

A Molecular-Level Plug/Socket System: Electronic Energy Transfer from a Binaphthyl Unit Incorporated into a Crown Ether to an Anthracenyl Unit Linked to an Ammonium Ion

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Abstract: The reversible acid/base- (hydrogen-bonding-) controlled association between racemic crown ethers incorporating a binaphthyl unit (the socket) and wirelike compounds bearing an anthracenyl unit (the plug) is described. The compounds used were the (\pm)-binaphthocrown ethers **BN20C6**, **BN23C7**, and **BN26C8**, the amines 9-methyl(aminomethyl)anthracene (**AM**) and 9-methyl(aminobenzyl)anthracene (**AB**), and their hexafluorophosphate salts **AMH**⁺**PF**₆⁻ and **ABH**⁺**PF**₆⁻. The

experiments were carried out in CH₂Cl₂ solution. Fluorescence data, ¹H NMR spectra, and molecular modeling all point to the formation of stable, pseudorotaxane-type H-bonded adducts of **BN23C7** with **AMH**⁺ and of **BN26C8** with **AMH**⁺ and **ABH**⁺. These systems

can be considered as molecular-level plug/socket devices since they are characterized by i) reversible, acid/base-controlled plug in/plug out behavior and ii) photoinduced flow of electronic energy from the binaphthyl to the anthracenyl unit in the plug in state. The above concepts can be easily extended to systems in which a) the plug in/plug out function is stereoselective and b) light excitation induces an electron flow instead of a flow of electronic energy.

Keywords: energy transfer • hydrogen bonds • molecular devices • pseudorotaxanes • supramolecular chemistry

Introduction

Computers are based on sets of components (wires, switches, transistors, etc.) constructed by the top-down approach. A necessary condition for further miniaturization down to the limit of information processing and computation at the molecular level is the bottom-up construction of sets of molecular-level components able to perform the various kinds of electronic functions.^[1] Apart from futuristic applications, the design and construction of molecular-level systems able to perform specific functions^[2] is a topic of great scientific interest since it introduces new concepts in the field of chemistry and stimulates the ingenuity of the research work-

ers interested in the bottom-up approach to nanotechnology.^[3] In the last few years much attention has been devoted to the development of molecular-level wires^[4] for conduction of electrons or electronic energy and to molecular-level switches^[5] able to permit or prevent electron or electronic energy flow along a wire. More recently, systems capable of functioning as logic gates^[6, 7] have been obtained as a spin-off of studies aimed at the development of fluorescent sensors^[7] and molecular-level machines.^[8] Less attention has been devoted to molecular-level systems able to play the plug/socket role for the flow of electronic energy or electrons.^[9] In this paper we wish to describe both the reversible acid/base- (hydrogen-bonding-) controlled plug in/plug out between racemic crown ethers incorporating a binaphthyl unit and wirelike compounds bearing an anthracenyl unit, and also the photoinduced flow of electronic energy in the plug in state.

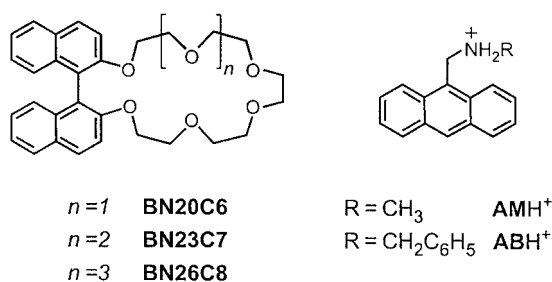
Results and Discussion

Synthesis: The compounds used were the (\pm)-binaphthocrown ethers **BN20C6**, **BN23C7**, and **BN26C8**, the amines 9-methyl(aminomethyl)anthracene (**AM**) and 9-methyl(aminobenzyl)anthracene (**AB**), and their hexafluorophosphate salts **AMH**⁺**PF**₆⁻ and **ABH**⁺**PF**₆⁻ (Scheme 1). The synthesis of

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Scheme 1. The investigated binaphthocrown ethers and anthracenyl ammonium ions.

these compounds is described in the Experimental Section; Scheme 2 outlines the strategy followed for the synthesis of **BN23C7** and **BN26C8**.

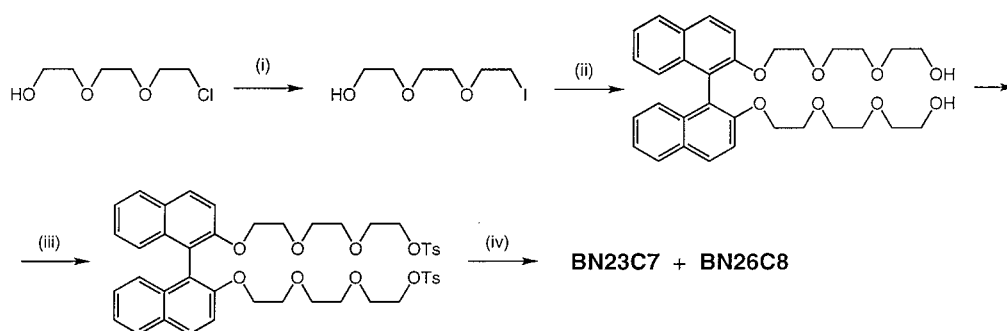
Photophysical experiments: All the photophysical experiments were carried out in air-equilibrated CH₂Cl₂ solution at room temperature. The absorption and emission spectra of crown ethers **BN20C6**, **BN23C7**, and **BN26C8** and of ammonium ions **AMH**⁺ and **ABH**⁺ display the characteristic bands^[10] of their binaphthyl and anthracenyl chromophoric units (see, for example, Figure 1 and Table 1). The fluorescence of the binaphthyl unit of the crown ether has a quantum yield of about 0.5 and a lifetime of 5 ns. Addition of base (Bu₃N) does not cause any change in the absorption and emission bands of the crown ethers, whereas addition of acid (CF₃SO₃H) causes some spectral changes arising from protonation of the crown ether oxygens. In the case of the **AMH**⁺ and **ABH**⁺ ammonium ions, addition of base causes a very small blue shift in the absorption and emission bands and a

Abstract in Italian: In soluzione di CH₂Cl₂ l'associazione tra eteri corona contenenti un'unità binaftile (in forma racemica) e composti filiformi costituiti da un gruppo amminico legato ad un'unità antracenicile, promossa dalla formazione di legami a idrogeno, può essere controllata mediante reazioni acido/base. I composti utilizzati sono gli eteri corona (±)**BN20C6**, **BN23C7** e **BN26C8**, le ammine 9-metil(amminometil)antracene (**AM**) e 9-metil(amminobenzil)antracene (**AB**), ed i loro sali di esafluorofosfato **AMH**⁺PF₆⁻ e **ABH**⁺PF₆⁻. Misure spettroscopiche di fluorescenza e ¹H NMR hanno evidenziato la formazione di addotti, stabilizzati da legami a idrogeno ed aventi struttura di tipo pseudorotassano, tra le specie **BN23C7** e **AMH**⁺, **BN26C8** e **AMH**⁺, **BN26C8** e **ABH**⁺, in accordo con i risultati degli studi di molecular modelling effettuati su tali sistemi. Essi possono essere considerati esempi di spine e prese a livello molecolare poiché i) i componenti molecolari possono essere connessi e disconnessi in modo reversibile mediante reazioni acido/base; ii) quando i componenti sono connessi, è possibile far scorrere un flusso di energia elettronica dall'unità binaftile a quella antracenicile mediante fotoeccitazione della prima unità. Tali concetti possono essere facilmente estesi a sistemi nei quali a) la connessione tra i componenti è stereoselettiva e b) l'eccitazione luminosa induce un flusso di elettroni invece di un flusso di energia elettronica.

decrease in the fluorescence intensity.^[9e,f] Such changes can be fully reversed upon addition of a stoichiometric amount of acid with respect to the added base.

From the well-known photophysical properties of the 1,1'-binaphthyl and anthracene chromophoric units,^[10] we anticipated that in the case of association between a binaphthocrown ether and an anthracenyl ammonium ion electronic energy transfer would cause the quenching of the binaphthyl-type fluorescence and the sensitization of the anthracene-type fluorescence.^[11] We have found that addition of increasing amounts of **AMH**⁺ to 1 × 10⁻⁴ mol L⁻¹ CH₂Cl₂ solutions of crown ethers **BN23C7** and **BN26C8** causes a progressive decrease in the emission intensity of the binaphthyl-type fluorescence (λ_{exc} = 292 nm, λ_{em} = 360 nm; Figure 2). The same result is obtained by titration of a 1:1 mixture of crown ether and amine by acid; the above-mentioned protonation of the crown ether, of course, does not occur until free amine is present. After the addition of an excess of the ammonium ion, the fluorescence intensity was completely quenched and the excited state lifetime was no longer measurable. The same behavior was observed in the case of **ABH**⁺ with **BN26C8**,^[12] whereas no quenching of the binaphthyl-type fluorescence was observed for **AMH**⁺ with **BN20C6** and for **ABH**⁺ with **BN20C6** and **BN23C7**. These results show that: a) the largest **BN26C8** crown ether gives adducts with both **AMH**⁺ and **ABH**⁺; b) **BN23C7** gives an adduct only with **AMH**⁺, and c) the smallest **BN20C6** crown ether is not capable of giving adducts with either **AMH**⁺ or **ABH**⁺. Clearly, the size of the crown ether ring and the bulkiness of the wire-type component have a strong effect in determining the possibility of association, which is driven by H-bond formation between the ammonium moiety and the crown ether oxygens.

Although the experimental errors are large because the values of the unquenched fluorescence intensity have to be corrected for absorption by the anthracenyl moiety,^[13] the titration curves (Figure 2, inset) suggest a 1:1 stoichiometry for the adducts and indicate that the association constants are larger than 10⁵ L mol⁻¹. Such high values for the association constants are also confirmed by acid titration experiments performed on a 1:1 mixture of crown ether and amine, in which corrections can be avoided since the absorption of the binaphthyl luminescence by the anthracenyl unit is constant along the titration. We have also found that the quenching of the binaphthyl-type fluorescence (λ_{exc} = 292 nm, λ_{em} = 360 nm) is accompanied by the sensitization of the fluorescence (λ_{em} > 400 nm) of the anthracenyl unit of the ammonium ion (Figure 2). For the three adducts, the quantum yield of anthracenyl-type emission is the same for excitation in the binaphthyl- and anthracenyl-based absorption bands, indicating the occurrence of a very efficient energy-transfer process. The energy-transfer rate constant, which has to compete with the fast intrinsic decay (2 × 10⁸ s⁻¹) of the binaphthyl fluorescence, can be estimated to be larger than 4 × 10⁹ s⁻¹ from the equation $k_{en} = (\Phi^\circ/\Phi - 1)/\tau^\circ$, where τ[°] is the lifetime of the unquenched binaphthyl fluorescence (5 ns, Table 1) and Φ[°] and Φ are the quantum yields of the binaphthyl fluorescence in the free crown and in the adduct, respectively.



Scheme 2. The synthesis of **BN23C7** and **BN26C8**. Conditions: i) NaI, acetone; ii) 2,2'-dihydroxy-1,1'-binaphthyl, K_2CO_3 , acetone; iii) TsCl, THF, NaOH, H_2O ; iv) ethylene glycol, KOH, dioxane.

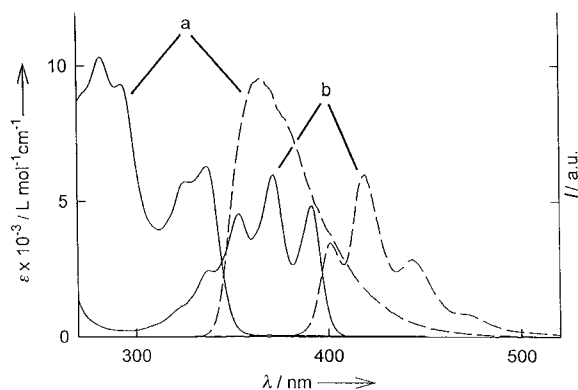


Figure 1. Absorption (full lines) and emission (dashed lines) spectra in CH_2Cl_2 solution at room temperature of crown ether **BN23C7** (a) and ammonium ion **AMH⁺** (b) ($\lambda_{exc} = 292$ nm for **BN23C7** and 370 nm for **AMH⁺**).

Table 1. Absorption and luminescence data for the crown ethers **BN20C6**, **BN23C7**, and **BN26C8**, and anthracenyl ammonium ions **AMH⁺** and **ABH⁺**.^[a]

	Absorption		Luminescence ^[b]		
	λ_{max} [nm] ^[c]	ϵ_{max} [$L mol^{-1} cm^{-1}$] ^[d]	λ_{max} [nm] ^[c]	$\Phi_{em}^{[d,e]}$	τ [ns] ^[d]
BN20C6	241	103000	368	0.53	5.0
	282	10300			
	336	6100			
BN23C7	241	96000	370	0.47	5.2
	282	10400			
	336	6200			
BN26C8	241	94000	370	0.49	5.2
	282	10800			
	336	6500			
AMH⁺	372	6000	421	0.36	12
ABH⁺	372	7400	423	0.30	10

[a] Air-equilibrated CH_2Cl_2 solution, room temperature. [b] $\lambda_{exc} = 290$ nm. [c] Experimental error: ± 2 nm. [d] Experimental error: $\pm 10\%$. [e] Measured with anthracene in degassed ethanol as a standard ($\Phi = 0.27$); see: W. R. Dawson, M. W. Windsor, *J. Phys. Chem.* **1968**, 72, 3251–3260.

Once the adducts are formed, addition of a stoichiometric amount of base causes the revival of the binaphthyl fluorescence and the disappearance of the anthracenyl fluorescence upon excitation in the binaphthyl bands, showing that the adducts can be reversibly dissociated.

Molecular modeling: It has long been known that crown ethers give adducts with RNH_3^+ ammonium ions in nonpolar solvents.^[14] More recently it has been shown that when the

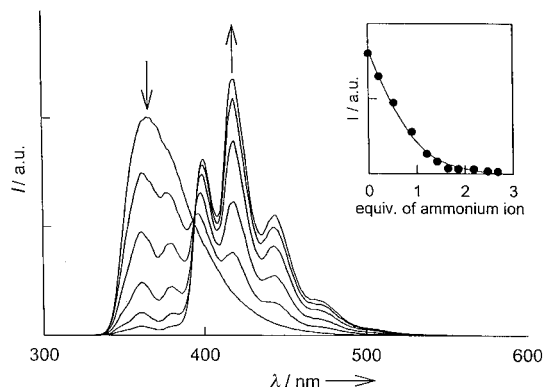


Figure 2. Changes in the fluorescence spectra of a CH_2Cl_2 solution of a $1.0 \times 10^{-4} mol L^{-1}$ solution of **BN23C7** upon addition of **AMH⁺** (the features that are present in the region of the binaphthyl fluorescence are due to reabsorption by the anthracenyl unit). The inset shows the titration curve for the decrease of the fluorescence intensity at 360 nm ($\lambda_{exc} = 292$ nm).

crown ether ring is large enough, suitably chosen $R_2NH_2^+$ ions can thread through the ring to give pseudorotaxanelike species.^[15] Molecular modeling (MacroModel 4.5-MM3* force field; see Supporting Information) shows that in the case of the smallest crown **BN20C6** neither **AMH⁺** nor **ABH⁺** can penetrate the cavity of the crown ether, as is also the case for **BN23C7** with **ABH⁺**. By contrast, for **BN23C7** with **AMH⁺** and **BN26C8** with both **AMH⁺** and **ABH⁺**, the minimum-energy conformation corresponds to a pseudorotaxanelike structure (see, e.g., Figure 3).

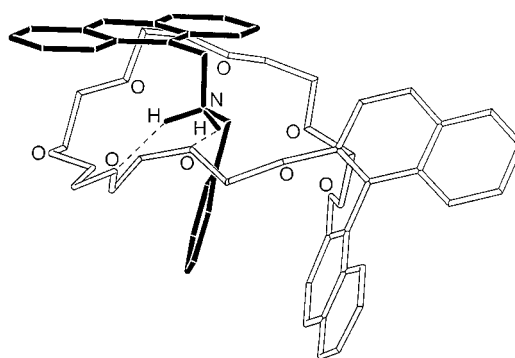


Figure 3. Computer-generated minimum-energy structure of the adduct of **BN26C8** and **ABH⁺** (MacroModel 4.5 MM3* force field).

^1H NMR spectroscopy: Evidence for interactions of varying intensity, depending on the ring size of the host and the bulkiness of the ammonium guest, has been obtained from ^1H NMR spectra at 200 MHz (Tables 2 and 3). Upon addition of an equimolar amount of either **BN23C7** or **BN26C8** to a $2.7 \times 10^{-3} \text{ mol L}^{-1}$ solution of **AMH** $^+$ in $\text{CDCl}_3/\text{CD}_3\text{CN}$ 6:1, significant upfield shifts for the protons of the anthracene group and for the benzylic methylene protons were observed. Strong variations were also observed for the complex multiplets corresponding to the protons of the polyether chain. A mixture of **BN23C7** and **AMH** $^+$ in a 1:2 mole ratio showed single signals of the guest, thus indicating rapid exchange at room temperature between complexed and uncomplexed species on the ^1H NMR time scale. In the case of the **ABH** $^+$ guest, formation of a strong complex with **BN26C8** was clearly revealed by significant shifts of the signals of the polyether chain, while with **BN23C7** the spectrum of a 1:1 mixture was not different from the sum of the spectra of the pure components.

Table 2. ^1H NMR chemical shifts (δ values) for the isolated molecular components represented below (200 MHz, $\text{CD}_3\text{CN}/\text{CDCl}_3$ 1:6, room temperature).

	BN23C7		BN26C8	
	AMH $^+$ PF $_6^-$	ABH $^+$ PF $_6^-$	BN23C7	BN26C8
H _a	5.28	5.23		
H _b	2.77	4.41		
H _c	8.16–8.12	7.98–7.94		
H _d	8.68	8.65		
H _e	8.26–8.22	8.14–8.11		
H _f + H _g	7.73 + 7.60	7.67–7.56		
H _a + H _b			4.15 + 4.03	4.14 + 4.05
-CH ₂ - crown			3.63–3.30	3.63–3.28

Table 3. ^1H NMR chemical shifts (δ values) for equimolar ($2.7 \times 10^{-3} \text{ mol L}^{-1}$) mixtures of **AMH** $^+$ and **BN23C7**, **AMH** $^+$ and **BN26C8**, **ABH** $^+$ and **BN23C7**, and **ABH** $^+$ /**BN26C8** (200 MHz, $\text{CD}_3\text{CN}/\text{CDCl}_3$ 1:6, room temperature). See Table 2 for hydrogen labeling.

	AMH $^+$ /BN23C7	AMH $^+$ /BN26C8	ABH $^+$ /BN23C7	ABH $^+$ /BN26C8
H _a	5.08	5.18	5.21	5.22
H _b	2.83	2.81	4.40	4.40
H _c	7.90–7.86	–	–	8.12–8.07
H _d	8.58	8.64	8.64	8.65
H _e	8.06–8.02	8.08–8.02	8.13–8.09	8.12–8.07
H _f + H _g	7.44 + 7.26	–	–	–
H _a + H _b	4.43 + 4.00	4.04 + 3.71	4.22–3.96	4.50 + 3.96
-CH ₂ - crown	3.49–3.15	3.50–2.90	3.61–3.29	3.68–2.30

Conclusion

Fluorescence data, ^1H NMR spectra, and molecular modeling point to the formation of stable H-bonded adducts of **BN23C7** with **AMH** $^+$ and **BN26C8** with **AMH** $^+$ and **ABH** $^+$ that are likely to involve pseudorotaxane-type structures. As depicted schematically in Figure 4 for the **BN26C8-ABH** $^+$ case, these

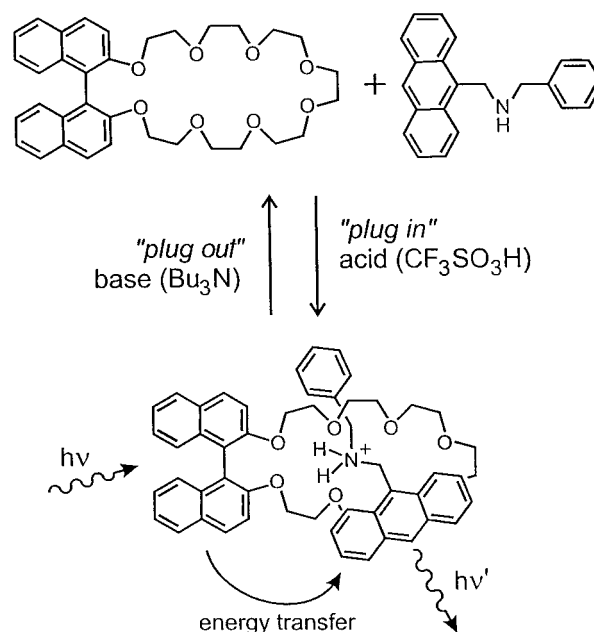


Figure 4. Reversible acid/base-controlled plug in/plug out between **BN26C8** and **ABH** $^+$, and photoinduced energy transfer from the binaphthyl to the anthracenyl unit in the plug in state.

systems can be considered as molecular-level plug/socket devices since they are characterized by i) reversible acid/base-controlled plug in/plug out function and ii) photoinduced flow of electronic energy from the binaphthyl to the anthracenyl unit in the plug in state. The above concepts can be straightforwardly extended to systems where a) the plug in/plug out function is stereoselective (enantiomeric recognition of ammonium ions by crown ethers containing binaphthyl is a well known property^[16]), and b) light excitation induces an electron flow (instead of a flow of electronic energy).

Experimental Section

Instruments: ^1H NMR spectra were measured with either a Bruker AC200 or a Bruker AC300 spectrometer. HPLC analyses were performed on a Hewlett Packard 1050 liquid chromatograph fitted with a UV-VIS detector operating at 230 nm. Samples were analyzed on a Supelcosil LC-18 DB column (25 cm \times 4.6 mm i.d.; particle size 5 μm). ES-MS spectra were obtained on a Fisons Instruments VG-Platform benchtop mass spectrometer equipped with a pneumatically assisted electrospray LC-MS interface and a single quadrupole. All the photophysical experiments were carried out in CH_2Cl_2 solution at room temperature with equipment and procedures as previously described.^[9e]

Materials: 9-Methyl(aminomethyl)anthracene (**AM**), 2-[2-(2-chloroethoxy)ethoxy] ethanol and 2,2'-dihydroxy-1,1'-binaphthyl were commercial samples. 9-Methyl(aminobenzyl)-anthracene (**AB**) was available from a previous investigation.^[9f] **BN20C6** was prepared according to a literature

procedure,^[14b] m.p. 124–126 °C (ref. [14b] 125–127 °C). **BN23C7** and **BN26C8** were prepared according to the procedure outlined in Scheme 2. The former compound was obtained as an unexpected by-product, probably derived from partial hydrolysis of the ditosylate intermediate, followed by cyclization of the resulting diol monotosylate.

2-[2-(2-Iodoethoxy)ethoxy]ethanol: 2-[2-(2-Chloroethoxy)ethoxy]ethanol (5.0 g, 29.6 mmol) and NaI (50 g, 0.34 mol) were refluxed overnight under stirring in acetone (30 mL). After cooling, the slurry was taken up in the minimum amount of water and extracted with Et₂O (3 × 50 mL). The organic layers were dried (MgSO₄), filtered, and evaporated to dryness to yield the title compound (7.1 g, 92% yield), which was used in the next step without further purification. ¹H NMR (CDCl₃): δ = 3.73–3.78 (t, 2H, ICH₂), 3.60–3.70 (m, 10H, OCH₂), 2.9 (brs, 1H, OH).

2,2'-Bis(8-hydroxy-3,6-dioxo-1-oxtyloxy)-1,1'-binaphthyl: A mixture of 2,2'-dihydroxy-1,1'-binaphthyl (1.1 g, 3.6 mmol), 2-[2-(2-iodoethoxy)ethoxy]ethanol (2.4 g, 4.4 mmol) and K₂CO₃ (5.0 g, 36.3 mmol) in acetone (10 mL) was stirred under argon at room temperature for three days. After the addition of 10 mL of acetone, the solid was filtered off and washed with acetone (10 mL). The organic phase was evaporated to dryness and the crude material was purified by flash chromatography on silica gel (elution with CHCl₃ containing increasing amounts of CH₃OH from 0 to 10%) to yield the title compound (2.0 g, 95% yield) as a colorless oil. ¹H NMR (CDCl₃): δ = 7.93–7.94 (dd, 4H, Ar), 7.40–7.43 (d, 2H, Ar), 7.16–7.32 (m, 6H, Ar), 4.08–4.18 (m, 4H, ArOCH₂), 3.08–3.64 (m, 20H, OCH₂), 2.63 (brs, 2H, OH), ES-MS: *m/z* = 573 [M+Na⁺].

2,2'-Bis(8-tosyloxy-3,6-dioxo-1-oxtyloxy)-1,1'-binaphthyl: A mixture of diol (2.0 g, 3.6 mmol), KOH (600 mg, 150 mmol) in 5 mL of H₂O, and THF (5 mL) was stirred at 0 °C. TsCl (2.7 g, 14.4 mmol) dissolved in 5 mL of THF was added dropwise to the mixture while keeping the temperature below 5 °C. The reaction mixture was then stirred at 0 °C for 2 h. This mixture was poured into ice-water and extracted with chloroform (3 × 10 mL). The organic layers were dried over MgSO₄, filtered and evaporated to dryness. The crude oil was purified by flash chromatography on silica gel (CHCl₃) to yield the title compound (1.9 g, 60% yield) as a colorless oil. ¹H NMR (CDCl₃): δ = 7.90–7.94 (d, 2H, Ar), 7.82–7.85 (d, 2H, Ar), 7.75–7.77 (d, 2H, Ar), 7.39–7.42 (m, 2H, Ar), 7.28–7.30 (m, 6H, Ar), 7.10–7.13 (m, 4H, Ar), 3.90–4.07 (m, 8H, OCH₂), 3.38–3.46 (m, 8H, OCH₂), 2.93–3.12 (m, 8H, OCH₂); ES-MS: *m/z* = 877 [M+Na⁺].

2,3,4,5-Bis(1,2-naphtho)-1,6,9,12,15,18,21-heptaoxacyclotricosa-2,4-diene (BN23C7) and **2,3,4,5-bis(1,2-naphtho)-1,6,9,12,15,18,21,24-octaoxacyclohexaicoso-2,4-diene (BN26C8)**: The ditosylate (1.0 g, 1.2 mmol), diethyleneglycol (72 mg, 1.2 mmol), powdered KOH (1.0 g, 178 mmol) and dioxane (70 mL) were stirred at 50 °C for 5 days. After cooling, the mixture was poured into water (50 mL) and extracted with CH₂Cl₂ (4 × 100 mL). The organic layers were dried over MgSO₄, filtered, and evaporated to dryness. The crude product was purified by flash chromatography on silica gel (elution with CHCl₃ containing increasing amounts of CH₃OH from 0 to 5%) to yield, in the given order, **BN23C7** (80 mg, 13% yield) and **BN26C8** (100 mg, 15% yield). Both compounds were obtained as waxy solids, unsuitable for elemental analysis, and were no less than 99% pure by careful HPLC analysis (CH₃OH/H₂O 65:35, 0.65 mL min⁻¹, retention time 7.6 and 7.8 min, respectively). These compounds are described in the literature^[14b, 17] as oils. **BN23C7**: ¹H NMR (CDCl₃): δ = 7.92–7.95 (d, 2H, Ar), 7.84–7.87 (d, 2H, Ar), 7.45–7.48 (d, 2H, Ar), 7.15–7.34 (m, 6H, Ar), 4.00–4.20 (m, 4H, ArOCH₂), 3.22–3.65 (m, 24H, OCH₂); ES-MS: *m/z* = 556 [M+Na⁺]. **BN26C8**: ¹H NMR (CDCl₃): δ = 7.92–7.95 (d, 2H, Ar), 7.84–7.87 (d, 2H, Ar), 7.45–7.48 (d, 2H, Ar), 7.15–7.34 (m, 6H, Ar), 4.00–4.20 (m, 4H, ArOCH₂), 3.30–3.70 (m, 20H, OCH₂); ES-MS: *m/z* = 600 [M+Na⁺].

Supporting information available: ¹H NMR spectra of the adducts, fluorescence quantum yields and lifetimes of the crown ethers in the presence of the anthracenyl ammonium ions, and molecular modeling structures.

Acknowledgments

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