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Crown-annelated 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives: a new efficient transducer in the electrochemical and spectroscopic monitoring of metal complexation

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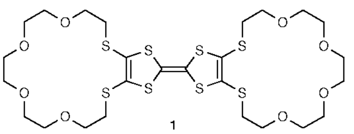
S_2O_4-Crown annelated derivatives of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene function as efficient ligands in the voltammetric and spectroscopic recognition of Na^+ and Ag^+.

Redox-active ligand systems are important in the field of electrochemically-controlled uptake and release of guest metal cations.[1] For large shifts of the redox potential to be observed upon metal binding the antennae [*e.g.* crown ether unit(s)] should be situated close to the redox-responsive centre (*i.e.* the transducer), thereby enhancing the intramolecular electrostatic (through-space) effect which modulates the redox signal. Typical molecular[2] redox species for this purpose are ferrocene,[3] metal coordinated dithiolate[4] and diimine,[5] and tetrathiafulvalene (TTF) derivatives,[6] *e.g.* **1**[6a,b] and **2**.[6d] For these systems cation binding induces a positive shift of the one-electron oxidation potential E_1^{ox}.



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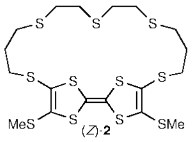
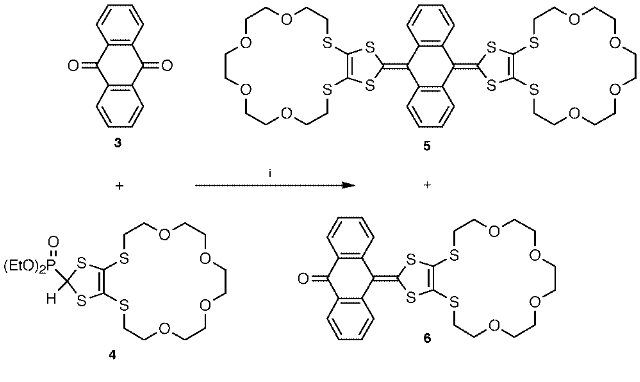


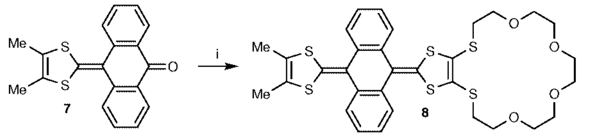
(*Z*)-2

Derivatives of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene are versatile building blocks in supramolecular and materials chemistry.[7] The special feature of this system is a *two-electron* oxidation wave [neutral → dication, E_1^{ox} *ca.* +0.35 V‡ (in MeCN, *vs.* Ag/AgCl) which is electrochemically quasi-reversible and chemically reversible].[8] Herein we report the first crown-annelated derivatives **5** and **8**.

Reaction of anthraquinone **3** with the new reagent **4**[9] under standard conditions[8,10] gave a mixture of the bis- and mono-crown annelated derivatives **5** and **6**, respectively (Scheme 1).§



Scheme 1 i, **4**, LDA, THF, −78 °C, 3 h, then addition of **3**, then −78 to 20 °C.



Scheme 2 i, **4**, LDA, THF, −78 °C, 3 h, then addition of **7**, then −78 to 20 °C.

The latter was characterised by X-ray diffraction.¶ Reaction of **4** with **7**[8a] gave the bis(1,3-dithiole) system **8** (Scheme 2).

An X-ray crystallographic study¶ of **8**·CH_2Cl_2 showed a motif of saddle-shaped molecules (Fig. 1) engulfing each other's dimethyldithiole ends. The anthracenediylidene moiety is folded along the C(9)···C(10) vector, the two benzene rings forming a dihedral angle of 39° (*cf.* 21° in **6**). The dithiole rings are folded along the S(1)···S(2) and S(3)···S(4) vectors by 15.5 and 8.7°, and the S(1)C(16)C(17)S(2) and S(3)C(19)C(20)S(4) planes form an acute dihedral angle of 81°.

The cation binding properties of **5** were assessed by ^1H NMR titration studies in $CDCl_3$ at 50 °C (at 20 °C a precipitate formed on addition of metal salts). In the presence of Na^+ and Ag^+ the resonances due to the $–SCH_2CH_2O–$ protons of the crown [(SCH_2) δ 3.05; (OCH_2) δ 3.66] shifted downfield by *ca.* 0.07 ppm in the presence of 10 equiv. of Na^+ and Ag^+, while the anthracenediylidene resonances were unaffected, confirming that cation binding occurs at the crown site. Li^+ and K^+ cations had essentially no effect on the ^1H NMR spectrum. UV–VIS absorption spectra for **5** in MeCN in the presence of both Na^+ and Ag^+ (as the perchlorate salts) resulted in a specific change in the spectra. No isosbestic points were observed, indicating that, most probably, both 1:1 and 1:2 complexes [*i.e.* **5**M^+ and **5**$(M^+)_2$] form simultaneously, and the absorption spectra of these species are different. Such behaviour is known for other bis(crown) chromoionophores.[11] Fig. 2 shows the changes in the spectrun of **5** upon complexation with Ag^+. The stability constants for the formation of **5**M^+ and **5**$(M^+)_2$ were estimated to be $\log K_1$ *ca.* 3.4 and $\log K_2$ *ca.* 5.5, respectively.

Cyclic voltammetry (CV) and square wave voltammetry (SQV) showed that **5** and **8** display a two-electron oxidation

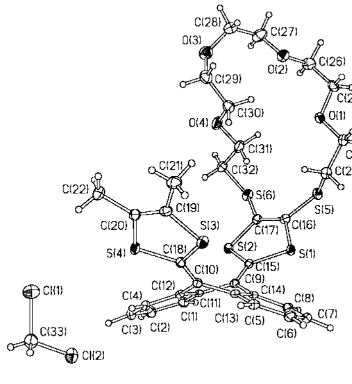


Fig. 1 Molecular structure of **8**·CH_2Cl_2 (50% displacement ellipsoids).

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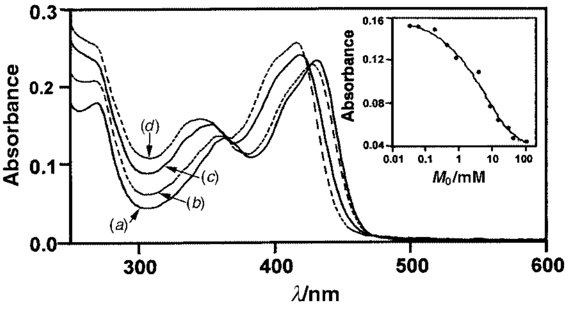

Fig. 2 Absorption spectra of **5** (2×10^{-5} M) in MeCN (1 cm cell) containing $AgClO_4$ at concentrations of (*a*) 0, (*b*) 0.5, (*c*) 8.0 and (*d*) 30 mM. Inset: absorption at 445 nm as a function of Ag salt concentration fitted with eqn. (1), where A_0, A_1 and A are the absorbances of the free ligand L and

$$A = A_0 + \frac{K_1 M_0 (A_1 - A_0)}{1 + K_1 M_0 + K_2 M_0^2} + \frac{K_2 M_0^2 (A_\infty - A_0)}{1 + K_1 M_0 + K_2 M_0^2} \quad (1)$$

complexes LM^+ and $L(M^+)_2$, respectively; K_1 and K_2 are equilibrium constants for complex formation.

wave: E_1^{ox} +0.405 V (**5**) and E_1^{ox} +0.345 V (**8**). A second reversible one-electron wave, ascribed to oxidation of the anthracene system[8b,c] (*i.e.* radical trication formation) was seen at E_2^{ox} 1.62 V for both compounds [CV data were recorded *vs.* Ag/AgCl, $Bu_4N^+ClO_4^-$ (0.1 M), MeCN, 20 °C, 100 mV s^{-1}]. The progressive addition of aliquots of metal triflate salts resulted in a positive shift of E_1^{ox} (and a similar positive shift of the coupled reductive peak on the cathodic scan), while E_2^{ox} remained unchanged, thereby acting as an internal reference. This is consistent with expulsion of the metal cation from the ionophore prior to the second oxidation wave. The maximum positive shifts (ΔE_1^{ox}) are as follows: Li^+ (15–20 mV), Na^+ (100 mV), K^+ (15–20 mV) and Ag^+ (115 mV). The values of ΔE_1^{ox} are essentially the same for the mono- and bis-crown systems **8** and **5**, respectively, whereas in the TTF series, *e.g.* **1**, a larger shift is observed for bis-crowns. This is likely to be a consequence of intramolecular steric interactions between the crown rings of **5**, and/or sandwich complexation between two crowns, favoured by the rigid saddle conformation. A comparison with related S_2O_4-crowned TTF systems[6] shows two important advantages of systems **5** and **8**: (i) the positive shifts for Na^+ and Ag^+ are significantly larger, and (ii) the system is significantly more sensitive, with saturation being achieved with < 10 equiv. of cation (Fig. 3) (*cf.* 200 equiv. for **1**[6a]).

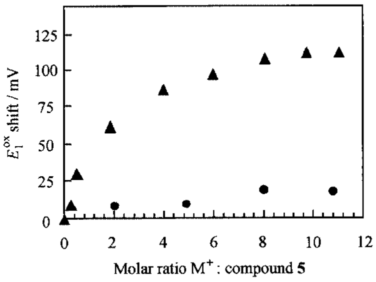

Fig. 3 Shift of E_1^{ox} in the CV of **5** with added equivalents of AgOTf (▲) and KOTf (●). Data were obtained in 0.2 M Bu_4NBF_4, MeCN, Pt disk electrode, 50 mV s^{-1}, Ag/AgCl reference electrode, referenced *vs.* decamethylferrocene.

We suggest that these results are a consequence of the unique combination of structural and redox properties of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene transducer unit: (i) the saddle-shape folding of the anthracenediylidene system places the crown ring(s) of **5** and **8** in close proximity to the redox-responsive moiety, and there is a marked conformational change upon oxidation,[7a] and (ii) the E_1^{ox} redox process which is monitored is a *two-electron* oxidation (*cf.* the one-electron wave of TTF, ferrocene *etc.*) thereby enhancing the electrostatic repulsion with the bound metal cation(s) leading to an increase in ΔE_1^{ox}.

In summary, using ligands **5** and **8** we have exploited for the first time the chromophoric and redox properties of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system to provide efficient and controllable cation recognition within appended crown ether units. To enhance further these effects we suggest that redox species which undergo a *multi-electron* wave (*e.g.* certain dendrimers)[12] should be targets for future transducers in redox-controlled molecular recognition.

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Notes and references

‡ E_1^{ox} = anodic peak potential on the first wave of the oxidative scan.

§ Compounds **4**, **5**, **6** and **8** gave spectroscopic and analytical data consistent with their structures. *Selected data* for **5**: orange crystals, 67% yield, mp 216–218 °C (from CH_2Cl_2–cyclohexane); $\delta_H(CDCl_3)$ 3.05 (8H, m), 3.66 (32H, m), 7.33 (4H, m) and 7.56 (4H, m). For **8**: orange crystals, 53% yield; mp 223–225 °C (from CH_2Cl_2); $\delta_H(CDCl_3)$ 1.94 (6H, s), 3.00 (4H, m), 3.58 (16H, m), 7.29 (4H, m), 7.52 (2H, m) and 7.68 (12H, m).

¶ Diffraction data were measured on a SMART 1K CCD area detector (graphite-monochromated Mo-Kα radiation, λ = 0.71073 Å). Structures were solved by direct methods and refined against F^2 of all data, using SHELXL97 (G. M. Sheldrick, University of Göttingen, 1997). *Crystal data* for **6**: $C_{27}H_{28}O_5S_4$, M = 560.7, T = 150 K, orthorhombic, $P2_12_12_1$ (No. 19), a = 7.600(1), b = 18.395(1), c = 18.566(4) Å, U = 2596(1) Å^3, Z = 4, D_c = 1.435 g cm^{-3}, μ = 0.40 mm^{-1}, 10781 reflections (4219 unique, R_{int} = 0.037) with 2θ = 52.7°, 418 variables, R = 0.038 [3920 data, $I > 2\sigma(I)$], $wR(F^2)$ = 0.083, $\Delta\rho$ max./min. = 0.28, −0.21 e Å^{-3}. The absolute structure was determined from anomalous X-ray scattering: Flack parameter 0.07(8). For **8**: $C_{32}H_{34}O_4S_6 \cdot CH_2Cl_2$, M = 759.9, T = 120 K, triclinic, $P\bar{1}$ (No. 2), a = 11.891(2), b = 12.546(1), c = 12.691(2) Å, α = 104.93(1), β = 97.02(1), γ = 106.60(1)°, U = 1713(1) Å^3, Z = 2, D_c = 1.473 g cm^{-3}, 9437 reflections (7080 unique, R_{int} = 0.025) with 2θ = 55°, 551 variables, R = 0.037 [6205 data, $I > 2\sigma(I)$], $wR(F^2)$ = 0.089, $\Delta\rho$ max./min. = 0.43, −0.29 e Å^{-3}. CCDC 182/1511. See http://www.rsc.org/suppdata/cc/a9/a908716h/ for crystallographic data in .cif format.

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