# Tetrathiafulvalene derivatives bearing a crown ether with intramolecular charge transfer properties: synthesis and cation binding studies<sup>†</sup>

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Received (in Montpellier, France) 13th October 2008, Accepted 2nd December 2008 First published as an Advance Article on the web 21st January 2009 DOI: 10.1039/b817892e

Two new TTF crown ether derivatives, **TNC** and **TBC**, have been synthesized and well characterized. The interaction between the TTF and crown ether moieties through a triple bond has been demonstrated to show a remarkable sensing ability towards  $Pb^{2+}$  over the other cations.

# Introduction

As a well known organic  $\pi$ -donor, tetrathiafulvalene (TTF) has aroused much interest over the past 30 years. Large numbers of TTF compounds with elaborate structures have been constructed and have shown promising applications in supramolecular systems.<sup>1,2</sup> Specifically, TTF macrocyclic systems containing a host unit capable of cation binding are attracting widespread attention because the complexation of the host with an ionic guest can induce a change in their physicochemical response (e.g., spectral or electrochemical).3-5 In general, upon metal ion binding in TTF macrocyclic systems, the first oxidation potential  $(E_{ox}^{1})$  increases, while the second  $(E_{ox}^2)$  remains unchanged. This is rationalized by the expulsion of the cation after the first oxidation.<sup>4</sup> Therefore, the  $E^{1}_{ox}$  shift upon metal complexation has been extensively used for sensing purposes.<sup>6</sup> The groups of Becher and Sallé have dedicated themselves to this field. Sallé et al. have classified TTF macrocycles into model A or model B families according to their grafting sites, in which the crown moieties are directly linked to TTF subunits.<sup>7</sup>



In earlier reports, Becher *et al.* took the lead in developing TTF crown derivatives of model **A** for recognition events.<sup>8</sup> Sallé *et al.* have made a number of TTF-based macrocycles of model **B** for redox-selective metal ion sensors.<sup>9</sup> It was established that the association constants and physicochemical

† Electronic supplementary information (ESI) available: Additional experimental details and data. CCDC reference number 644421. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b817892e

responses significantly depend on the electrostatic interaction between the TTF moiety and cations, both in models **A** and **B**, when TTF macrocycles bind a metal ion *via* a crown ether. Spatial proximity to the TTF moiety is an important factor governing the interaction of a guest cation with the TTF unit. Since the biggest HOMO coefficient of the TTF moiety is mainly located on the central S<sub>2</sub>C=CS<sub>2</sub> fragment,<sup>10</sup> model **B** would be more appropriate for enhancing the through-space electrostatic interactions between metal ions and the TTF unit. Indeed, Sallé and co-workers have reported a model **B** bis(pyrrolo)-TTF crown with more selective binding toward Pb<sup>2+</sup> and Ba<sup>2+</sup> in its neutral state.<sup>11</sup>



Other than direct interactions through space, however, we are not aware of reports concerning the interaction of the TTF moiety with a guest cation through bonds in TTF crown ether derivatives (model C). More recently, we reported that the electronic communication between the TTF moiety and acceptors can be effectively optimized by a  $\pi$ -conjugated bond.<sup>12</sup> In this context, we are interested in the incorporation of a crown ether functionality into the TTF moiety *via* a  $\pi$ -conjugated triple bond for studying through-bond



Scheme 1 The synthetic route to TNC and TBC, and references TN and TB.

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Downloaded by McMaster University on 21 March 2013 Published on 21 January 2009 on http://pubs.rsc.org | doi:10.1039/B817892E interactions between the TTF moiety and guest cations. Here, we wish to report the synthesis of two novel TTF crown ether compounds, **TNC** and **TBC** (Scheme 1). Although the spatial distance is longer than that in both models **A** and **B**, we demonstrate that the interaction between the TTF unit and the crown ether through a triple bond has a remarkable sensing ability towards  $Pb^{2+}$  over the other cations.

# **Results and discussion**

## Synthesis

The synthesis of target molecules TNC and TBC was carried out under the typical Sonogashira coupling conditions shown in Scheme 1.13 The starting materials 2-iodotetrathiafulvalene (I-TTF) and  $HC \equiv CR$  were prepared according to literature methods.<sup>14</sup> The reaction of I-TTF with 1 equiv.  $HC \equiv CR$  in a mixed solvent of NEt<sub>3</sub> and THF, catalyzed by CuI and  $Pd(PPh_3)_4$ , for 6 h at room temperature afforded TNC and **TBC** as orange-yellow solids with yields of 70 and 60%, respectively. <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, MS spectrometry, and satisfactory elemental analyses confirmed the identities of all the compounds. A single crystal of TBC was obtained and structurally characterised. Compared with the synthetic procedures for model A and B compounds, this reaction could be performed under mild conditions with a relatively shorter reaction time and in higher yield. Compounds TN and TB were also prepared as references for TNC and TBC, respectively.

## X-Ray crystal structure determination of TBC

Single crystals of TBC were obtained by diffusion of hexane into a CH<sub>2</sub>Cl<sub>2</sub> solution of TBC and determined by X-ray diffraction.<sup>15</sup> The molecular structure of TBC is depicted in Fig. 1. A noticeable feature of the TTF moiety lies in two of its bond lengths, 1.722(3) Å (S(4)–C(5)) and 1.332(4) Å (C(5)-C(6)). All the other S-C bonds in TBC (between 1.737(3) and 1.768(3) Å) are much longer than that of S(4)–C(5). The shorter  $\pi$ -conjugated C(1)–C(2) bond (1.316(4) Å) than that of C(5)–C(6) indicates that the triple bond-bridged **TBC** molecule is significantly conjugated. In addition, there is a dihedral angle of  $38.2^{\circ}$ (C(9)-C(10)-C(5)-C(6)) between the phenyl ring of the phenylacetylene and the plane of the TTF moiety. The TTF moiety also has a slightly twisted cis-conformation, with dihedral angles of  $17.8^{\circ}$  (C(5)–C(6)–C(4)–C(3)) and  $13.4^{\circ}$ (C(4)-C(3)-C(1)-C(2)), respectively.



Fig. 1 ORTEP drawing of the molecular structure of TBC with thermal ellipsoids at 30% probability.

### UV-vis spectral changes of TNC and TBC toward cations

The absorption spectra of TNC and TBC, together with those of TN and TB, in acetonitrile solution were investigated and are shown in Fig. S1.<sup>†</sup> Similar to TN and TB, TNC and TBC display two absorption bands at <370 nm and 370-500 nm (Table 1). The absorption spectral properties follow Beer's Law at concentrations below  $1 \times 10^{-4}$  M, suggesting the absence of aggregation. With reference to our previous work on triple bond-bridged TTF- $\pi$ -A compounds,<sup>12a</sup> the intense absorption band at <370 nm is assigned to a local transition in the TTF moiety, while the low energy absorption band arises from intramolecular charge transfer (ICT). The triple bond linkage modulates the electron distribution between the TTF core and the crown group in TNC and TBC. As indicated in Table 1, the ICT absorption bands of **TBC** ( $\lambda_{max} = 407 \text{ nm}$ ) and **TB** ( $\lambda_{max} = 403$  nm) are lower in energy than those of **TNC** ( $\lambda_{max} = 395$  nm) and **TN** ( $\lambda_{max} = 396$  nm). This may be rationalized by the fact that the higher electron density of the N centre in TNC and TN leads to a weaker electron accepting ability compared to the benzo-15-crown-5 and methoxy substituents in TBC and TB.

Taking advantage of the recognition ability of crown ethers for cations, we investigated the complexation behaviors of TNC and TBC toward metal ions, particularly Pb<sup>2+</sup>. Fig. 2 shows the UV-vis absorption spectral changes of TNC and **TBC** in acetonitrile as a function of added  $Pb(ClO_4)_2$ . Evidently, the interaction between the crown ether and  $Pb^{2+}$ leads to significant changes in the absorption spectra of TNC and TBC. The maximum of the local absorption band of TNC blue-shifts from 338 to 307 nm, while the ICT band red-shifts from 395 to 413 nm, respectively, with increasing  $Pb^{2+}$  concentration. Throughout the titration, well-defined isosbestic points at 317 and 433 nm were clearly observed, indicating the presence of only two absorption species in solution: the free TNC and the complex TNC·Pb<sup>2+</sup>. The observed red shift in the low energy ICT absorption band should be a result of the complexation of metal ions to the azo-crown ether moiety in TNC, which would enhance the electron accepting ability of the azo-crown ether moiety, thereby improving the extent of ICT from the TTF unit to the azo-crown moiety through the triple bond. Similar results were observed upon adding Pb<sup>2+</sup> to a solution of **TBC** in acetonitrile, only with smaller spectral changes than those of TNC (Fig. 2(b)). At the same time, no spectral changes were observed in the control experiments; TN and **TB** providing evidence of the binding of  $Pb^{2+}$  to the crown ether moiety. Therefore, it can be deduced that  $Pb^{2+}$ can interact with the crown ether moiety, inducing by a through-bond response from the TTF unit in TNC and TBC. The smaller spectral change of TBC indicates that the electronic communication between the TTF unit and the

Table 1 The absorption properties of TBC, TB, TNC and TN in  $CH_3CN$  solution (10<sup>-5</sup> M) at room temperature

	ТВС	ТВ	TNC	TN
$\lambda_{\max}^{a}(\varepsilon^{c})$	310 (0.859)	297 (1.057)	338 (1.176)	332 (1.480)
$\lambda_{\max}^{b}(\varepsilon^{c})$	407 (0.121)	403 (0.143)	395 (0.229)	396 (0.270)
$a \lambda < 370$	nm. <sup>b</sup> $\lambda = 370$ -	–500 nm. <sup>c</sup> ε/10	$^{5} dm^{-3} mol^{-1} dm^{-1}$	$cm^{-1}$ .



**Fig. 2** Absorption spectral changes of **TNC** and **TBC** in CH<sub>3</sub>CN solution with 0.1 M <sup>*n*</sup>Bu<sub>4</sub>NPF<sub>6</sub> as a function of Pb<sup>2+</sup> concentration (0–1.5 equiv.). (a) **TNC** ( $1.4 \times 10^{-5}$  M), (b) **TBC** ( $2.4 \times 10^{-5}$  M); the insets show plots of  $A_0/(A_0 - A)$  vs. 1/[Pb<sup>2+</sup>] for **TNC** and **TBC**.

benzo-15-crown-5 moiety is disturbed by the dihedral angle of  $38.2^{\circ}$  (C(9)–C(10)–C(5)–C(6)) observed in its crystal structure.

The insets in Fig. 2 show plots of  $A_0/(A_0 - A)$  vs.  $1/[Pb^{2+}]$ , where A and  $A_0$  refer to the absorbance in the presence and absence of Pb<sup>2+</sup> at 395 and 407 nm for **TNC** and **TBC**, respectively. Analysis of the plots using the Benesi–Hildebrand equation reveals that the complexation of the crown ether moiety and Pb<sup>2+</sup> is in the ratio 1 : 1 (see Fig. S2†),<sup>16</sup> with the binding constant, log K, being 4.07 for **TNC**, and 4.60 for **TBC**, respectively.

TNC and TBC can also complex with other metal cations, such as Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Zn<sup>2+</sup>, available as their perchlorate salts, resulting in similar absorption spectral changes in TNC and TBC compared to those seen for Pb<sup>2+</sup>. However, the spectral changes are much less significant (Fig. S3 and Fig. S4<sup>+</sup>) and a large excess of these other metal cations need to be added. The binding constants of TNC and TBC with these cations in acetonitrile were determined, and are summarized in Table 2. To provide a clear picture, the change of absorbance at a wavelength of 338 nm for TNC in



Fig. 3 The absorbance changes at 338 nm for TNC  $(1.4 \times 10^{-5} \text{ M})$  in the presence of a  $1.7 \times 10^{-5}$  M acetonitrile solution of various cations.

the presence of 1.2 equiv. of metal cation in an acetonitrile solution is presented in Fig. 3. Obviously, **TNC** shows the highest binding affinity towards  $Pb^{2+}$  compared to the other metal ions. The N heteroatom in the azo-crown ether moiety of **TNC** enhances its affinity towards softer  $Pb^{2+}$  ions, and thus affords a high selectivity and sensitivity towards them.

As described for the previous TTF crown ether derivatives, the UV-vis spectral responses resulting from the complexation of model **A** or **B** compounds and metal ions were quite small, in spite of dramatic changes observed in electrochemical studies. However, the interaction between the crown ether moiety and Pb<sup>2+</sup> leads to significant absorption spectral changes of the triple bond-bridged TTF crown derivatives **TNC** and **TBC**. For **TNC**, the absorbance at  $\lambda = 338$  nm decreased by more than three-fold (from 1.176 to 0.346) when 1.5 equiv. of Pb<sup>2+</sup> was added (Fig. 2), which is the largest UV-vis spectral change observed so far for TTF crown derivatives. Evidently, the triple bond can serve as a bridge to optimize the electronic communication between the TTF moiety and the crown ether, resulting in remarkable changes to the ICT by an external stimulus in the absorption spectra.

### **Electrochemical studies**

TNC and TBC, along with their references TN and TB, exhibit two reversible one-electron oxidation waves  $(E^1 \text{ and } E^2,$ Table 3), which are derived from the oxidation of TTF to  $TTF^{+\bullet}$  and  $TTF^{2+}$ , respectively. In addition, a third oxidation potential  $(E^3)$  at 1.07 V for TNC and 1.03 V for TN, respectively, corresponding to the oxidation of the N heteroatom, was detected. Progressive addition of  $Pb^{2+}$  to solutions of **TNC** and **TBC** resulted in positive shifts of their  $E^1$  and  $E^2$ values (Table 3, Fig. S5<sup>†</sup>). In contrast to models A and B, the positive shift of  $E^1$  in the presence of  $Pb^{2+}$  is small and the oxidation of TTF up to its dication  $(E^2)$  does not lead to expulsion of the metal cation. This fact provides indirect evidence that the metal cation and  $TTF^{2+}$  are well separated. TNC and TBC associate with metal ions through the triple bond. Since Pb<sup>2+</sup> interacts with the N atom of the azo-crown moiety directly, the  $E^3$  shift of TNC is much larger, close to 50 mV. Under identical conditions, no alteration could be observed in the cyclic voltammograms when Pb<sup>2+</sup> ions were introduced into TN or TB solutions. The addition of other

Table 2 The binding constants of TBC and TNC for various metal ions in acetonitrile with 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> at 298 K

	Li <sup>+</sup>	Na <sup>+</sup>	$Mg^{2+}$	Ca <sup>2+</sup>	$Zn^{2+}$	$Pb^{2+}$
TBC TNC	2.40	2.16	4.13 2.48	4.18 3.47	3.92 2.57	4.60 4.07

	TTF	TNC	<b>TNC</b> + $Pb^{2+}$	TN	TBC	<b>TBC</b> + $Pb^{2+}$	ТВ
$E^{1}_{1/2}/V$	0.320	0.407	0.424	0.414	0.422	0.439	0.432
$E^{2}_{1/2}/V$	0.700	0.771	0.804	0.762	0.803	0.819	0.790
$E_{1/2}^{3/2}/V$	—	1.12	1.17	1.09		—	—

**Table 3** The oxidative potentials of **TNC**, **TN**, **TBC**, **TB** and parent TTF in the presence and absence of  $Pb^{2+a}$ 

<sup>*a*</sup> The data are given vs. a saturated calomel electrode in CH<sub>3</sub>CN with  $^{n}Bu_{4}NPF_{6}$  (0.1 M) as the supporting electrolyte (100 mV s<sup>-1</sup>).



**Fig. 4** <sup>1</sup>H NMR spectra of **TNC**  $(2.0 \times 10^{-3} \text{ M})$  in CD<sub>3</sub>COCD<sub>3</sub> as a function of Pb<sup>2+</sup> concentration: (a) 0, (b) 0.3, (c) 0.6, (d) 1.0, (e) 1.5 and (f) 2.0 equiv.

metal cations (Li<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and Zn<sup>2+</sup>) caused no significant modification in the cyclic voltammograms of **TNC** or **TBC**, suggesting that the interaction between TTF and crown ether moieties through the triple bond has a remarkable sensing ability towards  $Pb^{2+}$  over the other cations.

# <sup>1</sup>H NMR titration study

A <sup>1</sup>H NMR titration study was also carried out to confirm the specific sensing properties of **TNC** towards  $Pb^{2+}$ . Fig. 4 shows the family of <sup>1</sup>H NMR spectra of **TNC** in  $CD_3COCD_3$  solution taken during the course of the titration. A comparison of the <sup>1</sup>H NMR spectra in the presence and absence of  $Pb^{2+}$  reveals that the chemical shifts associated with the phenyl and the crown ether protons are evidently shifted downfield by the progressive addition of  $Pb(ClO_4)_2$  to the solution. In contrast, the addition of  $Pb^{2+}$  to a **TN** solution under identical conditions caused no obvious changes in its <sup>1</sup>H NMR spectrum, except for broadening of the signals of the TTF moiety. Other metal cations did not interfere with the detection of  $Pb^{2+}$ . These observations clearly indicate that **TNC** interacts with  $Pb^{2+}$  through the triple bond, and that the whole **TNC** molecule is conjugated.

# Conclusions

Two novel TTF crown ether derivatives, **TNC** and **TBC**, have been synthesized by a straightforward Sonogashira coupling reaction. The  $\pi$ -conjugated triple bond serves as a bridge to optimize the electronic communication between the TTF unit and the crown ether moiety. The resulting ICT of **TNC** and **TBC** is effective for sensing purposes. In contrast to reported models **A** and **B**, TTF crown derivatives **TNC** and **TBC** show a remarkable sensing ability towards Pb<sup>2+</sup>. Despite being far separated, the TTF units in **TNC** and **TBC** can communicate effectively with metal cations through their triple bonds, leading to remarkable changes in their UV-vis absorption, <sup>1</sup>H NMR spectra and electrochemical properties.

# Experimental

# Synthesis

**TBC.** A mixture of I-TTF (110 mg, 0.33 mmol), 4-acetylenebenzo-15-crown-5 (88 mg, 0.3 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (17 mg) and CuI (6 mg) was added to a solution of anhydrous THF (20 mL) and TEA (0.2 mL), and stirred for 12 h at room temperature. After filtration, the filtrate was evaporated and purified by column chromatography over silica gel (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH) to afford **TBC** as a yellow solid (yield 60%; m.p. 154 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 7.05 (s, 1H), 7.00 (s, 1H), 6.98 (s, 1H), 6.87 (d, 1H), 6.68 (s, 2H), 3.98 (m, 4H), 3.67 (m, 4H) and 3.52 (m, 8H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz): δ 149.6, 148.3, 126.3, 125.2, 120.1, 119.9, 116.0, 114.1, 113.5, 113.3, 112.8, 106.0, 93.8, 78.9, 70.5, 69.7, 69.6, 68.7, 68.6, 68.5 and 68.3. MS (EI): m/z = 494. Anal. for C<sub>22</sub>H<sub>22</sub>O<sub>5</sub>S<sub>4</sub>: found (calc.): C, 53.26 (53.42); H, 4.49 (4.48)%.

TNC. TNC was synthesized by a procedure similar to that for TBC, except that 4-acetylene-phenyl-aza-15-crown-5 was used in place of 4-acetylene-benzo-15-crown-5. This product was obtained as an orange-yellow solid (yield 70%; m.p. 145 °C) after purification by column chromatography over silica gel (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH). <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz): δ 7.27 (d, 2H, J = 9.0 Hz), 6.68 (d, 2H, J = 9.0 Hz), 6.61 (s, 1H), 6.49 (s, 2H), 3.67 (m, 4H), 3.57 (m, 8H) and 3.54 (m, 8H). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz): δ 148.4, 131.7, 130.9, 126.5, 126.3, 125.2, 120.7, 119.9, 114.4, 109.8, 94.0, 71.3, 70.5, 70.2, 67.9 and 51.6. MS (EI): m/z = 522. Anal. for C<sub>24</sub>H<sub>27</sub>NO<sub>4</sub>S<sub>4</sub>: found (calc.): C, 55.30 (55.25); H, 5.24 (5.22); N, 2.67 (2.68)%.

## Acknowledgements

We are grateful for financial support from the National Science Foundation of China (20732007, 20728506 and 20672122), the Ministry of Science and Technology of China (2006CB806105, 2007CB808004, 2007CB936001, and 2009CB22008) and the Bureau for Basic Research of the Chinese Academy of Sciences.

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