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Synthesis of podands bearing aromatic end groups and complex formation with tropylium tetrafluoroborate in 1,2-dichloroethane

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ABSTRACT: A series of podands bearing phenyl, naphthyl and anthryl end groups were prepared and characterized. UV–visible spectrophotometry was used to investigate the host–guest chemistry of the podands in complexation with tropylium tetrafluoroborate in 1,2-dichloroethane. The results are discussed and compared with those for previously studied systems containing crown ethers. The stability constants for these open-chain polyethers are in the range 5.1–8.4 $dm^3\,mol^{-1}$, except for the podand having anthryl end groups [1,12-bis(anthryl-9)-2,5,8,11-tetraoxadodecane], which gives a 10-fold increase in the stability constant. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: molecular recognition; π–π stacking; podands; tropylium tetrafluoroborate

INTRODUCTION

Crown ethers and their acyclic analogues, podands,[1] are of wide interest because of their tendency to form complexes with cations and uncharged organic molecules. The research on crown ethers and podands has mostly focused on their complexation with alkali metals, alkaline earth metals and ammonium cations, but complexation has also been demonstrated with diazonium, hydronium, acylium and hydrazinium species.[2] Recently, investigations in host–guest chemistry have focused on molecular recognition and the potential of π–π interactions to secure strong and selective binding for organic molecules. We have demonstrated that π–π stacking and cation–π interactions play a significant role in the host–guest complexation between benzene-substituted crown ethers and electron-deficient aromatic carbenium ions such as tropylium[3,4] and pyridinum.[5] Tropylium ion has been shown to be an ideal guest for investigation of π–π interactions. It is a monocharged organic cation containing an even number of electrons and as such represents a new type of guest in host–guest chemistry. That tropylium ion is an effective π-acceptor is exemplified by the successful synthesis of many intramolecular and intermolecular charge-transfer complexes with aromatic hydrocarbons.[6,7] In addition, a large number of tropyliophanes, which have the tropylium ion as a part of the molecular skeleton, and other macrocyclic compounds containing tropylium ion have been synthesized.[8–10]

The capability of podands for complex formation with organic molecules depends on several factors, including the number and nature of the donor atoms, ring size, substituents and topological and conformational properties.[1] The selectivity and binding efficiency of podand molecules can be improved by adding functional groups in terminal position(s), while their wrap-around capability can be modified through substitution of the polyether chain. The aromatic end groups should be such as to allow π–π stacking interaction with aromatic guests. Likewise, enlargement of the aromatic surface in podands would be expected to improve and strengthen the complexation with an aromatic guest.

Here we report the synthesis and characterization of a series of podands bearing aromatic substituents at both ends of the oligoether chain. The capability of the podands for complexation with an organic guest was studied with tropylium tetrafluoroborate in 1,2-dichloroethane (DCE) by UV–visible absorption spectrophotometry. An important aim of the study was to determine the influence of the macrocyclic effect, donor atoms and aromatic substituents on the complexation of aromatic cations. A comparison between crown ethers and podands was undertaken as it was expected to be informative for the development of new tweezer-type hosts capable of π–π binding with cationic organic molecules.

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RESULTS AND DISCUSSION

Synthesis

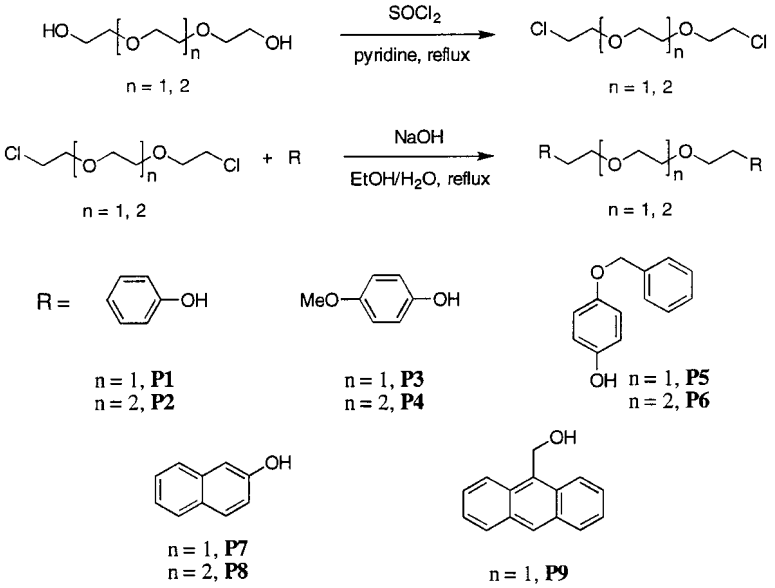
Our aim was to prepare acyclic analogues of previously investigated benzene-substituted crown ethers, which contain multiple binding sites bearing aromatic substituents. In particular, we were interested in the introduction of large aromatic substituents at the end of the acyclic polyether chain. We applied the 'end group concept'[11] to imitate the structure of crown ethers substituted with benzene or other aromatic groups. In essence, this is the recognition that when conformationally flexible systems are rigidified, they become stronger complexing agents and form more ordered crystals. Aromatic groups were introduced into the terminal positions by the Williamson ether synthesis (Scheme 1). The reactants were dichlorinated or ditosylated glycols were prepared from the respective glycols and commercially available aromatic alcohols. The 4-(benzyloxy)phenyl-substituted podands **P5** and **P6** are also precursors for the dibenzo-substituted crown ethers 2B28C8 and 2B34C10, respectively.[12]

Several combinations of bases and solvents tested in the preparation of an anthracene-substituted podand from chlorinated or tosylated glycols and 2-aminoanthracene or 2-hydroxyanthracene, but without success. However, a reaction between 9-(hydroxymethyl)anthracene and triethylene glycol ditosylate in the presence of sodium hydride led to the anthracene-substituted podand 1,12-bis(9-anthryl)-2,5,8,11-tetraoxadodecane (**P9**).

Properties of complexes

The complexation behaviour of the podands in DCE with tropylium tetrafluoroborate was followed by absorption changes in the UV–visible spectra. Except for **P9**, a yellow–orange colour developed spontaneously upon the addition of podand to a solution of tropylium tetrafluoroborate in dry DCE. The anthracene-substituted podand **P9** behaved differently; its addition to a solution of tropylium ion in DCE induced the development of intense red colour. The electronic spectrum of the substituted podands in the presence of tropylium ion exhibited a broad wavelength absorption at 300–600 nm. For example, the addition of 3-methoxybenzene-substituted podand (**P3**) to DCE solutions containing tropylium salt led to the appearance of a new absorption band with maximum at about 465 nm, not found in the spectrum of either tropylium tetrafluoroborate or **P3**. The intensity of the new band increased with the incremental additions of podand. The band is indicative of a charge-transfer interaction and the formation of a molecular complex between tropylium ion and the podand (Fig. 1). The substantial hypsochromic (blue) shift from 468 to 435 nm accompanying the change from DCE to MeCN as solvent (Fig. 2) is in accordance with the solvent sensitivity of a charge-transfer band.

The method of continuous variation, or Job's method,[13] was used to confirm the stoichiometry of the complex. As can be seen in Fig. 3, the occurrence of a maximum at a mole fraction of 0.5 implies that only one complex (1:1) was present under the conditions used. Typical double-reciprocal plots for the podand–tropylium ion complexes revealed a linear relationship for the entire range of concentrations tested. This was further evidence for the 1:1 stoichiometry of the complexes in solution. Values for the stability constants K and molar absorptivities of complex ε_C in DCE for podand–tropylium ion complexes were calculated by the Rose and Drago method.[3,14] Results are given in Table 1.



Scheme 1.

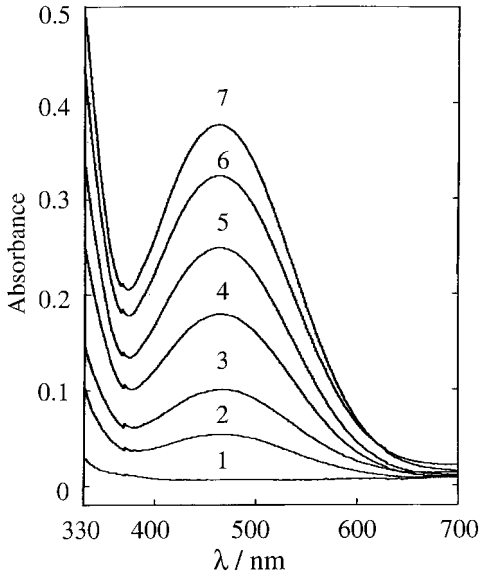


Figure 1. Absorption spectra of tropylium tetrafluoroborate (2.0×10^{-3} M) in DCE solutions at 25 °C in the presence of increasing amounts of **P3**: (1) 0, (2) 0.006, (3) 0.012, (4) 0.024, (5) 0.036, (6) 0.048 and (7) 0.06 M

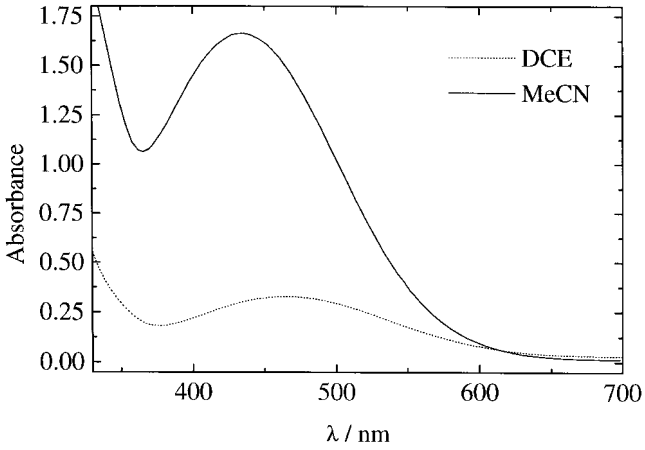


Figure 2. Absorption spectra of **P3**–tropylium tetrafluoroborate complex in DCE and MeCN solutions at 25 °C. The change of solvent from DCE to MeCN is accompanied by a hypsochromic shift (33 nm)

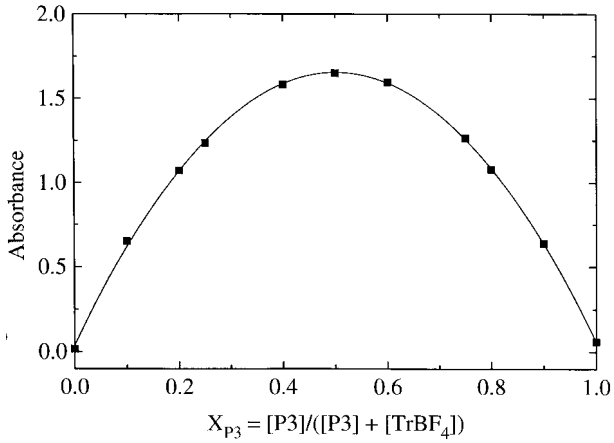


Figure 3. Job plot for **P3**–tropylium tetrafluoroborate in DCE at 25 °C, $\lambda = 425$ nm

The data in Table 1 suggest that stepwise extension of the polyether chain does not lead to an enhancement of the binding of the tropylium ion. Likewise, the values of the stability constant generally responded only slightly to changes in the aromatic substituent. Again, the anthracene-substituted podand **P9** constitutes an exception; the value of the stability constant of **P9** (85.5 ± 4.3 $dm^3\,mol^{-1}$) is 10 times larger than the values for the other podands studied. The number of oxygen atoms involved in the complexation with tropylium ion has an impact on the stability of the complexes. Comparison of the K values[3] of 0.7 ± 0.1 $dm^3\,mol^{-1}$ for 1,4-diphenoxybutane–tropylium (1,4-diPhBu) and 1.5 ± 0.2

Table 1. Stability constants, molar absorptivities of complexes and free energies of binding for the interaction of podands with tropylium ion in 1,2-dichloroethane solution at 25 °C[a]

Podand	λ_{max} (nm)	K ($dm^3\,mol^{-1}$)	ε_C ($dm^3\,mol^{-1}\,cm^{-1}$)	$-\Delta G°$ (kJ mol^{-1})	r^2
P1	410	7.6 ± 1.0	662 ± 43	5.01	0.9966
P2	425	5.9 ± 2.3	726 ± 199	4.42	0.9719
P3	465	5.1 ± 0.7	791 ± 82	4.05	0.9995
P4	475	5.2 ± 0.5	573 ± 43	4.06	0.9997
P5	460	7.7 ± 1.7	710 ± 123	5.05	0.9977
P6	450	6.7 ± 1.2	909 ± 108	4.73	0.9969
P7	470	7.1 ± 0.4	1408 ± 69	4.85	0.9999
P8	430	8.4 ± 3.3	1447 ± 353	5.28	0.9809
P9	502	86.2 ± 4.6	1765 ± 31	11.05	0.9995
2B18C6[b]	435	128.5 ± 4.1	1575 ± 18	12.04	—
2B24C8[b]	425	273.5 ± 13.8	1060 ± 13	13.91	—
1,4-DiPhBu[c]	425	0.7 ± 0.1	—	—	—
1,8-DiPhOc[c]	423	1.5 ± 0.2	—	—	—

[a] Values were calculated from the absorbance at selected wavelength by the method of Rose and Drago, Eqn. (1). Crown ethers are included for comparison.
[b] Ref. 3.
[c] Ref. 4.

$dm^3\ mol^{-1}$ for 1,8-diphenoxyoctane–tropylium (1,8-diPhOc) in DCE at 25 °C with our present *K* values shows that the stability of the complexes increases with increasing number of oxygen donors in the acyclic chain (Table 1). The length of the carbon chain in 1,8-diphenoxyoctane is the same as in **P2**, and equal to the length of the opened macrocycle of 12-crown-4 or half of the length of opened macrocycle of 24-crown-8. The crown ethers dibenzo-24-crown-8 (2B24C8) and dibenzo-30-crown-10 (2B30C10) are the cyclic counterparts of the podands **P1** and **P2**, and the stability constants of 274 $dm^3\ mol^{-1}$ for 2B24C8–tropylium[3] and 418 $dm^3\ mol^{-1}$ for 2B30C10–tropylium complexes[3] in DCE at 25 °C demonstrate that the steric factors and macrocyclic nature of the host molecule play an important role in the complexation of tropylium ion (Table 1).

The x-ray crystal structure of the solid 1:1 complex formed between 2B24C8 and tropylium tetrafluoroborate has revealed that the electron-deficient tropylium ring is inserted into the cavity of the macrocycle between two adjacent benzene rings.[15] The data in Table 1 indicate that the acyclic host molecules are not able to form a cleft-like cavity stable enough for tropylium cation. The wrap-around capability of podands has been exploited in many metal ion complexes.[16] In these podand–metal complexes, cations are surrounded by oxygen atoms and the addition of suitable end groups enhances the ligand rigidity sufficiently to permit the isolation of the complexes. Because of the size and nature of tropylium ion, a similar wrap-around phenomenon is not encountered in the podand–tropylium ion systems studied here. The flexibility of the polyether chain and the weakness of the π-stacking interaction in the absence of a well shaped cavity result in relatively weak binding between the podands and tropylium ion. Substitution of the benzene rings and increase in the aromatic surface from benzene to naphthalene both have only a minimal effect on the stability of the complexes. This observation provides further evidence that the π–π interaction, face-to-face or edge-to-face, cannot contribute with full efficacy to the tropylium complexation with acyclic hosts. The sizeable stability constant of **P9** shows that the structural factors of the ligands are of considerable importance in the podand–tropylium ion complexation. Multiple binding is important in the molecular recognition of both neutral and charged organic molecules and the requirements of steric and functional complementarity and spatial preorganization of the host compound are correspondingly high.[17] The attachment of anthracene to the polyether chain via the methyl group in position 9 and the area of the aromatic surface differentiate **P9** from the other podands studied. Evidently the spatial preorganization and therefore the π–π interaction also have a greater effect on the stability of the **P9**–tropylium complex than on the stability of the other podand complexes in the present study.

In an attempt to shed light on the complexation of podands with tropylium ion, we carried out semiempirical RHF-AM1 calculations for the **P1**–tropylium system using Gaussian 94.[18] As a starting point we took the crystal structure of the 2B24C8–tropylium tetrafluoroborate complex.[4] The cyclic structure of the crown ethers was broken by removing one of the polyether chains and the counter ion was also taken away. Figure 4 shows the geometry-optimized structure of the **P1**-tropylium ion complex. Dotted lines indicate the possible interactions. Similar characteristics were also displayed by the optimized 1,7-bis(phenyl)-1,4,7-trioxaheptane–tropylium and 1,7-bis(3-methoxyphenyl)-1,4,7-trioxaheptane–tropylium cation structures derived from the unsatisfactorily solved structure of the 2B18C6–tropylium tetrafluoroborate complex.[4] The observed edge-to-face interaction between the aromatic units in the calculated structures differs from the interaction in the crystal structures of the complexes formed between dibenzo-crown ethers and tropylium cation, where the face-to-face stacking is observed.[4] The calculated structures emphasize the importance of the interactions between oxygen atoms in the podand framework and tropylium cation. The lower stability constant of the 1,8-diphenoxyoctane (two oxygen atoms) than **P1** (four oxygen atoms) complexes in DCE solution (Table 1) agrees well with the importance of direct interactions between oxygen atoms and the tropylium ion. Additionally, we have previously observed by fast atom bombardment mass spectrometry that tropylium ions form complexes in the gas phase with acyclic polyethers without aromatic substituents in the polyether chain.[19]

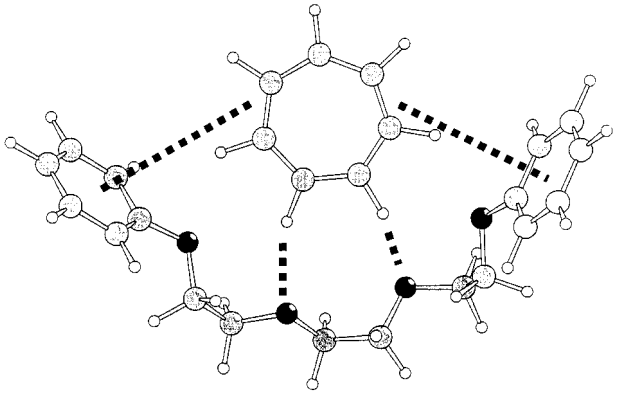


Figure 4. Calculated (RHF-AM1) minimum energy conformation of **P1**–tropylium ion complex

CONCLUSIONS

The intermolecular interactions in the complexation of organic guest molecules are essentially weaker than those in the complexation of metal ions. Among the noncovalent intermolecular forces that contribute to the complex formation between podand and tropylium ion are cooperative interactions, such as aromatic–aromatic

π–π interaction between the electron-rich and electron-deficient aromatic units, CH— O hydrogen bonding between the polyether oxygen atoms and the tropylium hydrogen atoms and electrostatic cation–π interactions between the π-face of an aromatic system and the positive charge of tropylium ion. The same forces also play a significant role in self-assembly processes where large ordered nanometre-scale structures are formed in a selective way from relatively small molecular compounds. Recently, podands and their complexation capability have been utilized in supramolecular chemistry, most notably in the preparation of rotaxanes and pseudorotaxanes.[20]

EXPERIMENTAL

Materials and methods. The starting materials were purchased from commercial sources and used without further purification, unless mentioned otherwise. Acetonitrile (MeCN) (Fluka, Buchs, Switzerland) and 1,2-dichloroethane (DCE) (Lab-Scan, Dublin, Ireland) were dried and distilled according to literature procedures.[21] 1,8-Dichloro-3,6-dioxaoctane and 1,11-dichloro-3,6,9-trioxaundecane were prepared by a literature method[22] from triethylene glycol (Fluka) and tetraethylene glycol (Fluka), respectively. Thin-layer chromatography (TLC) was carried out on aluminium plates coated with silica gel. Compounds were detected by UV radiation measurement. Flash column chromatography was performed on silica gel with the solvents specified. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM200 spectrometer. NMR chemical shifts are reported in ppm downfield from internal tetramethylsilane (TMS). The coupling constants are expressed in Hz. Electron ionization (EI) and fast atom bombardment (FAB) mass spectra were obtained using a Kratos MS 80 mass spectrometer operating with the DART data system. Ultraviolet–visible (UV–visible) spectra were recorded with a Philips PU 8740 spectrophotometer and matched glass cells of 10 mm pathlength. The cell containing the solution was maintained within to $\pm$0.05 °C of a set temperature by circulating water from a thermostated bath through a double-walled cell insert. The temperature inside the cell was monitored with a digital thermometer. Small amounts of the compounds were accurately weighed with a Perkin-Elmer AD-2 autobalance. Elemental analysis was carried out with a Perkin-Elmer 2400 apparatus. Melting points (m.p.) were determined with a Thermopan microscope (Reichert, Vienna, Austria) melting-point apparatus and are uncorrected.

General procedure for the synthesis of substituted podands P1–P8. A mixture of NaOH (2.04 g, 0.051 mol), aromatic alcohol (0.05 mol) and dichloroglycol (0.025 mol) was stirred and heated at reflux in 20 ml of H_2O–EtOH (1:1) for 16–24 h, after which the reaction mixture was allowed to cool to room temperature. The mixture was partitioned between dichloromethane and water. The organic layer was separated and washed with 5% NaOH solution, water and brine and dried over $MgSO_4$. Evaporation gave the crude product, which was subjected to further purification.

1,10-Diphenyl-1,4,7,10-tetraoxaundecane (P1). The compound was prepared in 75% yield by literature method.[23] White crystals; m.p. 43 °C (lit. 43.5–45 °C);[23] 1H NMR ($CDCl_3$, 25 °C), δ 7.22–7.32 (4H, aryl, m), 6.87–6.92 (6H, aryl, m), 4.13 (4H, α-CH_2, t, J = 4.37 Hz), 3.87 (4H, β-CH_2, J = 4.6 Hz, t), 3.76 (4H, γ-CH_2, s); ^{13}C NMR ($CDCl_3$, 25 °C), δ 68.1, 70.5, 71.6, 115.4, 121.5, 130.1; EI MS (70 eV), m/z 302 [M^+]; HRMS (EI), calculated 302.1518, observed 302.1512.

1,13-Diphenyl-1,4,7,10,13-pentaoxatridecane (P2). 1,11-Dichloro-3,6,9-trioxaundecane was converted to the title product and isolated as a colourless oil in 84% yield by distillation. B.p. 151 °C (0.1 mmHg); ^{1}H NMR ($CDCl_3$, 25 °C), δ 7.21–7.31 (4H, aryl, m), 6.81–6.98 (6H, aryl, m), 4.12 (4H, α-CH_2, m), 3.87 (4H, β-CH_2, m), 3.87 (8H, γ-η-CH_2, m); ^{13}C NMR ($CDCl_3$, 25 °C), δ 68.2, 70.5, 71.4, 115.5, 121.6, 130.1, 159.8; EI MS (70 eV), m/z 346 [M^+]; CI (NH_3) MS, m/z 365 [$M + NH_3$]$^+$; HRMS (EI), calculated 346.4224, observed 346.1777.

1,10-Bis(4-methoxyphenyl)-1,4,7,10-tetraoxaundecane (P3). Recrystallization from EtOH afforded the title compound as a white crystalline solid in 96% yield. M.p. 70 °C; ^{1}H NMR ($CDCl_3$, 25 °C), δ 6.78 (8H, aryl, s), 5.18 (4H, α-CH_2, m), 3.60–3.80 (6H, OCH_3, 4H, 8H, γ-η-CH_2, m); ^{13}C NMR ($CDCl_3$, 25 °C), δ 43.4, 56.5, 71.3, 72.1, 115.6, 116.7, 150.2, 154.4; EI MS (70 eV), m/z 362 [M^+], CI (NH_3) MS, m/z 380 [$M + NH_3$]$^+$; HRMS (EI), calculated 362.1729, observed 362.1712.

1,13-Bis(4-methoxyphenyl)-1,4,7,10,13-pentaoxatridecane (P4). Subjection of the colourless oil to silica gel column chromatography with EtOAc–*n*-hexane (1:1) as the eluent afforded **P4** in 82% yield. ^{1}H NMR ($CDCl_3$, 25 °C), δ 6.78–6.88 (8H, aryl, m), 4.06 (4H, α-CH_2, t, J = 4.8 Hz), 3.82 (4H, β-CH_2, t, J = 4.8 Hz), 3.75 (6H, OCH_3, s), 3.70 (8H, γ-η-CH_2, m); ^{13}C NMR ($CDCl_3$, 25 °C), δ 56.3, 68.7, 70.5, 71.3, 71.4, 115.2, 153.6, 154.5; EI MS (70 eV), m/z 406 [M^+]; HRMS (EI), calculated 406.1991, observed 406.1966.

1,8-Bis[(4-benzyloxy)phenoxy]-3,6-dioxaoctane (P5). 4-Benzyloxyphenol (Aldrich, Milwaukee, WI, USA) was used as a starting material. The crude product was recrystallized from CH_2Cl_2–Et_2O affording a white crystalline solid in 28% yield. M.p. 110 °C; ^{1}H NMR ($CDCl_3$, 25 °C), δ 7.30–7.40 (10H, aryl, m), 6.81–6.91 (8H, aryl, m), 5.00 (4H, CH_2, s), 4.08 (4H, α-CH_2, t, J = 4.8 Hz), 3.83 (4H, β-CH_2, J = 4.8 Hz, t), 3.74 (4H, γ-

CH_2, s); ^{13}C NMR ($CDCl_3$, 25 °C), δ 68.8, 70.6, 71.4, 71.5, 116.3, 116.5, 128.2, 128.6, 129.2, 153.9; EI MS (70 eV), *m*/*z* 514 [M^+]; HRMS (EI), calculated 514.2355, observed 514.2359.

1,11-Bis[(4-benzyloxy)phenoxy]-3,6,9-trioxaundecane (P6). The white solid was obtained after recrystallization from CH_2Cl_2–Et_2O, yield 88%. M.p. 84 °C; ^1H NMR ($CDCl_3$, 25 °C), δ 7.30–7.43 (10H, aryl, m), 6.80–6.91 (8H, aryl, m), 5.00 (4H, CH_2, s), 4.07 (4H, α-CH_2, t, J = 4.8 Hz), 1.98 (4H, α-CH_2, t, J = 4.8 Hz), 3.70 (8H, γ--CH_2, m); ^{13}C NMR ($CDCl_3$, 25 °C), δ 68.1, 69.8, 70.6, 70.7, 70.8, 115.6, 115.7, 127.5, 127.9, 128.5, 137.3, 153.1; EI MS (70 eV), *m*/*z* 558 [M^+]; HRMS (EI), calculated 558.2617, observed 558.2614.

1,10-Dinaphthalene-1,4,7,10-tetraoxaundecane (P7). Evaporation gave the solid, which was recrystallized from CH_2Cl_2–Et_2O in 37% yield. M.p. 77–78 °C; ^1H NMR ($CDCl_3$, 25 °C), δ 7.66–7.77 (6H, aryl, m), 7.27–7.48 (4H, aryl, m), 7.09–7.22 (4H, aryl, m), 4.23 (4H, α-CH_2, m), 3.91 (4H, β-CH_2, m), 3.57–3.80 (4H, γ-CH_2, m); ^{13}C NMR ($CDCl_3$, 25 °C), δ 67.5, 69.8, 70.6, 71.0, 106.8, 119.0, 123.6, 126.3, 126.8, 127.6, 129.1, 129.4, 134.5, 136.3, 156.7; EI MS (70 eV), *m*/*z* 402 [M^+]; HRMS (EI), calculated 402.1831, observed 402.1813.

1,13-Dinaphthalene-1,4,7,10,13-pentaoxatridecane (P8). Evaporation gave the white solid, which was recrystallized from CH_2Cl_2–Et_2O in 76% yield. M.p. 44–46 °C; ^1H NMR ($CDCl_3$, 25 °C), δ 7.65–7.78 (6H, aryl, m), 7.26–7.48 (4H, aryl, m), 7.09–7.21 (4H, aryl, m), 4.23 (4H, α-CH_2, m), 3.91 (4H, β-CH_2, m), 3.57–3.80 (10H, γ-η-CH_2, m); ^{13}C NMR ($CDCl_3$, 25 °C), δ 67.4, 69.7, 70.7, 70.8, 106.8, 119.0, 123.6, 126.3, 126.7, 127.6, 129.0, 129.3, 134.5, 156.7; EI MS (70 eV), *m*/*z* 446 [M^+]; HRMS (EI), calculated 446.2093, observed 446.2105.

1,12-Bis(anthryl-9)-2,5,8,11-tetraoxadodecane (P9). At room temperature, to a solution of 9-hydroxymethylanthracene (1.12 g, 5.36 mmol) (Aldrich) in dry DMF (40 ml) was added dropwise with stirring NaH 0.28 g (5.5 mmol, 50% in mineral oil, washed previously with *n*-pentane) in dry DMF (10 ml). Stirring was continued for 30 min after completion of the addition. A dry DMF solution (10 ml) of triethylene glycol ditosylate[24] (1.23 g, 2.68 mmol) was then introduced dropwise. The reaction mixture was warmed for 18 h at 80 °C before cooling to room temperature. The excess of NaH was quenched by the addition of a few drops of water, then the solvent was removed *in vacuo* and the residue was partitioned between water (30 ml) and dichloromethane (40 ml). The organic layer was washed twice with 2 M HCl, water and brine and dried over $MgSO_4$. Evaporation gave the crude product, which was subjected to silica gel column chromatography with EtOAc–*n*-hexane (1:1) as the eluent. Recrystallization from EtOH afforded the title compound as a light yellow crystalline solid in 23% yield. M.p. 73 °C; ^1H NMR ($CDCl_3$, 25 °C), δ 8.39 (6H, aryl, d, J = 10.5 Hz), 7.97 (4H, aryl, dd, J = 9.4 Hz), 7.38–7.55 (8H, aryl, m), 3.72–3.78 (4H, α-CH_2, m), 3.63–3.67 (4H, β-CH_2, m), 3.63 (4H, γ-CH_2, s); ^{13}C NMR ($CDCl_3$, 25 °C), δ 66.0, 70.2, 71.4, 71.6, 125.1, 125.6, 126.8, 129.0, 129.5, 129.6, 132.1; EI MS (70 eV), *m*/*z* 530 [M^+], HRMS (EI), calculated 530.2457, observed 530.2420.

1,3,5-Cycloheptatrienylium tetrafluoroborate. Tropylium salt was prepared according to literature procedures;[25] m.p. 203 °C (decomp.); ^1H NMR (CD_3CN, 30 °C), δ 9.24 (7H, s).

Complexation studies. Stability constant determination by UV–visible spectrophotometry. The stability constant for 1:1 complexation was defined by a method described in detail elsewhere.[3] The absorption measurements were made immediately after the mixing of podand and tropylium solutions. The Rose–Drago equation:

$$\frac{1}{K} = \frac{A - A_0}{\varepsilon_C - \varepsilon_A} - C_A - C_D + \frac{C_D C_A (\varepsilon_C - \varepsilon_A)}{A - A_0} \quad (1)$$

where A_0 is the absorbance of pure acceptor solution, A is the absorbance of the acceptor–donor solution, C_A and C_D are the initial concentrations of acceptor and donor, and ε_C and ε_A are the molar absorptivities of complex and acceptor in solution, respectively, contains two unknown constants, K and ε_C, which were evaluated by an iteration method with a PC implementing the SigmaPlot 4.0 program.[26] The program relies on a least-squares procedure with the Marquardt–Levenberg algorithm.[27] The errors in K and ε_C were evaluated numerically by standard deviations of single K and ε_C values usually obtained from 6–10 measurements.

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