

Photophysical and Electrochemical Characterisation of the Interactions between Components in Neutral π -Associated [2]Catenanes

Darren G. Hamilton,^[a] Marco Montalti,^[b] Luca Prodi,^{*[b]} Marco Fontani,^[c] Piero Zanello,^{*[c]} and Jeremy K. M. Sanders^{*[a]}

Abstract: The electrochemical and photophysical properties of a variety of neutral π -associated [2]catenanes have been explored by using cyclic voltammetry, absorption and luminescence spectrophotometry and the measurement of excited-state lifetimes. Several trends that could be correlated with interactions between the mechanically linked components of the structures were revealed from comparative study of catenane precursors, model compounds and the [2]catenanes themselves. Throughout, emphasis is placed on pairwise comparisons between systems which differ in a single structural feature. Substitution in a catenane of a pyromellitic diimide unit by a naphtha-

lene diimide yields more readily reduced derivatives, whose absorption spectra reveal charge transfer within the catenane to be a lower energy process of reduced intensity. Conversion of the butadiyne links within the diimide macrocycle of the catenanes to saturated chains results in an increase in both the energy and intensity of their charge-transfer bands; electrochemically these derivatives are all harder to reduce than the parent systems. Replacement of one

of the electron-donating components of the catenanes with a less effective aromatic donor bearing a carboxy group also decreases the energy and intensity of the charge-transfer feature and is accompanied by a slightly more ready reduction. A sequence of reduction and translational events is proposed to explain the intriguing electrochemical behaviour of a catenane that contains one pyromellitic and one naphthalene diimide. For some systems the photophysical and electrochemical techniques, whilst exploring distinct physical phenomena, are shown to be in good agreement by comparison of shifts of electrochemical reduction waves with those of charge-transfer absorption features.

Keywords: catenanes • donor–acceptor systems • electrochemistry • photophysics • supramolecular chemistry

Introduction

Supramolecular chemists might argue that, as a discipline, the area has matured to the point where it is possible to conceive, prepare and study complex molecular assemblies capable of functioning in a designed fashion.^[1–6] Useful arrays of building blocks and methods by which to connect them are now readily available, and the resulting molecules can be studied by using standard analytical tools, augmented by the introduction of,

for example, soft-ionisation mass spectrometric techniques.^[7] However, the development of analytical approaches for characterisation of the functions of complex molecules, perhaps comprising several interacting subunits, is still at an early stage and must rely on thorough characterisation of individual molecular units and investigations of how their properties are modified when incorporated in larger systems.^[8, 9]

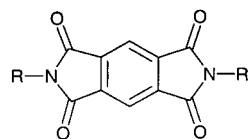
In this context we report here the electrochemical and photophysical characterisation of a series of neutral π -associated [2]catenanes. In addition to their aesthetic appeal, catenanes have been viewed as useful vehicles for establishing synthetic methodology, and two existing classes of contemporary catenanes have been examined in great detail, from both structural and analytical perspectives.^[10] Our current series of [2]catenanes offers opportunities to examine the effects of several structural changes within the context of an interlocked molecule. Though the systems discussed here are highly reminiscent of, and are inspired by, the bipyridinium catenanes studied by the Stoddart group, our systems present unique structural features. In particular, we describe the study of systems that are structurally derived from other [2]cate-

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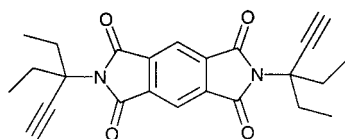
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nanes allowing us to quantify changes in properties as a result of altering the mutual structural relationship of the interlocked rings. A total of eight model compounds or catenane precursors (**1–8**), and ten [2]catenanes (**9–18**) are discussed

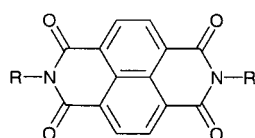


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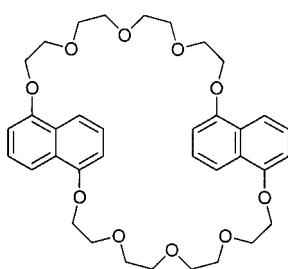


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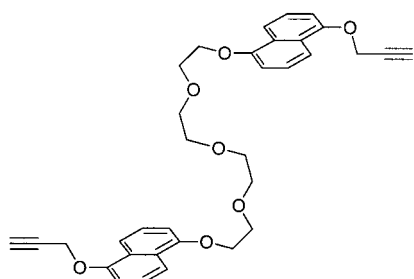


4 R = (CH₂)₅CH₃

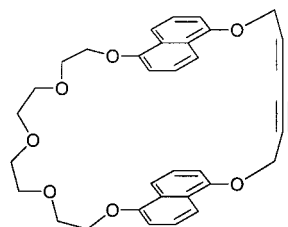
5 R = CH₂C≡CH



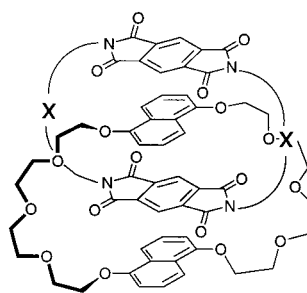
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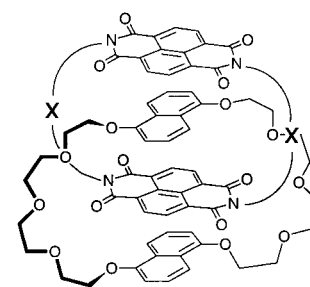


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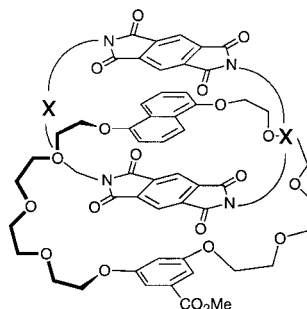
9 X = -CH₂-C≡C-C≡C-CH₂-

10 X = -(CH₂)₆-



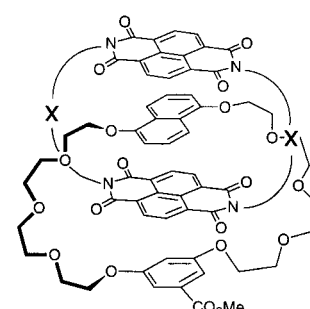
11 X = -CH₂-C≡C-C≡C-CH₂-

12 X = -(CH₂)₆-



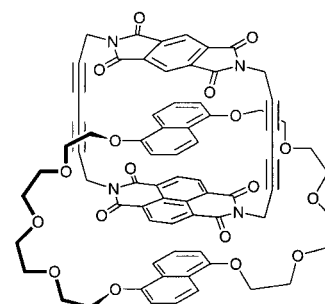
13 X = -CH₂-C≡C-C≡C-CH₂-

14 X = -(CH₂)₆-

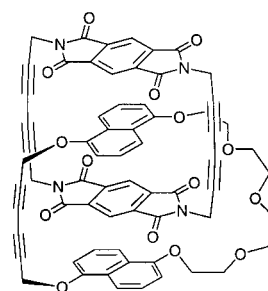


15 X = -CH₂-C≡C-C≡C-CH₂-

16 X = -(CH₂)₆-



17



18

Results and Discussion

Electrochemistry

Model compounds and catenane precursors: Electrochemical analysis by cyclic voltammetry (CV) of aromatic diimide derivatives **1–5** reveals the presence of two sequential reduction processes, each being chemically and electrochemically reversible on the CV experiment timescale. The formal electrode potentials for these redox changes are compiled in Table 1.^[11] With the exception of the electrogenerated monoanions of acetylenic pyromellitic diimides **2** and **3**, which undergo slow decomposition reactions, the monoanions proved to be stable over the increased timescale of macroelectrolysis.

Viehbeck and co-workers have determined the forms of the radical-anionic and dianionic species of various aromatic diimides by combining CV with IR and UV spectroscopic

Table 1. Formal electrode potentials (E° [V] vs. SCE) and peak-to-peak separations (ΔE_p [mV]) for the two consecutive one-electron reductions displayed by aromatic diimides **1–5** in dichloromethane (0.2 M [NBu₄][PF₆] supporting electrolyte).

	$^1E^\circ$	ΔE_p [a]	$^2E^\circ$	ΔE_p [a]
1	−0.95	62	−1.53	76
2	−0.82	72	−1.42	98
3	−0.96	72	−1.60	80
4	−0.70	64	−1.12	62
5	−0.60	82	−1.02	84

[a] Measured at 0.2 V s^{−1}.

analysis.^[11] These sequential reduction processes for pyromellitic and naphthalene diimides are shown schematically (Figure 1). They also examined the effects of *N*-substitution

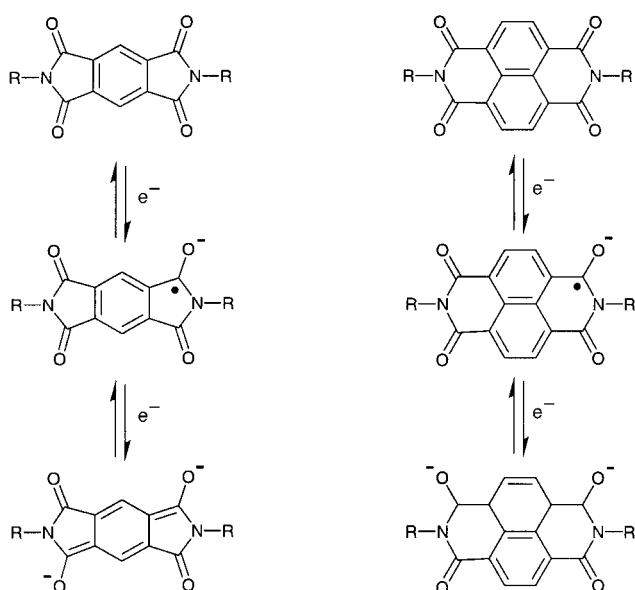


Figure 1. Reversible sequential one-electron reduction processes for pyromellitic and naphthalene diimides (from ref. [11]; *syn* and *anti* designations for the negative charges in the dianions are as described therein).

in the diimide framework. Our results for the model compounds and catenane precursors **1–5** agree with their findings: i) expansion of the aromatic framework from benzene to naphthalene yields more readily reduced derivatives and ii) *N*-substitution has a significant effect on the reduction potentials.

The former observation may be ascribed to extended delocalisation of the additional charge. The effect of *N*-substitution is perhaps greater than might be expected since the MO descriptions of aromatic imides have a node at nitrogen,^[12] implying that *N*-substituents should perhaps only weakly affect the LUMO energy, a parameter directly related to the first reduction potential of the substrate.^[11] However, it is clear from the values in Table 1 that the inductive effects of the substituents play an important role in determining the values of the redox potentials for both pyromellitic and naphthalene diimide derivatives. For both cases, diimides bearing electron-donating substituents ought to be harder to reduce, because of their increased electron density, than those

with electron-withdrawing substituents for which additional stabilisation of charge might be achieved. In both diimide series, **1–3** and **4–5**, it is easier by around 0.1 V (i.e., a less negative potential is required) to reduce the acetylenic derivatives than those bearing simply alkyl substituents. Diimide **3**, equipped with *two* alkyl groups and *one* acetylene substituent, presents a very similar reduction profile to mono-alkyl derivative **1**, perhaps indicating that the two different substituents have opposing electronic effects of similar magnitude.

[2]Catenanes, *general characteristics*: The incorporation of two units of **2** within an interlocked assembly with macrocyclic polyether **6**, to form the [2]catenane assembly **9**, would be expected to give rise to two two-electron redox couples if there were either no electronic communication between the individual diimide subunits, or if these units were rendered identical by some dynamic process occurring within the catenane on the CV timescale.^[13] However, as observed for related interlocked molecules containing electroactive subunits, pyromellitimide [2]catenane **9** and its naphthalene analogue **11** both exhibit a splitting of the first reduction followed by a further two-electron reduction process. Figure 2 shows the CV trace for [2]catenane **9**.

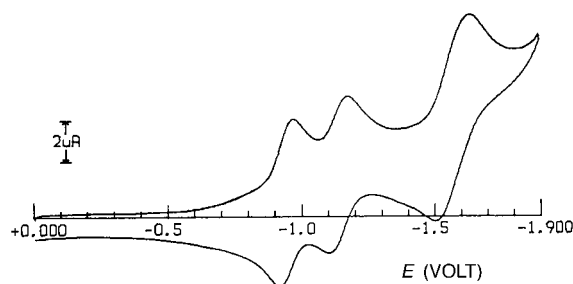


Figure 2. Cyclic voltammetric response recorded at a platinum electrode of [2]catenane **9** (0.4 mM in CH₂Cl₂; 0.2 M [NBu₄][PF₆] supporting electrolyte; scan rate 0.2 V s^{−1}).

The lack of direct conjugation between the two diimide subunits that comprise the electron-accepting macrocycle of [2]catenanes **9** and **11** suggests that the most likely explanation for the observed electrochemical behaviour is the same as previously advanced for [2]catenanes based on electron-accepting bipyridinium units.^[14] The observation of two separate reductions for the first redox process indicates, as supported by our earlier NMR and photophysical studies, a topological difference between the diimide units.^[15] Those sandwiched between the electron-rich naphthalene diethers are more stabilised and therefore harder to reduce than those on the outside of the catenane assembly. This difference in ease of reduction results in the observation of distinct single-electron reduction processes for each diimide subunit. The further two-electron reduction feature is the likely result of the presence of an additional electron in each diimide system. After the first reduction of both diimides the increased electron density must reduce their electron-accepting properties to such an extent that the stabilising donor–acceptor interactions between the catenane subunits which maintain

the inside/outside topological differences are lost. The result is that the second reduction processes for both diimides occur at the same potential and therefore appear as a *single* two-electron feature.

Electrochemical data for **9**, **11**, and five other related [2]catenanes are presented in Table 2. Analogous CV characteristics to those presented by **9** and **11** were observed for

Table 2. Formal electrode potentials (E° [V] vs. SCE) for the reduction processes displayed by [2]catenanes **9–13**, **17** and **18** in dichloromethane (0.2 M [NBu₄][PF₆] supporting electrolyte).

	$E_{0/1}^\circ$	$E_{1-/2-}^\circ$	$E_{1-/3-}^\circ$	$E_{2-/4-}^\circ$	$E_{3-/4-}^\circ$
9	–0.94	–1.14	–	–1.57	–
10	–1.07	–1.21	–	–1.65	–
11	–0.70	–0.98	–	–1.18	–
12	–0.83	–1.11	–	–1.32	–
13	–0.96	–1.09	–	–1.58	–
17	–0.76	–	–1.19	–	–1.57
18	–0.94	–1.19	–	–1.60	–

their hydrogenated analogues **10** and **12**, and also for the ester-substituted derivative **13**. The remaining entries in the table are for [2]catenane **17**, which contains an example of each of the aromatic diimides, and **18**, which has three butadiyne linkages in its structure; these two systems are discussed separately later in this section. There was insufficient material for complete electrochemical characterisation of [2]catenanes **14–16**. However, by comparison between pairs of [2]catenanes we can examine the separate effects of the replacement of a pyromellitic with a naphthalene diimide (**9** ↔ **11**, **10** ↔ **12**), hydrogenation of the butadiyne links (**9** ↔ **10**, **11** ↔ **12**) and the introduction of a less competent donor unit in the crown macrocycle (**9** ↔ **13**).

Effects of replacing pyromellitic with naphthalene diimides: Unremarkably, the reduction potentials for pyromellitimide [2]catenane **9** are found at more negative potential than those of its naphthalene analogue **11**, a predictable consequence of the better electron-accepting ability of the naphthalene diimide unit (e.g., **1** ↔ **4**). The same trend is revealed by comparing pairs of hydrogenated derivatives (e.g., **10** ↔ **12**).

Effects of hydrogenation of the linkers in the diimide macrocycle: For both **9** and **11**, hydrogenation of the butadiyne links to afford **10** and **12**, respectively,^[16] results in shifts of the first reduction waves for each of the diimide units to more negative potential. In the saturated derivatives it is harder, by around 0.1 V, to reduce the diimide units, indicating that they are stabilised relative to their counterparts in their precursor [2]catenanes **9** and **11**. This behaviour is in agreement with the reduction potentials recorded for the model compounds which reveal that the effect of converting an acetylenic link to a saturated carbon chain is to make it around 0.1 V harder to introduce both the first and second electrons to the saturated derivatives for both diimide series. Such additional stabilisation is also supported by the photophysical investigation described in the following section. As with the parent systems the second reduction potentials for **10** and **12** occur

simultaneously, consistent with the loss of donor–acceptor interactions and inside–outside differentiation after the first reduction. From these data it is not possible to separate the effects on the diimide reduction potentials of the [2]catenanes into contributions arising from i) the saturation of the *N*-substituent and ii) an alteration in the relationship between the electron-deficient diimides and the electron-rich diethers of the crown. However, we shall see that the photophysical studies certainly support a significant contribution from the latter.

Effects of replacing the dinaphtho crown with an asymmetric analogue: Replacing the symmetrical dinaphtho crown ether present in [2]catenane **9** with the asymmetric crown present in **13** has only a small effect on the first reduction potential (for the outer diimide), but the central diimide (corresponding to the second reduction potential) is 0.05 V easier to reduce in the asymmetric system **13**. If we regard the ester-substituted aromatic ring of the crown as being, at best, π -neutral then we would expect the dominant solution co-conformer to be that with the electron-rich naphthalene diether sandwiched between the two diimide units.^[16] The small shift in the first reduction potential between **9** and **13** is therefore unsurprising, since the outer diimide in both catenanes will be adjacent to, and influenced by, a single naphthalene diether. The shift in potential of the second reduction (the inner diimide) implies a weakened stabilising influence from the adjoining aromatic diethers, entirely consistent with the predicted electronic character of the ester-substituted aromatic unit. We have argued above that the addition of a second electron to each of the diimide units results in complete loss of ordering interactions and that therefore both diimides acquire a second electron at the same potential. This situation is also observed for [2]catenane **13**, in which the third reduction process corresponds to two electrons and occurs at an essentially identical potential to that found for **9**, thereby confirming the diimide unit's indifference to the nature of the aromatic diether units of the crown once internal ordering interactions have been lost. To illustrate the arguments presented in this and the preceding section a graphical representation of the positions and shifts of the reduction potentials of the parent pyromellitimide precursor **2** and its derivative [2]catenanes **9**, **10** and **13** is shown in Figure 3.

Analysis of tris-butadiyne-linked [2]catenane 18: The unusual [2]catenane **18**, revealed as a highly constrained system by X-ray crystallography and ¹H NMR studies, nonetheless exhibits quite similar electrochemical characteristics to **9**, a system containing identical electroactive units.^[17] The only difference is a 50 mV shift towards more negative potential of the second reduction wave, that is, that for the central diimide. In this rigidified system, such additional stabilisation of the central diimide could seem an unexpected result; some contribution to this behaviour could, however, come from the insertion of the triple bonds in the crown ether structure. We have seen that the electron-accepting ability of diimides **1–5** is affected by the nature of their *N*-substituents, and perhaps the donor ability of the naphthalene diethers is similarly modified. Unfortunately, an estimation of the

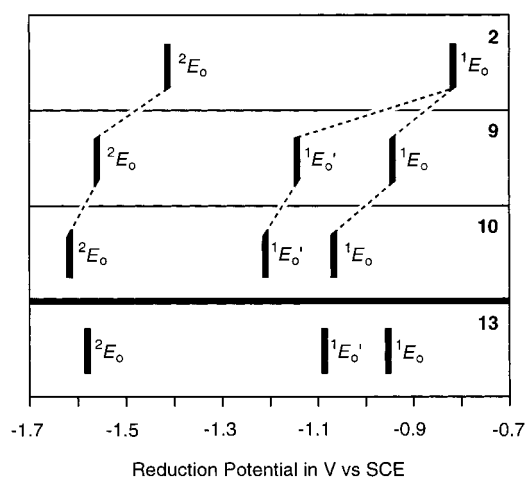


Figure 3. Graphical summary of the electrochemical data for **2**, **9**, **10** (a direct derivative sequence) and **13** (${}^1E_o'$ and 1E_o denote the first one-electron reduction processes, 2E_o is the second two-electron process).

respective donor abilities of **6** and **8** by measurement of their oxidation potentials is problematic, since these oxidation processes are irreversible for all the current systems (with the partial exception of **6**).

Analysis of mixed diimide [2]catenane 17: The electrochemical response of the asymmetric [2]catenane **17** appears on first inspection to be somewhat different from those of the above described systems in that a single two-electron reduction process interposes two distinct one-electron reductions (Figure 4). Earlier photophysical investigation of this system

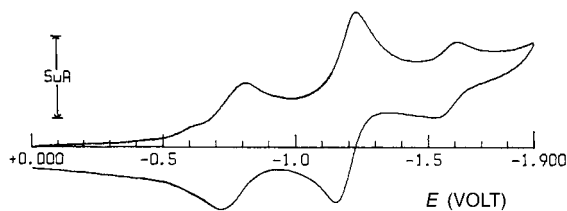


Figure 4. Cyclic voltammetric response recorded at a platinum electrode of [2]catenane **17** (0.4 mM in CH_2Cl_2 ; 0.2 M $[\text{NBu}_4][\text{PF}_6]$ supporting electrolyte; scan rate 0.2 V s^{-1} ; the slight leading shoulder reveals the presence of a small amount of diimide precursor **5**).

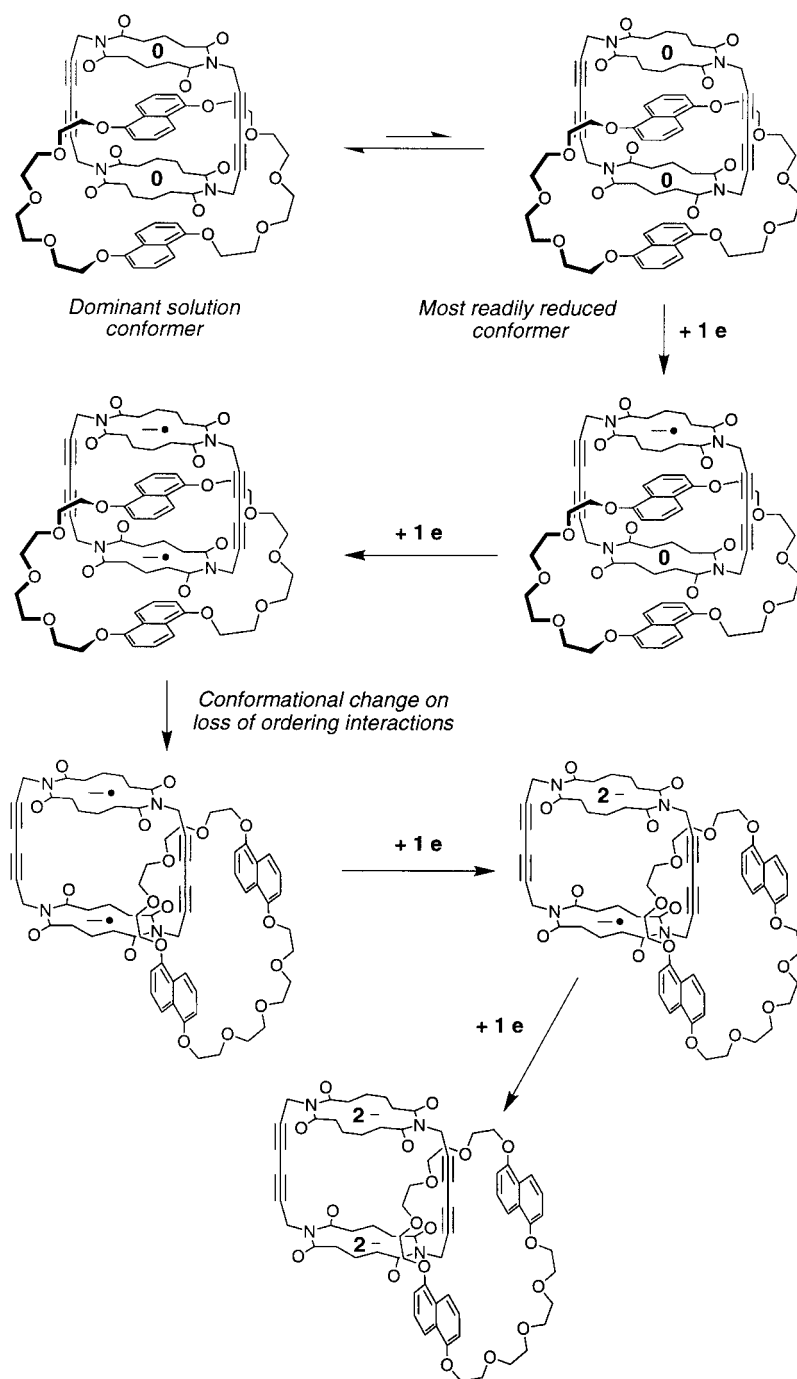
revealed that of the two possible translational isomers (either the benzene or naphthalene diimide could be sandwiched within the crown macrocycle), that with the naphthalene diimide in the central position is favoured by around 85:15 in dichloromethane.^[15] We would therefore expect to observe four formally distinct one-electron reduction processes for **17**, two for the inner naphthalene diimide and two for the peripheral pyromellitic diimide. A possible sequence of events to rationalise the observed CV trace can, to good approximation, be constructed by using the redox values obtained for symmetrical [2]catenanes **9** and **11**. Starting from the dominant translational isomer of **17**, with the naphthalene diimide included in the crown macrocycle, we might expect the first reduction to correspond to an “inside” naphthalene diimide. The fact that the observed value (${}^1E_o' = -0.76 \text{ V}$) is actually rather closer to that assigned to the “outside” diimide

in symmetrical [2]catenane **11** perhaps reveals that the timescale of electrochemical reduction readily overcomes the effect of a favoured solution co-conformation. The most readily reduced co-conformer may not dominate in solution, but, as long as it is generated rapidly with respect to the sweep rate of the electrochemical experiment, even a small equilibrium concentration will ensure the initial reduction will occur from this form. Within this first-generated catenane monoanion the best acceptor is the neutral pyromellitic diimide. We would therefore expect the assembly to translate to a co-conformation in which this diimide is bound within the crown macrocycle: the second reduction potential will therefore correspond to the addition of one electron to the “inside” pyromellitic diimide (${}^1E_o' \approx -1.14 \text{ V}$ in [2]catenane **9**). Now both diimides are sufficiently electron rich that they can no longer enter into donor–acceptor complex formation and the second reduction potential for each diimide matches that found for the individual [2]catenanes **11** and **9** (${}^2E_o' \approx -1.18$ and -1.57 V , respectively). The overall appearance of the CV trace for [2]catenane **17** is thus explained by the near coincidence of the first reduction potential of the pyromellitic diimide with that of the second for the naphthalene diimide, resulting in an apparent two-electron reduction wave sandwiched by two one-electron features. The proposed series of electrochemical and translational events is depicted in Scheme 1.

Photophysics

Absorption spectra: As previously reported for **9**, **11** and **17**, the absorption spectra of [2]catenanes **10**, **12–16** and **18** differ from the sum of the absorption spectra of their crown and diimide components.^[15] In all cases, the absorption bands of the components undergo noticeable decreases in intensity accompanied by small red shifts when incorporated in [2]catenanes; an intense tail in the 340–440 nm region and the presence of a new broad band in the 400–600 nm region are also revealed (Figures 5 and 6 and Table 3). Collectively, these observations support the establishment of reasonably strong donor–acceptor interactions between the electron-rich aromatic units of the crowns and the electron-deficient diimides. As mentioned above, the photophysical characterisation of [2]catenanes **9**, **11** and **17** has been reported and the key features of their photophysical behaviour are reproduced here for purposes of comparison.^[15]

[2]Catenanes **9–18** comprise quite a large series and it is worth reviewing at this point the theoretical basis of the effect on the absorption spectrum of changing a structural parameter in the catenane skeleton. The most diagnostic band in the absorption spectrum for this kind of compound is the new charge-transfer (CT) band that appears in the 400–600 nm region upon molecular interlocking (Figures 5 (bottom) and 6 (bottom), Table 3), though it should be noted that the observed CT absorption is most often a sum of closely related CT transitions, which involve several different inter-unit interactions within a structurally complex molecule containing several donors and acceptors. The most relevant features of this absorption band, its wavelength and intensity, can be correlated to structural parameters according to the theory of



Scheme 1. Schematic representation for the electrochemical and translational changes occurring upon reduction of mixed pyromellitic-naphthalene diimide [2]catenane **17** (for purposes of clarity the diimide units are shown in outline only).

Hush.^[18, 19] The energy (E_{op}) for the optical electron-transfer transition (and as a consequence, the position of the absorption maximum) is correlated with the energy gradient (ΔE) between the ground and the excited state of a system, and to the total reorganisation energy (λ) involved in the charge-transfer process [Eq. (1)]. The molar absorption

$$E_{\text{op}} = \Delta E + \lambda \quad (1)$$

$$\epsilon = \frac{2380 r^2}{E_{\text{op}} \Delta \bar{\nu}^{1/2}} H_{\text{DA}}^2 \quad (2)$$

coefficient (ϵ) can in turn be correlated with the magnitude of the electronic-coupling matrix element (H_{DA}) between the donor and the acceptor moieties [Eq. (2); r = donor/acceptor spacing, $\Delta \bar{\nu}^{1/2}$ = band halfwidth in cm^{-1}].

As with our approach to the examination of the electrochemical characteristics of the [2]catenanes, we can also examine pairs of molecules to partition out the effects of various structural features on their photophysical characteristics. Three general trends are immediately discerned when the positions of the band maxima (λ_{max}) of catenanes **9–16** are compared: shifts toward higher energies can be observed i) on replacing naphthalene with pyromellitic diimides (**9** ↔ **11**, **10** ↔ **12**, **13** ↔ **15**, **14** ↔ **16**), ii) on hydrogenation of the butadiyne links connecting the diimide components (**9** ↔ **10**, **11** ↔ **12**, **13** ↔ **14**, **15** ↔ **16**) and iii) for those catenanes containing the symmetrical dinaphtho crown (**9** ↔ **13**, **11** ↔ **15**), though this effect is rather small for the hydrogenated systems (**10** ↔ **14**, **12** ↔ **16**). When the molar absorption coefficients (ϵ_{max}) of these features are compared, the intensity of the band is found to be higher i) for those catenanes containing the pyromellitimide unit (**9** ↔ **11**, **10** ↔ **12**, **13** ↔ **15**, **14** ↔ **16**), ii) for the hydrogenated catenanes (**9** ↔ **10**, **11** ↔ **12**, **13** ↔ **14**, **15** ↔ **16**) and iii) for those catenanes containing the symmetrical dinaphtho crown (**9** ↔ **13**, **10** ↔ **14**, **11** ↔ **15**, **12** ↔ **16**). A useful rationale for these observations requires support from

data obtained with other techniques. [2]Catenane **18** will be discussed after considering the relationships within the series **9–16**.

The shift of the maximum of the CT band towards higher energies on replacing the naphthalene diimides with pyromellitimide units is wholly consistent with our electrochemical data, which revealed that the pyromellitimide derivatives, whether as model compounds or when incorporated in [2]catenanes, were significantly harder to reduce than their naphthalene analogues: it is harder to introduce additional charge to pyromellitimide derivatives, as expected.^[11]

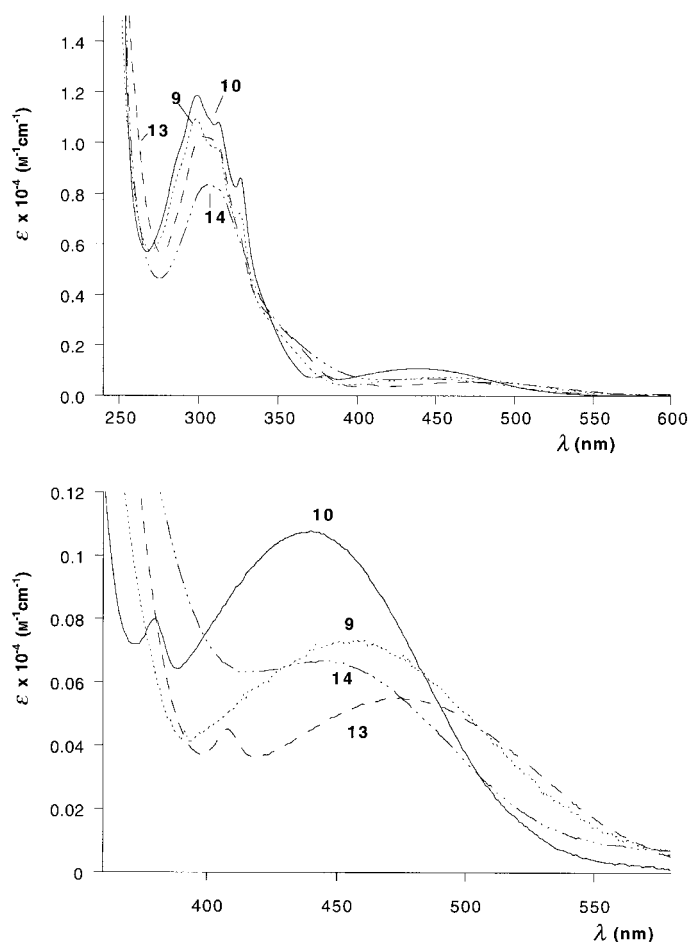


Figure 5. Top: absorption spectra of pyromellitimide derived [2]catenanes **9**, **10**, **13** and **14** (in CH_2Cl_2). Bottom: expansion of the CT region of the absorption spectra of **9**, **10**, **13** and **14** (in CH_2Cl_2).

The higher values of E_{op} [Eq. (1)], the energy of the optical electron-transfer transition, observed for the hydrogenated [2]catenanes (Table 3; **9** → **10** ca. 90 meV, **11** → **12** ca. 140 meV) correlate reasonably well (see Appendix) with the higher energy required for electrochemical reduction of the acceptor units in the [2]catenanes (Table 2; **9** → **10** and **11** → **12**, ΔE ca. 130 mV). The considerably higher intensity observed for hydrogenated [2]catenanes **10**, **12**, **14** and **16** can be explained by a stronger interaction between the electron-rich and electron-deficient units; such an increase of the degree of interaction is a likely result of a decrease in the rigidity of the constituent macrocycles so allowing adoption of a more optimal arrangement, a prediction supported by modelling studies.^[16] Further evidence in support of this view is provided by the greater distortion experienced by the strong absorption bands of the naphthalene diimide units (in the 340–400 nm region) of **12** when compared with those of **11**.

Those catenanes containing the asymmetric crown possess a unit with a higher oxidation potential, a poorer electron-donating unit, than those present in dinaphtho crown **6**. Accordingly, this unit is only likely to contribute to the CT absorption band of its derivative catenanes at higher wavelengths, with a correspondingly reduced contribution in the 440–600 nm region. This rationale provides an explanation for the lower absorption coefficients found in this part of the

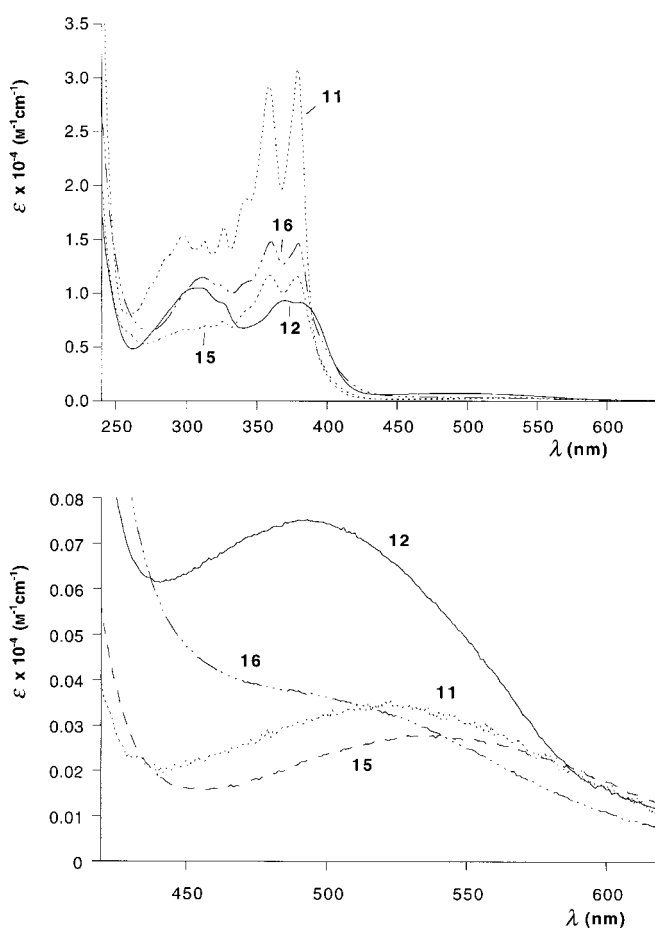


Figure 6. Top: absorption spectra of naphthalene diimide derived [2]catenanes **11**, **12**, **15** and **16** (in CH_2Cl_2). Bottom: expansion of the CT region of the absorption spectra of **11**, **12**, **15** and **16** (in CH_2Cl_2).

Table 3. Absorption maxima (λ_{max}) and molar absorption coefficients (ϵ_{max}) of the CT bands of the [2]catenanes in CH_2Cl_2 .

	λ_{max} [nm]	ϵ_{max} [$\text{M}^{-1}\text{cm}^{-1}$]
9	455	730
10	440	1080
11	523	350
12	493	750
13	478	550
14	446	670
15	542	280
16	490	380
17	500	880
18	448	460

spectrum (**9** ↔ **13**, **10** ↔ **14**, **11** ↔ **15**, **12** ↔ **16**). Our electrochemical results are not comprehensive for these comparisons, but the shift to lower energy of the CT band from **9** with **13** is in agreement with the readier reduction of the inside pyromellitimide unit. As discussed in the electrochemical section, the inside pyromellitimide is less stabilised by one electron-rich naphthalene system and one carboxylate-substituted phenyl diether than by two naphthalene diethers and is consequently rather easier to reduce.

The absorption spectrum of the asymmetric [2]catenane **18** differs from the sum of the absorption spectra of its crown and

diimide components **2** and **8**, once more supporting the establishment of a reasonably strong donor–acceptor interaction between the electron-rich naphthalene diethers and the electron-deficient pyromellitimide units. The charge-transfer absorption band may be directly compared with the corresponding CT feature for [2]catenane **9**, since these systems have identical chromophoric units. Comparative spectra (Figure 7) reveal the CT absorption band in unsymmetrical

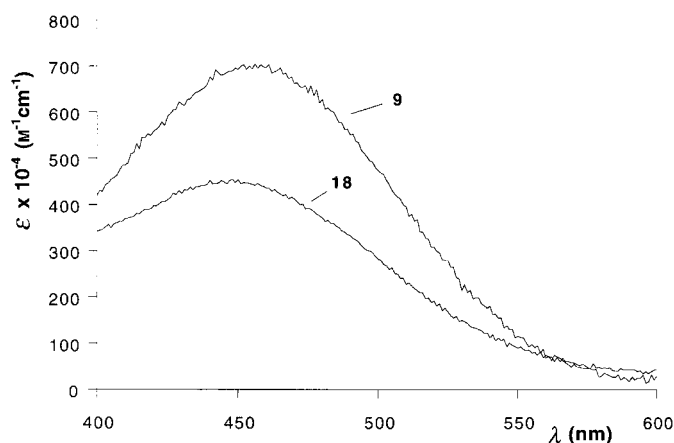


Figure 7. Comparison of the CT region of the absorption spectra of [2]catenanes **9** and **18** (in CH_2Cl_2).

[2]catenane **18** to be both weaker and shifted to slightly higher energy relative to the corresponding feature of symmetrical [2]catenane **9**. The difference between the two absorption maxima (0.048 eV, Table 3) is in agreement, according to Equation (1), with the difference in the reduction potential (50 mV, Table 2) of the pyromellitic diimide units lying inside the catenane structures. The diminished absorption coefficient of **18** can be attributed to a reduced electronic coupling of the donor and acceptor constituents, a likely consequence of less than optimal donor–acceptor overlap. Collectively, these findings support a view of [2]catenane **18** as a rather distorted system unable to accommodate the more efficient overlap of complementary π -frameworks presented by the closely related, but more structurally adaptable [2]catenane **9**. The solid-state analysis of [2]catenane **18** revealed the rather congested nature of this system and the relative geometric relationships between the interacting components may offer support for this conclusion.^[17] Additionally, we cannot exclude the possibility that the reduced number of hydrogen-bonding acceptor sites in macrocycle **8** plays a role in reducing the interaction between the electron-rich and -deficient components of **18** since such $\text{C-H}\cdots\text{O}$ hydrogen bonds are receiving increasing attention as a considerable organising force in molecules of this type.^[20]

Luminescence spectra and excited-state lifetimes: At room temperature acyclic bis-acetylene polyether **7** presents an intense structured luminescence band with maxima at 330 and 345 nm ($\tau = 8.0$ ns), ascribed to the π – π^* transition of the constituent 1,5-dialkoxy-naphthalene units; 1,5-dimethoxy-naphthalene exhibits identical fluorescence quantum yields and excited-state lifetimes. A similar luminescence band, but

1000-fold weaker ($I_{\text{rel}} = 0.1\%$), and with a shorter lifetime ($\tau \leq 0.4$ ns), was observed for the cyclic analogue **8**. The luminescence behaviour of this macrocycle differs substantially from that found for the symmetrical crown component **6**, in which only a little quenching was observed ($I_{\text{rel}} = 70\%$, $\tau = 7.5$ ns) with respect to 1,5-dimethoxynaphthalene and **7**. This observation is likely to reflect an increased interaction between the two chromophoric groups of **8**, though as the aromatic residues are tied together with an inflexible hexadiyne linker, the mechanism of interaction is unlikely to involve a co-facial arrangement. As already reported,^[15] no room temperature luminescence is observed for acetylenic pyromellitimide derivative **2**, while a very weak luminescence ($\lambda_{\text{max}} = 425$ nm, $\tau < 0.4$ ns) is observed for the hexyl analogue **1**. A structured, weak fluorescence band is exhibited by naphthalene diimide **5** (387 and 408 nm; $\tau < 0.4$ ns), which may also be assigned to a π – π^* transition.^[15]

The [2]catenane **11**, which contains naphthalene diimide, displays a similar, but lower intensity, fluorescence band to that observed for the free diimide **5**, and again the lifetime is shorter than 400 ps. Catenanes **9** and **11** exhibit, as already reported, a similar, though once again weakened, fluorescence band to that observed for the parent crown ether if excitation is performed at wavelengths shorter than 330 nm, that is, below the wavelength required for diimide excitation. The lifetime of this band for [2]catenane **11** is equal to that observed for the fluorescence of crown **6** (7.5 ns), whilst for catenane **9** the decay profile can only be fitted by employing two exponential terms and reveals the presence of a double lifetime ($\tau_1 = 1.3$ ns and $\tau_2 = 7.5$ ns, respectively). No fluorescence was observed for the catenanes **10** and **12–16**.

Surprisingly, [2]catenane **18** exhibits a new, very intense ($\Phi > 0.1$) luminescence band centred at 412 nm ($\tau = 8.4$ ns; Figure 8). The excitation spectrum of this band is also

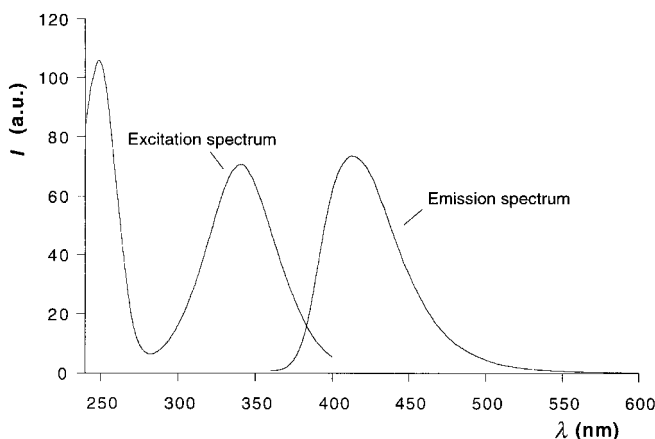


Figure 8. Excitation and emission spectra for [2]catenane **18** (in CH_2Cl_2).

surprising, since it does not match the absorption spectra of either the catenane or its components, rather it has a maximum at $\lambda = 342$ nm. The same bands were observed in acetonitrile, with a blue shift to 336 nm in the excitation spectrum. The possibility that this unusual fluorescent behaviour might have arisen from the presence of a trace of contaminant in the catenane sample was eliminated by HPLC

analysis: whilst a trace of an absorbing impurity was revealed in the sample, only the catenane-containing fraction displayed the unusual fluorescent behaviour.

The new luminescence band observed for [2]catenane **18** cannot be explained in terms of a pure charge-transfer transition, since its energy is higher than that of the CT band observed in its absorption spectrum. In principle, a strongly perturbed pyromellitimide unit, whose absorption maximum was shifted from 320 to 340 nm, could give rise to a feature of this kind. However, other explanations cannot be excluded on the basis of our experiments. We have shown that catenane **18** is the source of the observed fluorescence, but we can do no more than speculate about the mechanism of its generation. We have previously discussed the rather distorted solid-state structure of **18** and noted that the ^1H NMR spectrum reveals no site-exchange processes at room temperature.^[17] It is possible that the external diimide unit is structurally distorted, so altering the excitation wavelength, and, in addition, prevented from decaying from its excited state in a radiationless fashion by its non-optimal overlap with the remainder of the catenane donor–acceptor stack. However, in the absence of comparative models for **18** (other than **9**) these ideas must be treated as no more than conjecture. The 412 nm luminescence band observed for [2]catenane **18** at room temperature in solution was also observed at 77 K in a solid matrix ($\tau = 8.5$ ns), though the corrected excitation spectrum shows a slightly red-shifted maximum. The lack of phosphorescence activity at 77 K may indicate that the CT excited state promotes nonradiative deactivation to the ground state, a kinetically favoured process over conversion to the long-lived triplet excited states from which phosphorescence originates. However, we are once again addressing issues pertaining to a single, rather unique molecule and lack suitable model systems with which to compare these observations.

Luminescence spectra measured at 77 K revealed that acyclic bis-acetylene **7** ($\lambda_{\text{max}} = 345$ nm, $\tau = 9.8$ ns), dinaphtho crown **6** ($\lambda_{\text{max}} = 345$ nm, $\tau = 9.6$ ns) and naphthalene diimide **5** ($\lambda_{\text{max}} = 413$ nm, $\tau = 0.5$ ns) exhibit intense, structured fluorescence bands. Hexyl pyromellitimide **1** shows only weak fluorescence ($\lambda_{\text{max}} = 420$ nm, $\tau < 0.5$ ns), while acetylenic diimide **2** and macrocycle **8** do not exhibit any fluorescence. Relatively strong phosphorescence is observed for acyclic bis-acetylene **7** ($\lambda_{\text{max}} = 490$ nm, $\tau = 1200$ ms), the dinaphtho crown **6** ($\lambda_{\text{max}} = 488$ nm, $\tau = 1200$ ms), pyromellitimide derivatives **1** and **2** ($\lambda_{\text{max}} = 480$ nm, $\tau = 410$ ms) and naphthalene diimides **4** and **5** ($\lambda_{\text{max}} = 619$ nm, $\tau = 41$ ms). No phosphorescence is observed for macrocycle **8**. The lack of phosphorescence of this species can be ascribed to the same interchromophore interaction responsible for the fluorescence quenching observed at room temperature.

Neither fluorescence nor phosphorescence is observed for any of the catenanes at 77 K. Fluorescence quenching in the catenane structures has previously been ascribed to the presence of the CT excited state. The quenching is not complete at room temperature for catenanes **9** and **11**, while it is complete for **10** and **12–16** and as mentioned above, for all catenanes, at 77 K.

Incomplete quenching for **9** and **11** was attributed to the dynamic movement of the donor and acceptor units in the

catenane structure.^[15] For the hydrogenated catenanes **10**, **12**, **14** and **16** a stronger electron donor–acceptor interaction was invoked to explain the increase in intensity of the CT absorption band. Such an increased degree of interaction, perhaps accompanied by a slowing of the dynamic processes within the catenanes that break the donor–acceptor pairings, might well be associated with an increased fluorescence-quenching capacity. As previously advanced, this argument is also used to explain the general lack of any luminescence at 77 K, at which temperature all dynamic motion is expected to be frozen.^[15]

Conclusion

In this paper we have attempted to correlate the electrochemical and photophysical properties of quite a large series of related [2]catenanes and their precursors with structural features. Each change has been examined in isolation by making pairwise comparisons with derivatives that differ in only one of several possible structural features. Variations in the geometric relationships between the electron-donor and -acceptor units, conferred by alterations in the bridges linking the interlocked macrocycles, reveal how the structures of the molecules can impose topological distinctions on otherwise identical subunits, and how the electron donor–acceptor properties of the systems are relatively sensitive to their immediate environment. Of particular note are the changes observed for those systems in which an existing interlocked molecule is structurally modified, altering the relationship between their constituent donor and acceptor subunits and therefore their absorption characteristics and electrochemical profiles.

The electrochemical investigations revealed that the shifts of the diimide redox processes upon molecular interlocking are generally greater (for example, $\Delta^2E^\circ = 260\text{--}410$ mV) than those observed for related catenanes containing the same crown ether and bipyridinium units as acceptor moieties ($\Delta^2E^\circ < 300$ mV).^[14] Theoretical issues aside, this observation could be important for further developments: larger shifts might allow redox couples to be manoeuvred into “windows” in order that a particular electrochemical process can be realised without perturbing other redox active units within a molecule. If such events are linked to structural and/or functional changes then such fine control of behaviour could be exploited to significant advantage.^[21, 22] The distinct electrochemical signatures of pyromellitic and naphthalene diimides provide an additional dimension of redox control, whilst their common chemical properties allow standardised routes to be employed to achieve their incorporation in structurally complex molecules.^[15]

Experimental Section

Materials: Preparative details for all the [2]catenanes and their precursors discussed in this work have been reported previously.^[15–17] HPLC analysis and purification of [2]catenane **18** was performed with a Hewlett Packard 1050 HPLC (Supelcosil ABZ + PLUS column; 10 mm NH_4OAc

in H₂O containing 0.1% HCO₂H, then 95:5 MeCN/H₂O containing 0.05% HCO₂H).

Electrochemistry: The techniques and apparatus for recording electrochemical measurements have been described elsewhere.^[23] All the potential values are expressed with reference to the saturated calomel electrode (SCE); under the experimental conditions the reversible one-electron oxidation of ferrocene occurs at +0.37 V. For aromatic diimides **1–5** the application of controlled potential coulometry to the first reduction step reveals the consumption of one-electron per molecule. For the catenanes the number of electrons involved in the second two-electron reduction is inferred from the CV profile, controlled potential coulometry failed as an electron-counting test owing to decomposition of the electrogenerated anions to further reducible by-products. Prior to examination of the interlocked systems it was confirmed that the macrocyclic polyethers **6** and **8** did not display redox activity in the region of interest in the electrochemical experiments. Both species undergo irreversible oxidation at peak potentials of +1.05 and +1.21 V, respectively. Despite repeated preparative thin-layer chromatography a stubborn trace of precursor diimide **5** remained in the sample of [2]catenane **17** used in the CV experiment; this is revealed the slight leading shoulder in the trace (see Figure 4).

Photochemistry: Photophysical experiments were conducted in CH₂Cl₂ at room temperature, and in an opaque rigid CH₂Cl₂ matrix for the low-temperature (77 K) luminescence measurements. Absorption spectra were recorded with a Perkin Elmer λ 16 spectrophotometer. Uncorrected emission spectra, corrected excitation spectra and phosphorescence lifetimes were obtained with a Perkin Elmer LS50 spectrofluorimeter. The fluorescence lifetimes (uncertainty, $\pm 5\%$) were obtained with an Edinburgh single-photon-counting apparatus (D₂ filled flash lamp). Emission spectra in a CH₂Cl₂ rigid matrix at 77 K were recorded by using quartz tubes immersed in a quartz Dewar filled with liquid nitrogen. In order to allow comparison of emission intensities, corrections for instrumental response, inner filter effects and phototube sensitivity were performed.^[24]

Appendix

Correlation of $\Delta\lambda$ with ΔE : Within the series of [2]catenanes there should exist reasonable correlations, although other variables need to be considered [see Eqs. (1) and (2)] between related pairs of systems: the shift in the maximum of the CT absorption ($\Delta\lambda$) is connected through Equation (1) with the electrochemical reduction potential (ΔE). For example, if we consider catenanes **11** and **12** we note a difference in the first reduction potential of 0.13 V. The CT band of acetylenic catenane **11** appears at 523 nm; this wavelength may be converted to an energy (in wavenumbers, cm⁻¹) by taking its reciprocal and multiplying by 10⁷ (to convert nm to cm). Subsequent conversion to units of eV (1 eV = 8080 cm⁻¹) yields the energy of the CT band in appropriate units: $(10^7/523)/8080 = 2.37$ eV. In the saturated analogue **12** it is 0.13 V harder to introduce an electron to the diimide system, that is, an additional 0.13 V per electron is required and we would expect the energy of the CT transition, in eV, to increase by this amount: $2.37 + 0.13 = 2.50$ eV. The expected wavelength of the transition may now be calculated by converting this energy back into units of wavenumbers and expressing the value in nm: $(10^7/\lambda)/8080 = 2.50$ eV, therefore $\lambda = 10^7/(2.50 \times 8080) = 495$ nm, that is, a blue-shift of 28 nm. The value calculated in this manner is close to the experimentally observed value of 493 nm.

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