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Azo and azoxythiacrown ethers: synthesis and properties

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ABSTRACT

A series of 16- and 18-membered azo- and azoxythiacrown ethers have been synthesized by reductive macrocyclization of the respective bis(nitrophenoxy)oxaalkanes. The aromatic residues located in the polyether region of the molecule were introduced to macrocyclic skeletons and their affinities toward different groups of metal cations in ion-selective electrodes were described. X-ray structures for one dinitropodand and one azoxybenzothiacrown exhibiting strong π–π and π–H interactions have been found.

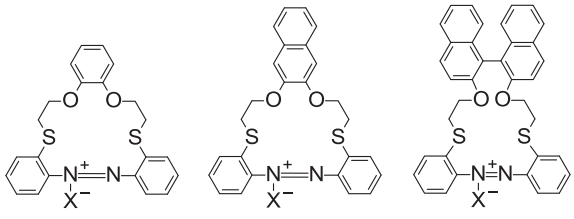
1. Introduction

Since the discovery of crown ethers, many of these compounds have been synthesized and documented in the literature. The structures of crown ethers determine their binding properties, such as binding selectivity and strength toward a wide range of metal ions, nonmetal ions, and neutral molecules. Thanks to their remarkable binding properties, the study of crown ethers has largely contributed to the development of host–guest chemistry. In such molecules, the number of oxygen atoms in the crown can be varied to alter the physical and chemical properties of the molecular structure. Replacement of oxygen atoms by sulfur in azo- and azoxycrown ethers leads to new products with different properties, especially in the area of cation selectivity. According to Pearson's theory,[1] sulfur atoms cause an increase in the affinity of macrocyclic ionophores toward 'soft' metal cations and a decrease in the affinity for the formation of complexes with 'hard' cations. This theory has previously been elaborated by us through studies of cation responsive sulfur containing 13- and 16-membered crown ethers.[2–5] Valuable results that we obtained from these previous successful syntheses, together with previously reported oxygen containing analogues of 13- and 16-membered thiacrown ethers[6] inspired us to synthesize more rigid molecules with enhanced lipophilicity. The new parts forming the macrocyclic skeletons are aromatic residues located in the polyether region of the molecule. In this way, the presence of flexible dioxyethylene chains and rigid aromatic residues alter the flexibility of the structure of investigated compounds and hence their complexation properties.

2. Results and discussion

2.1. Synthesis

The 16- and 18-membered azo- and azoxythiacrown ethers were prepared by multistep reactions (Scheme 1).



Scheme 1. Azo and azoxybenzothiacrown ethers.

The first step was the alkylation of catechol, 2,3-dihydroxynaphthalene or 2,2′-dihydroxy-1,1′-bisnaphthalene with 2-chloroethanol to obtain disubstituted diols (Scheme 2). In the next step the obtained diols were converted into chlorides via reaction with thionyl chloride in the presence of pyridine.

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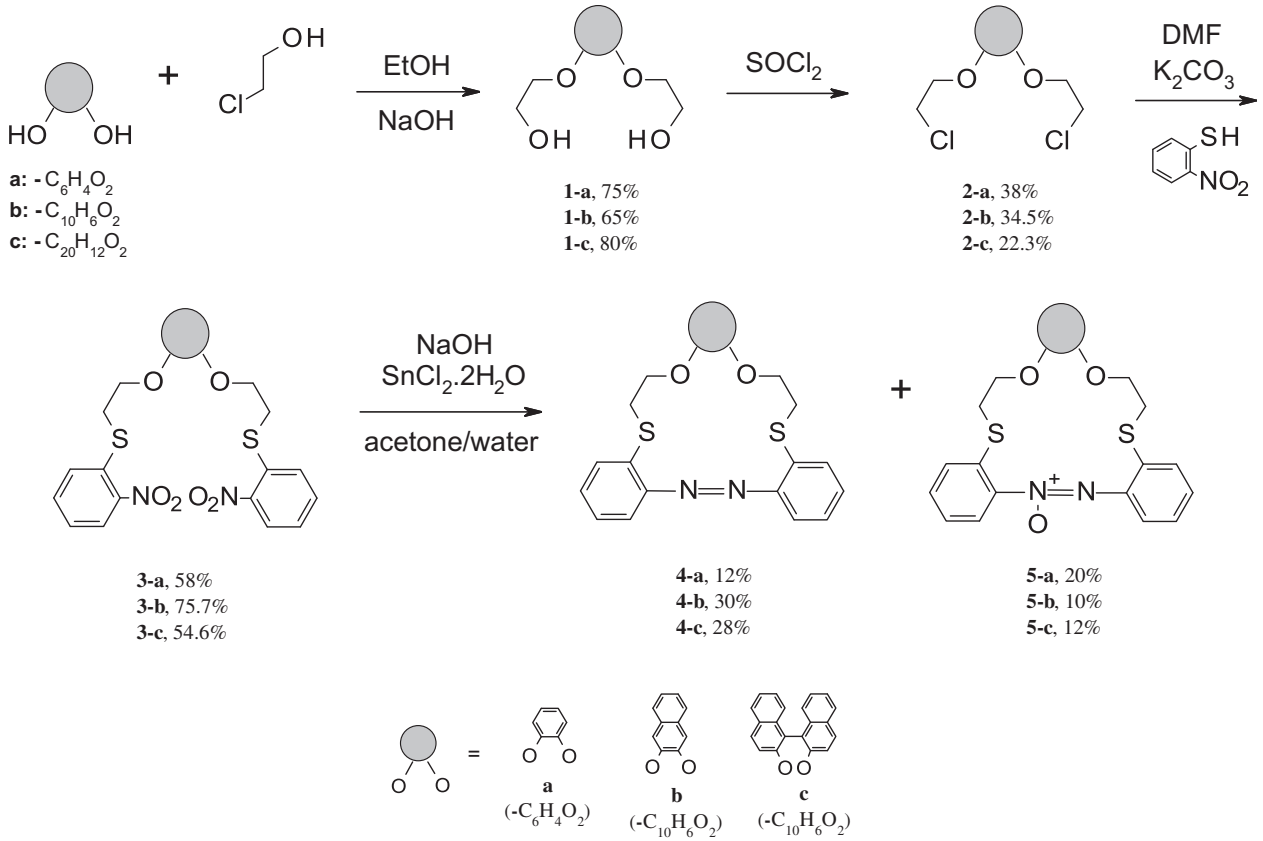
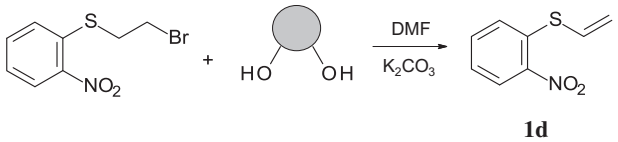


Scheme 2. General synthesis route for azo- and azoxythiacrown ethers.

Dinitropodands were obtained by condensing 2-nitrothiophenol with the respective aromatic dichloride in warm DMF in the presence of anhydrous potassium carbonate.

Then dinitro compounds **3-a**,**b**,**c** were subjected to reaction with sodium stannite (generated in situ from NAOH and $SnCl_2 \cdot 2H_2O$) to yield macrocyclic products. After these processes two main products were obtained: azo- and azoxy macrocycles (Scheme 1).

As shown, this procedure is composed of several stages. Such a synthetic route was chosen despite a much simpler way, which was previously used for the preparation of analogous oxygen compounds.[7] In this method, the condensation step of 2-(2-nitrophenyl)ethyl bromide/chloride with an aromatic diol (2,3-dihydroxynaphthalene, catechol or 1,1′-binaphthyl-2,2′-diol) gave respective dinitro compounds with good yield. The same reaction route was applied for the synthesis of analogous sulfur compounds (**4-a**,**b**,**c** and **5-a**,**b**,**c**) with same aromatic diols. However, the resulting reaction mixture mainly contained a yellow product, which after analyses was identified as vinyl sulfide **1d** (Scheme 3). Changing the solvent did not give better results.



1d

Scheme 3. Formation of vinyl sulfide product.

The presence of the vinyl sulfide was confirmed by NMR spectroscopy (please see the Experimental section). The synthesis of analogous compounds was previously reported by Kuad et al. and dehydrohalogenation reactions of alkyl halides took place under similar conditions.[8] Correspondingly, it can be concluded that replacement of sodium hydroxide by potassium carbonate in the synthesis procedure demonstrated by us also causes the formation of sulfur ylides and does not yield the desired products.

2.2. Potentiometric studies

Because of the observed progress in minimization of the sensor size, we decided to use all the synthesized compounds as ionophores in miniature potentiometric sensors. The membranes of similar composition to those used for classic ISE were poured onto graphite screen-printed electrodes. The characteristics of these electrodes and the selectivity coefficient values determined in the earlier described manner[4,9] were collected in Table 1 and shown in Fig. 2. All of the synthesized azo- and azoxybenzothiacrown ethers were applied to ion-selective membrane electrodes as ion carriers. Their selectivity toward Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Hg^{2+}, Ni^{2+} and Ag^+ were demonstrated. Potentiometric selectivity coefficients $K_{I,J}^{pot}$ were determined by the separate solution method

Table 1
Experimental selectivity coefficients $\log K_{Pb,X}^{pot}$

	4-a	5-a	4-b	5-b	4-c	5-c
Cu^{2+}	−0.292	−0.635	1.609	1.504	−1.074	−1.037
K^+	−1.388	−1.141	−0.021	−0.494	−1.288	−1.649
Na^+	−5.628	−8.650	−2.665	−2.690	−8.450	−4.650
Ag^+	10.982	6.217	12.232	6.020	5.979	8.951
Hg^{2+}	4.330	4.025	7.775	—	5.560	6.039
Ni^{2+}	—	−7.330	−4.259	—	−7.151	−8.670
Zn^{2+}	−6.212	−9.382	—	−7.594	−9.654	—
Ca^{2+}	−5.395	−8.261	—	−6.583	−8.404	—
Mg^{2+}	−1.599	−1.507	5.003	−0.334	—	—

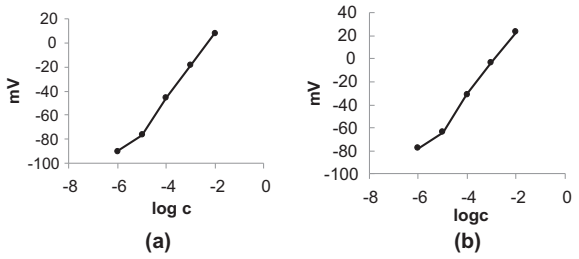


Fig. 1. Potentiometric responses of crown ethers **5-a** (a) and **5-b** (b) toward Pb^{2+}.

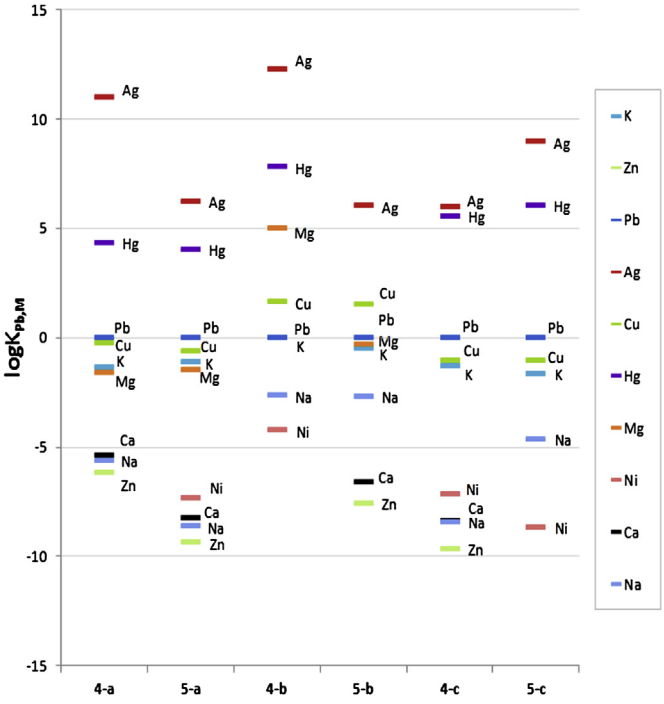


Fig. 2. Schematic presentation of the log *K* values of crown ethers for each cation.

(SSM) according to guidelines established by IUPAC.[10] Bakker's conditioning method[11] was also utilized to overcome the non-Nernstian response of membrane electrodes toward the most discriminated ions. The measurements were carried out by immersing the electrodes in a nitrate salt solution of the investigated metal ions from the lowest (10^{-6} M) to the highest solution concentration (10^{-2} M). The properties of ion-selective membrane electrodes doped with synthesized thiacrown ethers with azo- and azoxy-units are presented (Fig. 2). In order to calculate the selectivity coefficients, Pb^{2+} was selected as the primary cation since it was the cation showing the best near-Nernstian response (Fig. 1).

All electrodes showed a high silver affinity. It was also found that compound **4-b** exhibited a high affinity toward Mg^{2+} ($\log K^{pot}_{Pb,Mg} = 5.003$) and Cu^{2+} ($\log K^{pot}_{Pb,Cu} = 1.609$). In the case of analogue azoxy compound **5-b**, a higher affinity remained only toward Cu^{2+} ($\log K^{pot}_{Pb,Cu} = 1.504$). Compounds **4-a** and **5-a** possess a higher affinity toward Pb^{2+} than Mg^{2+} and Cu^{2+}. For compounds **4-c** and **5-c**, higher selectivity was exhibited toward Pb^{2+} than Cu^{2+}. However, they did not exhibit any measurable affinity toward Mg^{2+}. When the closely related oxygen analogues of compound **4-a** and **5-a** with catechol residue are compared to their previously synthesized oxygen analogues (where the sulfur atoms of compounds **4-b** and **5-a** were replaced by oxygen atoms),[6] the rules of Pearson's soft/hard acid/base theory can be more obviously reflected. For the oxygen-analogues the following order of the selectivity coefficients K>>Na>Zn>Cu>Mg is observed but for thia-analogues **4-a** and **5-a**, the orders changed to: $Cu^{2+}>K^{+}>Mg^{2+}>Na^{+}>Zn^{2+}$. According to the given orders, the affinity of hard oxygen donors toward alkali metals (hard bases) and the affinity of soft sulfur-analogues toward a softer cation (copper) is meaningful in terms of HSAB theory. Notably, the difference between sulfur and oxygen-analogues is not sharp but the contribution of hard oxygen atoms from the ether chain in compounds **4-a** and **5-a** seem to be still existing. Furthermore, the selectivity exhibited toward K^{+} was due to the conditioning method used; by means of bringing the ion-selective electrodes into contact with a discriminated cation solution (KCl).[11]

2.3. Crystallographic studies

Crystal structures have been determined for dinitropodand, $C_{22}H_{20}N_2O_6S_2$, **3-a**, and azoxybenzothiacrown ether, $C_{26}H_{22}N_2O_3S_2$, **5-b**. The crystallographic studies show that intermolecular interactions were not of any classical H-bond type. Nonetheless, several CH···π and ring stacking interactions were found to be quite useful to explain the packing mode and the origin of specific conformations of these molecules.

2.3.1. X-ray structural analysis of compound ***3-a***. Compound **3-a** crystallizes in the space group $P\bar{1}$ with two molecules in the unit cell (Z=2). Its molecular structure is presented in Fig. 3. Selected crystallographic and refinement details are shown in Table 2 while bond lengths, valence angles and torsion angles are given in the Supplementary data in Table 2a. Basic bond lengths and angles are similar to the ones reported for related macrocyclic molecules. As could be expected, angles at *S*-atoms, ca. 102°, are tighter than tetrahedral.

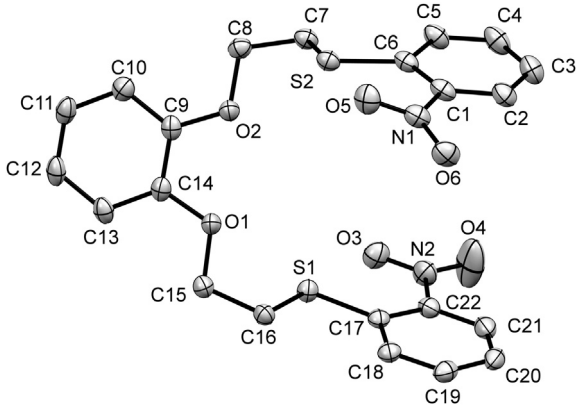


Fig. 3. ORTEP view of dinitropodand **3-a** with atom numbering scheme.

Two nitrophenyl rings are almost parallel to one another and the catechol ring is inclined, altogether forming an apparent letter *Z* shape (Fig. 5). Two adjacent molecules are linked by a weak C–H···π interaction involving the catechol ring (Fig. 5, Table 3). The nitrophenyl rings are stacked parallel within the solid state by alternating interpenetration of rings coming from two molecules (Fig. 4). This stacking is facilitated by opposite positions of the NO2 group in neighboring rings and therefore beneficial electric polarization of the rings. It is also noteworthy that the coplanarity of one $-NO_2$ group (O3–N2–O4) with the phenyl ring in the structure of dinitropodand is related to packing (Fig. 4). For the external $-NO_2$ group (O5–N1–O6) in the same molecule the related torsion is much wider (compare 20.0(3)° for O5–N1–C1–C6 and 2.7(3)° for O3–N2–C22–C17, Table 3).

Table 2
crystallographic data of dinitropodand **3-a** and azoxythiacrown **5-b**

Parameters	**3-a**	**5-b**
Formula	$C_{22}H_{20}N_2O_6S_2$	$C_{26}H_{22}N_2O_3S_2$
Formula weight	472.52	474.58
F (000)	492.00	1984.0
Space group	$P\bar{1}$ (triclinic)	*Pbca* (orthorhombic)
a (Å)	8.1325(4)	21.3571(8)
b (Å)	10.7979(5)	9.392(3)
c (Å)	12.4939(5)	21.6635(7)
α (°)	75.867(4)	90
β (°)	83.128(4)	90
γ (°)	81.873(4)	90
Volume (Å^3)	1049.1	4345.0(3)
Z	2	8
Density (Mg/m^3)	1.496	1.451
Temperature (K)	120	120
*R*1 (no. of refl.)	0.0447(3188)	0.0485(3239)
*wR*2 (no. of refl.)	0.1217(3889)	0.1366(4274)
Indices range	$-9<h<9$	$-16<h<26$
	$-12<k<13$	$-10<k<11$
	$-13<l<15$	$-26<l<22$
Absorption coefficient (mm^{-1})	0.298	0.279
Completeness to θ=25.5°	99.9%	—
Completeness to θ=26°	—	99.9%
Goodness-of fit on F^2	1.077	1.028

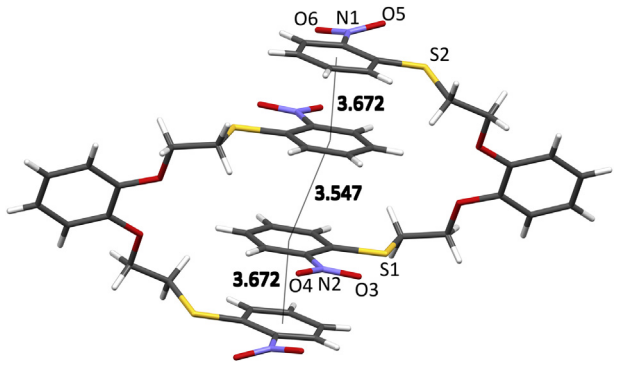


Fig. 4. Illustration of ring face-to-face, π–π stacking interactions between the aromatic rings in dinitropodand **3-a**.

*2.3.2. X-ray structural analysis of compound **5-b**.* Compound **5-b** (Fig. 6) crystallizes in the orthorhombic system, in the centrosymmetric space group *Pbca*, with eight molecules in the unit cell. Selected crystallographic and refinement details are shown in Table 2 while bond lengths, valence angles, and torsion angles are given in Table 2b in the Supplementary data. Analysis of conformation about the nitrogen double bond shows that this compound exists as the (*Z*) isomer. The azoxy moiety is almost coplanar with one phenyl ring (C7–C12), while the dihedral angle to next neighbor ring (C1–C6) is substantially wider (compare the improper torsion angle O3–N1–C7–C8 11.7° and the torsion angle O3–N1–C6–C5 −37.5°). The oxygen atom for the azoxy group is directed outside the macrocycle cavity. Such an orientation has already been noted, e.g., for potassium complex,[12] however for another azoxymacrocycle sodium complex the oxygen atom is directed inside the cage, toward the cation.[13] Valence angles on the sulfur atoms are 102.95(10) and 104.35(10)°, for S1 and S2, respectively, lower than the tetrahedral angle. Heteroatoms O1, O2, S1, S2, and N2 are directed toward the center of the macrocycle enabling potential coordination of a guest cation. In the structure of the 13-membered sulfur analogue, 1,2-azoxy-3,4,12,13-dibenzo-5,11-dithia-8-oxacyclotridecane, sulfur atoms tend to be as far apart as possible

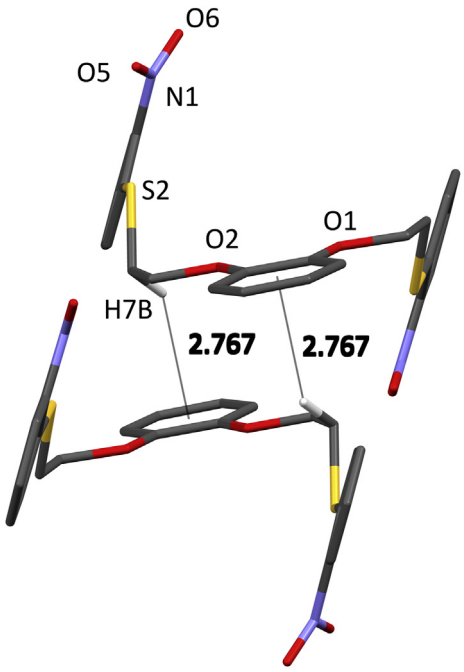


Fig. 5. C–H···π interactions between the aromatic rings and H atoms of ether chains in dinitropodand **3-a** (only interacting H atoms are displayed).

causing an unusual sequence of trans–trans-*anti-gauche* torsion angles in the ether chain.[3] Situation is different for 16-membered analogue,[5] in the polyether chain where the torsion angles around the C–C bonds are *gauche*, and around C–O(S) bonds are trans or *anti* indicating stress-free conformation of polyether chain. A similar situation—both O–C–C–S angles are *gauche*—is observed for compound **5-b**, and the sulfur atoms seem to be directed to the inside of the ring.

The intermolecular interactions (CH···π and π–π ring stacking) found in the crystal structures of the investigated compounds were quite meaningful (Table 3, Figs. 7 and 8). The most widely accepted intermolecular centroids distance for the face-to-face stacking interactions is in the range of 3.4–3.8 Å. In addition, the effective C–H···π distances should be shorter than 3.0 Å (as was implemented by A. Spek in PLATON program (for C–H···π see the Ref. 14). This indicates the presence of relatively strong intermolecular aromatic interactions in **3-a**. Some non-covalent intermolecular interactions operate in the solid state of compound **5-b**. Interactions' parameters are summarized in Table 3 and visualized in Fig. 8. Most significant are C–H···π interactions. The minimal centroids distance is ca. 4.9 Å, which precludes significant interactions between two rings in **5-b**.

3. Experimental section

3.1. General

All materials and solvents used were of analytical grade. Silica gel (0.035–0.070 mm, Fluka) was used for column chromatography. ^{1}H NMR spectra were recorded on a Varian instrument at 200 or 500 MHz. IR spectra were recorded on Genesis II (Mattson) apparatus. The purity and identity of crown ethers was established by high resolution mass spectra carried out on an AMD-604 spectrometer. UV–vis spectra were recorded on a Unicam UV-330 Spectrophotometer. For potentiometric measurements 654 pH-meter (Metrohm) and OP-08201 Ag/AgCl Radelkis reference electrode was used. The melting points (mp) are uncorrected.

Table 3
Intermolecular interactions in compounds **3-a** and **5-b**

Compound **3-a**					
C–H···π					
C–H	Cg	H···Cg, Å	γ, °	C–H···Cg, °	C···Cg, Å
C7–H7B	(C9–C14)#1	2.77	0.62	113	3.522(3)
Ring stacking					
Cg(I)	Cg(J)	Cg(I)–Cg(J), Å	α, °	β, °	$Cg(I)_{perp}$, Å
C17–C22	(C17–C22)#2	3.5475(13)	0	19.13	3.3516(9)
Symmetry codes: #1: *related by* (1−*x*, −*y*, 2−*z*); #2: *related by* (1−*x*, −*y*, 1−*z*)					
Compound **5-b**					
C–H···π					
C–H	Ring I	H···Cg(I), Å	γ, °	C–H···Cg, °	C···Cg(I), Å
C8–H8	(C15–17, C22–24)#1	2.86	5.19	147	3.695(2)
C25–H25B	(C1–C6)#2	2.59	7.22	148	3.472(3)
C26–H26A	(C17–C22)#3	2.86	27.92	142	3.693(2)
Ring stacking					
Ring I	Ring J	Cg(I)–Cg(J), Å	α, °	β, °	$Cg(I)_{perp}$, Å
(C15–C17, C22–C24)	(C1–C6)#4	4.8801(13)	63.50(10)	6.45	1.9908(9)
Symmetry codes: #1: *related by* (*x*, 3/2−*y*, −1/2+*z*); #2: *by* (−*x*, 2−*y*, −*z*) #3: *by* (*x*, 1+*y*, *z*), #4: *by* (*x*, −1+*y*, *z*)					

3.2. General procedure for the synthesis 1-a,b,c

Separately, each of the dihydroxy-substituents, *catechol* (**a**), 2,3-*dihyroxynaphthalene* (**b**), 2,2′-*dihydroxy*-1,1′-*bisnaphthalene* (**c**) (50 mmol), and NaOH (0.12 mol) were dissolved in 20–25 ml ethanol and 2-chloroethanol (0.12 mol) was added to this solution dropwise over 15 min. After refluxing the reaction mixture for 20 h, the resulting solid was separated by filtration. Ethanol was evaporated in vacuo and the resulting oily product was dissolved in 200 ml chloroform. The chloroform solution was washed with 3% NaOH and then with distilled water until the pH reached neutrality.

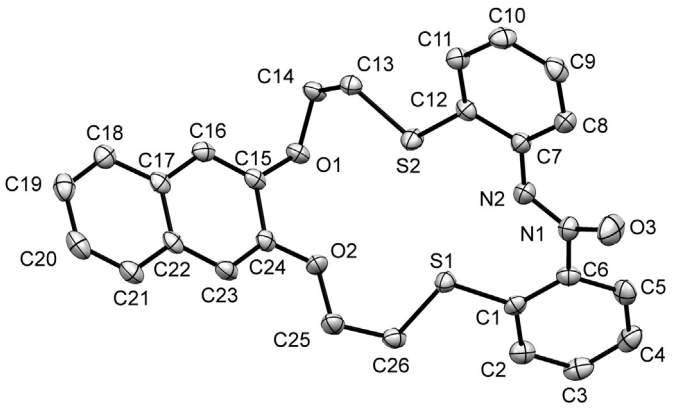


Fig. 6. ORTEP view of compound **5-b** with atom numbering.

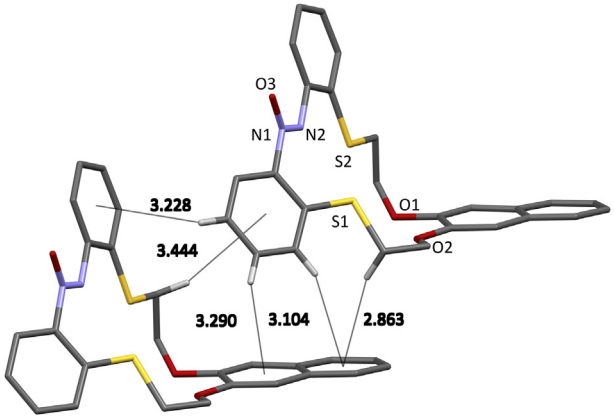


Fig. 7. C–H···π and edge-to-face interactions between the centroids of aromatic rings and H atoms (only interacting H atoms are displayed).

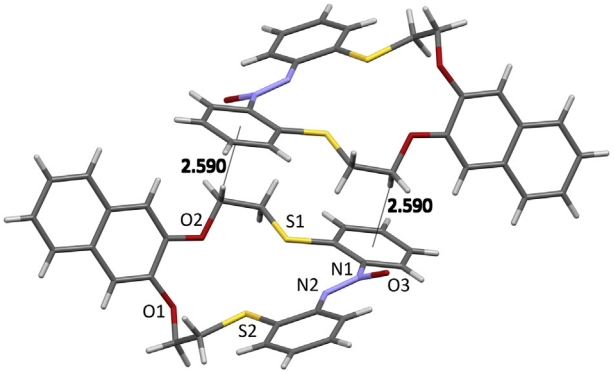


Fig. 8. C–H···π interactions in compound **5-b**.

*3.2.1. 1,2-Bis(2-hydroxyethoxy)benzene (**1-a**).* White solid, yield: 75%, mp: 76–79 °C (lit.[15] mp: 81–83 °C). ^{1}H NMR (500 MHz, DMSO): 3.74 (4H, t, *J*=4.39 Hz, OCH_2); 3.93 (4H, t, *J*=4.43 Hz, CH_2); 4.86 (2H, t, *J*=5.85 Hz, OH); 6.97–7.26 (4H, m, ArH).

*3.2.2. 2,3-Bis(2-hydroxyethoxy)naphthalene (**1-b**).* Brown solid, yield: 65%, mp: 158–164 °C (lit.[16] mp: 146–147 °C). ^{1}H NMR (500 MHz, DMSO): 3.78 (4H, t, *J*=5.19 Hz, OCH_2); 4.10 (4H, t, *J*=4.88 Hz, CH_2); 4.88 (2H, t, *J*=5.49 Hz, OH); 7.27–7.31 (4H, m, ArH); 7.69–7.72 (2H, m, ArH).

*3.2.3. 2,2′-Bis(2-hydroxyethoxy)-1,1′-binaphthalene (**1-c**).* Gray solid, yield: 80%, mp: 105–106 °C (lit.[17] mp: 112–114 °C). ^{1}H NMR (500 MHz, DMSO): 3.35–3.40 (4H, m, OCH_2); 3.95–4.05 (4H, m, CH_2); 4.55 (2H, t, *J*=5.37 Hz, CH_2OH); 6.88–6.90 (2H, m, ArH); 7.18–7.22 (2H, m, ArH); 7.28–7.32 (2H, m, ArH); 7.58–7.61 (2H, m, ArH); 7.90–7.94 (2H, m, ArH); 8.0–8.20 (2H, m, ArH).

*3.2.4. Identification of the vinyl sulfide (**1d**).* ^{1}H NMR (500 MHz, DMSO): 5.77 (1H, d, *J*=9.28 Hz, CH_2); 5.85 (1H, d, *J*=16.6 Hz, CH_2); 6.58 (1H, d, *J*1=9.28 Hz, *J*2=17.09 Hz, SCH); 7.32 (1H, t, *J*=8.3 Hz, ArH); 7.45 (1H, d, *J*=8.3 Hz, ArH); 7.56 (1H, t, *J*=8.3 Hz, ArH); 8.17 (1H, *J*=8.3 Hz, ArH).

3.3. General procedure for the syntheses of 2-a,b,c

Separately, each of the compounds **1-a**, **1-b**, **1-c** (30 mmol) and pyridine (60 mmol, 4.83 ml) were added into an ice-cooled round

bottomed flask and stirred. Thionyl chloride (78 mmol) was added to the flask dropwise at 0 °C over 30 min. The mixture was refluxed at 70 °C for 2 h. After the solvent was evaporated in vacuo, the residue was mixed with benzene and filtered under vacuum to remove the deposited pyridine hydrochloride. The benzene solution was washed with water and the benzene layer containing the title compound was isolated which subsequently evaporated *in vacuo*.

*3.3.1. 1,2-Bis(2-chloroethoxy)benzene (**2-a**).* Compound (**2-a**) was obtained as a white solid after recrystallization from methanol, yield: 38%, mp 52–56 °C (lit.[18] mp: 50–52 °C). ^{1}H NMR (500 MHz, DMSO): 3.68 (4H, t, J=4.45 Hz, OCH_2); 3.96 (4H, t, J=4.43 Hz, CH_2); 6.90–7.10 (3H, m, ArH); 7.26 (1H, s, ArH).

*3.3.2. 2,3-Bis(2-chloroethoxy)naphthalene (**2-b**).* Compound (**2-b**) was obtained as a pale brown solid after recrystallization from methanol yield: 34.5%, mp: 94–96 °C (lit.[19] mp: 90–92 °C). ^{1}H NMR (500 MHz, DMSO): 3.80–4.10 (4H, m, OCH_2); 4.20–4.40 (4H, m, CH_2); 7.20–7.50 (4H, m, ArH); 7.60–7.80 (2H, m, ArH).

*3.3.3. 2,2′-Bis(2-chloroethoxy)-1,1′-binaphthalene (**2-c**).* Compound (**2-c**) was obtained as a white solid after crystallization from methanol, yield: 22.3%, mp 100–103 °C (lit.[17] mp: 100–103 °C). ^{1}H NMR (200 MHz, DMSO): 3.39 (4H, t, J=6.27 Hz, OCH_2); 4.10–4.30 (4H, m, CH_2); 7.10–7.50 (8H, m, ArH); 7.80–8.05 (4H, m, ArH).

3.4. General procedure for the syntheses of 3-a,b,c

Separately, each of the compounds **2-a**, **2-b** or **2-c** (4.5 mmol) was added into a solution of *o*-nitrothiophenol (9 mmol, 1.4 g) in DMF, in the presence of anhydrous potassium carbonate (9 mmol, 1.24 g) and stirred for 20 h at 70 °C. After cooling, the reaction mixture was diluted with ice-water. Upon the addition of water, the precipitate was obtained. The precipitate was isolated by filtration and washed with water.

*3.4.1. 1,2-Bis(2-(2-nitrophenylthio)ethoxy)benzene (**3-a**).* Compound (**3-a**) was obtained from **2-a** as a yellow solid after recrystallization from methanol. Yield: 58%, mp 138–143 °C. ^{1}H NMR (200 MHz, DMSO): 3.45 (4H, t, J=6.23 Hz, SCH_2); 4.23–4.28 (4H, m, OCH_2); 6.89–7.0 (4H, m, ArH); 7.30–7.45 (2H, m, ArH); 7.60–7.80 (4H, m, ArH); 8.10–8.20 (2H, m, ArH). HRMS (EI) M^+ found 472.5022. $C_{22}H_{20}N_2O_6S_2$ requires 472.5016. IR (film) 2980, 1610, 1555, 1345, 1230, 1095, 851, 750 cm^{-1}.

*3.4.2. 2,3-Bis[2-(2-nitrophenylthio)ethoxy]naphthalene (**3-b**).* Compound (**3-b**) was obtained from **2-b** as a yellow solid. Yield: 75.7%, mp 172–175 °C. ^{1}H NMR (200 MHz, DMSO): 3.54 (4H, t, J=6.23 Hz, SCH_2); 4.36 (4H, t, J=6.31 Hz, OCH_2); 7.27–7.45 (6H, m, ArH); 7.53–7.90 (6H, s, ArH); 8.10–8.20 (2H, m, ArH). HRMS (EI) M^+ found 522.5558. $C_{26}H_{22}N_2O_6S_2$ requires 522.5603. IR (film) 3000, 1610, 1524, 1349, 1220, 1130, 860, 753 cm^{-1}.

*3.4.3. 2,2′-Bis[2-(2-nitrophenylthio)ethoxy]-1,1′-binaphthalene (**3-c**).* Compound (**3-c**) was obtained from **2-c** as a yellow solid. Yield 54.6%, mp: 158–160 °C ^{1}H NMR (200 MHz, DMSO): 3.50–3.52 (4H, m, SCH_2); 4.20–4.35 (4H, m, OCH_2); 6.80–7.0 (2H, m, ArH); 7.15–7.45 (8H, m, ArH); 7.52–7.70 (4H, m, ArH); 7.90–8.10 (6H, m, ArH). HRMS (EI) M^+ found 472.5022. $C_{22}H_{20}N_2O_6S_2$ requires 472.5016. IR (film) 2880, 1625, 1550, 1345, 1340, 1240, 1100, 850, 760 cm^{-1}.

3.5. General procedure for the syntheses of 4-a,b,c and 5-a,b,c

Separately, each of the dinitro-derivatives **3-a**, **3-b**, **3-c** (2 mmol) was suspended in a mixture of acetone and water (1:1) in a round bottomed flask and NaOH (60 mmol, 2.39 g) was dissolved in the mixture. Then stannous chloride dihydrate (7 mmol, 1.58 g) was added to the mixture. After the strongly exothermic reaction ceased, the reaction was refluxed at 70 °C for 3 h.

In the case of crown ethers **4-a**, **5-a** and **4-c**, **5-c**, the resulting precipitate was removed by filtration in vacuo and washed with acetone. After the evaporation of acetone in vacuo, resulting products were purified by column chromatography using methylene chloride as eluent.

In the case of naphthalene substituted crown ethers **4-b** and **5-b**, toluene was added to the cooled reaction mixture and the precipitated sodium chloride was removed by filtration in vacuo. Filtered NaCl was washed with toluene and the filtrates were combined. After washing the filtrates with water, the organic layer was separated and evaporated in vacuo. Resulting crude, dark brown product was chromatographed on silica gel column using firstly methylene chloride and then a mixture of methylene chloride–methanol (10:1) as the eluent.

*3.5.1. Azocrown ether (**4-a**).* Compound (**4-a**) was obtained as an orange solid in 12% yield, mp: 155–158 °C. ^{1}H NMR (500 MHz, DMSO): 3.35 (2H, t, J=5.37 Hz, SCH_2); 3.41 (2H, t, J=5.37 Hz, SCH_2); 4.20–4.23 (4H, m, OCH_2); 6.84–6.88 (2H, m, ArH); 6.96–7.0 (2H, m, ArH); 7.25–7.28 (1H, m, ArH); 7.32–7.38 (2H, m, ArH); 7.54–7.58 (2H, m, ArH); 7.60–7.64 (1H, m, ArH); 7.90–7.96 (2H, m, ArH); HRMS (EI) M^+ found 424.1487. $C_{22}H_{20}N_2O_2S_2$ requires 408.1566. IR (film): 2965, 1600, 1550, 1430, 1360, 1100, 760 cm^{-1}.

*3.5.2. Azoxycrown ether (**5-a**).* Compound (**5-a**) was obtained as a yellow solid in 20% yield, mp: 146–148 °C. ^{1}H NMR (500 MHz, DMSO): 3.36–3.42 (4H, m, SCH_2); 4.15–4.25 (4H, m, OCH_2); 6.82–6.90 (2H, m, ArH); 6.94–7.0 (2H, m, ArH); 7.22–7.30 (1H, m, ArH); 7.32–7.38 (2H, m, ArH); 7.52–7.58 (2H, m, ArH); 7.60–7.64 (1H, m, ArH); 7.88–7.90 (1H, m, ArH); 8.10–8.12 (1H, m, ArH); HRMS (EI) M^+ found 408.1623. $C_{22}H_{20}N_2O_3S_2$ requires 424.15153. IR (film): 2940, 1630, 1520, 1460, 1400, 1160, 1150, 750 cm^{-1}.

*3.5.3. Azocrown ether (**4-b**).* Compound (**4-b**) was obtained as an orange solid in 30% yield, mp: 188–190 °C. ^{1}H NMR (500 MHz, DMSO): 3.53 (4H, t, J=6.35 Hz, SCH_2); 4.35 (4H, t, J=6.35 Hz, OCH_2); 7.28–7.32 (3H, m, ArH); 7.36–7.40 (3H, m, ArH); 7.68–7.74 (4H, m, ArH); 7.78–7.81 (3H, m, ArH); 8.14–8.18 (1H, m, ArH); HRMS (EI) M^+ found 458.1668. $C_{26}H_{22}N_2O_2S_2$ requires 458.1722. IR (film): 2970, 1500, 1470, 1290, 1140, 1100, 750 cm^{-1}.

*3.5.4. Azoxycrown ether (**5-b**).* Compound (**5-b**) was obtained in 10% yield, mp 174–177 °C. ^{1}H NMR (500 MHz, DMSO): 3.45 (2H, t, J=5.37 Hz, SCH_2); 3.51 (2H, t, J=5.38 Hz, SCH_2); 4.32–4.40 (4H, m, OCH_2); 7.21–7.38 (6H, m, ArH); 7.52–7.58 (2H, m, ArH); 7.60–7.62 (2H, m, ArH); 7.63–7.67 (2H, m, ArH); 7.83–7.87 (2H, m, ArH). HRMS (EI) M^+ found 474.1655. $C_{26}H_{22}N_2O_3S_2$ requires 474.1671. IR (film): 12,960, 1625, 1500, 1470, 1390, 1140, 1100, 750 cm^{-1}.

*3.5.5. Azocrown ether (**4-c**).* Compound (**4-c**) was obtained in 28% yield, mp: 178–181 °C. ^{1}H NMR (500 MHz, DMSO): 3.50–3.52 (4H, m, SCH_2); 4.20–4.35 (4H, m, OCH_2); 6.90 (2H, t, J=7.32 Hz, ArH); 7.16–7.24 (4H, m, ArH); 7.28–7.38 (6H, m, ArH); 7.40–7.42 (2H, m, ArH); 7.50–7.60 (2H, m, ArH); 7.80–7.95 (4H, m, ArH). HRMS (EI) M^+ found 584.2146. $C_{36}H_{28}N_2O_2S_2$ requires 584.2192. IR (film): 2960, 1600, 1500, 1450, 1360, 1180, 1050, 740 cm^{-1}.

*3.5.6. Azoxycrown ether (**5-c**).* Compound (**5-c**) was obtained in 12% yield, mp 102–107 °C ^{1}H NMR (500 MHz, DMSO): 3.52–3.54 (4H, m, SCH_2); 4.25–4.35 (4H, m, OCH_2); 6.84–6.92 (2H, m, ArH); 7.12–7.22 (4H, m, ArH); 7.26–7.32 (6H, m, ArH); 7.42–7.46 (2H, m, ArH); 7.52–7.56 (1H, m, ArH); 7.82–7.98 (4H, m, ArH); 8.10–8.15 (1H, m, ArH). HRMS (EI) M^+ found 600.2201. $C_{36}H_{28}N_2O_3S_2$ requires

600.2141. IR (film): 2960, 1620, 1530, 1420, 1410, 1200, 1050, 760 cm^{-1}.

3.6. Membrane preparation and potentiometric measurement

The preparation of membranes for ion-selective electrodes was described earlier in detail.[20] Typical composition of membranes is: ionophore (5 mg), potassium tetrakis(*p*-chlorophenyl)borate (0.5 mg), poly(vinylchloride) (50 mg), and *o*-nitrophenyl octyl ether (0.1 ml). Then the cocktail was applied to screen-printed graphite electrodes via capillary. The solutions were allowed to evaporate overnight. The internal electrolyte was 1 mol dm^{-3} potassium chloride solution. The electrodes were soaked into 10^{-2} mol dm^{-3} KCl solution before measurements. The selectivity coefficients were determined using the separate solution method (SSM) 6 at 10^{-2} mol dm^{-3} activities of metal cations. Measurements were conducted using LAB LAWSON's potentiometer connected with computer.

3.7. Determination of X-ray structures

Experimental diffraction data were collected on a KM4 CCD kappa-geometry diffractometer (Oxford diffraction), equipped with a Sapphire2 CCD detector. An enhanced X-ray Mo Kα radiation source with a graphite monochromator was used. Determination of the unit cell and diffraction data collection were carried out at 120 K in a stream of dry nitrogen (Oxford CryoSystems). All calculations (data reduction, structure solution, and refinement) were carried out using CrysAlisPro[21] package. The structure was solved by direct methods, and all nonhydrogen atoms were refined with anisotropic thermal parameters by full-matrix least squares procedure based on F^2. Final refinements were carried out using the SHELX-97 package,[22] run under control of WinGX program.[23] CCDC-836043 and -836044 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via: www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data

Valence and torsion angles of compounds **3-a** and **5-b** are available in supplementary data file, in Table 2a and Table 2b, respectively. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.09.100. These data include MOL files and InChiKeys of the most important compounds described in this article.

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