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# The Synthesis and Spectroscopic Properties of a [2]Catenane Incorporating an Anthracene Chromophoric Unit

**R. Ballardini[a], V. Balzani*[b], A. Credi[b], M. T. Gandolfi[b], D. Marquis[c], L. Pérez-García[c][+], and J. F. Stoddart*[c][++]**

Istituto FRAE-CNR[a],
Via Gobetti 101, I-40129 Bologna, Italy
Fax: (internat.) +39(0)51/6399 844

Dipartimento di Chimica "G. Ciamician", Università di Bologna[b],
Via Selmi 2, I-40126 Bologna, Italy
Fax: (internat.) + 39(0)51/259 456
E-mail: vbalzani@ciam.unibo.it

School of Chemistry, University of Birmingham[c],
Edgbaston, Birmingham B15 2TT, UK

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A modified bis-*p*-phenylene-34-crown-10 ring in which one of the 1,4-dioxybenzene units has been replaced by a 9,10-dioxyanthracene unit has been employed as a template for the formation of cyclobis(paraquat-*p*-phenylene). The [2]catenane which results has been shown by $^1$H NMR spectroscopy to exist in solution exclusively in the translationally isomeric form in which (a) only the 1,4-dioxybenzene ring occupies the central cavity of the tetracationic cyclophane and (b) the crown ether ring is prevented from circumrotating through the cyclophane by the large 9,10-dioxyanthracene unit. The absorption spectrum and luminescence properties of this new [2]catenane and of its crown ether component in its free state have been investigated and compared with those of 1,4-dimethoxybenzene and a model anthracene derivative, carrying methylated triethylene glycol chains on the 9 and 10 positions of the anthracene ring. While the absorption spectrum of the crown ether is the sum of the spectra of the two component chromophoric moieties, its emission spectrum shows only the fluorescence band of the 9,10-dioxyanthracene-type unit. The excitation spectrum shows that the disappearance of the 1,4-dioxybenzene type emission in the crown ether is due to a very efficient ($k_q \geq 4 \times 10^{10}$ s$^{-1}$) energy-transfer process from the 1,4-dioxybenzene to the 9,10-dioxyanthracene type unit. The absorption spectrum of the [2]catenane is noticeably different from the sum of the spectra of its two cyclic components, particularly as far as the presence of a very broad charge-transfer (CT) band in the visible spectral region ($\lambda_{max}$ = 545 nm, $\varepsilon_{max}$ = 615 M$^{-1}$ cm$^{-1}$) is concerned. Comparison with the CT band of a model compound shows that the very broad CT band of the [2]catenane is in fact the result of two component bands originating from the interaction of the two different electron-donor units (1,4-dioxybenzene and 9,10-dioxyanthracene type) present in the crown ether with the electron-acceptor bipyridinium-type units of the cyclobis(paraquat-*p*-phenylene). The emission spectrum of the [2]catenane does not show any band because of the quenching action (rate constant $k_q \geq 5 \times 10^{10}$ s$^{-1}$) of the low-energy non-luminescent charge-transfer levels on the higher energy, potentially luminescent levels of the crown ether.

## Introduction

Self-assembly,[1] with its reliance on supramolecular entities[2][3] as intermediates, is one of the most powerful synthetic paradigms available for the template-directed construction of interlocked molecular compounds, such as catenanes and rotaxanes.[4] At present, one of the most useful properties offered by these intriguing molecules is that in which translational "isomerism" is controlled by some external stimulus, which may be chemical, electrochemical, or photochemical. This property can be developed and exploited to produce switches and machines that operate at a molecular level.

Ever since we reported[5] the highly efficient template-directed synthesis of a [2]catenane **1**$\cdot$4PF$_6$ (shown in Figure 1) in which the tetracationic cyclophane, cyclobis(paraquat-*p*-phenylene), is formed around the crown ether, bis-*p*-phenylene-34-crown-10, we have been trying to identify derivatives that can adopt at least two different mechanical states as a result of modifying some of the building blocks that also act as molecular recognition sites between the compo-

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[+] Current Address: University of Barcelona, Laboratory of Organic Chemistry, Faculty of Pharmacy, E-08028 Barcelona, Spain.

[++] New Address: Department of Chemistry and Biochemistry, University of California at Los Angeles, 405 Hilgard Avenue, Los Angeles CA 90095-1569, USA; Fax: (internat.) +1-310-206-1843; E-mail: stoddart@chem.ucla.edu.

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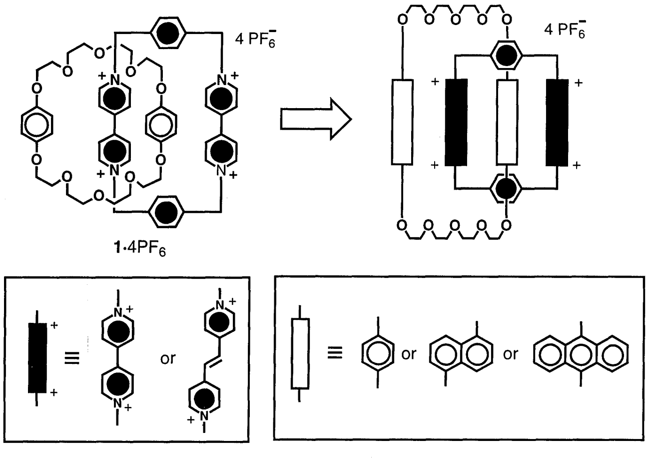
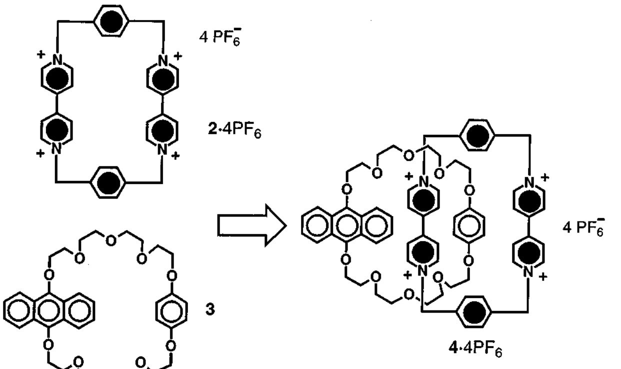
nent rings. The [2]catenane **1**·$4PF_6$ and a few of these derivatives are highlighted in Figure 1.

Figure 1. The [2]catenane **1**·$4PF_6$ and potential π-electron deficient and π-electron donor components for [2]catenanes



As part of a program of research, aimed at extending the π-systems[6] in both the tetracationic cyclophane and crown ether components of [2]catenanes, we have been investigating the consequences of replacing one of the two 1,4-dioxybenzene rings in bis-*p*-phenylene-34-crown-10 with a 9,10-dioxyanthracene unit (Figure 2). Anthracene was chosen for its steric characteristics as well as for the extended nature of its π-system. Moreover, anthracene-based components, because they are electrochemically and photochemically active, are attractive building blocks for incorporation into potentially switchable molecules.[7]

Figure 2. The tetracationic cyclophane **2**·$4PF_6$, the macrocyclic polyether **3** and the [2]catenane **4**·$4PF_6$



Here, we describe (1) the synthesis of a crown ether **3**, incorporating a 9,10-dioxyanthracene unit, as well as a 1,4-dioxybenzene ring, and (2) the ability of this crown ether to act as a catenation template during the formation of cyclobis(paraquat-*p*-phenylene), **2**·$4PF_6$, followed by (3) the characterization of the new [2]catenane **4**·$4PF_6$ by mass spectrometry and NMR spectroscopy, prior to (4) studying the physical properties of the crown ether **3** and the [2]catenane **4**·$4PF_6$. Both components are interesting from the spectroscopic viewpoint, since they contain two potentially luminescent groups: a 1,4-dioxybenzene-type, and a 9,10-dioxyanthracene unit. The properties of molecules like **3** and **4**·$4PF_6$, depend to a large extent on electronic interactions among the component parts.[8][9] It was anticipated that a comparative study of the absorption spectra and luminescent properties of model compounds containing the chromophoric units present in **2**·$4PF_6$, **3** and **4**·$4PF_6$ may reveal the extent of electronic interaction between such units and suggest steps that might now be taken toward the design of new chemical,[10] photochemical,[11] and electrochemical[6][10a][11d][12] molecular switches.

## Results and Discussion

### Synthesis

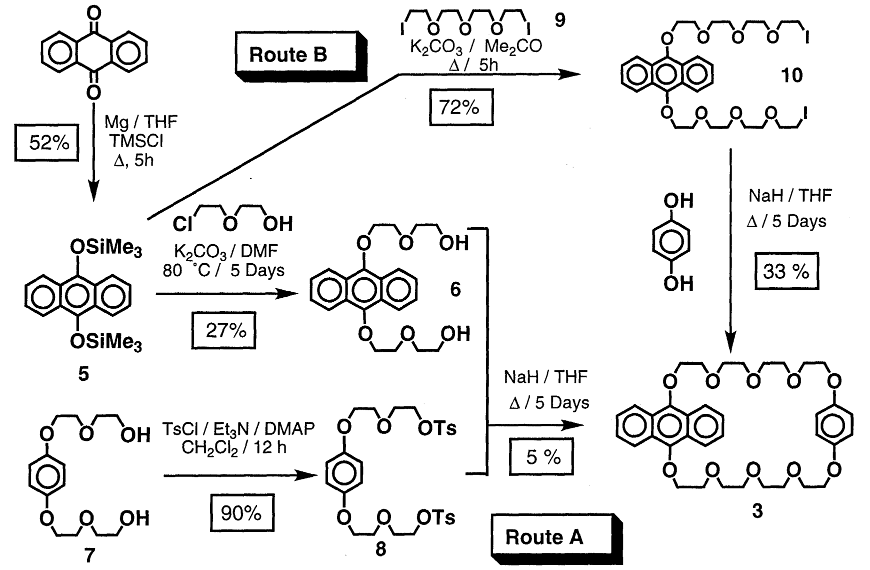
The crown ether **3** was prepared using two different routes (A and B) which are illustrated in Scheme 1. Both routes employ hydroquinone and 9,10-anthraquinone as starting materials. In the first of them, the synthesis of 9,10-bis(trimethylsilyloxy)anthracene (**5**) was approached in a manner similar to that reported in the literature,[7a][7l] i. e., by reaction of 9,10-anthraquinone with $Me_3SiCl$ in the presence of Mg turnings under an atmosphere of Ar. Bis-*O*-alkylation ($K_2CO_3$/DMF) of **5** with 2-(2-chloroethoxy)-ethanol afforded the diol **6**. Compound **8**, which was prepared according to a published procedure,[5] was reacted (NaH/THF) with **6** to give **3** in about 5% yield. In the second procedure, 9,10-bis(trimethylsilyloxy)anthracene (**5**) was reacted with an excess of the dioidide **9** under basic conditions ($K_2CO_3/Me_2CO$) to afford **10**. Iodide was chosen as leaving group in order to aid compound purification.[7a][7l] Reaction (NaH/THF) of **10** with hydroquinone gave the crown ether **3** in 33% yield. Obviously, the most efficient method by far is the second one, partly because it relies on fewer synthetic steps, but also because the final macrocyclization is higher yielding. Furthermore, the use of this particular strategy[7o] for the elaboration of *desymmetrized* crown ethers offers the advantage of relying upon just one compound as an intermediate, namely **10**, from which the desired macrocycles can be synthesized.

The [2]catenane **4**·$4PF_6$ was self-assembled using a well-established template-directed methodology (Scheme 2). Reaction of the dicationic salt **11**·$2PF_6$[5] with 1,4-bis(bromomethyl)benzene (**12**) results presumably in a tricationic intermediate which, following complexation with the crown ether **3**, generates **4**·$4PF_6$ in 59%.

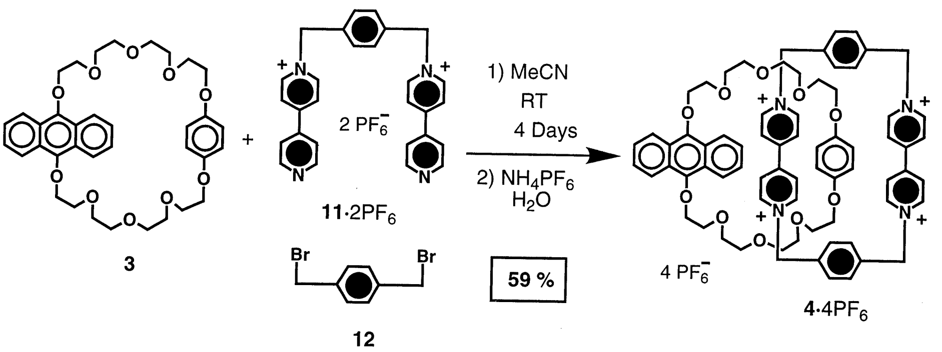
### Mass Spectrometry

The [2]catenane **4**·$4PF_6$ was characterized in the first instance by positive-ion FABMS. The use of this technique revealed peaks at *m/z* 1591, 1446, and 1301, characteristic of the successive loss of one, two, and three $PF_6^-$ counterions from the molecular ion. Peaks at *m/z* 955, and 809, corresponding to the loss of one and two $PF_6^-$ counterions from the free tetracationic cyclophane component, are also characteristic[13] of fragmentations undergone by the [2]catenane – in this case, loss of the neutral crown ether component.

Scheme 1. Synthesis of **3**, a crown ether containing one anthracene and one benzene unit (Routes A and B)



Scheme 2. The self-assembly of the [2]catenane **4**·4PF$_6$



## $^1$H NMR Spectroscopy

The complete suppression of Process I (Figure 3), the one that relates to the equilibration of the π-electron rich 1,4-dioxybenzene ring and the 9,10-dioxyanthracene unit between the positions either "inside" or "alongside" the tetracationic cyclophane, in the [2]catenane **4**·4PF$_6$ is shown by $^1$H NMR spectroscopy. It represents the most distinguishing feature of the dynamic behavior exhibited by this molecule. At room temperature in CD$_3$CN, the singlet at δ 3.34 can be attributed to the 1,4-dioxybenzene protons in the macrocyclic polyether component. The steric hindrance displayed by the anthracene moiety prevents the circumrotation of the macrocyclic polyether through the tetracationic cyclophane and dictates that it is always occupying the "alongside" position, leaving the 1,4-dioxybenzene ring "inside" the tetracationic cavity such that their protons are shifted to high field. As a consequence, the [2]catenane exists in solution at room temperature exclusively as one of two possible translational isomers, i. e., the one represented in Figure 3.

The second dynamic process exhibited by **4**·4PF$_6$ involves pirouetting of its crown ether component around the tetracationic cyclophane. Above room temperature, this process (Process II in Figure 3) is fast on the $^1$H NMR timescale as shown by the good resolution of the signals observed in both CD$_3$CN and (CD$_3$)$_2$CO for all the protons in the [2]catenane. By contrast, in (CD$_3$)$_2$CO solution at −20 °C, process II is "frozen out", as indicated by the appearance of two sets of signals for all the protons observed corresponding to the tetracationic cyclophane component of **4**·4PF$_6$. For instance, at 0 °C, the protons on the α-CH bipyridinium unit appear as two doublets of equal intensity centered on δ 9.20 and δ 9.37, respectively, for the "inside" and "alongside" bipyridinium units, respectively. The coalescence method[14] was used to calculate the $\Delta G_c^{\ddagger}$ value (12.8 kcal mol$^{-1}$) for process II (Table 1).

Figure 3. The $^1$H NMR spectrum of the [2]catenane **4**·4PF$_6$

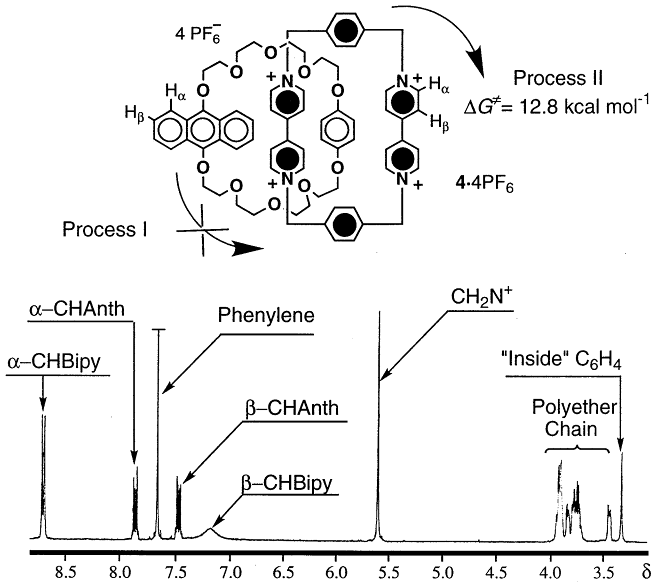


Table 1. Kinetic and thermodynamic parameters obtained from the temperature dependent 400 MHz $^1$H NMR spectra recorded on the [2]catenane **4**·4PF$_6$ in (CD$_3$)$_2$CO

| Probe protons | Δν (Hz) | $k_c$ (s$^{-1}$) | $T_c$ (K) | $\Delta G_c^{\ddagger}$ (kcal mol$^{-1}$) | Process |
|---|---|---|---|---|---|
| α-CH Bipy | 76 | 169 | 267 | 12.8 | II |
| CH$_2$N$^+$ | 32 | 71 | 261 | 12.9 | II |
| OC$_6$H$_4$O | 1304 | 2897 | 225 | 9.5 | Rocking |

A third dynamic process, namely that of *rocking*, has been identified[16] in some [2]catenanes. It involves the protons on the 1,4-dioxybenzene ring of the macrocyclic polyether exchanging their positions from those pointing toward the phenylene spacer in the tetracationic cyclophane to those pointing away from the cyclophane. In the case of the [2]catenane **4**·4PF$_6$, the signals of the protons corresponding to the 1,4-dioxybenzene ring appear as a singlet at δ 3.68 at room temperature in (CD$_3$)$_2$CO solution. However, at −70°C, the protons of the 1,4-dioxybenzene ring resonate as two signals of equal intensities at δ 2.09 and 5.35. The coalescence method[14] was used to calculate a $\Delta G_c^{\ddagger}$ value of 9.5 kcal mol$^{-1}$ (Table 1) for this rocking process.

### Absorption Spectra and Luminescence Properties

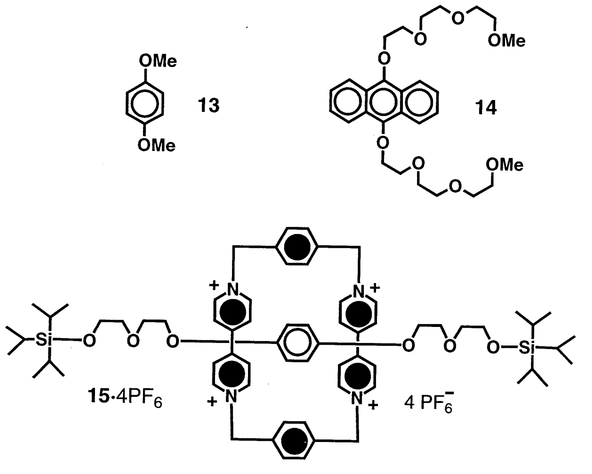
It is well known that the cyclophane **2**·4PF$_6$ shows (Table 2) an intense absorption band in the UV region and no luminescence.[5] The crown ether **3** and the [2]catenane **4**·4PF$_6$ are interesting species from the spectroscopic viewpoint since they contain two potentially luminescent chromophoric moieties: the 1,4-dioxybenzene-, and 9,10-dioxyanthracene-type units. Furthermore, in **4**·4PF$_6$, one expects charge-transfer (CT) interactions between the two different electron-donor units of the crown and the 4,4′-bipyridinium-type electron-acceptor units of the tetracationic cyclophane. In order to elucidate the spectroscopic behavior of **3** and **4**·4PF$_6$, we have compared (Figure 4) their properties to those exhibited by the 1,4-dimethoxybenzene (**13**) and a 9,10-dimethoxyanthracene-type reference compound **14**, as well as to the previously examined[5] rotaxane **15**·4PF$_6$. The most important data, obtained in MeCN solution, are shown in Table 2.

Table 2. Absorption and emission data[a]

| Compound | Absorption | Fluorescence | | | | |
|---|---|---|---|---|---|---|
| | | r.t. | | | 77 K | |
| | $\lambda_{max}$, nm (ε, M$^{-1}$ cm$^{-1}$) | $\lambda_{max}$ (nm) | τ (ns) | Φ | $\lambda_{max}$ (nm) | τ (ns) |
| **13** | 290 (2900) | 320 | 2.5 | 0.11[b] | 317[c] | 3.8[c] |
| **14** | 258 (110000) | 437 | 9.0 | 0.75[d] | 418[e,f] | |
| | 381 (7600)[e] | | | | | |
| **3** | 258 (110300) | 320 | | ≤10$^{-3}$ | | |
| | 381 (7600)[e] | 437 | 9.0 | 0.65[d] | 416[e,f] | 12 |
| **2**·4PF$_6$ | 260 (40000) | | | | | |
| **4**·4PF$_6$ | 258 (144500) | 437 | | [g] | | |
| | 384 (6800)[e] | | | | | |
| | 545 (615) | | | | | |

[a] Air-equilibrated MeCN solutions, unless otherwise noted. For errors, see the Experimental Section. – [b] The standard used was naphthalene in degassed cyclohexane, Φ = 0.23. See ref.[26]. – [c] Butyronitrile rigid matrix. – [d] The standard used was quinine sulfate in 1 N sulfuric acid, Φ = 0.55. See ref.[27]. – [e] Structured band. – [f] Highest energy feature. – [g] Estimated value ≤ 5 × 10$^{-3}$.

Figure 4. Structural formulas of the model compounds **13** and **14** for the chromophoric units present in **3** and a reference compound – [2]rotaxane **15**·4PF$_6$



*Crown Ether* **3**: The absorption spectrum of **3** is exactly that expected for the sum of the spectra of the two component 1,4-dioxybenzene and 9,10-dioxyanthracene chromophoric units shown in Figure 5. This observation indicates that the electronic interaction between the two chromophoric groups is very weak.

Both the reference compounds **13**[7g] and **14**[7g][7l] are luminescent species. In MeCN solution at room temperature, **13** shows (Figure 6) an emission maximum at 320 nm; the excited state lifetime is rather short (2.5 ns) and the fluorescence quantum yield is relatively high (0.11). This emission can be attributed to the lowest energy singlet ex-

Figure 5. Absorption spectra (MeCN, room temperature) of the model compounds **13** (dashed line) and **14** (full line). Note the reduction factor for the UV band of **14**

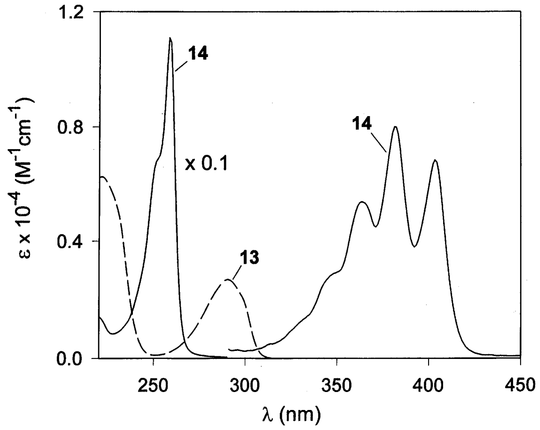


Figure 6. Emission spectra (MeCN, room temperature) of the model compounds **13** ($\lambda_{ex}$ = 290 nm, dashed line) and **14** ($\lambda_{ex}$ = 380 nm, full line)

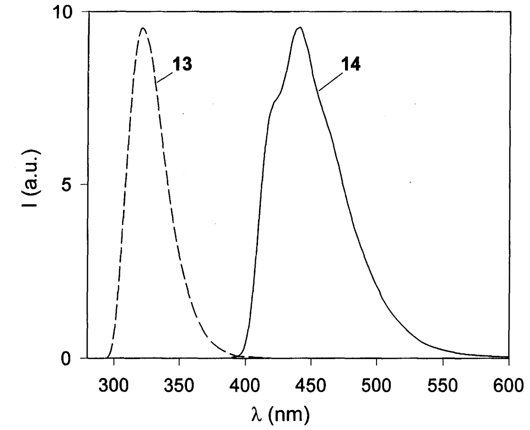
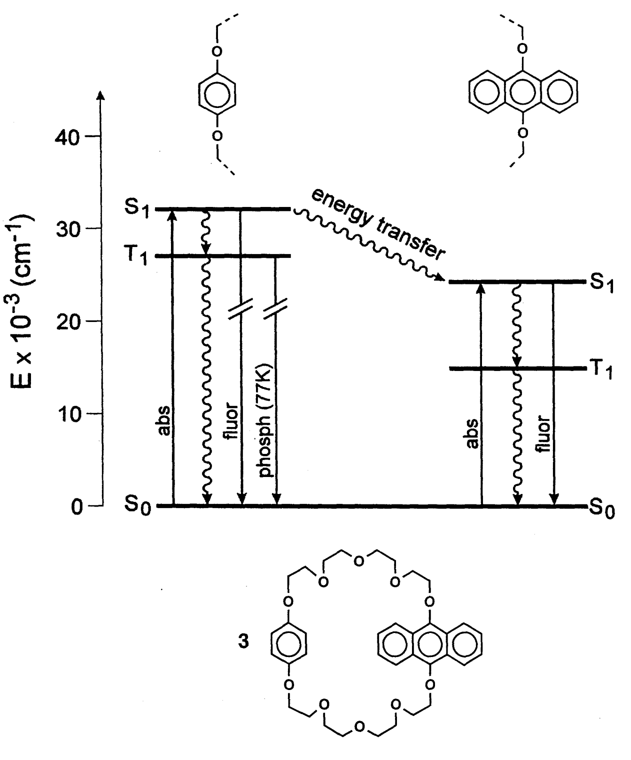


Figure 7. Schematic energy-level diagram for the macrocyclic polyether **3** and its chromophoric units



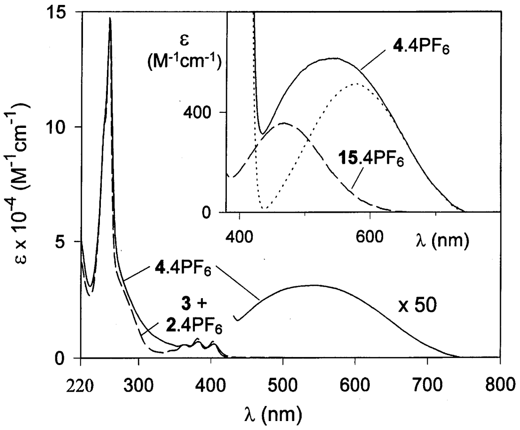
cited state, $S_1$(1,4-dioxybenzene), of **13**. The emission band of **14** occurs (Figure 6), as expected, at considerably lower energy ($\lambda_{max}$ = 437 nm) and can again be attributed to the lowest energy singlet excited state, $S_1$(9,10-dioxyanthracene), of **14**; the excited state lifetime is relatively long, 9.0 ns, and the fluorescence quantum yield is very high, 0.75 (in fair agreement with the previously reported[7l] values of $\tau$ = 15 ns and $\Phi$ = 0.69 for a degassed MeCN solution). In the emission spectrum of the crown ether **3**, the fluorescence band of the 1,4-dioxybenzene-type unit is very weak (quantum yield $\leq 10^{-3}$), whereas the fluorescence band of the 9,10-dioxyanthracene-type unit is present with the same characteristics ($\lambda_{max}$ = 437 nm, $\tau$ = 9.0 ns, $\Phi$ = 0.65) exhibited by compound **14**. These results show that in **3** the $S_1$(1,4-dioxybenzene) excited state is quenched by a very fast process. The rate constant of the quenching process, $k_q$, can be evaluated from equation (1) where $\tau°$ and $\Phi°$ are the excited state lifetime and quantum yield of the reference compound 1,4-dimethoxybenzene (**13**), and $\Phi$ is the quantum yield of the 1,4-dioxybenzene-type unit of **3**. Since $\tau°$ = 2.5 ns, $\Phi°$ = 0.11, and $\Phi \leq 10^{-3}$ (Table 2), a lower limiting value of $4 \times 10^{10}$ s$^{-1}$ can be obtained for the rate constant of the process responsible for the quenching of the $S_1$(1,4-dioxybenzene) excited state of **3**.

$$k_q = \frac{1}{\tau^0}\left(\frac{\Phi^0}{\Phi} - 1\right) \qquad (1)$$

We have also found that in **3** the fluorescence of the 9,10-dioxyanthracene-type unit has the same quantum yield (within the experimental error), regardless of whether excitation is performed in the 1,4-dioxybenzene- or 9,10-dioxyanthracene-type absorption bands. This observation shows that the quenching of the $S_1$(1,4-dioxybenzene) excited state is due to energy transfer to the $S_1$(9,10-dioxyanthracene) level (Figure 7).[17][18]

*[2]Catenane* **4**·4PF$_6$: It is well known that, in catenanes composed of electron-donor and electron-acceptor components, there are strong electronic interactions.[5] This is certainly the case for the [2]catenane **4**·4PF$_6$, since its absorption spectrum is considerably different from the sum of the spectra of the two ring components (Figure 8). Of particular interest is the presence of a new, broad absorption band in the visible spectral region ($\lambda_{max}$ = 545 nm, $\varepsilon_{max}$ = 615 M$^{-1}$cm$^{-1}$). By analogy with the behavior of a number of rotaxanes and catenanes of the same family,[5][19][20] such an absorption band can be assigned to CT transitions involving the electron-donor units present in the crown ether and the electron-acceptor units of the tetracationic cyclophane. As shown in Figure 8, the CT band of **4**·4PF$_6$ in the visible region is extremely broad, suggesting that it receives contributions from two distinct CT transitions. This is not

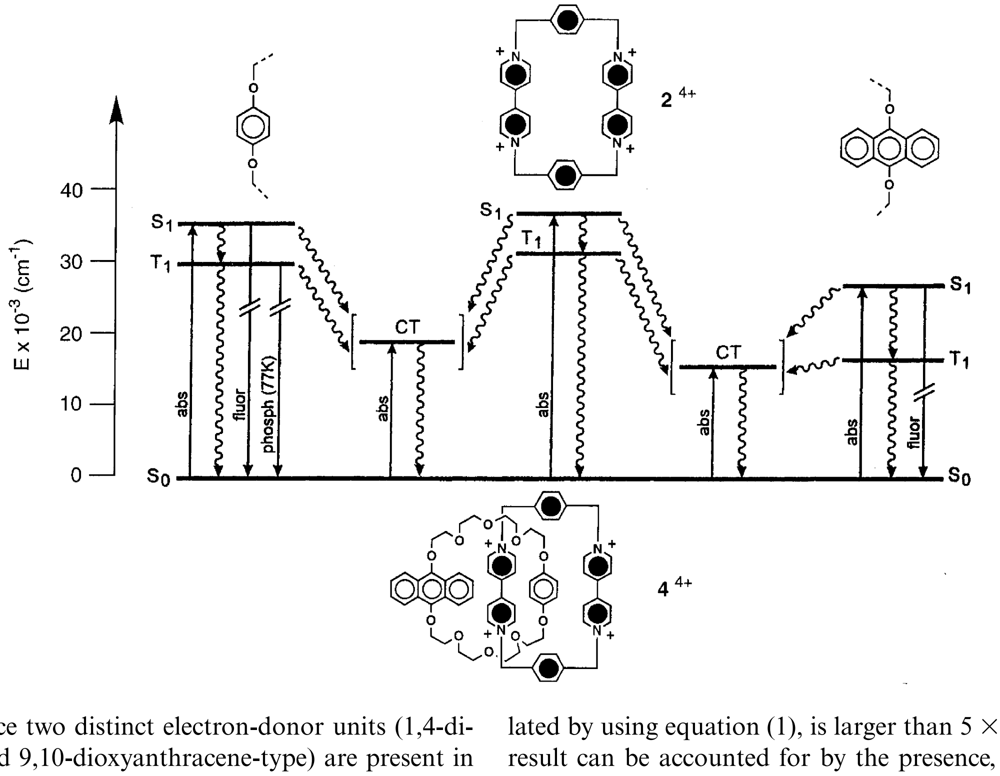
Figure 8. Absorption spectra (MeCN, room temperature) of the [2]catenane **4**·$4PF_6$ (full line) compared to the sum of the absorption spectra of its components – the macrocyclic polyether **3** and the tetracationic cyclophane **2**·$4PF_6$ (dashed line); inset: absorption spectrum (MeCN, room temperature) in the visible region of the [2]catenane **4**·$4PF_6$ (full line) and the [2]rotaxane **15**·$4PF_6$ (dashed line); the dotted line shows the difference between the two bands; for more details, see the text



unexpected, since two distinct electron-donor units (1,4-dioxybenzene- and 9,10-dioxyanthracene-type) are present in the crown ether **3** and the energy of the CT bands is related to the properties (particularly, to the oxidation potential) of the electron-donor unit.[5][19][20] It will be recalled that, for steric reasons, the 1,4-dioxybenzene-type unit occupies the "inside" position in **4**·$4PF_6$, in spite of the fact that the 9,10-dioxyanthracene-type unit is a better electron donor. As a model compound for the CT interaction of a 1,4-dioxybenzene-type unit "inside" the macrocycle **2**·$4PF_6$, we can take the previously studied[5] [2]rotaxane **15**·$4PF_6$ (Figure 4), which shows a CT band with $\lambda_{max}$ = 470 nm and $\varepsilon_{max}$ = 350 $M^{-1}cm^{-1}$. Subtraction of this band from that of **4**·$4PF_6$ (Figure 9, inset) shows that the latter contains another component band with $\lambda_{max}$ = 574 nm and $\varepsilon_{max}$ = 530 $M^{-1}cm^{-1}$). This component can be attributed to a CT transition from the "alongside" 9,10-dioxyanthracene-type unit, which is a better electron donor than the 1,4-dioxybenzene-type unit, to a 4,4′-bipyridinium-type unit of the tetracationic cyclophane. This spectral analysis is fully consistent with the results obtained[21] for a [2]rotaxane made of cyclobis(paraquat-*p*-phenylene) and a dumbbell-shaped component containing one 9,10-dioxyanthracene, and two 1,4-dioxybenzene-type units, where the CT band due to the interaction between the 9,10-dioxyanthracene-type unit and the tetracationic cyclophane showed a maximum at 580 nm.[22]

As far as luminescence is concerned, the behavior of the [2]catenane **4**·$4PF_6$ is completely different from that of the corresponding components. The strong fluorescence band of the 9,10-dioxyanthracene-type unit, which is still present in the crown ether **3**, can no longer be observed ($\Phi \leq 5 \times 10^{-3}$). The rate constant for the quenching process, calculated by using equation (1), is larger than $5 \times 10^{10}\ s^{-1}$. This result can be accounted for by the presence, clearly shown by the absorption spectra (vide supra), of low energy charge-transfer excited states which offer a route for fast radiationless decay of the $S_1$(9,10-dioxyanthracene) level, as illustrated by the energy level diagram of Figure 9.

Figure 9. Schematic energy-level diagram for the catenane **4**·$4PF_6$



## Conclusions

It is clear that there is no circumrotation of the crown ether ring related to bis-*p*-phenylene-34-crown ether, in which one of the 1,4-dioxybenzene rings has been replaced by a 9,10-dioxyanthracene unit, through the cavity of the tetracationic cyclophane in the [2]catenane $\mathbf{4}\cdot 4PF_6$. Furthermore, it has been established that $\mathbf{4}\cdot 4PF_6$ and the crown ether **3** with their two potentially luminescent groups — namely a 1,4-dioxybenzene- and a 9,10-dioxyanthracene-type units — are very interesting species from the spectroscopic viewpoint following measurements of their absorption, emission and excitation spectra, excited state lifetimes, and fluorescent quantum yields. In **3**, the two chromophoric units interact very weakly, as indicated by the fact that the absorption spectrum of the macrocycle is equal to the sum of the spectra of the 1,4-dioxybenzene-type to the 9,10-dioxyanthracene-type components. The fluorescent excited state of the 1,4-dioxybenzene-type unit, however, is quenched via energy transfer to the 9,10-dioxyanthracene-type one with rate constant $k_q \geq 4 \times 10^{10}\ s^{-1}$. In the case of $\mathbf{4}\cdot 4PF_6$, the absorption spectrum is considerably different from the sum of the spectra of the two cyclic components, particularly for the presence of a very broad CT band in the visible spectral region. Comparison with the CT absorption band of the model rotaxane compound $\mathbf{15}\cdot 4PF_6$ shows that the very broad CT band of $\mathbf{4}\cdot 4PF_6$ is in fact due to two component bands originating from the interaction of the two different electron-donor units present in the crown ether with the electron-acceptor 4,4′-bipyridinium-type units of the tetracationic cyclophane. The emission spectrum of $\mathbf{4}\cdot 4PF_6$ does not show any band because of the quenching effect of the low-energy non-luminescent charge-transfer levels on the higher energy, potentially luminescent levels of the crown ether **3**.

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## Experimental Section

*General Methods:* With the exception of 9,10-anthraquinone, which was purchased from Fluka, the following chemicals were purchased from Aldrich and used as received unless it is indicated that they have been recrystallized: 1,4-bis(bromomethyl)benzene (**12**), 2-(2-chloroethoxy)ethanol, 1,4-dihydroxybenzene, 4-dimethylaminopyridine, tosyl chloride (recrystallized from hexane-$CHCl_3$), triethylamine and trimethylsilyl chloride. Solvents were distilled and dried [THF (from Na/benzophenone ketyl), DMF (from $CaH_2$), MeCN (from $P_2O_5$), $Me_2CO$ (from $K_2CO_3$), $CH_2Cl_2$ (from $CaH_2$)], according to literature procedures.[23] The following compounds were prepared, according to published procedures: 9,10-bis(trimethylsilyloxy)anthracene (**5**),[7a][7l] 1,4-bis[2-(2-hydroxyethoxy)ethoxy]benzene (**7**),[5] 1,4-bis[2-(2-hydroxyethoxy)ethoxy]benzene bis(4-methylbenzenesulfonate) (**8**),[5] 1,13-diiodo-4,7,10-trioxatridecane (**9**),[7a][7l] 9,10-bis[2-[2-[2-(2-iodoethoxy)ethoxy]ethoxy]ethoxy]anthracene (**10**),[7a][7l] 1,1′-[1,4-phenylenebis(methylene)]bis(4,4′-bipyridinium) bis(hexafluorophosphate) (**11**),[5][24] and tetraethylene glycol bis(4-methylbenzenesulfonate).[25] − Thin-layer chromatography (TLC) was performed on aluminium sheets coated with silica gel 60 $F_{254}$ (Merck 5554); after being developed, the plates were air-dried, analyzed under an UV lamp and exposed to a $SiO_2/I_2$ tank. − Column chromatography was carried out on silica gel 60 (Merk 9385, 230−400 mesh). − Melting points were determined on a electric melting-point apparatus with a digital display (Electhrothermal 9200) and are uncorrected. − Low-resolution mass spectra were obtained on a Kratos Profile Mass Spectrometer using either Electron Impact Mass Spectrometry (EIMS) or Chemical Ionisation Mass Spectrometry (CIMS) using $NH_3$. FABMS were obtained using a Kratos MS80RF mass spectrometer, coupled to a DS90 system. The atom gun (Ion Tech Limited) was operated at 7 keV with a tube current of 2 mA. The primary beam of atoms was produced from research grade krypton. The sample was dissolved in a small amount of 3-nitrobenzylalcohol that had been coated on to a stainless steel probe and the spectrum was recorded in the positive ion mode at a scan speed of 30 s per decade. − $^1H$ NMR Spectra were recorded on either a Bruker AC 300 (300 MHz) or a Bruker AMX400 (400 MHz) spectrometer. − $^{13}C$ NMR Spectra were recorded on either the Bruker AC300 (75.5 MHz) or the Bruker AMX400 (100 MHz) spectrometer. − Microanalyses were performed by the University of Birmingham Microanalytical Service.

*9,10-Bis[2-(2-hydroxyethoxy)ethoxy]anthracene* (**6**): A solution of compound **5**[7a][7l] (5.00 g, 14.1 mmol) in dry DMF (150 ml) was added over 3 h to a stirred suspension of $K_2CO_3$ (15.77 g, 114.0 mmol) in dry DMF (150 ml) under nitrogen. A solution of 2-(2-chloroethoxy)ethanol (7.45 g, 50.0 mmol) in dry DMF (100 ml) was then added over 30 min and the temperature was raised to 80°C. Stirring and heating were continued for 5 days. After cooling down to room temperature, the reaction mixture was filtered and the residue washed with DMF (50 ml). The solvent was removed in vacuo and the residue was partitioned between $CHCl_3$ (50 ml) and $H_2O$ (50 ml). The pH was adjusted to ca. 2 with 2 N HCl, and the aqueous phase was washed with $CHCl_3$ (2 × 75 ml). The combined organic solutions were washed with $H_2O$ (50 ml), dried ($MgSO_4$) and concentrated in vacuo. Purification of the residue by column chromatography [$SiO_2$, $Me_2CO$/hexane (1:1)] gave the title compound **6** as a yellow solid (1.99 g, 27%). − M. p. 100 °C. − EIMS (70 eV): *m/z* (%) 386 (50) $[M]^+$. − $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 1.95$ (bs, 2 H, O*H*), 3.75−3.80 (m, 4 H, β-C$H_2$O), 3.84−3.89 (m, 4 H, γ-C$H_2$O), 3.98−4.04 (m, 4 H, α-C$H_2$O), 4.35−4.40 (m, 4 H, δ-C$H_2$OH), 7.46−7.53 (m, 4 H, *H*-1,4,5,8), 8.32−8.40 (m, 4 H, *H*-2,3,6,7). − $^{13}C$ NMR (75.5 MHz, $CDCl_3$, 25 °C): $\delta = 62.0$, 70.6, 72.7, 74.8, 122.6, 125.4, 134.0, 147.2. − Anal. calcd for $C_{22}H_{26}O_2\cdot H_2O$ (404.4): C 65.83, H 6.98; found C 65.94, H 6.84.

*1,4,7,10,13,20,23,26,29,32-Decaoxa[13]paracyclo[13](9.10)-anthracenophane* (**3**):

*Method A:* A solution of the diol **6** (1.20 g, 3.1 mmol) in dry THF (50 ml) was added over 15 min to a stirred suspension of NaH (0.33 g, 6.8 mmol, 50% in mineral oil, washed previously with *n*-hexane) in dry THF (ml) under nitrogen. After 1 h, a solution of the bistosylate **8**,[5] (1.55 g, 3.1 mmol) in dry THF (80 ml) was added over 30 min. The reaction mixture was heated under reflux for 4 days. The reaction mixture was then cooled down to room temperature and a few drops of $H_2O$ were added to destroy any residual NaH. The reaction mixture was concentrated in vacuo and the residue was partitioned between $H_2O$ (20 ml) and PhMe (20 ml). The organic extracts were washed with $H_2O$ (10 ml), dried ($CaCl_2$) and concentrated in vacuo. Column chromatography of the residue [$SiO_2$, $Me_2CO$/hexane (1:1)] afforded the title compound **3** as a yellow solid (0.10 g, 5%). − M. p. 162 °C. − FABMS (8 keV): *m/z* 654 $[M + NH_4]^+$, 637 $[M + 1]^+$. − $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 3.74$−3.91 (m, 24 H, C$H_2$O), 3.97−4.02

(m, 4 H, C$H_2$CH$_2$O), 4.28−4.35 (m, 4 H, C$H_2$OAr), 6.50 (s, 4 H, C$_6H_4$), 7.34−7.40 (m, 4 H, *H*-2,3,6,7), 8.33-8.41 (m, 4 H, *H*-1,4,5,8). − $^{13}$C NMR (75.5 MHz, CDCl$_3$, 25 °C): δ = 68.1, 69.7, 70.6, 70.8, 70.9, 71.0, 71.0, 74.9, 115.4, 122.7, 125.1, 125.4, 147.1, 152.9. − Anal. calcd for $C_{36}H_{44}O_{10}$ (636.7): C 67.93, H 6.92; found C 68.14, H 7.02.

*Method B:* A solution of 1,4-dihydroxybenzene (0.28 g, 2.6 mmol) in dry THF (160 ml) was added over 15 min to a stirred suspension of NaH (0.28 g, 50% in mineral oil, washed previously with *n*-hexane, 6.0 mmol) in dry THF (150 ml) under nitrogen. After 30 min, a solution of the diiodide **10**[7a][7l] (2.00 g, 2.6 mmol) in dry THF (150 ml) was added over 15 min, and reflux was maintained for 5 days. Workup according to method A afforded the title compound **3** (0.55 g, 33%).

*{[2]-[1,4,7,10,13,20,23,26,29,32-Decaoxa[13]paracyclo[13](9.10)anthracenophane]-[9,18,29,38-tetraazonia[1.1.0.1.1.0]paracyclophane]-Catenane} Tetrakis(hexafluorophosphate)* (**4**·4PF$_6$): 1,1′-[1,4-Phenylenebis(methylene)]bis(4,4′-bipyridinium) bis(hexafluorophosphate) (**11**),[5][25] (71 mg, 0.10 mmol) was added as a solid to a solution of the crown ether **3** (200 mg, 0.31 mmol) in dry MeCN (20 ml). After 10 min, 1,4-bis(bromomethyl)benzene (**12**) (37 mg, 0.14 mmol) was added as a solid to the mixture, which, after 4 h, became an intense purple color. After the reaction had been stirred at room temperature for 4 days, the solvent was removed in vacuo and the residue was purified by column chromatography [SiO$_2$, MeOH/2 N NH$_4$Cl/MeNO$_2$ (7:2:1)]. The catenane-containing fractions were combined, evaporated in vacuo and dried. The residue was dissolved in H$_2$O (50 ml) and a saturated NH$_4$PF$_6$ solution was added until no further precipitation was observed. The precipitate was filtered off, washed with H$_2$O (2 × 5 ml) and dried to afford the [2]-catenane **4**·4PF$_6$ as a purple solid (100 mg, 59%). − M. p. >300°C. − FABMS (8 keV): *m/z* 1735 $[M]^+$, 1591 $[M - PF_6]^+$, 1446 $[M - 2PF_6]^+$, 1301 $[M - 3PF_6]^+$, 955 $[M - PF_6 - \mathbf{3}]^+$, 809 $[M - 2PF_6 - \mathbf{3}]^+$. − $^1$H NMR (400 MHz, CD$_3$CN, 70°C): δ = 3.38 (s, 4 H, C$_6H_4$ "inside"), 3.48−3.95 (m, 32 H, C$H_2$O), 5.69 (s, 8 H, C$H_2$N$^+$), 7.25 (d, $^3J$ = 7.0 Hz, 8 H, bipyridinium β-C*H*), 7.50−7.54 (m, 4 H, Anth. H-2,3,6,7), 7.74 (s, 8 H, *p*-xylyl-*H*), 7.90−7.94 (m, 4 H, Anth. H-1,4,5,8), 8.78 (d, $^3J$ = 7.0 Hz, 8 H, bipyridinium α-C*H*). − $^{13}$C NMR (75.5 MHz, CD$_3$COCD$_3$, 25 °C): δ = 65.7, 68.7, 70.5, 70.7, 70.9, 72.0, 72.1, 72.2, 74.8, 105.1, 109.1, 123.1, 125.0, 125.2, 126.6, 128.9, 131.9, 132.3, 137.8, 145.3, 147.2, 151.7. − Anal. calcd for $C_{72}H_{76}N_4O_{10}F_{24}P_4 \cdot 2H_2O$ (1773.3): C 48.77, H 4.55, N 3.16; found C 48.63, H 4.36, N 3.30.

*Absorption and Luminescence Measurements:* Room temperature experiments were carried out in MeCN solutions. Absorption and emission spectra were recorded with a Perkin-Elmer λ6 spectrophotometer and a Perkin Elmer LS-50 spectrofluorimeter, respectively. Emission spectra in butyronitrile rigid matrix at 77 K were recorded using quartz tubes immersed in a quartz Dewar filled with liquid nitrogen. Fluorescence lifetimes were measured with an Edinburgh 199 single-photon counting equipment, and fluorescence quantum yields were determined using naphthalene in degassed cyclohexane (Φ = 0.23)[26] or quinine sulfate in H$_2$SO$_4$ 1 N (Φ = 0.55)[27] as standards. Experimental errors: absorption maxima, ±2 nm; emission maxima, ±2 nm; excited-state lifetimes, ±10%; fluorescence quantum yields, ±20%.

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