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# NOVEL 9,10-BIS(1,3-DITHIOL-2-YLIDENE)-9,10-DIHYDROANTHRACENE DERIVATIVES BRIDGED BY A CROWN ETHER UNIT AT THE 1,8-POSITIONS: A NEW TYPE OF REDOX-SWITCHABLE HOSTS UNDERGOING REVERSIBLE STRUCTURAL CHANGES[†]

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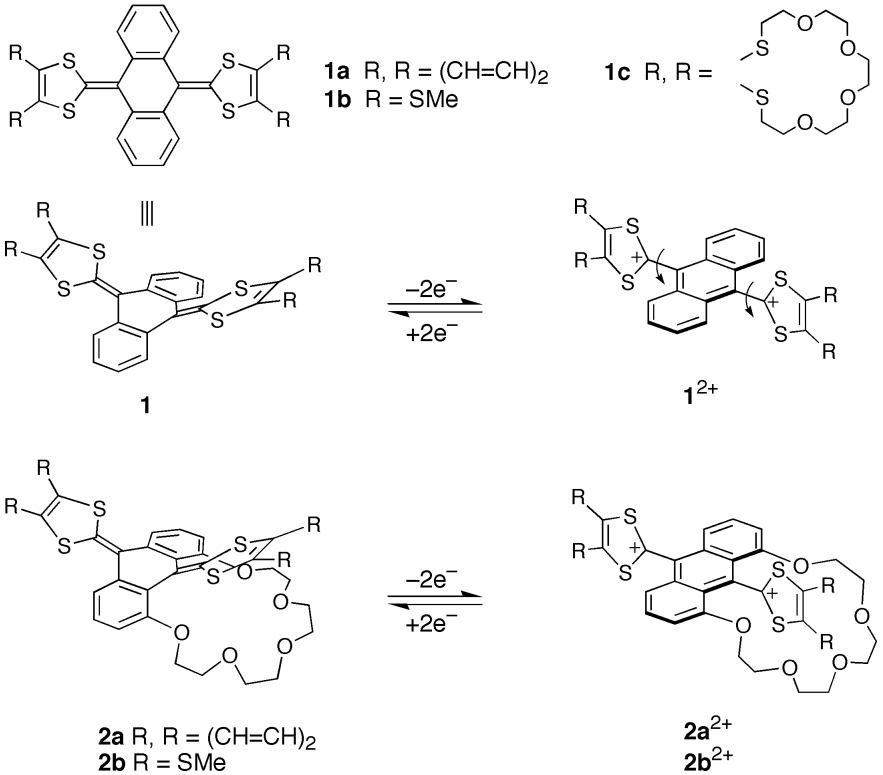
**Abstract** – Novel redox-switchable host molecules (**2**) composed of a 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene unit and a crown ether moiety bridging the 1,8-positions have been synthesized. Cyclic voltammetry and X-Ray analyses revealed that the molecules undergo a significant structural change upon oxidation. $^1$H-NMR titration experiments on the neutral and dication states show that the binding abilities of the dication states for alkali metal cations ($Li^+$, $Na^+$, $K^+$) are considerably lower than those of the neutral molecules. The binding properties of **2** were also investigated by cyclic voltammetry.

## INTRODUCTION

Recently, redox-switchable host molecules whose binding abilities can be controlled electrochemically have attracted much attention for applications, such as redox-controlled binding and releasing of guest molecules and electrochemical sensors.[1] Most of these systems contain a redox-active unit which shows no significant structural change upon electron transfer, and the binding abilities are regulated mainly by a change in the charge of this unit which affects the electrostatic interaction between the host and guest. On the other hand, there have been only a few examples of redox-switchable hosts in which both the structures and charges of the redox-active units are changed upon electron transfer.[2] For such

[†] Dedicate to Professor Barry M. Trost on the occasion of his 65th birthday.

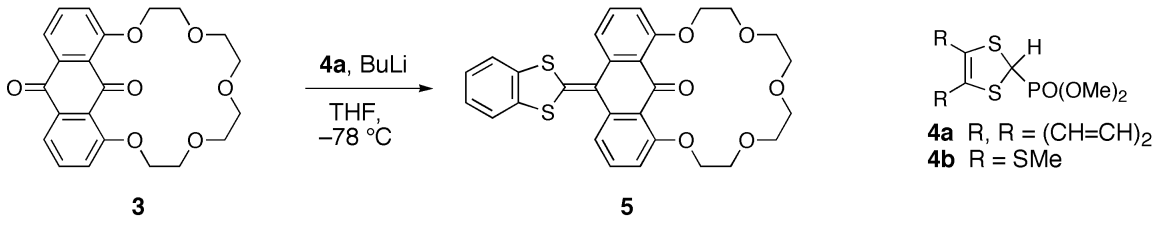
molecules it is expected that their binding abilities can be controlled effectively by structural changes in the binding site as well as by electrostatic effects. From this point of view, 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives (**1**)[3] are particularly attractive as a redox-active unit because of their drastic and reversible conformational changes upon two-electron oxidation as shown in Scheme 1. Neutral molecules (**1**) are butterfly shaped due to the steric repulsions between the sulfur and peri hydrogen atoms, while the corresponding dications ($\mathbf{1}^{2+}$) adopt a twisted conformation in which the two 1,3-dithiolium rings are orthogonal to the planar anthracene unit.[3b] Recently, Bryce *et al*. pointed out the usefulness of this system for construction of supramolecular systems and reported interesting crown-annelated molecules (**1c**).[3d–i] We have now introduced a crown ether bridge into the 1,8-positions of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene skeleton to give **2**. The affinity of the corresponding dications ($\mathbf{2}^{2+}$) for metal cations should be lower than that of the neutral molecules (**2**) owing to both the steric hindrance of the twisted dithiolium group and electrostatic repulsion by positive charges.




**Scheme 1**

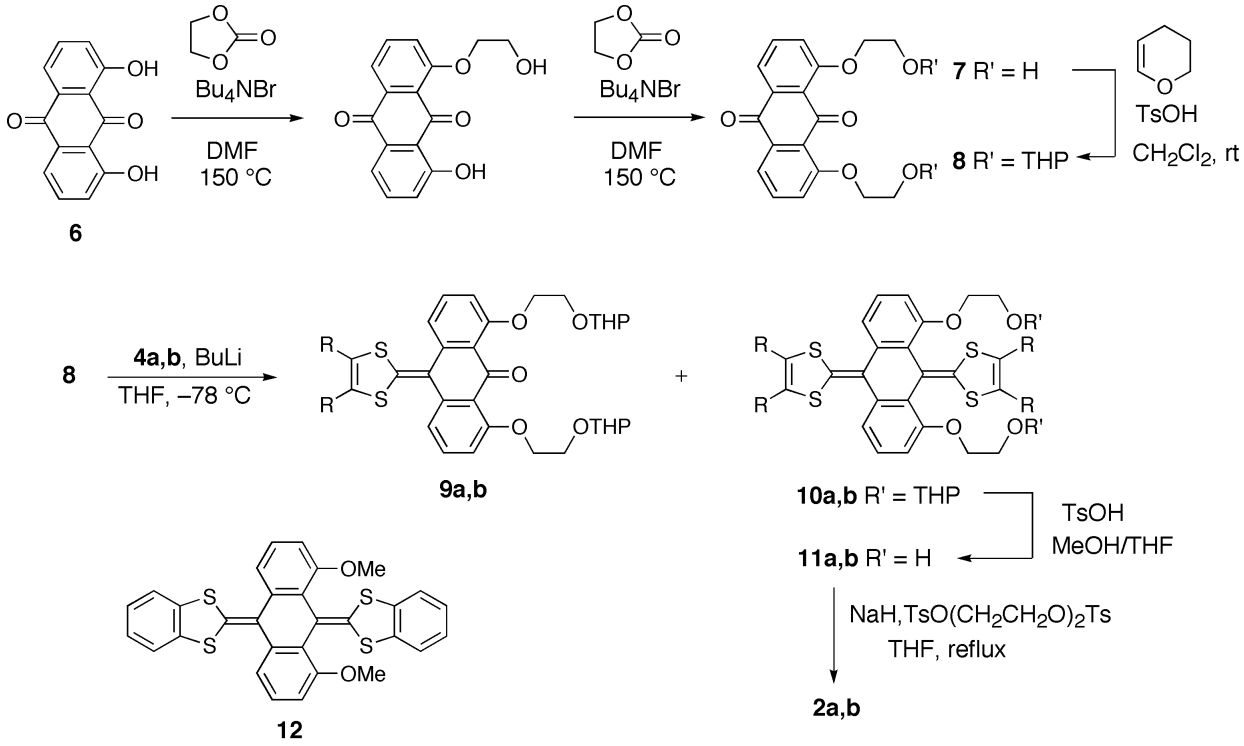
## RESULTS AND DISCUSSION

**Synthesis.** Initially, we attempted a Wittig–Horner reaction of a phosphonate ester (**4a**)[3a] with crown-annelated anthraquinone (**3**).[4] Despite the use of 2.5 equiv. of **4a**, only a monocondensation product (**5**) could be obtained, suggesting the presence of a severe steric hindrance of the crown ether moiety (Scheme 2).




**Scheme 2**

In order to avoid such a problem, we decided to construct the crown ether ring at the final step. A diol (**7**) was synthesized in 40% yield from 1,8-dihydroxyanthraquinone (**6**) in two steps,[5] and the hydroxyl groups of **7** were protected as THP ether groups to give **8**. Wittig–Horner reactions of **8** afforded biscondensation products (**10a,b**) in 54 and 24% yields, respectively, along with **9a,b**. Low yields of **10** and formation of the monocondensation products (**9**) indicate that the carbonyl group at the 9-position in **8** is still hindered by the 1,8-substituents. The protecting groups in **10** were removed under an acidic condition to give dilols (**11a,b**). Treatment of **11** with sodium hydride followed by slow addition of diethylene glycol ditosylate[6] gave the desired host compounds (**2a,b**) in 70 and 66% yields, respectively. For comparisons, a 1,8-dimethoxy derivative (**12**) was also prepared from 1,8-dimethoxyanthraquinone[7] and **4a** in 64% yield.




**Scheme 3**

**Redox properties.** The electrochemical properties of the new compounds (**2a,b**) and (**12**) were studied by cyclic voltammetry (CV) in benzonitrile. The redox potentials are summarized in Table 1 along with those for **1a,b** measured under the same conditions. They showed the CV waves typical for 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives as shown in Figure 1. Namely, re-

reduction peaks at $E_{pc1}$ corresponding to the first two-electron oxidation ones ($E_{pa1}$) were observed at lower potentials owing to structural changes upon electron transfer. This indicates that the substituents at the 1,8-positions do not prevent the conformational changes accompanied by two-electron oxidation. The cyclic voltammograms were almost unchanged during the repetition of scans within the scan range of –0.5—+1.20 V, suggesting the reversibily of the structural changes. Second oxidation waves at $E_{pa2}$ can be assigned to the oxidation of the anthracene units of the dications affording the trication radicals. The 1,8-dialkoxy groups in **2** and **12** have only a small effect on the $E_{pa1}$ values, but lower the $E_{pa2}$ values by 0.20—0.37 V compared with the corresponding parent compounds (**1**). This can be explained by considering that the HOMO of the neutral molecule is mainly localized on the *p*-quinobis(1,3-dithiole) moiety, while that of the dication lies on the anthracene unit with large atomic orbital coefficients at the 1,8-positions.[8]

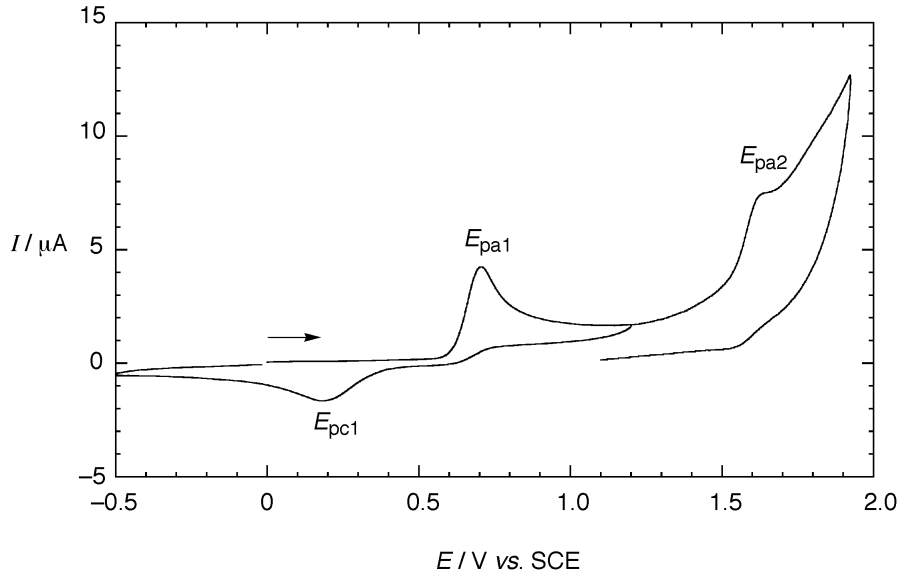



**Figure 1.** Cyclic voltammogram of **2a**. The reverse scan from the switching potential of +1.90 V is omitted partially for clarity.

**Table 1** Redox potentials of **1**, **2**, and **12**[a]

| Compound | $E_{pa1}$/V | $E_{pc1}$/V | $E_{pa2}$/V |
|---|---|---|---|
| **1a** | 0.70 | 0.22 | 1.97 |
| **1b** | 0.56 | 0.21 | 1.69 |
| **2a** | 0.71 | 0.18 | 1.62 |
| **2b** | 0.59 | 0.20 | 1.49 |
| **12** | 0.74 | 0.13 | 1.60 |

[a] $Bu_4NClO_4$ (0.1 mol $dm^{-3}$) in PhCN, Pt electrode, scan rate 100 mV $s^{-1}$, *E*/V *vs.* saturated calomel electrode (SCE).

Chemical oxidation of **2b** with two equiv. of tris(4-bromophenyl)aminium hexachloroantimonate afforded the corresponding dication (**2b**$^{2+}$) as a stable $SbCl_6$ salt in 98% yield.

**X-Ray molecular structures.** The X-Ray analysis of the dimethoxy derivative (**12**) revealed that the molecule adopts a butterfly-shape similar to the previously reported 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene systems as shown in Figure 2(a). The most characteristic feature is that the dithiole ring at the 9-position is tilted more largely than the others owing to the steric repulsion between the sulfur and oxygen atoms: the angles of the C(9)=C(15) and C(10)=C(22) double bonds with respect to the C(11)C(12)C(13)C(14) plane are 44.9 and 34.6°, respectively. The intramolecular S···O contact distances are shorter than the sum of the van der Waals radii (3.32 Å) [S(1)···O(1) = 2.767(3); S(2)···O(2) = 2.888(3) Å].

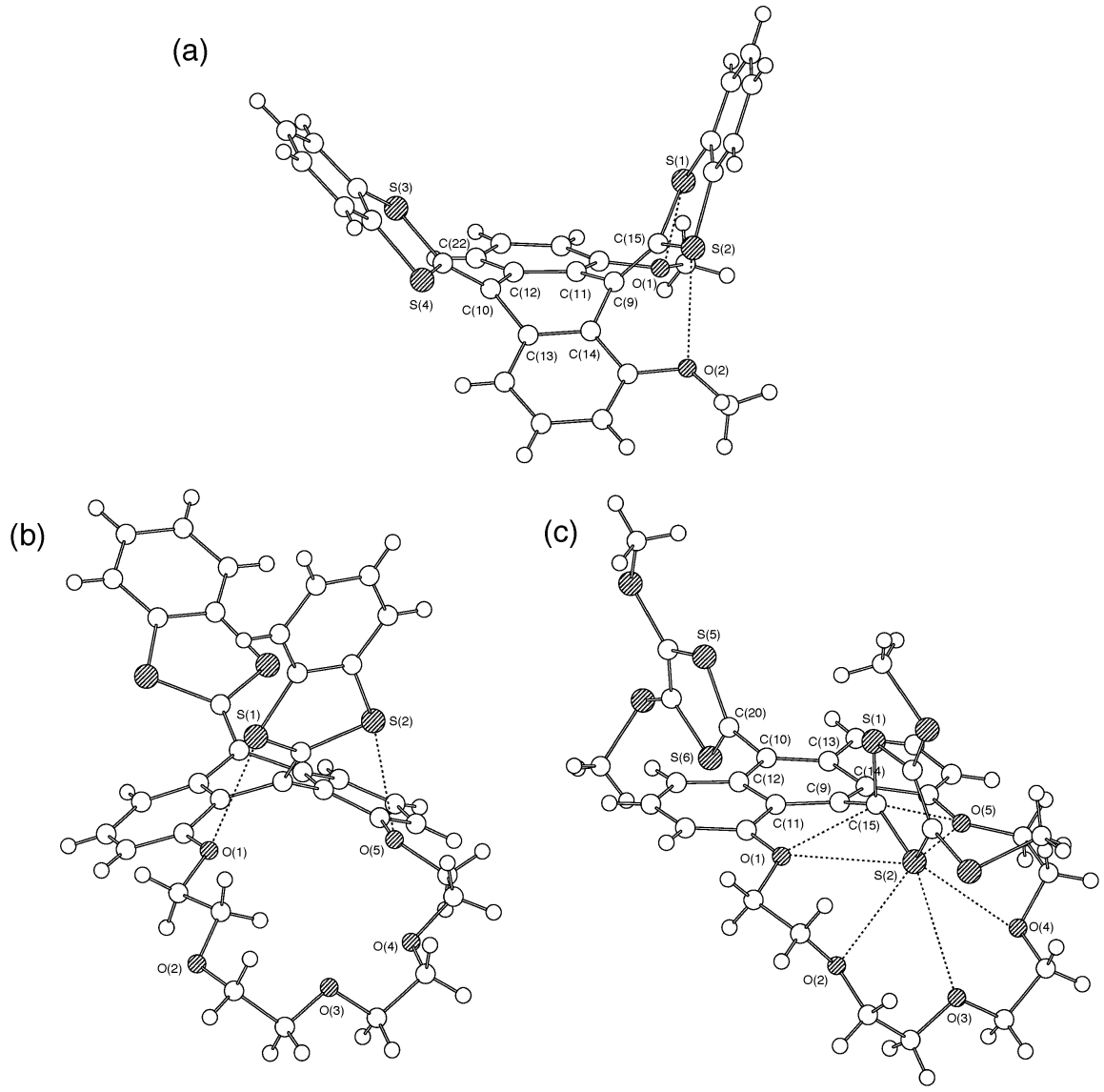



**Figure 2.** X-Ray molecular structures of (a) **12**, (b) **2a**, and (c) **2b**$^{2+}$ (counterions and solvent molecules are omitted). Broken lines indicate short intramolecular contacts. Selected interatomic distances (Å): (a) S(1)···O(1) 2.767(3); S(2)···O(2) 2.888(3); (b) S(1)···O(1) 2.835(2); S(2)···O(5) 2.877(2); (c) S(2)···O(1) 2.995(5); S(2)···O(2) 3.077(6); S(2)···O(3) 3.183(6); S(2)···O(4) 3.165(6); S(2)···O(5) 2.851(5); C(15)···O(1) 2.601(7); C(15)···O(5) 2.711(7).

The molecular structure of the crown compound (**2a**) is shown in Figure 2(b). The geometry of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene moiety of **2a** is essentially the same as that of **12**. One of the methylene units of the crown ether moiety is directed inward and hence the cavity is slightly collapsed. Since the 1,3-dithiole ring at the 9-position is away from the crown ring, it is expected that it does not prevent the binding of metal cations.

On the other hand, in the dication sate (**2b**$^{2+}$) the central anthracene unit is flattened, and the 1,3-dithiolium rings are nearly orthogonal to it as shown in Figure 2(c). The C(9)–C(15) bond is slightly deviated from the C(11)C(12)C(13)C(14) plane (20.8°). In contrast to the neutral molecule (**2a**), all the oxygen atoms are directed inward and contact with the S(2) atom of the dithiolium ring within the sum of the van der Waals radii [S(2)···O interatomic distances: 2.851(5)–3.183(6) Å]. Short intramolecular contacts are also found between the C(15) atom, which is the C-2 position of the 1,3-dithiolium ring, and the oxygen atoms at the 1,8-positions [2.601(7) and 2.711(7) Å]. A CPK model of the dication (**2b**$^{2+}$) shows that the cavity of the crown ether ring is almost occupied by the S(2) atom. Therefore, the binding ability of the dications (**2**$^{2+}$) is considered to be quite low compared to the neutral molecules (**2**).

**Complexation studies.** In order to compare the cation binding abilities of the neutral molecules (**2**) and dication states (**2**$^{2+}$), $^1$H-NMR titration experiments were carried out on the both states. Addition of alkali metal salts ($LiClO_4$ $NaClO_4$, and $KPF_6$) to an NMR sample solution of the neutral host (**2b**) in $CD_3CN$[9] induced downfield shifts of the signals assigned to the protons of the crown ether moiety, especially the Ar–O*C*$H_2$– methylene protons, indicating that the complexation occurs at this site. Non-linear least-squares analyses[10] of the obtained titration curves afforded the association constants *K* for the formation of 1:1 complexes (*K*: $Li^+$, 1100 ± 310; $Na^+$, 2000 ± 210; $K^+$, 2700 ± 440 $M^{-1}$). On the other hand, the $^1$H-NMR spectral signals of **2b**$^{2+}$ were not affected by addition of metal cations, indicating that no compexation occurs in the dication state as predicted by the X-Ray analysis.

The cation binding properties of **2** were also investigated by cyclic voltammetry. When excess amounts of alkali metal salts (*ca*. 10 equiv.) were added to a solution of **2**, the first oxidation potentials ($E_{pa1}$) shifted anodically (Table 2). Such anodic shifts were not seen for **1** and **12**, supporting that the potential shift observed for **2** are induced by the binding of metal ions with the crown ether moiety. In contrast to the $E_{pa1}$, the $E_{pa2}$ values of **2** remained unchanged in the presence of metal cations, suggesting that the metal ion is released from the dications (**2**$^{2+}$) owing to their low binding abilities as shown by the $^1$H-NMR titration experiments.[3h,11] Although the neutral hosts (**2**) bind all the metal cations examined here with sufficiently high association constants, only the sodium ion shows a large anodic shift of $E_{pa1}$. This finding indicates that **2** can be used for electrochemical sensing of $Na^+$. This selectivity may be attributed to the difference in the structures of the complexes depending on the metal cations.

**Table 2** Shifts of $E_{pa1}$ upon addition of alkali metal cations

| Compound | $\Delta E_{pa1}$/mV | | |
|---|---|---|---|
| | $Li^+$ | $Na^+$ | $K^+$ |
| **2a** | +20 | +110 | 0 |
| **2b** | +10 | +70 | +10 |

In conclusion, we have shown that the novel redox-switchable host compounds (**2**) and their dications ($\mathbf{2}^{2+}$) show the distinct changes in the molecular structures and binding abilities for alkali metal cations. This work also suggests that introduction of guest recognition sites into the 1,8-positioins of a 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene unit would be a promising way to construct a new type of redox-switchable receptors.

## EXPERIMENTAL

**General.** Melting points were measured on a Yanagimoto hot stage melting point apparatus and are uncorrected. IR and UV–VIS spectra were recorded on a JEOL Diamond-20 and a Shimadzu UV-260 spectrophotometers, respectively. NMR spectra were recorded with JEOL JNM-LA400 ($^1$H: 400 MHz; $^{13}$C: 100 MHz) or JNM-LA300 ($^1$H: 300 MHz; $^{13}$C: 75 MHz) spectrometer. MS and HRMS spectra (EI) were measured on a Shimadzu GCMS-QP1000EX and a JEOL JMS-777V spectrometer, respectively Elemental analyses were performed on a Perkin-Elmer Model 240 or a Yanaco MT-6 apparatus.

**Attempted synthesis of the compound (2a).** To a solution of phosphonate ester (**4a**)[3a] (165 mg, 0.63 mmol) in dry THF (5 mL) was added BuLi (1.57 M in hexane, 0.48 mL, 0.75 mmol) at –78 °C under nitrogen. After stirring for 15 min, anthraquinone (**3**)[4] (100 mg, 0.25 mmol) was added to the solution. The mixture was stirred for 2 h at –78 °C and allowed to warm to rt. After stirring for further 17 h, the solution was concentrated. Water (15 mL) was added to the residue, and the mixture was extracted with $CH_2Cl_2$. The extract was dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on alumina (ethyl acetate) to give **5** (55 mg, 41%) as yellow plates: mp 253–254 °C (from toluene); IR (KBr) 2873, 1670 (C=O), 1655, 1591, 1577, 1468, 1448, 1279, 1263, 1238, 1120, 1103, 1076, 737 cm$^{-1}$; $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 3.81–4.24 (16H, m, crown), 6.89 (2H, dd, $J$ = 5.3, 4.0 Hz, Ar-2,7-H), 7.12–7.15 (2H, AA'XX', benzodithiole), 7.22–7.26 (2H, AA'XX', benzodithiole), 7.45–7.47 (4H, m, Ar-3,4,5,6-H); $^{13}$C-NMR (100 Hz, $CDCl_3$) $\delta$ 68.9, 69.4, 70.4, 71.2, 111.5, 118.1, 119.8, 121.0, 123.3, 126.0, 131.4, 134.8, 138.6, 139.9, 157.1, 183.0; MS *m/z* (rel. intensity) 534 ($M^+$, 100%), 476 (42), 385 (41), 105 (30); Anal. Calcd for $C_{29}H_{26}O_6S_2$: C, 65.15; H, 4.90. Found: C, 65.26; H, 4.75.

**1-Hydroxy-8-(2-hydroxyethoxy)anthraquinone.** A solution of 1,8-dihydroxyanthraquinone (**6**) (5.00 g, 20.8 mmol), ethylene carbonate (3.69 g, 41.6 mmol), and tetrabutylammonium bromide (6.71 g, 20.8 mmol) in dry DMF (30 mL) was heated at 150 °C for 3 h under nitrogen. After cooling to rt, the mixture was poured into water (300 mL), and the resulting precipitate was filtered off, washed with water, and dried in vacuo. The solid was purified by column chromatography on silica gel (toluene followed by ethyl acetate) to give the title compound (4.17 g, 71%) as yellow needles: mp 171–173 °C (from ethyl acetate); IR (KBr) 3456 (OH), 1668 (C=O), 1631, 1585, 1448, 1288 $cm^{-1}$; $^1$H-NMR (400 MHz, DMSO-$d_6$) $\delta$ 3.81 (2H, q, $J$ = 5.2 Hz, $OCH_2CH_2OH$), 4.22 (2H, t, $J$ = 5.2 Hz, $OCH_2CH_2OH$), 4.89 (1H, t, $J$ = 5.2 Hz, $OCH_2CH_2OH$), 7.33 (1H, dd, $J$ = 8.3, 0.7 Hz, Ar-H), 7.61–7.85 (5H, m, Ar-H), 12.92 (1H, s, Ar-OH); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) $\delta$ 59.5, 71.2, 116.8, 118.3, 119.4, 120.1, 120.8, 124.3, 132.4, 135.0, 136.2, 136.3, 160.2, 161.5, 182.2, 188.1; MS *m/z* (rel. intensity) 284 ($M^+$, 15%), 266 (93), 240 (100), 184 (49), 139 (68), 63 (57); Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25. Found: C, 68.03; H, 4.07.

**1,8-Bis(2-hydroxyethoxy)anthraquinone (7).** A solution of ethylene carbonate (0.78 g, 8.8 mmol), tetrabutylammonium bromide (1.17 g, 3.63 mmol), and 1-hydroxy-8-(2-hydroxyethoxy)anthraquinone (1.00 g, 3.52 mmol) in dry DMF (5 mL) was heated at 150 °C for 5 h under nitrogen. After cooling to rt, the mixture was poured into water (100 mL), and the resulting precipitate was filtered off, washed with water, and dried in vacuo. The solid was purified by column chromatography on silica gel (ethyl acetate followed by methanol) to give **7** (649 mg, 56%) as yellow prisms: mp 207–210 °C (from ethyl acetate); IR (KBr) 3450 (OH), 2929, 1670 (C=O), 1585, 1442, 1331, 1271, 1240, 1059 $cm^{-1}$; $^1$H-NMR (400 MHz, DMSO-$d_6$) $\delta$ 3.78 (4H, q, $J$ = 5.4 Hz, $OCH_2CH_2OH$) , 4.19 (4H, t, $J$ = 5.4 Hz, $OCH_2CH_2OH$), 4.91 (2H, t, $J$ = 5.4 Hz, $OCH_2CH_2OH$), 7.57 (2H dd, $J$ = 8.l, 1.5 Hz, Ar-H), 7.68–7.74 (4H, m, Ar-H); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) $\delta$ 59.5, 71.3, 118.5, 120.8, 123.8, 134.1, 134.3, 158.4, 181.4, 183.3; MS *m/z* (rel. intensity) 328 ($M^+$, 10%), 310 (23), 253 (100), 249 (71), 139 (81); Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.9. Found: C, 66.09; H, 4.84.

**THP-protected compound (8)**. To the stirred solution of the compound (**7**) (1.00 g, 3.05 mmol) and 2,3-dihydro-4*H*-pyran (1.73 mL, 19.1 mmol) in dry $CH_2Cl_2$ (30 mL) was added *p*-toluenesulfonic acid monohydrate (10 mg) at rt. The solution was stirred for 2.5 h, washed with sat. $NaHCO_3$ aq followed by water, dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on alumina (toluene/ethyl acetate, 1:1) to give **8** (1.32 g, 88%) as yellow plates: mp 79–80 °C (from toluene/hexane, 1:1); IR (KBr) 2945, 2875, 1672 (C=O), 1589, 1313, 1288, 1236, 1227, 1126, 1072, 1038, 1020 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.54–1.87 (12H, m, THP), 3.55–4.83 (14H, m, THP, $-CH_2CH_2-$), 7.38 (2H, dd, $J$ = 8.3, 1.5 Hz, Ar-H), 7.61 (2H, dd, $J$ = 8.3, 7.7 Hz, Ar-H), 7.85 (2H, dd, $J$ =

7.7, 1.5 Hz, Ar-H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 19.4, 25.4, 30.5, 62.3, 65.8, 66.4, 99.2, 99.4, 120.6, 124.9, 133.5, 134.7, 158.7, 182.1, 184.0; MS *m/z* (rel. intensity) 312 (40), 266 (23), 139 (20), 85 (100), $M^+$ was not observed; Anal. Calcd for $C_{28}H_{32}O_8$: C, 67.73; H, 6.50. Found: C, 67.99; H, 6.45.

**Wittig–Horner reaction of the compound (8).** To a solution of phosphonate ester (**4a**) (412 mg, 1.57 mmol) in dry THF (8 mL) was added BuLi (1.56 M in hexane, 0.97 mL, 1.51 mmol) at –78 °C under nitrogen. After stirring for 20 min, a solution of the anthraquinone (**8**) (300 mg, 0.60 mmol) in THF (2 mL) was added to the solution. The mixture was stirred for 1 h at –78 °C and allowed to warm to rt. Water (40 mL) was added to the solution, and the mixture was extracted with $CH_2Cl_2$. The extract was dried over $Na_2SO_4$, and concentrated. The residue was purified by column chromatography on silica gel (toluene/ethyl acetate, 1:1) to give **9a** (86 mg, 23%) and **10a** (251 mg, 54%).

**9a:** yellow plates; mp 132–135 °C (from toluene); IR (KBr) 2939, 2870, 1668 (C=O), 1589, 1579, 1467, 1450, 1273, 1124, 1074, 1034 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.52–1.82 (12H, m), 3.52–3.55 (2H, m), 3.88–3.97 (4H, m), 4.08–4.12 (2H, m), 4.30 (4H, br s), 4.79 (2H, br s), 6.98–7.01 (2H, m, Ar-H), 7.11–7.14 (2H, AA'XX', benzodithiole), 7.23–7.25 (2H, AA'XX', benzodithiole), 7.45–7.46 (4H, m, Ar-H); MS *m/z* (rel. intensity) 632 ($M^+$, 5%), 464 (12), 376 (10), 84 (46). Anal. Calcd for $C_{35}H_{36}O_7S_2$: C, 66.43; H, 5.73. Found: C, 66.18; H, 5.63.

**10a:** yellow prisms; mp 112–114 °C (from ethyl acetate); IR (KBr) 3057, 2939, 2870, 1577, 1570, 1464, 1450, 1267, 1124, 1076, 1034, 741 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.43–1.75 (12H, m), 3.45–3.49 (2H, m), 3.77–3.94 (4H, m), 4.00–4.15 (2H, m), 4.25–4.31 (4H, m), 4.64–4.73 (2H, m), 6.96–7.06 (6H, m, benzodithiole, Ar-H), 7.13–7.19 (4H, m, benzodithiole, Ar-H), 7.29–7.38 (4H, m, benzodithiole, Ar-H); MS *m/z* (rel. intensity) 768 ($M^+$, 12%), 600 (28), 512 (12), 446 (13), 404 (69), 360 (100), 282 (11), 153 (16). Anal. Calcd for $C_{42}H_{40}O_6S_4$: C, 65.60; H, 5.24. Found: C, 65.44; H, 5.20.

A Wittig–Horner reaction of methylthio substiuted phosphonate ester (**4b**)[12] with the anthraquinone (**8**) gave mono- and biscondensed products (**9b**) and (**10b**).

**9b:** 68%, yellow plates; mp 91–93 °C (from ethyl acetate/hexane, 1:1); IR (KBr) 2941, 2870, 1668 (C=O), 1589, 1579, 1468, 1277, 1240, 1074, 1036 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.51–1.82 (12H, m), 2.38 (6H, s, $SCH_3$), 3.51–3.56 (2H, m), 3.87–3.96 (4H, m), 4.06–4.11 (2H, m), 4.29 (4H, br s), 4.78 (2H, br s), 6.98 (2H, br d, $J$ = 8.5 Hz, Ar-H), 7.24 (2H, d, $J$ = 7.3 Hz, Ar-H), 7.42 (2H, d, $J$ = 8.1 Hz, Ar-H); MS *m/z* (rel. intensity) 674 ($M^+$, 22%), 590 (33), 506 (67), 462 (42); HRMS–FAB+ Calcd for $C_{33}H_{38}O_7S_4$: *m/z* 674.1500; Found: 674.1522 (dev. +3.2 ppm).

**10b:** 24%, yellow needles; mp 220–224 °C (from ethyl acetate/hexane, 1:1); IR (KBr) 2940, 2920, 2871, 1576, 1462, 1431, 1267, 1124, 1074, 1034, 966, 872, 758 cm$^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 1.47–1.84

(12H, m), 2.37 (6H, s, $SCH_3$), 2.40 (6H, s, $SCH_3$), 3.49–3.52 (2H, m), 3.76–3.90 (4H, m), 4.00–4.11 (2H, m), 4.20–4.25 (4H, m), 4.64–4.71 (2H, m), 6.93 (2H, br d, $J$ = 7.6 Hz, Ar-H), 7.21–7.27 (4H, m, Ar-H); MS *m/z* (rel. intensity) 852 ($M^+$, 65%), 684 (23), 530 (30), 489 (21), 446 (83), 402 (66), 328 (19), 295 (57); HRMS–FAB+ Calcd for $C_{38}H_{44}O_6S_8$: *m/z* 852.0903; Found: 852.0900 (dev. –0.5 ppm).
$^{13}$C-NMR spectra of the compounds (**9a,b**) and (**10a,b**) show a large number of signals probably due to the presence of diastereomers.

**Deprotection of 10.** The compound (**10a**) (94 mg, 0.12 mmol) was dissolved in THF (20 mL) under heating, and methanol (8 mL) was added to the resulting solution. After cooling to rt, *p*-toluenesulfonic acid monohydrate (10 mg) was added. After stirring for 6 h at rt, saturated aqueous $NaHCO_3$ (70 mL) was added to the solution, and the mixture was extracted with $CH_2Cl_2$. The extract was dried over $Na_2SO_4$ and concentrated to give **11a** (69 mg, 95%) as yellow prisms: mp 175–178 °C (from toluene); IR (KBr) 3415 (OH), 2931, 2870, 1577, 1464, 1450, 1433, 1267, 1066, 739 $cm^{-1}$; $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 3.74–3.79 (2H, m, $CH_2$), 3.86 (2H, s, OH), 4.03–4.16 (4H, m, $CH_2$), 4.24–4.28 (2H, m, $CH_2$), 6.99–7.07 (6H, m, benzodithiole, Ar-H), 7.14–7.20 (4H, AA'XX', benzodithiole), 7.35 (2H, dd, $J$ = 8.3, 7.8 Hz, Ar-H), 7.44 (2H, dd, $J$ = 7.8, 1.0 Hz, Ar- H); $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta$ 61.4, 72.9, 113.8, 117.0, 119.3, 121.0, 121.2, 123.3, 125.3, 125.7, 126.3, 128.0, 134.0, 134.6, 135.2, 137.0, 137.1, 154.4; MS *m/z* (rel. intensity) 600 ($M^+$, 60%), 404 (100), 360 (61), 300 (29); Anal. Calcd for $C_{32}H_{24}O_4S_4 \cdot 1.5CH_3C_6H_5$: C, 69.07; H, 4.91. Found: C, 69.44; H, 4.58.

The methylthio derivative (**11b**) was synthesized by the similar method.
**11b:** 100%, yellow needles; mp 253–255 °C (from ethyl acetate); IR (KBr) 3396 (OH), 2920, 2870, 1576, 1464, 1450, 1429, 1269, 1065 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 2.39 (6H, s, $SCH_3$), 2.42 (6H, s, $SCH_3$), 3.70–3.77 (4H, m), 3.98–4.03 (2H, m), 4.09–4.14 (2H, m), 4.21–4.23 (2H, m), 6.91–6.95 (2H, m), 7.28–7.32 (4H, m); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 18.9, 19.1, 61.3, 72.8, 113.7, 116.4, 118.8, 122.9, 125.7, 125.8, 127.6, 127.9, 132.9, 133.6, 136.5, 154.3; MS *m/z* (rel. intensity) 684 ($M^+$, 100%), 489 (38), 446 (95), 402 (30), 342 (36), 295 (61). Anal. Calcd for $C_{28}H_{28}O_4S_8$: C, 49.09; H, 4.12. Found: C, 48.77; H, 4.26.

**Crown compound (2a).** Sodium hydride (60% oil dispersion, 24 mg, 0.60 mmol) was added to a solution of diol (**11a**) (150 mg, 0.25 mmol) in dry THF (25 mL), and the mixture was heated under reflux for 2 h under nitrogen. To the solution was added a solution of diethylene glycol ditosylate[6] (105 mg, 0.25 mmol) in THF (25 mL) over a period of 2 h. After addition, the mixture was refluxed for 6.5 h. Water was carefully added to the solution, and the mixture was extracted with $CH_2Cl_2$. The extract was

dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on alumina (toluene/ethyl acetate, 1:1) to give **2a** (118 mg, 70%) as yellow plates: mp 280 °C (decomp) (from $CHCl_3$/hexane, 1:1); IR (KBr) 2943, 2925, 2900, 2866, 1577, 1568, 1466, 1458, 1448, 1267, 1169, 1124, 1115, 1078, 741 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 3.64–3.74 (8H, m, crown), 3.88–3.93 (2H, m, crown), 4.15–4.24 (4H, m, crown), 4.28–4.33 (2H, m, crown), 6.91 (2H, dd, $J$ = 7.8, 0.9 Hz, Ar-H), 6.99 (2H, AA'XX', benzodithiole), 7.04 (2H, AA'XX', benzodithiole), 7.15–7.18 (4H, m, benzodithiole), 7.31 (2H, t, $J$ = 7.8 Hz, Ar-H), 7.36 (2H, dd, $J$ = 7.8, 0.9 Hz, Ar-H). $^{13}$C-NMR (100 MHz, DMSO-$d_6$) $\delta$ 52.1, 68.0, 69.0, 70.0, 111.2, 117.3, 121.4, 121.6, 124.2, 125.5, 126.4, 128.0, 134.0, 136.1, 136.5, 152.0, 154.1, 158.5, 177.9, 181.4; MS *m/z* (rel. intensity) 670 ($M^+$, 72%), 447 (13), 360 (100), 153 (15); HRMS–EI Calcd for $C_{36}H_{30}O_5S_4$: *m/z* 670.0976; Found: 670.0955 (dev. –3.2 ppm).

The methylthio derivative (**2b**) was synthesized by the similar method.
**2b**: 66%, yellow solid; mp 298–300 °C (decomp) (from toluene/hexane, 1:1); IR (KBr) 2918, 2871, 1577, 1464, 1267, 1115, 1078, 758, 741 $cm^{-1}$; $^1$H-NMR (400 MHz, $CDCl_3$) $\delta$ 2.38 (6H, s, $SCH_3$), 2.41 (6H, s, $SCH_3$), 3.64–3.77 (8H, m, crown), 3.88–3.93 (2H, m, crown), 4.13–4.26 (6H, m, crown), 6.86 (2H, br d, $J$ = 8.4 Hz, Ar-H), 7.21–7.28 (4H, m, Ar-H); $^{13}$C-NMR (100 MHz, $CDCl_3$) $\delta$ 18.9, 19.1, 68.8, 69.7, 71.0, 71.1, 111.6, 116.7, 117.9, 123.6, 125.0, 125.6, 127.3, 127.4, 132.0, 132.7, 136.5, 154.4; MS *m/z* (rel. intensity) 754 ($M^+$, 100%), 445 (44), 402 (64), 295 (33) HRMS–EI Calcd for $C_{32}H_{34}O_5S_8$: *m/z* 754.0172; Found: 754.0138 (dev. –4.5 ppm).

**Dication salt ($2b^{2+}$) ($SbCl_6^-$)$_2$.** To a solution of **2b** (20 mg, 0.026 mmol) in dry $CH_2Cl_2$ (3 mL) was added tris(4-bromophenyl)aminium hexachloroantimonate (42 mg, 0.051 mmol) at rt under nitrogen. The mixture was stirred for 30 min, and the resulting precipitate was collected by filtration and repeatedly washed with $CH_2Cl_2$ to give **$2b^{2+}$ ($SbCl_6^-$)$_2$** (36 mg, 98%) as a brown solid: mp 185–190 °C (decomp); $^1$H-NMR (400 MHz, $CD_3CN$) $\delta$ 2.85 (6H, s, $SCH_3$), 2.93 (6H, s, $SCH_3$), 3.40–3.47 (4H, m, crown), 3.51–3.65 (8H, m, crown), 4.15–4.20 (2H, m, crown), 4.41–4.46 (2H, m, crown), 7.18 (2H, d, $J$ = 7.6 Hz, Ar-H), 7.40 (2H, d, $J$ = 8.8 Hz, Ar-H), 7.67 (2H, dd, $J$ = 8.8, 7.6 Hz, Ar-H); $^{13}$C-NMR (100 MHz, $CD_3CN$) $\delta$ 20.3, 20.4, 67.4, 70.0, 70.9, 71.1, 111.6, 119.3, 122.0, 124.5, 126.0, 130.8, 134.0, 152.9, 153.8, 157.4, 185.0, 195.5. Anal. Calcd for $C_{32}H_{34}O_5Cl_{12}S_8Sb_2$: C, 26.99; H, 2.41. Found: C, 27.46; H, 2.58.

**9,10-Bis(1,3-benzodithol-2-ylidene)-1,8-dimethoxy-9,10-dihydroanthracene (12)**. To a solution of phosphonate ester (**4a**) (488 mg, 1.86 mmol) in dry THF (10 mL) was added BuLi (1.53 M in hexane, 1.46 mL, 2.23 mmol) at –78 °C under nitrogen. After stirring for 15 min, a solution of 1,8-dimethoxyanthraquinone[7] (200 mg, 0.75 mmol) was added to the solution. The mixture was stirred for

30 min at –78 °C and allowed to warm to rt. The solution was concentrated. Water (40 mL) was added to the residue, and the mixture was extracted with $CH_2Cl_2$. The extract was dried over $Na_2SO_4$ and concentrated. The residue was purified by column chromatography on silica gel (toluene) to give **12** (273 mg, 68%) as yellow prisms: mp 286–287 °C (from ethyl acetate); IR (KBr) 3057, 2993, 2930, 2833, 1577, 1568, 1537, 1468, 1448, 1433, 1263, 1070 $cm^{-1}$; $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 3.99 (6H, s, OMe), 6.91–6.94 (2H, AA'XX', benzodithiole), 6.96–6.99 (2H, AA'XX', benzodithiole), 7.02–7.05 (2H, AA'XX', benzodithiole), 7.14–7.19 (4H, m, benzodithiole, Ar-H), 7.33–7.35 (4H, m, Ar-H); $^{13}$C-NMR (100 MHz, DMSO-$d_6$) $\delta$ 55.3, 110.5, 117.2, 117.3, 121.4, 121.6, 123.1, 123.8, 125.6, 126.4, 128.3, 132.5, 133.0, 134.0, 135.8, 136.4, 154.8; MS *m/z* (rel. intensity) 540 ($M^+$, 63%), 374 (100), 270 (14), 225 (19); Anal. Calcd for $C_{30}H_{20}O_2S_4$: C, 66.63; H, 3.73. Found: C, 66.86; H, 3.48.

**Electrochemical measurements.** Cyclic voltammetry was performed in a three-compartment cell with a Pt disc working electrode, Pt wire counter electrode, and saturated calomel reference electrode (SCE). Measurements were made with a Toho Technical Research Polarization Unit PS-07 potentiostat/galvanostat with a scan rate of 100 mV $s^{-1}$. The cell contained a solution of a substrate (*ca.* 1 mM) and tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte in benzonitrile. All solutions were purged with nitrogen and retained under the inert atmosphere during the experiment. The half wave potential of the ferrocene/ferrocenium couple was observed at +0.45 V under the same conditions.

**X-Ray structural analyses**. Reflection data were collected on a Rigaku Mercury CCD area detector for **2a** and **$2b^{2+}$ $(SbCl_6^-)_2$(MeCN)** and a Rigaku RAXIS-IV imaging plate area detector for **12**, using Mo-K$\alpha$ radiation ($\lambda$ = 0.71070 Å) at 296 K. All the structures were solved by the direct method using the SHELXS-86 program.[13] The non-hydrogen atoms were refined anisotropically by full-matrix least-squares method on $F_2$ using the SHELXL-93 program.[14] Hydrogen atoms were included at calculated positions but not refined. All the structures have been deposited as CIF files at the Cambridge Crystallographic Data Centre.

**Crystal data for 2a:** $C_{36}H_{30}O_5S_4$, $M$ = 540.70, monoclinic, space group $P2_1/c$, $a$ = 10.540(2), $b$ = 10.230(2), $c$ = 20.977(2) Å, $\beta$ = 95.76(1)°, $V$ = 2564.8(7) Å$^3$, $Z$ = 4, $T$ = 296 K, $F$(000) = 1120, $\mu$(Mo-K$\alpha$) = 3.98 $cm^{-1}$, crystal dimensions = 0.40 × 0.40 × 0.10 mm, 31253 reflections collected, 7158 independent ($R_{int}$ = 0.0661), $R_1$ = 0.0664 and $wR_2$ = 0.1538 for 6274 data with $I > 2\sigma(I)$. CCDC 279517.

**Crystal data for $2b^{2+}$ $(SbCl_6^-)_2$(MeCN):** $C_{32}H_{34}O_5S_8Cl_{12}Sb_2 \cdot CH_3CN$, $M$ = 1465.03, triclinic, space group $P\bar{1}$, $a$ = 9.909(2), $b$ = 17.439(2), $c$ = 17.691(3) Å, $\alpha$ = 67.242(9), $\beta$ = 88.74(1), $\gamma$ = 73.19(1)°, $V$ = 2684.7(6) Å$^3$, $Z$ = 2, $T$ = 296 K, $F$(000) = 1444, $\mu$(Mo-K$\alpha$) = 19.54 $cm^{-1}$, crystal dimensions = 0.27 × 0.20

× 0.05 mm, 27128 reflections collected, 11936 independent ($R_{int}$ = 0.0410), $R_1$ = 0.0851 and $wR_2$ = 0.1563 for 9053 data with $I > 2\sigma(I)$. Since the geometry of an acetonitrile molecule was deformed during the refinements, the molecule was refined under the restraint conditions. CCDC 279518.

**Crystal data for 12:** $C_{30}H_{20}O_2S_4$, $M$ = 670.84, monoclinic, space group $P2_1/c$, $a$ =12.013(2), $b$ = 26.009(4), $c$ = 11.812(2) Å, $\beta$ = 103.322(4)°, $V$ = 3150.8(9) Å$^3$, $Z$ = 4, $T$ = 296 K, $F(000)$ = 1400, $\mu$(Mo-K$\alpha$) = 3.46 cm$^{-1}$, crystal dimensions = 0.30 × 0.15 × 0.10 mm, 4116 reflections collected, $R_1$ = 0.0675 and $wR_2$ = 0.1765 for 3304 data with $I > 2\sigma(I)$. CCDC 196090.

**$^1$H-NMR titrations.** A stock solution of the host (**2b**) (3.1–4.3 × 10$^{-4}$ M) in $CD_3CN$ was prepared in 2 mL volumetric flask, and a 0.6 mL portion was transferred to a NMR tube and an initial $^1$H-NMR spectrum was taken to determine the chemical shift of the free host. A solution of guest cations (1.0–1.3 × 10$^{-2}$ M) was prepared in 1 mL volumetric flask using the stock solution of the host (**2b**), and small aliquots were successively added to the host solution in the NMR tube. After each addition, the $^1$H-NMR spectra were taken and the chemical shift of the host (Ar–OC***H***$_2$–$CH_2$O–) was monitored as a function of cation concentration. The data were analyzed by a non-linear least-squares method using the following equation (1) for a 1:1 host–guest binding,[10] where $[H]_t$ and $[G]_t$ are the total concentrations of host and guest, respectively; $K$ is the association constant for the formation of host–guest complex; $\delta_H$ and $\delta_{HG}$ are the chemical shifts of free and complexed hosts, respectively.

$$\delta_{obs} = \delta_H + 0.5\,(\delta_{HG} - \delta_H)[\,[H]_t + [G]_t + 1/K - \{([H]_t + [G]_t + 1/K)^2 - 4[H]_t[G]_t\}^{1/2}\,]/[H]_t \quad (1)$$

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