1**−**4**

	UV−vis		PL				CIE coordinates[a,e]			
compound	λ_{max} (nm)[a]	λ_{max} (nm)[b]	λ_{max} (nm)[a]	λ_{max}(nm)[b]	bandgap[c] (eV)	HOMO[d]	x	y	T_m[f] (°C)	T_d[g] (°C)
Py-BtC6 (**1**)	375, 451	389, 470	530	605	2.32	−5.15	0.48	0.50		460
Py-PhOC4 (**2**)	306, 394	290, 396	433	462	2.83	−5.25	0.15	0.10	252	436
Py-TtC9 (**3**)	347, 429	364, 442	490	585	2.44	−5.30	0.41	0.56	100	299
Py-BtzTC8 (**4**)	307, 452	380, 471	541	635	2.25	−5.33	0.59	0.41		451

[a] Measured in chloroform solutions. [b] Measured from thin films on glass. [c] Measured from the absorption onset of the UV−vis spectrum. [d] Measured from the oxidation onset of the cyclic voltammetry (CV). [e] Obtained from chromameter measurements upon excitation at 365 nm. [f] Obtained from DSC measurement. [g] Obtained from TGA measurement (temperature at 5% weight loss under nitrogen, 10 °C/min ramp rate).

discotic shape, high photoluminescence efficiency, and good hole-injection/transport properties, have the potential to be a very interesting class of materials for opto-electronic applications.[7] Previously, there have been reports on the synthesis of tetrafunctionalized pyrene materials,[8] but very few of these offer OLED device results,[8a,f,i,n] and none to our knowledge report deep blue OLEDs from solution processing. One very attractive aspect of these materials is that they can be accessed from relatively simple synthetic routes as shown in Scheme 1. We selected bithiophene, phenylene, thienothiophene, and benzothiadiazole−thiophene as the chromophores with the aim of preparing electron-rich materials for application in OLEDs, organic photovoltaics (OPV), and organic thin-film transistors (OTFTs). To achieve solution processability, alkyl groups were incorporated on the conjugated moieties. As illustrated in Scheme 1, **1** (Py-BtC$_6$) and **2** (Py-PhOC$_4$) were synthesized and purified as red and white powders by Suzuki−Miyaura cross-coupling reaction of 1,3,6,8-tetrabromopyrene with commercially available 2-(5-(5-hexylthiophen-2-yl)thiophene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and 4-butoxyphenylboronic acid, respectively. Compounds **3** (Py-TtC$_9$) and **4** (Py-BtzTC$_8$) were synthesized and purified as dark yellow and red powders by coupling tributyl(6-nonylthieno[3,2-*b*]thiophene-2-yl)stannane and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-7-(5-octylthiophene-2-yl)benzo[*c*][1,2,5]thiadiazole[9] with 1,3,6,8-tetrabromopyrene using Stille and Suzuki−Miyaura cross-coupling routes, respectively. All of the compounds are readily soluble in common organic solvents such as $CHCl_3$, CH_2Cl_2, THF, and toluene, which allows for purification by column chromatography (using hexane/CH_2Cl_2 mixtures) and solution processing. ^{1}H and ^{13}C NMR spectra, elemental analysis, and MALDI-TOF were employed to confirm the structure and purity of all compounds (Supporting Information).

The photophysical properties of the compounds were measured by UV−vis absorption and photoluminescence (PL) spectroscopy in chloroform and in thin films. All four compounds exhibit prominent short and long wavelength absorption peaks (see Table 1 and Supporting Information). Compounds **1** and **4** show red-shifted wavelength absorption maxima (λ_{max}) at 451 and 452 nm in comparison to **2** and **3** (λ_{max} = 394 and 429 nm, respectively) due to their slightly more extended conjugation lengths. When compared to molecular pyrene (abs λ_{max} = 338 nm), all compounds in this study (**1**−**4**) demonstrated absorption λ_{max} values that are significantly red-shifted. In thin film absorption, compounds **1**, **3**, and **4** show red shifts of 13−19 nm, whereas compound **2** shows similar absorbance compared to their respective dilute soultions. Solution PL spectra for **2** and **3** show deep blue and sky blue emission, respectively, at 433 and 490 nm, whereas **1** and **4** exhibit green and orange emission at 530 and 541 nm, respectively. The bathochromic shifts of the solution PL λ_{max} range from 40 to 148 nm for compounds **1**−**4** compared to the unsubstituted pyrene core (PL_{max} = 393). In thin film PL, all the compounds are red-shifted 29−95 nm compared their respective dilute solutions (Table 1). This is likely due to aggregation in the solid state versus dilute solutions. CIE coordinates for dilute solutions of **1**−**4** are also shown in Table 1, indicating the excellent deep blue coordinates for **2** (0.15, 0.10).

The electrochemical properties of compounds **1**−**4** were investigated by cyclic voltammetry (CV) in anhydrous dichloromethane (Supporting Information). The HOMO levels or ionization potentials (IP) were calculated by using the known equation IP = E_{ox}^{onset} + 4.4.[10] The results are presented in Table 1. The calculated HOMO values are in the range of −5.15 to −5.33 eV, indicating that the materials are suitable for application in OLEDs. For example, these energy levels match quite well with commonly used hole injection/transport layers and anodes such as PEDOT:PSS (−5.1 eV) and ITO (−4.9 eV). This fine-tuning of electrochemical properties demonstrates the significant effect of attaching the different conjugated moieties to the central pyrene core.

The thermal properties of the tetrafunctional pyrene derivatives were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) and are shown in Table 1. Only **2** and **3** show melting points (T_m = 252 and 100 °C, respectively) in DSC heating cycles up to 300 °C, whereas **1** and **4** do not show any thermal transitions in this range. The thermal decomposition (T_d) temperatures (5% weight loss in nitrogen atmosphere) were observed above 400 °C for all compounds except **3**, which shows T_d onset at 299 °C.

The strong PL emission, tunable energy levels, excellent solubility, enhanced thermal properties, and good film-forming properties make these materials promising candidates for application in solution-processed devices. As a starting point, **2** was selected as a potential deep blue emitting material for application in OLEDs, as this is still a highly sought after goal in the OLED community.[11] The structure of the OLED is as follows: indium tin oxide (ITO)/PEDOT:PSS (50 nm)/ **2** (50 nm)/1,3,5-tris(phenyl-2-benzimidazolyl)-benzene (TPBI) (20 nm)/Ca (20 nm)/Ag (100 nm) where PEDOT/PSS and TPBI act as hole-injecting/transport and electron-injecting/transporting layers, respectively. The OLED device data is shown in Figure 1. The maximum brightness and luminescence efficiency are 5015 cd/m^2 (at 11 V) and 2.56 cd/A (at 10 cd/m^2), respectively (Figure 1a). These efficiency numbers are quite promising for unoptimized small molecule solution processed blue OLEDs.[12] The turn-on voltage for the device of around 3 V is quite low, suggesting that the barrier for hole injection from PEDOT/PSS is low, which is expected from the measured HOMO levels. The nondoped OLED devices show efficient bright blue light emission with CIE coordinates (0.15, 0.18) (EL spectrum shown in Figure 1b).

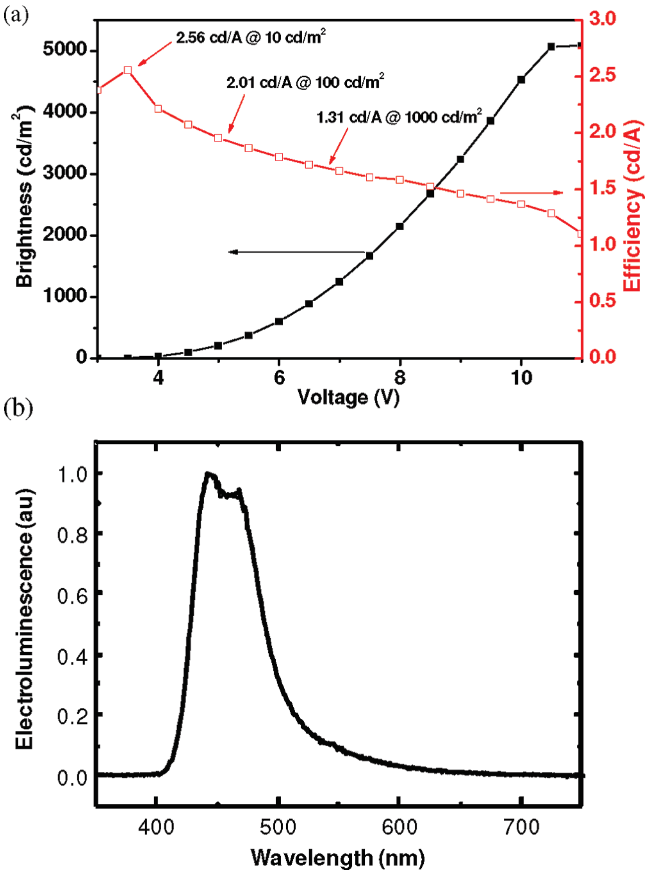

Figure 1. (a) Brightness and efficiency characteristics and (b) EL spectrum of OLED devices based on (**2**). OLED device configuration: ITO/PEDOT (50 nm)/(**2**) (50 nm)/TPBI (20 nm)/Ca (20 nm)/Ag (100 nm) (CIE = 0.15, 0.18).

In summary, we report here the possibilities of tetrafunctionalized pyrene-based materials for application in solution-processed organic electronic devices. The introduction of different moieties (bithiophene, phenylene, thienothiophene, and benzothiadiazole−thiophene) has a substantial influence on the resultant opto-electronic and thermal properties. OLEDs based on 1,3,6,8-tetrakis(4-butoxyphenyl)pyrene (**2**) as the active emitter show efficiencies of 2.56 cd/A, deep blue emission (CIE = 0.15, 0.18), low turn-on voltages (3.0 V), and a maximum brightness of 5015 cd m^{-2} at 11 V. These findings are quite encouraging for unoptimized OLEDs and suggest that further improvements are likely. For example, optimizing the layer thicknesses and doping the emitters into suitable hosts may further improve device efficiency and color coordinates.[8a] We are currently testing these pyrene-based materials for further application in OLEDs and organic field effect transistors (OFETs).

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Supporting Information Available: Experimental procedures, spectroscopic data, thermal analysis, and cyclic voltammograms for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) (a) Zhang, X. N.; Kohler, M.; Matzger, A. J. *Macromolecules* **2004**, *37*, 6306. (b) Sonar, P.; Singh, S. P.; Leclère, P.; Surin, M.; Lazzaroni, R.; Lin, T. T.; Dodabalapur, A.; Sellinger, A. *J. Mater. Chem.* **2009**, *19*, 3228.

(10) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1996**, *8*, 579.

(11) Turker, L.; Tapan, A.; Gumus, S. *Polycyclic Aromat. Compd.* **2009**, *29*, 139.

(12) (a) Zhang, M.; Xue, S.; Dong, W.; Wang, Q.; Fei, T.; Gu, C.; Ma, Y. *Chem. Commun.* **2010**, *46*, 3923. (b) Wang, L.; Jiang, Y.; Luo, J.; Zhou, Y.; Zhou, J.; Wang, J.; Pei, J.; Cao, Y. *Adv. Mater.* **2009**, *21*, 4854.