Synthesis and Metal Ion Complexation Studies of [60]Fullerene Derivatives of Tetrathiafulvalene Crown Ethers

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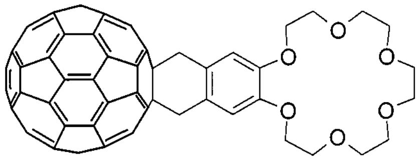
The synthesis of two novel [60]fullerene derivatives containing the electron donor tetrathiafulvalene and metal-complexing crown ethers is described, and their complexation ability with alkali metal cations is studied by solid-liquid extraction techniques, cyclic voltammetry and ^{1}H NMR spectroscopy.

Introduction

Crown ethers, tetrathiafulvalenes (TTFs) and C_{60} are three different classes of compounds each of which exhibits interesting and unique chemical properties.[1] We have recently prepared some new hybrids of fullerene- and TTF-derived crown ethers, and have measured their self-assembling properties as monolayers (SAMs) and their metal-ion sensing abilities.[2] As part of our interest in the preparation of fullerene derivatives with potentially interesting biological and materials properties, we now report the synthesis and properties of two new TTF crown ether derivatives of C_{60} obtained from a Diels–Alder reaction. The interest in compounds of this type arises from their metal-complexing abilities,[3,4] amphiphilic character,[3,5] potential to form new conducting solid-state phases after doping with electropositive metals or through the formation of charge transfer (CT) complexes or salts (CT complexes or salts derived from TTF donor derivatives are well-known organic conductors and superconductors[6]), and from their potential intramolecular energy and electron- or charge transfer.[7–9]

A benzo[18]crown-6 structure **1** and a TTF structure **2** (Chart) have recently been reported by Diederich,[3] Rovira[9a,9b] and Gorgues.[9c,9d] As our first strategy of this effort, we now report the synthesis of two novel C_{60} derivatives of crown ether annelated TTF **3b** and **3c**, in both of which a crown ether annelated TTF donor group is directly linked by two single bonds to C_{60} through a hexacyclic ring (Chart). We discuss their metal ion complexation abilities derived from solid-liquid extraction experiments, cyclic voltammetry (CV) and ^{1}H NMR spectroscopy.



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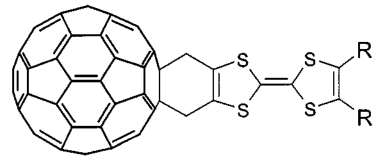
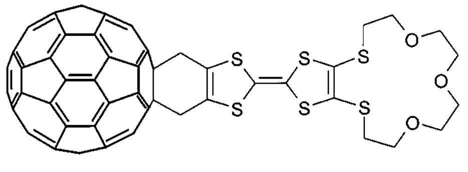
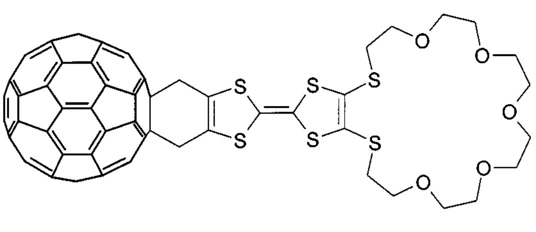


R = H, CH_3, SCH_3, or SCH_2CH_2S

2 (**3a**, R = SCH_2CH_2S)



3b



3c

Results and Discussion

Synthesis and Characterization

The TTF-C_{60} dyad **3a** was recently reported by Gorgues et al.[9d] and was synthesized here as a model compound only for comparison purposes. In general, the synthesis of compounds **3a–c** takes advantage of the well-established Diels–Alder reaction of C_{60} with a diene such as **4a**, **4b** or **4c**. The dienes are generated in situ by iodine-induced 1,4-elimination of Br_2 from the corresponding bis(bromomethyl)TTF derivatives **5a–c**, using either KI in the presence

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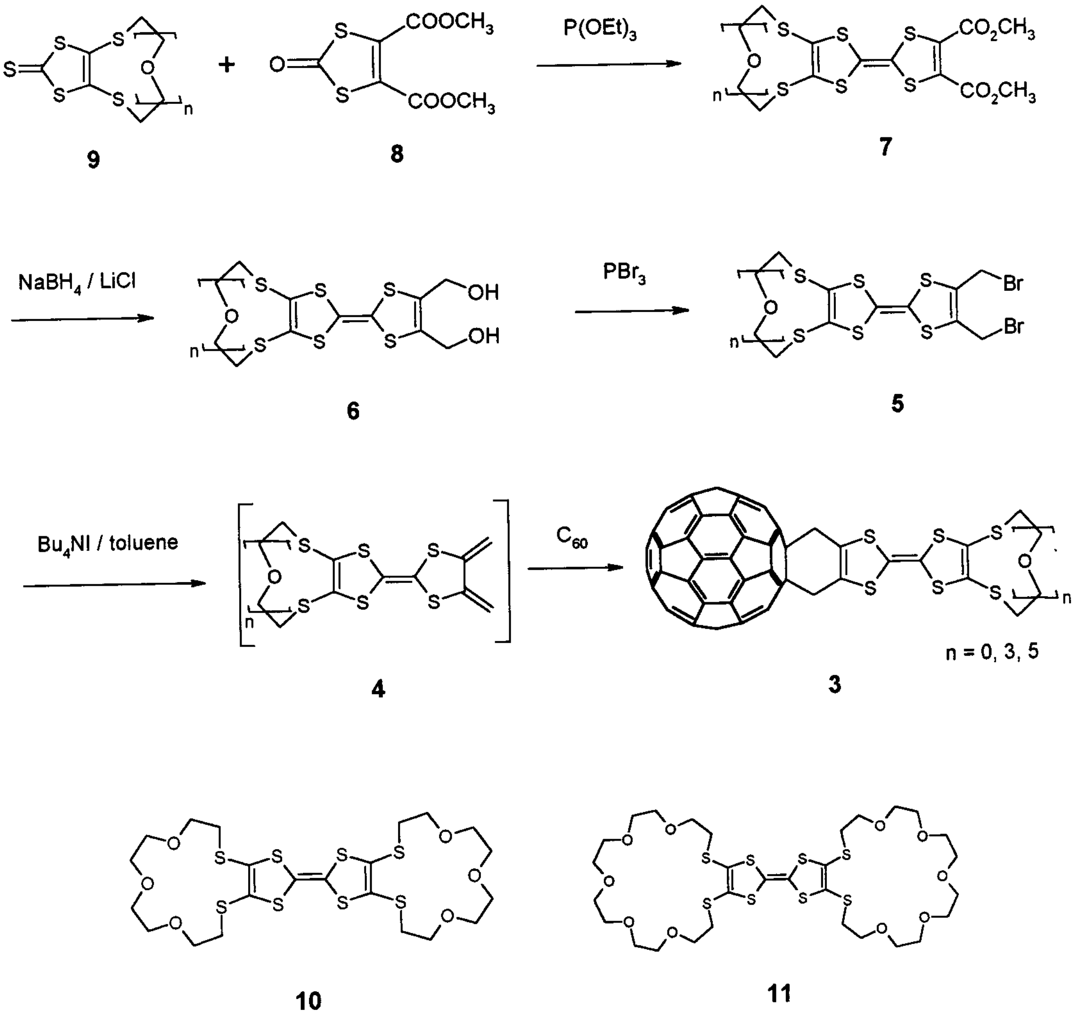

Scheme 1. Synthetic procedures for compounds **3a** (*n* = 0), **3b** (*n* = 3), and **3c** (*n* = 5)

of 18-crown-6 as the phase transfer reagent, developed by Müllen et al.,[10] or Bu$_4$NI as described by Diederich et al.[3] We compared these two different reagents for the synthesis of **3a**. The yields of the Diels–Alder products were comparable. However, the KI/18-crown-6 procedure is not suitable for the synthesis of **3b** and **3c**, especially for **3c**, due to the complexation of K$^+$ with the crown ether containing product. Thus, compounds **3b** and **3c** were prepared according to the procedures shown in the Scheme starting from 5,8,11-trioxa-2,14,16,18-tetrathiabicyclo[13.3.0]octadec-1(15)-ene-17-thione (**9b**) and 5,8,11,14,17-pentaoxa-2,20,22,24-tetrathiabicyclo[19.3.0]tetraicos-1(21)ene-23-thione (**9c**), both of which were synthesized according to the procedures reported by Becher et al.[4] with a slight modification, that is, bis(tetrabutylammonium) bis(1,3-dithiole-2-thione-4,5-dithiolate)zincate(II), the Zn salt, $(n\mathrm{Bu}_4\mathrm{N})_2\mathrm{Zn(dmit)}_2$, (rather than the dithiolate salt as used by Becher et al.[4]) was directly reacted with the corresponding dibromo glycols in acetone at reflux for about two days under nitrogen using high-dilution techniques. The yields for both **9b** and **9c** are high compared to those of Becher's.[4] Cross coupling between the 1,3-dithiole-2-thione **9b** or **9c** and the 1,3-dithiole-2-one **8** in neat triethyl phosphite at 110–130 °C afforded the unsymmetrically substituted crown ether TTF diester **7b** or **7c**, respectively, in reasonably high yields (40–60%). Theoretically speaking, two additional symmetric TTF derivatives **10** or **11** (Scheme) could be formed in addition to the unsymmetrical ones for such kinds of cross-coupling reactions. However, we did not observe the symmetric crown ether TTFs in either case, only the symmetric tetraester TTF which was eluted from the column as the first band. This must be due to the low reactivity of the 1,3-dithiole-2-thione **9b** and **9c** self-coupling. Reduction of the two ester groups of **7b** and **7c** with NaBH$_4$ and LiCl in a mixed solvent of THF and methanol (4:1 v/v)[11] gave the corresponding dialcohol TTF derivatives **6b** and **6c**. In general, the reduction products should be mixtures of mono- and di-alcohol TTFs and the separation could be difficult. However, in both cases, only trace amounts of the monoalcohol TTF was present in the reaction mixture and in the case of **6b**, due to the great differential solubility of the products in CH$_2$Cl$_2$, separation of **6b** from its monoalcohol product was accomplished by washing the crude product mixture with CH$_2$Cl$_2$. In the case of **6c**, due the great difference in polarity between its mono- and di-alcohol products, analytically pure **6c** can be readily obtained by flash column chromatography on silica gel (70–230 mesh) eluting with 5:2 (v/v) CH_2Cl_2/acetone. The crown ether TTF diols **6b** and **6c** were then carefully transformed with phosphorus tribromide in dry THF into the corresponding dibromo compounds **5b** and **5c**,[12] which are the key intermediates in the synthesis of **3b** and **3c**. Finally, synthesis of the target compounds incorporating the crown ether structures takes advantage of the well-known Diels–Alder reaction of C_{60} which reacts as a dienophile with the transient diene **4b** or **4c** to form the derivatives bridged across a 6,6-ring junction, as judged by UV/Vis spectroscopic analysis, see below. The conditions for the addition of C_{60} to the crown ether TTF dimethenes **4b** or **4c**, generated in situ by iodine-induced 1,4-elimination of Br_2 from the corresponding bis(bromomethyl)TTF derivatives **5b** or **5c**, were optimized for the model reaction leading to **3a**. The highest yields of **3a**, **3b** and **3c** were obtained by refluxing C_{60} and the bis(bromomethyl) derivatives **5a–c** with Bu_4NI in toluene which, for solubility reasons, is the solvent of choice (see Scheme 1).

Although the low solubility of **3b** and **3c** prevented us from recording their ^{13}C NMR spectra, the structure was well established using other techniques (see Experimental Section). [4+2] Diels–Alder cycloadditions to C_{60} are well-known to occur at the reactive 6,6-ring junction of the [C_{60}]fullerene,[9a] and the UV/Vis spectra of **3b** and **3c** confirm the 6,6-closed character of the cycloadducts. As shown in Figure 1 (a), the UV/Vis spectra of both **3b** and **3c** are virtually identical and quite similar to that of **3a**. In the UV region, the spectra (cyclohexane) of compounds **3b** and **3c** (as well as **3a**) are essentially dominated by the three characteristic absorptions of C_{60}. In the visible region, the spectra show a weak and sharp absorption band at 432 (**3b**) or 431 nm (**3c**) and a very weak but distinguishable absorption at 701 (**3b**) or 708 nm (**3c**) [not shown, but can be observed at higher concentration or magnification, see Figure 1 (b)]. These are characteristic of C_{60} derivatives and are typical of fullerene monoadducts bridged at a 6,6-junction with a closed transannular bond.[3,9a,9c] However, the three absorption bands of **3b** or **3c** in the UV region are broader than those of C_{60} and some fine structure is observable. This may be due to the presence of the TTF moiety in the compounds because TTFs have characteristic absorptions in the UV region as shown in the inset of Figure 1 (a). In addition, the spectra of **3b** and **3c** are generally less structured and the long-wavelength absorptions between 450 and 650 nm are hypsochromically shifted, Figure 1 (b). Other structural characterization data are presented in the Experimental Section.

Complexation Studies

The complexation properties of compounds **3b** and **3c** and some of their synthetic intermediates with alkali metal ions (Li^+, Na^+ and K^+) were investigated by solid-liquid extraction techniques, cyclic voltammetry and ^1H NMR spectroscopy. In preliminary studies, the receptor behavior of **3b** and **3c** was analyzed in extraction experiments which were monitored by UV/Vis spectroscopy. Thus, solid-liquid saturation extractions were performed with **3a** (for comparison purposes), **3b** and **3c** in pure methanol and in 0.1 M $NaPF_6$ methanol solution, as shown in Figure 2. On the whole, the solubility follows the trend **3c** > **3b** > **3a** in both pure methanol and in the salt solution. This correlates well with the flexibility and the number of atoms in the annelated ring, which is largest in **3c** and smallest for **3a**. Compound **3a** has a very low solubility in both pure methanol and in the salt solution (Figure 2). However, for both the crown ether containing compounds **3b** and **3c** the solubility in the salt solution is higher than in the pure solvent. The crown ether **3b** is about seven times more soluble in the $NaPF_6$ solution than in the pure solvent (comparison of the optical densities at 432 nm) and **3c** is about 21 times more soluble in the $NaPF_6$ solution than in the pure solvent. This solubility enhancement for both **3b** and **3c** must be the direct result of complexation with the Na^+ ions by the crown ether moiety. A nonspecific salt effect on the solubility of **3b** or **3c** can be excluded based on the control experiment with **3a**. In addition, as can be seen from Figure 2, the absence of complexation-induced shifts of the electronic absorption bands of **3b** or **3c** suggests that the Na^+ ion bound

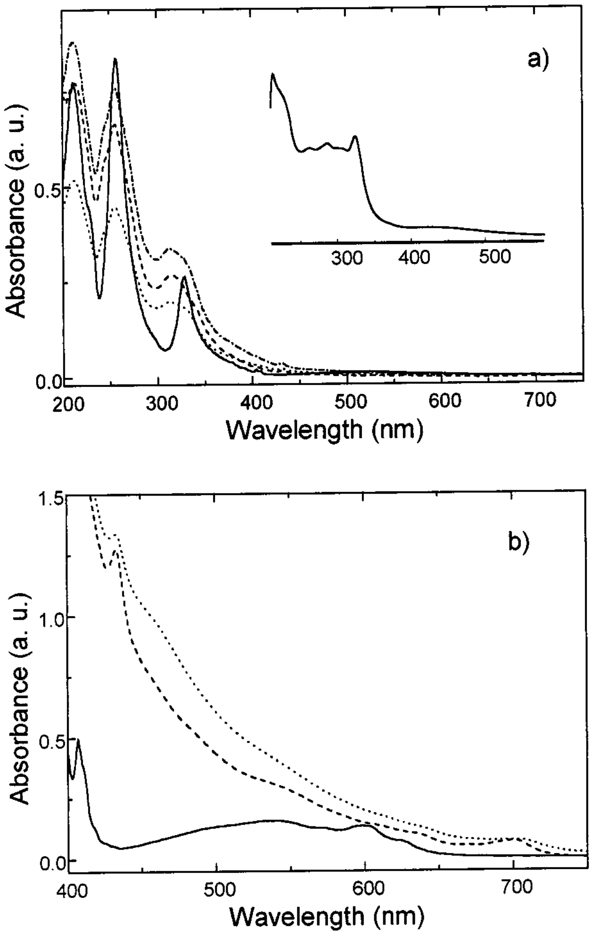

Figure 1. a) UV/Vis spectra of compounds **3a** (dashed), **3b** (dotted), **3c** (broken), and C_{60} (solid) in cyclohexane; [compound] ≈ 10^{-5} M; inset: UV/Vis spectrum of **7b** in THF; b) Visible spectra of compounds **3b** (dashed), **3c** (dotted), and C_{60} (solid) in ODCB; [compound] ≈ 5×10^{-4} M

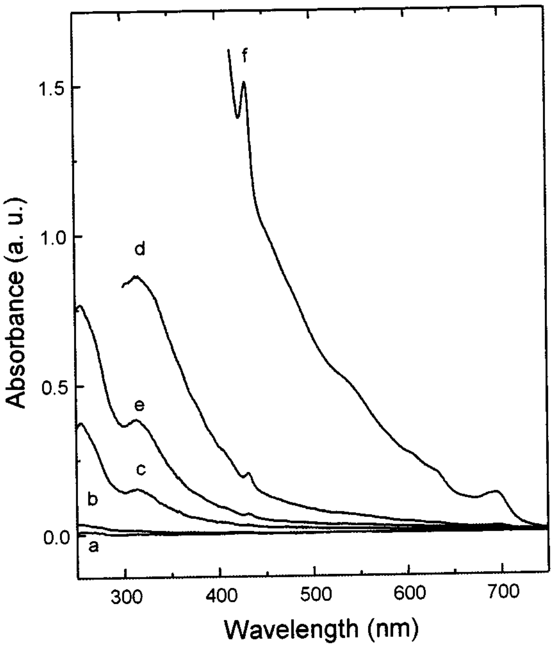

Figure 2. UV/Vis spectra of solutions prepared by solid-liquid extraction: a) **3a** extracted with pure methanol, b) **3a** extracted with 0.1 M $NaPF_6$ in methanol, c) **3b** extracted with pure methanol, d) **3b** extracted with 0.1 M $NaPF_6$ in methanol, e) **3c** extracted with pure methanol, f) **3c** extracted with 0.1 M $NaPF_6$ in methanol; $T \approx 295$ K, $d = 1$ cm

in the crown moiety does not interact with the fullerene chromophore, an expected result.

Cyclic voltammetry was employed to study both the solution electrochemistry and the complexation properties of compounds **3b**, **3c**, **3a** and C_{60} and of some related TTFs for comparison. The results are reported in Figure 3 and the electrochemical potential data are collected in Table 1.

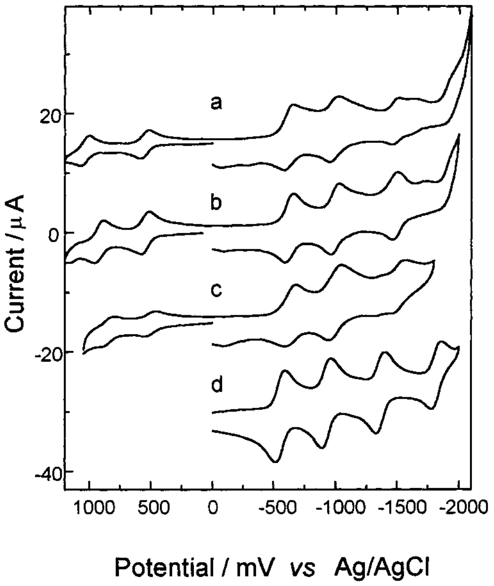

Figure 3. CVs (sweep rate 0.1 V s^{-1}) of **3a** (a), **3b** (b), **3c** (c) and C_{60} (d) on a GC electrode in ODCB solution; $T \approx 295$ K

Table 1. $E_{1/2} = (E^{red} + E^{ox})/2$, E^{red} or E^{ox}: peak potentials (mV *vs* Ag/AgCl) of the redox couples of C_{60} and compounds **3a–c** detected by CV (sweep rate 0.1 Vs^{-1}) in *o*-dichlorobenzene solution at room temperature; errors for $E_{1/2}$ values are estimated at ±5 mV

	$E^{ox}{}_{1/2}{}^1$	$E^{ox}{}_{1/2}{}^1$	$E^{red}{}_{1/2}{}^1$	$E^{red}{}_{1/2}{}^2$	$E^{red}{}_{1/2}{}^3$
TTF	488	824			
7a	742	1146			
7b	741	1107			
7c	719	1033			
3a	549	1034	–623	–993	–1493
3b	547	928	–628	–999	–1495
3c	503	845	–631	–997	–1523

All the C_{60} derivatives show three reversible reduction peaks with $\Delta E_p < 85$ mV in the cathodic direction and two reversible oxidation peaks ($\Delta E_p < 80$ mV) in the anodic scan. This clearly confirms the presence of both C_{60} and TTF moieties in the compounds. All the C_{60} derivatives retain the basic electronic properties of C_{60} while the observed reduction potentials (Table 1) are shifted to more negative values than those of unsubstituted C_{60}. This is the same behavior observed for most C_{60} derivatives and can be explained as a consequence of a partial loss of "conjugation".[1c] In addition, for compounds **3a–c** the C_{60}-based reduction potentials are almost identical, which indicates that there are no substantial intramolecular interactions between the TTF groups and C_{60}, in agreement with the UV/Vis spectroscopic analysis. However, the TTF-based oxidation potentials, especially for the second oxidation, follow the trend **3a** > **3b** > **3c**. This is in agreement with the trend for the oxidations of **7a**, **7b** and **7c** and must reflect the electron donating ability of the crown ether group.

Complexation was also studied by cyclic voltammetry. As discussed above, **3b** and **3c** exhibit two one-electron reversible oxidation waves in the anodic direction centered on the TTF moiety, and three reversible reductions in the cathodic direction originating from the C_{60} moiety. The CVs were then recorded after saturating the *o*-dichlorobenzene (ODCB)/Bu_4NPF_6 solutions with $LiPF_6$, $NaPF_6$ or KPF_6. The results are shown in Figure 4 and the shifts with different metal ions are summarized in Table 2. As can be seen from Figure 4 and Table 2, it can be concluded that: *i*) the salts have no effect on the C_{60} moiety of either **3a**, **3b** or **3c**, in agreement with the UV/Vis spectroscopic analysis of the solid-liquid extraction experiments; *ii*) the shifts observed were always for the TTF-centered oxidations, and these, as expected, were always anodic (more positive); *iii*) the shifts, if any, of the first oxidation peak were always larger than those for the second one; *iv*) all the compounds tested did not show any effect when Li^+ was added; *v*) the shifts for compounds **3c** or **7c** are larger than those for compounds **3b** or **7b**; and *vi*) the largest shifts observed for compound **3c** were found when sodium ions were used, with a general order: $Na^+ > K^+ > Li^+$.

That the shifts we have observed are really due to complexation is confirmed not only by the fact that **3a** and **7a**, neither of which contain a crown ether, did not show any changes in oxidation potentials after adding any metal ions

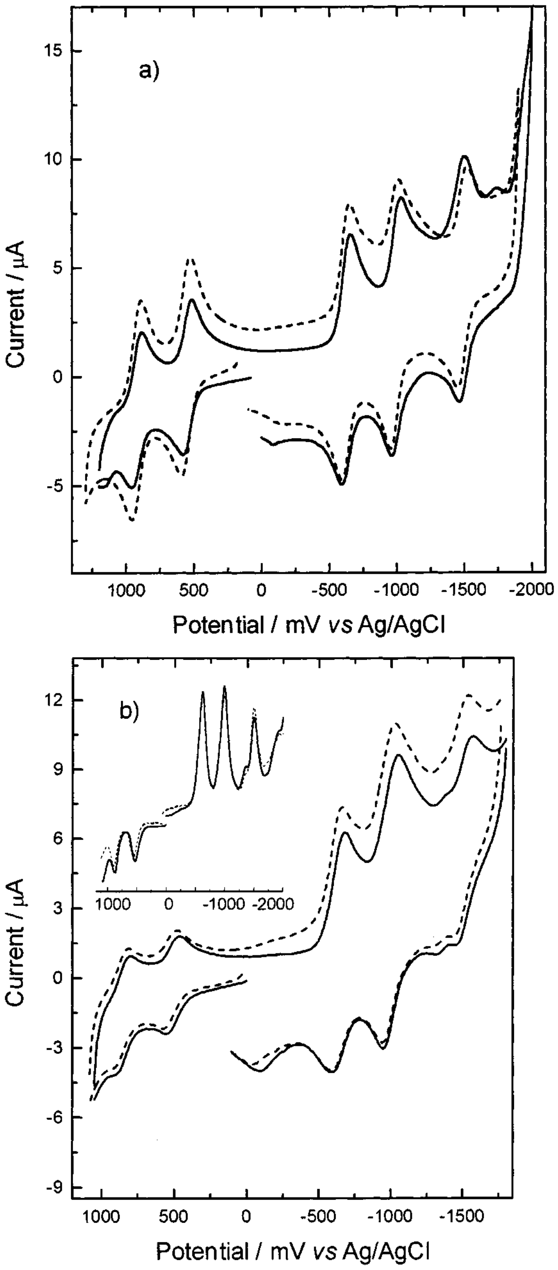

Figure 4. a) CVs (sweep rate 0.1 V s^{-1}) of compound **3b** in the absence (solid) and presence (dashed) of $NaPF_6$ (saturated) on a GC electrode in ODCB solution; **b)** CVs (sweep rate 0.1 V s^{-1}) of compound **3c** in the absence (solid) and presence (dashed) of $NaPF_6$ (saturated) on GC electrode in ODCB solution; inset: Osteryoung square wave voltammograms of **3c** in the absence (solid) and presence – of $NaPF_6$ (saturated) on platinum electrode in ODCB; $T \approx 295$ K

Table 2. Shifts (mV) of peak potentials on addition of alkali metal ions

	Li^+ E^1_{ox}	E^2_{ox}	Na^+ E^1_{ox}	E^2_{ox}	K^+ E^1_{ox}	E^2_{ox}
3a	0	0	0	0	0	0
3b	0	0	+10	0	0	0
3c	0	0	+25	+15	+15	+10
7a	0	0	0	0	0	0
7b	0	0	+10	0	0	0
7c	0	0	+25	+18	+15	+10
10[a]	0	0	+10	0	0	0
11	0	0	+15[a]	0	+60[a]	0

[a] $E_{1/2}$ values from ref.[4]

under almost identical experimental conditions, but also by the fact that **7b** and **7c**, both of which contain a crown ether moiety, showed almost the same behavior and close to the same potential shifts (Table 2).

When comparing the shifts observed for **3b**, **7b** or **3c**, **7c** to those obtained by Becher et al.[4] for the symmetric crown ether TTFs **10** and **11** (Table 2), two things are evident: *i*) for **3b** and **7b**, the shifts are identical to those observed for **10**; *ii*) for **3c** and **7c**, two things are different from **11**: firstly, both E^1_{ox} and E^2_{ox} changed for **3c** or **7c** after adding metal ions, however, for **11**, only the first oxidation potentials were positively shifted; secondly, as mentioned above, the ion effect for **3c** or **7c** follows the order $Na^+ > K^+ > Li^+$, but for **11**, the order is $K^+ > Na^+ > Li^+$. On the whole the shifts are small, especially for **3b**, but the data seem to be in good agreement with the ^{1}H-NMR analysis discussed below.

Additional qualitative evidence for the complexation was also obtained by ^{1}H NMR spectroscopic analysis in $CDCl_3$. Following solid/liquid extraction of $NaPF_6$ with a solution of **3b**, the NMR line shape changed and a small complexation-induced downfield-shift (0.05 ppm) was observed for the -SCH_2CH_2O- protons. As expected, no NMR spectral changes were observed for **7a** but an identical complexation-induced shift and shape change were observed under similar conditions for the corresponding protons of **7b**, indicating that the observed changes in **3b** are due to complex formation.[4]

In conclusion, we have synthesized the first two examples in which the three systems (C_{60}, TTF and crown ether) are covalently linked and the compounds do indeed show the expected binding properties with alkali metal ions as indicated by UV/Vis, CV and proton NMR analysis. Other experiments, such as doping with alkali metals and amphiphilicity, are currently underway.

Experimental Section

General Instrumentation and Descriptions: All chemicals were of reagent grade. All solvents were dried over molecular sieves (4 Å) and purified according to standard procedures prior to use. All temperatures quoted were uncorrected. [60]Fullerene was purchased from SES Research, Inc. and used as received without further purification. Column chromatography was performed on silica gel (230–400 or 70–230 mesh) purchased from E. Merck. UV/Vis spectra were recorded on a Shimadzu UV-2101PC spectrometer with a 1-cm quartz cell. IR spectra were recorded on a Perkin–Elmer 2000 FT-IR spectrometer in the region of 4000–400 cm^{-1} as KBr pellets. NMR spectra were recorded on a Bruker Avance-300 spectrometer. Mass spectra were recorded on a VG MASSLAB TRIO-2 spectrometer in the positive FAB mode with *N*-bromoacetamide (NBA) as the matrix. High resolution FAB-MS were recorded on a micromass Quattro I spectrometer in the positive FAB mode with a resolution of 10 K. Cyclic voltammetry and Osteryoung square wave voltammetry (OSWV) were performed on a BAS

100 W electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN) at room temperature with a three-electrode configuration in an *o*-dichlorobenzene solution containing the substrate (0.1–0.5 mM) and a supporting electrolyte (nBu_4NPF_6, 0.05 M). A glassy carbon (GC, ø 3 mm) or platinum disc (ø 1 mm) was used as a working electrode, the counter electrode was a platinum wire (ø 1 mm). A Ag/AgCl electrode was used as the reference electrode. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. The scan rate was generally 100 mV/s unless stated otherwise. OSWV experiments were performed with parameters of step potential: 4 mV, S. W. amplitude: 25 mV, frequency: 15 Hz, and quiet time: 2 seconds.

Synthesis of 7b and 7c: To a 50 mL round-bottom flask was added **9b** or **9c** (4 mmol), **8** (4 mmol) and 10 mL of freshly distilled triethyl phosphite. The mixture was stirred and heated to 110–130 °C (oil temperature) under Ar for about 50 min. After evaporating the excess triethyl phosphite under high vacuum, the residue was then subjected to column chromatography on silica gel (70–230 mesh) eluting with 2:1 (v/v) CH_2Cl_2/hexane. After the first fraction was eluted, the eluent was changed to CH_2Cl_2 (for **7b**) or 20:1 (v/v) CH_2Cl_2/acetone (for **7c**). The last fraction was collected as the target compound with yields of 60.4% (**7b**) or 40.1% (**7c**).

7b: FAB-MS; *m/z*: 542 (M^+, 100%). – HR-MS; *m/z*: found (calcd.) 541.9692 (541.9690). – ^1H NMR ($CDCl_3$): $\delta = 2.99$ (t, $J = 6.4$ Hz, 4 H), 3.65–3.70 (m, 8 H), 3.74 (t, $J = 6.8$ Hz, 4 H), 3.86 (s, 6 H). – FT-IR (KBr): $\nu = 2978$ (m), 2953 (m), 2919 (m), 2887 (m), 1719 (vs, C=O), 1576 (m-s), 1433 (m-s), 1250 (s), 1020 (s), 965 (m-s), 764 (m) cm^{-1}.

7c: FAB-MS; *m/z*: 630 (M^+, 100%). – HR-MS: *m/z*: found (calcd.) 630.0212 (630.0217). – ^1H NMR ($CDCl_3$): $\delta = 3.92$ (s, 6 H), 3.67–3.76 (m, br, 20 H), 3.04 (t, $J = 6.0$ Hz, 4 H). – FT-IR (KBr): $\nu = 2918$ (m), 2871 (m), 1734 (s, C=O), 1576 (m), 1433 (s), 1265 (s), 1109 (s), 1019 (s), 967 (m), 761 (m), 571 (m) cm^{-1}.

Synthesis of 6b and 6c: To a 100 mL three-necked round-bottom flask was added **7b** or **7c** (1 mmol), 20 mL dry THF and 5 mL methanol. The mixture was stirred and cooled to 0 °C. Then, $NaBH_4$ (8 mmol) and LiCl (8 mmol) were added under nitrogen. After stirring at 0 °C for about 4 h, the cooling bath was removed and stirring was continued for an additional 1 h at room temperature. Then the reaction mixture was cooled down again and 20 mL saturated NH_4Cl aqueous solution was added dropwise at 0 °C. After the addition, the mixture was extracted with AcOEt three times and the combined organic layers were washed with brine (2 × 40 mL), separated, and dried (Na_2SO_4). After removal of the solvent, the dialcohol TTF **6b** or **6c** was purified by either washing the mixture with CH_2Cl_2 (**6b**, 78%) or by flash column chromatography eluting with 5:2 (v/v) CH_2Cl_2/acetone (**6c**, 82.4%).

6b: FAB-MS; *m/z*: 486 (M^+, 100%). – HR-MS; *m/z*: found (calcd.) 485.9791 (485.9791). – ^1H NMR ([D_6]DMSO): $\delta = 5.46$ (t, $J = 6.0$ Hz, 2 H), 4.18 (d, $J = 5.7$ Hz, 4 H), 3.48–3.58 (m, 12 H), 2.92 (t, $J = 6.0$ Hz, 4 H). – FT-IR (KBr): $\nu = 3344$ (br, s), 2909 (m-s), 2871 (m-s), 1453 (m), 1347 (m), 1097 (s), 1023 (m) cm^{-1}.

6c: FAB-MS; *m/z*: 574 (M^+, 100%). – HR-MS; *m/z*: found (calcd.) 574.0318 (574.0316). – ^1H NMR ($CDCl_3$): $\delta = 4.33$ (br. s, 2 H), 3.71–3.74 (br. m, 4 H), 3.66–3.69 (m, 20 H), 3.03 (t, $J = 6.0$ Hz, 4 H). – FT-IR (KBr): $\nu = 3342$ (br, s), 2900 (m-s), 2870 (m-s), 1452 (m), 1353 (m), 1096 (s), 1023 (m), 938 (w), 771 (w) cm^{-1}.

Synthesis of 5b and 5c: To a solution of **6b** or **6c** (0.5 mmol) dissolved in dry THF (15 mL) was added dry CCl_4 (15 mL) under nitrogen. The mixture was stirred and cooled to 0 °C. Then phosphorus tribromide (1 mmol) was slowly added dropwise from a syringe. After the addition was complete, stirring was continued for 2 h at 0 °C and then the temperature was allowed to increase to room temperature and the mixture stirred for an additional 2–3 h. The clear red solution was poured into 80 mL EtOAc followed by 40 mL water. The organic layer was separated and washed with brine (2×50 mL), dried ($MgSO_4$) and the solvent was evaporated. The residue was filtered off on a silica gel with hexane/EtOAc (2:1) as the eluent affording purple solids in yields of 55% (**5b**) or 44% (**5c**).

5b: FAB-MS; *m/z*: 611 (M^+, 6%). – ^1H NMR ($CDCl_3$): $\delta = 4.21$ (s, 4 H), 3.67–3.75 (m, 12 H), 2.99 (s, br, 4 H). – FT-IR (KBr): $\nu = 2918$ (m-s), 2857 (m-s), 1653 (m), 1116 (s) cm^{-1}.

5c: FAB-MS; *m/z*: 701 (M^+, 50%). – ^1H NMR ($CDCl_3$): $\delta = 4.22$ (s, 4 H), 3.66–3.70 (m, 20 H), 3.04 (t, $J = 6.0$ Hz, 4 H).

Synthesis of 3b and 3c: A mixture of C_{60} (0.1 mmol) and Bu_4NI (0.4 mmol) was allowed to react with **5b** or **5c** (0.1 mmol) in 40 mL of dry toluene at reflux under nitrogen for 6 h in the dark. After cooling to room temperature, the mixture was washed with water, separated and dried ($MgSO_4$). The solvent was then evaporated and the residue submitted to flash column chromatography eluting with toluene to remove unchanged C_{60}, then with toluene/AcOEt (1:1) to collect the second band as the monoadduct **3b** (42%) or **3c** (23%). The bis-adducts were separated and characterized by FAB-MS, but the isomers were not separated.

3b: FAB-MS; *m/z*: 1172 (M^+, 100%). – HR-MS; *m/z*: found (calcd.) 1171.9736 (1171.9736). – ^1H NMR (1:1 $CS_2/CDCl_3$): $\delta = 4.34$–4.61 (m, 4 H), 3.72–3.82 (m, 12 H), 3.06 (s, br, 4 H). – FT-IR (KBr): $\nu = 2910$ (m), 2842 (m), 1428 (m), 1114 (m), 761 (m), 571 (m), 527 (vs) cm^{-1}.

3c: FAB-MS; *m/z*: 1262 (M^+, 100%). – HR-MS; *m/z*: found (calcd.) 1260.0261 (1260.0261). – ^1H NMR ($CDCl_3$): $\delta = 3.05$ (t, $J = 6.0$ Hz, 4 H), 3.56–3.87 (m, 24 H). – FT-IR (KBr): $\nu = 2910$ (w), 2890 (w), 1429 (m), 1214 (m), 1183 (s), 1152 (m), 576 (s), 526 (vs) cm^{-1}.

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