

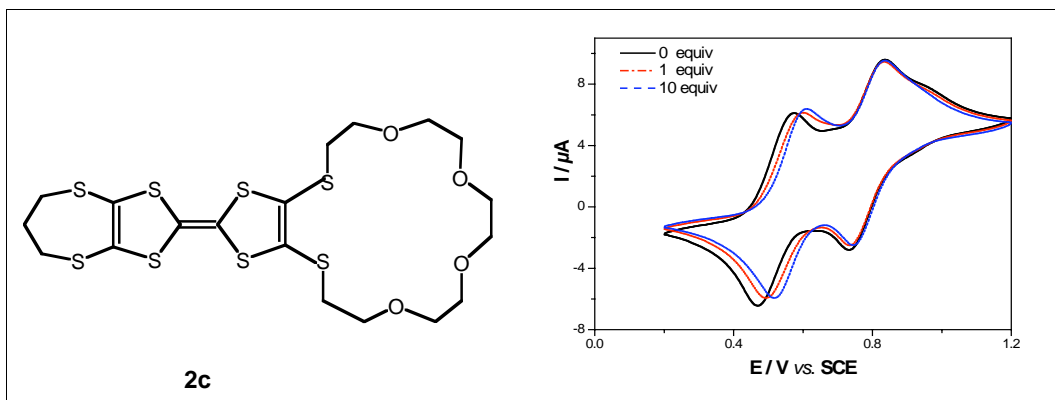
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A series of new crown-ether annelated TTF derivatives **2a**, **2b**, **2c**, **3** and **5** have been synthesized and characterized by melting points, NMR, IR and ESI-MS. The crystal structure of compound **3**, 2, 3-dithia-(5',8'-dioxaoctyl)-6,7-ethylenedithiatetrathiafulvalene, has been determined by X-ray crystallography. Redox properties of all these compounds have been investigated by cyclic voltammetry and each compound shows two reversible single-electron redox couples. The results indicate that **3** is responsive for Li^+ , but not to other alkali metal cations, such as Na^+ and K^+ . Although with the same cavity, compounds **2c** and **5** show marked changes upon the addition of sodium perchlorate, while there is no significant response for **2a** and **2b** at the same condition.

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Introduction.

Tetrathiafulvalene (TTF) and its numerous derivatives have been investigated extensively as strong electron-donor molecules since the spectacular discovery of high conductivity and superconductivity in some charge-transfer salts [1]. Different chemical modifications have been carried out on the TTF unit to prepare many versatile building blocks for macro- and supramolecular chemistry at the molecular level. The "classical" chemical modifications carried out on the TTF skeleton are aimed at tuning of the donor ability to increase the electrical conductivity [2]. Some other complicated systems, such as TTF-cyclophanes, TTF-catenanes and TTF-rotaxanes/pseudorotaxanes, have also been developed in synthetic TTF chemistry [3,4]. During the past two decades, much attention has been directed towards redox-active macrocyclic ligand systems [5], especially when complexation of a guest molecule (or an ion) at one site in the molecule, a change in the optical [6] or redox [7] properties of the system can be detected by spectroscopic, structural, or electrochemical techniques [8]. In the context of redox-responsive ligands, the good π -electron donor tetrathiafulvalene appears as an ideal redox-active system because TTF moiety is fully delocalized,

polarizable and it can be successively oxidized into thermodynamically stable radical cation and dication species in totally reversible way [9]. Bryce *et al.* introduced anthraquinone into this system to enlarge the delocalized core and get better results such as larger shift and more sensitivity [10]. Incorporation of the TTF unit into macrocycles containing a crown ether recognition motif allows the electrochemical recognition of various metal cations, such as Li^+ , Na^+ , K^+ and Ba^{2+} [11,12]. The main group ion Pb^{2+} and the transition metal ion Ag^+ were also found having good responsibility for these macrocyclic TTFs [12c, 13]. Anion sensible TTF compounds have also been studied [14].

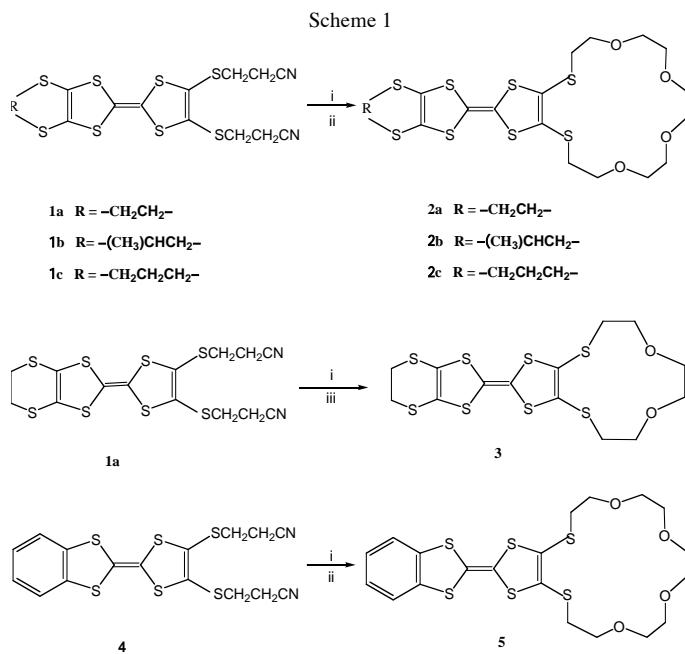
To ensure a good communication between the chelating unit (crown ether) and the redox moiety (the TTF core), the functionalization of the TTF moiety has been undertaken with different strategies of synthesis [15,16]. Herein, we report the synthesis, structure and metal-cation recognition of a series of new crown-annelated TTF derivatives.

Results and Discussion.

Synthesis.

The starting materials **1a**, **1b**, **1c** and **4** were prepared by the standard triethyl phosphite-mediated cross-coupling

reaction according to the reported literature [17-20] and characterized by melting points, IR, NMR. Analytical and spectroscopic data are in good agreement with the literature. The two thiolate groups in the starting materials were protected with 2-cyanoethyl groups. Under nitrogen, reaction with two equivalents of cesium hydroxide monohydrate in methanol resulted in an important intermediate, dicesium thiolate, which was very sensitive to air and moisture. The crown-annulated TTF derivative **3** was formed after the alkylation with 1,2-bis(2-iodoethoxy)ethane. Similar to the preparation of compound **3**, upon treatment **1a**, **1b**, **1c** and **4** with cesium hydroxide monohydrate in methanol solution, followed by alkylation with penta(ethylene glycol)di-*p*-toluenesulfonate overnight under high-dilution conditions (Scheme 1) giving a mixture of mono-, di-, tri-, tetra and even pentamer. The reaction mixture was injected on the column and the monocrown annulated was separated by chromatography. High dilution generally increased the proportion of monomer at the expense of "multimers".



Reagents and Conditions: (i) DMF, CsOH·H₂O/CH₃OH, r.t., 1.5 h (ii) penta(ethyleneglycol)di-*p*-toluenesulfonate/DMF, 18 h. (iii) 1, 2-bis(2-iodoethoxy)-ethane/DMF, 10 h.

Table 1

Cyclic voltammetric data for compound **2a**, **2b**, **2c** and **5** (ΔE^1_{ox} refers to the anodic shift in the first oxidation potential after saturation of the solution with NaClO₄).

Compound	E^1_{ox}/V	E^1_{ox}/V	$\Delta E^1_{\text{ox}}/\text{mV}$
2a	0.57	0.82	10
2b	0.54	0.73	15
2c	0.49	0.72	30
5	0.52	0.79	45

Electrochemical Studies.

The redox behaviour of compound **3** was investigated by cyclic voltammetry (CV). As expected, **3** exhibits two reversible one-electron redox couples ($E^1_{1/2} = 0.558$ V, $E^2_{1/2} = 0.846$ V), which are typical for TTFs [21]. In the presence of 9 equiv. lithium perchlorate, the maximum of about 15 mV shift of the $E^1_{1/2}$ (ΔE^1_{ox}) to more positive (anodic) potential was observed, whereas E^2_{pa} and E^2_{pc} remained unchanged. No CV response was detected in the presence of other alkali metal, such as Na⁺, K⁺. Electrochemical recognition for compounds **2a**, **2b**, **2c** and **5** has been evaluated in CH₂Cl₂/CH₃CN solution in both the absence and the presence of metal cations by cyclic voltammetry in the same condition (Table 1). All these compounds show two reversible one-electron well-defined redox couples on a glassy carbon electrode. Significant changes of the CVs of **2c** and **5** (Figure 1) could be observed upon addition of Na⁺. Addition of a

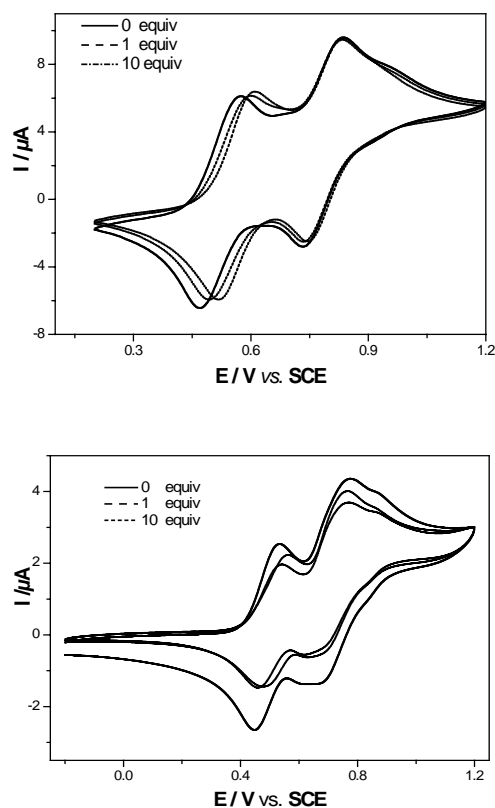


Figure 1. Cyclic voltammograms of **2c** (top) and **5** (down) recorded in a mixture of CH₂Cl₂/CH₃CN (10⁻³ mol L⁻¹) at a scan rate of 50 mV s⁻¹ with *n*-Bu₄NClO₄ (0.1 M) as the supporting electrolyte in the presence of increasing amounts of Na⁺.

controlled amount of NaClO₄ to a solution of compound **2c** and **5** in CH₂Cl₂/CH₃CN (1:1) with *n*-Bu₄NClO₄ (0.1 M) caused substantial positive shifts ($\Delta E^1_{1/2} = 30$ mV and

45 mV, respectively) of the first oxidation potential (E_{ox}^1), whereas E_{ox}^2 remained unchanged. The reason why the first oxidation wave is shifted to more anodic potential may be interpreted as a result of the electrostatic inductive effect of the metal bound to crown ether withdrawing the electron density from the TTF moiety. On the other hand, the dicationic state of the TTF core is reached at a constant E_{ox}^2 value, irrespective of the amount of metal cation added. This behavior can be explained by the expulsion of the metal cation from the cavity, owing to the increased repulsive electrostatic interaction with the doubly charged TTF moiety. Interestingly, the E_{ox}^1 shifts reach a limit when approximately stoichiometric amounts of Na^+ are added to receptors. This result provides further evidence for the high stability of the 1:1 complexes, confirming the good complexation selectivity of these receptors. But compounds **2a** and **2b** show very slight response (only ~10mV) upon the addition of sodium perchlorate. The three compounds (**2a**, **2b** and **2c**) reported here have similar structures, but exhibit different electrochemical properties after their reaction with metal ions. This may due to the modification of TTF unit or the extra structural factors. Therefore, it is possible for us to optimize and explore better probes by the slight modifications on TTF derivatives.

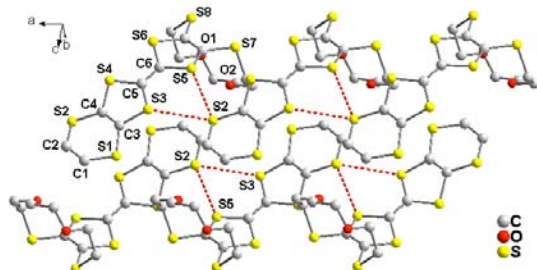


Figure 2. The packing diagram of compound **3** view along the *c* axis (the dotted line representing S...S non-bonded contacts less than 3.7 Å).

X-ray crystal Structure.

As illustrated in Figure 2, compound **3** is in a boat conformation. The macrocycle adopts a crown conformation, favorable for metal coordination which is like some other TTF-monocrown compound [22]. The S_2O_2 crown-ether group is bent toward one side of the TTF unit(s), nearly vertical to the plane of the TTF C_2S_4 core. On the TTF unit, the conjugated π system of this molecule is extended to all of the eight sulfur atoms therefore the response to the guest metal ions will be more sensitive. The bond length of C(5)-C(6) (central double bond of the TTF moiety, 1.338(5) Å) is in accordance with those of unoxidized TTF compounds. For example, in

tetramethylthio-TTF, the related values are 1.33-1.35 Å. They are obviously shorter than the corresponding bonds in the one-electron oxidized compound (1.38-1.40 Å) [23]. The shortest intermolecular S...S contacts between S(2)...S(3') and S(2)...S(5') (Figure 3) are 3.625 Å and 3.571 Å, respectively, which are less than the sum of the van der Waals radii (3.70 Å). From the packing diagram of compound **3**, the crystal consists of columns of molecules along *a* direction.

X-Ray Structure Determination.

The single crystal of compound **3** suitable for the X-ray structure analysis was grown from dichloromethane/diethyl ether. Intensity data were measured on a Bruker Smart Apex CCD diffractometer equipped with graphite-monochromated Mo-K ($\lambda = 0.71073$ Å) radiation using $\omega/2\theta$ scan mode at 293(2) K. The highly redundant data sets were reduced using SAINT and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS supplied by Bruker. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 using SHELXTL-97. All non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of U_{iso} .

Full crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 280915. Copies of this information may be obtained from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

EXPERIMENTAL

General Procedure.

All the commercial reagents used were analytically pure and without further purification. Schlenk techniques were used in carrying out manipulation under nitrogen atmosphere. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C analyzer. The IR spectra were taken on a Vector22 Bruker Spectrophotometer (400-4000 cm^{-1}) with KBr pellets. NMR spectra were measured on a Bruker AM 500 spectrometer. Chemical shifts were measured as δ units (ppm) relative to tetramethylsilane. Melting points were determined with a X-4 digital micro melting point apparatus and uncorrected. ESI-MS spectra were recorded on a Varian MAT 311A instrument. Cyclic voltammetry (CV) experiments were performed on a CHI660 electrochemistry workstation with a three electrode system. A glassy carbon electrode was used as the working electrode, a platinum wire as auxiliary electrode and Ag/AgCl electrode as reference electrode. CV measurements were made in CH_2Cl_2/CH_3CN solution and using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte.

2,3-Dithia-(3',6',9',12'-tetraoxatetradecyl)-6,7-ethylenedithiatetrafulvalene (**2a**)

At room temperature, to a solution of **1a** (450 mg, 1 mmol) in DMF (50 mL) was added a solution of CsOH·H₂O (336 mg, 2 mmol) in methanol (15 mL) over a period of 45 min with stirring. The mixture was further stirred for 1 h and the solution color was changed into dark red. The above solution and the solution of penta(ethylene glycol)di-*p*-toluenesulfonate (95%) (575 mg, 1 mmol) in DMF (50 mL) were added simultaneously into a 250-mL three-necked flask (already loaded with 100 mL of DMF) over 18 h under high-dilution conditions. The reaction mixture was stirred for an additional 3 h, and then concentrated *in vacuo*. The resulting residue was taken up into dichloromethane (100 mL), washed with brine (2 × 30 mL), and dried over MgSO₄. Evaporation of the solvent and subsequent column chromatography (silica gel, CH₂Cl₂/AcOEt 19:1) gave **2a** as an orange oil (291 mg, 52%). δ_H (CDCl₃-TMS): 2.71 (4H, t, SCH₂, *J* = 4.0 Hz), 3.03 (4H, t, SCH₂, *J* = 6.0 Hz), 3.55 (4H, s, OCH₂), 3.63 (8H, s, OCH₂), 3.68 (4H, t, SCH₂, *J* = 6.0 Hz); δ_C (CDCl₃-TMS): 29.77, 68.21, 70.13, 76.85, 113.37, 117.41, 127.53, 129.51, 132.48, 144.48; *m/z* (ESI-MS) 582.9 (M+Na⁺).

Anal. Calcd. for C₁₈H₂₄O₄S₈: C, 38.58; H, 4.29. Found: C, 38.70; H, 4.31.

2,3-Dithia-(3',6',9',12'-tetraoxatetradecyl)-6,7-methylethylenedithiatetrafulvalene (**2b**)

Compound **2b** was obtained in a similar method as a yellow oil in 42% yield. δ_H (CDCl₃-TMS): 1.48 (3H, d, CH₃, *J* = 4.0 Hz), 3.02 (H, m, SCH), 3.19 (2H, d, SCH₂, *J* = 6.0 Hz), 3.59 (4H, s, OCH₂), 3.63 (8H, s, OCH₂), 3.69 (4H, t, SCH₂, *J* = 6.0 Hz), 3.74 (4H, t, SCH₂, *J* = 6.0 Hz); δ_C (CDCl₃-TMS): 36.03, 69.63, 70.14, 70.91, 71.19, 111.50, 122.29, 126.37, 128.36, 130.21, 136.87; *m/z* (ESI-MS) 596.9 (M+Na⁺).

Anal. Calcd. for C₁₉H₂₆O₄S₈: C, 39.73; H, 4.57. Found: C, 39.48; H, 4.51.

2,3-Dithia-(3',6',9',12'-tetraoxatetradecyl)-6,7-propylenedithiatetrafulvalene (**2c**)

Compound **2c** was obtained in a similar method as a yellow oil in 38% yield. δ_H (CDCl₃-TMS): 2.42 (2H, m, CH₂CH₂CH₂, *J* = 4.0 Hz), 2.70 (4H, t, SCH₂, *J* = 4.0 Hz), 3.03 (4H, t, SCH₂, *J* = 6.0 Hz), 3.65 (4H, s, OCH₂), 3.67 (8H, s, OCH₂), 3.74 (4H, t, SCH₂, *J* = 6.0 Hz); δ_C (CDCl₃-TMS): 20.50, 31.02, 36.63, 70.13, 76.71, 112.15, 114.10, 127.58, 129.45, 144.41; *m/z* (ESI-MS) 597.1 (M+Na⁺).

Anal. Calcd. for C₁₉H₂₆O₄S₈: C, 39.73; H, 4.57. Found: C, 39.55; H, 4.49.

2,3-Dithia-(5',8'-dioxaoctyl)-6,7-ethylenedithiatetrafulvalene (**3**)

To a DMF (20 mL) solution of **1a** (350 mg, 0.75 mmol) was added a methanol (15 mL) solution of CsOH·H₂O (253 mg, 1.5 mmol) over a period of 45 min with stirring. The mixture was further stirred for 1 h and a DMF (5 mL) solution of 1, 2-bis(2-iodoethoxy)ethane (278 mg, 0.75 mmol) was added. After stirring for 10 h, the solvent was evaporated and the residue was dissolved in CH₂Cl₂, washed with brine and dried over MgSO₄. Concentration *in vacuo* gave a yellow residue, which was subjected to column chromatography (SiO₂, eluent: dichloromethane). The first yellow band was collected and concentrated to provide **3** as orange yellow crystals (72 mg,

20%), mp 138 °C. δ_H (CDCl₃-TMS): 3.08 (4H, t, SCH₂O, *J* = 6.0 Hz), 3.33 (4H, s, SCH₂), 3.63 (4H, s, OCH₂), 3.74 (4H, t, OCH₂, *J* = 6.0 Hz);

Anal. Calcd. for C₁₄H₁₆O₂S₈: C, 35.54; H, 3.45. Found: C, 35.70; H, 3.50.

2,3-Dithia-(3',6',9',12'-tetraoxatetradecyl)-6,7-benzodithiatetrafulvalene (**5**)

By a procedure similar to **2a**, penta(ethyleneglycol)di-*p*-toluenesulfonate reacted with appropriate **4** to give compound **5** as a yellow oil (395 mg, 76%). δ_H (CDCl₃-TMS): 3.05 (4H, t, SCH₂, *J* = 6.2 Hz), 3.63 (4H, s, OCH₂), 3.65 (8H, s, OCH₂), 3.75 (4H, t, SCH₂, *J* = 6.2 Hz), 7.12 (2H, q, Ar-H), 7.25 (2H, q, Ar-H); δ_C (CDCl₃-TMS): 36.03, 69.63, 70.14, 70.91, 71.19, 111.50, 122.29, 126.37, 128.36, 130.21, 136.87; *m/z* (ESI-MS) 542.9 (M+Na⁺);

Anal. Calcd. for C₂₀H₂₄O₄S₆: C, 46.15; H, 4.62. Found: C, 46.27; H, 4.68.

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