Macrocycles, pseudorotaxanes and catenanes containing a pyrrolo-tetrathiafulvalene unit: absorption spectra, luminescence properties and redox behavior

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The photophysical properties of (i) three macrocycles (**1**–**3**) of different size, each one incorporating a bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene (TTFP) and a 1,4-dimethoxybenzene (DMB) electron-donating unit, (ii) the six pseudorotaxanes obtained by threading **1**–**3** with the electron acceptors dimethyldiazapyrenium ($DMDAP^{2+}$) and dibenzyldiazapyrenium ($DBDAP^{2+}$) and (iii) the three catenanes obtained by interlocking **1**–**3** with the electron-accepting cyclophane cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) have been investigated. The monooxidized and dioxidized species obtained by oxidation with Fe(III) of the TTFP unit contained in the above compounds have also been studied. The redox-driven dethreading/rethreading process has been investigated in the case of the pseudorotaxane based on the macrocycle **2** and the $DMDAP^{2+}$ dication. In the catenanes, oxidation of the TTFP unit causes strong spectral changes, but does not promote disruption of the interlocked structures.

Tetrathiafulvalene (TTF) and its derivatives have been used extensively as electron-donating units in charge-transfer (CT) complexes.[1,2] It is also well-known that TTF can be oxidized reversibly[1e,3] to $TTF^{\cdot+}$ and TTF^{2+} and that the TTF^{2+} dicationic species behaves as an electron acceptor.[2c,4] Because of these specific properties, TTF-type units have recently been incorporated into pseudorotaxanes,[2c,d,f,4,5] rotaxanes[1a,6] and catenanes.[2c,d,4,6] In suitably designed systems of this kind, the electrochemically or chemically induced redox switching of the TTF-type unit can cause mechanical movements of the component parts, leading to machine-like behavior.[2c,4,6]

Continuing our investigations in this field, we have studied the absorption, emission and redox properties of macrocycles **1**–**3**[2e] which contain bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene (TTFP) and 1,4-dimethoxybenzene (DMB) units (Fig. 1). Such macrocycles can be threaded by dimethyldiazapyrenium ($DMDAP^{2+}$) or dibenzyldiazapyrenium ($DBDAP^{2+}$) electron-accepting dications to obtain the corresponding pseudorotaxane species, and they can also be interlocked with the cyclobis(paraquat-*p*-phenylene) cyclophane ($CBPQT^{4+}$) to obtain the corresponding catenanes[2e] (Fig. 1 and 2). The absorption, emission and redox properties of these species, including the redox-driven dethreading/rethreading process of a pseudorotaxane, are described.

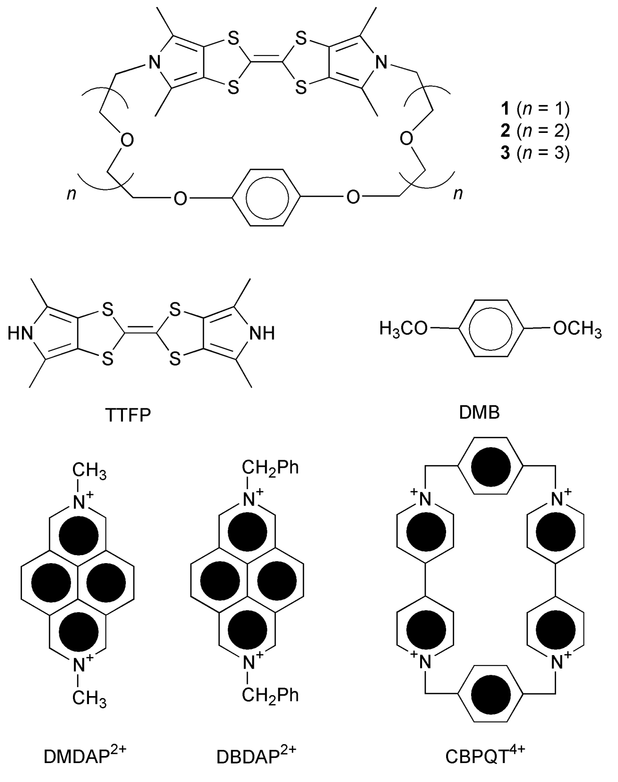

Fig. 1 Formulas and abbreviations of macrocycles **1**–**3**, the bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene (TTFP) and 1,4-dimethoxybenzene (DMB) model compounds, the dimethyldiazapyrenium ($DMDAP^{2+}$) and dibenzyldiazapyrenium ($DBDAP^{2+}$) electron-accepting molecules, and the cyclobis(paraquat-*p*-phenylene) electron-accepting cyclophane ($CBPQT^{4+}$).

Experimental

The preparation and characterization of macrocycles **1**–**3**,[2e] dimethyldiazapyrenium ($DMDAP^{2+}$)[7a] and dibenzyldiazapyrenium ($DBDAP^{2+}$),[7b] and catenanes[2e] **1**/$CBPQT^{4+}$, **2**/$CBPQT^{4+}$ and **3**/$CBPQT^{4+}$ have been previously reported. Fe(III) and Fe(II) perchlorates were Aldrich reagents. Fe(III) perchlorate was dried under vacuum on P_2O_5. The effective

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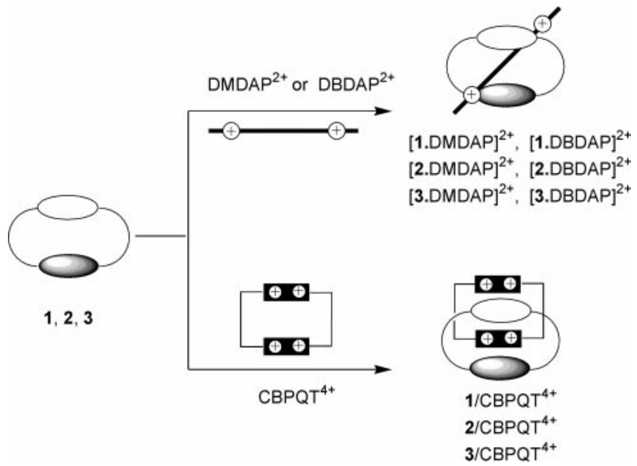


Fig. 2 Schematic representation and abbreviations used for macrocycles **1**–**3** and their pseudorotaxanes and catenanes.

content of Fe(III) was determined spectrophotometrically as $Fe(phen)_3{}^{2+}$ after reduction with Co(II).[8] Acetonitrile and dichloromethane (Merck Uvasol) were used without further purification. The absorption spectra were recorded with a Lambda 40 Perkin Elmer spectrophotometer and the emission spectra with a LS-50 Perkin Elmer spectrofluorimeter. Emission lifetimes were measured with an Edinburgh Instruments DS199 single-photon counting instrument. All the experiments were carried out at room temperature in air-equilibrated solutions having concentrations in the range 10^{-4}–10^{-5} M.

Results and discussion

Macrocycles 1, 2 and 3

The photophysical properties of macrocycles **1**, **2** and **3** were studied in acetonitrile (MeCN) solution. The results obtained have been compared with those of the bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene (TTFP) and *p*-dimethoxybenzene (DMB) model compounds (Fig. 1) of the component units.

Fig. 3 shows the absorption spectra of the three macrocycles compared to the sum of the spectra of the TTFP and DMB chromophoric units. A perturbation in the shape and intensity of the band with a maximum around 300 nm, characteristic of both chromophoric groups, more pronounced in the smallest and in the largest rings, can be seen. Furthermore, the weak and broad absorption band in the visible region, characteristic of the TTFP chromophoric group, increases considerably in intensity in the case of the largest macrocycle.

As far as the emission properties are concerned, it is well-known[9] that DMB shows a fluorescence band with a maximum at 320 nm and a 2 ns lifetime; TTFP, like TTF,[4] does not show any emission. We have found that in macrocycles **1**, **2** and **3** the DMB-type fluorescence is completely quenched, as happens in the case of similar macrocycles containing the TTF unit.[4] This behavior may be accounted for by an intramacrocycle energy-transfer process from the upper lying, potentially fluorescent excited state of the DMB unit to the lower lying, non-emissive excited state of the TTFP unit, which corresponds to the visible absorption band with λ_{max} around 420 nm.

Pseudorotaxanes formed by macrocycles 1, 2 and 3 with $DMDAP^{2+}$ and $DBDAP^{2+}$

The $DMDAP^{2+}$ and $DBDAP^{2+}$ dications are known to be strong electron acceptors.[2b,7b,10] They thread crown ethers containing electron-donating groups, giving rise to pseudorotaxanes that usually exhibit high association constants.[2b,7b] Both $DMDAP^{2+}$ and $DBDAP^{2+}$ show intense absorption bands in the 300–450 nm region and a strong fluorescence band with a maximum at 428 nm and a lifetime of 10 ns (MeCN, room temperature).[7b,11] The absorption and emission spectra of $DMDAP^{2+}$ are shown in Fig. 4. When the $DMDAP^{2+}$ and $DBDAP^{2+}$ dications thread electron-donating macrocycles, their strong fluorescent band is completely quenched.[7b,10] The switching of the fluorescence signal

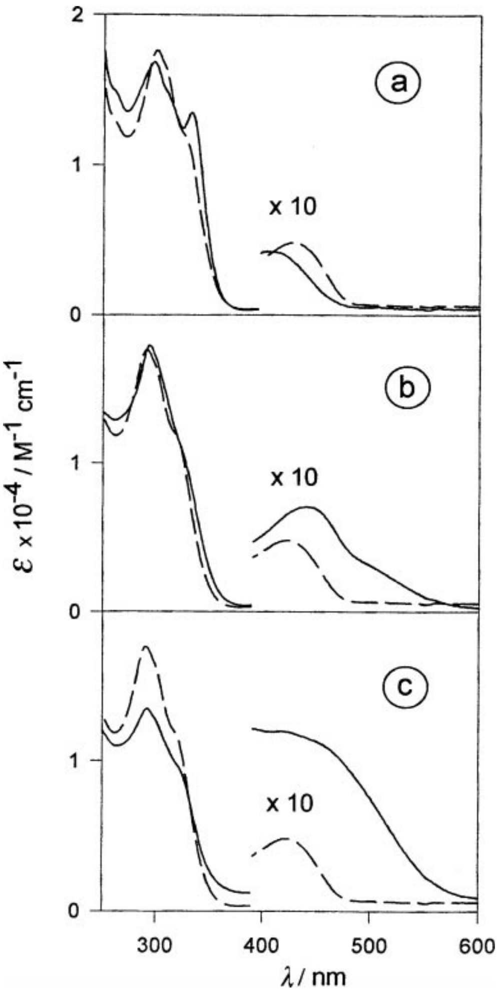


Fig. 3 Absorption spectra (MeCN, 20 °C) of macrocycles (solid lines) **1** (a), **2** (b) and **3** (c) compared to the sum (dashed lines) of the spectra of the TTFP and DMB model compounds.

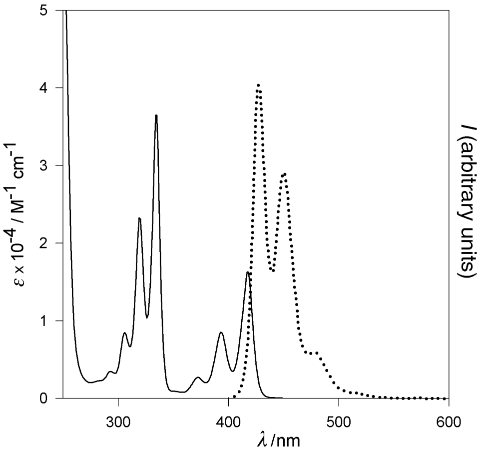


Fig. 4 Absorption (solid line) and emission (dotted line) spectra of $DMDAP^{2+}$ in MeCN at 20 °C.

is an excellent probe with which to monitor threading/dethreading processes.

Mixing of MeCN solutions containing macrocycles **1**–**3** (1×10^{-4} M) and $DMDAP^{2+}$ or $DBDAP^{2+}$ (5×10^{-5} M) caused noticeable changes in the absorption spectra compared with the sum of the spectra of the separated components. As an example, Fig. 5 shows this comparison for the pseudorotaxane $[\mathbf{2} \cdot DMDAP]^{2+}$. Particularly interesting is the appearance of a new broad absorption band in the visible region ($\lambda_{max} = 470$ nm) that can be assigned to charge-transfer interactions between the electron-donating units of the macrocycle and the electron-accepting $DMDAP^{2+}$ dication.

The changes in the absorption spectra were accompanied by quenching of the fluorescence band of the diazapyrenium species. Such a quenching cannot arise from a dynamic process because the fluorescent excited states of $DMDAP^{2+}$ and $DBDAP^{2+}$ are short-lived (10 ns) and the concentration of the quencher (*i.e.* the macrocycle) is very low.[12] Therefore, the quenching has to arise from the association of the two components in the ground state, revealed by the changes in the absorption spectrum. The static mechanism of the quenching process is confirmed by the fact that the quenching of the fluorescence intensity during the titration is not accompanied by a parallel decrease in the fluorescence lifetime. The residual fluorescence signal derives, therefore, from the fraction of diazapyrenium units that do not undergo association. Quantitative analysis of the quenching of the fluorescence intensity observed when $DMDAP^{2+}$ or $DBDAP^{2+}$ were added to solutions containing the macrocycles has allowed us to obtain values for the association constants (Table 1).

By analogy with other complexes of this kind,[7b] we assume that the most stable structure for the adduct is that in which the $DMDAP^{2+}$ or $DBDAP^{2+}$ dication threads the macrocycle (pseudorotaxane superstructure, Fig. 2). Interestingly, the association constant is always higher for $DMDAP^{2+}$ than for $DBDAP^{2+}$, presumably because of a contribution coming from hydrogen bonding interactions involving the hydrogen atoms of the diazapyrenium methyl groups and the oxygen atoms of the crown ethers. As far as the macrocycles are concerned, the values of the association constants show that the most suitable cavity to host the diazapyrenium moiety is that offered by the medium-sized crown ether **2**, as suggested by CPK space-filling molecular models. We have also found that in a mixed, less polar solvent (CH_2Cl_2–MeCN 6 : 1, v/v), the association constants are much higher than in MeCN. In such a solvent, however, the mono- and dioxidized forms of the TTFP unit are not stable. Therefore, our oxidation experiments (*vide infra*) were carried out in MeCN.

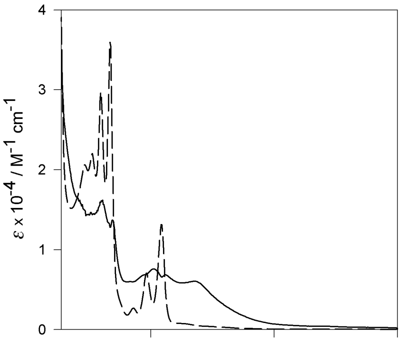


Fig. 5 Comparison between the absorption spectra (MeCN, 20 °C) of the pseudorotaxane $[\mathbf{2} \cdot DMDAP]^{2+}$ (solid line) and the sum of the spectra of the separated components (dashed line).

Table 1 Association constants (M^{-1}) of the macrocycles **1**, **2** and **3** with $DMDAP^{2+}$ and $DBDAP^{2+\,a}$

	$DMDAP^{2+}$	$DBDAP^{2+}$
1	1000	750
2	5300	5000
3	3250	1750

[a] In acetonitrile at 20 °C; the estimated experimental error is ± 10%. For more details, see text.

Dethreading/rethreading of pseudorotaxane $[\mathbf{2} \cdot DMDAP]^{2+}$

TTFP can be reversibly oxidized in electrochemical experiments to its mono- and dioxidized forms ($E^1_{1/2} = 0.33$ V, $E^2_{1/2} = 0.78$ V *vs.* Ag/AgCl in MeCN).[3b] Oxidation can also be performed chemically by using Fe(III) perchlorate in MeCN solution (Fe^{3+} undergoes an irreversible reduction at 1.1 V *vs.* SCE in MeCN),[13] as was previously carried out on systems containing the TTF unit.[1b] In the case of TTFP, a green monocation, thermally stable for days, and a yellow dication, thermally stable for hours, are obtained. The absorption spectra of TTFP, $TTFP^{\cdot +}$ and $TTFP^{2+}$ are shown in Fig. 6(a). Comparison with the spectral changes obtained by oxidation of macrocycle **2** [Fig. 6(b)] shows that, in the latter, the lowest energy band of the mono- and dicationic species are slightly displaced to lower energies. In the dicationic form of the macrocycle, a charge-transfer interaction can arise between the DMB electron-donating and $TTFP^{2+}$ electron-accepting units, as is the case in analogous macrocycles containing the TTF unit.[14] Evidence for the presence of a CT band with a maximum at about 750 nm is obtained by subtracting the spectrum of $TTFP^{2+}$ from that of $\mathbf{2}^{2+}$.

Oxidation of the TTFP unit of the macrocycles engaged with $DMDAP^{2+}$ or $DBDAP^{2+}$ in pseudorotaxane superstructures can be expected to cause dethreading since (i) the electron-donor properties of TTFP (and the consequent CT stabilization of the pseudorotaxane structure) are cancelled upon oxidation and (ii) a strong Coulombic repulsion arises between the two cationic components of the structure. The

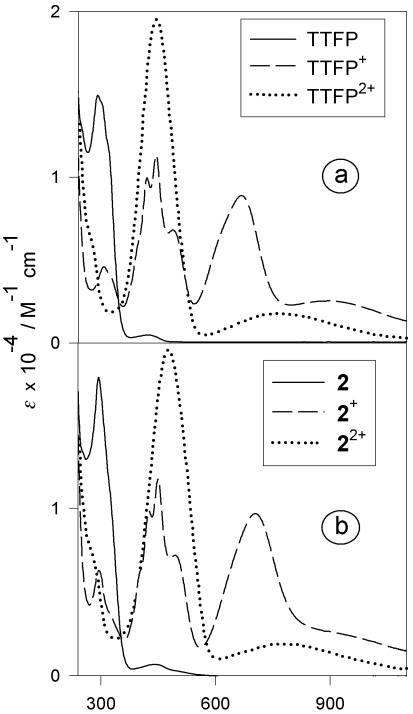
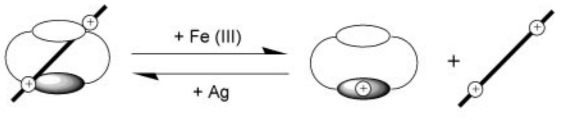


Fig. 6 Absorption spectra (MeCN, 20 °C) of (a) TTFP and its mono- and dioxidized forms; (b) macrocycles **2** and its mono- and dioxidized forms.

oxidation experiments were performed in MeCN on the most stable of the pseudorotaxanes (Table 1), namely [**2**·DMDAP]$^{2+}$ (Fig. 7).

Having first verified that Fe(III) and Fe(II) perchlorate salts do not react with DMDAP^{2+}, we titrated a MeCN solution containing **2** (1×10^{-4} M) and DMDAP^{2+} (5×10^{-5} M) with Fe(III) perchlorate. The value of the association constant shows that, in such a solution, 32% of the DMDAP^{2+} molecules are present in the complexed form. As already pointed out, in a less polar solvent, the fraction of complexed species would be higher, but the mono- and dioxidized forms of the TTFP unit are not stable in such solvents.

During the titration experiments, we measured the changes in the absorption spectra (Fig. 8) and in the fluorescence intensity of DMDAP^{2+} (Fig. 9, $\lambda_{em} = 452$ nm). The changes in the absorption spectra show that the TTFP unit of the crown ether is first monooxidized [Fig. 8(a)] and then dioxidized [Fig. 8(b)]. Fig. 9 shows that complete recovery of the DMDAP^{2+} fluorescence, as expected for dethreading of DMDAP^{2+} molecules involved in pseudorotaxane species, occurs upon monooxidation of the TTFP unit of the macrocycle. The slow increase in the fluorescence intensity at the beginning of the titration shows that Fe(III) preferentially oxidizes the excess free macrocycle rather than the macrocycle component of the pseudorotaxane species; this result is expected since the latter, being involved in electron donation to the DMDAP^{2+} thread, is more difficult to oxidize. The second oxidation to TTFP^{2+} occurs when the macrocycles are disengaged.



[2.DMDAP]$^{2+}$ 2^{+} DMDAP^{2+}

Fig. 7 Oxidation-induced dethreading and reduction-induced rethreading of pseudorotaxane [**2**·DMDAP]$^{2+}$.

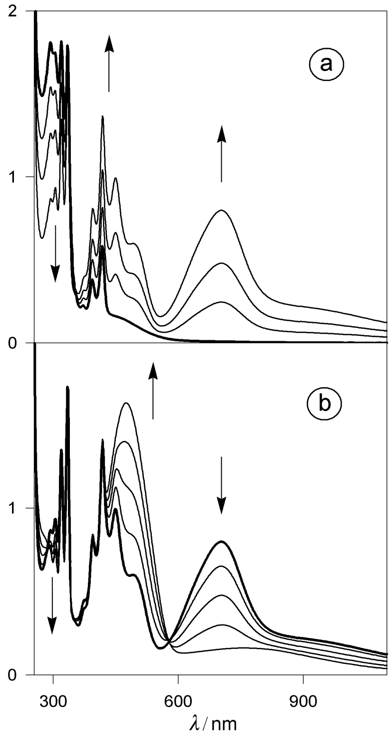


Fig. 8 Changes in the absorption spectrum (MeCN, 20 °C) of a solution containing 5×10^{-5} M DMDAP^{2+} and 1×10^{-4} M macrocycle **2** (32% pseudorotaxane formed) upon oxidation of the TTFP unit of **2** with Fe(III) perchlorate: (a) spectral changes observed during the addition of the first equivalent of Fe(III); (b) spectral changes observed during the addition of the second equivalent of Fe(III).

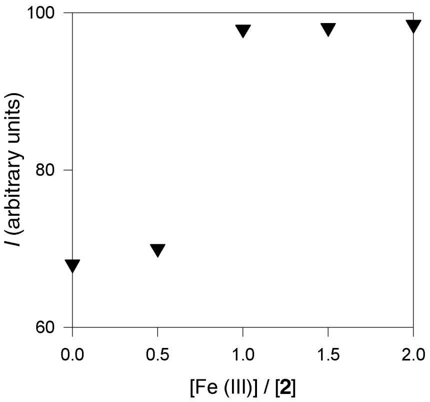


Fig. 9 Changes in the fluorescence intensity (MeCN, 20 °C) of DMDAP^{2+} in a solution containing 5×10^{-5} M DMDAP^{2+} and 1×10^{-4} M macrocycle **2** (32% pseudorotaxane formed) upon oxidation of the TTFP unit with Fe(III) perchlorate toTTFP$^{\cdot+}$ [1 equiv. of Fe(III)] and TTFP^{2+} [2 equiv. of Fe(III)].

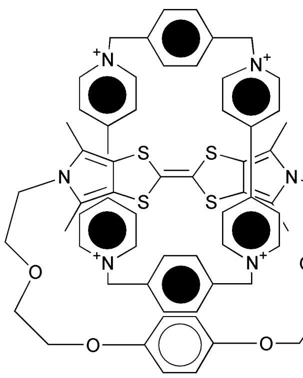
Addition of Ag powder at the end of the oxidation process causes reduction of the TTFP^{2+} unit of the macrocycles back to the neutral form. As a consequence, the electrostatic repulsion between macrocycle and thread is no longer present and the CT interaction between the electron-donating groups of **2** and the electron-accepting DMDAP^{2+} unit is restored. This causes the rethreading process (Fig. 7), as shown by the changes in the absorption spectrum and by the decrease in the fluorescence intensity to the original value.

Catenanes formed by macrocycles 1, 2 and 3 with CBPQT^{4+}

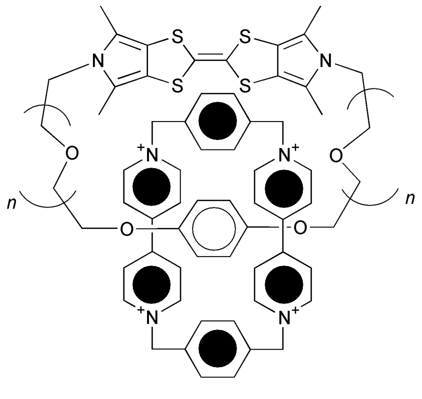
The tetracationic cyclophane CBPQT^{4+} (Fig. 1) contains two electron-accepting units. Such a cyclophane has been extensively used as a component of pseudorotaxanes, rotaxanes and catenanes based on charge-transfer interactions.[15,16]

^{1}H NMR spectra in CD$_3$CN at room temperature showed that for catenane **1**/CBPQT^{4+} (Fig. 10), in which cyclophane CBPQT^{4+} is interlocked with the smallest macrocycle **1**, the only translational isomer is that in which the CBPQT^{4+} cyclophane encircles the TTFP unit of the macrocycle.[2e] For catenanes **2**/CBPQT^{4+} and **3**/CBPQT^{4+}, which involve the larger macrocycles **2** and **3**, this isomer is only present in a small fraction (10 and 5%, respectively, in deuterated DMSO at 30 °C).[2e]

The photophysical properties of the three catenanes have been studied in 5×10^{-5} M MeCN solutions at 20 °C. The absorption spectra of the catenanes are compared with the sum of the spectra of the component macrocycles in Fig. 11. Notable features are (i) a decrease in the intensity of the UV absorption band (which is mostly due to the CBPQT^{4+} cyclophane) and (ii) the appearance of weak and broad absorption bands in the visible region. The latter can be attributed to CT transitions from the π-electron-donating units (TTFP and DMB) of the macrocycle to the π-electron-deficient bipyridinium units of the tetracationic cyclophane. On the basis of the much lower oxidation potential of TTFP[3b] compared with DMB,[15] the band around 400–500 nm can be assigned to the charge-transfer interactions between DMB and CBPQT^{4+}, and that at lower energy to the interaction between TTFP and CBPQT^{4+}. It should also be noted that the CT band involving the TTFP unit is very similar for **2**/CBPQT^{4+} and **3**/CBPQT^{4+} (λ_{max} about 900 nm, $\varepsilon = 1200$ and 1500 M^{-1} cm^{-1}, respectively), but it is strongly blue-shifted and more intense in the case of **1**/CBPQT^{4+} (λ_{max} about 700 nm, $\varepsilon = 2000$ M^{-1} cm^{-1}) (see Fig. 11). This behavior is consistent with the different structure of **1**/CBPQT^{4+}



1/CBPQT^{4+}



2/CBPQT^{4+} (*n* = 2)
3/CBPQT^{4+} (*n* = 3)

Fig. 10 Prevalent isomers, at room temperature, of the catenanes formed by CBPQT^{4+} and macrocycles **1**, **2** and **3**.

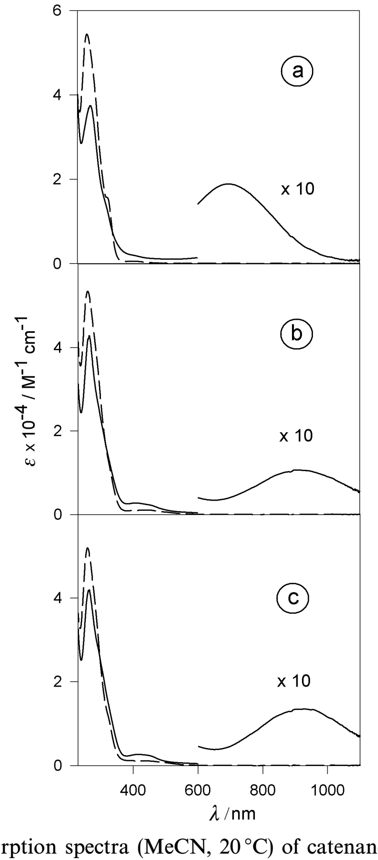


Fig. 11 Absorption spectra (MeCN, 20 °C) of catenanes (solid lines) **1**/CBPQT^{4+} (a), **2**/CBPQT^{4+} (b), and **3**/CBPQT^{4+} (c) compared with the sum (dashed lines) of the spectra of the component macrocycles.

compared with those of **2**/CBPQT^{4+} and **3**/CBPQT^{4+} (Fig. 10). In the catenane involving the smallest macrocycle, the TTFP unit is surrounded by the two electron-accepting units of the cyclophane and the system is very rigid. This situation favors overlapping between the donor and acceptor orbitals (which accounts for the higher ε value), but destabilizes the CT excited state because of the electrostatic repulsion between the formally monooxidized TTFP unit and the cationic cyclophane. In the catenanes involving the two larger macrocycles, where the cyclophane surrounds the DMB unit, the TTFP unit interacts with only one, 'alongside', bipyridinium unit of CBPQT^{4+}, the orbital overlap is smaller and the CT state is less destabilized. These results are consistent with the increasing oxidation potential of the TTFP unit in going from free TTFP to the TTFP units of catenanes **3**/CBPQT^{4+}, **2**/CBPQT^{4+} and **1**/CBPQT^{4+}.[2e] As expected, the higher energy CT band (400–500 nm), which corresponds to the interaction of the DMB unit of the macrocycle with the CBPQT^{4+} cyclophane, is more intense for **2**/CBPQT^{4+} and **3**/CBPQT^{4+} (Fig. 11), whereas it can hardly be seen for **1**/CBPQT^{4+}.

In all the examined catenanes, the fluorescence emission of the DMB unit is completely quenched, as previously found for similar compounds.[15,16] This observation can be explained by the presence of low-energy, non-emitting CT excited states that offer efficient deactivation paths to the potentially fluorescent exited state of the DMB unit.

Chemical oxidation with Fe(III) perchlorate of the TTFP unit in catenanes **2**/CBPQT^{4+} and **3**/CBPQT^{4+} leads, as expected, to the disappearance of the CT band with a maximum at 900 nm. Both the monooxidized and dioxidized forms of the TTPF unit, and therefore of the corresponding catenanes, can be obtained. In the case of **1**/CBPQT^{4+} however, only one-electron oxidation was observed (with disappearance of the CT band at 700 nm), showing that the oxidizing power of Fe(III) in MeCN is not sufficient to obtain the dioxidized TTFP unit in this cyclophane (the reduction potential of the TTFP$^{2+/+}$ couple in **1**/CBPQT^{4+} is +1.46 V *vs.* Ag/AgCl, MeCN).[2e]

Conclusions

The nonsymmetric macrocycles **1**–**3**, which contain bis(2,5-dimethylpyrrolo[3,4-*d*])tetrathiafulvalene (TTFP) and 1,4-dimethoxybenzene (DMB) electron-donating units, are fascinating compounds. Their TTFP unit can be mono- and dioxidized resulting in profound spectral changes. The pseudorotaxane-type adducts of the macrocycles with the fluorescent dimethyldiazapyrenium (DMDAP^{2+}) and dibenzyldiazapyrenium (DBDAP^{2+}) electron-accepting molecules exhibit CT absorption bands, no fluorescence, and can be dethreaded/rethreaded by chemical oxidation/reduction of the TTFP unit. The catenanes obtained by interlocking the macrocycles with the cyclobis(paraquat-*p*-phenylene) electron-accepting cyclophane (CBPQT^{4+}) exhibit different absorption spectra and oxidation behavior related to their different structure.

Acknowledgements

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