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Anthracene-Containing [2]Rotaxanes: Synthesis, Spectroscopic, and Electrochemical Properties

Roberto Ballardini,[a] Vincenzo Balzani,*[b] Wim Dehaen,[c] Adele E. Dell'Erba,[b] Françisco M. Raymo,[d] J. Fraser Stoddart,*[d] and Margherita Venturi[b]

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Two dumbbell-shaped compounds (**8** and **11**), each composed of two polyether chains intercepted by a 1,4-dioxybenzene recognition site, terminated by tetraarylmethane-based stoppers, and emanating from a central 9,10- or a 2,6-dioxyanthracene unit, have been synthesized. Two [2]rotaxanes (**9** · 4 PF_6 and **12** · 4 PF_6) have been prepared by interlocking these dumbbell-shaped compounds (**8** and **11**) with a bipyridinium-based tetracationic cyclophane (**15** · 4 PF_6) – namely, cyclobis(paraquat-*p*-phenylene). A [3]rotaxane (**10** · 8 PF_6) incorporating two cyclophane components (**15** · 4 PF_6) was also obtained when the 9,10-dioxyanthracene-containing dumbbell-shaped compound (**8**) incorporating two 1,4-dioxybenzene recognition sites was employed. The ^{1}H-NMR spectroscopic investigation of the [2]rotaxanes (**9** · 4 PF_6 and **12** · 4PF_6) revealed that the cyclophane component encircles one of the two 1,4-dioxybenzene recognition sites in the 9,10-dioxyanthracene-containing [2]rotaxane (**9** · 4 PF_6) and the 2,6-dioxyanthracene unit in the other [2]rotaxane (**12** · 4 PF_6). These structures have been confirmed by UV/Vis and electrochemical experiments. Comparison with the spectroscopic properties of simple model compounds shows the presence of electronic interactions which lead to *(i)* the occurrence of very efficient energy transfer processes in the dumbbell-shaped components and *(ii)* perturbations in the absorption spectra with appearance of two charge-transfer absorption bands and complete luminescence quenching in the [2]rotaxanes. For the 2,6-dioxyanthracene-containing [2]rotaxane (**12** · 4 PF_6), it has been demonstrated that the cyclophane can be displaced from the dioxyanthracene to the 1,4-dioxybenzene station upon electrochemical oxidation.

Introduction

[*n*]Rotaxanes[1] are molecules composed of [*n* – 1] rings encircling a linear component terminated at both ends by bulky stoppers in the shape of a dumbbell. The ring and dumbbell-shaped components are not covalently linked to each other. Rather, a mechanical bond – in most instances reinforced by noncovalent bonding interactions – holds the components together. Although, by virtue of this mechanical bond, the ring and dumbbell-shaped components cannot dissociate, they are able to move, one relative to the other(s), between appropriate recognition sites that act as "stations". Indeed, the "shuttling" of the ring component along the linear portion of the dumbbell-shaped component has been observed in a large number of [2]rotaxanes – the so-called "molecular shuttles".[2] By introducing chemically-, electrochemically-, and/or photochemically-active units into the dumbbell-shaped component of [2]rotaxanes, the "shuttling" process can be controlled reversibly by external stimuli, thus offering the opportunity of constructing "molecular switches".[3] In research targeted toward the design and realization of molecular devices able to perform logical operations, we have developed[4] a self-assembly approach to [*n*]rotaxanes. The method relies upon the high complementarity between π-electron rich dioxyarene-based neutral components and π-electron deficient bipyridinium-based cationic components. A number of cooperative noncovalent bonding interactions – namely, [C–H···O] hydrogen bonding,[5] [π···π] stacking,[6] and [C-H···π] interactions[7] – are invariably responsible for the molecular recognition events which govern these template-directed syntheses.[8] In order to construct novel [*n*]rotaxanes incorporating photochemically-active units, we have envisaged the possibility of introducing dioxyanthracene units within the dumbbell-shaped components of [*n*]rotaxanes. Here, we report the template-directed syntheses and the characterization of two [2]rotaxanes and one [3]rotaxane incorporating either a 9,10- or a 2,6-dioxyanthracene unit, together with a couple of 1,4-dioxybenzene recognition sites, in their dumbbell-shaped components. Since they contain several chromophoric and redox active units, these compounds are particularly interesting from the viewpoint of their absorption, luminescence, and electrochemical properties.

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[a] Istituto FRAE-CNR,
via Gobetti 101, I-40129 Bologna, Italy
[b] Dipartimento di Chimica "G. Ciamician" dell'Universitá,
via Selmi 2, I-40126 Bologna, Italy
Fax: (internat.) + 39-051/2099456
E-mail: vbalzani@ciam.unibo.it
[c] Department Scheikunde, Katholieke Universiteit Leuven,
Celestijnenlaan 200F, B-3001 Heverlee, Belgium
Fax: (internat.) + 32-(0)16327990
[d] Department of Chemistry and Biochemistry, University of California, Los Angeles,
405 Hilgard Avenue, Los Angeles, CA 90095-1569, USA
Fax: (internat.) + 1-310206-1843
E-mail: stoddart@chem.ucla.edu

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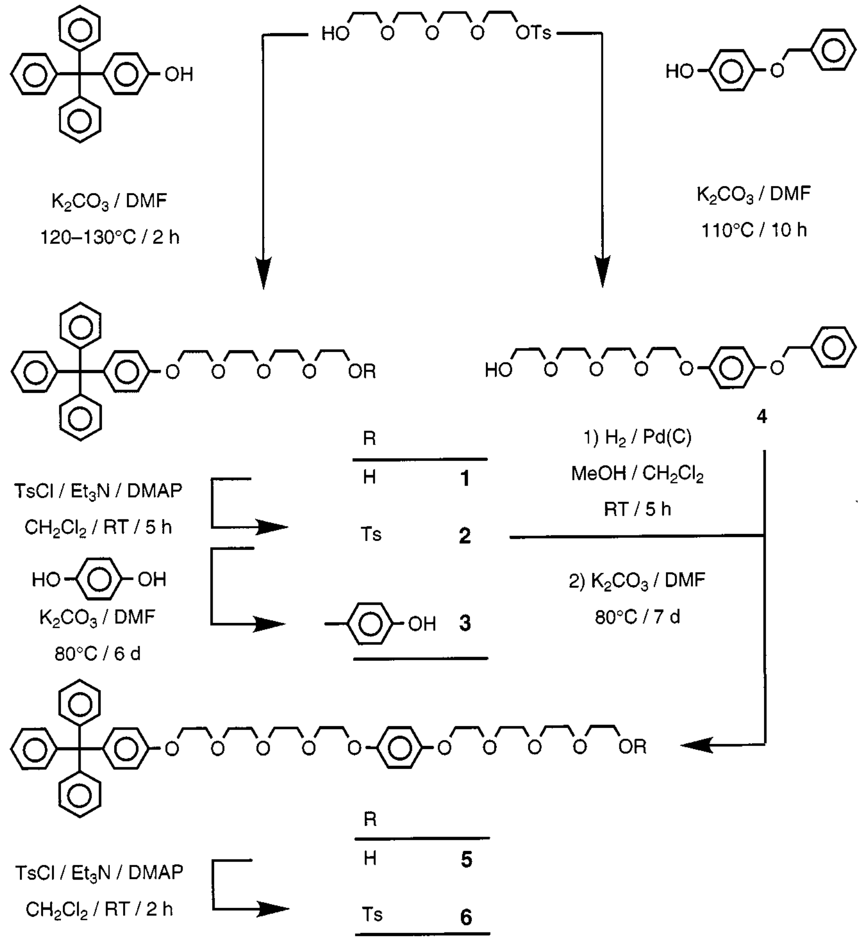
Results and Discussion

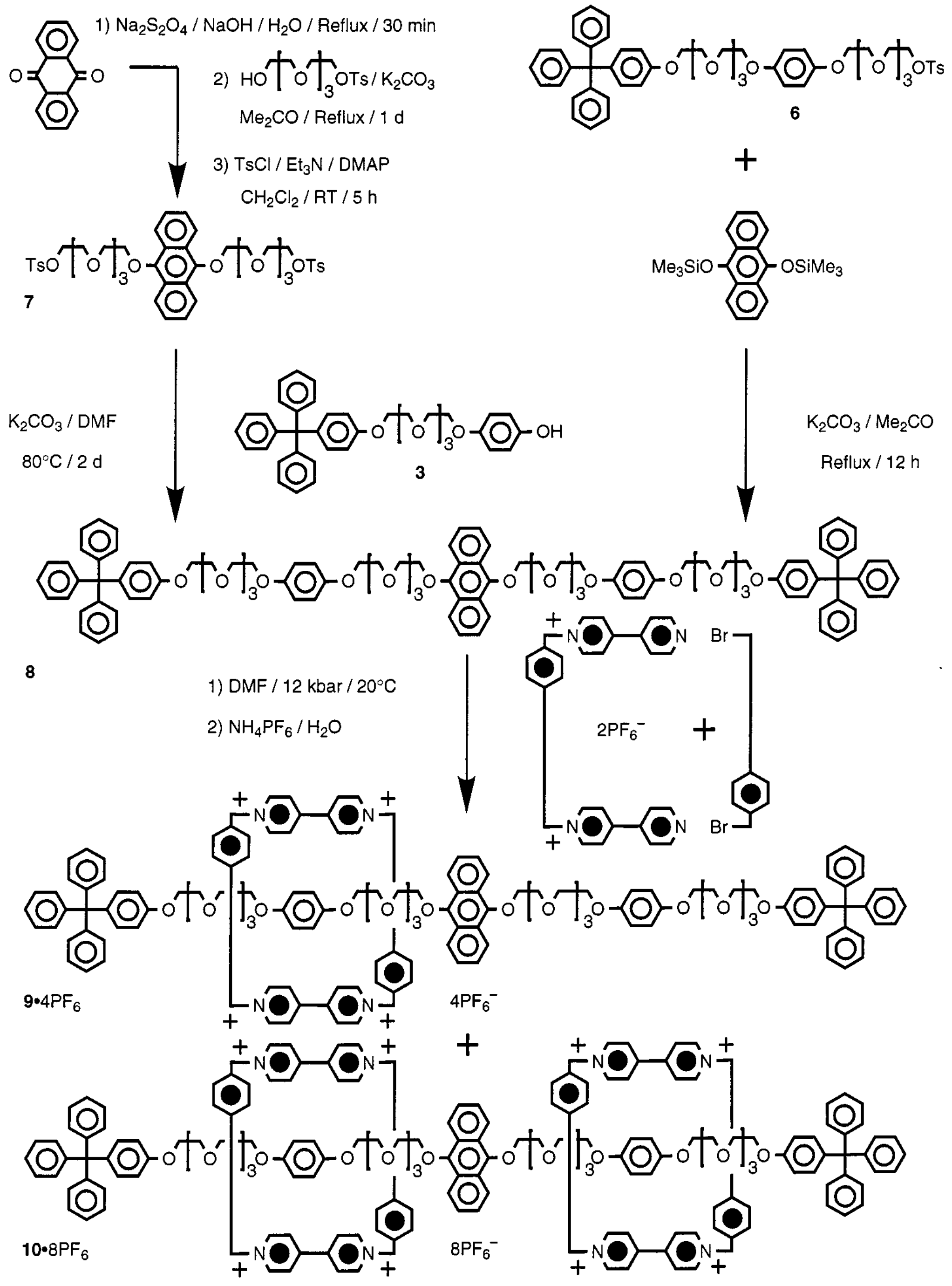
Synthesis and Spectroscopic Characterization

The syntheses of the anthracene-containing dumbbell-shaped compounds and [*n*]rotaxanes, along with their precursors, are illustrated in Schemes 1–3. Reaction (Scheme 1) of 4-triphenylmethylphenol with tetraethylene glycol monotosylate in the presence of K_2CO_3 gave **1**, which was converted into the tosylate **2**. Alkylation of 1,4-dihydroxybenzene with **2**, and of 4-benzyloxyphenol with tetraethylene glycol monotosylate, afforded **3** and **4**, respectively. Hydrogenolysis of **4**, followed by alkylation with **2**, yielded the 1,4-dioxybenzene-based polyether **5** which was converted into the tosylate **6**.



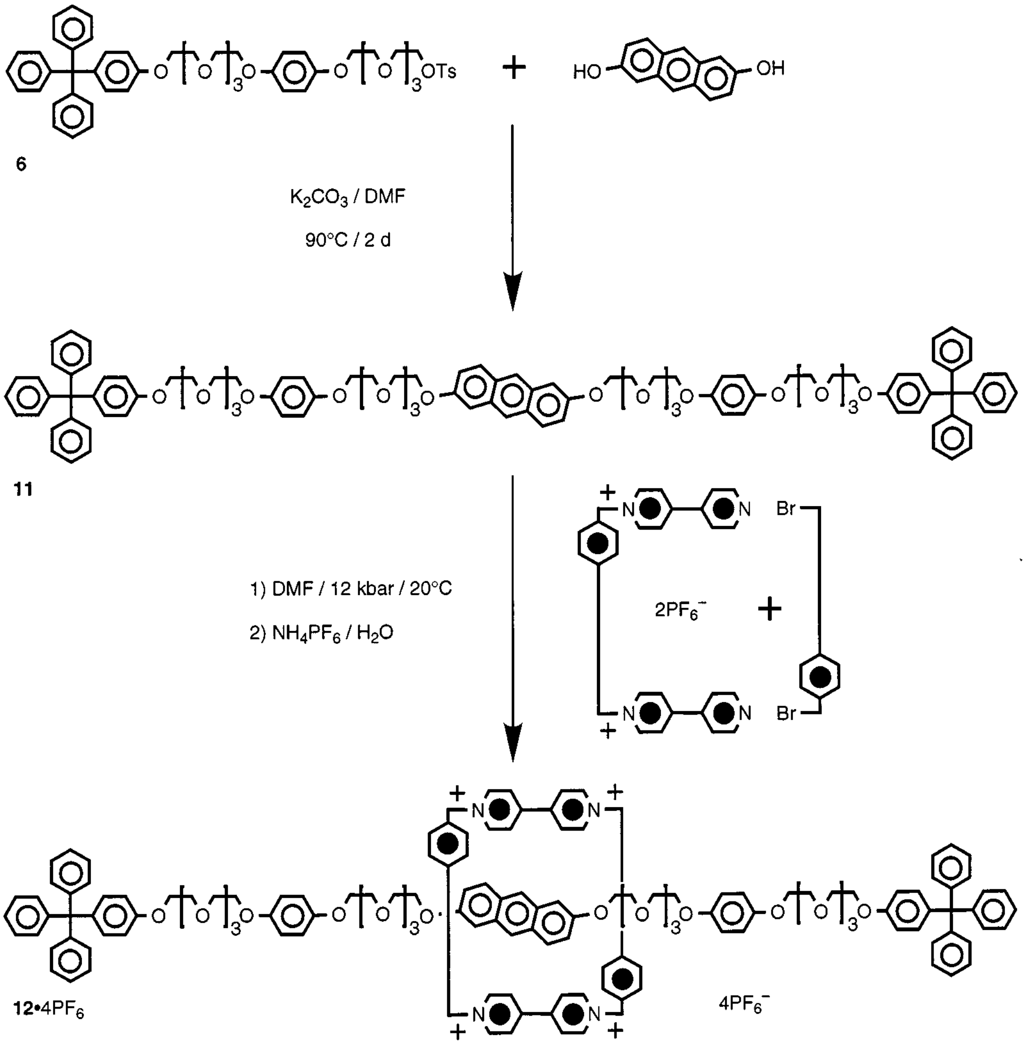
Scheme 1. Synthesis of 1,4-dioxybenzene-based polyether precursors

Reduction (Scheme 2) of anthraquinone with $Na_2S_2O_4$, followed by alkylation with tetraethylene glycol monotosylate, and subsequent tosylation of the diol gave the 9,10-dioxyanthracene-containing polyether **7**. Reaction of **7** with **3** in the presence of K_2CO_3 afforded the dumbbell-shaped compound **8**. Alternatively, **8** was obtained by reacting 9,10-bis(trimethylsilyloxy)anthracene with **6** in the presence of K_2CO_3. Subjecting a solution of **8**, 1,4-bis(4,4′-pyridylpyridinium)xylylene bis(hexafluorophosphate), and 1,4-bis-(bromomethyl)benzene in DMF under a pressure of 12 kbar gave the 9,10-dioxyanthracene-containing [2]rotaxane **9** $\cdot$ 4 PF_6 in a yield of 8%, after counterion exchange. In addition, the 9,10-dioxyanthracene-containing [3]rotaxane **10** $\cdot$ 8 PF_6 was also isolated in trace quantities (1%). The liquid secondary ion mass spectrum (LSIMS) of the [2]rotaxane **9** $\cdot$ 4 PF_6 revealed peaks at *m*/*z* values of 2691 and 2545 for $[M - PF_6]^+$ and $[M - 2\ PF_6]^+$, respectively, corresponding to the consecutive loss of one and two PF_6^- anions, respectively. The central 9,10-dioxyanthracene ring system, incorporated within the dumbbell-shaped component of **9** $\cdot$ 4 PF_6, is too bulky to pass through the cavity of the tetracationic cyclophane component.[9],[10] As a result, the "shuttling" of the tetracationic cyclophane along the linear portion of the dumbbell-shaped component is not possible in this particular [2]rotaxane. The ^{1}H-NMR spectrum of **9** $\cdot$ 4 PF_6 in $(CD_3)_2CO$ shows that the tetracationic cyclophane resides exclusively around one of the two 1,4-dioxybenzene units. Indeed, in the ^{1}H-NMR spectrum of **9** $\cdot$ 4 PF_6, two singlets, centered on δ = 4.10 and 6.80, are observed[11] for the protons of the 1,4-dioxybenzene rings located inside and outside, respectively, the cavity of the tetracationic cyclophane. By contrast, only one singlet, centered on δ = 6.80, is observed[12] for the protons of the two equivalent 1,4-dioxybenzene rings in the free dumbbell-shaped compound **8**. Furthermore, in the [2]rotaxane



Scheme 2. Template-directed synthesis of the [2]rotaxane **9** · 4 PF_6 and of the [3]rotaxane **10** · 8 PF_6

9 · 4 PF_6, the protons in positions 1 and 8 of the 9,10-dioxyanthracene ring system, can be distinguished from those in positions 4 and 5. Indeed, two sets of signals, centered on $\delta = 8.01$ and 8.22, are observed in the ^{1}H-NMR spectrum of **9** · 4 PF_6 for these protons. Similarly, the protons on the phenoxy rings of the stoppers located in the *ortho* positions with respect to the oxygen atoms, give rise to two sets of signals, centered on $\delta = 6.71$ and 6.83, in the ^{1}H-NMR spectrum of **9** · 4 PF_6. On the contrary, in the free dumbbell-shaped compound **8**, the protons in positions 1, 4, 5, and 8 of the 9,10-dioxyanthracene ring system are equivalent and give rise to one set of signals only, centered on $\delta = 8.37$. Similarly, the protons on the two equivalent phenoxy rings of the stoppers resonate as one set of signals, centered on $\delta = 6.82$, in the ^{1}H-NMR spectrum of the free dumbbell-shaped compound **8**. When, a second cyclophane component is introduced onto the dumbbell-shaped component of the [2]rotaxane **9** · 4 PF_6, the symmetry is restored. Indeed, the ^{1}H-NMR spectrum of the [3]rotaxane **10** · 8 PF_6 shows the equivalence of *(i)* the protons of the two 1,4-dioxybenzene rings (singlet at $\delta = 4.10$, overlapped partially by the resonances from the OCH_2 protons), *(ii)*



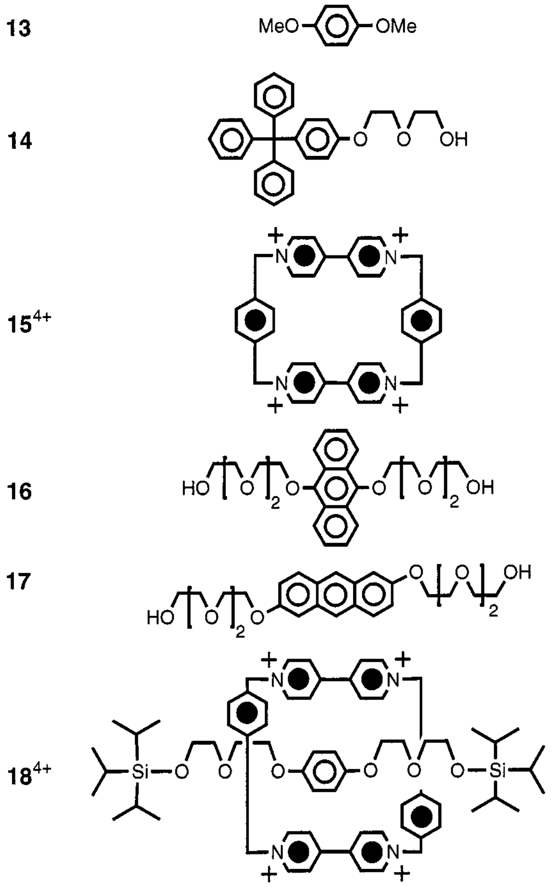
Scheme 3. Template-directed synthesis of the [2]rotaxane **12** · 4 PF_6

the protons in the positions 1, 4, 5, and 8 on the 9,10-dioxyanthracene ring system (one set of signals centered on δ = 7.95), and *(iii)* the protons of the two phenoxy rings of the stoppers (one doublet at δ = 6.68).

Alkylation of 2,6-dihydroxyanthracene with **6** gave (Scheme 3) the 2,6-dioxyanthracene-containing dumbbell-shaped compound **11**. Reaction of 1,4-bis(4,4′-pyridylpyridinium)xylylene bis(hexafluorophosphate) with 1,4-bis(bromo)xylylene in the presence of **11**, under ultrahigh pressure (12 kbar) conditions, afforded the 2,6-dioxyanthracene-containing [2]rotaxane **12** · 4 PF_6 in a yield of 17%, after counterion exchange. In this case, however, no [3]rotaxane could be isolated or was even detected. The liquid secondary ion mass spectrum (LSIMS) of the [2]rotaxane **12** · 4 PF_6 revealed peaks at *m*/*z* values of 2836, 2691, and 2546 for $[M]^+$, $[M - PF_6]^+$, and $[M - 2\,PF_6]^+$, respectively, corresponding to the molecular ion and to the consecutive loss of one and two PF_6^- anions, respectively. The ^{1}H-NMR spectrum of the [2]rotaxane **12** · 4 PF_6 in $(CD_3)_2CO$ revealed that the tetracationic cyclophane component resides exclusively around the 2,6-dioxyanthracene ring system. Indeed, comparison of the ^{1}H-NMR spectra of the free dumbbell-shaped compound **11** with that of the [2]rotaxane **12** · 4 PF_6 shows a dramatic upfield shift ($\Delta\delta$ = –3.86 ppm) of the singlet (δ = 4.30) associated with the protons on the positions 9 and 10 on the 2,6-dioxyanthracene ring system in the ^{1}H-NMR spectrum of **12** · 4 PF_6. Similarly, the doublet associated with the protons in the positions 4 and 8 on the 2,6-dioxyanthracene ring system is shifted upfield ($\Delta\delta$ = –0.22 ppm) and appears at δ = 7.59 in the ^{1}H-NMR spectrum of **12** · 4 PF_6. The significant changes in these δ values of the resonances associated with the 2,6-dioxyanthracene protons are a result of shielding effects exerted by the sandwiching bipyridinium units. By contrast, the protons on the two equivalent 1,4-dioxybenzene rings are unaffected by the presence of the tetracationic cyclophane. They resonate as a singlet (partially overlapping with the signals associated with the protons of the two phenoxy rings of the stoppers) centered on δ = 6.79 in the ^{1}H-NMR spectra of both the free dumbbell-shaped compound **11** and of the [2]rotaxane **12** · 4 PF_6.

Absorption and Emission Properties

The systems discussed in this paper contain several chromophoric units. Model compounds (**13**–**17**) for such units are listed in Scheme 4. Comparison with the properties of the simple rotaxane **18**$^{4+}$ shown in Scheme 4 have also proved useful.



Scheme 4. Structural formulas of model and reference compounds

Model Compounds: The absorption and fluorescence spectra of the model compounds in MeCN solution at room temperature are shown in Figures 1–3 and the most relevant data have been collected and are listed in Table 1. As one can see from inspection of Figure 1, compounds **13**, **14**, and **15**$^{4+}$ do not absorb above 350 nm, whereas **16** (Figure 2) and **17** (Figure 3) show very strong absorption bands in the 240–270 nm region and weak and structured absorption bands between 300 and 420 nm. Compounds **13** and **14** exhibit a strong fluorescence band in the 300–350 nm spectral range (Figure 1), and a phosphorescence band (in *n*PrCN rigid matrix at 77 K) with λ_{max} = 408 nm (τ = 2.1 s) and 403 nm (τ = 2.3 s), respectively. Compounds **16** and **17** show broad and very strong fluorescence bands with maxima around 435 nm (Figures 2 and 3) and no phosphorescence, even at 77 K. Compound **15**$^{4+}$ does not show any luminescence at all.123

Table 1. Absorption and fluorescence properties in MeCN solution at room temperature

Compound	Absorption λ_{max}, nm (ε_{max}, M^{-1} cm^{-1})	Fluorescence λ_{max}, nm	τ, ns	ϕ[a]
13	290 (2800)	320	2.5	0.11
14	270 (2600)	314	4.5	0.08
15^{4+}	260 (40000)			
16	381 (7600)[b]	437	9.0	0.75
17	322 (4000)[b]; 403 (3300)[b]	435	12.0	0.70
8	286 (13000); 382 (4300)[b]	437	9.5	0.75
11	286 (9800); 323 (3900)[b]; 402 (3100)[b]	435	14.0	0.70
9^{4+}	383 (5200)[b]; 487 (500)			
12^{4+}	404 (2800)[b]; 600 (sh)			

[a] Fluorescence quantum yield. – [b] Structured band.

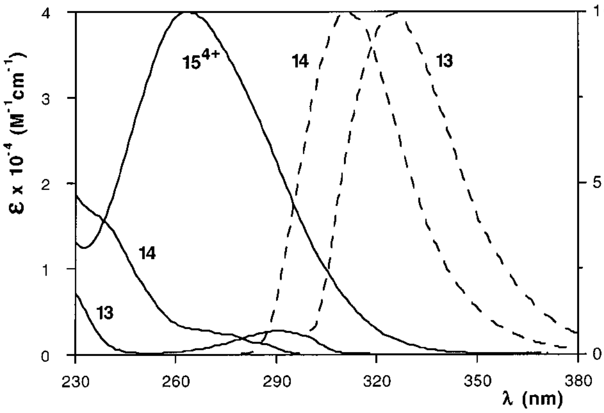


Figure 1. Absorption (full lines) and emission (dashed lines) spectra of compounds **13**, **14**, and **15**$^{4+}$

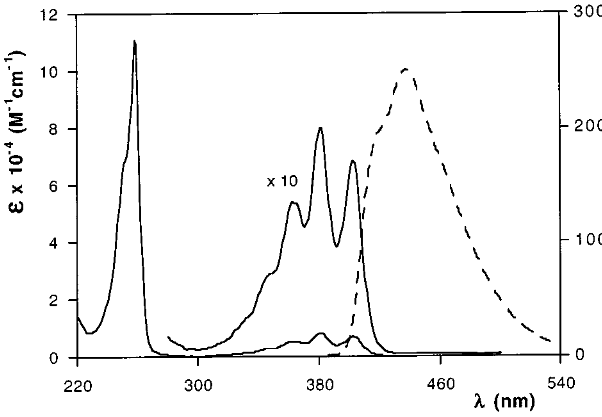


Figure 2. Absorption (full lines) and emission (dashed line) spectra of the model compound **16**

Dumbbell-Shaped Compounds 8 and 11: All the five chromophoric units present in the dumbbell-shaped compounds **8** and **11** are electron donors. Therefore, one cannot expect to have any low energy intercomponent charge-transfer (CT) excited state in these compounds, contrary to what happens in the case of dumbbell-shaped compounds containing both electron-donor and electron-acceptor units.[13]

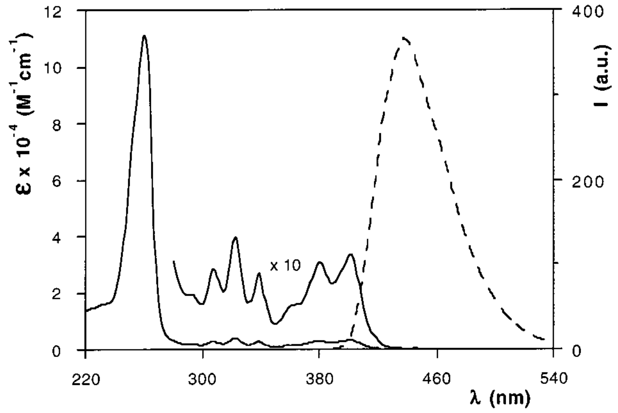


Figure 3. Absorption (full lines) and emission (dashed line) spectra of the model compound **17**

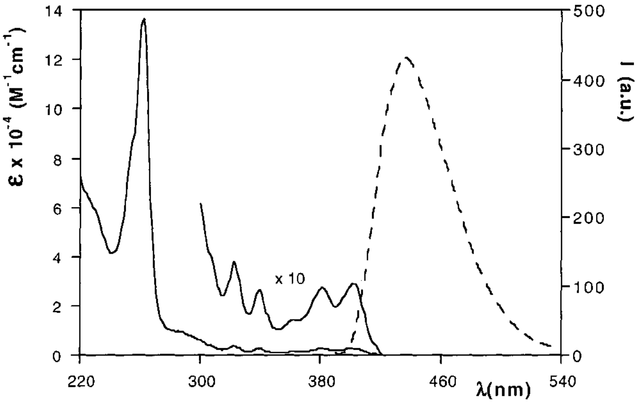
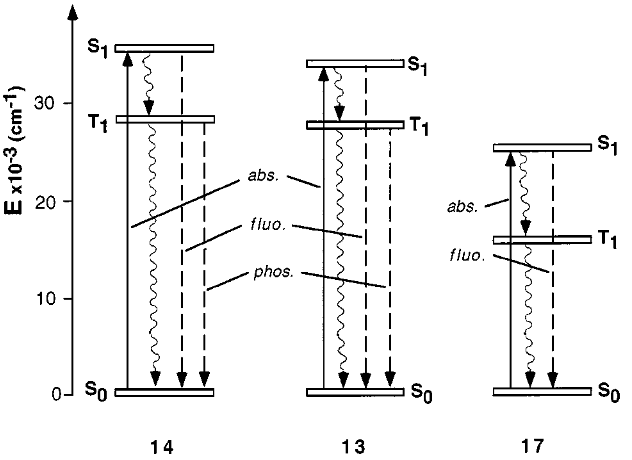


Figure 4. Absorption (full lines) and emission (dashed line) spectra of the dumbbell-shaped compound **11**

The absorption spectrum (Figure 4) of the dumbbell-shaped compound **11**, in fact, is practically identical to the sum of the spectra of its component units. The fluorescence spectrum (Figure 4) of **11** shows the 435 nm band of the 2,6-dioxyanthracene-type component, with the same lifetime and quantum yield (Table 1), whereas there is no evidence for the bands of the 1,4-dioxybenzene-type and stopper units. The excitation spectrum at λ_{em} = 435 nm coincides with the absorption spectrum throughout the entire spectral region. These results show that, in compound **11**, there is a very efficient energy transfer from the 1,4-dioxybenzene-type and stopper units to the central 2,6-dioxyanthracene-type component (Figure 5). Since the intrinsic decay rate ($k = 1/\tau$) of the fluorescent excited state in the **13** and **14** model compounds is $> 2{\cdot}10^8$ s^{-1} (Table 1), > 90% quenching of the fluorescence of the 1,4-dioxybenzene-type and stopper units means that the rate of energy transfer to the central 2,6-dioxyanthracene-type component is larger than $2{\cdot}10^9$ s^{-1}. At 77 K, the only fluorescence band observed is that of the 2,6-dioxyanthracene-type unit; no phosphorescence can be observed, indicating that the lowest triplet excited states (T_1) of the 1,4-dioxybenzene-type and stopper units, if populated, are quenched by the non-emissive, lower lying T_1 excited state of the central component.



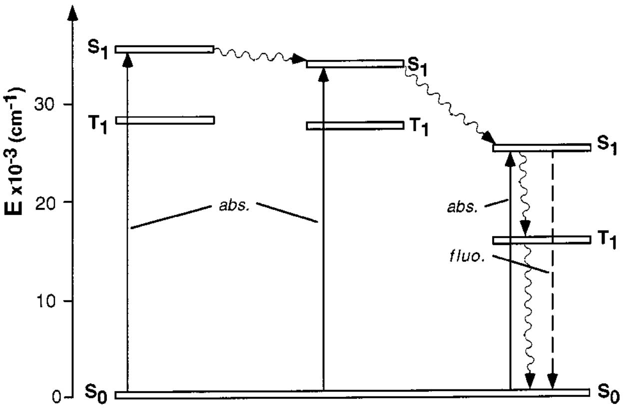


Figure 5. Schematic energy-level diagram for the dumbbell-shaped compound **11**

The absorption and emission behavior of the dumbbell-shaped compound **8** (Table 1) is practically identical to that of compound **11**.

[2]Rotaxanes 9^{4+} and 12^{4+}: The absorption spectra of the [2]rotaxane 9^{4+} and 12^{4+} are shown in Figure 6 and

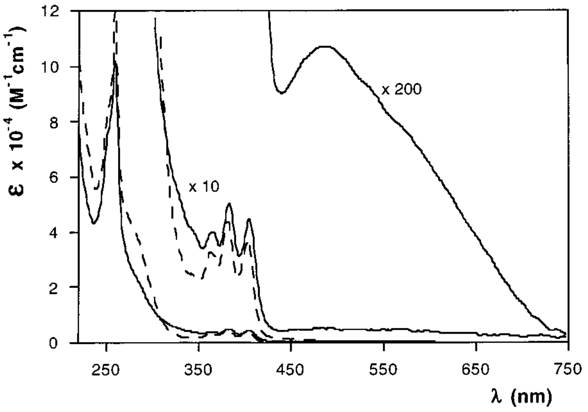


Figure 6. Absorption spectrum of the [2]rotaxane 9^{4+} (full lines) compared with the sum of the absorption spectra of its separated components **8** and 15^{4+} (dashed lines)

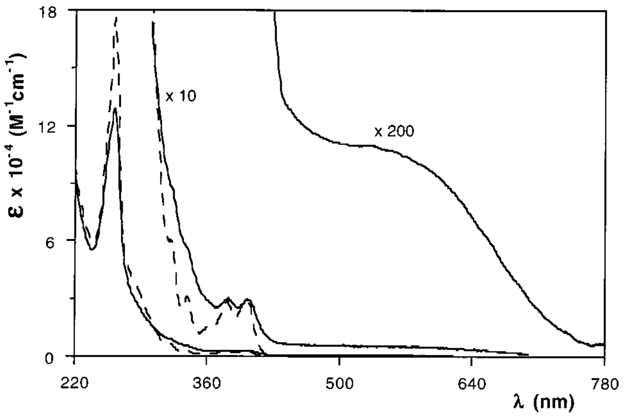


Figure 7. Absorption spectrum of the [2]rotaxane **12**$^{4+}$ (full lines) compared with the sum of the absorption spectra of its separated components **11** and **15**$^{4+}$ (dashed lines)

Figure 7, where the sum of the spectra of their separated components – namely, the tetracationic cyclophane **15**$^{4+}$ and the dumbbell-shaped compounds **8** and **11**, respectively – are also illustrated for comparison purposes. There are noticeable differences between the spectrum of each rotaxane and the sum of the spectra of the respective components, indicating the presence of substantial electronic interactions. Of particular interest is the appearance in the spectra of both rotaxanes of a new, broad absorption in the visible region that can be assigned to CT transitions involving the electron-donor units present in the dumbbell-shaped component and the electron-acceptor **15**$^{4+}$ cyclophane. Since the 2,6-dioxyanthracene-type ring system is a better electron donor than the 1,4-dioxybenzene-type one (as shown by the electrochemical potentials, Table 2 and previous results[14]) one expects the CT band, involving the former ring system, to lie at lower energy. As shown in Figures 6 and 7, the CT absorption bands are extremely broad, suggesting that they receive contributions from more than one CT transitions. The CT band of **9**$^{4+}$ has its maximum at 487 nm, close to that of the model compound[15] **18**$^{4+}$ (Scheme 4), whereas that of **12**$^{4+}$ does not show any maxima, because of overlapping with the tail of the UV band, but apparently peaks at about 600 nm. We can conclude that the predominant contribution to the CT absorption comes from the interaction of the **15**$^{4+}$ cyclophane with the 1,4-dioxybenzene-type ring for **9**$^{4+}$, and with the 2,6-dioxyanthracene-type ring system for **12**$^{4+}$. In agreement with the ^{1}H-NMR spectroscopic results discussed in the previous section, this conclusion is in accordance with the fact that the cyclophane surrounds the 1,4-dioxybenzene-type ring in **9**$^{4+}$ and the 2,6-dioxyanthracene-type ring system in **12**$^{4+}$. However, the broadness of the CT bands suggests that some kind of alongside interactions between the unthreaded donor units of the dumbbell-shaped compounds and the **15**$^{4+}$ cyclophane are present.

As far as luminescence is concerned, the behavior of the [2]rotaxanes is completely different from that of the corresponding dumbbell-shaped components since the strong fluorescence of the anthracene moiety can no longer be observed. This result can be accounted for by the presence, clearly shown by the absorption spectra (vide supra) of CT excited states, below the fluorescent level of the dioxyanthracene-type components, which offer a route for fast radiationless decay (Figure 8).

Table 2. Electrochemical potentials (V, vs SCE) in Ar-purged MeCN solution at room temperature

Compound	Reduction[a]		Oxidation[b]			
13[c]			+1.31			
14[d]			+1.50			
15$^{4+[c]}$	–0.29	–0.71				
17			+0.95 (0.5)[e]			
18$^{4+[c]}$	–0.33	–0.81	+1.60			
12^{4+}	–0.32	–0.83	+1.03 (0.5)[e]	+1.29 (0.9)	+1.59 (0.9)	+1.65 (2.1)

[a] Reversible bielectronic processes ($E_{1/2}$ values reported). – [b] Not fully reversible or irreversible processes (potential values evaluated from the DPV peaks); the number of exchanged electrons, calculated using **15**$^{4+}$ as reference compound, is given in parentheses. – [c] Ref. [15] – [d] Ref.[13] – [e] The irreversibility of the process precludes the determination of the actual number of exchanged electrons.

Electrochemistry

Electrochemical experiments were carried out only on the [2]rotaxane **12**$^{4+}$ because the other compounds were not available in sufficient amounts. As in the case of the spectroscopic properties, it is convenient to discuss the electrochemical properties of **12**$^{4+}$ by comparison with the properties of the **15**$^{4+}$ cyclophane, the model compounds of the ring systems which are present in the dumbbell-shaped component **11** – namely **13**, **14**, and **17** – and the simple [2]rotaxane **18**$^{4+}$ (Scheme 4). The potential values for the redox processes of **12**$^{4+}$ and related compounds are shown in Table 2. The reduction processes are reversible, whereas the oxidation processes are either not fully reversible or irreversible.

Model Compounds: The potential values reported in Table 2 for **15**$^{4+[15]}$ the model compounds **13**,[15] and **14**,[13] and the [2]rotaxane **18**$^{4+[15]}$ were obtained in previous investigations. Compound **17** shows an irreversible oxidation wave at +0.95 V.

Rotaxane 12^{4+}: In the potential window examined, **12**$^{4+}$ shows (Table 2 and Figure 9) two reversible reduction and four oxidation processes. The two reduction waves are both bielectronic and can be assigned to the first and second reduction of the bipyridinium units present in the cyclophane **15**$^{4+}$. They are displaced toward more negative potentials, compared with the free cyclophane **15**$^{4+}$, because of the engagement of the bipyridinium units in CT interactions.[15] The simultaneous reduction of such units shows that, even in the rotaxane, they are equivalent. These results suggest that, in **12**$^{4+}$, alongside interactions (vide supra) do not destroy the symmetry of cyclophane **15**$^{4+}$.

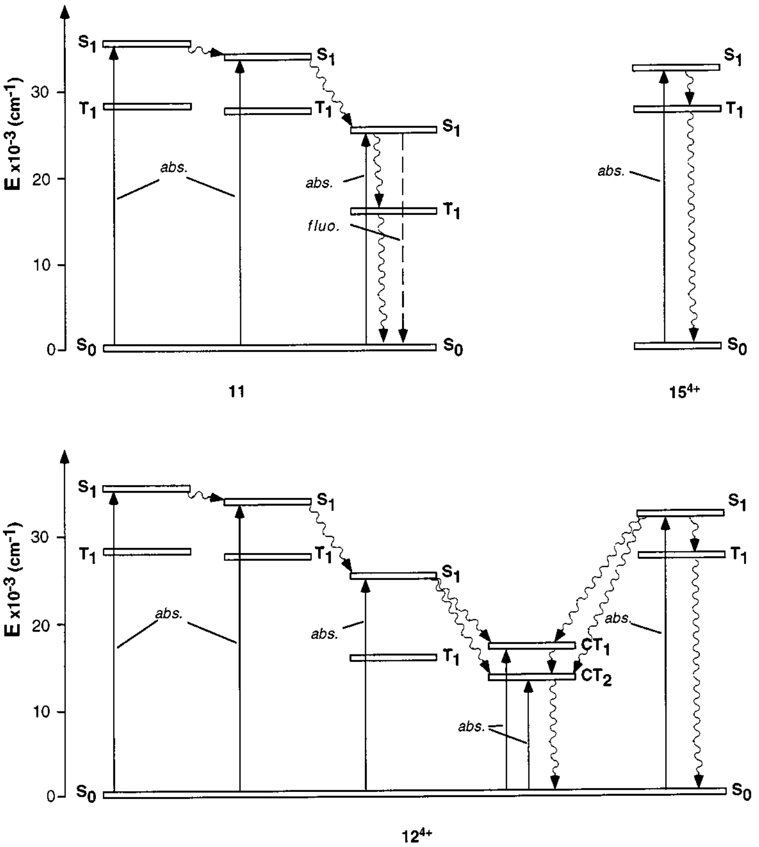


Figure 8. Schematic energy-level diagram for the [2]rotaxane **12**$^{4+}$ (bottom) and its dumbbell-shaped **11** (see also Figure 5) and macrocycle **15**$^{4+}$ components (top). CT$_1$ and CT$_2$ represent the charge-transfer excited states involving **15**$^{4+}$ with the 1,4-dioxybenzene-type and 2,6-dioxyanthracene-type ring systems, respectively

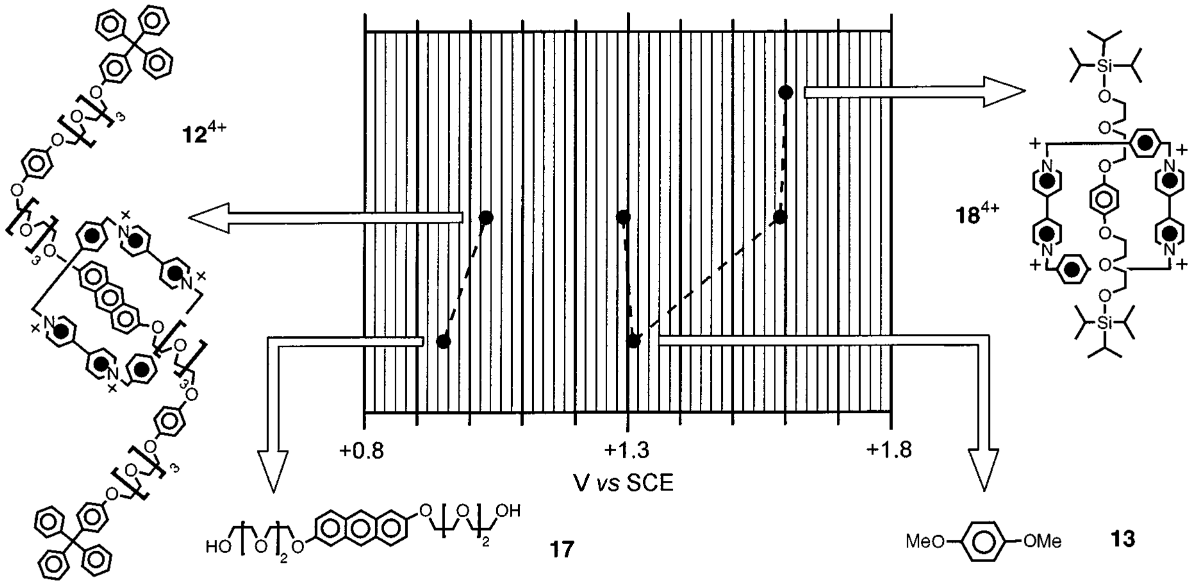


Figure 9. Correlation of the potential values for the oxidations of the model compounds **17** and **13**, and the [2]rotaxanes **12**$^{4+}$ and **18**$^{4+}$

The behavior on oxidation is very interesting (Figure 9 and Table 2). As indicated by the properties of the model compounds **13**, **17**, and **14**, oxidation should first of all involve the 2,6-dioxyanthracene-type ring system of the dumbbell-shaped component. Rotaxane **12**$^{4+}$ shows an oxidation wave somewhat displaced to more positive potentials compared with the model compound **17**, as expected if the 2,6-dioxyanthracene-type ring system is involved in a charge-transfer interaction with the cyclophane **15**$^{4+}$. The second oxidation of **12**$^{4+}$ takes place at +1.29 V, i.e., practically at the same potential of the model compound **13**, indicating that one of the two 1,4-dioxybenzene-type rings of the dumbbell-shaped component does not interact with the cyclophane $\mathbf{15}^{4+}$. The third wave occurs at +1.59 V, i.e., practically at the same potential of the oxidation of the 1,4-dioxybenzene-type ring in $\mathbf{18}^{4+}$ and so it can be assigned to a 1,4-dioxybenzene-type ring surrounded by the cyclophane. Finally, the last wave must be assigned to the oxidation of the stoppers. These assignments are also supported by the number of electrons exchanged in each process (Table 2).

These results, which are in agreement with those obtained by NMR and UV/Vis spectroscopies, demonstrate that, in $\mathbf{12}^{4+}$, the macrocycle initially surrounds the 2,6-dioxyanthracene-type ring system. They also show that, after oxidation of this electron donor, the cyclophane $\mathbf{15}^{4+}$ moves to one of the two 1,4-dioxybenzene-type rings. This system constitutes, therefore, another example of electrochemically-driven shuttling in a rotaxane-type structure.[3]

Conclusions

Two dumbbell-shaped compounds, incorporating two 1,4-dioxybenzene rings, linked to central 9,10- or 2,6-dioxyanthracene ring systems by polyether chains, have been synthesized. The 9,10-dioxyanthracene-containing dumbbell-shaped compound has been employed to template the synthesis of both a [2]- and a [3]-rotaxane incorporating cyclobis(paraquat-*p*-phenylene) as the cyclophane component(s). By contrast, only a [2]rotaxane was isolated when the 2,6-dioxyanthracene-containing dumbbell-shaped compound was employed as the template for the cyclophane formation. ^{1}H-NMR spectroscopic investigations of the [2]rotaxanes revealed that, in the 2,6-dioxyanthracene-containing [2]rotaxane, the macrocyclic component encircles exclusively the 2,6-dioxyanthracene unit while, in the 9,10-dioxyanthracene-containing [2]rotaxane, the cyclophane component resides exclusively around one of the two 1,4-dioxybenzene rings, since the 9,10-dioxyanthracene ring system is too bulky to be accommodated inside the cavity of the cyclophane component. The rotaxanes and their dumbbell-shaped and cyclophane components incorporate several chromophoric and electroactive units and their spectroscopic, excited-state, and redox properties have been investigated in some detail. In particular, charge-transfer and energy-transfer processes have been characterized by absorption spectra, luminescence spectra, and excited-state lifetimes. UV/Vis spectroscopy and electrochemical measurements have confirmed that, in the 2,6-dioxyanthracene-containing [2]rotaxane, the cyclophane surrounds such an electron donor. Furthermore, the electrochemical behavior has revealed that, after oxidation of the 2,6-dioxyanthracene ring system, the cyclophane moves to encircle a 1,4-dioxybenzene-type ring.

Experimental Section

General Methods: Chemicals were purchased from Aldrich and used as received. Solvents were dried according to procedures described in the literature.[16] The compounds tetraehtylene glycol monotosylate,[17] 9,10-bis(trimethylsilyloxy)anthracene,[18] 1,4-bis(4,4′-pyridylpyridinium)xylylene bis(hexafluorophosphate),[15] 2,6-dihydroxyanthracene,[19] and 9,10-bis{2-[2-(2-hydroxyethoxy)-ethoxy]ethoxy}anthracene[10] were prepared according to literature procedures. – Thin layer chromatography (TLC) was carried out using aluminum sheets precoated with silica gel 60 F (Merck 5554). The plates were inspected by UV light and developed with iodine vapor. – Column chromatography was carried out using silica gel 60 F (Merck 9385, 230–400 mesh). – Melting points were determined on an Electrothermal 9200 apparatus and are not corrected. – Electron impact mass spectra (EIMS) and chemical ionization mass spectra (CIMS) were recorded on a Kratos Profile spectrometer. Liquid secondary ion mass spectra (LSIMS) were obtained from a VG Zabspec mass spectrometer, equipped with a 35 keV cesium ion gun. Samples were dissolved in either a 3-nitrobenzyl alcohol or 2-nitrophenyl octyl ether matrix, previously coated on to a stainless steel probe tip. – ^{1}H-NMR spectra were recorded on either a Bruker AC300 (300 MHz) or a Bruker AMX400 (400 MHz) spectrometer, using either the solvent or TMS as internal standards. ^{13}C-NMR spectra were recorded on either a Bruker AC300 (75.5 MHz) spectrometer or a Bruker AMX400 (100.6 MHz) spectrometer, using either the solvent or TMS as internal standards. – Absorption and luminescence experiments at room temperature were carried out in MeCN solutions. Electronic absorption spectra were recorded with a Perkin–Elmer λ6 spectrophotometer. Emission spectra and phosphorescence lifetimes were obtained with a Perkin–Elmer LS50 spectrofluorimeter. Emission spectra in *n*PrCN rigid matrix at 77 K were recorded using quarz tubes immersed in a quarz Dewar filled with liquid N_2. Fluorescence quantum yields were determined using naphthalene in degassed cyclohexane as a standard ($\Phi = 0.23$).[20] Nanosecond lifetime measurements were performed with an Edinburgh single-photon counting equipment (D_2 lamp, $\lambda_{ex} = 300$ nm). Experimental errors: absorption maxima, ±2 nm; emission maxima, ±2 nm; excited-state lifetimes, ±10%; fluorescence quantum yields, ±20%. – Electrochemical experiments were carried out in Ar-purged MeCN solution with a Princeton Applied Research 273 multipurpose instrument interfaced to a personal computer, using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. A more detailed description of the experimental procedures was reported previously.[13] The experimental error on the potential values was estimated to be ±10 mV and ±20 mV for reversible and irreversible processes, respectively.

1-[2-{2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy}ethoxy]-4-triphenylmethylbenzene (1): A mixture of 4-triphenylmethylphenol (10.08 g, 30 mmol), tetraethylene glycol monotosylate (11.60 g, 33 mmol), and K_2CO_3 (4.60 g, 33 mmol) in dry DMF (70 mL) was heated at 120–130 °C for 2 h. After cooling down to room temperature, the mixture was diluted with H_2O (300 mL) and washed with CH_2Cl_2 (3 × 100 mL). The organic layer was washed with H_2O (4 × 200 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 19:1) to afford **1** (9.60 g, 62%) as a colorless oil. – CIMS: m/z = 513 $[M + H]^+$ – ^{1}H NMR ($CDCl_3$): δ = 2.60 (1H, br s), 3.60 (2 H, m), 3.65–3.75 (10 H, m), 3.83 (2 H, m), 4.12 (2 H, m), 6.80 (2 H, m), 7.10 (2 H, m), 7.15–7.27 (15 H, m). – ^{13}C NMR ($CDCl_3$): δ = 61.8, 64.3, 67.3, 69.8, 70.4, 70.6, 70.7, 70.8, 72.5, 113.4, 125.9, 127.4, 131.2, 132.2, 139.2, 147.1, 156.7.

1-{2-[2-{2-[2-(4-Methylphenylsulfonyloxy)ethoxy]ethoxy}-ethoxy]ethoxy}-4-(triphenylmethyl)benzene (2): *p*-Toluenesulfonyl chloride (5.72 g, 30 mmol) was added to a stirred solution of **1** (7.68 g, 15 mmol), Et_3N (7.58 g, 75 mmol), and 4-dimethylaminopyridine (50 mg, 0.4 mmol) in CH_2Cl_2 (100 mL) mantained at 0 °C. The temperature was allowed to rise gradually to room temperature and the solution was stirred for a further 5 h. The solution was diluted with CH_2Cl_2 (100 mL), washed with aqueous HCl (1 M, 100 mL) and with a saturated solution of $NaHCO_3$ (100 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 49:1) to afford **2** (9.21 g, 92%) as a colorless oil. – EIMS: *m*/*z* = 666 $[M]^+$. – ^1H NMR ($CDCl_3$): δ = 2.43 (3 H, s), 3.59–3.72 (12 H, m), 4.06 (2 H, m), 4.18 (2 H, m), 6.77 (2 H, m), 7.09 (2 H, m), 7.14–7.26 (15 H, m), 7.32 (2 H, m), 7.69 (2 H, m). – ^{13}C NMR ($CDCl_3$): δ = 21.6, 64.3, 67.3, 68.7, 69.3, 69.8, 70.6, 70.7, 70.8, 77.3, 113.4, 125.9, 127.4, 128.0, 129.8, 131.1, 132.2, 133.2, 139.2, 144.8, 147.1, 156.8.

1-{2-[2-{2-[2-(4-Hydroxyphenoxy)ethoxy]ethoxy}ethoxy]ethoxy}-4-(triphenylmethyl)benzene (3): A mixture of **2** (6.66 g, 10 mmol), 1,4-dioxybenzene (6.60 g, 60 mmol), and K_2CO_3 (2.76 g, 20 mmol) in DMF (100 mL) was heated at 80 °C for 6 d under an atmosphere of N_2. After cooling down to room temperature, the solvent was removed under reduced pressure and the residue was taken up in H_2O (300 mL) and washed with $CHCl_3$ (3 × 100 mL). The organic solution was washed with H_2O (4 × 200 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, $CH_2Cl_2/MeCO_2Et$ 10:1) to afford **3** (4.23 g, 70%) as a colorless oil. – EIMS: *m*/*z* = 604 $[M]^+$. – ^1H NMR ($CDCl_3$): δ = 3.65–3.85 (12 H, m), 3.96 (2 H, m), 4.07 (2 H, m), 5.95 (1 H, br s), 6.71 (4 H, s), 6.75 (2 H, m), 7.08 (2 H, m), 7.12–7.27 (15 H, m). – ^{13}C NMR ($CDCl_3$): δ = 64.3, 67.3, 68.1, 69.8, 69.9, 70.7, 70.8, 113.4, 115.8, 116.1, 125.9, 127.4, 131.1, 132.2, 139.2, 147.1, 150.1, 152.7, 156.7.

1-Benzyloxy-4-[2-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}ethoxy]-benzene (4): A mixture of 4-benzyloxyphenol (6.00 g, 30 mmol), tetraethylene glycol monotosylate (11.60 g, 33 mmol), and K_2CO_3 (4.60 g, 33 mmol) in DMF (50 mL) was heated at 80 °C for 10 h under an atmosphere of N_2. After being cooled down to room temperature, the solvent was removed under reduced pressure and the residue was taken up in H_2O (300 mL) and washed with $CHCl_3$ (3 × 100 mL). The organic solution was washed with H_2O (4 × 200 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 9:1) to afford **4** (8.30 g, 74%) as a colorless oil. – EIMS: *m*/*z* = 376 $[M]^+$. – ^1H NMR ($CDCl_3$): δ = 2.64 (1 H, br s), 3.61 (2 H, m), 3.66–3.77 (10 H, m), 3.82 (2 H, m), 4.12 (2 H, m), 5.03 (2 H, s), 6.89 (4 H, m), 7.30–7.45 (5 H, m). – ^{13}C NMR ($CDCl_3$): δ = 61.7, 68.9, 70.3, 70.6, 70.7, 70.8, 72.6, 115.7, 115.9, 127.5, 127.9, 128.5, 137.3, 153.1, 153.2.

1-[2-{2-[2-(Hydroxyethoxy)ethoxy]ethoxy}ethoxy]-4-{2-[2-{2-[2-(4-triphenylmethylphenoxy)ethoxy]ethoxy}ethoxy]ethoxy}benzene (5): H_2 was bubbled through a solution of **4** (4.47 g, 12 mmol) containing Pd (10% on charcoal, 1 g) in MeOH (40 mL) and CH_2Cl_2 (40 mL) for 5 h at room temperature. The mixture was filtered through Celite and the solvent was removed under reduced pressure. A solution of the residue and **2** (8.00 g, 12 mmol) containing K_2CO_3 (5.00 g, 36 mmol) in dry DMF (40 mL) was heated at 80 °C for 7 d under an atmosphere of Ar. After being cooled down to room temperature, the solvent was removed under reduced pressure and the residue was taken up in H_2O (300 mL) and washed with $CHCl_3$ (3 × 100 mL). The organic solution was washed with H_2O (4 × 200 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 19:1) to afford **5** (6.08 g, 65%) as a colorless oil. – EIMS: *m*/*z* = 780 $[M]^+$. – ^1H NMR ($CDCl_3$): δ = 2.62 (1 H, br s), 3.60 (2 H, m), 3.55–3.64 (18 H, m), 3.78–3.83 (6 H, m), 4.03–4.12 (6 H, m), 6.77 (2 H, m), 6.81 (4 H, s), 7.09 (2H, m), 7.13–7.26 (15 H, m). – ^{13}C NMR ($CDCl_3$): δ = 61.8, 64.3, 67.3, 68.1, 69.9, 70.4, 70.6, 70.7, 70.8, 72.5, 113.4, 115.6, 125.9, 127.4, 131.1, 132.2, 139.2, 147.1, 153.1, 153.2, 156.8.

1-{2-[2-{2-[2-(4-Methylphenylsulfonyloxy)ethoxy]ethoxy}ethoxy]-ethoxy}-4-{2-[2-{2-[2-(4triphenylmethylphenoxy)ethoxy]ethoxy}-ethoxy]ethoxy}benzene (6): *p*-Toluenesulfonyl chloride (1.90 g, 10 mmol) was added to a stirred solution of **5** (3.80 g, 5 mmol), Et_3N (3.03 g, 30 mmol), and 4-dimethylaminopyridine (60 mg, 0.5 mmol) in CH_2Cl_2 (100 mL) mantained at 0 °C. The temperature was allowed to rise gradually to room temperature and the solution was stirred for a further 2 h. The solution was diluted with CH_2Cl_2 (170 mL), washed with aqueous HCl (1 M, 100 mL) and with H_2O (2 × 100 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 50:1) to afford **6** (4.13 g, 88%) as a colorless oil. – EIMS: *m*/*z* = 934 $[M]^+$. – ^1H NMR ($CDCl_3$): δ = 2.45 (3 H, s), 3.56–3.75 (18 H, m), 3.78–3.85 (6 H, m), 4.03–4.17 (8 H, m), 6.78 (2 H, m), 6.80 (4 H, s), 7.07 (2 H, m), 7.13–7.27 (15 H, m), 7.32 (2 H, m), 7.79 (2 H, m). – ^{13}C NMR ($CDCl_3$): δ = 21.6, 64.3, 67.2, 68.1, 68.7, 69.2, 69.9, 70.6, 70.7, 70.8, 77.3, 113.4, 115.6, 125.8, 126.4, 127.4, 128.0, 129.8, 131.1, 132.2, 133.1, 139.1, 144.7, 147.0, 153.1, 156.7.

9,10-Bis{2-[2-{2-[2-(4-Methylphenylsulfonyloxy)ethoxy]ethoxy}-ethoxy]ethoxy}anthracene (7): A solution of anthraquinone (2.08 g, 10 mmol), $Na_2S_2O_4$ (2.00 g, 11.5 mmol), NaOH (3.00 g, 75 mmol) in H_2O (20 mL) was heated under reflux for 30 min under an atmosphere of Ar. A solution of tetraethylene glycol monotosylate (14 g, 40 mmol) in Me_2CO (20 mL) was added and heating under reflux was mantained for a further 1 d. Then, $Na_2S_2O_4$ (1.00 g, 5.8 mmol) was added and heating under reflux was mantained for a further 2 d. After being cooled down to room temperature, H_2O (100 mL) was added and the mixture was washed with CH_2Cl_2 (3 × 50 mL). The organic solution was washed with H_2O (2 × 100 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (50 mL) and the solution was cooled down to 0 °C. *p*-Toluenesulfonyl chloride (3.23 g, 17 mmol), Et_3N (5.05 g, 50 mmol), and 4-dimethylaminopyridine (102 mg, 0.9 mmol) were added. The temperature was allowed to rise gradually to room temperature and the solution was stirred for a further 2 h. The solution was diluted with CH_2Cl_2 (170 mL), washed with aqueous HCl (1M, 100 mL) and with H_2O (2 × 100 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, $CH_2Cl_2/MeCO_2Et$ 150:1) to afford **7** (300 mg g, 3%) as a yellow oil which was used immediately in the next step. – LSIMS: *m*/*z* = 858 $[M]^+$ – ^1H NMR ($CDCl_3$): δ = 2.40 (6 H, s), 3.50–3.78 (24 H, m), 3.95 (4 H, m), 4.32 (4 H, m), 7.30 (4 H, m), 7.45 (4 H, m), 7.77 (4 H, m), 8.33 (4 H, m).

9,10-Bis[2-{2-[2-{2-[4-{2-[2-{2-[2-(4-triphenylmethylphenoxy)-ethoxy]ethoxy}ethoxy]ethoxy}phenoxy]ethoxy}ethoxy]ethoxy}ethoxy]-anthracene (8). Method A: A mixture of **3** (500 mg, 0.8 mmol), **7** (261 mg, 0.3 mmol), and K_2CO_3 (690 mg, 5 mmol) in DMF (5 mL) was heated at 80–90 °C for 2 d under an atmosphere of Ar. After being cooled down to room temperature, the solvent was removed under reduced pressure and the residue was taken up in H_2O (50 mL) and washed with CH_2Cl_2 (3 × 50 mL). The organic solution was washed with H_2O (4 × 200 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 19:1) to afford **8** (410 mg, 78%) as a colorless oil. – LSIMS: *m*/*z* = 1735 $[M]^+$. – ^1H NMR ($CDCl_3$): δ = 3.69–3.86 (44 H, m), 3.94–4.13 (16 H, m), 4.34 (4 H, m), 6.82 (12 H, m), 7.12 (4 H, m), 7.15–7.23 (30 H, m), 7.46 (4 H, m), 8.37 (4 H, m). – ^{13}C NMR ($CDCl_3$): δ = 64.3, 67.3, 68.1, 69.9, 70.7, 70.8, 71.0, 74.9, 113.4, 115.6, 122.8, 125.2, 125.3, 125.9, 127.4, 131.1, 132.2, 139.2, 147.1, 153.1, 156.8.

Method B: A solution of 9,10-bis(trimethylsilyloxy)anthracene (118 mg, 0.33 mmol) and **6** (939 mg, 1 mmol) in Me_2CO (10 mL) was added to suspension of K_2CO_3 (1.38 g, 10 mmol) in Me_2CO (5 mL) heated under reflux and an atmosphere of Ar. The resulting mixture was heated under reflux for a further 12 h and, after being cooled down to room temperature, the solvent was removed under reduced pressure and the residue was taken up in H_2O (50 mL) and washed with CH_2Cl_2 (3 × 50 mL). The organic solution was washed with H_2O (4 × 200 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 19:1) to afford **8** (95 mg, 17%) as a colorless oil.

[2]Rotaxane 9 · 4 PF_6 and [3]Rotaxane 10 · 8 PF_6: A solution of **8** (350 mg, 0.20 mmol), 1,4-bis(4,4′-pyridylpyridinium)xylylene bis(hexafluorophosphate) (423 mg, 0.60 mmol), 1,4-bis(bromomethyl)benzene (198 mg, 0.75 mmol) in dry DMF (10 mL) was subjected to a pressure of 12 kbar for 2 d at 20 °C. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, MeOH/2 M NH_4Claq/$MeNO_2$ 7:2:1) to afford two solids which were dissolved individually in a mixture of H_2O and Me_2CO. After the addition of NH_4PF_6 to both solutions and the evaporation of Me_2CO, the [2]rotaxane **9** · 4 PF_6 (44 mg, 8%) and the [3]rotaxane **10** · 8 PF_6 (10 mg, 1%) precipitated out of the respective solutions. **9** · 4 PF_6. – M. p. > 250 °C. – LSIMS: m/z = 2691 $[M - PF_6]^+$, 2545 $[M - 2\ PF_6]^+$. – ^{1}H NMR $[(CD_3)_2CO]$: δ = 3.60–4.15 (68 H, m), 6.05 (8 H, s), 6.71 (2 H, m), 6.80 (4 H, s), 6.83 (3 H, m), 7.06 (3 H, m), 7.13–7.32 (30 H, m), 7.44 (4 H, m), 7.96 (16 H, m), 8.01 (2 H, m), 8.22 (2 H, m), 9.24 (8 H, m). – **10** · 8 PF_6: M. p. > 250 °C. – LSIMS: m/z = 3790 $[M - PF_6]^+$, 3645 $[M - 2\ PF_6]^+$. – ^{1}H NMR $[(CD_3)_2CO]$: δ = 3.60–4.10 (72 H, m), 6.05 (16 H, s), 6.68 (4 H, m), 7.02 (4 H, m), 7.13–7.29 (30 H, m), 7.33 (4 H, m), 7.95 (20 H, m), 8.02 (16 H, m), 9.20 (16 H, m).

2,6-Bis[2-{2-[2-{2-[4-{2-[2-{2-[2-(4-triphenylmethylphenoxy)ethoxy]ethoxy}ethoxy]ethoxy}phenoxy]ethoxy}ethoxy]ethoxy}ethoxy]anthracene (11): A mixture of 2,6-dihydroxyanthracene (105 mg, 0.5 mmol), **6** (934 mg, 1 mmol), and K_2CO_3 (690 mg, 5 mmol) in DMF (3 mL) was heated at 90 °C for 2 d under an atmosphere of N_2. After being cooled down to room temperature, the solvent was removed under reduced pressure and the residue was taken up in H_2O (50 mL) and washed with CH_2Cl_2 (3 × 50 mL). The organic solution was washed with H_2O (4 × 200 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 19:1) to afford **11** (590 mg, 68%) as a yellow oil. – LSIMS: m/z = 1736 $[M]^+$. – ^{1}H NMR ($CDCl_3$): δ = 3.67–3.84 (44 H, m), 3.94 (4 H, m), 4.00–4.12 (12 H, m), 4.26 (4 H, m), 6.73–6.79 (12 H, m), 7.09 (4 H, m), 7.81 (2 H, m), 8.16 (2 H, s). – ^{13}C NMR ($CDCl_3$): δ = 64.3, 67.3, 67.4, 68.1, 69.8, 69.9, 70.7, 70.8, 70.9, 104.9, 113.4, 115.6, 120.8, 124.3, 125.9, 127.4, 128.8, 129.3, 131.1, 132.2, 139.2, 147.1, 153.1, 155.7, 156.8.

[2]Rotaxane 12 · 4 PF_6: A solution of **11** (350 mg, 0.20 mmol), 1,4-bis(4,4′-pyridylpyridinium)xylylene bis(hexafluorophosphate) (423 mg, 0.60 mmol), 1,4-bis(bromomethyl)benzene (198 mg, 0.75 mmol) in dry DMF (10 mL) was subjected to a pressure of 12 kbar for 2 d at 20 °C. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, MeOH/2 M NH_4Claq/$MeNO_2$ 7:2:1) to afford solid which was dissolved in a mixture of H_2O and Me_2CO. After the addition of NH_4PF_6 and the evaporation of Me_2CO, the [2]rotaxane **12** · 4 PF_6 (48 mg, 17%) precipitated out of solution. – M. p. > 250 °C. – LSIMS: m/z = 2836 $[M]^+$, 2691 $[M - PF_6]^+$, 2546 $[M - 2\ PF_6]^+$. – ^{1}H NMR $[(CD_3)_2CO]$: δ = 3.60–4.10 (64 H, m), 4.30 (2 H, s), 5.95 (8 H, s), 6.65–6.95 (16 H, m), 7.13–7.23 (34 H, m), 7.59 (2 H, m), 7.95 (8 H, s), 7.97 (8 H, m), 9.17 (8 H, m).

9,10-Bis{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}anthraquinone (16): A mixture of anthraflavic acid (4.80 g, 20 mmol), 2-[2-(2-chloroethoxy)ethoxy]ethanol (8.40 g, 50 mmol), K_2CO_3 (6.90 g, 50 mmol), and NaI (0.68 g, 5 mmol) in DMF (30 mL) was heated at 120 °C for 3 h. After being cooled down to room temperature, the mixture was diluted with H_2O (150 mL) and washed with CH_2Cl_2 (2 × 150 mL). The organic layer was washed with H_2O (2 × 150 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 9:1) to afford **16** (7.90 g, 78%) as a yellow solid. – M. p. = 127 °C. – LSIMS: m/z = 474 $[M]^+$. – ^{1}H NMR ($CDCl_3$): δ = 2.50 (2 H, br s), 3.63 (4 H, m), 3.66–3.76 (12 H, m), 3.92 (4 H, m), 4.30 (4 H, m), 7.23 (2 H, m), 7.69 (2 H, m), 8.17 (2 H, m). – ^{13}C NMR ($CDCl_3$): δ = 61.9, 68.2, 69.6, 70.5, 71.1, 72.6, 110.7, 121.3, 127.4, 129.8, 135.9, 163.7, 182.2.

2,6-Bis{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}anthracene (17): A suspension of 2,6-bis{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}anthraquinone (5.04 g, 10 mmol) and $NaBH_4$ (5.00 g, 132 mmol) in *i*PrOH (100 mL) was heated under reflux for 4 h. After being cooled down to room temperature, the solvent was removed under reduced pressure and the residue was treated with ice/H_2O (100 mL). The mixture was neutralized with HCl_{conc} and heated under reflux for 1 h. After being cooled down to room temperature, the mixture was washed with CH_2Cl_2 (2 × 200 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was dissolved in *i*PrOH (100 mL) and treated with another portion of $NaBH_4$ (5.00 g, 132 mmol) and the procedure described previously was repeated. The resulting residue was crystallized from $CHCl_3$/Me_2CO (1:1) to afford **17** (3.23 g, 68%). – M. p. = 142 °C. – LSIMS: m/z = 474 $[M]^+$. – ^{1}H NMR ($CDCl_3$): δ = 2.00 (2 H, br s), 3.62 (4 H, m), 3.70–3.79 (12 H, m), 3.95 (4 H, m), 4.30 (4 H, m), 7.15–7.19 (4 H, m), 7.83 (2 H, m), 8.18 (2 H, m). – ^{13}C NMR ($CDCl_3$): δ = 61.8, 67.3, 69.8, 70.5, 70.9, 72.5, 104.9, 120.7, 124.3, 128.8, 129.3, 131.2, 155.6.

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