Novel butterfly pyrene-based organic semiconductors for field effect transistors†

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Novel butterfly pyrene derivatives functionalized with trifluoromethylphenyl and thienyl aromatic groups in the 1-, 3-, 6- and 8-positions of pyrene cores **1** and **2** have been synthesized by Suzuki coupling reactions, and their crystal structures, optical and electrochemical properties investigated; additionally, the field effect transistor using **2** as the active material exhibited a p-type performance.

Recently, organic semiconductors have gained a lot of interest through applications such as organic light emitting diodes (OLEDs),[1] solar cells[2] and organic field effect transistors (OFETs).[3] The interest in studying OFETs stems from the fact that these devices are easier to fabricate than traditional silicon based transistors, which require severe processing techniques, and also the likelihood of replacing amorphous silicon in applications such as identification tags, smart cards and display drivers that are intended for short term use and large scale manufacture. The design and synthesis of novel materials that possess a low threshold voltage, a high on/off ratio, and high mobility and stability under ambient and operating conditions are the major challenges in organic semiconductor research.
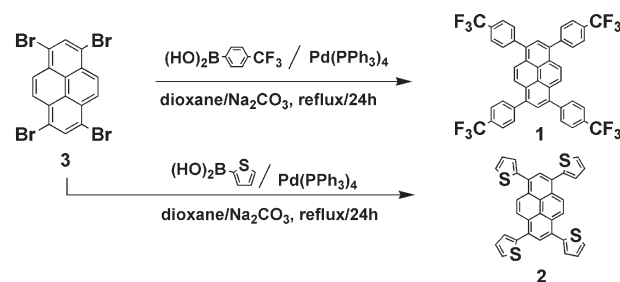
Existing organic semiconductors can be roughly classified into linear,[4–10] star-shaped,[11] branched[12] or lamellar[13] molecules on the basis of their shape. Most organic semiconductors are linear molecules, such as pentacene,[4] oligothiophene,[5] polyfluorenes,[6] tetracene,[7] anthracene[8] and their derivatives.[9] Among them, pentacene is the most well-known linear organic semiconductor with the highest thin film mobility using a polymeric surface treatment,[10] but is only moderately stable in air or under illumination, and has a low solubility in organic solvents. Phthalocyanine and its derivatives are typical lamellar molecules, which have been investigated widely as p-type or n-type active materials in OFETs.[13] Nowadays, a few star-shaped and branched molecules are synthesized and used as semiconducting materials in OFETs because of their easy processibility and high solubility in organic solvents.[11–12] Here, we report the synthesis and characterization of the first examples of novel butterfly pyrene derivatives with trifluoromethylphenyl and thienyl aromatic groups. Their

performance as p-type semiconductors in FET devices is also presented.

The synthesis of pyrene derivatives **1** and **2** were conveniently realized by Suzuki coupling reactions according to Scheme 1. The reaction of 4-trifluoromethylphenylboronic acid and 2-thiopheneboronic acid with 1,3,6,8-tetrabromopyrene in refluxing dioxane under a nitrogen atmosphere gave **1** and **2** in 75 and 77% yields, respectively. Both compounds **1** and **2** dissolve in common organic solvents, allowing these semiconductors to be easily purified by a combination of recrystallization and gradient sublimation. The compounds were characterized by ^{1}H NMR, MALDI-TOF, elemental analysis and X-ray crystallography. Differential scanning calorimetry (DSC) measurements showed sharp melting endotherm peaks at 231 °C for **1** and 308 °C for **2**, respectively. Thermogravimetric analysis (TGA) measurements gave the thermal decomposition temperatures (T_d) 388 °C for **1** and 428 °C for **2**, respectively. All the results shown in Table 1 indicate that the butterfly pyrene-based materials possess excellent thermal stability. This is a necessary feature of functional materials for applications in thin film molecular devices.

Single crystals of each were obtained by slow evaporation of solvent from dichloromethane solutions. Fig. 1(a) and Fig. 1(b) show the ORTEP drawings of **1** and **2** and their atomic numbering schemes, respectively. Both molecules display an inner flat, symmetric molecular geometry, while the peripheral trifluoromethylphenyl and thienyl units adopt twisted forms, connecting with the pyrene core like a flying butterfly. The torsion angles of 52.8 and 60.2° are observed between the pyrene and trifluoromethylphenyl rings, and 55.1 and 57.8° between the pyrene and thienyl rings. The molecules pack in the herringbone motif, as shown in the ESI,†‡ similar to pentacene.[14]

The physical properties of newly prepared compounds **1** and **2** are listed in Table 1. The absorption maximum of **1**, containing electron-withdrawing groups, is located at 381 nm, while

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures with cyclic voltammograms and crystal packing views of **1** and **2**. See DOI: 10.1039/b515433b

Scheme 1 Synthetic routes to compounds **1** and **2**.

Table 1 Physical properties of the two compounds used in FETs

| Compound | T_d/°C | T_m/°C | Solution | | Solid | |
			λ_{abs}/nm	λ_{em}/nm	λ_{em}/nm	E_{ox}/V[a]
1	388	231	381	425	452	1.27
2	428	308	314 and 406	467	545	1.04 and 1.23

[a] 0.1M (*n*-Bu)₄NPF₆ in CH_2Cl_2, Pt electrode, scan rate 50 mV s⁻¹, V *vs.* Ag/AgCl.
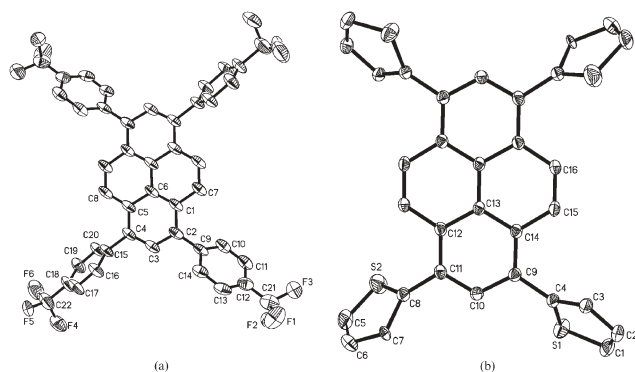
Fig. 1 (a) X-Ray structure of pyrene derivative **1**. (b) X-Ray structure of pyrene derivative **2**.

compound **2**, with electron-donating thienyl units, has double absorption maxima at 314 nm and 406 nm. The optical band gaps obtained from the absorption edges are 2.84 eV for **1** and 2.58 eV for **2**. The lower band gap for **2** is probably attributable to intramolecular charge transfer from the thienyl ring to the pyrene core. Simultaneously, the larger Stokes shift observed in **2** can be explained by the geometry of **2** becoming more planar than **1** in the excited state. Moreover, these two compounds exhibit strong blue and green fluorescence in the solid state. The emission maxima in the solid state are observed at longer wavelengths than in solution (27–78 nm red shift), indicating strong intermolecular interaction in the solid state.

The electrochemical stability of the butterfly compounds was examined by cyclic voltammetry (CV). The results are shown in Table 1 and the ESI.† The CV of **1**, containing acceptor groups, exhibited one oxidation peak (1.27 V *vs.* Ag/AgCl), while **2**, containing donor groups, showed two oxidation peaks (1.04 V and 1.23 V *vs.* Ag/AgCl). Both compounds showed no reduction

peaks. The oxidation potential of **1** is a little higher than that of **2**. This can be attributed to the electron-withdrawing effect of the trifluoromethylphenyl group.[15]

OFET devices were fabricated on SiO₂/Si substrates using a top-contact geometry. An n-type Si wafer with a SiO₂ layer of 450 nm and a capacitance of 10 nF cm⁻² was used as the gate. Thin films of these derivatives (50 nm) were formed on the SiO₂ by high vacuum evaporation at room temperature. Gold source and drain contacts (50 nm) were deposited on the organic layer through a shadow mask. The channel length (*L*) and width (*W*) were 0.4 and 66 mm, respectively. The FET measurements were carried out at room temperature in air or in a vacuum chamber using a semiconductor parameter analyzer. The FET device based on **1** did not show any FET performance. On the other hand, the FET device using **2** as active material exhibited p-type performance. The output characteristics of the device are shown in Fig. 2. The mobility was 3.7×10^{-3} cm² V⁻¹ s⁻¹ with an on/off ratio of 10^4, and the threshold voltage was −21 V. This is the first example of a p-type FET using a butterfly pyrene-type molecule as the active material. The film deposited on the SiO₂/Si substrate was investigated by X-ray diffraction (XRD) in reflection mode. Fig. 3 shows the XRD pattern of the thin film of **2** deposited at room temperature. Almost no reflection peak was observed, suggesting a disorder orientation on the SiO₂/Si substrate.

In summary, we have prepared two butterfly pyrene derivatives with trifluoromethylphenyl and thienyl as terminal groups that show strong fluorescence in the solid state. The thienyl derivative could also be used as an active layer for a p-type FET. To the best of our knowledge, this is the first example of a p-type FET based on butterfly pyrene-type molecules.
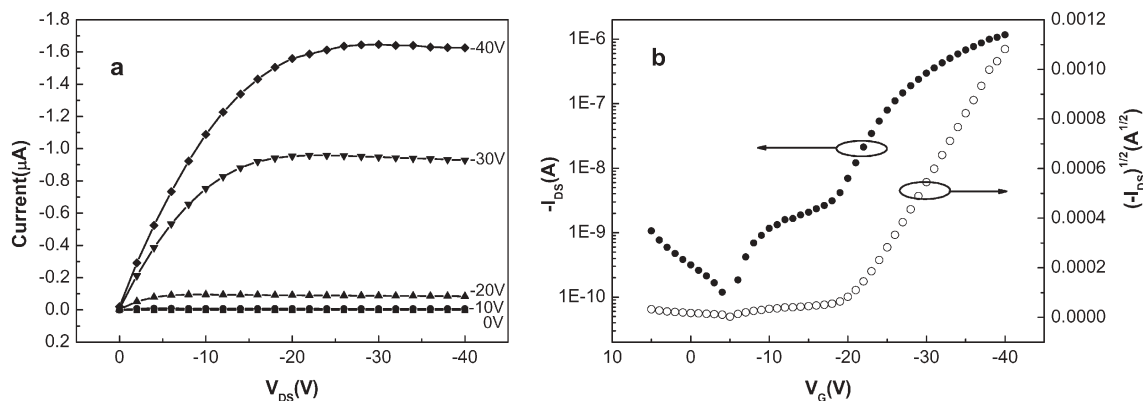
Fig. 2 (a) Drain-to-source current (I_{DS}) *vs.* drain-to-source voltage (V_{DS}) characteristics as a function of gate voltage (V_g) for the FET of **2** fabricated on SiO₂ at room temperature. (b) $-I_{DS}$ and $(-I_{DS})^{1/2}$ *vs.* V_g plots for the same device.
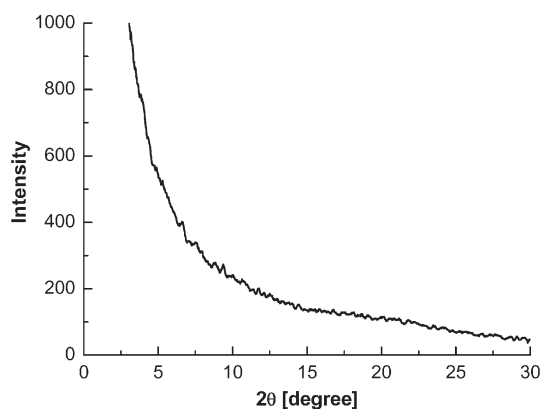
Fig. 3 X-Ray diffraction plot of the film (50 nm thickness) deposited at room temperature for **2**.

Notes and references

‡ **Crystal data for 1**: The measurement of **1** was made on a Bruker SMART with Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at 294 K. The structure was solved by direct methods and SHELXS-97, and refined by using SHELXL-97. Hydrogen atoms were located at calculated positions. Absorption correction was applied using SADABS. C$_{22}$H$_{11}$F$_6$, $M = 389.31$, crystal dimensions $0.24 \times 0.16 \times 0.14$ mm, monoclinic, space group $C2/c$, $a = 20.664(4)$, $b = 12.130(2)$, $c = 14.363(3)$ Å, $\alpha = 90$, $\beta = 92.894(3)$, $\gamma = 90°$, $V = 3595.4(11)$ Å^3, $Z = 8$, $D_c = 1.438$ g cm^{-3}, $\mu = 0.127$ mm^{-1}, $\theta_{max} = 26.36$, 9896 reflections measured, 3651 of which were independent ($R_{int} = 0.0477$), GOF = 1.001, 335 parameters, $R_1 = 0.0528$, $wR_2 = 0.1167$ for all reflections. CCDC 287257. **Crystal data for 2**: The measurement of **2** was made on a SMART APEX CCD with Mo-K$_\alpha$ radiation ($\lambda = 0.71069$ Å) at 293(2) K. The structure was solved by direct methods and SHELXS-97, and refined by using SHELXL-97. Hydrogen atoms were located at calculated positions. Absorption correction was applied using SADABS. C$_{16}$H$_9$S$_2$, $M = 265.35$, crystal dimensions $0.226 \times 0.182 \times 0.094$ mm, monoclinic, space group $P2_1/c$, $a = 13.794(5)$, $b = 8.637(5)$, $c = 11.009(5)$ Å, $\alpha = 90$, $\beta = 112.400(5)$, $\gamma = 90°$, $V = 1212.6(10)$ Å^3, $Z = 4$, $D_c = 1.453$ g cm^{-3}, $\mu = 0.414$ mm^{-1}, $\theta_{max} = 28.46$, 7270 reflections measured, 2859 of which were independent ($R_{int} = 0.0295$), GOF = 1.081, 163 parameters, $R_1 = 0.0815$, $wR_2 = 0.2584$ for all reflections. CCDC 287258. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b515433b

1 U. Mitschke and P. Bauerle, *J. Mater. Chem.*, 2000, **10**, 1471.
2 J. Rostalski and D. Meissner, *Sol. Energy Mater. Sol. Cells*, 2000, **61**, 87.
3 D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater.*, 2002, **14**, 99; Y. Sun, Y. Liu and D. Zhu, *J. Mater. Chem.*, 2005, **15**, 53.
4 Y. Y. Lin, D. J. Gundlach, S. F. Nelson and T. N. Jackson, *IEEE Electron Device Lett.*, 1997, **18**, 606.
5 F. Garnier, A. Yassar, R. Hajlaoui, G. Horowitz, F. Deloffre, B. Servet and P. Alnot, *J. Am. Chem. Soc.*, 1993, **115**, 8716.
6 S. E. Burns, P. Cain, J. Mills, J. Wang and H. Sirringhaus, *MRS Bull.*, 2003, Nov., 829.
7 D. J. Gundlach, J. A. Nichols, L. Zhou and T. N. Jackson, *Appl. Phys. Lett.*, 2002, **80**, 2925; R. W. I. de Boer, T. M. Klapwijk and A. F. Morpurgo, *Appl. Phys. Lett.*, 2003, **83**, 4345.
8 H. Meng, F. Sun, M. B. Goldfinger, G. D. Jaycox, Z. Li, W. J. Marshall and G. S. Blackman, *J. Am. Chem. Soc.*, 2005, **127**, 2406; S. Ando, J. Nishida, E. Fujiwara, H. Tada, Y. Inoue, S. Tokito and Y. Yamashita, *Chem. Mater.*, 2005, **17**, 1261.
9 M. M. Payne, S. R. Parkin, J. E. Anthony, C. Kuo and T. N. Jackson, *J. Am. Chem. Soc.*, 2005, **127**, 4986; H. Moon, R. Zeis, E. Borkent, C. Besnard, A. J. Lovinger, T. Siegrist, C. Kloc and Z. Bao, *J. Am. Chem. Soc.*, 2004, **126**, 15322; J. Locklin, D. Li, S. C. B. Mannsfeld, E. Borkent, H. Meng, R. Advincula and Z. Bao, *Chem. Mater.*, 2005, **17**, 3366; K. Xiao, Y. Liu, T. Qi, W. Zhang, F. Wang, J. Gao, W. Qiu, Y. Ma, G. Cui, S. Chen, X. Zhan, G. Yu, J. Qin, W. Hu and D. Zhu, *J. Am. Chem. Soc.*, 2005, **127**, 13281.
10 T. W. Kelley, D. V. Muyres, P. F. Baude, T. P. Smith and T. D. Jones, *Mater. Res. Soc. Symp. Proc.*, 2003, **771**, L6.5.
11 S. A. Ponomarenko, S. Kirchmeyer, A. Elschner, B. H. Huisman, A. Karbach and D. Drechsler, *Adv. Funct. Mater.*, 2003, **13**, 591; M. Sonntag, K. Kreger, D. Hanft and P. Strohriegl, *Chem. Mater.*, 2005, **17**, 3031; Y. Sun, K. Xiao, Y. Liu, J. Wang, J. Pei, G. Yu and D. Zhu, *Adv. Funct. Mater.*, 2005, **15**, 818.
12 Y. Wu, Y. Li, S. Gardner and B. S. Ong, *J. Am. Chem. Soc.*, 2005, **127**, 614.
13 Z. Bao, A. J. Lovinger and A. Dodobalapur, *Appl. Phys. Lett.*, 1996, **69**, 3066; Z. Bao, A. J. Lovinger and B. Janelle, *J. Am. Chem. Soc.*, 1998, **120**, 207; K. Davidson, R. Jones and S. McDonald, *Synth. Met.*, 2001, **121**, 1399.
14 J. Cornil, J. Ph. Calbert and J. L. Brédas, *J. Am. Chem. Soc.*, 2001, **123**, 1250; S. E. Fritz, S. M. Martin, C. D. Frisbie, M. D. Ward and M. F. Toney, *J. Am. Chem. Soc.*, 2004, **126**, 4084.
15 S. Ando, J. Nishida, H. Tada, Y. Inoue, S. Tokito and Y. Yamashita, *J. Am. Chem. Soc.*, 2005, **127**, 5336.