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Spectroscopic and Electrochemical Properties of Catenanes Containing the 2,7-Diazapyrenium Unit

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The spectroscopic and electrochemical properties of two cyclophanes containing one and, respectively, two 2,7-diazapyrenium electron-acceptor units, and of their [2]catenanes with macrocycles containing two dioxybenzene or dioxynaphthalene electron-donor units have been investigated. The absorption spectra of the catenanes show weak and broad bands in the visible region, assigned to charge-transfer (CT) interactions. The very strong and structured fluorescence (298 K) and the structured fluorescence and phosphorescence (77 K) of the diazapyrenium unit are maintained in the two cyclophanes, but they are no longer present in the [2]catenanes, presumably because of a quenching process caused by the lower energy CT excited states. Each diazapyrenium unit undergoes two distinct reduction processes – only the first one of which is fully reversible – that are hardly affected at all when the diazapyrenium units are incorporated in a cyclophane. In the [2]catenanes, the CT interaction displaces the reduction processes of the diazapyrenium units toward more negative potentials. The results obtained for the diazapyrenium and previously investigated 4,4′-bipyridinium salts, selected cyclophane derivatives, and some [2]catenanes obtained by interlocking the cyclophanes with macrocycles containing two dioxyaromatic electron-donor units are compared and discussed.

Keywords: Catenanes; Photochemistry; Electrochemistry; Charge-transfer

INTRODUCTION

In the last few years, the cyclobis(paraquat-*p*-phenylene) cyclophane 1^{4+} (Fig. 1) has been extensively used to construct rotaxanes and catenanes in conjunction with acyclic and cyclic aromatic polyethers [1–3]. The cyclophane contains two equivalent 4,4′-bipyridinium units, both of which exhibit electron-acceptor properties and, as a result, can undergo two distinct, reversible one-electron reduction processes [2–4]. In order to extend our studies in this field, we subsequently synthesized larger versions of cyclophanes based on the bipyridinium unit

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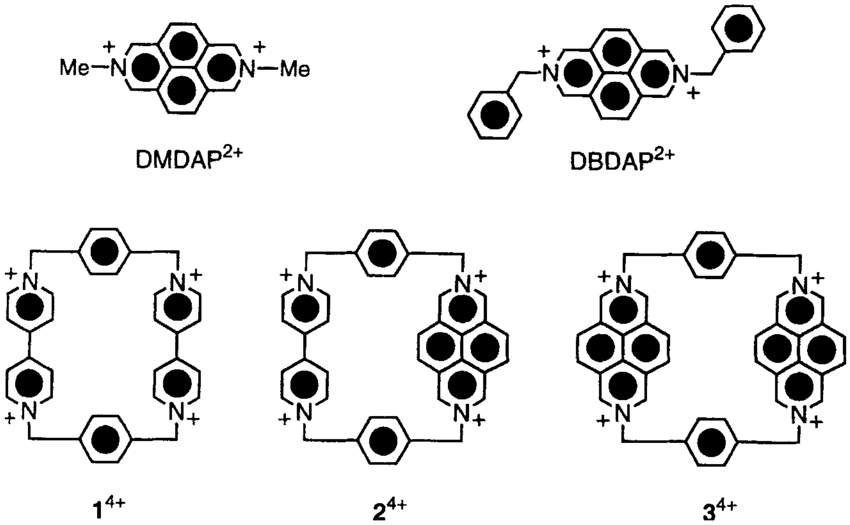

FIGURE 1 Structural formulas of the examined tetracationic cyclophanes and model compounds for the DAP^{2+} unit.

[5], as well as cyclophanes based on electron-acceptor units capable of exhibiting photochemical or photophysical properties [3]. The presence of a luminescence signal in the donor or acceptor units involved in pseudorotaxane, rotaxane or catenane structures turns out to be a useful probe to reveal the occurrence of CT interactions, as well as to monitor structural changes induced by external stimuli. In this regard, the commonly used bipyridinium unit is silent [2,3], whereas the 2,7-diazapyrenium (DAP^{2+}) unit exhibits strong fluorescence in fluid solution at room temperature, [6,7] and fluorescence and phosphorescence in rigid matrix at 77 K. We have now studied the photophysical and electrochemical behavior of (*i*) the cyclophane **2**$^{4+}$, which contains a bipyridinium and a diazapyrenium unit, of (*ii*) the symmetric bis-diazapyrenium cyclophane **3**$^{4+}$ (Fig. 1), and of (*iii*) their [2]catenanes with 1,4-dibenzo[34]-crown-10 (**B**) and 1,5-dinaphtho[38]crown-10 (**N**) – namely, **2B**$^{4+}$, **2N**$^{4+}$, **3B**$^{4+}$, and **3N**$^{4+}$, as illustrated in Figure 2. The results obtained are discussed together with those previously reported for cyclophane **1**$^{4+}$ and its **1B**$^{4+}$ and **1N**$^{4+}$ catenanes (Fig. 2).

RESULTS AND DISCUSSION

Cyclophanes Containing the Diazapyrenium Unit

Cyclophanes **2**$^{4+}$ and **3**$^{4+}$ contain the DAP^{2+} unit which is large, flat and very electron poor [8]. This unit, which has also been employed as a guest in some very interesting pseudorotaxanes [6,7], is appealing not only for its excellent ability to interact with both π and σ electron-donating species, but also because of its interesting spectroscopic and electrochemical properties, which – as we will see below – are substantially maintained in the cyclophanes **2**$^{4+}$ and **3**$^{4+}$.

Absorption and Luminescence Properties

The reference compounds for the DAP^{2+} unit contained in cyclophanes **2**$^{4+}$ and **3**$^{4+}$ are the 2,7-dimethyl- (DMDAP^{2+}) and 2,7-dibenzyl- (DBDAP^{2+}) diazapyrenium dications (Fig. 1) [6,7]. The absorption spectrum of DBDAP^{2+} shows two intense and structured bands which can be assigned to transitions to the first and

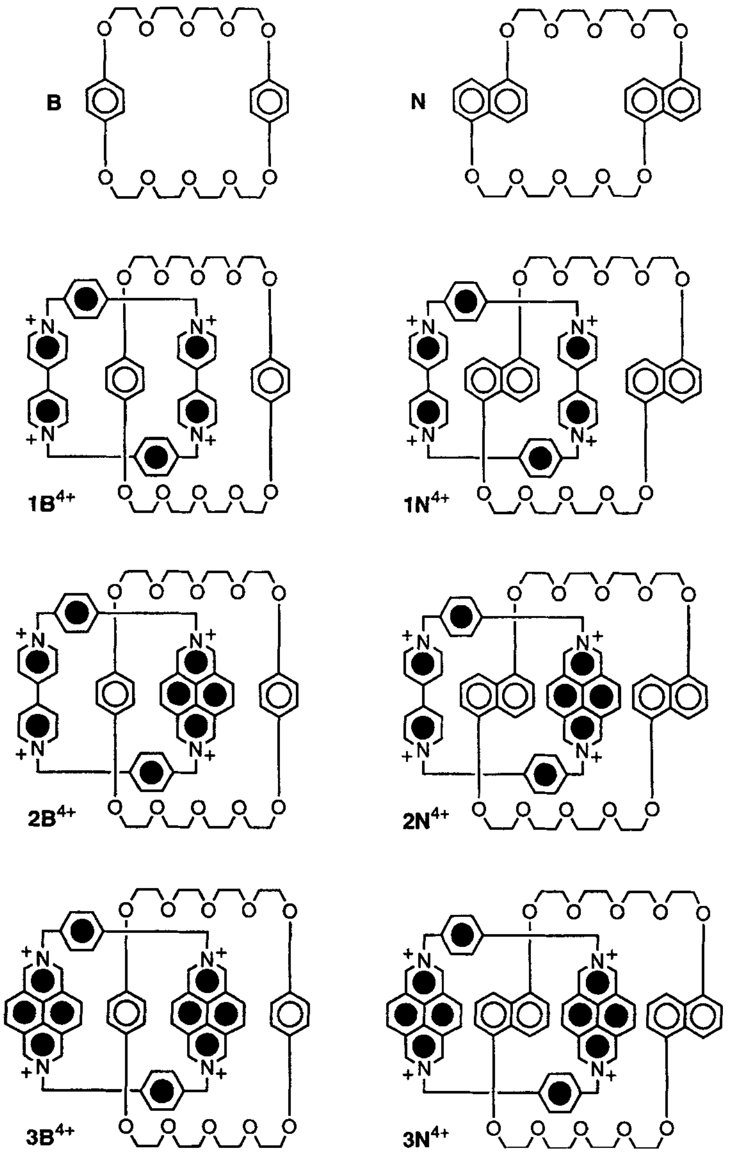

FIGURE 2 Structural formulas of the crown ether components and of their catenanes with the tetracationic cyclophanes.

second $^1\pi\pi^*$ excited state, respectively (Tab. I, Fig. 3). The absorption spectrum of DMDAP^{2+} is identical to that of DBDAP^{2+}, except for a slight blue shift of both bands.

The luminescence behavior of the DAP^{2+} unit is interesting. Both DMDAP^{2+} and DBDAP^{2+} display a very strong and structured fluorescence band; at 77 K, besides fluorescence, a structured phosphorescence band can also be seen (Tab. I, Fig. 3).

The absorption spectra of the cyclophanes 2^{4+} and 3^{4+} (Tab. I) show bands characteristic of their chromophoric groups, namely the DAP^{2+} and 4,4'-bipyridinium units, but they are different from the sum of the spectra of the model compounds of the component units. The strong

TABLE I Absorption and luminescence data

Compound	Absorption, 298 K[a] λ_{max} (nm)	Absorption, 298 K[a] ε ($M^{-1}cm^{-1}$)	Fluorescence, 298 K[a, b] λ_{max} (nm)	Fluorescence, 298 K[a, b] I_{rel}[d]	Fluorescence, 77 K[b, c] λ_{max} (nm)	Phosphorescence, 77 K[b, c] λ_{max} (nm)
$DMDAP^{2+}$	418[e]	15000	423[f]	100	424[f]	586[f]
$DBDAP^{2+}$	421[e]	12500	427[f]	47	427[f]	580[f]
B	290	5200	325	13	317	408
N	295	17600	330[f]	43	327[f]	480[f]
$\mathbf{2}^{4+}$	424[e]	14000	435[f]	57	427[f]	576[f]
$\mathbf{3}^{4+}$	423[e]	19000	434[f]	57	431[f]	575[f]
$\mathbf{1B}^{4+}$[g]	478[h]	700	–	–	–	–
$\mathbf{1N}^{4+}$[g]	529[h]	1100	–	–	–	–
$\mathbf{2B}^{4+}$	500[h, i]	900	–	–	–	–
$\mathbf{2N}^{4+}$	510[h]	2100	–	–	–	–
$\mathbf{3B}^{4+}$	510[h, i]	1100	–	–	–	–
$\mathbf{3N}^{4+}$	515[h]	2000	–	–	–	–

[a] MeCN solution.
[b] Excitation was performed in the lowest energy absorption band.
[c] Butyronitrile rigid matrix.
[d] Relative emission intensity; the fluorescence intensity of $DMDAP^{2+}$ is taken as 100.
[e] Lowest energy feature of a structured band.
[f] Highest energy feature of a structured band.
[g] Data from Ref. [3].
[h] Lowest energy (CT) band.
[i] Red-side shoulder of a more intense band.

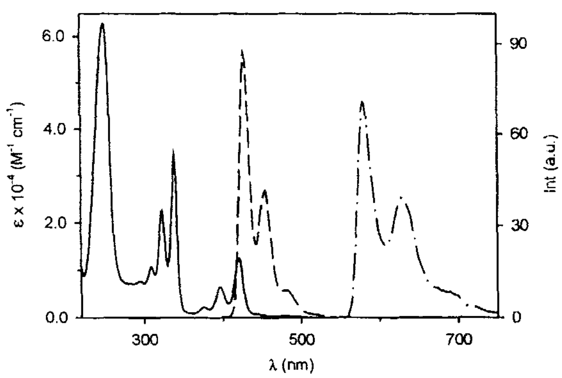

FIGURE 3 Absorption (MeCN, 298 K; solid line), fluorescence (MeCN solution, 298 K, $\lambda_{ex} = 340$ nm; dashed line), and phosphorescence (butyronitrile rigid matrix, 77 K, $\lambda_{ex} = 340$ nm; dashed-dotted line) spectra of $DBDAP^{2+}$.

and structured room-temperature fluorescence (MeCN solution), as well as the low-temperature fluorescence and phosphorescence (butyronitrile rigid matrix) bands characteristic of the DAP^{2+} unit, are maintained in the cyclophanes $\mathbf{2}^{4+}$ and $\mathbf{3}^{4+}$ (Tab. I). The excited-state lifetimes are almost the same as those found for the model compounds. In the asymmetric cyclophane $\mathbf{2}^{4+}$, the excitation spectrum shows that energy transfer from the bipyridinium group to the emitting DAP^{2+} unit does not occur.

Electrochemical Properties

The electrochemical properties of the DAP^{2+} unit resemble, but are not as satisfying as, those of the 4,4′-bipyridinium unit. Although $DMDAP^{2+}$ [8] and $DBDAP^{2+}$ show two reduction processes, they are not electroactive upon oxidation. The first reduction process is reversible and monoelectronic; the second one is irreversible and characterized by a low current intensity, most likely because of the instability of the reduced forms of the DAP^{2+} unit [9]. The lack of reversibility of the second reduction process prevents an accurate electrochemical characterization of the compounds based on this unit. The halfwave reduction potentials of the first process measured for $DMDAP^{2+}$ and $DBDAP^{2+}$ are gathered together in Table II. The first reduction potential of $DMDAP^{2+}$ is very similar to that of 1,1′-dimethyl-4,4′-bipyridinium. In going from

TABLE II Electrochemical data[a]

Compound	Reduction $E_{1/2}$, V *vs.* SCE[b]	Oxidation E, V *vs.* SCE[c]
B[d]	–	+1.23; +1.36
N[e]	–	+1.05; +1.15
$DMDAP^{2+}$	−0.46	–
$DBDAP^{2+}$	−0.41	–
$\mathbf{1}^{4+}$[f]	−0.29[g]; −0.71[g]	–
$\mathbf{2}^{4+}$	−0.30[g]; −0.72	–
$\mathbf{3}^{4+}$	−0.29[g]	–
$\mathbf{1B}^{4+}$[h]	−0.31; −0.44; −0.84[g]	+1.42; +1.72
$\mathbf{1N}^{4+}$[i]	−0.35; −0.56; −0.81; −0.89	+1.30; +1.55
$\mathbf{2B}^{4+}$	−0.31; −0.57; −0.86	+1.42; +1.65
$\mathbf{2N}^{4+}$	−0.35; −0.68[j]; −0.84	+1.31; +1.62
$\mathbf{3B}^{4+}$	−0.37; −0.52	+1.42; +1.67
$\mathbf{3N}^{4+}$	−0.42; −0.66	+1.31; +1.63

[a] MeCN solution, 298 K; 0.05 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, glassy carbon electrode.
[b] Halfwave reduction potentials; reversible and monoelectronic processes, unless otherwise indicated.
[c] Not fully reversible processes; potential values estimated from DPV peaks.
[d] Data from Ref. [10].
[e] Data from Ref. [11].
[f] Data from Ref. [3].
[g] Two-electron process.
[h] Data from Refs. [2] and [3].
[i] Data from Refs. [3] and [13].
[j] Another reduction process, difficult to assign, is observed at −0.58 V.

$DMDAP^{2+}$ to $DBDAP^{2+}$, a shift of the first reduction potential toward less negative values is observed – just as in the case of the bipyridinium compounds – because of the electron-withdrawing effect of the benzyl substituents (see below).

In cyclophane $\mathbf{1}^{4+}$, two reversible bielectronic processes are observed which can be assigned to the first and second reductions of the two equivalent bipyridinium units [2–4]. In cyclophane $\mathbf{3}^{4+}$, a reversible two-electron wave, assignable to the first reduction of the two equivalent DAP^{2+} units, is observed; the second reduction of the two DAP^{2+} units is badly characterized (the potential value is not shown in the Table). In the asymmetric cyclophane $\mathbf{2}^{4+}$, a reversible two-electron reduction wave is followed by a reversible monoelectronic wave and a very weak irreversible wave (the potential value is not shown in the Table). The comparison with the behavior of the two parent cyclophanes $\mathbf{1}^{4+}$ and $\mathbf{3}^{4+}$ allows us to assign the bielectronic wave to the simultaneous one-electron reduction of the DAP^{2+} and bipyridinium units, the following one-electron wave to the second reduction of the bipyridinium unit, and the irreversible wave to the second reduction of the DAP^{2+} unit.

It should be noted that a progressive shift of the first reduction potential toward less negative values is observed along the series $DMDAP^{2+}$, $DBDAP^{2+}$, $\mathbf{2}^{4+}$ (or $\mathbf{3}^{4+}$), exactly in keeping with what happens in the series 1,1′-dimethyl-4,4′-bipyridinium, 1,1′-dibenzyl-4,4′-bipyridinium, and $\mathbf{1}^{4+}$.

Macrocycles Containing the Electron-Donor Units

The absorption and emission spectra [3] and the electrochemical behavior [10, 11] of macrocycles 1,4-dibenzo[34]crown-10 (**B**) and 1,5-dinaphtho[38]crown-10 (**N**) are summarized in Tables I and II.

Catenanes

The catenanes **2B**$^{4+}$ and **2N**$^{4+}$, based on the asymmetric cyclophane **2**$^{4+}$, which contains one 4,4'-bipyridinium and one DAP^{2+} unit, are particularly interesting since they can exist as two different translational isomers – one in which the DAP^{2+} unit is inside the crown ether and the other where the DAP^{2+} unit resides alongside. Since the DAP^{2+} unit is known to be a better π-electron acceptor than the bipyridinium unit [7], it might be expected that the most populated translational isomer would be the one in which the DAP^{2+} unit occupies the inside position. This expectation is confirmed by X-ray crystallographic and ^{1}H NMR spectroscopic data [12]; the results of electrochemical experiments (see below) are in agreement with such a structure.

Absorption and Luminescence Properties

The absorption spectra of the catenanes are considerably different from the sum of the spectra of the separated components. The bands in the UV region, characteristic of the chromophoric units, are broader, less intense and slightly red-shifted; in catenanes **2N**$^{4+}$ (Fig. 4) and **3N**$^{4+}$, the typical structure of the absorption band of the dioxynaphthalene unit is lost. The only difference is the presence of a new absorption feature, weak and broad, in the 450–700 nm region (Tab. I, Fig. 5). These results can be explained on the basis of a CT interaction between the electron-donor units incorporated in the crown ether and the electron-acceptor units present in the cyclophane.

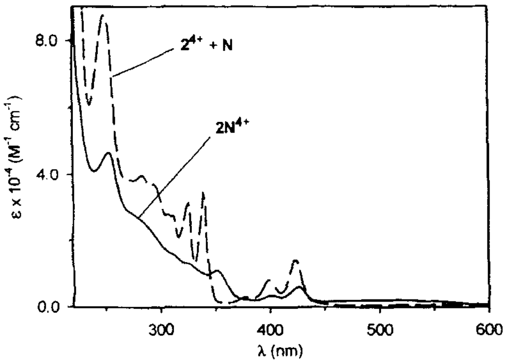

FIGURE 4 Absorption spectrum (MeCN, 298 K) of catenane **2N**$^{4+}$ (solid line) compared with the sum of the spectra of its molecular components **2**$^{4+}$ and **N** (dashed line).

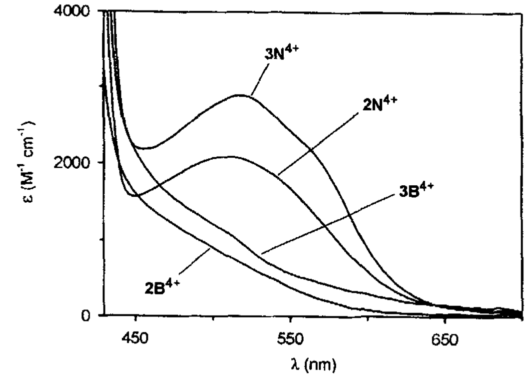

FIGURE 5 CT Absorption bands (MeCN, 298 K) of the four DAP^{2+}-containing [2]catenanes.

The energy and shape of the visible absorption feature is dependent upon the nature of the moieties involved in the CT interaction. For example, with the macrocyclic polyether **B**, only a shoulder around 500 nm is present, while, in catenanes containing the crown ether **N**, a band with a maximum of around 510 nm (ε ca. 2000 M^{-1} cm^{-1}) is observed. It should also be noted that these absorption features are displaced toward higher energy with respect to those observed for the corresponding catenanes of the cyclophane **1**$^{4+}$ [3].

In all the catenanes, the luminescence characteristic of the emitting components (**2**$^{4+}$, **3**$^{4+}$, **B**, **N**) is completely quenched, both at 298 K and 77 K. This observation is consistent with the presence of low energy CT excited states which provide the upper-lying levels of the chromophores with fast radiationless decay routes, as previously observed for many related systems [2,3,5–7,10,13].

Electrochemical Properties

In catenanes **3B**$^{4+}$ and **3N**$^{4+}$, the bielectronic wave of the corresponding cyclophane separates into two monoelectronic waves, both displaced toward more negative potentials (Tab. II). This is an expected result if one considers that, in the catenanes, the electron-acceptor units (*i*) are more difficult to reduce as a consequence of the CT interaction, and (*ii*) are no longer equivalent since the alongside unit interacts with only one donor moiety, whereas the inside one interacts with two donor moieties. For catenanes $\mathbf{2B}^{4+}$ (Fig. 6) and $\mathbf{2N}^{4+}$, three reversible monoelectronic processes are observed (Tab. II). Comparison with the first two reduction potentials of the catenanes based on the symmetric cyclophanes $\mathbf{1}^{4+}$ and $\mathbf{3}^{4+}$ shows that, for catenanes $\mathbf{2B}^{4+}$ and $\mathbf{2N}^{4+}$, the first monoelectronic process can be attributed to the first reduction of the alongside bipyridinium unit, the second to the first reduction of the inside DAP^{2+} unit, and the third to the second reduction of the bipyridinium unit. This order indicates that, in $\mathbf{2B}^{4+}$ and $\mathbf{2N}^{4+}$, the DAP^{2+} unit occupies the inside position, as expected on the basis of the increased π-electron-acceptor ability of the DAP^{2+} unit compared to the bipyridinium unit. It should also be noted that the third reduction is displaced toward more negative potentials with respect to the second process of $\mathbf{2}^{4+}$, indicating that some CT interaction is still effective.

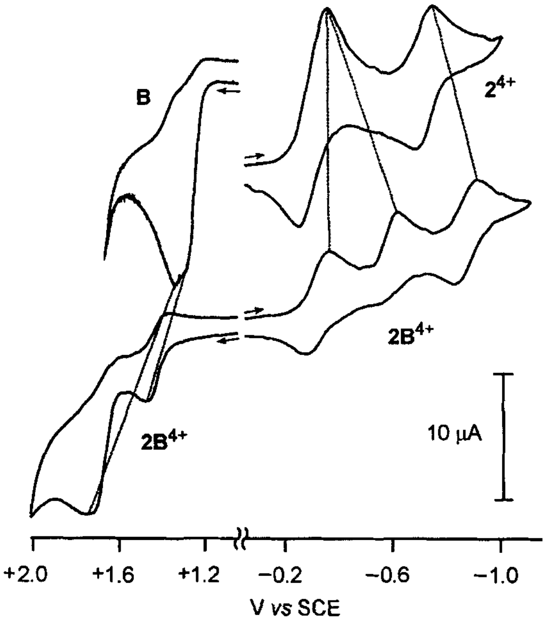

FIGURE 6 Cyclic voltammetric scan of catenane $\mathbf{2B}^{4+}$ and of its components $\mathbf{2}^{4+}$ and **B** (MeCN, 0.05 M tetrabutylammonium hexafluorophosphate, glassy carbon electrode, scan rate $20\,\mathrm{mV\,s^{-1}}$).

On the oxidation side, the two not fully reversible processes observed for the crown ethers (Tab. II) are maintained in the catenanes, although these are displaced toward more positive potentials, compared to the isolated **B** and **N** components, because of the CT interaction with the electron-accepting cyclophane. As discussed above for the reduction processes, the topology of the catenane structures allows the assignment of the less positive process to oxidation of the alongside dioxyaromatic unit, and of the more positive process to oxidation of the inside unit. It is worth noting that, in the catenanes, the potential shift (with respect to the isolated crown ether) for the first oxidation process is smaller than that for the second process; this difference accounts for the stronger CT interaction experienced by the inside unit compared to the alongside one. Somewhat surprisingly, the potential at which the alongside dioxybenzene (for the catenanes of crown ether **B**) or dioxynaphthalene (for the catenanes of crown ether **N**) unit is oxidized does not depend on the nature of the adjacent electron-acceptor unit (4,4′-bipyridinium for the catenanes of cyclophane $\mathbf{1}^{4+}$ and DAP^{2+} for the catenanes of cyclophanes $\mathbf{2}^{4+}$ and $\mathbf{3}^{4+}$). A more detailed analysis, unfortunately, is prevented by the lack of reversibility for these oxidation processes.

It is interesting to note that, although the model compounds for the bipyridinium and DAP^{2+} units undergo their first reduction process at the same potential (as in $\mathbf{1}^{4+}$ and $\mathbf{3}^{4+}$), the shift toward more negative potentials, which is observed when these units are incorporated in the catenanes, is much larger for the DAP^{2+} unit. This finding is in agreement with the higher values of the association constants of the pseudorotaxanes formed by DAP^{2+}-based compounds and aromatic crown ethers [7]. These results indicate that the value of the reduction potential of the free electron-acceptor unit cannot be directly related to the extent of the CT interaction. It should also be noted that the energy of the CT absorption bands of $\mathbf{3B}^{4+}$ and $\mathbf{3N}^{4+}$ is higher than for those in $\mathbf{1B}^{4+}$ and $\mathbf{1N}^{4+}$, respectively, indicating that there is no direct relation with the redox potentials. This consideration underlines that other factors besides the redox potentials, such as size and shape of the π-electron acceptor units, are involved in determining the interactions which govern the behavior of these kinds of systems.

CONCLUSION

The spectroscopic and electrochemical properties of two tetracationic cyclophanes containing the DAP^{2+} electron-acceptor unit, and of their [2]catenanes with two different electron donor macrocycles, have been studied. The results obtained indicate the presence of CT interactions between the electron-donor units of the crown ethers and the electron-acceptor bipyridinium and/or DAP^{2+} units of the cyclophanes. Although the first reduction potentials of the DAP^{2+} and bipyridinium units are practically the same, in the asymmetric $\mathbf{2B}^{4+}$ and $\mathbf{2N}^{4+}$ catenanes only the translational isomer in which the DAP^{2+} unit occupies the inside position is present. We have recently shown that the less stable co-conformation, which has the bipyridinium unit inside the cavity of the crown, can be obtained using external chemical inputs [14].

EXPERIMENTAL

Absorption and Luminescence Spectra

Measurements were carried out at 298 K in MeCN (Merck Uvasol^{TM}) solutions with concentrations in the range 1×10^{-5} to 1×10^{-4} M. UV-Vis absorption spectra were recorded on air-equilibrated solutions with a Perkin Elmer λ6 spectrophotometer. Uncorrected luminescence and corrected excitation spectra were obtained with a Perkin Elmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube. Relative luminescence intensities are referred to $DMDAP^{2+}$ and were determined by comparing the area subtended by the emission band of the sample with that of $DMDAP^{2+}$ under the same excitation conditions. Low-temperature (77 K) luminescence spectra were obtained on a butyronitrile (Fluka) rigid matrix using quartz tubes immersed in a quartz Dewar filled with liquid nitrogen. The estimated errors are: wavelengths, ±2 nm; extinction coefficients, ±10%; relative luminescence intensities, ±15%.

Electrochemistry

Cyclic voltammetric (CV) and differential pulse voltammetric (DPV) experiments were carried out in argon purged MeCN (Romil Hi-Dry^{TM}) solutions at 298 K with a PAR 273 multipurpose instrument interfaced to a PC. The working electrode was a glassy carbon electrode (Amel, 0.08 cm^2) and the counter electrode was a Pt spiral contained in a fine glass frit; a silver wire was employed as a quasi-reference electrode. The concentration of the electroactive sample was 5×10^{-4} M; 0.05 M tetrabutylammonium hexafluorophosphate was added as supporting electrolyte, and ferrocene was used as an internal standard for the potential values. Cyclic voltammograms (CV) were obtained at sweep rates of 20, 50, 100, 200, 500 mV s^{-1}; differential pulse voltammograms (DPV) were performed with scan rates of 20 mV s^{-1}, a pulse height of 75 mV, and a duration of 40 ms. For reversible processes, the same halfwave potential values were obtained from the DPV peaks and from an average of the cathodic and anodic cyclic voltammetric peaks. The potential values for not fully reversible processes were estimated from the DPV peaks. The number of exchanged electrons for reversible processes was measured by comparing the current intensity of the CV waves and the area of the DPV peaks with those found for the two reversible and bielectronic reduction processes of 1^{4+} [2–4], after correction for differences in the diffusion coefficients [15]. The experimental error on the potential values for reversible and not fully reversible processes was estimated to be ±5 and ±20 mV, respectively.

Acknowledgments

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