Diketopyrrolopyrrole as a p-channel organic semiconductor for high performance OTFTs[†]

Sabin-Lucian Suraru,^a Ute Zschieschang,^b Hagen Klauk^{*b} and Frank Würthner^{*a}

Received 13th October 2010, Accepted 15th November 2010 DOI: 10.1039/c0cc04395h

A new diketopyrrolopyrrole derivative 1 exhibits excellent hole mobilities of 0.7 cm² V⁻¹ s⁻¹ and a current *on/off* ratio of 10⁶ under ambient conditions in bottom-gate, top-contact organic thin film transistors (OTFTs) fabricated by vacuum deposition.

The search for new π -conjugated organic semiconductor materials and their application in organic thin film transistors (OTFTs) has emerged as an important research field.¹ Although the highest charge carrier mobilities are observed in single crystals,² thin films appear more promising with regard to applications. Typically, acenes³ and heteroacenes⁴ as well as oligothiophenes⁵ are among the best performing p-type organic semiconductors, exhibiting high field effect mobilities $\mu > 1$ cm² V⁻¹ s⁻¹ and *on/off* ratios >10⁵. The outstanding performance of these molecules has been related to rather small reorganization energies upon formation of their radical cations combined with favourable packing in the solid state.⁶ Although both of these features are appropriately met by acenes,³ more robust and synthetically easier accessible materials are desired from the application point of view.

Diketopyrrolopyrroles (DPPs) are a versatile class of π -conjugated materials, whose most prominent and large scale commercial application is in the area of high grade red pigments, e.g., Pigment Red 254 ("Ferrari red"), that exhibit excellent mechanical and thermal stabilities, bright shades and high colour strengths.⁷ These pigments containing hydrogen atoms at the lactam nitrogens are insoluble in most common solvents owing to strong intermolecular hydrogen-bonding interactions between the lactam units and π - π -stacking between the π -systems.⁸ Thus, N,N'-disubstituted derivatives bearing alkyl groups,9 dendritic residues,10 or polar and ionic substituents¹¹ have been synthesised to achieve solubility in organic solvents and even in water. Due to their favourable optical properties, DPP derivatives were recently considered for dye-sensitised solar cells¹² and as small molecule donor materials in bulk heterojunction (BHJ) solar cells, where remarkably high power conversion efficiencies of 4.4% could be achieved.¹³ Interestingly, by decreasing the orbital energies

^b Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany. E-mail: H.Klauk@fkf.mpg.de; Fax: +49 711 689 1472;

with electron-withdrawing substituents, DPPs could also be utilized as an acceptor component in BHJ solar cells.¹⁴ Despite exhibiting p-type and n-type charge transport properties in photovoltaic devices, DPPs have received little attention as organic semiconductor materials in OTFTs.¹⁵⁻¹⁷ In one example, a DPP pigment with a lactam NH-group has been deposited by thermal evaporation in vacuum and compared with the solution-cast and heat-treated Boc-group-protected analogue, both showing only modest hole mobilities of $\sim 10^{-5}$ and $\sim 10^{-6}$ cm² V⁻¹ s⁻¹, respectively.¹⁵ In a second example, it was demonstrated that DPPs functionalised at cores with terthiophenes afford hole mobilities of up to 0.02 cm² V⁻¹ s⁻¹ in solution-fabricated OTFTs.¹⁶ In a further example, OTFTs from solution-processed polymers bearing alternating DPP and quaterthiophene units were shown to possess ambipolar charge transport properties with hole mobilities up to 0.1 cm² V⁻¹ s⁻¹ and electron mobilities up to 0.09 cm² V⁻¹ s⁻¹.¹⁷ Notably, for the last two examples it remains ambiguous to what extent the charge transport properties, in particular for hole transport, are governed by the DPP or the oligothiophene subunits. Because oligothiophenes are very common p-type organic semiconductors, it appears more reasonable to relate the observed hole transport properties to the oligothiophene subunits rather than to the strongly quadrupolar DPPs. Herein, however, we describe a p-type semiconductor based on a pristine DPP derivative (1, Scheme 1) that shows excellent hole transport characteristics in thin film organic field effect transistors prepared by vacuum deposition.

The new DPP derivative **1** was synthesised by cyanation of the respective brominated precursor 2^{18} by performing a Rosemund-von Braun cyano-dehalogenation reaction with copper(1) cyanide in DMF at 130 °C affording **1** with 31% yield (Scheme 1). The product was easily purified by column chromatography as the branched alkyl chains provide good solubility of this material in organic solvents. The molecular



Scheme 1 Synthesis of DPP 1

^a Universität Würzburg, Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Am Hubland, 97074 Würzburg, Germany. E-mail: wuerthner@chemie.uni-wuerzburg.de;

Fax: +49 931 31 84756; Tel: +49 931 31 85340

Tel: +49 711 689 1401

[†] Electronic supplementary information (ESI) available: Synthetic detail, ¹H NMR and ¹³C NMR spectra, HRMS, UV-vis spectra and a cyclic voltammogram of **1**. See DOI:10.1039/c0cc04395h

Table 1 Summary of the performance for TFTs with DPP 1 fabricated at different deposition temperatures $T_{\rm D}$

$T_{\mathbf{D}}/^{\circ}\mathbf{C}$	$\mu/{ m cm}^2~{ m V}^{-1}~{ m s}^{-1}$	$I_{ m on}/I_{ m off}$	$^{a}U_{\mathrm{T}}/\mathrm{V}$
20	0.2	10 ⁶	-14
50	0.5	10^{6}	-19
70	0.7	10^{6}	-27
90	0.6	10^{6}	-25
^{<i>a</i>} $U_{\rm T}$: Threst	hold voltage.		

structure of DPP 1 was confirmed by ¹H and ¹³C NMR, high resolution mass spectrometry, and elemental analysis.

The redox behaviour of DPP **1** was studied by cyclic voltammetry (CV) in dichloromethane with ferrocene as an internal standard. Two reversible reduction waves at -1.24 V and -1.77 V as well as one reversible oxidation at 0.86 V are observed (Fig. S4, see ESI†). These values correspond to HOMO and LUMO energy levels of -5.66 eV and -3.56 eV if the most commonly used ionization potential of ferrocene (4.8 eV) is applied.¹⁹ The optical absorption in dichloromethane shows a maximum at $\lambda_{max} = 586$ nm (Fig. S5, see ESI†). An excellent agreement is found for the optical band gap (2.12 eV calculated from λ_{max}) and the electrochemical band gap (2.10 eV from CV).

To investigate the charge transport properties of compound 1 bottom-gate, top-contact TFTs with a 110 nm thick $SiO_2/AIO_x/SAM$ gate dielectric were fabricated and measured in air. The organic compound was deposited at four different substrate temperatures (Table 1). Fig. 1 shows the output and transfer characteristic of the TFT prepared at $T_D = 70$ °C that exhibits a hole mobility of $0.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as determined in the saturation regime and a current *on/off* ratio (I_{on}/I_{off}) of 10⁶. These values are amazingly high if we consider the small size of the π -conjugated scaffold, the quite high amount of electronically inactive alkyl chains and the presence of a mixture of diastereomers (due to the racemic nature of the ethyl hexyl side chains).

The dependence of the mobility on the deposition temperature $T_{\rm D}$ (Table 1) shows an increase of the mobility from 20 °C to 50 °C reaching a maximum at 70 °C, whereas a slight decrease was observed at 90 °C. To correlate these results with the morphology of the organic layer, the latter was investigated by atomic force microscopy (AFM). With increasing deposition temperature, DPP 1 forms larger grains and thus the number of crystalline domains decreases (Fig. 2). A lower number of grain boundaries should be favourable for



Fig. 1 Output (left) and transfer (right) characteristics for the bottom-gate, top-contact TFT of DPP 1 measured in air.



Fig. 2 AFM amplitude and topography (inset) images of vacuum deposited thin films of 1 onto $SiO_2/AIO_x/SAM$ gate dielectric at different substrate temperatures T_D (indicated in the respective image).

the charge transport and this leads to an increase of the field effect mobility.

In summary, we discovered an efficient p-channel organic semiconductor material based on the new DPP derivative 1, exhibiting high hole mobilities and on/off ratios in vacuum-deposited TFTs. The easy synthetic access is an additional advantage of this organic material for a wide range of applications and it opens up new prospectives for target molecules in respect of high performance organic semiconductors.

Notes and references

- Organic Field-Effect Transistors, ed. Z. Bao and J. Locklin, Taylor and Francis, Boca Raton, USA, 2007; A. R. Murphy and J. M. J. Fréchet, Chem. Rev., 2007, 107, 1066; A. Facchetti, Mater. Today, 2007, 10, 28; Organic Electronics, ed. H. Klauk, Wiley-VCH, Weinheim, Germany, 2006; Y. Sun, Y. Liu and D. Zhu, J. Mater. Chem., 2005, 15, 53.
- 2 V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson and J. A. Rogers, *Science*, 2004, 303, 1644.
- 3 J. E. Anthony, Angew. Chem., Int. Ed., 2008, 47, 452.
- 4 K. Takimiya, H. Ebata, K. Sakamoto, T. Izawa, T. Otsubo and Y. Kunugi, J. Am. Chem. Soc., 2006, **128**, 12604; M. L. Tang, A. D. Reichardt, T. Siegrist, S. C. B. Mannsfeld and Z. Bao, Chem. Mater., 2008, **20**, 4669; S. Subramanian, S. K. Park, S. R. Parkin, V. Podzorov, T. N. Jackson and J. E. Anthony, J. Am. Chem. Soc., 2008, **130**, 2706; P. Gao, D. Beckmann, H. N. Tsao, X. Feng, V. Enkelmann, M. Baumgarten, W. Pisula and K. Müllen, Adv. Mater., 2009, **21**, 213.
- 5 M. Halik, H. Klauk, U. Zschieschang, G. Schmid, S. Ponomarenko, S. Kirchmeyer and W. Weber, *Adv. Mater.*, 2003, 15, 917.
- 6 J.-L. Brédas, D. Beljonne, V. Coropceanu and J. Cornil, *Chem. Rev.*, 2004, **104**, 4971.
- 7 Z. Hao and A. Iqbal, Chem. Soc. Rev., 1997, 26, 203; O. Wallquist and R. Lenz, Macromol. Symp., 2002, 187, 617.
- 8 A. Iqbal, L. Cassar, A. C. Rochat, J. Pfenninger and O. Wallquist, J. Coat. Technol., 1988, 60, 37.
- 9 T. Beyerlein and B. Tieke, *Macromol. Rapid Commun.*, 2000, 21, 182; A. B. Tamayo, M. Tantiwiwat, B. Walker and T.-Q. Nguyen, *J. Phys. Chem. C*, 2008, 112, 15543.
- 10 J. Hofkens, W. Verheijen, R. Shukla, W. Dehaen and F. C. de Schryver, *Macromolecules*, 1998, **31**, 4493.
- B. Song, Z. Wang, S. Chen, X. Zhang, Y. Fu, M. Smet and W. Dehaen, *Angew. Chem., Int. Ed.*, 2005, 44, 4731; B. Song, H. Wei, Z. Wang, X. Zhang, M. Smet and W. Dehaen, *Adv. Mater.*, 2007, 19, 416.
- 12 S. Qu, W. Wu, J. Hua, C. Kong, Y. Long and H. Tian, J. Phys. Chem. C, 2010, 114, 1343.
- 13 B. Walker, A. B. Tamayo, X.-D. Dang, P. Zalar, J. H. Seo, A. Garcia, M. Tantiwiwat and T.-Q. Nguyen, *Adv. Funct. Mater.*, 2009, **19**, 3063.
- 14 P. Sonar, G.-M. Ng, T. T. Lin, A. Dodabalapur and Z.-K. Chen, J. Mater. Chem., 2010, 20, 3626; B. P. Karsten,

J. C. Bijleveld and R. A. J. Janssen, Macromol. Rapid Commun., 2010, 31, 1554.

- 15 H. Yanagisawa, J. Mizuguchi, S. Aramaki and Y. Sakai, Jpn. J.
- Appl. Phys., 2008, 47, 4728.
 16 M. Tantiwiwat, A. Tamayo, N. Luu, X.-D. Dang and T.-Q. Nguyen, J. Phys. Chem. C, 2008, 112, 17402.
- 17 L. Bürgi, M. Turbiez, R. Pfeiffer, F. Bienewald, H.-J. Kirner and C. Winnewisser, Adv. Mater., 2008, 20, 2217; J. C. Bijleveld,

A. P. Zoombelt, S. G. J. Mathijssen, M. M. Wienk, M. Turbiez, D. M. de Leeuw and R. A. J. Janssen, J. Am. Chem. Soc., 2009, 131, 16616.

- 18 L. Huo, J. Hou, H.-Y. Chen, S. Zhang, Y. Jiang, T. L. Chen and Y. Yang, Macromolecules, 2009, 42, 6564.
- 19 B. W. D'Andrade, S. Datta, S. R. Forrest, P. Djurovich, E. Polikarpov and M. E. Thompson, Org. Electron., 2005, 6, 11.

Electronic supplementary information (ESI) for:

Diketopyrrolopyrrole as p-channel organic semiconductor for high performance OTFTs

Sabin-Lucian Suraru,^a Ute Zschieschang,^b Hagen Klauk^{*,b} and Frank Würthner^{*,a}

^a Universität Würzburg, Institut für Organische Chemie and Röntgen Research Center for Complex Material Systems, Am Hubland, 97074 Würzburg, Germany; Fax: +49 (0)931 31 84756; Tel: +49 (0)931 31 85340; E-mail: wuerthner@chemie.uni-wuerzburg.de

^b Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany; Fax: +49 (0)711 689 1472; Tel: +49 (0)711 689 1401; E-mail: H.Klauk@fkf.mpg.de

Table of contents

1. General methods	S1
2. Experimental procedures, analytical and spectroscopic data	S2
3. ¹ H NMR, ¹³ C NMR spectra and ESI-HRMS of DPP 1	S3
4. Cyclic voltammogram and UV-vis spectrum	S5
5. Fabrication and characterization of organic TFTs	S6
6. References	S7

1. General methods

The starting compound 2,5-di(2-ethylhexyl)-3,6-bis(5-cyano-thiophen-2-yl)pyrrolo[3,4-c]-pyrrole-1,4-dione **2** was prepared according to the literature.¹ All other reagents and solvents were obtained from commercial suppliers and purified and dried according to standard procedures.² Column chromatography was performed on silica gel (Merck Silica 60, particle size 0.040-0.063 mm). Solvents for spectroscopic studies were of spectroscopic grade and used as received.

Elemental analysis was performed on a CHNS 932 analyzer (Leco Instruments GmbH, Mönchengladbach, Germany). ¹H and ¹³C spectra were recorded in CD_2Cl_2 on a Bruker Avance 400 spectrometer. Residual undeuterated solvent was used as internal standard (5.32 ppm for ¹H, 53.84 ppm for ¹³C). High-resolution ESI-TOF mass spectrometry was carried out on a microTOF focus instrument (Bruker Daltronik GmbH). UV-vis measurements were performed in CH_2Cl_2 (10⁻⁵ M) in a

conventional quartz cell (light pass 10 mm) on a Perkin-Elmer Lambda 950 spectrometer. For cyclic voltammetry, a standard commercial electrochemical analyzer (EC epsilon; BAS Instruments, UK) with a three electrode single-compartment cell was used. Dichloromethane (HPLC grade) was dried over calcium hydride under argon and degassed before using. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was prepared according to the literature,³ and recrystallized from ethanol/water. The measurements were carried out in dichloromethane at a concentration of about 10⁻⁴ M with ferrocene (Fc) as an internal standard for the calibration of the potential. Ag/AgCl reference electrode was used. A Pt disc and a Pt wire were used as working and auxiliary electrodes, respectively.

2. Experimental procedures, analytical and spectroscopic data

2,5-Di(2-ethylhexyl)-3,6-bis(5-cyano-thiophen-2-yl)pyrrolo[3,4-c]-pyrrole-1,4-dione (1)

A mixture of compound 2 (249 mg, 0.365 mmol) and copper(I)cyanide (1.50 g, 16.7 mmol) in dry DMF (8 mL) was heated under argon for 8 h at 130 °C. The reaction mixture was allowed to cool down to room temperature and a saturated solution of sodium cyanide in water was added. The aqueous phase was extracted with dichloromethane. The solvent was removed under reduced pressure and the residue was purified by column chromatography (dichloromethane) affording 48.8 mg (31%) of a dark violet solid.

¹H NMR (400 MHz, CD₂Cl₂): $\delta = 8.82$ (d, ³*J* = 4.2 Hz, 2H), 7.76 (d, ³*J* = 4.2 Hz, 2H), 4.03-3.91 (m, 4H), 1.84-1.72 (m, 2H), 1.40-1.18 (m, 16H), 0.91-0.82 (m, 12H). ¹³C NMR (101 MHz, CD₂Cl₂): $\delta = 161.5$, 139.8, 138.3, 135.7, 134.8, 113.9, 113.7, 110.9, 46.4, 39.7, 30.5, 28.7, 23.9, 23,4, 14.2, 10.5. HRMS (ESI, acetonitrile/CHCl₃ 1:1, pos. mode): *m*/*z* 575.2510 [M+H]⁺ (calcd. for C₃₂H₃₉N₄O₂S₂ 575.2510). Elemental Anal. Calcd. for C₃₂H₃₈N₄O₂S₂: C, 66.87; H, 6.66; N, 9.75; S, 11.16; O, 3.94. Found: C, 66.60; H, 6.62; N, 9.77; S, 11.09. CV (CH₂Cl₂, 0.1 M TBAHFP, vs. Fc/Fc⁺): *E*_{*I*/2}^{red} (X⁻/X²⁻) = -1.77 V, *E*_{*I*/2}^{red} (X/X⁻) = -1.24 V, *E*_{*I*/2}^{ox} (X/X⁺) = 0.86 V. UV-vis (CH₂Cl₂): λ_{max} (ε) = 586 (28500), 546 nm (26500 M⁻¹ cm⁻¹).

3. ¹H NMR, ¹³C NMR spectra and ESI-HRMS of DPP 1



Fig. S1 ¹H NMR spectrum (400 MHz) of DPP **1** in CD_2Cl_2 .



Fig. S2 13 C NMR spectrum (101 MHz) of DPP **1** in CD₂Cl₂.



Fig. S3 High-resolution ESI-TOF mass spectrum of DPP 1 in acetonitrile/chloroform 1:1.

4. Cyclic voltammogram and UV-vis spectrum



Fig. S4 Cyclic voltammogram of 1 in dichloromethane using ferrocene as an internal standard.

Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2011



Fig. S5 Absorption spectrum of 1 in dichloromethane.

5. Fabrication and characterization of organic TFTs

Organic TFTs were fabricated on heavily doped silicon substrates, which also served as a common gate electrode of the transistors. The gate dielectric consists of a 100 nm thick layer of SiO₂, plus an 8 nm thick layer of AlO_x, plus a 2.1 nm thick self-assembled monolayer of pentadecylfluoro-octadecylphosphonic acid. The SiO₂ layer was obtained by thermal oxidation of the Si substrate, the AlO_x was deposited by atomic layer deposition, and the SAM was obtained by immersing the substrate in a 2-propanol solution of the phosphonic acid molecules. (In principle, phosphonic acid SAMs can also be obtained on SiO₂, but we have found that AlO_x is a more suitable surface for high-quality phosphonic acid SAMs). A 30 nm thick layer of the organic semiconductor DPP **1** was then deposited onto the SiO₂/AlO_x/SAM gate dielectric by thermal sublimation in a vacuum evaporator. TFTs were completed by evaporating 30 nm thick gold source and drain contacts through a polyimide shadow mask, defining a channel length of 100 μ m and a channel width of 1000 μ m. The current-voltage characteristics were measured using an Agilent 4156C Semiconductor Parameter Analyzer in ambient

conditions. The sample of DPP **1** was measured again after six months storage under ambient conditions, showing a significantly reduced performance of 10^{-5} cm² V⁻¹ s⁻¹.

The AFM images were processed with WSXM, a freeware scanning probe microscopy software.⁴

6. References

- L. Huo, J. Hou, H.-Y. Chen, S. Zhang, Y. Jiang, T. L. Chen, Y. Yang, *Macromolecules*, 2009, 42, 6564.
- 2 D. D. Perrin, W. L. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals* –Pergamon Press Ltd.: Oxford, 1980, 2nd edn.
- 3 A. J. Fry, in *Laboratory Techniques in Electroanalytical Chemistry*, ed. Peter Kissinger and William R. Heineman, Marcel Dekker Ltd., New York; 1996, 2nd edn.
- 4 I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, J. Gomez-Herrero, A. M. Baro, *Rev. Sci. Instrum.*, 2007, 78, 013705-1.