Functionalization of the cyclodextrin platform with tetrathiafulvalene units: an efficient access towards redox active Langmuir–Blodgett films

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Electroactive cyclodextrins persubstituted with pendant tetrathiafulvalene moieties were synthesized and electrochemically characterized by cyclic voltammetry. They show a very good ability to be transferred as Langmuir–Blodgett films, independently of the hydrophobic character of the redox active part.

Because transport properties of organic charge-transfer salts of the tetrathiafulvalene (TTF) family are clearly dependent on the molecular organization in the solid, a considerable number of TTF derivatives bearing various functionalities have been designed in an effort to control the solid-state ordering.[1]

In this context, the Langmuir–Blodgett (LB) technique constitutes an efficient tool to obtain highly organized materials, and has already been explored in the case of the TTF family[2] in order to obtain conducting LB films after oxidation (*e.g.* by I_2 vapour). However, the amphiphilic character of such TTF derivatives, which generally constitutes a structural prerequisite to allow film formation,[2c,f] leads to the occurrence of alternated insulating layers—corresponding to the hydrophobic linear hydrocarbon tails (generally at least C_{16})—between redox active TTF layers. Moreover, addition of a fatty acid to the amphiphilic molecule is often needed to achieve a good transfer of the film onto the solid substrate.

Considering these limitations, we have focused on the use of the cyclodextrin (CD) platform to carry TTF moieties for LB film formation.

Cyclodextrins are cyclic oligosaccharides consisting of six, seven or eight (α-CD, β-CD and γ-CD, respectively) α-1,4-linked D-glucopyranose units forming a truncated cone. The narrow rim bears primary OH groups (C-6) and the wide rim secondary OH groups (C-2, C-3), both of these hydrophilic faces being separated by a hydrophobic cavity known for its inclusion ability.

Various amphiphilic β- and γ-cyclodextrins functionalized with alkyl chains at the primary hydroxy positions or modified on the secondary face have been found to form LB films.[3] However, to our knowledge, no advantage of this ability to generate good quality LB fims has been taken in the preparation of redox-active monolayers.

Moreover, besides this ability to favour film deposition, the CD cavity is well known to form inclusion complexes with a wide variety of inorganic or organic guest compounds,[4] which, in the case of electroactive cyclodextrins, could allow charge-transfer interactions to occur.

Therefore, considering the highly active surface inherent in LB films, use of this technique in the case of systems associating the redox properties of the TTF moiety with the complexing ability of the CD entity could lead to new sensors selective to various chemical derivatives.

This paper deals with the synthesis and electrochemical characterization of molecular blocks built from association of CD and TTF moieties, as well as with preliminary results related to their Langmuir monolayers and LB films.

The reactivity of both primary and secondary hydroxy groups of CD has been extensively investigated, allowing mono- or per-substitution of CD either on the primary or/and the secondary face with good selectivity.[5] We have focused on the synthesis of β-CD and γ-CD derivatives **3**, bearing the redox active TTF moieties on the narrower rim (primary face), where the intramolecular distances between the neighbouring pendant TTF systems are expected to be in the range of S···S intermolecular contacts in crystalline TTF based materials. Moreover, this functionalization allows access to the wider secondary face for the potential inclusion of a guest.

Results and Discussion

Synthesis

Preparation of the target compounds **3** was achieved according to a convergent synthesis *via* nucleophilic persubstitution of the 6-deoxy-6-iodocyclomaltooligosaccharides **2**, with the free thiolate derivative of TTF **1** (Scheme 1).

Selective periodinations on the primary face of native β- and γ-CD were performed according to the described procedure (PPh_3, I_2, DMF),[6] to produce **2** in fairly good yields. On the other hand, unsymmetrically substituted TTF building blocks **1** were synthesized in high yields by adaptation of the Becher methodology,[7] which involves the use of the 2-cyanoethyl fragment as a versatile protecting group for the thiolate functionality.

Finally, treatment of **1** with a methanolic solution of caesium hydroxide monohydrate led to the thiolate intermediate which was subsequently reacted with a deficiency of periodo-CD **2**, to give the target compounds **3** as brownish powders {β-**3a**: 78%; β-**3b**: 53%; β-**3c**: 50%; γ-**3a**: 28%, after silica gel chromatography purification [CH_2Cl_2–CH_3OH (8/2: v/v)+AcOH (0.1%)]}.

These compounds have been fully characterized by ^1H and ^{13}C NMR (COSY, HMQC, DEPT) spectroscopy, their ^{13}C spectra being remarkably simple thanks to the seven- and eight-fold symmetry of β-**3** and γ-**3**, respectively. Molecular ions of these highly extended systems were characterized by FAB or plasma desorption MS (β-**3a**: MH^+ 3632; β-**3b**: MH^+ 4417; β-**3c**: 5008; γ-**3a**: MH^+ 4150).

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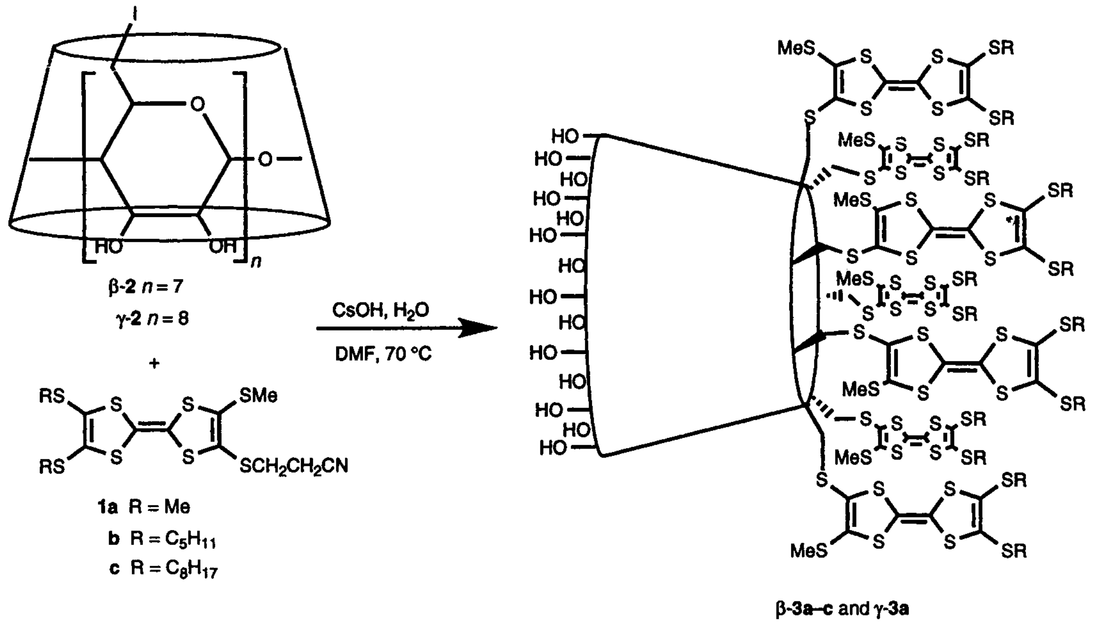

Scheme 1

Solution electrochemistry

The solution redox properties of the TTF labelled CD **3** have been studied by cyclic voltammetry.[8] Cyclic voltammograms display two reversible oxidation waves at E_{pa_1} [β-**3a**: 0.52; β-**3b**: 0.52; β-**3c**: 0.54; γ-**3a**: 0.53 *vs.* standard calomel electrode (SCE)] and E_{pa_2} (β-**3a**: 0.78; β-**3b**: 0.86; β-**3c**: 0.81; γ-**3a**: 0.78) in a CH_2Cl_2–CH_3CN (4 : 1, v : v) mixture, which correspond to the two-step oxidation of the TTF unit. The first oxidation wave is significantly broader than the second one (Fig. 1), behaviour which is unchanged upon dilution. The shape of the first redox system may be explained by the presence of strong through-space intramolecular interactions between neighbouring TTF moieties for β- or γ-**3** molecules arranged in a closed compact conformation.[9] As a consequence of Coulombic repulsions between positive TTF units, the TTF–CD assembly changes to an open conformation at E_{pa_1}, with the charged-TTF moieties lying away from the CD rigid part. The TTFs now behave like individual molecules, and are oxidized at the same potential (E_{pa_2}), which explains the narrower shape of the second oxidation wave.[9]

Langmuir monolayers and LB films

Compounds β-**3** were spread on the water surface of a Langmuir–Blodgett trough from a chloroform solution (*ca.* 0.1 mM). The surface pressure (*Π*) *versus* area per molecule isotherms for compounds β-**3** are presented in Fig. 2, and show no first-order phase transition. These compounds formed stable monolayers with relatively high collapse pressures (*ca.* 40 N m^{-1}), independently of the hydrophobic R alkyl length, even in the case of the β-**3a** molecule which bears no alkyl chains.

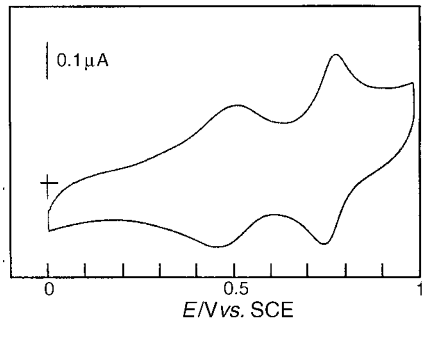

Fig. 1 Cyclic voltammetry of β-**3a** (10^{-4} mol dm^{-3}) in CH_2Cl_2–CH_3CN (4:1), $Bu^n_4NPF_6$ (0.1 mol dm^{-3}), scan rate 100 mV s^{-1}

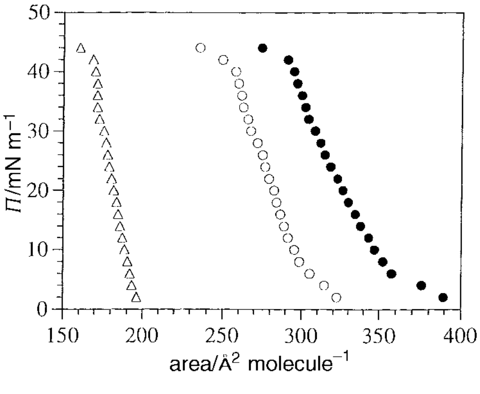

Fig. 2 *Π*–*A* isotherms of (△) β-**3a**, (○) β-**3b** and (●) β-**3c**

The limiting area, A_0, extrapolated from the *Π*–*A* curve for compound β-**3a**, is in good agreement with that calculated for the cyclodextrin secondary face orientated parallel to the interface.[3b] This result shows the ability of the molecular block to adopt a very compact conformation for which all TTF units are located over the CD cavity, the compaction mode being governed by the rigid cylindrical polar part of the molecule.

On the other hand, β-**3b** and β-**3c** are characterized by considerably larger A_0 values than for β-**3a** (β-**3b**: 250, β-**3c**: 291 Å^2), indicating that in these cases the molecular organisation is dominated by the hydrophobic tails. Moreover, the dependence of A_0 on increasing chain length from *n*-pentyl to *n*-octyl indicates disorder in the hydrophobic tails.

The monolayers of compounds β-**3** were transferred (30 mN m^{-1}, with a dipping speed of 1 cm min^{-1}) without the need for addition of a fatty acid and with a transfer ratio of 1.0 even in the case of the non-amphiphilic β-**3a**.

X-Ray diffraction studies of the Y-type LB films show the presence of one to three Bragg peaks in the diffractogram. This demonstrates as expected an increase in the layer thickness with the length of the alkyl chain (15, 18 and 20 Å per layer respectively for β-**3 a**,**b** and **c**). However, this increase is slower than expected, suggesting either a tilting or some *gauche* conformation in the alkyl chains, which is confirmed by IR measurements.

The IR spectra of these films show that the alkyl chains within the LB films are relatively poorly organized, the CH_2 vibrations being located around 2924 and 2853 cm^{-1} in accordance with the presence of some *gauche* conformations.

Under an atmosphere of saturated iodine vapour, the colour of the LB films changed to brown correlating with the appearance of new bands in the IR spectra (Fig. 3), characteristic of the oxidation state of the multilayers: (*i*) a broad band centred at *ca.* 11000 cm^{-1} corresponds to an intermolecular charge transfer band labelled type B in the Torrance's classification,[2d] and (*ii*) two strong peaks, now located at 1399 and 1336 cm^{-1} which are clearly associated with a_g modes, the $\nu_{central}$ C=C stretching vibration of the TTF group becoming IR active through the linear electron–molecular vibration interaction.

Such results show the formation of totally ionized dimers of TTF within the LB film.[10] After doping and under air or nitrogen, the brown colour of the multilayers fades away and the bands in the IR spectrum associated with the oxidized state slowly disappear and the IR spectrum of the undoped LB films is restored. Deiodination of the multilayers demonstrates the poor stability of the ionized dimers of TTF in these materials, which may be a consequence of the rigidity of the molecular platform, for which TTF units are confined near the CD cavity with a low degree of mobility, thus preventing good quality overlap. We are currently working on the synthesis of new analogous systems, in which the TTF units are associated with the CD cavity through slightly longer linkers, in order to increase their mobility and to stabilize the conducting state within the multilayers.

Conclusion

We have synthesized and characterized new electroactive cyclodextrins. These systems are of special interest since they are designed to associate the complexing ability of the CD cavity with the redox properties of the TTF core. Indeed, these systems, which display a high density of TTF units, and whose electrochemical behaviour (essentially the same as the parent TTF derivatives) shows good oxidability, may allow an entry to various fields of materials chemistry, and, among others, to electroconducting radical-cation salts. Unfortunately, attempts to electrocrystallize our systems under galvanostatic conditions have been unsuccessful so far. Nevertheless, the ability of the CD fragment to promote film transfer has been successfully transposed in the present case with good quality LB films incorporating electroactive units being obtained. This result allows us to consider the use of the same general strategy (covalent grafting of an appropriate system on to the CD entity) to produce LB films possessing physical properties requiring a high degree of molecular organization in the material, such as electroconductivity or second-order nonlinear optics.

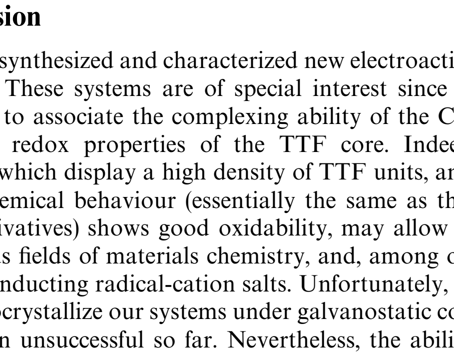

Fig. 3 IR absorption spectra between 1000 and 1500 cm^{-1} of β-**3a** LB films (*a*) before doping and (*b*) after doping

Experimental

^1H and ^{13}C NMR spectra were recorded on a JEOL GSX270WB spectrometer operating at 270 and 67.5 MHz, respectively. Chemical shifts (δ) are given in ppm (relative to $SiMe_4$) and *J* values in Hz. Cyclic voltammetry experiments were performed on a PAR model 273 potentiostat/galvanostat, under an argon atmosphere *vs.* SCE, Pt working and counter electrodes, solvents and supporting electrolyte being electrochemical grade.

LB films formation and characterization

The compression isotherm curves were recorded using a home-made Teflon trough, working at different temperatures and under a continuous nitrogen flow saturated with water. The surface pressure was measured by a Wilhemy balance using a Pt probe. The compression was carried out step by step. The sub-phase was Millipore Q-grade water with a resistivity higher than 18 MΩ cm. Chloroform (HPLC grade from Prolabo) was used as spreading solvent. The solutions (concentrations *ca.* 10^{-3} mol dm^{-3}) were stored at −18 °C between experiments to limit solvent evaporation. Built-up films have been obtained by the vertical lifting method using a large area Atemata trough working at room temp. under a continuous dried nitrogen flow. Stepwise compression was performed to reach the transfer surface pressure. Films were deposited onto optically polished calcium fluoride for the IR linear measurements and onto an optically polished glass substrate for the low angle X-ray experiments. IR spectra were recorded with a computer-controlled Nicolet 750 interferometer. The X-ray diffraction patterns were obtained using a conventional generator (Kristalloflex Siemens Ltd) delivering non-monochromatized line-focused Cu-Kα radiation and equipped with an oscillating sample. The intensities of the Bragg reflections were collected by using an Inel CPS 120 curved position-sensitive detector.

Synthesis of TTF substituted cyclodextrins β-3 and γ-3

Compounds **1a–c** have been synthesized according to the described procedure.[7b]

Heptakis{6-deoxy-6-[3′,6′,7′-tris(methylthio)tetrathiafulvalen-2′-ylthio]}cyclomaltoheptaose β-3a. 2-(2-Cyanoethylthio)-3,6,7-tris(methylthio)TTF **1a** (610 mg, 1.43 mmol) was dissolved in dry DMF (40 ml) and degassed with N_2 for 15 min. A solution of caesium hydroxide monohydrate (311 mg, 1.86 mmol) in dry methanol (8 ml) was added dropwise to the mixture, the colour of the solution becoming darker. After stirring for an additional 10 min, heptakis(6-iodo-6-deoxy) cyclomaltoheptaose β-**2** (233 mg, 0.12 mmol) dissolved in dry DMF was added dropwise. The reaction mixture was then stirred at room temp. for 2 h with the appearance of an orange precipitate, and heated at 70 °C for an additional 2 h. After cooling to room temp., stirring was maintained overnight, and the precipitate was collected by filtration, washed with a small amount of DMF, and with diethyl ether. The orange material thus obtained was then chromatographed over silica gel [eluent: CH_2Cl_2–methanol; 7:3 (v/v)+0.1% acetic acid], to afford β-**3a** as an orange powder (78% yield), mp 183–186 °C; δ ($CDCl_3$) 6.68 (s, 1H, OH); 5.23 (s, 1H, OH); 4.97 (m, 1H, H1); 3.95 (m, 2H, H3-H5); 3.73 (m, 1H, H2); 3.49 (m, 2H, H4-H6a); 3.20 (m, 1H, H6b); 2.48 (s, 3H, SCH_3); 2.43 (s, 3H, SCH_3); 2.41 (s, 3H, SCH_3). δ ([$^2H_6$]DMSO) 130.3, 126.7, 126.0 and 124.0 (lateral C=C), 110.4 and 108.6 (central C=C), 102.3 (C1), 84.5 (C4), 72.3 (C2 or C3), 72.2 (C2 or C3), 70.1 (C5), 23.3 (C6), 18.9 and 18.7 and 18.6 (SCH_3). FAB MS: MNa^+ 3654, MH^+ 3632.

Heptakis{6-deoxy-6-[3′-methylthio-6′,7′-bis(pentylthio)tetrathiafulvalen-2′-ylthio]}cyclomaltoheptaose β-3b. This compound was obtained using the same methodology as for β-**3a**, starting from 2-(2-cyanoethylthio)-3-methylthio-6,7-bis(pentylthio)TTF **1b** and heptakis(6-iodo-6-deoxy)cyclomaltoheptaose β-**2**, and was purified by silica gel chromatography [eluent: CH_2Cl_2–methanol; 8:2 (v/v)+0.1% acetic acid], to afford β-**3b** as a dark-brown solid (53% yield), mp 95 °C; δ ($CDCl_3$) 6.70 (s, 1H, OH); 5.21 (s, 1H, OH); 4.97 (m, 1H, H1); 3.94 (m, 2H, H3-H5); 3.73 (m, 1H, H2); 3.51 (m, 2H, H4-H6a); 3.13 (m, 1H, H6b); 2.79 (m, 4H, SCH_2); 2.46 (s, 3H, SCH_3); 1.62 (m, 4H, SCH_2CH_2); 1.35 [m, 8H, $S(CH_2)_2CH_2CH_2$]; 0.89 (m, 6H, CH_3). δ ($CDCl_3$) 132.7, 128.6, 128.2 and 123.7 (lateral C=C), 111.4 and 110.4 (central C=C), 102.4 (C1), 85.6 (C4), 73.8 (C2 or C3), 73.7 (C2 or C3), 71.4 (C5), 38.3 (C6), 37.0 (SCH_2), 31.4 (CH_2–CH_3), 30.1 (SCH_2CH_2), 23.0 [$S(CH_2)_2CH_2$], 22.0 (SCH_3), 14.8 (CH_3). FAB MS: MNa^+ 4439, MH^+ 4417.

Heptakis{6-deoxy-6-[3′-methylthio-6′,7′-bis(octylthio)tetrathiafulvalen-2′-ylthio]}cyclomaltoheptaose β-3c. This compound was obtained using the same methodology as for β-**3a**, starting from 2-(2-cyanoethylthio)-3-methylthio-6,7-bis(octylthio)TTF **1c** and heptakis(6-iodo-6-deoxy)cyclomaltoheptaose β-**2**, and was purified by silica gel chromatography [eluent: CH_2Cl_2–methanol; 8:2 (v/v)+0.1% acetic acid], to afford β-**3c** as a brown powder (50% yield), mp 65–70 °C; δ ($CDCl_3$) 6.70 (s, 1H, OH); 5.22 (s, 1H, OH); 4.98 (m, 1H, H1); 3.95 (m, 2H, H3-H5); 3.74 (m, 1H, H2); 3.52 (m, 2H, H4-H6a); 3.13 (m, 1H, H6b); 2.80 (m, 4H, SCH_2); 2.47 (s, 3H, SCH_3); 1.62 (m, 4H, SCH_2CH_2); 1.28 (m, 20H, $S(CH_2)_2(CH_2)_5$; 0.89 (m, 6H, CH_3). δ ($CDCl_3$) 128.0 and 123.0 (lateral C=C), 110.0 (central C=C), 101.7 (C1), 85.6 (C4), 73.2 (C2, C3), 71.0 (C5), 37.8 (C6), 36.4 (SCH_2), 31.8, 29.7, 29.3, 29.2, 28.6, 22.7 $(CH_2)_6$,19.3 (SCH_3), 14.2 (CH_3). PDMS: 5008; FAB MS: 3876 $(M-2\times565)^+$.

Octakis{6-deoxy-6-[3′,6′,7′-tris(methylthio)tetrathiafulvalen-2′-ylthio]}cyclomaltooctaose γ-3a. This compound was obtained using the same methodology as for β-**3a**, starting from 2-(2-cyanoethylthio)-3,6,7-tris(methylthio)TTF **1a** and octakis(6-iodo-6-deoxy)cyclomaltooctaose γ-**2**, and was purified by silica gel chromatography [eluent: CH_2Cl_2–methanol; 8:2 (v/v)+0.1% acetic acid], to afford β-**3c** as a brown powder (28% yield), mp 211 °C; δ ($CDCl_3$) 5.00 (m, 1H, H1); 3.96 (m, 2H, H3-H5); 3.74 (m, 1H, H2); 3.49 (m, 2H, H4-H6a); 3.23 (m, 1H, H6b); 2.44 (m, 9H, SCH_3). FAB MS: MH^+ 4150.

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