The First Tetrathiafulvalene–σ–Polynitrofluorene Diads: Low HOMO–LUMO Gap, Amphoteric Redox Behavior, and Charge Transfer Properties

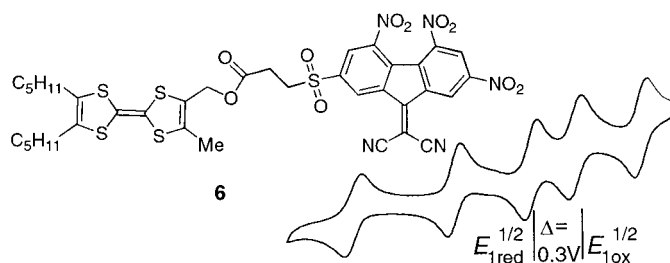Dmitrii F. Perepichka,[†] Martin R. Bryce,*,[†] Eric J. L. McInnes,[‡] and Jing P. Zhao[‡]

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ABSTRACT

The synthesis, solution redox behavior, EPR, and intramolecular charge transfer properties of novel donor–acceptor diads of TTF–σ–A type (TTF = substituted tetrathiafulvalene, σ = saturated spacer, A = polynitrofluorene acceptor) are reported. The HOMO–LUMO gap for compound **6** is as small as 0.3 eV, and spectroelectrochemical experiments reveal its electrochromic behavior in the near-IR region.

Since an inspiring proposal of Aviram and Ratner for "unimolecular" rectification[1] in TTF–σ–TCNQ (TCNQ is 7,7′,8,8′-tetracyano-*p*-quinodimethane), TTF derivatives bearing an electron acceptor substituent have been prime targets, especially in recent years.[2] Different acceptor groups have been covalently attached to TTF: fullerene,[2a–c] phthalocyanines,[2a] pyromellitic diimide,[2d,e] quinones,[2a,f,g] tetracyano-anthraquinodimethane,[2a] thioindigo,[2h] viologen and related acceptors,[2a,d,i] but these possess only moderate electron affinity (EA). TTFs having a strong electron acceptor moiety (i.e., of similar EA to TCNQ) are very difficult to obtain. The only example[3] of a direct coupling of TTF derivatives with substituted TCNQ gave EPR-active products, which were not well characterized. The troublesome synthesis of the starting TCNQ synthon (seven steps, overall yield 13%) and problems with purification of the products preclude a detailed investigation of these compounds. Many different TTF–benzoquinone diads have been reported,[2a,f,g] but all attempts to increase their acceptor ability by conversion to the corresponding TCNQ or *N,N′*-dicyanoquinodiimine derivatives have failed due to the incompatibility of TTF with

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(1) Aviram, A.; Ratner, M. *Chem. Phys. Lett.* **1974**, *29*, 277. For recent discussions of this proposal, see: Metzger, R. M. *J. Mater. Chem.* **1999**, *9*, 2027.

(2) (a) Bryce, M. R. *Adv. Mater.* **1999**, *11*, 11 and references therein. (b) Guldi, D. M.; González, S.; Martín, N. *J. Org. Chem.* **2000**, *65*, 1978. (c) Martín, N.; Sánchez, L.; Herranz, M. A.; Guldi, D. M. *J. Phys. Chem. A* **2000**, *104*, 4648. (d) Nielsen, M. B.; Hansen, J. G.; Becher, J. *Eur. J. Org. Chem.* **1999**, 2807. (e) Hansen, J. G.; Bang, K. S.; Thorup, N.; Becher, J. *Eur. J. Org. Chem.* **2000**, 2135. (f) Tsiperman, E.; Regev, L.; Becker, J. Y.; Bernstein, J.; Ellern, A.; Khodorkovsky, V.; Shames, A.; Shapiro, L. *Chem. Commun.* **1999**, 1125. (g) Sheib, S.; Cava, M. P.; Baldwin, J. W.; Metzger, R. M. *J. Org. Chem.* **1998**, *63*, 1198. (h) Aqad, E.; Ellern, A.;

Shapiro, L.; Khodorkovsky, V. *Tetrahedron Lett.* **2000**, *41*, 2983. (i) Ashton, P. A.; Balzani, V.; Becher, J.; Credi, A.; Fyfe, M. C. T.; Mattersteig, G.; Menzer, S.; Nielsen, M. B.; Raymo, F. M.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 3951.

(3) Panetta, C. A.; Baghdadchi, J.; Metzger, R. M. *Mol. Cryst. Liq. Cryst.* **1984**, *107*, 103.

the strongly acidic conditions (TiCl$_4$) of these reactions. On the other hand, it is known that condensation of polynitrofluoren-9-ones with malononitrile takes place under milder conditions[4] and the resulting dicyanomethylene derivatives have an electron affinity similar to that of TCNQ. With this in mind we now report the first TTF−fluorene conjugates which possess both strong electron donor and strong acceptor properties.

The synthesis of the D−σ−A diads **5** and **6** is presented in the Scheme 1. Acceptor **4** was synthesized from 2,4,5,7-

Scheme 1[a]

1, R = H
2, R = C(O)Me

3, R = OMe
4, R = Cl

5

6

3 →[ii] **7**
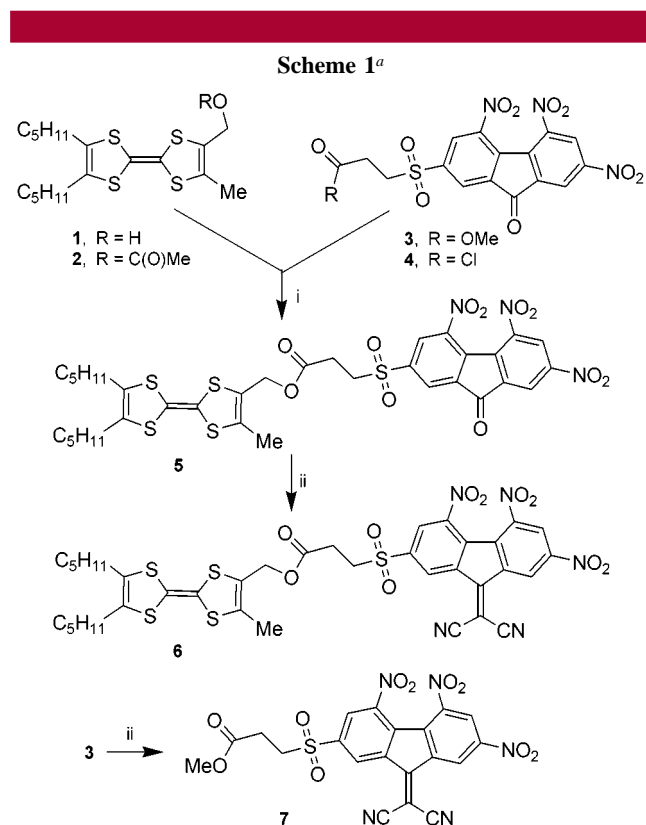
[a] (i) **1** + **4**, pyridine, MeCN, 20 °C, 12 h; (ii) CH$_2$(CN)$_2$, DMF, 20 °C, 6 h.

tetranitrofluoren-9-one via nucleophilic substitution[5] with methyl 3-mercaptopropionate followed by oxidation of the formed sulfide to sulfone (H$_2$O$_2$ in acetic acid), hydrolysis of the ester bond (CF$_3$CO$_2$H/H$_2$O), and conversion to the acid chloride (neat oxalyl chloride) with an overall yield of 70%. It was coupled with substituted TTF−methanol **1** (which was obtained from 4-methyl-4′,5′-dipentylTTF[6]), yielding TTF−fluorenone conjugate **5** in 65% yield. The acceptor ability of the fluorene moiety in **5** was increased

by conversion to dicyanomethylene derivative **6** (80% yield). The structures of the new compounds **5** and **6** were established by analytical and spectroscopic data.[7]

The high donor and acceptor ability of the TTF and fluorene moieties, respectively, in **6** results in facile intramolecular electron transfer in this compound, which is manifested in a strong EPR signal in solution (Figure 1). There
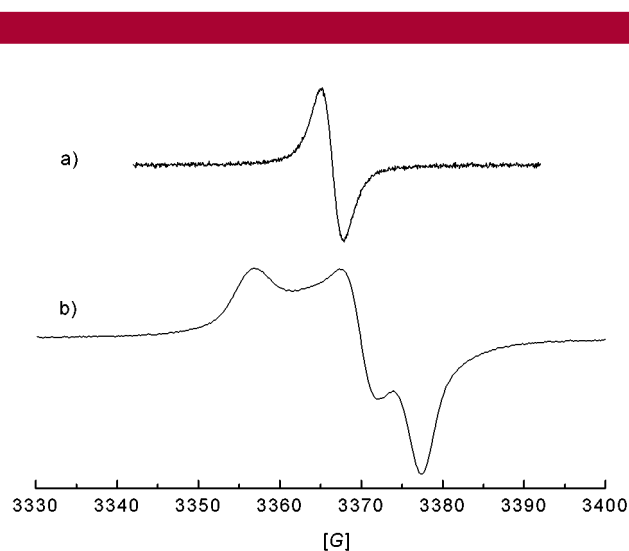
Figure 1. X-band EPR spectra of compound **6** in acetone solution at 293 K (a) and frozen CH$_2$Cl$_2$ solution at 110 K (b).

is an intense line in the acetone solution, centered at $g_{iso} = 2.007$ (Figure 1a). A frozen CH$_2$Cl$_2$ solution gives rise to a rhombic spectrum, g values $g_1 = 2.014$, $g_2 = 2.006$, and $g_3 = 2.002$ (Figure 1b). The anisotropic g values average well to the isotropic value and are almost the same as those reported for substituted TTF radical cations.[8]

There is no indication of a second radical species (corresponding to the fluorene radical anion), even at Q-band frequency.[9] It is noteworthy that intermolecular complex **8**[4] gives rise to a very similar EPR signal with the same g values in the solid state (but it is EPR silent in solution at rt and at

(4) Perepichka, I. F.; Kuz'mina, L. G.; Perepichka, D. F.; Bryce, M. R.; Goldenberg, L. M.; Popov, A. F.; Howard, J. A. K. *J. Org. Chem.* **1998**, *63*, 6484 and references herein.

(5) Perepichka, I. F.; Popov, A. F.; Orekhova, T. V.; Bryce, M. R.; Andrievskii, A. M.; Batsanov, A. S.; Heaton, J.; Howard, J. A. K.; Sokolov, N. I. *J. Org. Chem.* **2000**, *65*, 3053.

(6) 4-Methyl-4′,5′-dipentylTTF was synthesized by analogy with trimethylTTF: Moore, A. J.; Bryce, M. R.; Batsanov, A. S.; Cole, J. C.; Howard, J. A. K. *Synthesis* **1995**, 675. The pentyl chains increased the solubility of **5** and **6** in organic solvents.

(7) **5**: mp 145 °C (dec). Found: C, 49.67; H, 4.28; N, 4.90. C$_{34}$H$_{35}$N$_3$O$_{11}$S$_5$ requires: C, 49.70; H, 4.26; N, 5.12. MS *m/z* (ES): 821 (M$^+$). ^{1}H NMR (acetone-d_6): δ = 9.04 (1H, d, J = 2 Hz), 8.82 (1H, d, J = 2 Hz), 8.79 (1H, s.br), 8.63 (1H, s.br), 4.79 (2H, s), 3.92 (2H, t, J = 7 Hz), 2.96 (2H, t, J = 7 Hz), 2.41 (4H, m), 2.03 (3H, s), 1.57−1.45 (4H, m), 1.39−1.28 (8H, m), 0.94−0.86 (6H, m). **6**: mp 150 °C (dec). Found: C, 50.64; H, 4.11; N, 7.86. C$_{37}$H$_{35}$N$_5$O$_{10}$S$_5$ requires: C, 51.08; H, 4.05; N, 8.05 MS *m/z* (EI): 869 (M$^+$). ^{1}H NMR (acetone-d_6): δ = 9.5−9.0 (4H, br), 4.73 (2H, br), 4.02 (2H, br), 3.07 (2H, t, J = 6 Hz), 2.53 (4H, br), 2.1−1.8 (3H, br), 1.57−1.34 (4H, m), 1.34−1.15 (8H, m), 0.88−0.70 (6H, m). ^{1}H NMR (acetone-d_6 + CF$_3$COOH): 9.28 (1H, s), 9.21 (1H, s), 8.98 (1H, br), 8.69 (1H, br), 4.02 (2H, t, J = 6 Hz), 3.08 (2H, t, J = 6 Hz), 1.79−1.49 (4H, br.m), 1.38 (8H, br), 0.99−0.86 (6H, m), CH$_2$ and CH$_3$ protons adjacent to the TTF moiety are not observable. IR (KBr) ν/cm^{-1} 2928, 2203, 1742, 1543, 1340, 1133.

(8) Ribera, E.; Rovira, C.; Veciana, J.; Tarrés, J.; Canadell, E.; Rousseau, R.; Molins, E.; Mas, M.; Schoeffel, J.-P.; Pouget, J.-P.; Morgado, J.; Henriques, R. T.; Almeida, M. *Chem. Eur. J.* **1999**, *5*, 2025.

(9) (a) A possible explanation for the quenching of the radical anion signal could be the formation of dimers by the fluorene radical anion moieties (the formation of dimers of radical anions of a similar acceptor, TCNQ, is well-known: Boyd, R. H.; Phillips, W. D. *J. Phys. Chem.* **1965**, *43*, 2927). (b) In every EPR experiment the solutions were thoroughly degassed.

110 K). Spin-counting experiments on **6** showed that only 2% of molecules in solution exist in a radical form, which suggests an essentially neutral ground state. Because of a weaker acceptor moiety, compound **5** did not show any significant EPR signal in fluid or frozen solutions.

In accord with the EPR data, paramagnetic broadening (or even complete disappearance) of the signals for the protons adjacent to both the TTF and fluorene nuclei was observed in the ^{1}H NMR spectra of **6** (this is not observed in **5**). The resolution of the fluorene part of the molecule was somewhat improved by addition of trifluoroacetic acid.[4] A significant lowering of the C≡N stretching frequency in the IR spectra in KBr for **6** ($\nu = 2203$ cm^{-1}) compared with compound **7** ($\nu = 2235$ cm^{-1}) indicates a significant charge transfer in the solid state. Complex **8** is characterized by a similar value ($\nu_{C≡N} = 2209$ cm^{-1}), and in the case of full charge transfer (as exemplified by ion radical salt **9**) $\nu_{C≡N}$ is further lowered to 2185 cm^{-1}.[10]

8,   X = TTF;
9,   X = Li.
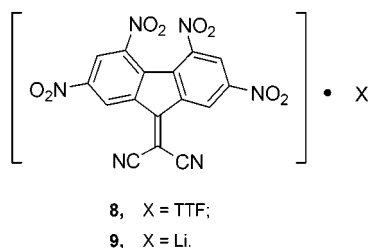
In cyclic voltammetry (CV) experiments, both compounds **5** and **6** show reversible amphoteric multiredox behavior (Figure 2) consisting of three single-electron reduction waves
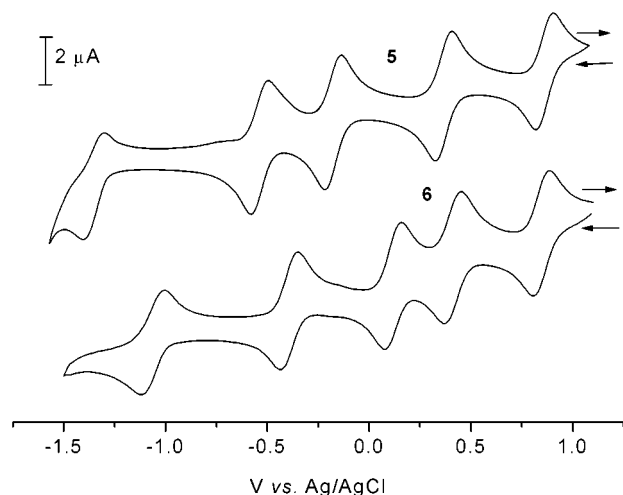

Figure 2. Cyclic voltammograms of compounds **5** and **6**.[11]

(from the fluorene moiety) yielding radical anion, dianion, and radical trianion species and two single-electron oxidations of the TTF fragment:
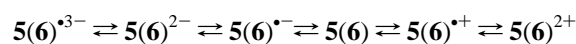
$$\mathbf{5(6)}^{\bullet 3-} \rightleftarrows \mathbf{5(6)}^{2-} \rightleftarrows \mathbf{5(6)}^{\bullet -} \rightleftarrows \mathbf{5(6)} \rightleftarrows \mathbf{5(6)}^{\bullet +} \rightleftarrows \mathbf{5(6)}^{2+}$$

Table 1. Redox Potentials (V vs Ag/AgCl) for Compounds **2**, **3**, and **5**−**7** in CH$_2$Cl$_2$ Solution[11]

compd	$E_{1ox}^{1/2}$	$E_{2ox}^{1/2}$	$E_{1red}^{1/2}$	$E_{2red}^{1/2}$	$E_{3red}^{1/2}$
2	0.36	0.90			
3			−0.18	−0.55	−1.37
5	0.37	0.87	−0.18	−0.54	−1.36
6	0.41	0.85	0.11	−0.40	−1.07
7			0.18	−0.40	−1.07

The thermodynamic potentials $E^{1/2}$ are given in Table 1,[11] together with data for model compounds **2**, **3**, and **7** to show the mutual influence of TTF and fluorene fragments on the redox properties of **5** and **6**. Attachment of the TTF moiety to fluorenone (**3** → **5**) has no apparent influence on the acceptor ability of the fluorene moiety, whereas the same change for the dicyanomethylene analogue (**7** → **6**) results in a 70 mV negative shift of the first reduction potential, indicating an interaction between the donor and acceptor moieties in **6**. There is a concomitant 50 mV positive shift in the first oxidation potential of TTF due to the presence of the acceptor fragment (**2** → **6**). In accordance with the fact that this charge transfer interaction should disappear with reduction of the acceptor fragment to the radical anion, the TTF moiety (**7** → **6**) has no influence on the second and third reduction waves. It is highly remarkable that for **6** the difference between the oxidation and reduction potentials ($E_{1ox}^{1/2} - E_{1red}^{1/2}$) is only 300 mV, i.e., an extremely low HOMO−LUMO gap (ca. 0.3 eV) has been reached for this compound.[12] Also, the thermodynamic stability of the radical anion of **6** is higher, compared with that of **5**, which is due to an increase in the difference between $E_{1red}^{1/2}$ and $E_{2red}^{1/2}$ [$\log K_{dispr} = -(E_{1red}^{1/2} - E_{2red}^{1/2})/0.059$].

Intramolecular charge transfer (ICT) in compounds **5** and **6** is also manifested in broad absorption bands in the visible and near-IR region of their electronic spectra, with the maxima and intensities strongly dependent on the solvent used [e.g., for **5**: λ_{ICT}/nm (ϵ/M^{-1} cm^{-1}) = 705 (150), 900 sh (130) in acetone; 750 (300), 990 (260) in CH$_2$Cl$_2$]. Their intramolecular nature was established by a linear concentration dependence in the 10^{-3} to 10^{-5} M range. These bands are not observed in the solution of either the separate donor (**2**) and acceptor (**7**) components or their radical ions (see the spectroelectrochemical experiment below), but a very similar spectrum was obtained for intermolecular complex **8** (Figure 3). Therefore, we attribute the ICT bands to the absorption of charge transfer π−π intramolecular complex of **6**.[13] The observed red shift and a large increase in the

(10) A similar change, from 2225 to 2180 cm^{-1}, was observed for the TCNQ^0/TCNQ$^{\bullet -}$ couple: Chappel, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442.

(11) Procedure: ca. 10^{-3} M compound in dry CH$_2$Cl$_2$, Pt working electrode, 0.1 M Bu$_4$NPF$_6$, 20 °C, scan rate 100 mV s^{-1}; Fc/Fc$^+$ shows 0.50 V in these conditions.

(12) HOMO−LUMO gap of 0.3 eV is most unusual for monomeric organic compounds, but well-known for rare-earth organometallic compounds: Jiang, J.; Liu, W.; Poon, K.-W.; Du, D.; Arnold, D. P.; Ng, D. K. P. *Eur. J. Inorg. Chem.* **2000**, 205, and references therein.
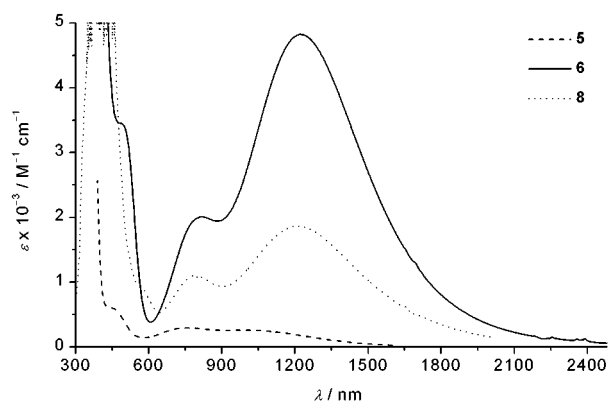
Figure 3. Electronic spectra of compounds **5** and **6** (in CH_2Cl_2) and complex **8** (obtained by mixing 0.08 M solutions of the D and A components in PhCN; the plot represents an optical density of 1 cm cell).

Figure 4. Electronic absorption spectra in visible and near-IR region for compound **6** at different applied potentials (in CH_2Cl_2; 0.1 M Bu_4NPF_6 as an electrolyte).

intensities of the ICT bands for **6** compared to **5** clearly indicate a much stronger donor−acceptor interaction in compound **6**, in accordance with the CV results.

Compounds for which transparency in the visible and near-IR regions can be changed by applying various potentials (electrochromic materials) are of great current interest.[14] A relatively high intensity of the ICT band at 1220 nm led us to evaluate **6** as an electrochromic material. Applying a potential of +0.6 V, to generate the radical cation, results in complete disappearance of the ICT absorbance; instead, two new bands characteristic of the TTF radical cation[2i] (450 and 640 nm) arise (Figure 4). Analogously, switching to −0.3 V gives rise to the radical anion and the corresponding spectral change (new bands at 470, 515, 550, and 790 nm).[4]

Both processes are fully reversible, i.e., the initial spectra recovered after setting the potential back to +0.2 V. We consider **6** to be a very promising electrochromic material for the near-IR region.

In conclusion, we have synthesized the first TTF−σ−fluorene donor−acceptor diads. The presence of both electron donor and acceptor fragments results in multistage amphoteric redox behavior with distinctive electrochromism. The HOMO−LUMO gap for compound **6** is evaluated by CV to be 0.3 eV. Strong charge transfer in compound **6** is manifested in lowering of the C≡N stretching in the IR spectrum and intensive ICT bands in the electronic absorption spectrum. Although the ground state of **6** in solution is essentially neutral, the paramagnetic zwitterion state is easily available and ca. 2% of molecules exists in a radical form at rt.

Supporting Information Available: ^{1}H NMR spectra of **5**, **6**, **7**, and of a mixture **2** + **7**; details of PM3 geometry optimization of **6** and the derived diagrams for the "extended" and "head-to-tail" conformations.

OL015581R

(13) (a) This is also supported by geometry optimization of **6** with the semiempirical PM3 method showing that "extended" and folded "head-to-tail" conformations, where intramolecular π−π charge transfer can take place, are very close in energy. (b) The discrepancy between the $h\nu_{ICT}$ (1 eV) and the electrochemically determined HOMO−LUMO gap (0.3 eV) could be explained by the fact that whereas the ICT transition occurs solely from the intramolecularly complexed state of the molecule (where donor−acceptor interaction increases the gap), CV characterizes the "uncomplexed" or equilibrium state.

(14) (a) Mortimer, R. J. *Chem. Soc. Rev.* **1997**, *26*, 147. (b) Hünig, S.; Kemmer, M.; Wenner, H.; Perepichka, I. F.; Bäuerle, P.; Emge, A.; Gesch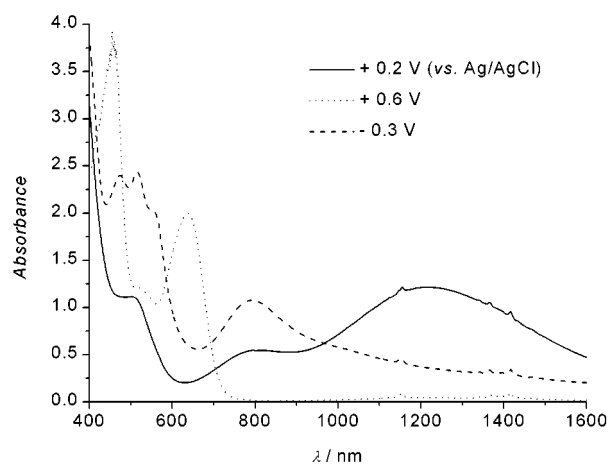eid, G. *Chem. Eur. J.* **1999**, *5*, 1969.