

# Self-assembled monolayers of a tetrathiafulvalene-based redox-switchable ligand

Gaëlle Trippé,<sup>a</sup> Maïtena Oçafrain,<sup>a</sup> Mohamed Besbes,<sup>a</sup> Vincent Monroche,<sup>a</sup> Joël Lyskawa,<sup>a</sup> Franck Le Derf,<sup>a</sup> Marc Sallé,<sup>\*a</sup> Jan Becher,<sup>b</sup> Barbara Colonna<sup>c</sup> and Luis Echegoyen<sup>c</sup>

<sup>a</sup> Laboratoire d'Ingénierie Moléculaire et Matériaux Organiques, CNRS UMR 6501, Université d'Angers, 2 Bd Lavoisier, F-49045, Angers, France. E-mail: marc.salle@univ-angers.fr; Fax: +33 2 41 73 54 05

<sup>b</sup> Department of Chemistry, Odense University (University of Southern Denmark), Campusvej 55, DK-5230, Odense M, Denmark

<sup>c</sup> Department of Chemistry, Clemson University, 219 Hunter Laboratories, Clemson, SC 29634, USA

Received (in London, UK) 22nd May 2002, Accepted 30th July 2002

First published as an Advance Article on the web 30th August 2002

A straightforward synthesis of new thiol derivatives incorporating the tetrathiafulvalene (TTF) moiety is presented. These electroactive systems form highly stable self-assembled monolayers (SAMs) on gold electrodes. The electrode obtained by SAM formation from a thiol derivative whose structure associates the redox-active TTF unit and a crown-ether ligating part, allows the voltammetric recognition of barium.

## Introduction

The modification of electrode surfaces using electroactive molecular systems is a very active research area, notably in connection to sensing applications.<sup>1</sup> In this context, many efforts have been devoted to the immobilization of the tetrathiafulvalene (TTF)<sup>2</sup> framework onto metallic surfaces. Tetrathiafulvalene can be easily oxidized in two successive one-electron steps into a stable radical-cation and dication, respectively. This ability has been exploited in the design of redox-responsive ligands, thus allowing the voltammetric detection of metallic cations in homogeneous solutions.<sup>2,3</sup> The usual cation-binding ligand connected to the TTF unit is a crown or thiacycrown ether, and cation binding by this macrocycle ring is detected *via* the voltammetric shift of the TTF center due to the electrostatic interaction and proximity of the crown-ether bound cation.

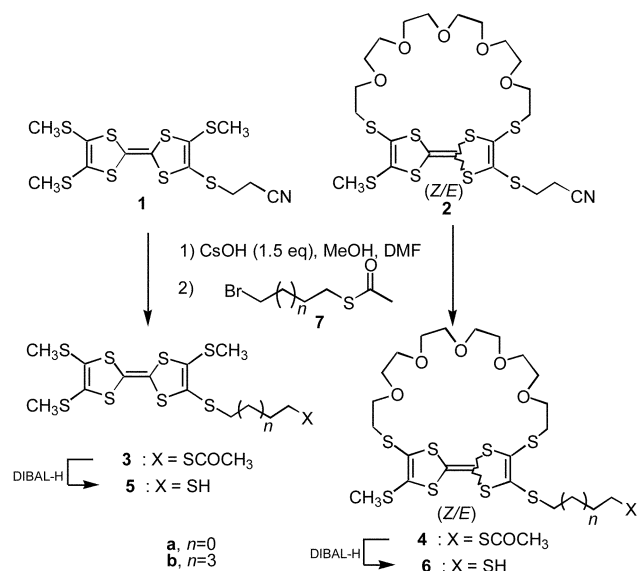
An evident further step for sensing applications is the immobilisation of these TTF-based redox-switchable ligands onto a conducting surface, as realized by the electrodeposition of a dendrimer,<sup>4</sup> or by the preparation of self-assembled monolayers (SAMs).<sup>5,6</sup> SAM modified electrodes<sup>6c</sup> incorporating the redox-active TTF core appear to be of special interest, and since the initially reported work,<sup>7</sup> significant advances have been realized,<sup>5,6,8,9</sup> notably in the preparation of SAMs possessing cation recognizing properties.<sup>5,6a,b</sup> These SAMs are usually prepared by adsorption of TTF-based polyether systems on gold or platinum. The compounds contain three specific functionalities: (i) a redox-active TTF part for reversible generation of positive charges upon electrooxidation, (ii) a proximal polyether chain for complexation of metal cations, and (iii) an alkyl chain terminated by an anchoring functionality in order to promote SAM formation (*i.e.* thiol<sup>5</sup> or disulfide<sup>6a,b</sup> functions).

Considering our recent findings that recognition properties of TTF ligands are optimised when the crown-ether part is annelated in the 2,7-positions of the TTF framework,<sup>3e,f,j,4</sup> we describe here the synthesis, SAM formation, electrochemical characterization and Ba<sup>2+</sup> sensing properties of a series of

such TTF-based ligands. These crown-ether annelated TTFs (**6a**, **6b**) possess alkylthiol chains of various lengths as anchoring sites. The TTF thiol derivatives without the ligating crowns were also prepared (**5a**, **5b**) and these were used as models for synthetic and deposition optimisation.

## Results and discussion

Thiol derivatives **5**, **6** were prepared starting from the cyanoethylsulfanyl precursors **1**<sup>10</sup> and **2**<sup>11</sup> which were subsequently treated by caesium hydroxide and compounds **7** ( $n = 0, 3$ ) (Scheme 1). Thioacetyl chains **7** were synthesized *via* a Mitsunobu reaction<sup>6</sup> from the corresponding  $\alpha,\omega$ -bromo alcohols.



Scheme 1

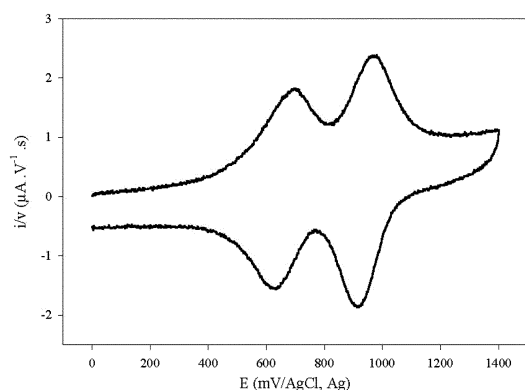
The thioester intermediates **3**, **4** were then reduced to the target TTF thiols **5**, **6** with DIBAL-H (dichloromethane,  $-80^{\circ}\text{C}$ ).<sup>12</sup> Compounds **5**, **6** possess a very strong tendency to self-oxidize to the disulfides within a few days ( $^1\text{H-NMR}$  monitoring), even under a controlled Ar atmosphere. Although not specifically mentioned, similar behavior may occur with other TTF thiol derivatives (no clear SH signature in the  $^1\text{H-NMR}$ ),<sup>5,8</sup> and may be attributed to an electron-transfer process involving catalytic amounts of  $\text{TTF}^{2+}$  which favours the irreversible oxidation of thiol into disulfide.<sup>13</sup>

Self-assembled monolayers (SAMs) were prepared in a glove-box, by soaking gold (111) bead electrodes<sup>14</sup> in a solution of the thiol TTF derivative (**5a,b**, **6a,b**) ( $1\text{--}2 \times 10^{-3}$  M) in dichloromethane or THF. After soaking for 24–48 h, the resulting electrodes were rinsed abundantly, and immersed in a freshly prepared electrolytic solution ( $\text{Bu}_4\text{NPF}_6$ , 0.1 M in acetonitrile or THF).

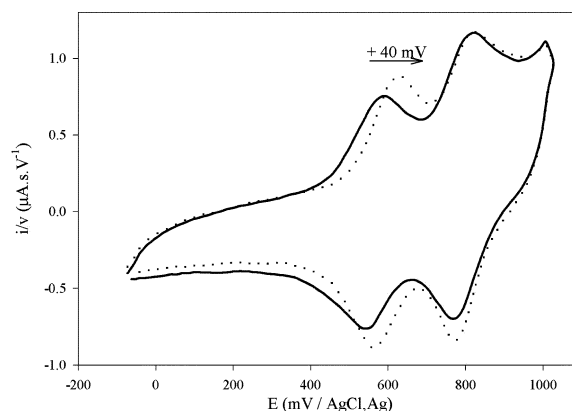
The cyclic voltammograms (CV) of the SAMs obtained with the model compounds **5a** and **5b** show the expected two one-electron oxidation processes corresponding to the successive reversible oxidation of neutral TTF ( $\text{TTF}^0$ ) to the radical-cation ( $\text{TTF}^{\bullet+}$ ) and to dication ( $\text{TTF}^{2+}$ ) ( $E_{1/2}^1 = 0.66$  V,  $E_{1/2}^2 = 0.94$  V/AgCl/Ag)<sup>15</sup> (Fig. 1).

SAMs of TTF thiol derivatives are known<sup>5,7</sup> to undergo a gradual decrease of the current response when the potential is scanned beyond the first oxidation peak potential. Noteworthy, the CVs of SAMs obtained from **5a** and **5b** appear highly stable within the potential window examined (from  $\text{TTF}^0$  to  $\text{TTF}^{2+}$ ), as well as for scan rates ranging from 0 to  $20\text{ V s}^{-1}$ . SAMs derived from **5a** and **5b** are stable even after more than 100 potential scan cycles and after several days. The higher stability observed in these cases is surprising when one considers that compounds **5a,b** present relatively small anchoring alkylthiol chains (trimethylene and hexamethylene, respectively), which should therefore alter the order in the monolayer packing within the SAM. The electrochemical response of these SAMs is consistent with a redox system confined at the electrode surface, as shown by the linearity of both oxidative peak currents with the scan rate  $v$  ( $v = 0$  to  $20\text{ V s}^{-1}$ ), by the constant values of the anodic ( $E_p^a$ ), and cathodic ( $E_p^c$ ) peaks and of  $\Delta E (= E_p^a - E_p^c)$  on varying  $v$ . The surface coverage ( $\Gamma$ ) reaches a value of  $\Gamma = 1 \times 10^{-10}\text{ mol cm}^{-2}$  in both cases.<sup>14</sup>

This study was extended to the corresponding thiol derivatives **6a,b** incorporating a poly(oxaethylene) chain. Analogously to model compounds **5a,b**, SAMs of **6a** or **6b** were obtained by immersing a gold electrode in a 1–2 mM solution of the corresponding thiol derivative in dichloromethane (24 h). In the case of **6a**, the resulting electrodes exhibit the typical two oxidations of TTF, and the analytical criteria



**Fig. 1** Cyclic voltammogram for self-assembled monolayers of compound **5a**. Gold electrode,  $\Gamma = 1 \times 10^{-10}\text{ mol cm}^{-2}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{Bu}_4\text{NPF}_6$  (0.1 mol  $\text{L}^{-1}$ ).



**Fig. 2** Cyclic voltammogram for self-assembled monolayers of compound **6a** in the absence (solid line) and in the presence of 5 mM  $\text{Ba}(\text{ClO}_4)_2$  (dotted line) Gold electrode;  $\Gamma = 3 \times 10^{-11}\text{ mol cm}^{-2}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{Bu}_4\text{NPF}_6$  (0.1 mol  $\text{L}^{-1}$ ).

show the characteristics of a surface confined redox system (linearity of  $i = f(v)$ , constant value of  $\Delta E$  for both waves,  $\Gamma = 3 \times 10^{-11}\text{ mol cm}^{-2}$ ) (Fig. 2). A similar surface-confined behavior is also found for compound **6b**, but in this case the SAMs are stable only in THF.

Since the parent crown-ether TTF ligand was previously shown to recognize  $\text{Ba}^{2+}$ ,<sup>3f,j</sup> we have studied the electrochemical behavior of SAMs of **6a** and **6b** in the presence of this cation. No clear evidence for  $\text{Ba}^{2+}$  recognition could be observed in the case of the SAMs of **6b**. An attempt to improve the recognition properties of the corresponding SAMs was made by preparing mixed monolayers either by immersing SAMs of **6b** in decanethiol (10 min), or by immersion of a clean gold bead in a mixture of **6b** and an alkyl thiol ( $\text{C}_5\text{SH}$  or  $\text{C}_{10}\text{SH}$ ). In the first case, the CV response exhibiting both redox waves of TTF appears stable but no shift of the oxidation potentials is observed upon addition of  $\text{Ba}^{2+}$ . In the latter case, the SAMs obtained are not electroactive, which could be the result of selective adsorption of the alkyl thiol due to kinetic and/or thermodynamic reasons.

On the contrary, SAMs of **6a** recorded in the presence of barium perchlorate showed a positive shift of +40 mV for the first oxidation process (Fig. 2). This was the anticipated behavior due to the electrostatic effect of the bound metal cation in close proximity to the TTF system. Noteworthy, and contrary to observations made on previously published SAMs of crown-TTF ligands,<sup>6a,b</sup> the potential of the second oxidation process remains constant for SAMs of **6a** in the presence of  $\text{Ba}^{2+}$ . This behavior is consistent with observations made with the parent TTF-ligand in homogeneous solution,<sup>3f,j</sup> and results from an electrostatically-induced decomplexation of  $\text{Ba}^{2+}$  upon oxidation of the redox-active TTF core.

## Conclusions

We have synthesized a series of TTF thiol derivatives, with varying alkylthiol anchoring chain lengths and with or without a crown-ether coordinating group attached. These thiol derivatives form highly stable SAMs on gold bead electrodes over a large potential window (from neutral TTF to  $\text{TTF}^{2+}$ ), at high scan rates (up to  $20\text{ V s}^{-1}$ ), and upon repeated cycling. Recognition of barium was detected by CV for SAMs of **6a**. These results are similar to those previously observed for the parent crown-TTF ligand in homogeneous solution. Since the present compounds form immobilised and stable SAMs, they offer the potential for applications in metal ion sensing.

## Experimental

### General details

$^1\text{H}$ -NMR (500.13 MHz) and  $^{13}\text{C}$ -NMR (125.75 MHz) spectra were recorded on a BRUKER AVANCE DRX 500 spectrometer.

Mass spectra (MS) using electronic impact (EI) and fast atom bombardment (FAB-LSIMS) were achieved either on a VG-Autospec EBE (VG analytical) spectrometer or on a JEOL JMS 700 B/ES spectrometer. Mass spectra using the time of flight mode (MALDI-TOF) were recorded on a BRUKER BIFLEX III.

Cyclic voltammetry experiments were performed on a potentiostat-galvanostat EG&G PAR models 273 or 273 A, with solvents and electrolytes of electrochemical grades, and at room temperature. Potentials are measured towards a silver wire pseudoreference electrode and then referenced to an AgCl/Ag (NaCl 3 M) BAS electrode, and a platinum wire (diameter: 1 mm) was used as the counter electrode. When necessary, electrochemical experiments were performed in a JACOMEX glove-box (usual  $\text{O}_2$  and  $\text{H}_2\text{O}$  contents: 5 ppm).

### Synthesis

**Thioacetyl derivatives 7a and 7b.** Diisopropyl azodicarboxylate (DIAD) (2.00 g, 16.6 mmol) was added dropwise to triphenylphosphine (4.34 g, 16.6 mmol) in THF at  $0^\circ\text{C}$ . Once the complex was precipitated, the reaction mixture was diluted with THF (100 mL) and a mixture of a 3-bromopropan-1-ol (6-bromohexan-1-ol respectively) (11.0 mmol) and thioacetic acid (11.0 mmol) in THF (100 mL) was added to the white precipitate. The temperature was kept to  $0^\circ\text{C}$  for two hours and then allowed to rise to rt. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane, washed with water and dried over sodium sulfate. The solvent was concentrated (1/3), and petroleum ether (bp  $35\text{--}60^\circ\text{C}$ ) was added to precipitate the triphenylphosphine oxide, subsequently removed by filtration. The filtrate was concentrated *in vacuo* and the oil was purified by distillation (**7a**: bp<sub>(1.6 mbar)</sub> =  $60^\circ\text{C}$ ; Colorless oil; 2.65 g, 24%) or by silicagel chromatography (**7b**: (toluene), light yellow oil, 60%).

**7a:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 2.12 (quint, 6.7 Hz, 2H); 2.34 (s, 3H); 3.01 (t, 7.0 Hz, 2H); 3.45 (t, 6.5 Hz, 2H). MS (EI)  $\text{M}^{++}$   $\text{C}_5\text{H}_9\text{BrOS}$  calc. 195.9564, found 195.9557.

**7b:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.35–1.50 (m, 4H); 1.52–1.65 (m, 2H); 1.78–1.93 (m, 2H); 2.32 (s, 3H); 2.86 (t, 7.1 Hz, 2H); 3.40 (t, 7.1 Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 27.6, 27.8, 28.9 and 29.3 ( $\text{CH}_2$ ); 30.5 ( $\text{CH}_3$ ); 32.5 ( $\text{CH}_2\text{S}$ ); 33.6 ( $\text{CH}_2\text{Br}$ ); 195.8 (CO).  $\text{C}_8\text{H}_{15}\text{BrOS}$  MS (EI $^+$ ) 239.1 ( $\text{M} + \text{H}$ ) $^{++}$ . IR (KBr)  $\text{cm}^{-1}$ : 1684 (C=O).

**Thioester TTFs 3a,b and 4a,b.** Caesium hydroxide monohydrate (1.1 equiv.) in dry methanol (5 mL) was added to the tetrathiafulvalene derivative (**1** or **2**) in dry and degassed DMF (50 mL). After stirring for 15 minutes at rt, the bromothioacetyl derivative (**7a** or **7b**) in DMF (10 mL) was added in one portion. The reaction mixture was stirred for one hour. The solvents were removed under reduced pressure, and the residue was dissolved in dichloromethane, washed with water and dried over sodium sulfate. The organic phase was concentrated under reduced pressure and the orange residue was purified by silicagel chromatography.

**3a** (eluent: petroleum ether–dichloromethane (9/1) + 2% v triethylamine). (mp  $58^\circ\text{C}$ )  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.90 (quint, 7.0 Hz, 2H); 2.32 (s, 3H); 2.41 (s, 9H); 2.84 (t, 7.0 Hz, 2H); 3.00 (t, 7.0 Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 19.1 ( $\text{SCH}_3$ ); 27.6 ( $\text{CH}_2\text{SCO}$ ); 29.5 ( $\text{CH}_2\text{CH}_2\text{S}$ ); 30.6 ( $\text{SCOCCH}_3$ ); 34.9 ( $\text{SCH}_2$ ); 110.7 and 110.9 (central C=C); 124.5, 127.5, 127.6, 131.0 (lateral C=C); 195.2 (CO). MS (FAB)  $\text{M}^{++}$   $\text{C}_{14}\text{H}_{18}\text{OS}_9$  calc. 489.8844, found 489.8842.

**3b** (eluent: toluene).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.40 (m, 4H); 1.60 (m, 4H); 2.32 (s, 3H); 2.44 (s, 9H); 2.81 (t, 2H); 2.87 (t, 2H).

**4a** (eluent dichloromethane + 2% v triethylamine). *Z/E* mixture: 25/75.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.92 (quint, 7.1 Hz, 2H); 2.00 (*Z*) and 2.14 (*E*) (s, 3H); 2.44 and 2.45 (s, 3H); 2.85–2.91 (m, 2H); 2.95–3.03 (m, 6H); 3.62–3.72 (m, 20H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 19.1 and 19.2 ( $\text{CH}_3\text{S}$ ); 27.7 ( $\text{CH}_2\text{SCO}$ ); 29.3 and 29.5 ( $\text{CH}_2\text{CH}_2\text{S}$ ); 30.6 ( $\text{SCOCCH}_3$ ); 35.0 and 35.2 ( $\text{SCH}_2$ ); 70.2, 70.6, 70.7, 70.8, 70.8, 70.8, 70.9, 71.0 and 71.0 ( $\text{OCH}_2$ ); 110.5, 111.0 and 111.4 (central C=C); 125.0, 127.3, 128.5 and 130.3 (lateral C=C); 195.3 (CO). MS (FAB)  $\text{M}^{++}$   $\text{C}_{24}\text{H}_{36}\text{O}_6\text{S}_9$  calc. 708.0026, found 707.9998.

**4b** (eluent: dichloromethane–ethyl acetate: 8/2 + 2% v triethylamine). *Z/E* mixture: 75/25.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.38–1.43 (m, 4H); 1.57–1.68 (m, 4H); 2.32 (s, 3H); 2.44 (s, 3H, *E*); 2.46 (s, 3H, *Z*); 2.85 (m, 6H, *E*); 2.98 (m, 6H, *Z*); 3.72–3.61 (m, 20H, *Z* and *E*).  $^{13}\text{C}$  RMN ( $\text{CDCl}_3$ ): 19.3 and 19.2 ( $\text{SCH}_3$ ); 27.9–38.8 ( $\text{CH}_2$ ); 70.2–70.9 ( $\text{CH}_2\text{O}$ ); 111.0 and 111.5 (central C=C); 124.7, 126.7, 130.0 and 131.7 (lateral C=C); 196.0 (C=O). MS (MALDI-TOF)  $\text{M}^{++}$  (750.01)  $\text{C}_{27}\text{H}_{42}\text{O}_6\text{S}_9$ . IR (KBr)  $\text{cm}^{-1}$ : 1688 (C=O).

**Thiols TTF derivatives 5 and 6.** A solution of the appropriate thioacetyl derivative (**3** or **4**) (0.2–0.5 mM) in distilled dichloromethane (50 mL) was cooled to  $-80^\circ\text{C}$ . Diisobutylaluminum hydride 1.0 M in hexane (5 equiv.) was added dropwise. After stirring at  $-80^\circ\text{C}$  for 45 minutes, the reaction mixture was quenched with a solution of HCl (3 M) in methanol (12 mL). Temperature was allowed to rise to rt, and the organic layer was washed with water, dried over sodium sulfate and evaporated. The crude orange oil was purified by silicagel chromatography.

**5a:** Orange oil, 64% yield;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.37 (t, 7.0 Hz, 1H); 1.93 (m, 2H); 2.43 (s, 9H); 2.70 (dd, 7.0 Hz and 7.0 Hz, 2H); 2.93 (t, 7.0 Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 19.2 ( $\text{SCH}_3$ ); 23.0 ( $\text{SCH}_2\text{CH}_2$ ); 33.3 and 34.4 ( $\text{SCH}_2$ ); 110.7 and 111.0 (central C=C); 124.5, 127.5, 127.6 and 131.0 (lateral C=C). MS (FAB)  $\text{M}^{++}$   $\text{C}_{12}\text{H}_{16}\text{S}_9$  calc. 447.8758, found 447.8738.

**5b:** Orange oil, 85% yield,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.34 (t, 8.0 Hz, 1H); 1.38–1.48 (m, 4H); 1.60–1.72 (m, 4H); 2.43 (s, 9H); 2.54 (q, 7.0 Hz, 2H); 2.83 (t, 7.0 Hz, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 19.2 ( $\text{SCH}_3$ ); 27.8, 27.8, 27.9 and 29.5 ( $\text{SCH}_2\text{CH}_2$ ); 33.8 and 36.1 ( $\text{SCH}_2$ ); 110.5 and 111.0 (central C=C); 125.7, 127.5 and 129.6 (lateral C=C). MS (EI $^+$ )  $\text{M}^{++}$   $\text{C}_{15}\text{H}_{22}\text{S}_9$  calc. 489.9199, found 489.9208.

**6a:** Orange oil, 97% yield, *Z/E* mixture: 70/30.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.36 and 1.41 (2t (*Z* and *E*), 8.1 Hz, 1H); 1.93 (quint, 7.0 Hz, 2H); 2.43 and 2.46 (2s (*Z* and *E*), 3H); 2.68 (q, 7.9 Hz, 2H); 2.94–3.01 (m, 6H); 3.62–3.71 (m, 20H).

**6b:** Orange oil, 42% yield, *Z/E* mixture: 25/75.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.33 (t, 7.8 Hz, 1H); 1.43 (m, 4H); 1.62 (m, 4H); 2.43 and 2.46 (2 s (*Z* and *E*), 3H); 2.54 (dq, 6.5 Hz, 2H); 2.86 (t, 6.5 Hz, 2H); 2.95–3.00 (t, 7.0 Hz, 4H); 3.62–3.72 (m, 20H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 19.1 and 19.2 ( $\text{SCH}_3$ ); 24.5, 27.7, 27.8, 27.9, 28.1, 29.5 and 29.7 ( $\text{CH}_2$ ); 33.8, 35.0, 35.2 and 36.2 ( $\text{SCH}_2$ ); 70.1, 70.6, 70.6, 70.7, 70.8, 70.8, 70.8, 70.9 and 71.0 ( $\text{OCH}_2$ ); 110.4, 110.9, 111.0 and 111.3 (central C=C); 124.4, 124.8, 126.3, 126.9, 128.7, 129.8, 130.4, 131.5 (lateral C=C). MS (FAB)  $\text{M}^{++}$   $\text{C}_{25}\text{H}_{40}\text{O}_5\text{S}_9$  calc. 708.0369, found 708.0362.

### Acknowledgements

S. Chesne is greatly acknowledged for technical support as well as the SCAS (Angers) for spectroscopic analyses. This research was funded by the MENRT, the CNRS, SMARTON (G. T.) and CMEP 99MDU431 (M. B.). L. E. thanks the National Science Foundation, grant CHE-0135786, for generous support of this work.

## References and notes

- For a review, see for instance L. M. Goldenberg, M. R. Bryce and M. C. Petty, *J. Mater. Chem.*, 1999, **9**, 1957.
- (a) For recent reviews dedicated to applications of TTF derivatives, including immobilization, see for instance J. L. Segura and N. Martin, *Angew. Chem., Int. Ed. Eng.*, 2001, **40**, 1372; (b) M. R. Bryce, *J. Mater. Chem.*, 2000, **10**, 589; (c) M. Brondsted Nielsen, C. Lornholt and J. Becher, *Chem. Soc. Rev.*, 2000, **29**, 153.
- (a) T. K. Hansen, T. Jørgensen, P. C. Stein and J. Becher, *J. Org. Chem.*, 1992, **57**, 6403; (b) R. Dieing, V. Morisson, A. J. Moore, L. M. Goldenberg, M. R. Bryce, J. M. Raoul, M. C. Petty, J. Garin, M. Saviron, I. K. Lednev, R. E. Hester and J. N. Moore, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1587; (c) M. B. Nielsen and J. Becher, *J. Liebigs Ann.*, 1997, 2177; (d) F. Le Derf, M. Sallé, N. Mercier, J. Becher, P. Richomme, A. Gorgues, J. Orduna and J. Garin, *Eur. J. Org. Chem.*, 1998, 1861; (e) F. Le Derf, M. Mazari, N. Mercier, E. Levillain, P. Richomme, J. Becher, J. Garin, J. Orduna, A. Gorgues and M. Sallé, *Chem. Commun.*, 1999, 1417; (f) F. Le Derf, M. Mazari, N. Mercier, E. Levillain, P. Richomme, J. Becher, J. Garin, J. Orduna, A. Gorgues and M. Sallé, *Inorg. Chem.*, 1999, **38**, 6096; (g) K. Svane Bang, M. Brondsted Nielsen, R. Zubarev and J. Becher, *Chem. Commun.*, 2000, 215; (h) B. Johnston, L. M. Goldenberg, M. R. Bryce and R. Katakya, *J. Chem. Soc., Perkin Trans. 2*, 2000, 189; (i) M. R. Bryce, A. S. Batsanov, T. Finn, T. K. Hansen, J. A. K. Howard, M. Kamenjicki, I. K. Lednev and S. A. Asher, *Chem. Commun.*, 2000, 295; (j) F. Le Derf, M. Mazari, N. Mercier, E. Levillain, G. Trippé, A. Riou, P. Richomme, J. Becher, J. Garin, J. Orduna, N. Gallego-Planas, A. Gorgues and M. Sallé, *Chem. Eur. J.*, 2001, **7**, 447; (k) G. Trippé, E. Levillain, F. Le Derf, A. Gorgues, M. Sallé, J. O. Jeppesen, K. Nielsen and J. Becher, *Org. Lett.*, 2002, **4**, 2461.
- F. Le Derf, E. Levillain, G. Trippé, A. Gorgues, M. Sallé, R. M. Sebastian, A. M. Caminade and J. P. Majoral, *Angew. Chem., Int. Ed. Eng.*, 2001, **40**, 224.
- (a) A. J. Moore, L. M. Goldenberg, M. R. Bryce, M. C. Petty, A. P. Monkman, C. Marenco, J. Yarwood, M. J. Joyce and S. N. Port, *Adv. Mater.*, 1998, **10**, 395; (b) A. J. Moore, L. M. Goldenberg, M. R. Bryce, M. C. Petty, J. Maloney, J. A. K. Howard, M. J. Joyce and S. N. Port, *J. Org. Chem.*, 2000, **65**, 8269.
- (a) H. Liu, S. Liu and L. Echegoyen, *Chem. Commun.*, 1999, 1493; (b) S. Liu, H. Liu, K. Bandyopadhyay, Z. Gao and L. Echegoyen, *J. Org. Chem.*, 2000, **65**, 3292; (c) For a reference about electrochemical features of SAMs, see for instance A. E. Kaifer and M. Gómez-Kaifer, *Supramolecular Electrochemistry*, Wiley-VCH, 1999, ch. 15.
- C. M. Yip and M. D. Ward, *Langmuir*, 1994, **10**, 549.
- E. Dahlstedt and J. Hellberg, *Synth. Met.*, 2001, **119**, 181.
- (a) H. Fujihara, H. Nakai, M. Yoshihara and T. Maeshima, *Chem. Commun.*, 1999, 737; (b) H. Nakai, M. Yoshihara and H. Fujihara, *Electrochemistry*, 2000, **68**, 8; (c) H. Nakai and H. Fujihara, *J. Organomet. Chem.*, 2000, **611**, 566.
- J. Lau, O. Simonsen and J. Becher, *Synthesis*, 1995, 521.
- Compound **2**, and consequently derivatives **4** and **6**, exist as a mixture of *Z/E* isomers which are in slow equilibrium (ref. 3f).
- P. Hudhomme, P. Blanchard, M. Sallé, S. Le Moustarder, A. Riou, M. Jubault, A. Gorgues and G. Duguay, *Angew. Chem., Int. Ed. Eng.*, 1997, **36**, 878.
- K. Yoshida, *Electrooxidation in Organic Chemistry*, John Wiley and Sons, Ltd., New York, 1984.
- The gold bead electrodes were prepared and cleaned according to described procedure.<sup>6b</sup> The geometric areas of the gold electrodes were deduced from comparison between the slopes of the linear plots of the cathodic peak current *versus* the square root of the scan rate, obtained for the diffusion-controlled reduction of  $\text{Fe}(\text{CN})_6^{3-}$  ( $10^{-2}$  M in 0.5 M NaCl, 25°C) for: (i) the working gold bead electrodes, and (ii) gold disk electrodes of known surface (2 mm diameter from Radiometer Analytical SA). Typical electrode surfaces range from 0.02 to 0.04 cm<sup>2</sup>. Surface coverages of the SAMs of TTF derivatives were calculated by integration of the current during the first scan.
- $E_{1/2}$  is defined as  $0.5(E_p^a + E_p^c)$ .