

# A tetrathiafulvalene–tetracyanoanthraquinodimethane (TTF–TCNAQ) diad with a chemically tunable HOMO–LUMO gap

Jincai Wu,<sup>a,†</sup> Shi-Xia Liu,<sup>a,\*</sup> Antonia Neels,<sup>b</sup> Franck Le Derf,<sup>c</sup> Marc Sallé<sup>c</sup> and Silvio Decurtins<sup>a</sup>

<sup>a</sup>Departement für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

<sup>b</sup>Institut de Microtechnique, Université de Neuchâtel, Rue Jaquet Droz 1, CH-2002 Neuchâtel, Switzerland

<sup>c</sup>Laboratoire de Chimie, Ingénierie Moléculaire et Matériaux d'Angers (CIMMA), Université d'Angers, CNRS UMR 6200, 2 Bd Lavoisier, 49045 Angers, France

Received 10 July 2007; revised 21 August 2007; accepted 28 August 2007

Available online 1 September 2007

**Abstract**—An imidazole-incorporated TTF–TCNAQ diad was synthesised, which shows remarkable optical and electrochemical responses as a function of pH.

© 2007 Elsevier Ltd. All rights reserved.

## 1. Introduction

Molecules with energetically low HOMO–LUMO gaps are of prime importance for the good performance of organic electronic devices.<sup>1,2</sup> As a consequence, much effort has been devoted to the preparation of a variety of  $\pi$ -conjugated oligo- or polymers<sup>3</sup> as well as to covalent linkage of a  $\pi$ -electron donor (D) to a  $\pi$ -electron acceptor (A) through a  $\sigma$ -bonded molecular bridge.<sup>4–6</sup> The latter has received a great deal of attentions due to their potential application in fields such as molecular electronics, nonlinear optics, photovoltaics and artificial photosynthetic models.<sup>7</sup> Among all kind of electron donors and acceptors, tetrathiafulvalene (TTF) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) derivatives have been widely used for the study of photoinduced intramolecular charge transfer processes in such D–A systems.<sup>5–7</sup> It remains a challenge to tune the HOMO–LUMO gap by applying external stimuli, and therefore to control the performance of the corresponding electronic devices. Obviously, the development of ‘responsive’ D–A systems is very appealing. Such responsive systems are also highly desirable in redox sensor materials with valuable optical and electronic properties. In this context, we have focused our efforts on systems offering a good electrochemical

amphotericity and being prone to exhibit an efficient switching behaviour.

The imidazole unit possesses two heteroatoms, which not only retain a versatile reactivity, for example, towards alkylation, deprotonation and protonation, but also give rise to hydrogen bonding. These unique structural features offer a possibility of tuning the HOMO–LUMO gap via chemical stimuli. Therefore, an efficient synthetic route to an imidazole-incorporated TTF–TCNAQ diad **1** has been developed. This new compound shows remarkable optical and electrochemical responses as a function of pH as well as to the nature of substituents of the imidazole ring. Particularly, the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) significantly improves the electron-donating ability of the TTF and decreases the HOMO–LUMO gap.

## 2. Result and discussion

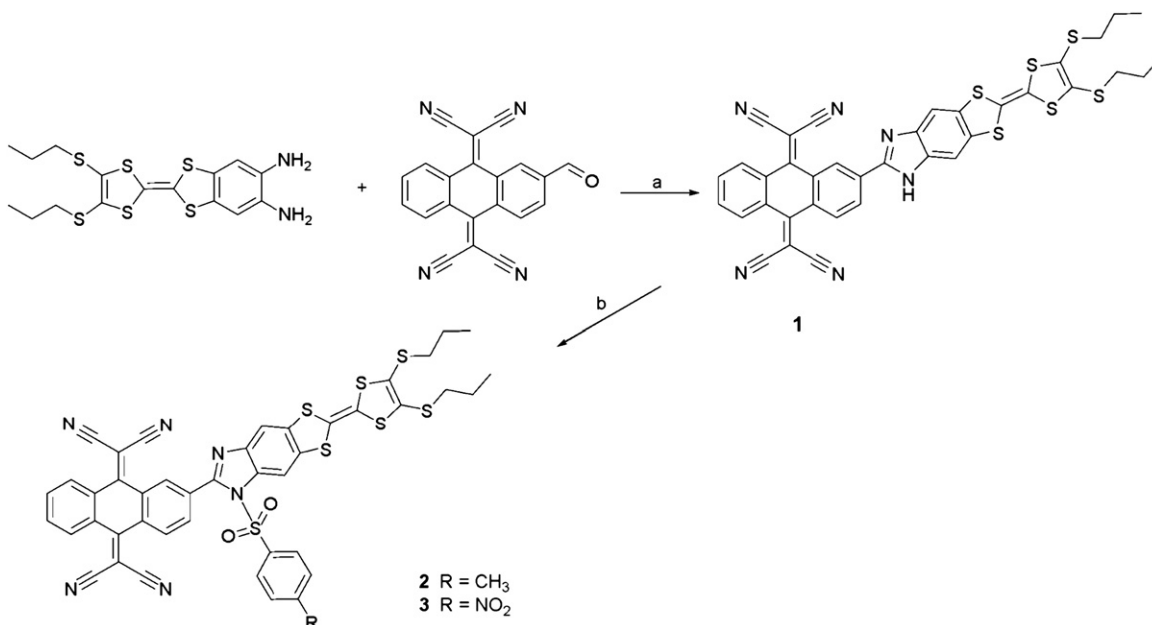
The target compound **1** was prepared via the direct condensation reaction of the diamine TTF precursor<sup>5d</sup> and a formyl-functionalised tetracyanoanthraquinodimethane<sup>8</sup> in 85% isolated yield (Scheme 1). Further alkylation with 4-substituted phenylsulfonyl chloride affords compounds **2** and **3** quantitatively.

Single crystals suitable for X-ray structural determination were obtained by slow evaporation of a saturated solution of **1** in CH<sub>3</sub>CN. The compound crystallises in the centrosymmetric triclinic space group with two TTF–TCNAQ

**Keywords:** Tetrathiafulvalene; 7,7,8,8-Tetracyano-*p*-quinodimethane; HOMO–LUMO gap; Intramolecular charge transfer; Cyclic voltammetry.

\* Corresponding author. Tel.: +41 31 6314296; fax: +41 31 6314399; e-mail: [liu@iac.unibe.ch](mailto:liu@iac.unibe.ch)

† Present address: State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, PR China.

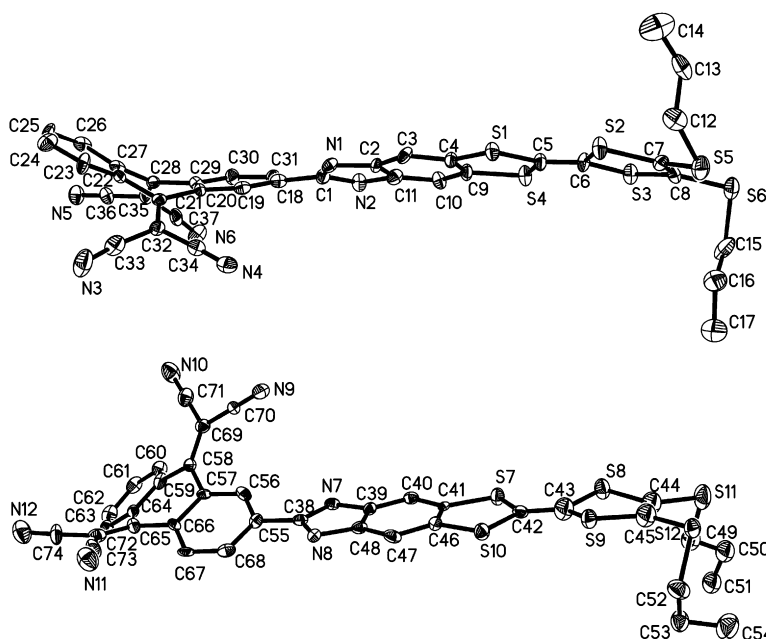


**Scheme 1.** A synthetic route to TTF–TCNAQ diads (a) nitrobenzene, 150 °C, 20 h; 85%; (b) NEt<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 4-substituted phenylsulfonamide, rt overnight, quantitatively.

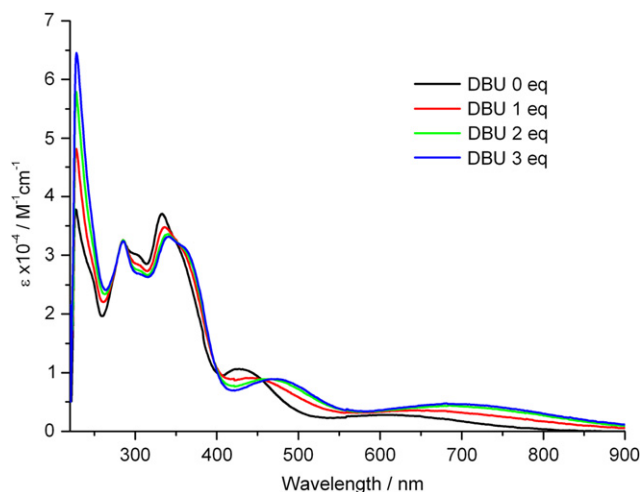
molecules, one water molecule and one half of an acetonitrile molecule per asymmetric unit (Fig. 1). The imidazole ring is nearly coplanar with the TTF moiety while, due to crystal packing effects, the propyl substituents are arranged distinctly in an out-of-plane conformation. As expected, the tetracyanoanthraquinone unit adopts a butterfly-like conformation as observed in other related D–A systems.<sup>9</sup> Bond lengths and conformations within the donor and acceptor units are in good agreement with those of their corresponding neutral species. The twist angles between the benzimidazole and TCNAQ units are 23.0(4)° and 25.5(3)°, respectively, for both crystallographically independent molecules. In the crystal lattice, the molecules are linked by

N–H···N (2.889 Å), N–H···O (2.863 Å), O–H···N (2.995 Å) hydrogen bonds and also by unconventional O–H···N≡C, C–H···S, C–H···N hydrogen bonds in a range of 3.067–3.646 Å. No significant  $\pi$ – $\pi$  interactions have been observed due to the nonplanar conformation of the TCNAQ moiety.

An intramolecular charge transfer (ICT) from the TTF unit to the TCNAQ moiety of compound **1** is evidenced by the appearance of a strong broad absorption band centered at 615 nm (Fig. 2). Additionally, an absorption band at 430 nm can be assigned to an ICT transition from the TTF unit to the imidazole fragment since it disappears upon



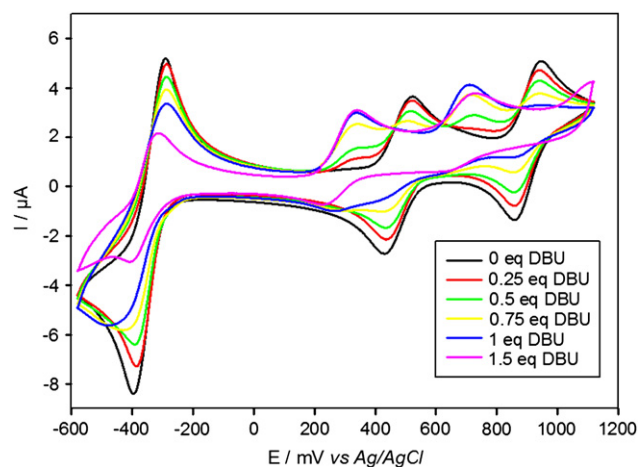
**Figure 1.** An ORTEP (30% probability ellipsoids) structure of **1**, showing both crystallographically independent molecules. Hydrogen atoms and solvent molecules are omitted for clarity.



**Figure 2.** Absorption spectra of **1** ( $1 \times 10^{-5}$  M) in  $\text{CH}_2\text{Cl}_2$  as a function of DBU concentration.

protonation in the presence of *para*-toluene sulfonic acid as well as in the case of the substituted compounds **2** and **3** (see Supplementary data). In the UV region, strong absorption bands are characteristic for  $\pi$ - $\pi^*$  transitions located on the TTF and TCNAQ subunits.<sup>10</sup> Interestingly, upon the addition of DBU, the ICT band at 430 nm gradually disappears throughout this addition and a new band around 475 nm concomitantly emerges. A well-defined isosbestic point at 455 nm can clearly be observed (Fig. 2), indicating the presence of two species in chemical equilibrium, namely compound **1** and presumably the deprotonated species or the hydrogen bonded complex between **1** and DBU.<sup>11</sup> During the UV-vis titration, the colour of the solution changes from green to brown. Moreover, the ICT band around 615 nm is also red-shifted by 80 nm. A possible explanation for this observation lies on the enhancement of the electron-donating ability of the TTF unit upon deprotonation or formation of the hydrogen bonded complex, hence increasing the HOMO energy of the molecule. This is confirmed by electrochemical data (Fig. 3).

The redox properties of compounds **1–3** were studied by cyclic voltammetry (CV) in  $\text{CH}_2\text{Cl}_2$  (Table 1). All of them



**Figure 3.** Cyclic voltammograms of **1** ( $10^{-3}$  M) as a function of DBU concentration, recorded in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$  (1:1) with  $\text{Bu}_4\text{NPF}_6$  (0.1 M) as the supporting electrolyte on Pt electrode with a scan rate 100 mV/s.

**Table 1.** Redox potentials of compounds **1–3**<sup>a</sup>

Compound	$E_1^{\text{red}}$	$E_1^{\text{ox}}$	$E_2^{\text{ox}}$	$\Delta E$
<b>1</b>	-0.30	0.52	0.94	0.82
<b>2</b>	-0.27	0.65	1.02	0.92
<b>3</b>	-0.06	0.84	1.20	0.90

<sup>a</sup> The data are given in V versus Ag/AgCl in  $\text{CH}_2\text{Cl}_2$ ;  $\text{Bu}_4\text{NPF}_6$  (0.1 M) as the supporting electrolyte on Pt electrode; scan rate 100 mV/s.  $\Delta E = E_1^{\text{ox}} - E_1^{\text{red}}$ .

show a clear electrochemically amphoteric behaviour consisting of two single-electron oxidation waves (typical for TTF derivatives) and one two-electron reduction wave (TCNAQ). In the cases of compounds **2** and **3**, the presence of the electron-withdrawing substituent on the imidazole ring enhances the electron-accepting ability of the TCNAQ fragment, but reduces the electron-donating ability of the TTF fragment much more strongly, leading to an increase in the electrochemical HOMO–LUMO gap,  $\Delta E$ . Similar results were also observed upon the addition of *para*-toluene sulfonic acid to **1** (see Supplementary data). Remarkably, the addition of DBU enhances the electron-donating ability of the donor part, but keeps the redox properties of the acceptor subunit being essentially unaltered, resulting in a significant decrease of the HOMO–LUMO gap of **1** (Fig. 3). These observations are in good agreement with the results of UV-vis spectroscopy measurements. In the positive direction, with progressive addition of DBU, both redox processes of the TTF unit are clearly divided into two different redox systems as a result of the coexistence of free **1** ( $E_1^{\text{ox}} = 0.47$  V,  $E_2^{\text{ox}} = 0.91$  V) and a new electroactive system ( $E_1^{\text{ox}} = 0.27$  V,  $E_2^{\text{ox}} = 0.67$  V). It is noteworthy from Figure 3 that (i) no additional change is observed in the oxidation peaks (TTF part) for more than 1 equiv of added DBU,<sup>12</sup> and (ii) both oxidation potentials are substantially negatively shifted. In contrast, in the negative direction, the reversible reduction wave is slightly negatively shifted by 0.04 V. Therefore, the electrochemical HOMO–LUMO gap  $\Delta E$  (**1**: 0.82 V, **1**·DBU: 0.66 V) significantly decreases with the addition of DBU.

### 3. Conclusion

In summary, an imidazole-incorporated TTF–TCNAQ diad **1** was synthesised. This compound shows remarkable optical and electrochemical responses as a function of pH as well as to the nature of substituents of the imidazole ring. Furthermore, it has been demonstrated that the electrochemical and optical HOMO–LUMO gap  $\Delta E$  can be tuned by the addition of DBU. This finding represents an important first example of a TTF–TCNAQ diad with a chemically tunable HOMO–LUMO gap, suggesting a new approach for controlling charge-transfer processes.

### 4. Experimental

#### 4.1. Equipment

Melting points were determined using a Büchi 510 instrument and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a Bruker AC 300 spectrometer operating at

300.18 and 75.5 MHz, respectively: chemical shifts reported in parts per million relative to TMS. The following abbreviations were used s (singlet), d (doublet), t (triplet) and m (multiplet). UV–vis absorption spectra were recorded on a Perkin-Elmer Lambda 10 spectrometer. Elemental analyses were performed on a Carlo Erba EA 1110 CHN apparatus. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr pellets. EI spectra were recorded using an Auto SpecQ spectrometer. MALDI-MS was carried out with a FTMS 4.7 TBioAPEX II TOF apparatus. Cyclic voltammetric measurements were conducted on a EG&G PAR 273A in a three-electrode single-compartment cell equipped with platinum electrodes (diameter 1 mm), a silver wire counter electrode and a Ag/AgCl reference electrode.

## 4.2. Crystallography

A very small dark orange crystal of compound **1** was mounted on a Stoe Mark II-Imaging Plate Diffractometer System<sup>13</sup> (Stoe & Cie, 2002) equipped with a graphite monochromator. Data collection was performed at  $-100\text{ }^{\circ}\text{C}$  using Mo K $\alpha$  radiation ( $\lambda=0.71073\text{ \AA}$ ); 240 exposures (10 min per exposure) were obtained at an image plate distance of 135 mm,  $\varphi=0^{\circ}$  and  $0<\omega<180^{\circ}$  and  $\varphi=90^{\circ}$  and  $0<\omega<180^{\circ}$  with the crystal oscillating through  $1.5^{\circ}$  in  $\omega$ . The resolution was  $D_{\min}\text{--}D_{\max}$  24.00–0.82  $\text{\AA}$ . The structure was solved by direct methods using the program SHELXS-97<sup>14</sup> and refined by full matrix least squares on  $F^2$  with SHELXL-97.<sup>15</sup> The hydrogen atoms of the water molecules were found from difference Fourier maps and refined constraining their O–H bond distances to their theoretical values. The remaining hydrogen atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. An empirical absorption correction was applied using DELREFABS (PLATON,<sup>16</sup>  $T_{\min}=0.489$ ,  $T_{\max}=0.836$ ). Crystal data has been deposited at the Cambridge Crystallographic Data Centre, reference CCDC 646227. Copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-(0)1223-336033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

## 4.3. Materials

All reagents and solvents were of commercial quality. 5,6-Diamino-2-(4,5-bis(propylthio)-1,3-dithio-2-ylidene)-benzo[*d*]-1,3-dithiole,<sup>5d</sup> and 2-formyl-9,10-bis(dicyanomethylene)anthracene<sup>8</sup> were prepared according to literature procedures.

**4.3.1. Compound 1.** To a solution of 5,6-diamino-2-(4,5-bis(propylthio)-1,3-dithio-2-ylidene)-benzo[*d*]-1,3-dithiole (0.243 g, 1 mmol) in nitrobenzene (50 ml) was added slowly a solution of 2-formyl-9,10-bis(dicyanomethylene)anthracene (0.332 g, 1 mmol) in nitrobenzene (50 ml). The mixture was stirred at  $150\text{ }^{\circ}\text{C}$  for 20 h. After cooling to room temperature, the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (2:1, v/v) as eluent, affording compound **1** as a dark green solid. Yield: 0.63 g (85%). Mp  $246\text{--}248\text{ }^{\circ}\text{C}$ . IR (KBr,  $\text{cm}^{-1}$ ): 3429, 2922, 2225, 1606, 1552, 1454, 1323, 1227, 1084, 839,

773, 689.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 13.50 (s, 1H), 9.10 (d,  $J=1.6\text{ Hz}$ , 1H), 8.46–8.49 (m, 2H), 8.29–8.32 (m, 2H), 7.86–7.98 (m, 4H), 2.88 (t,  $J=7.2\text{ Hz}$ , 4H), 1.62 (m, 4H), 0.99 (t,  $J=7.5\text{ Hz}$ , 6H). MS (EI): *m/z* 744 ( $\text{M}^+$ , 19%). Anal. Calcd for  $\text{C}_{37}\text{H}_{24}\text{N}_6\text{S}_6\cdot 0.5\text{hexane}$ : C 60.96, H 3.96, N 10.66. Found C 60.85, H 4.01, N 10.19.

**4.3.2. Compound 2.** To a solution of compound **1** (0.074 g, 0.1 mmol) in dichloromethane (10 ml) was added 10 equiv of triethyl amine (0.14 ml, 10 mmol). Then a solution of 4-methyl-phenylsulfonyl chloride (0.024 g, 0.12 mmol) in dichloromethane (10 ml) was dropped into the above-mentioned solution at  $0\text{ }^{\circ}\text{C}$  during 1 h. The mixture continued to be stirred overnight at room temperature. After the removal of all solvents under vacuum, the crude product was purified by flash chromatography on silica gel with hexane/ethyl acetate (1:1, v/v) as eluent, affording compound **2** as a dark green solid. Yield: 0.088 g (98%). Mp  $169\text{--}173\text{ }^{\circ}\text{C}$ . IR (KBr,  $\text{cm}^{-1}$ ): 3435, 2921, 2224, 1634, 1545, 1426, 1379, 1172, 1085, 771, 665, 583.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 7.61–8.62 (m, 9H), 7.60 (d,  $J=8.1\text{ Hz}$ , 2H), 7.30 (d,  $J=8.1\text{ Hz}$ , 2H), 2.86 (dt,  $J=6.9\text{ Hz}$ , 4H), 2.31 (s, 3H), 1.66 (m, 4H), 0.96 (dt,  $J=6.9\text{ Hz}$ , 6H). MS (MALDI): calcd for  $\text{C}_{44}\text{H}_{30}\text{N}_6\text{O}_2\text{S}_7$  898.05; found 898.04. Anal. Calcd for  $\text{C}_{44}\text{H}_{30}\text{N}_6\text{O}_2\text{S}_7\cdot 0.5\text{CH}_2\text{Cl}_2\cdot 0.75\text{hexane}$ : C 58.48, H 4.16, N 8.35. Found C 58.88, H 3.85, N 8.23.

**4.3.3. Compound 3.** The procedure is same as for compound **2**. It was obtained as a green solid. Yield: 98%. Mp  $206\text{--}210\text{ }^{\circ}\text{C}$ . IR (KBr,  $\text{cm}^{-1}$ ): 3434, 2923, 2231, 1673, 1532, 1429, 1384, 1275, 1184, 853, 737, 613, 578.  $^1\text{H}$  NMR (DMSO- $d_6$ )  $\delta$ : 8.54 (s, 1H), 8.43 (m, 1H), 8.31–8.22 (m, 6H), 8.04 (s, 1H), 7.91 (m, 4H), 2.87 (dt,  $J=6.9\text{ Hz}$ , 4H), 1.59 (m, 4H), 0.96 (dt,  $J=6.9\text{ Hz}$ , 6H). MS (MALDI): calcd for  $\text{C}_{43}\text{H}_{27}\text{N}_7\text{O}_4\text{S}_7$  929.02; found 929.02. Anal. Calcd for  $\text{C}_{43}\text{H}_{27}\text{N}_7\text{O}_4\text{S}_7$ : C 55.52, H 2.93, N 10.54. Found C 55.68, H 2.93, N 10.08.

## Acknowledgements

This work was supported by the Swiss National Science Foundation (grant no. 200020-116003 and COST Action D31) as well as by the ESF program—SONS (NANOSYN).

## Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.08.091.

## References and notes

- (a) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891; (b) Baffreau, J.; Dumur, F.; Hudhomme, P. *Org. Lett.* **2006**, *8*, 1307; (c) Perepichka, D. F.; Bryce, M. R.; Batsanov, A. S.; McInnes, E. J. L.; Zhao, J. P.; Farley, R. D. *Chem.—Eur. J.* **2002**, *8*, 4656; (d) Perepichka, D. F.; Bryce, M. R.; Pearson, C.; Petty, M. C.; McInnes, E. J. L.; Zhao, J. P. *Angew. Chem., Int. Ed.* **2003**, *42*, 4635.
- (a) Ho, G.; Heath, J. R.; Kondratenko, M.; Perepichka, D. F.; Arseneault, K.; Pézolet, M.; Bryce, M. R. *Chem.—Eur. J.*

- 2005, 11, 2914; (b) Tsiperman, E.; Becker, J. Y.; Khodorkovsky, V.; Shames, A.; Shapiro, L. *Angew. Chem., Int. Ed.* **2005**, 44, 4015; (c) Perepichka, D. F.; Bryce, M. R.; McInnes, E. J. L.; Zhao, J. P. *Org. Lett.* **2001**, 3, 1431.
3. (a) Roncali, J. *Chem. Rev.* **1997**, 97, 173; (b) van Mullekom, H. A. M.; Vekemans, J. A. J. M.; Meijer, E. W. *Chem.—Eur. J.* **1998**, 4, 1235; (c) Akoudad, S.; Roncali, J. *Chem. Commun.* **1998**, 2081; (d) Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1985**, 82, 5717.
4. (a) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, 14, 99; (b) Afzali, A.; Dimitrakopoulos, C. D.; Breen, T. L. *J. Am. Chem. Soc.* **2002**, 124, 8812; (c) Duong, H. M.; Bendikov, M.; Steiger, D.; Zhang, Q.; Sonmez, G.; Yamada, J.; Wudl, F. *Org. Lett.* **2003**, 5, 4433; (d) Meier, H. *Angew. Chem., Int. Ed.* **2005**, 44, 2482; (e) Frère, P.; Skabara, P. J. *Chem. Soc. Rev.* **2005**, 34, 69; (f) Wu, H.; Zhang, D. Q.; Su, L.; Ohkubo, K.; Zhang, C. X.; Yin, S. W.; Mao, L. Q.; Shuai, Z. G.; Fukuzumi, S.; Zhu, D. B. *J. Am. Chem. Soc.* **2007**, 129, 6839.
5. (a) Gautier, N.; Dumur, F.; Lloveras, V.; Vidal-Gancedo, J.; Veciana, J.; Rovira, C.; Hudhomme, P. *Angew. Chem., Int. Ed.* **2003**, 42, 2765; (b) Loosli, C.; Jia, C. Y.; Liu, S.-X.; Haas, M.; Dias, M.; Levillain, E.; Neels, A.; Labat, G.; Hauser, A.; Decurtins, S. *J. Org. Chem.* **2005**, 70, 4988; (c) Jia, C. Y.; Liu, S.-X.; Tanner, C.; Leiggenger, C.; Sanguinet, L.; Levillain, E.; Leutwyler, S.; Hauser, A.; Decurtins, S. *Chem. Commun.* **2006**, 1878; (d) Jia, C. Y.; Liu, S.-X.; Tanner, C.; Leiggenger, C.; Neels, A.; Sanguinet, L.; Levillain, E.; Leutwyler, S.; Hauser, A.; Decurtins, S. *Chem.—Eur. J.* **2007**, 13, 3804.
6. (a) Díaz, M. C.; Illescas, B. M.; Martín, N.; Perepichka, I. F.; Bryce, M. R.; Levillain, E.; Viruela, R.; Ortí, E. *Chem.—Eur. J.* **2006**, 12, 2709; (b) de Miguel, P.; Bryce, M. R.; Goldenberg, L. M.; Beeby, A.; Khodorkovsky, V.; Shapiro, L.; Niemz, A.; Cuelloc, A. O.; Rotello, V. *J. Mater. Chem.* **1998**, 8, 71; (c) Herranz, M. A.; González, S.; Pérez, I.; Martín, N. *Tetrahedron* **2001**, 57, 725; (d) Bryce, M. R. *Adv. Mater.* **1999**, 11, 11; (e) Gorgues, A.; Hudhomme, P.; Salle, M. *Chem. Rev.* **2004**, 104, 5151; (f) Tsiperman, E.; Becker, J. Y.; Khodorkovsky, V. *Tetrahedron Lett.* **2007**, 48, 4161.
7. (a) Marín, N.; Sánchez, L.; Guldi, D. M. *Chem. Commun.* **2000**, 113; (b) Fuks-Janczarek, I.; Luc, J.; Sahraoui, B.; Dumur, F.; Hudhomme, P.; Berdowski, J.; Kityk, I. V. *J. Phys. Chem. B* **2005**, 109, 10179; (c) Gouloumis, A.; González-Rodríguez, D.; Vázquez, P.; Torres, T.; Liu, S. G.; Echegoyen, L.; Ramey, J.; Hug, G. L.; Guldi, D. M. *J. Am. Chem. Soc.* **2006**, 128, 12674.
8. Illescas, B. M.; Martín, N. *J. Org. Chem.* **2000**, 65, 5986.
9. Perepichka, D. F.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K.; Cuello, A. O.; Gray, M.; Rotello, V. M. *J. Org. Chem.* **2001**, 66, 4517.
10. (a) Kini, A. M.; Cowan, D. O.; Gerson, F.; Möckel, R. *J. Am. Chem. Soc.* **1985**, 107, 556; (b) Torrance, J. B.; Scott, B. A.; Welber, B.; Kaufman, F. B.; Seiden, P. E. *Phys. Rev. B* **1979**, 19, 730; (c) Yamada, J.; Sugimoto, T. *TTF Chemistry: Fundamentals and Applications of Tetrathiafulvalene*; Springer: Berlin, 2004.
11. <sup>1</sup>H NMR titration studies carried out in presence of DBU show spectrum changes, but we were unable to fully ascertain the structure of the resulting compound.
12. From 2 equiv a loss of reversibility is observed for the different redox systems.
13. *Stoe & Cie. IPDS Software*; Stoe & Cie GmbH: Darmstadt: Germany, 2005.
14. Sheldrick, G. M. *Acta Crystallogr.* **1990**, A46, 467.
15. Sheldrick, G. M. *SHELXL-97, Program for crystal structure refinement*; University of Göttingen: Göttingen, Germany, 1997.
16. Spek, A. L. *J. Appl. Crystallogr.* **2003**, 36, 7.