Synthesis and properties of first representatives of crownophanes containing the fluorenone and naphthalene fragments

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A new family of crownophanes containing the fluorenone and naphthalene fragments linked by oligo(oxyethylene) bridges were synthesized. Reactions of these ligands with the paraquat dication gave inclusion complexes of the pseudorotaxane type that were detected by FAB mass spectrometry, ^{1}H NMR spectroscopy, and electronic absorption spectroscopy.

Key words: crownophane, fluorenone, naphthalene, paraquat, pseudorotaxane.

Design, synthesis, and application of various macrocyclic receptors that can selectively discriminate between metal ions, anions, and organic molecules belong to the main problems of the chemistry of "guest—host" complexes. Cyclophanes, which are macrocycles containing two or more aromatic fragments linked by various bridges, hold a central position among such receptors.[1—6] The size, shape, charge, and hydrophobicity of a cyclophane, as well as its tendency toward various intermolecular interactions with a guest molecule, can be easily changed by introduction in the receptor structure of rationally selected aromatic fragments, bridges between them, and functional groups, which allows effective control of its complexing properties. Because of this, cyclophanes are widely used in membrane transport and as catalysts, sensors, and components of catenanes and rotaxanes that are prototypes of molecular machines and nanoelectronic devices.[7—15]

Recently,[16—22] we have described the syntheses and properties of first representatives of fluorenonophanes containing two fluorenone fragments or the fluorenone and stilbene fragments linked by flexible polyether chains or conformationally rigid *p*-xylylene bridges. We have demonstrated that fluorenonophanes form stable inclusion complexes with electron-deficient organic molecules[16—20] and are promising templates for self-assembly of [2]catenanes on their basis.[21,22]

Here we describe the synthesis and properties of new crownophanes containing the fluorenone and naphthalene fragments connected by oligo(oxyethylene) chains with different lengths.

Crownophanes **1a—d** were obtained as shown in Scheme 1.

Alkylation of 2,7-dihydroxy-9*H*-fluoren-9-one **2** [23] with oligo(ethylene glycol) chlorohydrins **3a—d** in DMF in the presence of K_2CO_3 or in EtOH in the presence of KOH gave diols **4a—c** or **4d** in 78—80% yields. Reactions of these diols with *p*-toluenesulfonyl chloride in a mixture of 1,4-dioxane and chloroform in the presence of Et_3N at 0—5 °C for 30 h afforded ditosylates **5a—d** in good yields (70—88%). The latter reacted with 1,5-dihydroxynaphthalene **6** at high dilution in DMF in the presence of K_2CO_3. After workup of the reaction mixture and purification by column chromatography, we obtained fluorenone-containing crownophanes **1a—d** in moderate yields. The yield of the smallest crownophane **1a** was low; the yields of crownophanes **1b—d** were virtually independent of the ring size.

The ^{1}H NMR spectra of crownophanes **1a—d** show a set of signals at δ 3.65—4.38, which are typical of oligo(ethylene glycol) fragments, a characteristic set of signals (two doublets and a doublet of doublets) for the fluorenone protons, and a triplet and two doublets for the naphthalene protons. The signals for all the aromatic protons in crownophanes **1a—d** are shifted upfield compared to their positions in the spectra of model compounds: 2,7-dimethoxyfluorenone (**7**) and 1,5-dimethoxynaphthalene (**8**) (Table 1). This is probably due to reciprocal shielding by the opposite aromatic fragments.

The largest shifts of the signals for these protons were observed for the smallest crownophane **1a**. With an increase in the ring size, the relative shifts of the aforementioned signals decrease. The signals for the H(4) and H(8) protons of the naphthalene ring and for the H_c proton of fluorenone show the largest upfield shifts in the ^{1}H NMR spectra of crownophanes **1a—d**. The considerable upfield shifts for all the aromatic protons in compounds **1** suggest that they exist in solutions mainly as conformers with contiguous aromatic fragments arranged parallel or nearly parallel to each other.

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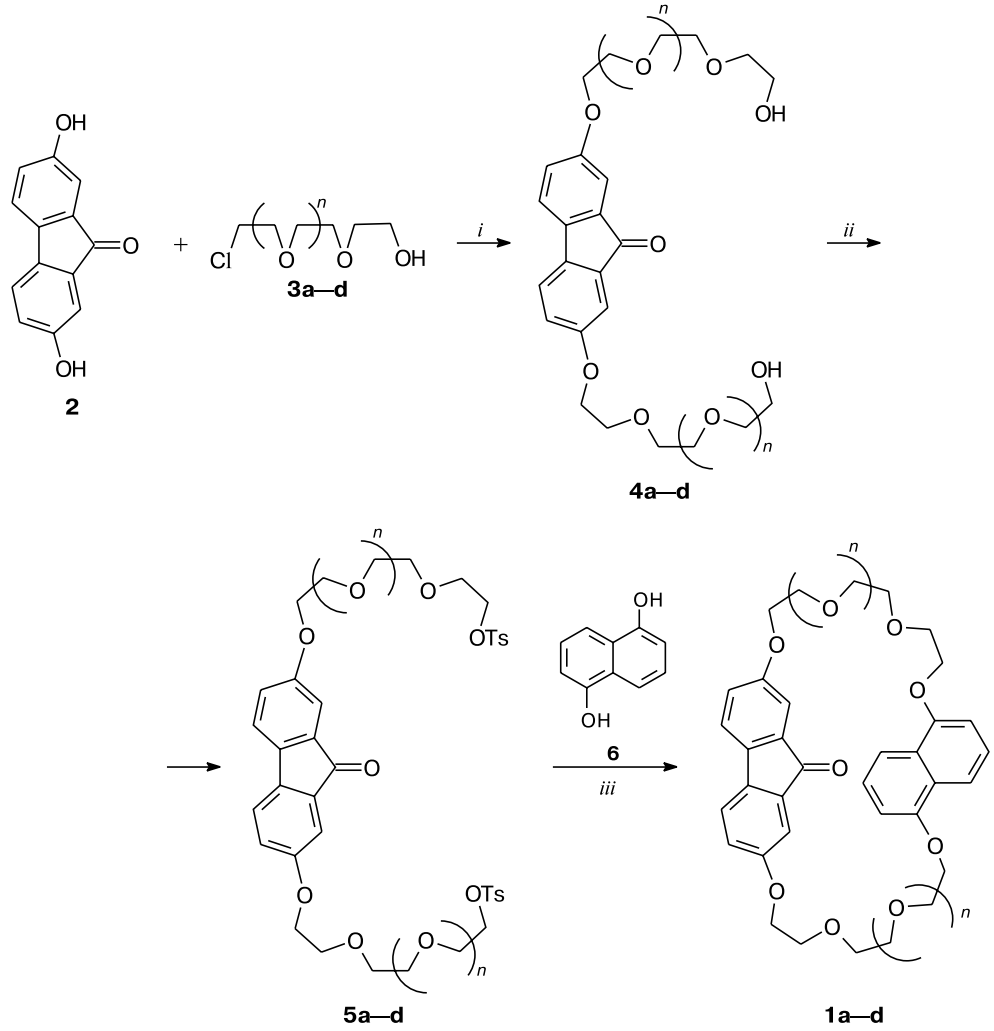
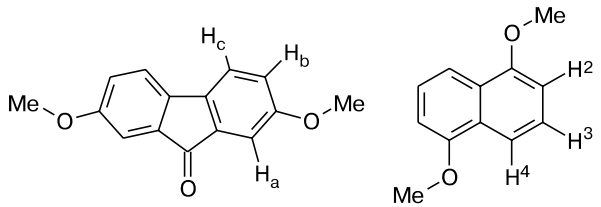
Scheme 1



n = 0 (**a**), 1 (**b**), 2 (**c**), 3 (**d**)

i. K_2CO_3/DMF (KOH/EtOH), 80 °C; *ii.* TsCl/NEt_3, 1,4-dioxane—$CHCl_3$, 0—5 °C, 30 h; *iii.* K_2CO_3/DMF, 80 °C.



Paraquat dication **9** and its derivatives (*N*,*N*′-dialkyl-4,4′-bipyridinium salts) belong to the most frequently studied electron-withdrawing guests that form stable inclusion complexes with donor macrocyclic molecules. In particular, a great number of pseudorotaxanes and rotaxanes have been reported to be complexes of paraquat ions with crown ethers, cryptands, cyclophanes, and other macrocyclic host molecules.[24—28] Crownophanes **1a—d** containing two π-electron-donating aromatic fragments should also be "good" hosts for dication **9**.

We tried to obtain such complexes under the conditions of competitive complex formation and qualitatively estimated their relative stabilities by FAB mass spectrometry.[29—31] Mass spectra were recorded for solutions of equimolar amounts of crownophanes **1a—d** and four equivalents of paraquat **9** · $2PF_6$ in 3-nitrobenzyl alcohol. In the case of compounds **1b—d** with tri-, tetra-, and penta(ethylene glycol) bridges between the aromatic frag-

Table 1. Absolute (δ) and relative chemical shifts (Δδ) of the aromatic protons of crownophanes **1a—d** and model compounds **7** and **8**

Compound	H_a		H_b		H_c		H(2), H(6)		H(3), H(7)		H(4), H(8)	
	δ	−Δδ	δ	−Δδ	δ	−Δδ	δ	−Δδ	δ	−Δδ	δ	−Δδ
1a	6.91	0.25	6.81	0.13	6.88	0.41	6.48	0.35	7.06	0.30	7.34	0.49
1b	6.92	0.24	6.85	0.09	6.80	0.49	6.57	0.26	7.08	0.28	7.58	0.25
1c	7.01	0.15	6.83	0.11	6.94	0.35	6.63	0.20	7.16	0.20	7.71	0.12
1d	7.05	0.11	6.84	0.10	7.03	0.26	6.68	0.15	7.23	0.13	7.74	0.09
7	7.16	—	6.94	—	7.29	—	—	—	—	—	—	—
8	—	—	—	—	—	—	6.83	—	7.36	—	7.83	—

ments, the mass spectra show peaks due to successive losses of the hexafluorophosphate anion from 1 : 1 complexes of these crownophanes with paraquat **9**·$2PF_6$ (Table 2). Such a spectral pattern is characteristic of most catenanes and pseudorotaxanes, indicating the formation of sufficiently stable 1 : 1 complexes of these crownophanes with paraquat **9**·$2PF_6$.[32—34] The most intense peak of the 1 : 1 complex was observed for crownophane **1c** with the tetra(ethylene glycol) bridges between the aromatic fragments. For crownophane **1d**, the peak was slightly less intense. The mass spectrum of a complex of crownophane **1b** contains a substantially weaker peak. No peak was detected for a complex of crownophane **1a**, in which the aromatic fragments are linked by the diethylene glycol bridges. Since the peak intensity ratio of complex ions of similar ligands seems to correlate with the stabilities of the complexes, one can believe that compound **1a** forms no complex with paraquat **9**·$2PF_6$ under the conditions of the FAB MS experiment, in contrast to larger crownophanes **1b—d**.

In the ^1H NMR spectra of equimolar mixtures of crownophanes **1b—d** with paraquat **9**·$2PF_6$, the signals

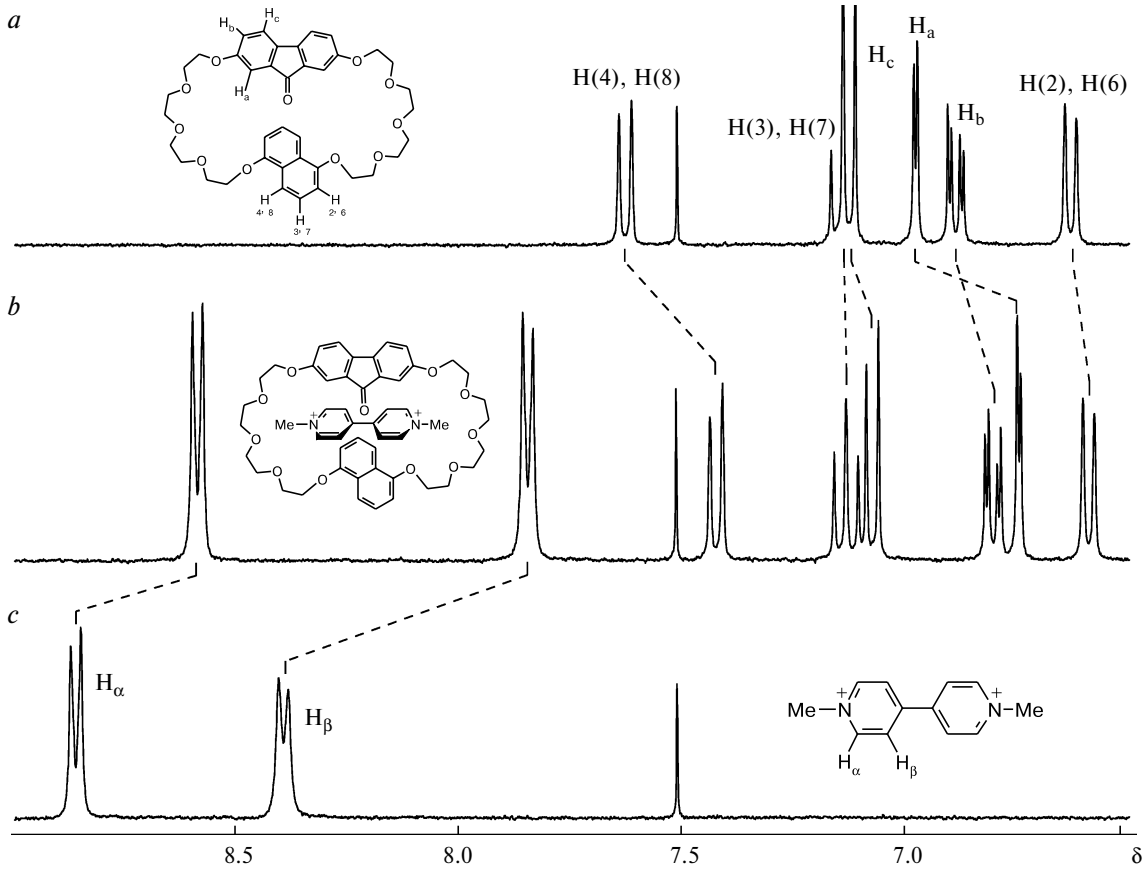


Fig. 1. Fragments of the ^1H NMR spectra of crownophane **1c** (*a*), its equimolar mixture with paraquat **9**·$2PF_6$ (*b*), and paraquat **9**·$2PF_6$ (*c*) in $CD_3CN—CDCl_3$ (4 : 3).

Table 2. FAB MS data for mixtures of crownophanes **1a—d** with paraquat **9**·2PF_6 [a]

Compound	$[M]^+$ [b]	$[M - PF_6]^+$	$[M_{crown} + H]^+$ [c]
1a	[988]	—	513
1b	[1076]	931 (4)	601
1c	[1164]	1019 (21)	689
1d	[1252]	1107 (18)	777

[a] The relative intensities (%) of the corresponding peaks are given in parentheses.
[b] No molecular ion peaks of the complexes were observed.
[c] The peaks of the protonated crownophanes.

for all the aromatic protons in the crownophanes and paraquat are shifted upfield compared to their positions in the spectra of the individual compounds (Fig. 1). The upfield shifts of the aromatic protons in the macrocyclic host molecule and paraquat **9**·2PF_6 have been shown[35,36] to be a reliable spectroscopic indication of the formation of inclusion complexes of the pseudorotaxane type. The shifts of the signals for the H_α and H_β protons in paraquat **9**·2PF_6 for similar complexes are proportional, to a first approximation, to their stabilities.

The spectrum of an equimolar mixture of the smallest crownophane **1a** with paraquat **9**·2PF_6 is virtually identical with the sum of the spectra of its components. Apparently, no inclusion complex is formed. With an extention of the crownophane macrocycle, the upfield shifts of the signals for the H_α and H_β protons in paraquat **9**·2PF_6 and, probably, the stabilities of the resulting complexes increase. According to the Δδ values obtained for these protons, crownophane **1c** should form the most stable inclusion complex with paraquat **9**·2PF_6 (Table 3). In general, the ^{1}H NMR data on the stabilities of the complexes of crownophanes **1a—d** with paraquat **9**·2PF_6 agree well with the FAB MS data.

On addition of a solution of paraquat **9**·2PF_6 to solutions of crownophanes **1b—d** in acetonitrile, the initial orange solutions turned dark red. This was accompanied by substantial changes in both the visible and UV regions of the electronic absorption spectra of these systems. The intensities of the bands in the UV region decrease compared to the sum of the spectra of the individual compounds, which is characteristic of pseudorotaxanes, rotaxanes, and catenanes.[33] Simultaneously, the visible region of the spectra contains an additional band superimposed on the absorption band of the carbonyl group of fluorenone. Apparently, this band is due to the formation of pseudorotaxane complexes stabilized by charge-transfer donor—acceptor interactions of the π-donating aromatic subunits of the cyclophanes with the π-withdrawing

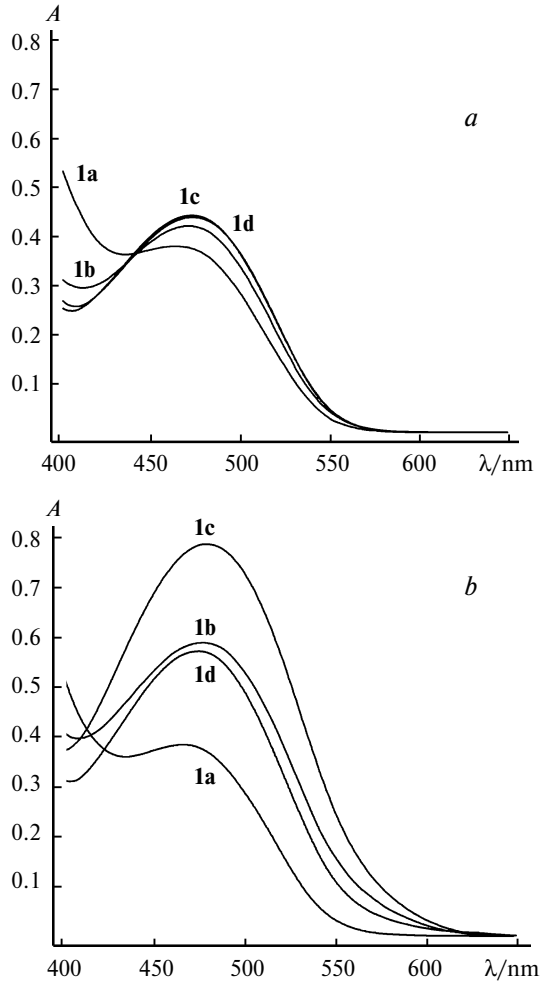


Fig. 2. Electronic absorption spectra of solutions of crownophanes **1a—d** ($1.5 \cdot 10^{-5}$ mol L^{-1}) (*a*) and their mixtures with paraquat **9**·2PF_6 (7 equiv.) (*b*).

Table 3. The upfield shifts Δδ of the signals for the aromatic protons of crownophanes **1a—d** in the ^{1}H NMR spectra of their equimolar mixtures with paraquat **9**·2PF_6

Compound	−Δδ							
	H_a	H_b	H_c	H(2), H(6)	H(3), H(7)	H(4), H(8)	H_α	H_β
1a	0	0.01	0	0	0	0.01	0.01	0.02
1b	0.17	0.06	0.02	0.04	0.01	0.17	0.14	0.49
1c	0.23	0.08	0.05	0.04	0	0.20	0.27	0.55
1d	0.09	0.02	0	0.03	0.04	0.13	0.15	0.30

bipyridinium fragments of paraquat **9**·2PF_6, which is in the cavity of the macrocycle.[32,33,36] With an increase in the molar crownophane : paraquat ratio, this band becomes more intense and its maximum experiences a slight bathochromic shift. The largest relative change in the intensity of this band was observed for a complex of crownophane **1c** with paraquat **9**·2PF_6. The electronic absorption spectra in case of the smallest crownophane **1a** show no changes. Obviously, in this case, no pseudorotaxane is formed or the resulting complex have no donor—acceptor interactions between the aromatic fragments of the crownophane and paraquat (Fig. 2).

In conclusion, note that the formation of pseudorotaxanes in the reactions of paraquat **9**·2PF_6 with crownophanes **1b—d** make the latter promising for use in the synthesis of supramolecular structures of the rotaxane and catenane types.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300 instrument (300 and 75.5 MHz, respectively) in $CDCl_3$. ^{1}H NMR spectra of complexes were recorded in $CDCl_3$—CD_3CN (3 : 4, v/v). Mass spectra (EI) were recorded on an MX-1321 mass spectrometer (direct inlet probe, 70 eV). FAB mass spectra were recorded on a VG 7070EQ mass spectrometer (Xe, 8 kV) in the 3-nitrobenzyl alcohol matrix. IR spectra were recorded on a Specord IR-75 spectrophotometer (KBr pellets). UV spectra were recorded on a Specord M-40 spectrophotometer. Preparative column chromatography was carried out on Kieselgel 60 silica gel (0.063—0.100 mm, Merck). The purity of all the compounds obtained was checked by TLC (Sorbfil UF-254). Melting points were measured in open capillaries and are given uncorrected. Compounds **2**,[23] **7**,[37] and **9**·2PF_6 [38] were prepared as described earlier.

Synthesis of diols 4a—c (general procedure). 2,7-Dihydroxyfluorenone **2** (16.96 g, 0.08 mol) was added under argon to a suspension of freshly calcined K_2CO_3 (66.2 g, 0.48 mol) and NaI (24 g, 0.16 mol) in dry DMF (400 mL). The mixture was stirred at 80 °C for 1 h and chlorohydrin **3a—c** (0.24 mol) was added. The reaction mixture was heated for an additional 35 h and filtered. The filtrate was evaporated to dryness *in vacuo*. The residue was dissolved in chloroform and the resulting solution was washed with aqueous 5% NaOH and twice with water, dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified as specified below.

2,7-Bis(6-hydroxy-1,4-dioxahexyl)-9*H*-fluoren-9-one (4a) was purified by recrystallization from propan-2-ol. The yield was 24.2 g (78%), red crystals, m.p. 117—119 °C. Found (%): C, 65.19; H, 6.29. $C_{21}H_{24}O_7$. Calculated (%): C, 64.94; H, 6.23. UV (MeOH), λ_{max}/nm (logε): 270 (5.01), 469 (2.43). IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 1.97 (br.s, 2 H, OH); 3.65—3.72, 3.74—3.82, 3.84—3.92, 4.14—4.21 (all m, 4 H each, CH_2O); 6.97 (dd, 2 H, H_b, J = 8.1 Hz, J = 2.5 Hz); 7.17 (d, 2 H, H_a, J = 2.2 Hz); 7.29 (d, 2 H, H_c, J = 8.1 Hz). MS (EI), m/z (I_{rel} (%)): 388 $[M]^+$ (44), 300 (7), 212 (35), 89 (8), 45 (100).

2,7-Bis(9-hydroxy-1,4,7-trioxanonyl)-9*H*-fluoren-9-one (4b) was purified by recrystallization from propan-2-ol. The yield was 29.3 g (77%), red crystals, m.p. 91—92 °C. Found (%): C, 62.82; H, 6.65. $C_{25}H_{32}O_9$. Calculated (%): C, 63.01; H, 6.77. UV (MeOH), λ_{max}/nm (logε): 270 (4.95), 473 (2.53). IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 2.18 (br.s, 2 H, OH); 3.63 (t, 4 H, CH_2O, J = 4.2 Hz); 3.68—3.82 (m, 12 H, CH_2O); 3.87, 4.17 (both t, 4 H each, CH_2O, J = 4.5 Hz); 6.98 (dd, 2 H, H_b, J = 8.1 Hz, J = 2.2 Hz); 7.17 (d, 2 H, H_a, J = 2.2 Hz); 7.28 (d, 2 H, H_c, J = 8.1 Hz). MS (EI), m/z (I_{rel} (%)): 476 $[M]^+$ (41), 432 (3), 344 (3), 212 (11), 89 (26), 45 (100).

2,7-Bis(12-hydroxy-1,4,7,10-tetraoxadodecyl)-9*H*-fluoren-9-one (4c) was purified by recrystallization from ethanol—ether (1 : 3). The yield was 36.1 g (80%), a finely crystalline orange solid, m.p. 61—63 °C. Found (%): C, 61.87; H, 6.94. $C_{29}H_{40}O_{11}$. Calculated (%): C, 61.69; H, 7.14. UV (MeOH), λ_{max}/nm (logε): 270 (4.89), 300 (3.83), 312 (3.80), 469 (2.47). IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 2.07 (br.s, 2 H, OH); 3.61 (t, 4 H, CH_2O, J = 4.5 Hz); 3.65—3.77 (m, 20 H, CH_2O); 4.17, 4.28 (both t, 4 H each, CH_2O, J = 4.7 Hz); 6.97 (dd, 2 H, H_b, J = 8.1 Hz, J = 2.5 Hz); 7.17 (d, 2 H, H_a, J = 2.5 Hz); 7.28 (d, 2 H, H_c, J = 8.1 Hz). MS (EI), m/z (I_{rel} (%)): 564 $[M]^+$ (14), 388 (2), 212 (10), 89 (18), 45 (100).

2,7-Bis(15-hydroxy-1,4,7,10,13-pentaoxapentadecyl)-9*H*-fluoren-9-one (4d). A solution of KOH (12 g, 0.215 mol) in anhydrous EtOH (30 mL) was added to a suspension of compound **2** (21.2 g, 0.1 mol) and NaI (1 g) in anhydrous EtOH (150 mL). The mixture was stirred at 40 °C for 15 min and chlorohydrin **3d** (61.6 g, 0.24 mol) was added. The reaction mixture was refluxed for 50 h. The solvent was removed under reduced pressure, the residue was dissolved in water (200 mL), and the product was extracted with $CHCl_3$ (700 mL). The extract was filtered and washed with 5% NaOH until the aqueous layer stopped becoming colored (~6—7 times), 1% HCl, and brine. The organic phase was dried over $MgSO_4$, filtered through a column with Al_2O_3, and concentrated under reduced pressure. Column chromatography (SiO_2, $CHCl_3$—MeOH (100 : 5)) gave diol **4d** as a dark red oil that crystallized with time. The yield was 52.2 g (80%). Found (%): C, 60.72; H, 7.41. $C_{33}H_{48}O_{13}$. Calculated (%): C, 60.57; H, 7.35. UV (MeOH), λ_{max}/nm (logε): 270 (4.92), 300 (3.84), 312 (3.82), 465 (2.59). IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 2.82 (br.s, 2 H, OH); 3.57—3.77 (m, 32 H, CH_2O); 3.86, 4.15 (both t, 4 H each, CH_2O, J = 4.7 Hz); 6.96 (dd, 2 H, H_b, J = 8.1 Hz, J = 2.5 Hz); 7.15 (d, 2 H, H_a, J = 2.5 Hz); 7.27 (d, 2 H, H_c, J = 8.1 Hz). MS (EI), m/z (I_{rel} (%)): 652 $[M]^+$ (7), 212 (10), 89 (21), 45 (100).

Synthesis of ditosylates 5a—d (general procedure). A solution of *p*-toluenesulfonyl chloride (14.3 g, 0.075 mol) in dry dioxane (30 mL) was added dropwise at 0—5 °C for 2 h to a solution of diol **4a—d** (0.03 mol) and Et_3N (12.6 mL, 0.09 mol) in $CHCl_3$ (120 mL). The reaction mixture was warmed to ~20 °C and stirred at this temperature for 30 h. Then an equal volume of $CHCl_3$ was added. The resulting solution was successively washed with aqueous 5% HCl, aqueous 10% NH_3, water, and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in boiling propan-2-ol and cooled. Crystalline ditosylates were washed with EtOH; oils were suspended several times in warm EtOH and the EtOH was decanted. The product was dissolved in benzene, concentrated under reduced pressure, and dried *in vacuo*.

2,7-Bis(6-tosyloxy-1,4-dioxahexyl)-9*H*-fluoren-9-one (5a). The yield was 18.4 g (88%), orange crystals, m.p. 109—112 °C. Found (%): C, 60.47; H, 5.41. $C_{35}H_{36}O_{11}S_2$. Calculated (%):

C, 60.33; H, 5.21. UV ($C_4H_8O_2$), λ_{max}/nm (logε): 272 (4.96), 301 (3.90), 314 (3.88), 464 (2.57). IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 2.42 (s, 6 H, Me); 3.73—3.83 (m, 8 H, CH_2O); 4.07 (t, 4 H, CH_2O, J = 4.5 Hz); 4.21 (t, 4 H, CH_2O, J = 4.8 Hz); 6.95 (dd, 2 H, H_b, J = 8.1 Hz, J = 2.2 Hz); 7.12 (d, 2 H, H_a, J = 2.2 Hz); 7.27—7.36 (m, 6 H, H_{Ar}, H_c); 7.80 (d, 4 H, H_{Ar}, J = 8.1 Hz). MS (FAB), m/z (I_{rel} (%)): 697 $[M + H]^+$ (100), 542 $[M - Ts + H]^+$ (51).

2,7-Bis(9-tosyloxy-1,4,7-trioxanonyl)-9*H*-fluoren-9-one (5b). The yield was 19.7 g (84%), a dark red oil that crystallized under a layer of hexane, m.p. 68—70 °C. Found (%): C, 59.56; H, 5.47. $C_{39}H_{44}O_{13}S_2$. Calculated (%): C, 59.68; H, 5.65. UV ($C_4H_8O_2$), λ_{max}/nm (logε): 225 (4.72), 272 (5.14), 301 (4.10), 314 (4.08), 469 (2.71). IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 2.43 (s, 6 H, Me); 3.57—3.75 (m, 12 H, CH_2O); 3.79—3.87 (m, 4 H, CH_2O); 4.08—4.21 (m, 8 H, CH_2O); 6.97 (dd, 2 H, H_b, J = 8.1 Hz, J = 2.5 Hz); 7.15 (d, 2 H, H_a, J = 2.5 Hz); 7.29 (d, 2 H, H_c, J = 8.1 Hz); 7.33, 7.80 (both d, 4 H each, H_{Ar}, J = 8.3 Hz). MS (FAB), m/z (I_{rel} (%)): 784 $[M]^+$ (100), 630 $[M - Ts + H]^+$ (12).

2,7-Bis(12-tosyloxy-1,4,7,10-tetraoxadodecyl)-9*H*-fluoren-9-one (5c). The yield was 23.1 g (80%), a dark red oily substance. Found (%): C, 58.98; H, 5.83. $C_{43}H_{52}O_{15}S_2$. Calculated (%): C, 59.16; H, 6.00. UV ($C_4H_8O_2$), λ_{max}/nm (logε): 229 (4.40), 272 (4.96), 302 (3.88), 314 (3.87), 464 (2.64). IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 2.43 (s, 6 H, Me); 3.60 (s, 8 H, CH_2O); 3.62—3.76 (m, 12 H, CH_2O); 3.85 (t, 4 H, CH_2O, J = 4.7 Hz); 4.11—4.20 (m, 8 H, CH_2O); 6.97 (dd, 2 H, H_b, J = 8.1 Hz, J = 2.2 Hz); 7.15 (d, 2 H, H_a, J = 2.2 Hz); 7.28 (d, 2 H, H_c, J = 8.1 Hz); 7.33, 7.79 (both d, 4 H each, H_{Ar}, J = 8.1 Hz). MS (FAB), m/z (I_{rel} (%)): 895 $[M + Na]^+$ (3), 872 $[M]^+$ (100), 718 $[M - Ts - H]^+$ (14).

2,7-Bis(15-tosyloxy-1,4,7,10,13-pentaoxapentadecyl)-9*H*-fluoren-9-one (5d). The yield was 18.3 g (70%), a dark red oily substance. Found (%): C, 58.89; H, 6.29. $C_{47}H_{60}O_{17}S_2$. Calculated (%): C, 58.74; H, 6.29. UV ($C_4H_8O_2$), λ_{max}/nm (logε): 226 (4.45), 272 (4.59), 302 (3.88), 314 (3.86), 465 (2.41). IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 2.44 (s, 6 H, Me); 3.58 (s, 8 H, CH_2O); 3.60—3.76 (m, 20 H, CH_2O); 3.86 (t, 4 H, CH_2O, J = 4.7 Hz); 4.16 (t, 8 H, CH_2O, J = 4.7 Hz); 6.97 (dd, 2 H, H_b, J = 8.1 Hz, J = 2.2 Hz); 7.15 (d, 2 H, H_a, J = 2.2 Hz); 7.28 (d, 2 H, H_c, J = 8.1 Hz); 7.33, 7.80 (both d, 4 H each, H_{Ar}, J = 8.1 Hz). MS (FAB), m/z (I_{rel} (%)): 999 $[M + K]^+$ (3), 983 $[M + Na]^+$ (18), 960 $[M]^+$ (100), 806 $[M - Ts + H]^+$ (6).

Synthesis of fluorenone-containing crownophanes 1a—d (general procedure). A solution of 1,5-dihydroxynaphthalene (1.6 g, 0.01 mol) and ditosylate **5a—d** (0.01 mol) in anhydrous DMF (400 mL) was added dropwise for 10 h to a stirred suspension of dry K_2CO_3 (5.52 g, 0.04 mol) in anhydrous DMF (600 mL). The reaction temperature was maintained at 80 °C. After the addition was completed, the mixture was stirred at this temperature for an additional 40 h, cooled, filtered, and concentrated *in vacuo*. The residue was dissolved in $CHCl_3$ (300 mL). The resulting solution was filtered, successively washed with 5% HCl, 5% NaOH, and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The product was purified by column chromatography (SiO_2, $CHCl_3$—MeOH (100 : 2)) and recrystallized.

2,5,8,10,13,16-Hexaoxa-1(2,7)-fluorena-9(5,1)-naphthalenacyclohexadecaphan-1^9-one (1a). The yield was 0.46 g (9%), a yellowish orange powder, m.p. 202—202.5 °C (from butan-1-ol). Found (%): C, 72.84; H, 5.62. $C_{31}H_{28}O_7$. Calculated (%): C, 72.64; H, 5.51. UV (MeCN), λ_{max}/nm (logε): 227 (4.68), 271 (4.76), 298 (4.16), 312 (4.05), 324 (3.83), 472 (2.38). IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 3.93—3.99 (m, 4 H, CH_2O); 4.01—4.13 (m, 8 H, CH_2O); 4.34 (t, 4 H, CH_2O, J = 4.2 Hz); 6.48 (d, 2 H, H(2), H(6), J = 7.8 Hz); 6.81 (dd, 2 H, H_b, J = 8.1 Hz, J = 2.2 Hz); 6.86—6.92 (m, 4 H, H_c, H_a); 7.06 (t, 2 H, H(3), H(7), J = 8.1 Hz); 7.34 (d, 2 H, H(4), H(8), J = 8.4 Hz). ^{13}C NMR, δ: 67.5, 69.0, 69.4, 69.8, 104.5, 111.4, 113.9, 119.7, 121.4, 124.7, 126.0, 135.2, 137.2, 153.7, 157.9, 192.1. MS (EI), m/z (I_{rel} (%)): 512 $[M]^+$ (100), 256 (10), 211 (5), 160 (8), 45 (7).

2,5,8,11,13,16,19,22-octaoxa-1(2,7)-fluorena-12(5,1)-naphthalenacyclodocosaphan-1^9-one (1b). The yield was 1.17 g (20%), reddish orange scaly crystals, m.p. 152—153 °C (from EtOH). Found (%): C, 69.76; H, 5.97. $C_{35}H_{36}O_9$. Calculated (%): C, 69.99; H, 6.04. UV (MeCN), λ_{max}/nm (logε): 226 (4.80), 271 (4.87), 295 (4.16), 312 (4.07), 326 (3.82), 474 (2.34). IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 3.78 (br.s, 8 H, CH_2O); 3.85—3.94 (m, 8 H, CH_2O); 4.06 (t, 4 H, CH_2O, J = 5.3 Hz); 4.13—4.18 (m, 4 H, CH_2O); 6.57 (d, 2 H, H(2), H(6), J = 7.5 Hz); 6.81 (d, 2 H, H_c, J = 8.1 Hz); 6.85 (dd, 2 H, H_b, J = 8.1 Hz, J = 2.2 Hz); 6.92 (d, 2 H, H_a, J = 1.9 Hz); 7.08 (t, 2 H, H(3), H(7), J = 8.1 Hz); 7.58 (d, 2 H, H(4), H(8), J = 8.4 Hz). ^{13}C NMR, δ: 67.4, 68.2, 69.6, 69.9, 71.1, 105.2, 110.6, 114.3, 120.0, 121.0, 124.7, 126.4, 135.5, 137.2, 154.0, 158.9, 193.0. MS (EI), m/z (I_{rel} (%)): 600 $[M]^+$ (100), 300 (7), 212 (2), 160 (5).

2,5,8,11,14,16,19,22,25,28-Decaoxa-1(2,7)-fluorena-15(5,1)-naphthalenacyclooctacosaphan-1^9-one (1c). The yield was 1.31 g (19%), red scaly crystals, m.p. 118.5—119.5 °C (from EtOH). Found (%): C, 68.13; H, 6.21. $C_{39}H_{44}O_{11}$. Calculated (%): C, 68.01; H, 6.44. UV (MeCN), λ_{max}/nm (logε): 226 (4.79), 271 (4.87), 296 (4.17), 312 (4.08), 326 (3.84), 472 (2.43). IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 3.68—3.79 (m, 16 H, CH_2O); 3.81—3.88 (m, 4 H, CH_2O); 3.29 (t, 4 H, CH_2O, J = 4.9 Hz); 4.03—4.13 (m, 8 H, CH_2O); 6.63 (d, 2 H, H(2), H(6), J = 7.5 Hz); 6.83 (dd, 2 H, H_b, J = 8.1 Hz, J = 2.2 Hz); 6.94 (d, 2 H, H_c, J = 8.1 Hz); 7.01 (d, 2 H, H_a, J = 1.9 Hz); 7.16 (t, 2 H, H(3), H(7), J = 8.1 Hz); 7.71 (d, 2 H, H(4), H(8), J = 8.4 Hz). ^{13}C NMR, δ: 67.7, 68.2, 69.6, 69.7, 70.8, 70.9, 71.0, 105.4, 110.4, 114.4, 120.3, 121.0, 124.9, 126.6, 135.7, 137.4, 154.2, 159.1, 193.2. MS (EI), m/z (I_{rel} (%)): 688 $[M]^+$ (100), 344 (7), 211 (6), 160 (6), 45 (32).

2,5,8,11,14,17,19,22,25,28,31,34-Dodecaoxa-1(2,7)-fluorena-18(5,1)-naphthalenacyclotetratriacontaphan-1^9-one (1d). The yield was 1.74 g (21%), an orange powder, m.p. 111—112 °C (from MeOH). Found (%): C, 66.61; H, 6.87. $C_{43}H_{52}O_{13}$. Calculated (%): C, 66.48; H, 6.75. UV (MeCN), λ_{max}/nm (logε): 225 (4.85), 271 (4.92), 296 (4.23), 313 (4.17), 326 (3.91), 472 (2.50). IR, ν/cm^{-1}: 1700 (C=O). ^{1}H NMR, δ: 3.62—3.79 (m, 24 H, CH_2O); 3.82 (t, 4 H, CH_2O, J = 4.5 Hz); 3.93 (t, 4 H, CH_2O, J = 4.8 Hz); 4.07 (t, 4 H, CH_2O, J = 4.5 Hz); 4.15 (t, 4 H, CH_2O, J = 4.8 Hz); 6.68 (d, 2 H, H(2), H(6), J = 7.5 Hz); 6.84 (dd, 2 H, H_b, J = 8.1 Hz, J = 2.2 Hz); 7.00—7.07 (m, 4 H, H_c, H_a); 7.23 (t, 2 H, H(3), H(7), J = 8.1 Hz); 7.74 (d, 2 H, H(4), H(8), J = 8.4 Hz). ^{13}C NMR, δ: 67.7, 68.0, 69.6, 69.7, 70.7, 70.8, 70.8, 71.0, 71.0, 105.4, 110.2, 114.5, 120.4, 120.9, 125.0, 126.6, 135.7, 137.4, 154.2, 159.1, 193.4. MS (EI), m/z (I_{rel} (%)): 776 $[M]^+$ (100), 388 (3), 211 (8), 160 (6), 45 (93).

1,5-Dimethoxynaphthalene (8). A solution of NaOH (2.64 g, 0.066 mol) in water (24 mL) was added for 20 min to a mixture of 1,5-dihydroxynaphthalene (4.8 g, 0.03 mol) and dimethyl

sulfate (7.9 g, 0.063 mol) in water (25 mL). The addition rate was regulated so as to prevent the temperature from increasing above 30 °C. The reaction mixture was stirred for 45 min and then at 70 °C for an additional 2 h. After cooling, the precipitate was filtered off, dried, and recrystallized from heptane with Al_2O_3. The yield was 1.9 g (34%), m.p. 183—184 °C (*cf.* Ref. 39: 183—184 °C). Found (%): C, 76.81; H, 6.71. $C_{12}H_{12}O_2$. Calculated (%): C, 76.57; H, 6.43. ^{1}H NMR ($CDCl_3$), δ: 3.97 (s, 6 H, Me); 6.83 (d, 2 H, H(2), H(6), J = 7.47 Hz); 7.36 (t, 2 H, H(3), H(7), J = 8.09 Hz); 7.83 (d, 2 H, H(4), H(8), J = 8.72 Hz). MS, m/z (I_{rel} (%)): 188 $[M]^+$ (100), 173 (55).

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