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Synthesis and Properties of First Bis(fluoreno)crownophanes

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Abstract—Alkylation of 2,7-dihydroxy-9*H*-fluoren-9-one with 2-(2-chloroethoxy)ethanol, 2-[2-(2-chloroethoxy)-ethoxy]ethanol, and 2-{2-[2-(2-chloroethoxy)ethoxy]ethoxy}ethanol in dimethylformamide in the presence of potassium carbonate gave 78–80% of the corresponding diols which were treated with *p*-toluenesulfonyl chloride in a dioxane–chloroform mixture in the presence of triethylamine at 0–5°C (30 h). The resulting bis(*p*-toluene-sulfonates) were brought into condensation with 2,7-dihydroxy-9*H*-fluoren-9-one in a very dilute solution in dimethylformamide containing anhydrous potassium carbonate at 80–85°C. Appropriate treatment of the reaction mixture, followed by chromatographic purification afforded 53–27% of the first representatives of a new class of cyclophanes, bis(oxofluoreno)crownophanes. Raising the temperature to 95–105°C resulted in an appreciable decrease of the product yield. The yield of the target products did not increase on replacement of potassium carbonate by cesium carbonate.

Cyclophanes are macrocyclic compounds incorporating one or several aromatic fragments [1]. They show enhanced selectivity in complex formation and constitute one of the main classes of macrocyclic receptors. Cyclophanes are widely used as catalysts, ion and neutral molecule carriers, chemosensors [2], and components of supramolecular structures like rotaxanes and catenanes, the latter being basis structures in the design of nano-electronic devices [3]. Crownophanes in which large aromatic fragments are linked through polyoxaethylene bridges attract specific attention. Crownophanes successfully combine properties of classical crown ethers and cyclophanes. Such a symbiosis makes them excellent receptors for both ionic and neutral species [4]. It is also important that flexible polyether chains allow relatively easy adjustment of the shape and size of the intramolecular cavity of crownophanes to meet steric requirements of a substrate.

The structure, selectivity of formation, and stability of molecular complexes and supramolecular systems are determined by various intermolecular nonvalence interactions [5]. Among these, the most important are hydrogen bonding, electrostatic interactions, π–π stacking, interactions like π–cation, π···H–C, and π···H–O, hydrophobic effects, and van der Waals forces. All these interactions taken alone are weak, but they give rise to a powerful cumulative effect which in most cases is responsible for the three-dimensional chemical structure and properties of complexes [5, 6]. With the goal of controlling complexing properties of cyclophanes, large and (as a rule) nonpolar aromatic fragments were introduced into the macrocyclic framework. On the other hand, to enhance intermolecular interactions which generally have electrostatic origin [5], it seems reasonable to introduce into the macroring large aromatic fragments with an extended π-electron system, containing polar groups. In this respect, it may be promising to incorporate into the crownophane structure a fluorenone fragment which was not used previously for such purposes. This assumption is based on the following: (1) Fluorenone possesses a large, strongly polarized π-electron system which is capable of effectively reacting with cations and other aromatic systems; (2) the carbonyl oxygen atom in fluorenone is a strong hydrogen acceptor which could give rise to strong hydrogen bonds with substrates, whereas hydrogen bonding is known to be often the crucial factor in molecular recognition processes and self-organization of supramolecular systems; (3) the carbonyl group in fluorenone can act as an antenna capable of recognizing an electron-deficient guest species, directing it toward the macrocyclic cavity of the host, and stabilizing the intercalation via electrostatic interactions; (4) fluorenone and its derivatives exhibit good luminescent

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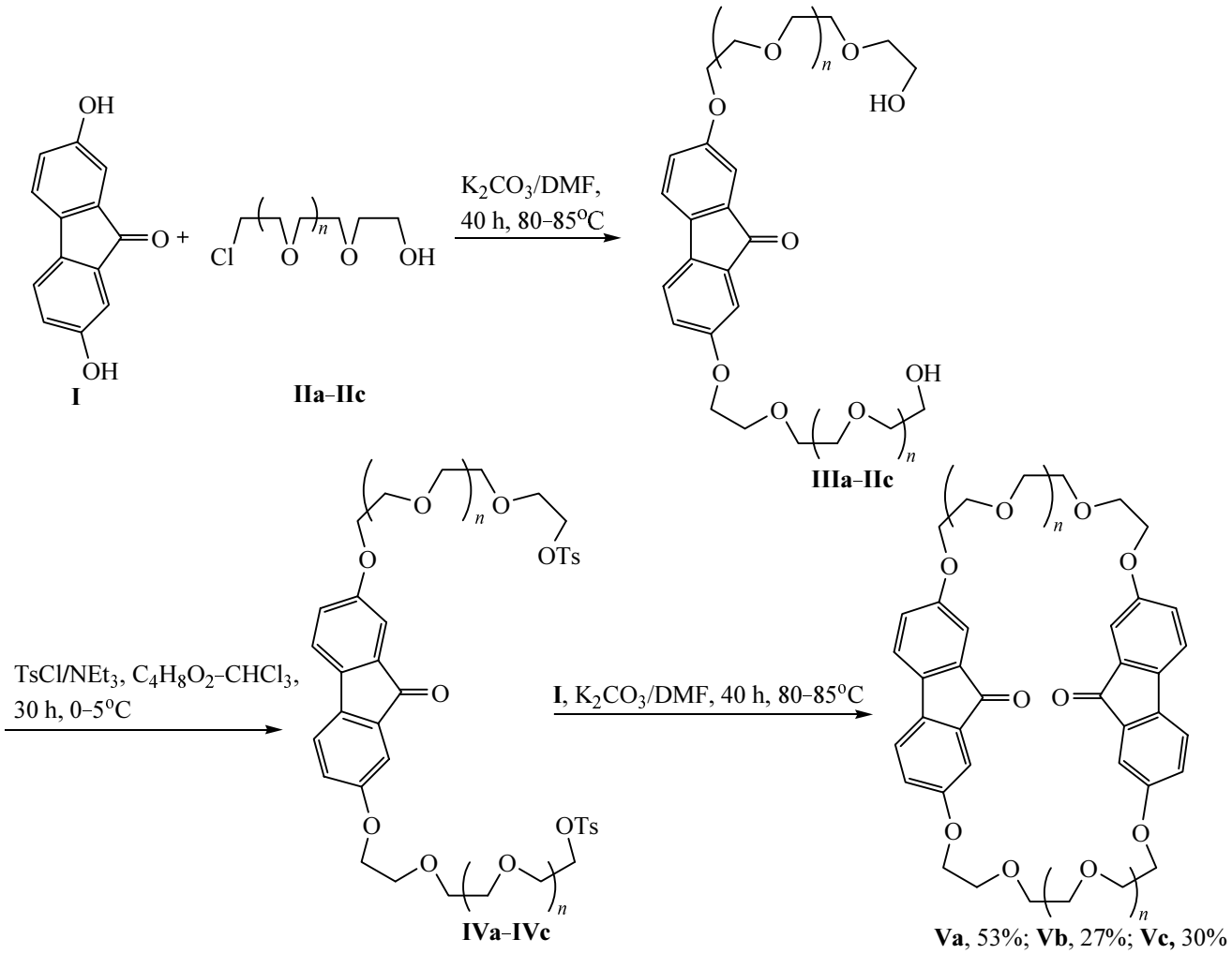
properties which may be important in the design of high-sensitive fluorescent chemosensors; and finally (5) the carbonyl group in fluorenonophanes can readily be converted into other functional groups, thus providing the possibility for fine tuning of the complexing power of such macrocyclic receptors.

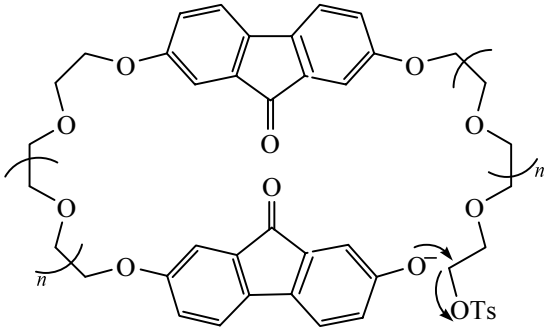
The present communication describes the synthesis and spectral properties of the first representatives of a new cyclophane family, bis(oxofluoreno)crownophanes **Va**–**Vc**. As starting compound we used relatively accessible 2,7-dihydroxy-9*H*-fluoren-9-one (**I**) [7]. Its alkylation with monochloro derivatives of di-, tri-, and tetraethylene glycols (compounds **IIa**–**IIc**) in DMF in the presence of potassium carbonate gave diols **IIIa**–**IIIc** in 78–80% yield (Scheme 1). Diols **IIIa**–**IIIc** were treated with *p*-toluenesulfonyl chloride in a mixture of dioxane and chloroform using triethylamine as a base (0–5°C, 30 h). As a result, we obtained the corresponding bis(*p*-toluenesulfonates) **IVa**–**IVc** in a good yield (70–88%). The latter were brought into condensation with dihydroxyfluorenone **I** in a strongly dilute DMF solution in the presence of anhydrous potassium carbonate (80–85°C). After appropriate treatment and chromatographic purification, we isolated bis(oxofluoreno)crownophanes. When the condensation was carried out at higher temperature (95–105°C), the yield of compounds **Va**–**Vc** was appreciably lower. It is known [8] that cesium cation favors formation of many macrocyclic systems. However, we failed to increase the yield of the target products to an appreciable extent by replacement of potassium carbonate by cesium carbonate. Presumably, in this case the effect of the cation is either weak or absent.

Crownophane **Va** was isolated in a considerably greater yield than those of compounds **Vb** and **Vc**; the

Scheme 1.



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



A

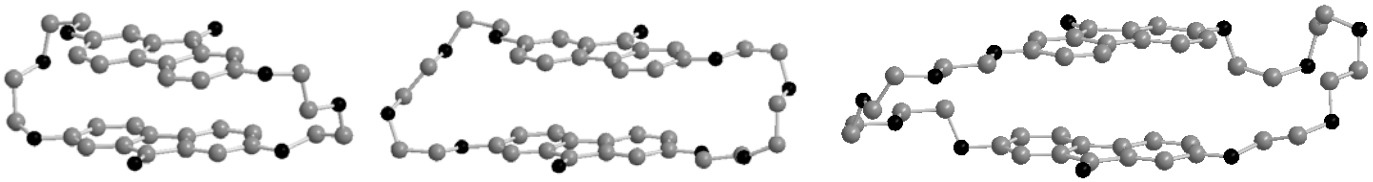
yields of the two latter were approximately similar. The observed difference may be attributed to formation of quasicyclic structure **A** (which is ready to cyclization) as a result of intramolecular π–π stacking of the fluorene fragments in intermediate open-chain compound. As we showed in preliminary communication [9], an analogous interaction was revealed in crystalline compound **Vb**; it is also typical of structures related to fluorenone, e.g., dibenzofurans [10]. In keeping with the entropy factor, such preorganization is more probable for molecules with short bridges between the fluorene fragments. As the length of the bridge increases, the number of degrees of freedom of the molecule also rises, and its preorganization becomes less favorable. As a result, the yield of crownophanes **Vb** and **Vc** decreases.

The fluorene fragments in molecule **Vb** in crystal are arranged parallel to each other at a distance of 3.45 Å [9], which is typical of cyclophanes if π–π stacking exists [11]. Mutual orientation of the carbonyl groups corresponds to nonpolar *anti* conformation of the molecule. The crystalline structure of compound **Vb** is well consistent with the most favorable theoretical structure determined by conformational analysis in terms of the Monte Carlo procedure (Spartan'02 software package, MMFF force field [12]; Fig. 1). The mean-square deviation of the coordinates of all non-hydrogen atoms in the calculated structure from those determined experimentally is 1.55 Å . Therefore, the above calculation method is believed to satisfactorily describe the real structure of crownophanes **Va**–**Vc** at least in the gas phase.

According to the calculations, an *anti* conformation with almost coplanar arrangement of the partially overlapping fluorene fragments is the most favorable for crownophanes **Va**–**Vc**. The absence of clearly defined intramolecular cavity in **Va**–**Vc** is not a serious obstacle to formation of intercalation compounds like pseudorotaxanes [13]. Bonding intramolecular π–π interactions between the aromatic fragments (which are unfavorable from the viewpoint of entropy factor) in solution may be lacking due to restriction of the internal mobility of the molecule. In this case, a dynamic equilibrium between numerous conformations of the macroring should be established, and these conformations may include those with an open cavity whose shape and size may vary over a fairly wide range to fit steric requirements of a substrate.

The above stated is confirmed by analysis of the ^{1}H NMR spectra of crownophanes **Va**–**Vc**, which displayed a set of signals typical of oligoethylene glycol fragments in the region δ 3.65–4.10 ppm and aromatic proton signals characteristic of 2,7 disubstituted fluorenones (Fig. 2). As compared to 2,7-dimethoxyfluorenone **VI** taken as model compound, signals from all fluorene protons in the spectra of **Va**–**Vc** are displaced upfield by 0.16–0.39 ppm due to shielding by the opposite aromatic fragment (see table). Regardless of the macroring size, the largest upfield shift is observed for the H^a and H^c protons relative to the corresponding shift of the H^b signal. These data indicate fast (on the NMR time scale, 300 MHz) rotation of the fluorene fragments with respect to each other. Computer simulation (Spartan'02, MMFF force field [12]) showed that such rotation makes the H^a and H^c protons the most shielded and that the average distance from these protons to the plane of the opposite aromatic fragment does not depend on the ring size to an appreciable extent.

Thus we have synthesized the first representatives of a new crownophane series, which are promising as



Va **Vb** **Vc**

Fig. 1. Calculated structures of crownophanes **Va**–**Vc**.

macrocyclic receptors for small organic molecules and metal ions. Complexing power of these compounds will be the subject of our further studies.

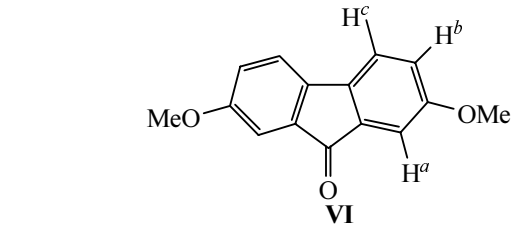
EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1321 instrument with direct sample admission into the ion source (ion source temperature 200°C). The IR spectra were measured in KBr using a Specord IR spectrometer. The UV spectra were recorded on a Specord-40 spectrophotometer.

Silica gel L (250 μm, Chemapol) was used for preparative column chromatography. The purity of the products was checked by TLC on Silufol UV 254 plates. Compounds **IIa** and **IIb** were commercial products, and compounds **IIc** [14] and **VI** [15] were prepared by known procedures.

Diols IIIa–IIIc (*general procedure***).** 2,7-Dihydroxy-9*H*-fluoren-9-one (**I**), 16.96 g (80 mmol), was added under argon to a suspension of freshly calcined potassium carbonate, 66.24 g (480 mmol), and sodium iodide, 24 g (160 mmol), in 400 ml of anhydrous dimethylformamide. The mixture was stirred for 1 h at 80°C, 240 mol of compound **IIa**–**IIc** was added, and the mixture was stirred for 35 h at that temperature. It was then filtered, and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in chloroform, and the solution was washed with a 5% aqueous solution of sodium hydroxide and two portions of water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was recrystallized from 2-propanol to isolate compounds **IIIa–IIIc** as orange–red crystals.

2,7-Bis[2-(2-hydroxyethoxy)ethoxy]-9*H*-fluoren-9-one (IIIa). Yield 24.2 g (78%), mp 117–119°C. UV spectrum (CH_3OH), λ_{max}, nm (log ε): 270 (5.0), 469 (2.43). IR spectrum: ν(C=O) 1700 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.97 br.s (2H, OH), 3.65–3.72 m (4H, CH_2O), 3.74–3.82 m (4H, CH_2O), 3.84–3.92 m (4H, CH_2O), 4.14–4.21 m (4H, CH_2O), 6.97 d.d (2H, H^b, J = 8.09 Hz), 7.17 d (2H, H^a, J = 2.18 Hz), 7.29 d (2H, H^c, J = 8.09 Hz). Mass spectrum, m/z (I_{rel}, %): 388 $[M]^+$ (44), 300 (7), 212 (35). Found, %: C 65.19; H 6.29. $C_{21}H_{24}O_7$. Calculated, %: C 64.94; H 6.23.



VI

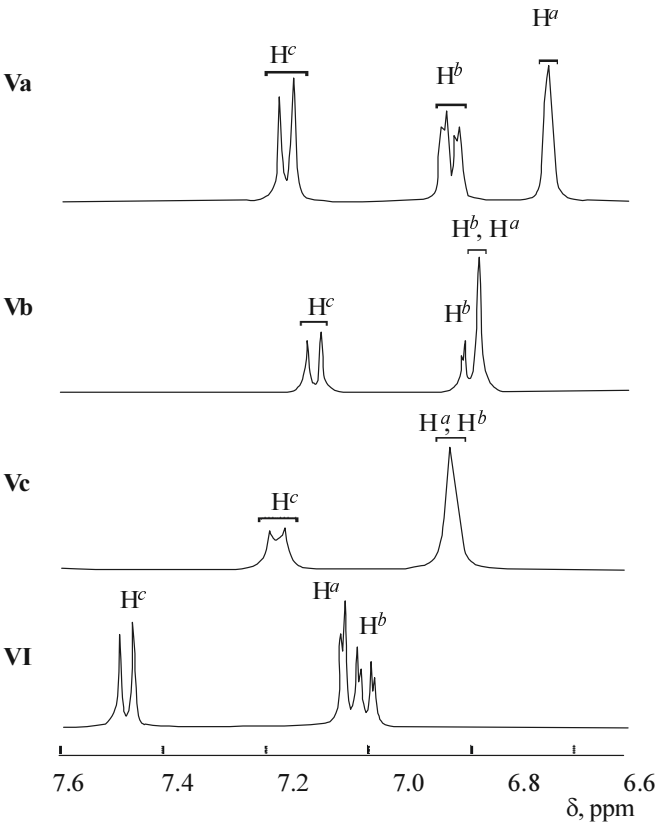


Fig. 2. Fluorene proton region in the ^{1}H NMR spectra of compounds **Va**–**Vc** and **VI** (DMSO-d_6, 25°C)

Relative chemical shifts of protons in the fluorene fragment of 2,7-dimethoxyfluorenone (**VI**) and crownophanes **Va**–**Vc** (DMSO-d_6, 25°C)

Comp. no.	Chemical shifts δ,[a] ppm			Difference in the chemical shifts Δδ,[b] ppm		
	H^a	H^b	H^c	H^a	H^b	H^c
Va	6.66	6.85	7.17	–0.39	–0.16	–0.31
Vb	6.78	6.80	7.11	–0.27	–0.21	–0.37
Vc	~6.84	~6.84	7.18	~(–0.21)	~(–0.17)	–0.30
VI	7.05	7.01	7.48	–	–	–

[a] For designation of protons, see Fig. 2.
[b] Δδ = δ(**VI**) – δ(**V**).

2,7-Bis{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}-9*H*-fluoren-9-one (IIIb). Yield 29.3 g (77%), mp 91–92°C. UV spectrum (CH_3OH), λ_{max}, nm (log ε): 270 (4.95), 473 (2.53). IR spectrum: ν(C=O) 1700 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.18 br.s (2H, OH), 3.63 t (4H, CH_2O, J = 4.2 Hz), 3.68–3.82 m (12H, CH_2O), 3.87 t (4H, CH_2O, J = 4.5 Hz), 4.17 t (4H, CH_2O, J = 4.5 Hz), 6.98 d.d (2H, H^b, J = 8.09 Hz), 7.17 d (2H, H^a, J = 2.18 Hz), 7.28 d (2H, H^c, J = 8.09 Hz). Mass spectrum, m/z (I_{rel}, %): 476 $[M]^+$ (41), 432 (3), 344 (3), 212 (11). Found, %: C 62.82; H 6.65. $C_{25}H_{32}O_9$. Calculated, %: C 63.01; H 6.77.

2,7-Bis(2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethoxy)-9*H*-fluoren-9-one (IIIc). Yield 36.1 g (80%), mp 61–63°C. UV spectrum (CH_3OH), λ_{max}, nm (log ε): 270 (4.89), 300 (3.83), 312 (8.30), 469 (2.47). IR spectrum: ν(C=O) 1700 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.07 br.s (2H, OH), 3.61 t (4H, CH_2O, J = 4.51 Hz), 3.65–3.77 m (20H, CH_2O), 4.17 t (4H, CH_2O, J = 4.67 Hz), 4.28 t (4H, CH_2O, J = 4.67 Hz), 6.97 d.d (2H, H^b, J = 8.09 Hz), 7.17 d (2H, H^a, J = 2.49 Hz), 7.28 d (2H, H^c, J = 8.10 Hz). Mass spectrum, m/z (I_{rel}, %): 564 $[M]^+$ (14), 388 (2), 212 (10). Found, %: C 61.87; H 6.94. $C_{29}H_{40}O_{11}$. Calculated, %: C 61.69; H 7.14.

Bis(*p*-toluenesulfonates) IVa–IVc (*general procedure*). A solution of 75 mol of *p*-toluenesulfonyl chloride in 30 ml of anhydrous dioxane was added dropwise over a period of 2 h to a solution of 30 mmol of diol **IIIa**–**IIIc** and 90 mmol of triethylamine in 120 ml of chloroform, maintained at 0–5°C. The cooling bath was removed, and the mixture was stirred for 30 h at room temperature. It was then diluted with an equal volume of chloroform, and the resulting solution was washed in succession with 5% hydrochloric acid, 10% aqueous ammonia, water, and a saturated solution of sodium chloride, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was treated as indicated below.

2-[2-(7-{2-[2-(4-Methylphenylsulfonyloxy)ethoxy]ethoxy}-9-oxo-9*H*-fluoren-2-yloxy)ethoxy]ethyl 4-methylbenzenesulfonate (IVa). Orange crystals from 2-propanol. Yield 18.4 g (88%), mp 109–112°C. UV spectrum (1,4-dioxane), λ_{max}, nm (log ε): 272 (4.96), 301 (3.90), 314 (3.88), 464 (2.57). IR spectrum: ν(C=O) 1700 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.42 s (6H, Me), 3.73–3.83 m (8H, CH_2O), 4.07 t (4H, CH_2O, J = 4.52 Hz), 4.21 t (4H, CH_2O, J = 4.82 Hz), 6.95 d.d (2H, H^b, J = 8.10 Hz), 7.12 d (2H, H^a, J = 2.18 Hz), 7.27–7.36 m (6H, H_{arom}, H^c), 7.80 d (4H, H_{arom}, J = 8.09 Hz). Mass spectrum, m/z (I_{rel}, %): 696 $[M]^+$ (5), 524 (26), 497 (7), 282 (10), 212 (31). Found, %: C 60.47; H 5.41. $C_{35}H_{36}O_{11}S_2$. Calculated, %: C 60.33; H 5.21.

2-(2-{2-[7-(2-{2-[2-(4-Methylphenylsulfonyloxy)ethoxy]ethoxy}ethoxy)-9-oxo-9*H*-fluoren-2-yloxy]ethoxy}ethoxy)ethyl 4-methylbenzenesulfonate (IVb). Dark red oily substance which crystallizes under a layer of hexane. Yield 19.7 g (84%), mp 68–70°C. UV spectrum (1,4-dioxane), λ_{max}, nm (log ε): 225 (4.72), 272 (5.14), 301 (4.10), 314 (4.08), 469 (2.71). IR spectrum: ν(C=O) 1700 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.43 s (6H, Me), 3.57–3.75 m (12H, CH_2O), 3.79–3.87 m (4H, CH_2O), 4.08–4.21 m (8H, CH_2O), 6.97 d.d (2H, H^b, J = 8.10 Hz), 7.15 d (2H, H^a, J = 2.49 Hz), 7.29 d (2H, H^c, J = 8.10 Hz), 7.33 d (4H, H_{arom}, J = 8.25 Hz), 7.80 d (4H, H_{arom}, J = 8.35 Hz). Mass spectrum, m/z (I_{rel}, %): 524 (4), 212 (16), 199 (75), 155 (49). Found, %: C 59.56; H 5.47. $C_{39}H_{44}O_{13}S_2$. Calculated, %: C 59.68; H 5.65.

2-{2-[2-(2-{7-[2-(2-{2-[2-(4-Methylphenylsulfonyloxy)ethoxy]ethoxy}ethoxy)ethoxy]-9-oxo-9*H*-fluoren-2-yloxy}ethoxy)ethoxy]ethoxy}ethyl 4-methylbenzenesulfonate (IVc). Dark red oily substance. Yield 18.3 g (70%). UV spectrum (1,4-dioxane), λ_{max}, nm (log ε): 229 (4.40), 272 (4.96), 302 (3.88), 314 (3.87), 464 (2.64). IR spectrum: ν(C=O) 1700 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.43 s (6H, Me), 3.60 s (8H, CH_2O), 3.62–3.76 m (12H, CH_2O), 3.85 t (4H, CH_2O, J = 4.67 Hz), 4.11–4.20 m (8H, CH_2O), 6.97 d.d (2H, H^b, J = 8.09 Hz), 7.15 d (2H, H^a, J = 2.18 Hz), 7.28 d (2H, H^c, J = 8.10 Hz), 7.33 d (4H, H_{arom}, J = 8.11 Hz), 7.79 d (4H, H_{arom}, J = 8.10 Hz). Mass spectrum, m/z (I_{rel}, %): 414 (3), 212 (8), 199 (4), 155 (4). Found, %: C 58.98; H 5.83. $C_{43}H_{52}O_{15}S_2$. Calculated, %: C 59.16; H 6.00.

Crownophanes Va–Vc (*general procedure*). A solution of 2.12 g (10 mmol) of compound **I** and 10 mmol of bis(*p*-toluenesulfonate) **IVa**–**IVc** in 400 ml of anhydrous DMF was added dropwise under stirring over a period of 10 h to a suspension of 5.52 g (0.04 mol) of dry potassium carbonate in 600 ml of anhydrous DMF, maintaining the temperature at 80°C. When the addition was complete, the mixture was stirred for 40 h at that temperature, cooled, and filtered, and the solvent was distilled off from the filtrate under reduced pressure. The

residue was combined with the precipitate, washed with two portions of methanol (50 and 30 ml), placed into a Soxhlet apparatus, and continuously extracted with toluene over a period of 40 h. The extract was cooled to room temperature, and the precipitate was filtered off and repeatedly crystallized from toluene until complete extraction of the product. The toluene mother liquors were combined and evaporated under reduced pressure, and the residue was washed with acetone (4 × 5 ml), dried, and purified by column chromatography on silica gel using chloroform–methanol (100 : 1) as eluent.

8,11,14,26,29,32-Hexaoxaheptacyclo-[31.3.1.1^{3,7}.1^{15,19}.1^{21,25}.0^{4,36}.0^{18,22}]tetraconta-1(37),3(40),4,6,15(39),16,18,21(38),22,24,33,35-dodecaene-2,20-dione (Va). Orange–red crystals. Yield 2.98 g (53%), mp 296–298°C (decomp.). UV spectrum (1,4-doxane), λ_{max}, nm (log ε): 264 (5.08), 302 (4.05), 314 (4.04), 473 (2.71). IR spectrum: ν(C=O) 1700 cm^{-1}. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.81 t (8H, CH_2O, J = 3.12 Hz), 4.09 t (8H, CH_2OAr, J = 3.12 Hz), 6.66 br.s (4H, H^a), 6.84 d.d (4H, H^b, ^3J = 8.10, ^4J = 2.17 Hz), 7.16 d (4H, H^c, J = 8.10 Hz). Mass spectrum, m/z (I_{rel}, %): 564 [M]$^+$ (100), 282 (7), 239 (8), 212 (11), 45 (8). Found, %: C 72.26; H 5.25. $C_{34}H_{28}O_8$. Calculated, %: C 72.33; H 5.00.

8,11,14,17,29,32,35,38-Octaoxaheptacyclo-[37.3.1.1^{3,7}.1^{18,22}.1^{24,28}.0^{4,42}.0^{21,25}]hexatetraconta-1(43),3(46),4,6,18(45),19,21,24,25,27,39,41-dodecaene-2,23-dione (Vb). Light red crystals. Yield 1.76 g (27%), mp 197–199°C. UV spectrum (1,4-dioxane), λ_{max}, nm (logε): 264 (5.09), 302 (4.06), 314 (4.04), 470 (2.66). IR spectrum: ν(C=O) 1700 cm^{-1}. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.65 s (8H, CH_2O), 3.75 t (8H, CH_2O, J = 4.20 Hz), 4.04 t (8H, CH_2O, J = 4.20 Hz), 6.81 br.s (4H, H^a), 6.84 br.d (4H, H^b, J = 8.10 Hz), 7.15 d (4H, H^c, J = 8.10 Hz). Mass spectrum, m/z (I_{rel}, %): 652 [M]$^+$ (100), 580 (16), 326 (14), 212 (18). Found, %: C 69.77; H 5.69. $C_{38}H_{36}O_{10}$. Calculated, %: C 69.93; H 5.56.

8,11,14,17,20,32,35,38,41,44-Decaoxaheptacyclo[43.3.1.1^{3,7}.1^{21,25}.1^{27,31}.0^{4,48}.0^{24,28}]dopentaconta-1(49),3(52),4,6,21(51),22,24,27(50),28,30,45,47-dodecaene-2,26-dione (Vc). Orange–red crystals. Yield 2.22 g (30%), mp 176–177°C (from toluene). UV spectrum (1,4-dioxane), λ_{max}, nm (logε): 263 (5.13), 270 (5.08), 302 (4.10), 314 (4.08), 468 (2.76). IR spectrum: ν(C=O) 1700 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.73 br.s (16H, CH_2O), 3.87 t (8H, CH_2O, J = 4.53 Hz), 4.00 t (8H, CH_2O, J = 4.53 Hz), 6.76 d.d (4H, H^b, ^3J = 8.40, ^4J = 2.18 Hz), 6.89 d (4H, H^a, J = 2.18 Hz), 6.97 d (4H, H^c, J = 8.40 Hz). Mass spectrum, m/z (I_{rel}, %): 740 [M]$^+$ (100), 369 (5), 238 (17), 212 (21), 129 (22). Found, %: C 68.34; H 6.22. $C_{42}H_{44}O_{12}$. Calculated, %: C 68.10; H 5.99.

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