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Probing the conformational changes upon oxidation in cross-conjugated architectures featuring vinylogous TTF units

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Abstract—We report the synthesis and electropolymerisation of 1,3,5-tris(1,3-dithiole-2-ylidenephenylene)benzene **4**. The resulting polymer features extended tetrathiafulvalene (TTF) units and can be considered as a cross-conjugated, cross-linked structure. Upon p-doping, electrochemical and UV–vis spectroelectrochemical experiments indicate that the polymer undergoes a unique conformational change within the dendralene unit from one definitive orthogonal arrangement to another.

The family of compounds known as the dendralenes[1] are cross-conjugated compounds possessing interesting and unusual electronic and conformational properties. Unlike linear π-conjugated systems, cross-conjugated structures are complicated by the extent and limitation of electron delocalisation. Excellent progress has been made in the study of ene–diyne[2] and *p*-phenylenevinylidene[3] structures, but investigations on alternative cross-conjugated structures remain limited. There has been significant interest in the synthesis and characterisation of redox-active dendralenes and, in particular, molecular[4,5] and polymeric[6] structures containing vinylogous tetrathiafulvalene (TTF) units have been studied. Molecular and polymeric switches[7] are potential, fascinating applications for cross-conjugated or dendralene systems.[8] For example, a three-way chromophoric molecular switch has been realised for a tetraethynylethene derivative.[9] Whilst there is significant interest in the electrochemical control of conformational changes in molecular cross-conjugated systems,[10] particularly in the potential application of electromechanical systems,[11] a quantitative conformational change in a single multi cross-conjugated macromolecule has not yet been identified. In this letter, we report the preparation of a cross-conjugated, cross-linked polymer (poly(**4**)), which undergoes a dramatic and highly specific conformational change upon electrochemical oxidation.

Compound **4** was prepared (Scheme 1) by a Wittig–Horner olefination between 1,3,5-tris-(4-formylphenyl)-benzene **2** and 4,5-dimethyl-2-dimethoxyphosphinyl-1,3-dithiole **3**[12] in THF. Trialdehyde **2** was synthesised in two steps from 4-bromoacetophenone, according to the literature.[13] Compound **4** was isolated in 27% yield after recrystallisation from toluene.[14]

Electrochemical experiments were performed in CH_2Cl_2 (vs Ag/AgCl) under argon, using a glassy carbon disc working electrode and platinum wire counter electrode, with a substrate concentration of 10^{-3} M and tetrabutylammonium hexafluorophosphate as the supporting electrolyte (0.1 M). Compound **4** undergoes a single, irreversible oxidation process at +0.71 V. Electropolymerisation was achieved by repetitive cycling over the oxidation wave of the monomer (Fig. 1). Polymer growth was conducted at two different scan rates with varying results. At 200 mV, we observed polymer growth through the emergence of a new redox wave at +0.49 V.[15] There appears to be some broadening of the redox wave and the possibility of 2–3 separate peaks within the oxidation process. At a slower polymerisation scan rate (100 mV), these peaks are more resolved and we can clearly see three peaks emerging. This could be

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Keywords: Dendralenes; TTF; Polymers.

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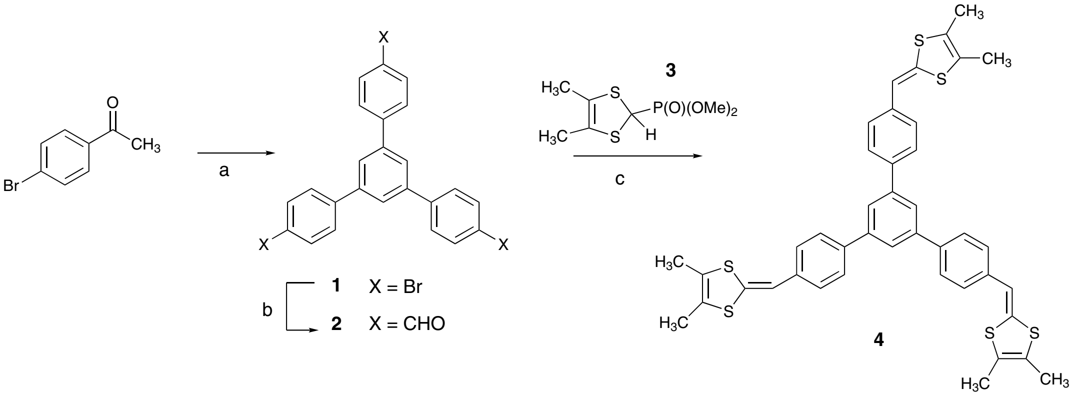


Scheme 1. Reagents and conditions: (a) $K_2S_2O_7/H_2SO_4$, 180 °C; (b) BuLi, benzene, 60 °C; then, 0 °C, *N*-formylpiperidine, 0 °C → rt; then, HCl 3 M; (c) **3**, THF, −80 °C, BuLi; then, **2**, −80 °C → rt.

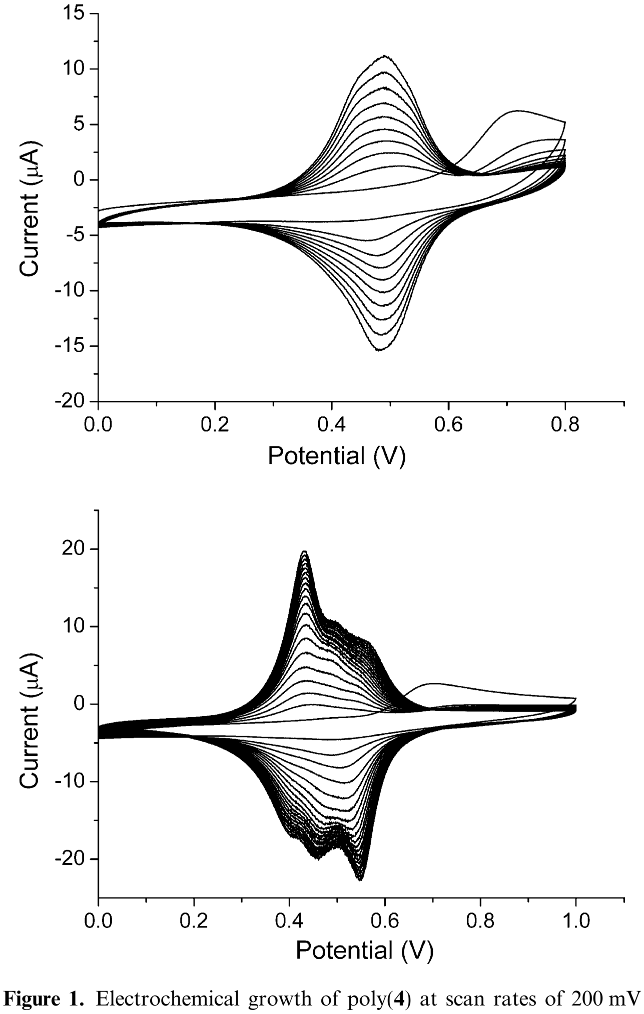


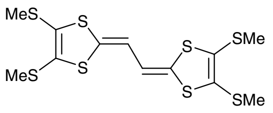
Figure 1. Electrochemical growth of poly(**4**) at scan rates of 200 mV (top) and 100 mV (bottom).

indicative of the formation of radical cations, dications and conformational change within the broad range of the oxidation process.

The polymeric structure and substitution around the central benzene ring (1,3,5) results in one definitive redox active structure (highlighted in red, Fig. 2). This, in effect, represents a [4]-dendralene system, similar to some extended TTF derivatives studied by Bryce et al.[4] Compounds **5**–**7** were studied in Ref. 4 and the crystal structures of two [3]-dendralene compounds clearly show the T-shaped conformation of the cross-conjugated units. Compounds such as **6** and **7** undergo strong conformational changes upon oxidation, which can be monitored by absorption spectroscopy.[4] Within the structure of poly(**4**), the dendralene fragments are expected to be twisted to the same extent. Consequently, the electrochemical behaviour of the red fragment (Fig. 2) will originate from either: (i) the extended TTF system **8**, or (ii) the half unit **9**, if two such units are twisted or orthogonal.

The cyclic voltammogram of poly(**4**) is depicted in Figure 3. There is a single, well defined redox process at $E^{1/2} = +0.54$ V (vs Ag/AgCl) due to the oxidation of the polymer (difference of 70 mV between oxidation and reduction peak maxima). From the value of this oxidation wave, it is more likely that a redox active unit corresponding to fragment **9** is responsible for this oxidation process rather than a species such as **8** ($R = CH_3$). This assumption is made on the basis that the unsubstituted version of **8** ($R = H$) undergoes two reversible oxidation waves at +0.20 and +0.36 V (vs Ag/AgCl),[16] whereas compound **10** undergoes a single oxidation process at +0.09 V versus ferrocene[17] ($E^{1/2}$ for poly(**4**) is +0.04 V versus ferrocene as an internal standard). These results suggest that the cross-conjugated conformation in poly(**4**) consists of planar 1,3-dithiol-2-ylidene-biphenyl units rather than a planar extended TTF. An irreversible peak is also seen at −1.93 V, but the broad irreversible peak at ca. −1.0 V is attributed to the presence of trace water.

The absorption characteristics of poly(**4**) in the neutral and doped states were studied in acetonitrile on ITO glass (Fig. 4). In the neutral state, there is an intense peak at 389 nm, accompanied by a small peak at 526 nm. The absorption maximum at 389 nm decreases slightly upon oxidation and new, weak bands emerge at 594 and 708 nm between 400 and 700 mV. Over 700 mV, the bands at 594 and 708 nm disappear abruptly and the peak at 389 nm is greatly diminished.



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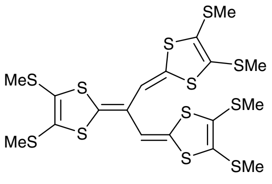

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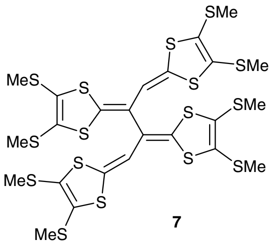

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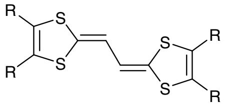

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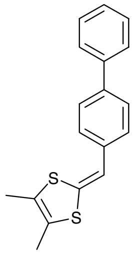

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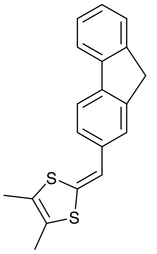

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At the same time, a new strong band appears at 462 nm. By analogy with the absorption characteristics of compounds **5**–**7**,[4] it is reasonable to believe that the weak bands for poly(**4**) at 594 and 708 nm are indicative of the initial formation of radical cations. However, a very sharp change is seen at 700 mV, where a new main band emerges at 462 nm, corresponding to the dication. We expect that the distribution of charges is localised within the dithiole units and there is no delocalisation of charge through to the benzene rings. We can therefore surmise that the planar unit is represented by the extended TTF structure seen in structure **11**. In fact, it is well known

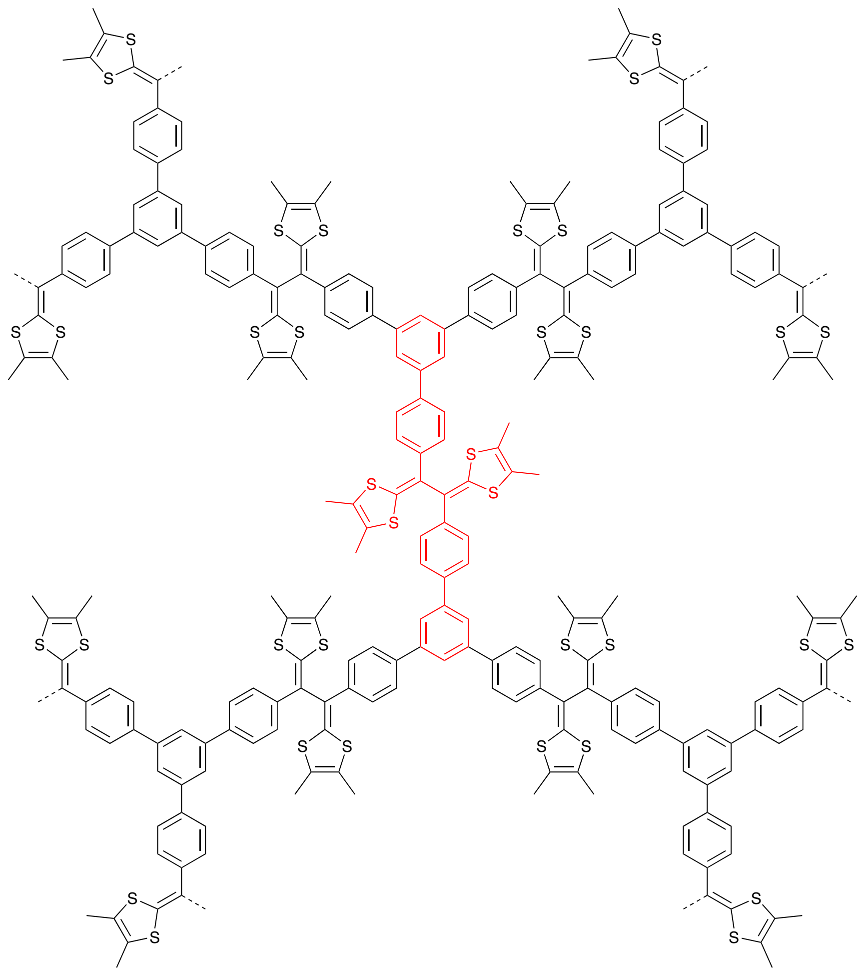


Figure 2. Fragment of poly(**4**) depicting the nature of the redox active unit, which is limited by meta linkages.

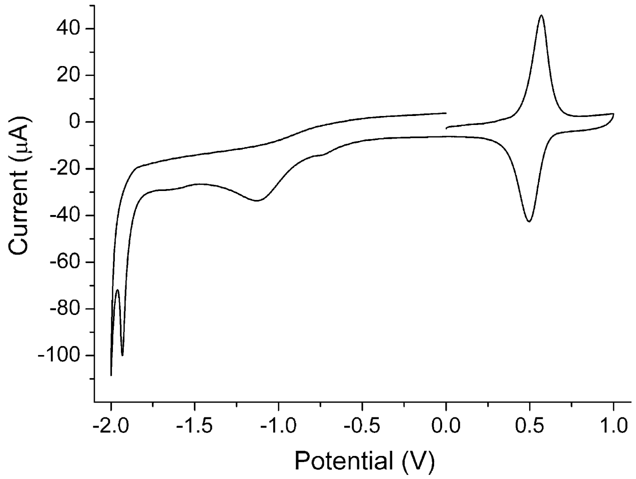


Figure 3. Cyclic voltammogram of poly(**4**) grown on a glassy carbon disk working electrolyte in monomer free acetonitrile solution (vs Ag/AgCl with 0.1 M n-Bu_4NPF_6 as supporting electrolyte).

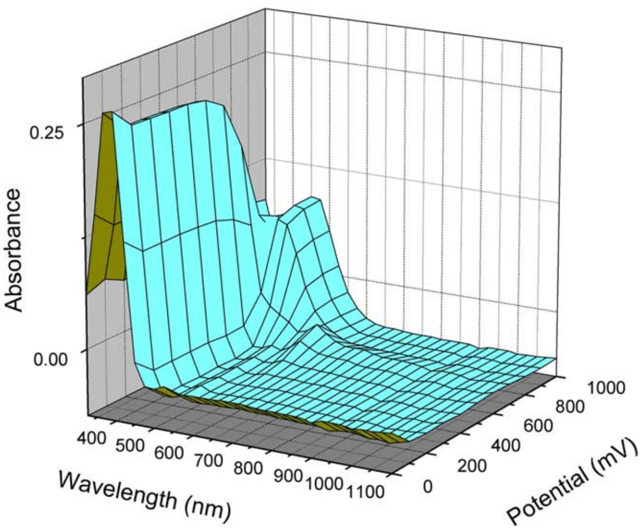
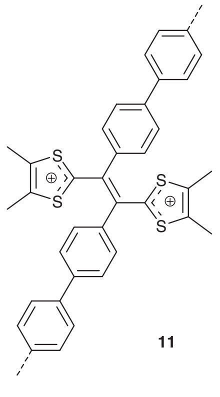


Figure 4. UV–vis spectroelectrochemical plot of poly(**4**) deposited on ITO. Experiments were run in acetonitrile solution versus Ag/AgCl reference electrode and in the presence of n-Bu_4NPF_6 (0.1 M).

that vinylogous TTF units are non-planar in the neutral form and undergo planarisation upon oxidation to the radical cation or dication states.[18] We can also conclude that the formation of radical cations and dications are very close processes and this can be seen in the polymerisation process using a scan rate of 100 mV.



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Acknowledgement

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References and notes

1. Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 948; Hopf, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 705; Fielder, S.; Rowan, D. D.; Sherburn, M. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 4331.
2. Tykwinski, R. R.; Diederich, F. *Liebigs Ann. Recl.* **1997**, 649; Zhao, Y.; McDonald, R.; Tykwinski, R. R. *Chem. Commun.* **2000**, 77; Zhao, Y.; Ciulei, S. C.; Tykwinski, R. R. *Tetrahedron Lett.* **2001**, *42*, 7721; Diederich, F. *Chem. Commun.* **2001**, 219; Zhao, Y.; McDonal, R.; Tykwinski, R. R. *J. Org. Chem.* **2002**, *67*, 2805; Camacho, D. H.; Saito, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 924; Zhao, Y.; Slepkov, A. D.; Akoto, C. O.; McDonald, R.; Hegmann, F. A.; Tykwinski, R. R. *Chem. Eur. J.* **2005**, *11*, 321.
3. Klokkenburg, M.; Lutz, M.; Spek, A. L.; van der Maas, J. H.; van Walree, C. A. *Chem. Eur. J.* **2003**, *9*, 3544.
4. Bryce, M. R.; Coffin, M. A.; Skabara, P. J.; Moore, A. J.; Batsanov, A. S.; Howard, J. A. K. *Chem. Eur. J.* **2000**, *6*, 1955.
5. Misaki, Y.; Matsumura, Y.; Sugimoto, T.; Yoshida, Z. *Tetrahedron Lett.* **1989**, *30*, 5289; Amaresh, R. R.; Liu, D.; Konovalova, T.; Lakshmikantham, M. V.; Cava, M. P.; Kispert, L. D. *J. Org. Chem.* **2001**, *66*, 7757; Navarro, A.-E.; Moggia, F.; Moustrou, C.; Heyndrickx, A.; Fages, F.; Leriche, P.; Brisset, H. *Tetrahedron* **2005**, *61*, 423.
6. Ohta, A.; Yamashita, Y. *Heterocycles* **1995**, *40*, 123; Lorcy, D.; Mattiello, L.; Poriel, C.; Rault-Berthelot, J. *J. Electroanal. Chem.* **2002**, *530*, 33; González, S.; Martìn, N.; Sánchez, L.; Segura, J. L.; Seoane, C.; Fonseca, I.; Cano, F. H.; Sedó, J.; Vidal-Gancedo, J.; Rovira, C. *J. Org. Chem.* **1999**, *64*, 3498.
7. Zauner, K.-P. *Crit. Rev. Solid State* **2005**, *30*, 33; Mendes, P. M.; Flood, A. H.; Stoddart, J. F. *Appl. Phys. A-Mater.* **2005**, *80*, 1197; Benniston, A. C. *Chem. Soc. Rev.* **2004**, *33*, 573; *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, 2001.
8. Carter, F. L. In *Computer Applications in Chemistry*; Heller, S. R., Potenzone, R., Jr., Eds.; Elsevier: Amsterdam, 1983; pp 225–262; Carter, F. L.; Siatkowski, R. E. In *From Atoms to Polymers*; Liebman, J. F., Greenberg, A., Eds.; VCH: Weinheim, 1989; pp 307–392.
9. Gobbi, L.; Seiler, P.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 674.
10. Bellec, N.; Boubekeur, K.; Carlier, R.; Hapiot, P.; Lorcy, D.; Tallec, A. *J. Phys. Chem. A* **2000**, *104*, 9750.
11. Liu, Y.; Flood, A. H.; Bonvallet, P. A.; Vignon, S. A.; Northrop, B. H.; Tseng, H.-R.; Jeppesen, J. O.; Huang, T. J.; Brough, B.; Baller, M.; Magonov, S.; Solares, S. D.; Goddard, W. A.; Ho, C.-M.; Stoddart, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 9745.
12. Ishikawa, K.; Akiba, K.; Inamoto, N. *Tetrahedron Lett.* **1976**, *41*, 3695.
13. Palomero, J.; Mata, J. A.; González, F.; Peris, E. *New J. Chem.* **2002**, *26*, 291–297; Weber, E.; Hecker, M.; Koepp,

E.; Orlia, W.; Czugler, M.; Csöregh, I. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1251.

14. Butyllithium (1.6 M solution in hexanes, 1.2 mL) was added dropwise to a stirred solution of 4,5-dimethyl-2-dimethoxyphosphinyl-1,3-dithiole **3** (0.36 mg, 1.48 mmol) in 10 mL of anhydrous THF at −78 °C under argon. Stirring was continued at −78 °C during 15 min. Into the resulting yellow-orange suspension was syringed a solution of 1,3,5-tris-(4-formylphenyl)benzene **2** (175 mg, 0.45 mmol) in 8 mL of anhydrous THF, and slowly warmed to 20 °C over 12 h. The solvent was evaporated, and CH_2Cl_2 was added (150 mL). The organic layer was washed with water (3 × 100 mL), dried ($MgSO_4$) and solvent evaporated. Recrystallisation from toluene afforded product **4** as a light brown solid (80 mg; yield: 27%). mp: 264–267 °C; IR (Nujol/NaCl): 1600 cm^{-1} (C=C), 1561, 1537 cm^{-1} (C=C, Ar); ^1H NMR (300 MHz, $CDCl_3$ δ ppm): 1.90 (s, 9H), 1.93 (s, 9H), 6.42 (s, 3H), 7.28 (d, $J = 8.3$ Hz, 6H), 7.61 (d, $J = 8.3$ Hz, 6H), 7.70 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ ppm): 12.92, 13.68, 111.04, 120.95, 121.31, 124.30, 126.87, 127.22, 134.62, 136.32, 137.51, 141.89; MS (FAB+) m/z (%): 732 ($M^{+\cdot}$, 36), 391 (100), 329 (54); UV/vis. CH_2Cl_2, λ_{max} (nm): 393, $\lg\varepsilon = 4.92$.
15. A related compound (1,3,5-tris(1,4-dithiafulven-6-yl)benzene) has been polymerised electrochemically, but there is no discussion of absorption characteristics or conformational effects in the polymer: Fourmigué, M.; Johannsen, I.; Boubekeur, K.; Nelson, C.; Batail, P. *J. Am. Chem. Soc.* **1993**, *115*, 3752.
16. Yoshida, Z.; Kawase, T.; Awaji, H.; Sugimoto, I.; Sugimoto, T.; Yoneda, S. *Tetrahedron Lett.* **1983**, *24*, 3469.
17. Lorcy, D.; Rault-Berthelot, J.; Poriel, C. *Electrochem. Commun.* **2000**, *2*, 382.
18. See for example: Lorcy, D.; Le Maguerès, P.; Rimbaud, C.; Ouahab, L.; Delhaes, P.; Carlier, R.; Tallec, A.; Robert, A. *Synth. Met.* **1997**, *86*, 1831; Yamashita, Y.; Tomura, M.; Zaman, M. B.; Imaeda, K. *Chem. Commun.* **1998**, 1657; Frère, P.; Skabara, P. J. *Chem. Soc. Rev.* **2005**, *34*, 69.