# The Electrochemically-Driven Decomplexation/Recomplexation of Inclusion Adducts of Ferrocene Derivatives with an Electron-Accepting Receptor<sup>†</sup>

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The tetracationic cyclophane, cyclobis(paraquat-4,4'-biphenylene), binds 1,1'-disubstituted ferrocenebased polyethers as a result of (i)  $[\pi \cdot \pi]$  stacking between the  $\pi$ -electron-deficient bipyridinium units and the  $\pi$ -electron-rich cyclopentadienyl rings and (ii)  $[C-H \cdot O]$  hydrogen bonds between the  $\alpha$ -bipyridinium hydrogen atoms and the polyether oxygen atoms. However, even the presence of a bulky tetraarylmethane group—which is too large to thread through the cavity of the cyclophane host—at the end of each of the two polyether substituents of the ferrocene-containing guest does not discourage adduct formation of the inclusion type. Thus, in these adducts, the ferrocene unit of the guest is located inside the cavity of the host with its two polyether chains protruding outward from the same side of the host. The alternative pseudorotaxane geometry is not observed in solutions of these 1:1 adducts. The host—guest adducts display absorption bands in the visible spectral region, characteristic of charge-transfer interactions. In the case of one of these adducts, reversible decomplexation/recomplexation takes place upon electrochemical oxidation/reduction of the ferrocene-based unit or upon reduction/oxidation of the tetracationic cyclophane.

# Introduction

The tetracationic cyclophane, cyclobis(paraquat-4,4'biphenylene) (1<sup>4+</sup>), can be synthesized<sup>1</sup> from its acyclic precursors in a reasonable yield (32%) when a ferrocenebased polyether is employed as the template. It is known<sup>1,2</sup> that this tetracationic cyclophane binds (Figure 1) ferrocene (**2**) as a result of  $[\pi \cdot \pi]$  stacking interactions between the  $\pi$ -electron-deficient bipyridinium units and the  $\pi$ -electron-rich cyclopentadienyl rings. Upon the introduction of one polyether chain onto each of the cyclopentadienyl rings of ferrocene (**2**), as in the case of the derivative **3**, the stability of the resulting second sphere adduct<sup>3</sup> increases<sup>1</sup> drammatically as a result—it is believed—of additional [C-H··O] hydrogen bonds that

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Figure 1. Adduct  $[1:2]^{4+}$  and the two co-conformations (A and B) for the adduct  $[1:3]^{4+}$ .

are formed between the  $\alpha$ -bipyridinium hydrogen atoms and some of the polyether oxygen atoms. However, since the rotation of one cyclopentadienyl ring with respect to the other is possible in solution, two different 1:1 adducts (**A** and **B**) can, in principle, be formed when a 1,1'disubstituted ferrocene derivative, such as **3**, is bound as a guest inside the host  $1^{4+}$ . In both these 1:1 adducts, the ferrocene unit in the guest is located inside the cavity of the host with, in one case, its two substituents

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protruding outward in hairpin-like fashion from the same (**A**) and, in the other case, from opposite (**B**) sides of the host. Only in co-conformation<sup>4</sup> **B** would the covalent attachment of bulky groups to the ends of the polyether chains of the guest bond together mechanically the cyclic and the acyclic components, affording a [2]rotaxane. In light of these considerations, we envisaged the possibility of designing and constructing ferrocene-based rotaxanes<sup>5</sup> with the ultimate goal of generating electrochemically controllable molecular shuttles.<sup>6,7</sup> Here, we report (i) the

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Scheme 1. Synthesis of the Dumbbell-Shaped Compound 9 Incorporating One Ferrocene Unit



synthesis of four ferrocene-containing acyclic polyethers, (ii) the complexation of their hairpin-like forms (**A**) exclusively by cyclobis(paraquat-4,4'-biphenylene) ( $\mathbf{1}^{4+}$ ), (iii) the absorption characteristics of the adducts, and (iv) the reversible decomplexation/recomplexation of one of the adducts, both upon oxidation/reduction of the ferrocene-based unit in the guest and upon reduction/ oxidation of the bipyridinium units in the host.

# **Results and Discussion**

Synthesis. The 1,1'-disubstituted ferrocene derivative **3** templates<sup>1</sup> the formation of **1**<sup>4+</sup> from its acyclic precursors in a yield of 32%. To construct a [2]rotaxane, we envisaged the possibility of modifying the template 3 by attaching bulky tetraarylmethane-based stoppers to the ends of each of the two polyether chains. Alkylation of 4 with 5 afforded (Scheme 1) the ester 6, which was hydrolyzed to give the acid 7, which was then converted into the acid chloride 8. Esterification of 3 with 8 afforded the dumbbell-shaped compound 9, which incorporates a ferrocene recognition site and two bulky stoppers. When this reaction was repeated in the presence of the preformed cyclophane  $1^{4+}$ , only trace amounts of the expected [2]rotaxane were obtained.<sup>8</sup> Similarly, when 9 was employed as a template in the macrocyclization of  $\mathbf{1}^{4+}$ from its acyclic precursors, extremely small quantities (<1%) of the expected [2]rotaxane were detected.<sup>8</sup> These unexpected results were ascribed initially to the relative ease of decomposition of the ferrocene templates 3 and **9**. Reduction of the  $\pi$ -electron-rich character of the

<sup>(8)</sup> A solution of **9** (275 mg, 0.18 mmol), **13**·2PF<sub>6</sub> (202 mg, 0.26 mmol), and **14** (89 mg, 0.26 mmol) in MeCN (10 mL) was stirred for 10 d at ambient temperature. The solvent was distilled off under reduced pressure and the residue washed with CHCl<sub>3</sub> (25 mL). The resulting solid was dissolved in a mixture of Me<sub>2</sub>CO and H<sub>2</sub>O (500 mL, 1: 1 v/v), and NH<sub>4</sub>PF<sub>6</sub> was added as a solid. The solution was concentrated under reduced pressure, and the resulting precipitate was filtered off and purified by column chromatography [SiO<sub>2</sub>: MeOH/2 M NH<sub>4</sub>Cl/MeNO<sub>2</sub> (7:2:1)] to afford traces (<1%) of the [2]rotaxane in addition to quantities of 1·4PF<sub>6</sub> after counterion exchange. The [2]rotaxane could only be characterized by liquid secondary ion mass spectrometry (LSIMS), which showed peaks at *m*/*z* values of 2828, 2679, and 2534 for [M]<sup>+</sup>, [M – PF<sub>6</sub>]<sup>+</sup>, and [M – 2PF<sub>6</sub>]<sup>+</sup>, respectively, corresponding to the molecular ion and to the losses of one and two hexafluorophosphate counterions, respectively.



Scheme 3. Template-Directed Synthesis of 1·4PF<sub>6</sub>



cyclopentadienyl rings by the insertion of a methylene group between them and their polyether substituents was expected to increase the stabilities of the templates. Indeed, reaction of **10** with **11** afforded (Scheme 2) the stable compound **12** in a yield of 77%. This compound was employed (Scheme 3) to template the formation of  $1^{4+}$  from its precursors **13**·2PF<sub>6</sub> and **14**. The tetracationic cyclophane was isolated as its hexafluorophosphate salt (**1**·4PF<sub>6</sub>) in a yield of 32% after precipitation with an excess of NH<sub>4</sub>PF<sub>6</sub>. Interestingly, this yield is exactly the same as that obtained when the template **3** was em-

ployed,<sup>1</sup> indicating that a reduction of the  $\pi$ -electron-rich character of the template does not affect significantly the efficiency of this template-directed synthesis. These observations suggested the synthesis of the templates 18 and 21, each incorporating one ferrocene recognition site and two tetraarylmethane-based stoppers. Compound 18 was obtained (Scheme 4) after the alkylation of 4 with 15, followed by tosylation and reaction of the tosylate with 11. Similarly, compound 21 was prepared (Scheme 5) after the alkylation of 4 with an excess of 19, followed by tosylation and reaction of the tosylate with 11. However, when 18 was used to template the macrocyclization of  $13^{2+}$  and 14, the expected [2]rotaxane was not even detected.9 Instead, the free tetracationic cyclophane 1.4PF<sub>6</sub>, in 2% yield only, and the unchanged template 18 were isolated from the reaction mixtures.

### Scheme 4. Synthesis of the Dumbbell-Shaped Compound 18 Incorporating One Ferrocene Unit



These unexpected results can be explained in two alternative ways. Either (i) the [2]rotaxanes are formed but the macrocyclic component can dethread because the stoppers are not large enough or (ii) the complexation of 1,1'-disubstituted ferrocene derivatives by **1**<sup>4+</sup> occurs as illustrated for co-conformation A in Figure 1. It is known<sup>1</sup> that  $\mathbf{1}^{4+}$  binds 1.4-dioxybenzene-based guests inside its cavity and that a reddish-orange color appears immediately when the preformed  $\mathbf{1}^{4+}$  cyclophane is mixed with guests of this kind. Thus, to verify if the tris(4-tertbutylphenyl)methyl groups are large enough to act as stoppers toward the cyclophane  $\mathbf{1}^{4+}$ , the 1,4-dioxybenzene-based dumbbell-shaped compound 23 was synthesized (Scheme 6) by reacting 17 with 22. It transpired that, when  $1.4PF_6$  and 23 were mixed in MeCN at room temperature, no color change was observed, indicating that threading of 23 through the cavity of  $1^{4+}$  does not occur. By contrast, when either of the ferrocene-based

<sup>(9)</sup> The attempted template-directed synthesis of the [2]rotaxane was carried out by stirring a solution of  $13 \cdot 2PF_6$ , 14, and 18 (3:3:1) in DMF at ambient temperature for 10 days. DMF was chosen as the solvent because 18 is not soluble in MeCN. No evidence was obtained for the formation of any [2]rotaxane. However,  $1 \cdot 4PF_6$  was isolated in a yield of 2% (based on the molar amounts of  $13 \cdot 2PF_6$  and 14). The template-directed synthesis of the tetracationic cyclophane  $1 \cdot 4PF_6$  was not expected to be an efficient template, and the latter was not available in sufficient quantities.

Scheme 5. Synthesis of the Dumbbell-Shaped Compound 21 Incorporating One Ferrocene Unit and Two Hydroquinone Rings



compounds, **18** or **21**, were mixed with  $1.4PF_6$  in DMF, a green color (vide infra), characteristic<sup>1</sup> of charge-transfer interactions between the cyclopentadienyl rings and the bipyridinium units, appeared immediately in keeping with the formation of an adduct. Since the tris-(4-tert-butylphenyl)methyl groups are too large to thread through the cavity of the cyclophane, the adducts formed between  $1^{4+}$  and either **18** or **21** must be similar to **A**-i.e., the two substituents of the guest protrude outside the cavity of the host from the same side.

#### Scheme 6. Synthesis of the Dumbbell-Shaped Compound 23 Incorporating One Hydroquinone Ring



<sup>1</sup>H NMR Spectroscopy. The <sup>1</sup>H NMR spectroscopic analyses of the adducts revealed significant chemical shift changes relative to the separate host and guest



**Figure 2.** <sup>1</sup>H NMR spectra ( $c = 0.01 \text{ mol } L^{-1}$ , 300 K) of (a) **12** recorded in CDCl<sub>3</sub> and of (b) **1**·4PF<sub>6</sub> and (c) an equimolar mixture of them recorded in CD<sub>3</sub>CN.

components. As an example, the <sup>1</sup>H NMR spectra of the free guest **12** (recorded in CDCl<sub>3</sub>) and of the free host **1**·4PF<sub>6</sub> and an equimolar mixture of guest and host recorded in CD<sub>3</sub>CN (0.01 mol L<sup>-1</sup>) at 300 K are illustrated in Figure 2. The largest chemical shift change is observed for the signals associated with the cyclopentadienyl ring protons, which move by ca.  $\Delta \delta$  –1.5 ppm on complexation as a result of the shielding effects exerted upon them by the bipyridinium and biphenylene units. The signals associated with the  $\beta$ -bipyridinium protons also move significantly ( $\Delta \delta$  ca. –0.2 ppm), and their chemical shift changes were exploited to determine (Table 1) the as-

Table 1.Association Constants<sup>a</sup> and Derived FreeEnergies of Association for the 1:1 Adducts Formedbetween 1<sup>4+</sup> and 2, 3, 11, 12, 18, or 21 in Solution at 300 K

guest	$K_{\rm a}$ (L mol <sup>-1</sup> )	$-\Delta G^{\circ}$ (kcal mol <sup>-1</sup> )	solvent
2	$80^{b}$	2.6	CD <sub>3</sub> CN
3	1600 <sup>b</sup>	4.3	CD <sub>3</sub> CN
11	160	3.0	CD <sub>3</sub> CN
12	3900	4.9	CD <sub>3</sub> CN
	290	3.4	(CD <sub>3</sub> ) <sub>2</sub> NCDO
18	230	3.2	(CD <sub>3</sub> ) <sub>2</sub> NCDO
21	230	3.2	(CD <sub>3</sub> ) <sub>2</sub> NCDO

 $^a$  Determined by  $^1\mathrm{H}$  NMR spectroscopy using the dilution method.  $^b$  See ref 1.

sociation constants ( $K_a$ ) for 1:1 adducts formed between  $1.4PF_6$  and the ferrocene derivatives 11 and 12 using the dilution method.<sup>10</sup> As observed previously<sup>1</sup> for ferrocene (2), the  $K_a$  value measured for 11 in CD<sub>3</sub>CN is relatively low. However, introduction of polyether chains—as in the ferrocene derivatives 3 and 12—reinforces<sup>1</sup> the intraadduct noncovalent bonding interactions (presumably in the form of [C-H···O] hydrogen bonds between the

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Table 2. <sup>1</sup>H NMR Chemical Shift Changes ( $\Delta\delta$ ) Experienced by Protons in 1<sup>4+</sup> upon Adduct Formation<sup>a</sup> with the Ferrocene Derivatives 12, 18, and 21 in (CD<sub>3</sub>)<sub>2</sub>NCDO at 300 K

			$\Delta \delta$		
1:1 adduct	$H_{\alpha}{}^{b}$	$\mathbf{H}_{\beta}{}^{b}$	$\mathbf{H}_{\gamma}{}^{b}$	$\mathbf{H}_{\delta}{}^{b}$	${ m H}_{\epsilon}{}^{b}$
<b>[1:12]</b> <sup>4+</sup>	-0.10	-0.21	+0.02	+0.06	-0.04
[1:18] <sup>4+</sup>	-0.08	-0.15	+0.01	+0.04	-0.04
$[1:21]^{4+}$	-0.10	-0.18	+0.02	+0.05	-0.04
<sup>a</sup> [ <b>1</b> •4PF <sub>6</sub> ] =	= [ferrocene	e derivativ	e] = 0.01 n	nol $L^{-1}$ . <sup>b</sup> S	ee Figure

2.



**Figure 3.** <sup>1</sup>H NMR chemical shift changes ( $\Delta \delta$ ) of the  $\beta$ -bipyridinium protons of **1**<sup>4+</sup> upon 1:1 adduct formation with the ferrocene derivatives **12**, **18**, and **21** in (CD<sub>3</sub>)<sub>2</sub>NCDO at 300 K as a function of concentration.

 $\alpha$ -bipyridinium hydrogen atoms and the polyether oxygen atoms) with the tetracationic cyclophane  $\mathbf{1}^{4+}$  and the  $K_{a}$ values increase accordingly. The  $K_a$  value also obtained by the dilution method<sup>10</sup> using the same probe protons-for the 1:1 adduct formed between 1.4PF<sub>6</sub> and 12 drops by approximately 1 order of magnitude (Table 1) in (CD<sub>3</sub>)<sub>2</sub>-NCDO, the solvent that has to be used in the case of the ferrocene derivatives 18 and 21 containing substituted tetraarylmethane groups because of their low solubilities in CD<sub>3</sub>CN. Clearly, the high polarity of (CD<sub>3</sub>)<sub>2</sub>NCDO means that it more efficiently solvates the ferrocene derivatives, making them less susceptible to forming inclusion adducts with the tetracationic cyclophane  $1^{4+}$ . The chemical shift changes, experienced by the protons in  $\mathbf{1}^{4+}$  upon adduct formation with 1 equiv of the ferrocene derivatives 12, 18, and 21 in (CD<sub>3</sub>)<sub>2</sub>NCDO (0.01 mol  $L^{-1}$ ), are listed in Table 2. Figure 3 presents graphically the chemical shift changes for the  $\beta$ -bipyridinium protons of  $1^{4+}$  upon adduct formation (1:1 mixtures) with the ferrocene derivatives 12, 18, and 21 in (CD<sub>3</sub>)<sub>2</sub>NCDO at 300 K at various concentrations below 0.01 mol L<sup>-1</sup>. They are quite similar, and so no significant differences were observed in the  $K_a$  values (Table 1) of the 1:1 adducts formed between 1.4PF<sub>6</sub> and 12, 18, and 21, suggesting that the bulky stoppers do not affect appreciably the molecular recognition event; i.e., in common with the ferrocene derivatives 18 and 21, which can only exist in co-conformation A on 1:1 adduct formation with the tetracationic cyclophane  $1^{4+}$ , compound 12, which could exist in co-conformation B with 1<sup>4+</sup>, also exists only in co-conformation A. Finally, addition of  $1.4PF_6$  (10.8 equiv) to a very dilute solution (7.7  $\times$  10^{-4} mol L^{-1}) of **21** in CD\_3CN resulted in significant upfield shifts of the hydroquinone ring protons at 300 K. They "move" from  $\delta$  6.80 and 6.81 to  $\delta$  6.63 and 6.70 in the experiment just described. Chemical shift changes are also evident for the cyclopentadienyl and polyether

protons. However, specific assignments to these protons could not be made. At 224 K, the exchange between host and guest on the <sup>1</sup>H NMR time scale (400 MHz) was still fast, indicating the formation of a rather "loose" 1:1 adduct in which the ferrocene nucleus of 21 is bound within the cavity of 1<sup>4+</sup> in an A-type co-conformation that still permits the hydroquinone rings in the guest to interact with the outside surfaces of the bipyridinium rings of the host in a donor-acceptor fashion. The fact that the hydroquinone ring protons are shifted even further upfield to  $\delta$  6.43 and 6.57 in the 224 K spectrum would not be in conflict with this hypothesis. In summary, all the <sup>1</sup>H NMR spectroscopic evidence indicates that all the ferrocene derivatives we have investigated so far in solution form 1:1 adducts with the tetracationic cyclophane  $1^{4+}$  using co-conformations of the type Aand *never* of the type **B**.

**Absorption and Luminescence Properties.** We have investigated the absorption and luminescence properties of the cyclophane  $1^{4+}$ , the ferrocene derivative **12**, and their  $[1:12]^{4+}$  adduct in MeCN at room temperature.

The absorption spectrum of  $\mathbf{1}^{4+}$  in MeCN shows (Figure 4) a very intense band with  $\lambda_{max} = 260 \text{ nm} (\epsilon = 83\ 000 \text{ L} \text{mol}^{-1} \text{ cm}^{-1})$ , expected on the basis of the chromophoric units contained in the cyclophane, namely, biphenyl<sup>11</sup> and 4,4'-bipyridinium<sup>12</sup> groups, and a weak band with  $\lambda_{max} = 340 \text{ nm} (\epsilon = 3000 \text{ L} \text{mol}^{-1} \text{ cm}^{-1})$  that may arise from a charge-transfer interaction between the biphenyl and bipyridinium units.<sup>13</sup> The absorption spectrum of **12** (Figure 4) displays the two well-known bands of the ferrocene nucleus ( $\lambda_{max} = 323$  and 435 nm,  $\epsilon = 100$  and 115 L mol<sup>-1</sup> cm<sup>-1</sup>, respectively).<sup>14</sup> These bands have the same  $\lambda_{max}$  as those of unsubstituted ferrocene, but are about 20% more intense, as observed for alkyl-disubstituted ferrocenes.<sup>14</sup>



**Figure 4.** Absorption spectra in MeCN at 298 K of the tetracationic cyclophane  $1^{4+}$  and the ferrocene derivative **12**.

As for the unsubstituted ferrocene,<sup>15</sup> its derivative **12** does not show any luminescence. The biphenyl units incorporated in  $1^{4+}$  are potentially fluorescent,<sup>11</sup> but their emission is quenched in the cyclophane because of the presence of low energy charge-transfer levels.

<sup>(11)</sup> Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Compounds*, Academic Press: London, 1965.

<sup>(12)</sup> Anelli, P.-L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. J. Am. Chem. Soc. 1992, 114, 198–213.

<sup>(13)</sup> Ashton, P. R.; Baldoni, V.; Balzani, V.; Claessens, C. G.; Credi, A.; Hoffmann, H. D. A.; Raymo, F. M.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *Eur. J. Org. Chem.* **2000**, in press.

<sup>(14)</sup> Lever, A. B. P. *Inorganic Electronic Spectroscopy*, Elsevier: Amsterdam, 1984.

<sup>(15)</sup> Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic Press: London, 1970.



**Figure 5.** Absorption spectra in MeCN at 298 K. (a) Sum of the spectra of the separated components  $\mathbf{1}^{4+}$  (3.2 ×  $10^{-4}$  mol  $L^{-1}$ ) and **12** (3.2 ×  $10^{-3}$  mol  $L^{-1}$ ); (b) spectrum of the mixture of the two components [concentrations as in (a)]; (c) enlarged view (× 5) of the difference between curves (b) and (a).

Upon titration of a  $3.2 \times 10^{-4}$  mol L<sup>-1</sup> MeCN solution of  $1^{4+}$  with 12, we observed the appearance of an absorption tail at  $\lambda > 550$  nm, where none of the free components absorbs. After subtraction of the spectrum of 12 from the absorption spectrum of the mixture, a broad band with  $\lambda_{max} = 570$  nm was obtained (Figure 5); such a band can be assigned to a donor/acceptor interaction between the  $\pi$ -electron-deficient bipyridinium units of  $1^{4+}$  and the  $\pi$ -electron-rich cyclopentadienyl rings of 12. The titration curve obtained by monitoring the absorbance of the donor/acceptor band can be fitted according to the formation of a 1:1 adduct between  $1^{4+}$ and 12, with an absorption coefficient at 570 nm of 170  $\pm$  30 L mol<sup>-1</sup> cm<sup>-1</sup> and an association constant consistent with that observed by NMR spectroscopy.

The 1:1 adduct formation between  $1^{4+}$  and both ferrocene derivatives **18** and **21** was also evident from their absorption spectra. Thus, in the mixed solvent, MeCN–DMF (4:1), both **18** and **21** (each at concentrations of 1.6  $\times$  10<sup>-3</sup> mol L<sup>-1</sup>) gave rise to an absorption coefficient at 570 nm of 90 L mol<sup>-1</sup> cm<sup>-1</sup> when they were mixed together with an equimolar amount of  $1^{4+}$ .

**Electrochemical Properties.** We have investigated the electrochemical behavior of the cyclophane 1<sup>4+</sup>, the ferrocene derivative 12, and their [1:12]<sup>4+</sup> adduct by (i) cyclic voltammetry, (ii) differential pulse voltammetry, and (iii) bulk electrolysis in MeCN at room temperature.

Cyclophane  $1^{4+}$  shows two reversible two-electron reduction processes at -0.31 V and -0.72 V vs SCE (Figure 6) that can be ascribed to the simultaneous oneelectron reduction of the two equivalent bipyridinium units.<sup>16</sup> No oxidation process is observed. As expected, compound **12** exhibits (Figure 7) the reversible oneelectron oxidation process characteristic of ferrocene<sup>17</sup> and no reduction processes. It is interesting to note that the ferrocene unit of **12** is oxidized at a potential value (+0.41 V vs SCE) very similar to that of unsubstituted ferrocene, indicating that the presence of the polyether chains does not influence the electrochemical properties of the redox-active unit.

The electrochemical behavior of the adduct  $[1:12]^{4+}$  on oxidation and reduction was studied in the presence of an excess of  $1^{4+}$  and 12, to obtain more than 90% of the electroactive unit under investigation in the complexed



Figure 6. Cyclic voltammetric patterns at 298 K of MeCN solutions containing 3.0  $\times$   $10^{-4}$  mol  $L^{-1}$  of  $1^{4+}$  (full line), and  $3.0\times 10^{-4}\,mol\;L^{-1}$  of  $1^{4+}$  with  $3.0\times 10^{-3}\,mol\;L^{-1}$  of 12 (dashed line). Scan rate: 50 mV s<sup>-1</sup>. The reference wave of the  $[Ru(bpy)_3]^{2+/+}$  process ( $E_{1/2} = -1.32$  V vs SCE) is also shown. form. The adduct [1:12]<sup>4+</sup> shows a reversible monoelectronic oxidation process at +0.46 V vs SCE (Figure 7), that can be assigned to the ferrocene unit of its acyclic component. This process occurs (i) at a potential value 50 mV more positive than that of uncomplexed 12 and (ii) with a current intensity which is about 20% smaller. These results are consistent with the formation of an inclusion adduct between  $1^{4+}$  and 12 and can be accounted for by (i) the presence of a donor/acceptor interaction between the  $\pi$ -electron-deficient bipyridinium units of  $1^{4+}$  and the  $\pi$ -electron-rich cyclopentadienyl rings of 12 and (ii) the decrease of the diffusion coefficient of **12** when it is surrounded by the  $1^{4+}$  cyclophane.<sup>18</sup>



**Figure 7.** Cyclic voltammetry (top; scan rate: 50 mV s<sup>-1</sup>) and differential pulse voltammetry (bottom; scan rate: 20 mV s<sup>-1</sup>; pulse height: 75 mV) at 298 K of MeCN solutions containing: (a)  $3.0 \times 10^{-4}$  mol L<sup>-1</sup> of **12** (full line); (b)  $3.0 \times 10^{-4}$  mol L<sup>-1</sup> of **12** and  $3.0 \times 10^{-3}$  mol L<sup>-1</sup> of **14**<sup>+</sup> (dashed line); (c) same solution as in (b), after exhaustive electrolysis at +0.50 V vs SCE (dashed-dotted line). Subsequent exhaustive electrolysis at 0.0 V gives a voltammetric pattern identical to that observed for solution (b) (dashed line). The feature with  $E_{1/2} = +1.29$  V vs SCE corresponds to the [Ru(bpy)<sub>3</sub>]<sup>3+/2+</sup> reference process.

Since the  $[1:12]^{4+}$  adduct is stabilized by donor/acceptor interactions, it may be expected that oxidation of the

<sup>(16)</sup> Amabilino, D.; Ashton, P. R.; Balzani, V.; Boyd, S. E.; Credi, A.; Lee, J. Y.; Menzer, S.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 4295–4307.

<sup>(17)</sup> Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Non Aqueous Systems*; Dekker: New York, NY, 1970.



**Figure 8.** Schematic representation of the electrochemically induced decomplexation/recomplexation processes of the [1:12]<sup>4+</sup> complex.



**Figure 9.** Two possible co-conformations (**A** and **B**) for a 1:1 adduct formed between cyclobis(paraquat-4,4'-biphenylene) and a 1,1'-disubstituted ferrocene derivative and the covalent attachment of stoppers at the ends of the two substituents of the guest.

electron-donor component leads to disruption of the adduct.<sup>7i,k-m,19-21</sup> This possibility was investigated by bulk

electrolysis at +0.50 V vs SCE to oxidize the ferrocene unit of  $[1:12]^{4+}$ . After exhaustive electrolysis, the system showed again a reversible monoelectronic oxidation process at +0.46 V, but its current intensity was the same as that observed (Figure 7) for uncomplexed 12. Such a current increase indicates that the electroactive species that is diffusing to the electrode is now the free  $12^+$ cation, while the fact that the process maintains reversibility and occurs at the potential characteristic of the adduct suggests that the complexation/decomplexation equilibrium is fast on the time scale of the electrochemical scan. Subsequent exhaustive electrolysis at 0.0 V gives back adduct  $[1:12]^{4+}$ , as demonstrated (Figure 7) by the voltammetric patterns.<sup>22</sup>

On the reduction side, the two reversible two-electron processes of  $1^{4+}$  are maintained in the  $[1:12]^{4+}$  adduct (Figure 5). The first process is slightly shifted (30 mV) toward more negative potential values, while the second one occurs practically at the same potential as that observed for the free cyclophane. The negative shift of the potential corresponding to the first reduction process can be explained on the basis of the donor/acceptor interaction taking place in the  $[1:12]^{4+}$  adduct. The occurrence of the second reduction process at the same potential observed for the free cyclophane suggests that,

after monoelectronic reduction of both the bipyridinium units of  $1^{4+}$ , the adduct is disrupted and the successive reduction takes place on the free cyclophane. These results are in agreement with previous studies,<sup>71,19–21</sup> which show that the donor/acceptor interaction between bipyridinium-containing macrocycles and  $\pi$ -electron-rich guests is destroyed upon reduction of the bipyridinium units. This behavior is confirmed by voltammetric studies carried out on **12** in a solution containing an excess of  $1^{4+}$  upon electrolysis of the cyclophane at -0.40 V vs SCE, which leads to quantitative one-electron reduction of the bipyridinium units.

Interestingly, the presence of **12** does not cause a decrease in the current intensity corresponding to the reduction processes of  $1^{4+}$ . This observation is not in conflict with the formation of the  $[1:12]^{4+}$  adduct since it may be expected that the diffusion coefficient of  $1^{4+}$  is not significantly altered by the inclusion of **12**.

In summary—as schematized in Figure 8—the electrochemical results show that the  $[1:12]^{4+}$  adduct undergoes reversible decomplexation/recomplexation processes on a time scale faster than that of the electrochemical experiments.

#### Conclusions

1,1'-Disubstituted ferrocene derivatives template the formation of cyclobis(paraquat-4,4'-biphenylene) as a result of second-sphere coordination.<sup>3</sup> The yields observed in this template-directed synthesis rise up to 32% (cf. 2% in the absence of a template) when polyether chains are attached to the ferrocene nucleus. We believe that some of the polyether oxygen atoms of the template sustain [C-H-O] hydrogen-bonding interactions with the  $\alpha$ -bipyridinium hydrogen atoms of the tetracationic cyclophane. These hydrogen bonds supplement the  $[\pi \cdot \pi]$ stacking interactions between the cyclopentadienyl rings and the bipyridinium units. In the second-sphere adducts formed between cyclobis(paraguat-4,4'-biphenylene) and 1,1'-disubstituted ferrocene derivatives, the two substituents of the guest protrude outward (A in Figure 9) from the cavity of the host in the same direction. Pseudorotaxane-like adducts (B in Figure 9), in which the two substituents of the guest protrude outward from opposite sides of the host, are not formed. Thus, complexation, followed by the covalent attachment of bulky groups to the termini of these substituents, cannot link mechanically the guest to the host; i.e., no rotaxanes can be formed. Similarly, when the acyclic precursors of cyclobis-(paraquat-4,4'-biphenylene) are reacted in the presence of a preformed dumbbell-shaped compound incorporating

(20) Asakawa, M.; Ashton, P. R.; Balzani, V.; Credi, A.; Mattersteig,
 G.; Matthews, O. A.; Montalti, M.; Spencer, N.; Stoddart, J. F.; Venturi,
 M. *Chem. Eur. J.* **1997**, *3*, 1992–1996.

a 1,1'-disubstituted ferrocene nucleus, extremely small quantities (<1%) of the expected [2]rotaxane are detected. The association constant for the 1:1 adduct [1:12]<sup>4+</sup> is affected dramatically by the nature of the solvent. Changing from CD<sub>3</sub>CN to (CD<sub>3</sub>)<sub>2</sub>NCDO reduces the association constant from 3900 to 290 L mol<sup>-1</sup>. This adduct has been investigated by absorption and emission electronic spectroscopy and electochemistry. It shows a charge-transfer absorption band in the visible spectral region and no luminescence. An electrochemical study has demonstrated that oxidation of the ferrocene-based unit of the guest and first reduction of the bipyridinium moieties of the host occur at more positive and, respectively, more negative potentials than in the free components. Detailed analysis of the electrochemical results shows that such oxidation and reduction processes cause disruption of the adduct and that recomplexation takes place upon back reduction and oxidation of the oxidized ferrocene and reduced bipyridinium units, respectively. The complexation/decomplexation process is reversible and fast on the time scale of the electrochemical scan.

#### **Experimental Section**

**General Methods.** Solvents were dried according to literature procedures.<sup>23</sup> The compounds **3**,<sup>1</sup> **4**,<sup>24</sup> **13**·2PF<sub>6</sub>,<sup>25</sup> **14**,<sup>25</sup> and **19**<sup>12</sup> were prepared as described previously in the literature. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60. Column chromatography was performed on silica gel 60 (230–400 mesh). Melting points are uncorrected. Liquid secondary ion mass spectrometry (LSIMS) and fast-atom bombardment mass spectrometry (FABMS) were performed using a 3-nitrobenzyl alcohol or 2-nitrophenyloctyl ether matrix. <sup>1</sup>H NMR spectra were recorded either at 300 or 400 MHz, while <sup>13</sup>C NMR spectra were recorded at 75 MHz.

**Association Constants.** Equimolar  $CD_3CN$  or  $(CD_3)_2$ -NCDO solutions of  $1.4PF_6$  and **11**, **12**, **18**, or **21** were diluted from ca.  $10^{-2}$  to ca.  $10^{-4}$  mol L<sup>-1</sup> in 10–15 consecutive steps. The resulting solutions were analyzed by <sup>1</sup>H NMR spectroscopy at 300 K. By nonlinear curve-fitting of the plot of the chemical shift change associated with the resonances of the  $\beta$ -bipyridinium protons against the concentration, the association constants ( $K_a$ ) of the adducts were determined<sup>10</sup> employing the following relationship

$$-\Delta \delta_{\beta} = (-\Delta \delta_{\text{sat}}/c) [2K_{\text{a}}c + 1 - [(2K_{\text{a}}c + 1)^2 - 4K_{\text{a}}^2 c^2]^{0.5}]/2K_{\text{a}}$$

where  $\Delta \delta$  denotes the chemical shift difference of the  $\beta$ -bipyridinium protons upon complexation at a concentration *c* of each of the two components,  $\mathbf{1}^{4+}$  and the ferrocene derivative, and  $\Delta \delta_{sat}$  is the chemical shift difference at saturation.

**Absorption and Luminescence Measurements.** Electronic absorption and luminescence spectra were recorded in MeCN solutions at room temperature.

**Electrochemical Measurements.** Electrochemical experiments were carried out in argon-purged MeCN solutions at room temperature with a multipurpose instrument interfaced to a personal computer. In the experiments where cyclic

<sup>(18)</sup> The decrease in current intensity associated with the oxidation of **12** in the adduct with respect to the free compound is that expected according to the Stokes–Einstein expression of the diffusion coefficient  $(D \propto M^{-1/3})$ .

<sup>(19)</sup> Ashton, P. R.; Ballardini, R.; Balzani, V.; Boyd, S. E.; Credi, A.; Gandolfi, M. T.; Gómez-López, M.; Iqbal, S.; Philp, D.; Preece, J. A.; Prodi, L.; Ricketts, H. G.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1997**, *3*, 152–170.

<sup>(21)</sup> Ashton, P. R.; Balzani, V.; Becher, J.; Credi, A.; Fyfe, M. C. T.; Mattersteig, G.; Menzer, S.; Nielsen, M. B.; Raymo, F. M.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 3951– 3957.

<sup>(22)</sup> The one-electron oxidized form of ferrocene, either produced by electrolysis or chemical oxidation using  $Fe(ClO_4)_3$ , undergoes some degradation in MeCN solution on the time scale of minutes. The same behavior is exhibited by compound **12**.

<sup>(23)</sup> Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Practical Organic Chemistry*, Longman: New York, NY, 1989.

<sup>(24)</sup> Ashton, P. R.; Ballardini, R.; Balzani, V.; Belohradsky, M.; Gandolfi, M. T.; Philp, D.; Prodi, L.; Raymo, F. M.; Reddington, M. V.; Spencer, N.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1996**, *118*, 4931–4951.

<sup>(25)</sup> Amabilino, D. B.; Ashton, P. R.; Brown, C. L.; Córdova, E.; Godínez, L. A.; Goodnow, T. T.; Kaifer, A. E.; Newton, S. P.; Pietraszkiewicz, M.; Philp, D.; Raymo, F. M.; Reder, A. S.; T. Rutland, M.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 1271–1293.

voltammetry (CV) and differential pulse voltammetry (DPV) techniques were employed, the working electrode was a glassy carbon electrode (0.08 cm<sup>2</sup>, Amel); its surface was routinely polished with a 0.05  $\mu$ m alumina–water slurry on a felt surface immediately prior to use. The electrolyses were carried out using a Pt grid as a working electrode. In all cases, the counter electrode was a Pt wire and the reference electrode was a saturated calomel electrode (SCE) separated with a fine glass frit. The concentration of the examined compounds was 3.0 imes10<sup>-4</sup> mol L<sup>-1</sup>; 0.05 M tetraethylammonium hexafluorophosphate was added as the supporting electrolyte. Cyclic voltammograms were obtained at sweep rates of 20, 50, 200, 500, and 1000 mV  $s^{-1};\, DPV$  experiments were performed with a scan rate of 20 mV s<sup>-1</sup>, a pulse height of 75 mV, and a duration of 40 ms. All processes observed were reversible, according to the criteria of (i) separation of 60 mV between cathodic and anodic peaks, (ii) close-to-unity ratio of the intensities of the cathodic and anodic currents, and (iii) constancy of the peak potential on changing sweep rate in the cyclic voltammograms. The same halfwave potential values have been obtained from the DPV peaks and from an average of the cathodic and anodic cyclic voltammetric peak. Both CV and DPV techniques have been used to estimate the current intensity associated with each redox process.  $[Ru(bpy)_3]^{2+}$  was employed  $^{26}$  as an internal standard for both potential values and current intensities. The experimental error on the potential values was estimated to be  $\pm 10$  mV.

**Cyclobis(paraquat-4,4'-biphenylene)**<sup>1</sup> (1•4PF<sub>6</sub>). A solution of **12** (0.1436 g, 0.32 mmol), **13**·2PF<sub>6</sub> (0.1333 g, 0.17 mmol), and **14** (0.0581 g, 0.17 mmol) in dry MeCN (20 mL) was stirred for 14 d at ambient temperature. The solvent was distilled off under reduced pressure, washed with CHCl<sub>3</sub>, and purified by column chromatography [SiO<sub>2</sub>: MeOH/2 M NH<sub>4</sub>Cl/MeNO<sub>2</sub> (7: 2:1)]. The resulting solid was dissolved in H<sub>2</sub>O, and after the addition of NH<sub>4</sub>PF<sub>6</sub>, **1**·4PF<sub>6</sub> (0.0673 g, 32%) precipitated out as white solid: mp >250 °C; FABMS *m*/*z* 963 [M + H – 2PF<sub>6</sub>]<sup>+</sup>, 818 [M – 3PF<sub>6</sub>]<sup>+</sup>; <sup>1</sup>H NMR (CD<sub>3</sub>CN)  $\delta$  8.92 (8H, d, *J* = 7 Hz), 7.65 (8H, d, *J* = 7 Hz), 7.53 (8H, d, *J* = 7 Hz), 5.80 (8H, s).

Ethyl 2-[4-[Tris(4-tert-butylphenyl)methyl]phenoxy]acetate (6). A mixture of 4 (8.61 g, 0.02 mol) and K<sub>2</sub>CO<sub>3</sub> (55.07 g, 0.40 mol) in dry MeCN (1.6 L) was heated under reflux and an atmosphere of N<sub>2</sub>, and then 5 (6.0 mL, 0.05 mol) was added. Heating under reflux was mantained for a further 20 h, and after being cooled to room temperature, the mixture was filtered and the solvent was distilled off under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed with  $H_2O$ , and dried (MgSO<sub>4</sub>) before the solvent was distilled off under reduced pressure to afford 6 (10.03 g, 100%) as a white solid: mp 223 °C; LSIMS m/z 590 [M]<sup>+</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ 7.23 (6H, d, J = 9 Hz), 7.13-7.04 (8H, m), 6.77 (2H, d, J = 9 Hz), 4.59 (2H, s), 4.27 (2H, q, *J* = 7 Hz), 1.32–1.28 (30H, m); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 169.1, 155.8, 148.4, 144.0, 140.7, 132.3, 130.7, 124.1, 111.3, 65.5, 63.1, 61.3, 34.3, 31.4, 14.2. Anal. Calcd for C41H50O3: C, 83.35; H, 8.53. Found: C, 83.40; H, 8.45

**2-[4-[Tris(4-***tert***-butylphenyl)methyl]phenoxy]acetic Acid (7).** A mixture of **6** (10.03 g, 0.02 mol) and 0.6 M aqueous NaOH (1 L) in EtOH (1.5 L) was heated under reflux for 5 h. After being cooled to room temperature, the mixture was concentrated under reduced pressure, diluted with 1.6 M aqueous HCl, and stirred for 15 min at ambient temperature. Filtration of the mixture afforded a white solid that was washed with H<sub>2</sub>O and dried to give **7** (9.41 g, 98%): mp 270 °C dec; LSIMS *m*/*z* 563 [M + H]<sup>+</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.22 (6H, d, *J* = 9 Hz), 7.13–7.02 (8H, m), 6.76 (2H, d, *J* = 9 Hz), 4.62 (2H, s), 1.29 (27H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  173.1, 155.2, 148.4, 143.9, 141.3, 132.5, 130.7, 124.1, 113.3, 65.3, 63.1, 34.3, 31.4. Anal. Calcd for C<sub>39</sub>H<sub>46</sub>O<sub>3</sub>: C, 83.24; H, 8.24. Found: C, 83.20; H, 8.29.

1,1'-Bis[2-[2-[2-[2-[4-[tris(4-*tert*-butylphenyl)methyl]phenoxy]acetoxy]ethoxy]ethoxy]ethoxy]ferrocene (9). A solution of 7 (1.90 g, 3.38 mmol), (COCl)<sub>2</sub> (1.5 mL, 17.19 mmol), and DMF (5 drops) in dry CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was heated for 17 h under reflux in an atmosphere of N2. After being cooled to ambient temperature, the solvent was distilled off under reduced pressure to give a yellowish solid. A solution of the solid residue, 3 (423 mg, 0.88 mmol), and 2,6-dimethylpyridine (245  $\mu$ L, 2.1 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was heated for 4 h under reflux in an atmosphere of N<sub>2</sub>. After being cooled to room temperature, the solution was diluted with CH<sub>2</sub>Cl<sub>2</sub>, washed with H<sub>2</sub>O, and dried (MgSO<sub>4</sub>) before the solvent was distilled off under reduced pressure. The resulting solid was purified by column chromatography (SiO<sub>2</sub>: CHCl<sub>3</sub>) to give 9 (740 mg, 54%) as a yellow solid: mp 84 °C; LSIMS *m*/*z* 1571  $[M]^+$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.22 (12H, d, J = 9 Hz), 7.12–7.03 (16H, m), 6.75 (4H, d, J = 9 Hz), 4.61 (4H, s), 4.40–4.33 (4H, m), 4.15-4.04 (4H, m), 3.94-3.91 (4H, m), 3.88-3.80 (4H, m), 3.76-3.69 (8H, m), 3.68-3.61 (8H, m), 1.30 (54H, s); <sup>13</sup>C NMR  $[(CD_3)_2CO] \delta$  169.3, 156.9, 149.1, 145.1, 140.9, 132.7, 131.4, 125.0, 114.1, 71.3, 71.2, 70.7, 70.6, 69.5, 65.6, 64.7, 63.8, 63.0, 56.6, 34.7, 31.6. Anal. Calcd for C100H122FeO12: C, 76.41; H, 7.82. Found: C, 76.21; H 7.90.

1,1'-Bis[[2-(2-methoxyethoxy)ethoxy]methylene]ferrocene (12). A solution of 10 (1.60 g, 5.80 mmol) in dry THF (50 mL) was added to a mixture of 11 (0.15 g, 0.59 mmol) and NaH (95% dry, 0.035 g, 1.39 mmol) in dry  ${\rm \widetilde{T}HF}$  (50 mL). The mixture was heated for 12 h under reflux in an atmosphere of Ar. Another portion of NaH (95% dry, 0.035 g, 1.39 mmol) was added to the mixture, and heating under reflux was mantained for a further 10 h. After being cooled to room temperature, H<sub>2</sub>O was added, and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were washed with H<sub>2</sub>O, dried (MgSO<sub>4</sub>), and concentrated under reduced pressure. Purification of the residue by column chromatography [SiO<sub>2</sub>: CH<sub>2</sub>Cl<sub>2</sub>/Me<sub>2</sub>CO (3:2)] afforded 12 (0.205 g, 77%) as an orange oil: FABMS  $m/z 450 \text{ [M]}^+$ ; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.28 (4H, br s), 4.19 (4H, br s), 4.11 (4H, br s), 3.63-3.52 (16H, m), 3.37 (6H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  71.9, 70.6, 70.5, 70.0, 69.2, 69.0, 59.0. Anal. Calcd for C<sub>22</sub>H<sub>34</sub>FeO<sub>6</sub>•0.25H<sub>2</sub>O: C, 58.09; H, 7.64. Found: C, 57.98; H, 7.51.

2-[2-[2-[2-[4-[Tris(4-tert-butylphenyl)methyl]phenoxy]ethoxy]ethoxy]ethoxy]ethanol (16). A mixture of 4 (4.75 g, 8.8 mmol), 15 (6.10 g, 17.5 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.21 g, 8.8 mmol) in dry MeCN (150 mL) was heated for 12 h under reflux in an atmosphere of Ar. After being cooled to ambient temperature, the solvent was distilled off under reduced pressure. The residue was dissolved in CHCl<sub>3</sub>, washed with  $\hat{H}_2O$ , and dried (MgSO<sub>4</sub>) before the solvent was removed under reduced pressure. The residue was purified by column chromatography [SiO<sub>2</sub>: (i) CH<sub>2</sub>Cl<sub>2</sub>/MeCO<sub>2</sub>Et (1:1), (ii) gradual increase of MeCO<sub>2</sub>Et in the eluant] to give 16 (3.94 g, 66%) as a white solid: mp 175–176.5 °C; FABMS m/z = 680 [M] +; HRFABMS m/z calcd for [M] + (C<sub>45</sub>H<sub>60</sub>O<sub>5</sub>) = 680.4441, m/z found = 680.4451; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.23 (6H, d, J = 9 Hz), 7.08 (8H, d, J = 9 Hz), 6.78 (2H, d, J = 9 Hz), 4.11 (2H, t, J = 5 Hz), 3.84 (2H, t, J = 5 Hz), 3.75-3.66 (10H, m), 3.60 (2H, t, J = 5 Hz), 2.29 (1H, s), 1.30 (27H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 156.5, 148.3, 144.1, 139.8, 132.2, 130.7, 124.0, 113.0, 72.5, 70.7, 70.6, 70.6, 70.3, 69.8, 67.2, 63.0, 61.7, 34.3, 31.4. Anal. calcd for C45H60O5.0.25H2O: C, 78.85; H, 8.90. Found: C, 78.71; H, 8.82.

2-[2-[2-[2-[4-[Tris(4-*tert*-butylphenyl)methyl]phenoxy]ethoxy]ethoxy]ethoxy]ethyl 4-Methylphenylsulfonate (17). A solution of tosyl chloride (2.70 g, 14.2 mmol) in CH<sub>2</sub>-Cl<sub>2</sub> (20 mL) was added to an ice-cooled solution of 16 (3.797 g, 5.58 mmol), DMAP (0.020 g, 0.16 mmol), and Et<sub>3</sub>N (4 mL) in CH<sub>2</sub>Cl<sub>2</sub> over a period of 30 min. The mixture was stirred for 12 h at ambient temperature, poured into 5 M aqueous HCl, and then diluted with H<sub>2</sub>O. The organic phase was washed with 1 M aqueous HCl and H<sub>2</sub>O before it was dried (MgSO<sub>4</sub>). The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO<sub>2</sub>: (i) CH<sub>2</sub>-Cl<sub>2</sub>, (ii) MeCO<sub>2</sub>Et/CH<sub>2</sub>Cl<sub>2</sub> with a gradual increase of MeCO<sub>2</sub>-Et in the eluant] to afford 17 (3.755 g, 81%) as a white solid: mp 168–168.5 °C; FABMS *m*/*z* 835 [M + H]<sup>+</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.79 (2H, d, *J* = 8 Hz), 7.32 (2H, d, *J* = 8 Hz), 7.23 (6H, d,

<sup>(26)</sup> Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277.

J = 9 Hz), 7.07 (8H, d, J = 9 Hz), 6.76 (2H, d, J = 9 Hz), 4.15 (2H, t, J = 5 Hz), 4.09 (2H, t, J = 5 Hz), 3.83 (2H, t, J = 5 Hz), 3.71–3.62 (6H, m), 3.59 (4H, s), 2.42 (3H, s), 1.30 (27H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  156.5, 148.3, 144.7, 144.1, 139.7, 133.0, 132.2, 130.7, 129.8, 128.0, 124.0, 113.0, 70.8, 70.7, 70.6, 69.8, 69.2, 68.7, 67.2, 63.0, 34.3, 31.4, 21.6. Anal. Calcd for C<sub>52</sub>H<sub>66</sub>O<sub>7</sub>S: C, 74.79; H, 7.97. Found: C, 74.54; H, 7.91.

1,1'-Bis[[2-[2-[2-[2-[4-[tris(4-tert-butylphenyl)methyl]phenoxy]ethoxy]ethoxy]ethoxy]ethoxy]methylene]ferrocene (18). A mixture of 11 (0.191 g, 0.78 mmol), 17 (3.569 g, 4.27 mmol), and NaH (95% dry, 0.046 g, 1.82 mmol) in dry THF (50 mL) was heated for 12 h under reflux in an atmosphere of Ar. Another portion of NaH (95% dry, 0.046 g, 1.82 mmol) was added, and the mixture was heated under reflux for a further 10 h. After the mixture was cooled to ambient temperature, H<sub>2</sub>O was added, and the mixture was washed with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were washed with H<sub>2</sub>O and dried (MgSO<sub>4</sub>). The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO2: CH2Cl2/Me2CO (7:1)] to afford 18 (0.730 g, 60%) as a yellow solid: mp 164-166 °C; FABMS m/z 1571 [M + H]<sup>+</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.23 (12H, d, J = 9Hz), 7.08 (16H, d, J = 9 Hz), 6.77 (4H, d, J = 9 Hz), 4.27-4.11 (12H, br m), 4.09 (4H, t, J = 5 Hz), 3.83 (4H, t, J = 5 Hz), 3.72-3.55 (24H, m), 1.30 (54H, s). Anal. Calcd for C102H130-FeO10: C, 77.93; H, 8.34. Found: C, 77.87; H, 8.30.

2-[2-[2-[2-[2-[2-[2-[2-[2-[4-[Tris(4-tert-butylphenyl)methyl]phenoxy]ethoxy]ethoxy]ethoxy]ethoxy]phenoxy]ethoxy]ethoxy]ethoxy]ethyl 4-Methylphenylsulfonate (20). A solution of 4 (0.495 g, 0.91 mmol), 19 (2.810 g, 3.65 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.13 g, 0.94 mmol) in dry MeCN (100 mL) was heated for 12 h under reflux in an atmosphere of Ar. After the solution was cooled to ambient temperature, the solvent was distilled off under reduced pressure. The solid residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the solution was washed with H<sub>2</sub>O and dried (MgSO<sub>4</sub>). The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography [SiO<sub>2</sub>: CH<sub>2</sub>Cl<sub>2</sub>/MeCO<sub>2</sub>Et (5:1)] to afford **20** (0.615 g, 61%) as a colorless oil: FABMS m/z 1103 [M + H]+; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.79 (2H, d, J = 8 Hz), 7.33 (2H, d, J = 8 Hz), 7.22 (6H, d, J = 9 Hz), 7.07 (8H, d, J = 9 Hz), 6.82 (4H, s), 6.77 (2H, d, J = 9 Hz), 4.15-4.06 (8H, m), 3.85-3.59 (24H, m), 2.43 (3H, s), 1.30 (27H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 156.5, 153.0, 153.0, 148.2, 144.7, 144.1, 139.7, 133.0, 132.2, 130.7, 129.8, 127.9, 124.0, 115.5, 113.0, 70.8, 70.7, 70.7, 70.6, 70.5, 69.8, 69.7, 69.2, 68.8, 68.6, 68.0, 67.2, 63.0, 34.2, 31.3, 21.6. Anal. calcd for C<sub>66</sub>H<sub>86</sub>O<sub>12</sub>S: C, 71.84; H, 7.86. Found: C, 71.80; H, 7.95.

CH<sub>2</sub>Cl<sub>2</sub>/Me<sub>2</sub>CO (10:1)] to afford **21** (0.079 g, 37%) as a yellow solid: mp 139.5–140.5 °C; FABMS m/z 2108 [M]<sup>+</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.23 (12H, d, J = 9 Hz), 7.07 (16H, d, J = 9 Hz), 6.82 (8H, s), 6.77 (4H, d, J = 9 Hz), 4.29 (4H, br s), 4.17 (4H, br s), 4.11–4.08 (8H, m), 4.06 (8H, t, J = 5 Hz), 3.85–3.47 (52H, m), 1.30 (54H, s). Anal. Calcd for C<sub>130</sub>H<sub>170</sub>FeO<sub>20</sub>: C, 74.05; H, 8.13. Found: C, 73.98; H, 8.19.

1,4-Bis[2-[2-[2-[2-[2-[2-[2-[2-[4-[tris(4-tert-butylphenyl)methyl]phenoxy]ethoxy]ethoxy]ethoxy]ethoxy]benzene (23). A solution of 17 (1.30 g, 1.56 mmol), 22 (0.045 g, 0.41 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.18 g, 1.30 mmol) in dry MeCN (50 mL) was heated for 2 d under reflux in an atmosphere of Ar. After the solution was cooled to ambient temperature, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, washed with H<sub>2</sub>O, and dried (MgSO<sub>4</sub>). The solvent was removed under reduced pressure, and the residue was purified by column chromatography [SiO<sub>2</sub>: CH<sub>2</sub>Cl<sub>2</sub>/MeCO<sub>2</sub>Et (5:1)] to afford **23** (0.406 g, 69%) as a white solid: mp 166–167 °C; FABMS *m*/*z* 1436 [M + 2H]<sup>+</sup>; <sup>1</sup>H NMR  $(CDCl_3)$   $\delta$  7.22 (12H, d, J = 9 Hz), 7.07 (16H, d, J = 9 Hz), 6.81 (4H, s), 6.77 (4H, d, J = 9 Hz), 4.09 (4H, t, J = 5 Hz), 4.05 (4H, t, J = 5 Hz), 3.84–3.67 (24H, m), 1.29 (54H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 156.6, 153.1, 148.3, 144.1, 139.7, 132.2, 130.7, 124.0, 115.5, 113.1, 70.8, 70.7, 69.8, 69.8, 68.0, 67.2, 63.0, 34.3, 31.4. Anal. Calcd for C<sub>96</sub>H<sub>122</sub>O<sub>10</sub>: C, 80.30; H, 8.56. Found: C, 80.01; H, 8.41.

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