

Shape-Persistent Macrocycles Functionalised with Coumarin Dyes: Acid-Controlled Energy- and Electron-Transfer Processes

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Abstract: We have investigated the spectroscopic properties (absorption spectra, emission spectra, emission lifetimes) of three triads in CH₂Cl₂: C2-M-C2, C343-M-C343, and C2-M-C343, in which M is a shape-persistent macrocyclic hexagonal backbone composed of two 2,2'-bipyridine (bpy) units embedded in opposing sides, and C2 and C343 are coumarin 2 and coumarin 343, respectively. All the components are strongly fluorescent species ($\Phi = 0.90, 0.79,$ and 0.93 for M, C2, and C343, re-

spectively, as established by investigating suitable model compounds). In each triad excitation of M leads to almost quantitative energy transfer to the lowest coumarin-localised excited state. Upon addition of acid, the two bpy units of the M component undergo independent protonation leading to

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monoprotonated (e.g., C2-M·H⁺-C2) and diprotonated (e.g., C2-M·2H⁺-C2) species. Further addition of acid leads to protonation of the coumarin component so that each triad is involved in four protonation equilibria. Protonation causes strong (and reversible, upon addition of base) changes in the absorption and fluorescence properties of the triads because of inversion of the excited-state order and/or the occurrence of electron-transfer quenching processes.

Introduction

Much attention is currently devoted to the synthesis and properties of shape-persistent macrocycles.^[1] Because of their rigid backbones with reduced conformational flexibility, such compounds can form ordered structures, such as tubular channels or two-dimensional nanopatterns on surfaces, and act as scaffolds for placing functional units at predetermined spatial positions. This latter feature, together with the possibility of changing the nature of the functional units by exploiting accessible synthetic routes, makes these compounds suitable for applications as sensors and catalysts. Particularly interesting are shape-persistent macrocycles incorporating coordination units such as 2,2'-bipyridine

(bpy)^[2] in which exocyclic coordination can be exploited to construct dinuclear metal complexes.^[2b-d]

Over the past few years it has been shown that suitably designed molecular and supramolecular species can perform as nanoscale devices and machines upon stimulation with photons, electrons or protons.^[3,4] In this regard, shape-persistent macrocycles are particularly interesting because they can play the dual role of simple scaffolds for placing suitable functional moieties at fixed spatial positions and also the role of active components by incorporating acid/base-, photo-, and/or redox-active units in their backbone. It is indeed expected that stimulation of such units with the appropriate input can influence the properties of the appended moieties or the energy- or electron-transfer processes eventually occurring between them.

As an extension of our previous work,^[2] triads C2-M-C2, C343-M-C343 and C2-M-C343 (Scheme 1) have been designed and synthesised.^[5] All three triads have the same shape-persistent macrocyclic hexagonal backbone (M) as a central component, which is composed of two bpy units embedded in opposing sides with four hexyloxymethyl chains at the remaining four corners for solubility reasons. Their exocyclic peripheries are decorated with three different combinations of coumarin 2 (C2) and 343 (C343) chromophores at two opposite corners of the structure.

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Because of their absorption and emission properties, coumarin 2 and coumarin 343 have been extensively studied,^[6] are employed in dye lasers, and used as energy donor and acceptor moieties, respectively, in the construction of multi-component systems.^[7] The components M, C2 and C343 of the triads contain basic sites, that can be protonated leading to a variety of species.

Here we report 1) the light absorption and emission properties of triads C2-M-C2, C343-M-C343, and C2-M-C343 in CH₂Cl₂, 2) the changes induced by acid addition on the absorption and emission spectra of these compounds, and 3) the energy- and electron-transfer processes that are at the basis of the acid-dependent spectroscopic features. For comparison purposes the behaviour of unsubstituted macrocycle **1**, as a model of the backbone (M) of the triads, and *N*-benzyl-coumarin 2 (**2**) and benzyl ester of coumarin 343 (**3**), as model compounds of the C2 and C343 moieties (Scheme 1) has been examined.

Results and Discussion

Unsubstituted macrocycle 1

Acid-controlled absorption and emission spectra: Macrocycle **1** (Scheme 1) shows a strong structured absorption band in the UV spectral region at $\lambda_{\max}=308$ nm ($\epsilon_{308}=190000\text{ M}^{-1}\text{ cm}^{-1}$, Figure 1a, —) and a very intense blue

Abstract in Italian: *Il presente lavoro riporta lo studio effettuato in CH₂Cl₂ delle proprietà spettroscopiche (spettri di assorbimento ed emissione, tempi di vita degli stati eccitati) di tre triadi: C2-M-C2, C343-M-C343 e C2-M-C343. M rappresenta un macrociclo rigido a struttura esagonale in cui sono incorporate in posizioni diametralmente opposte due unità 2,2'-dipiridina (bpy), mentre C2 e C343 indicano, rispettivamente, la cumarina 2 e la cumarina 343. Tutte le unità componenti le triadi sono fortemente luminescenti ($\Phi=0.90, 0.79$ e 0.93 per M, C2 e C343, rispettivamente, come stabilito studiando opportuni composti modello). In ciascuna triade l'eccitazione selettiva di M porta ad un trasferimento di energia al più basso stato eccitato localizzato sulle cumarine con un'efficienza praticamente unitaria. Aggiunte crescenti di acido inducono, dapprima, l'indipendente protonazione delle due unità bpy del componente M con formazione delle specie monoprotonate (per esempio, C2-M·H⁺-C2) e diprotonate (per esempio, C2-M·2H⁺-C2) e, successivamente la protonazione delle cumarine. Ciascuna triade è quindi coinvolta in quattro equilibri di protonazione che, invertendo l'ordine energetico degli stati eccitati e/o favorendo l'insorgere di processi di trasferimento elettronico che spengono le emissioni, sono accompagnati da modifiche consistenti (e reversibili per aggiunta di base) delle proprietà spettroscopiche (assorbimento ed emissione) delle triadi esaminate.*

emission at $\lambda_{\max}=381$ nm and $\Phi=0.90$ (Figure 1b, —; Table 1), similar to those exhibited by an analogous previously investigated macrocycle.^[2b]

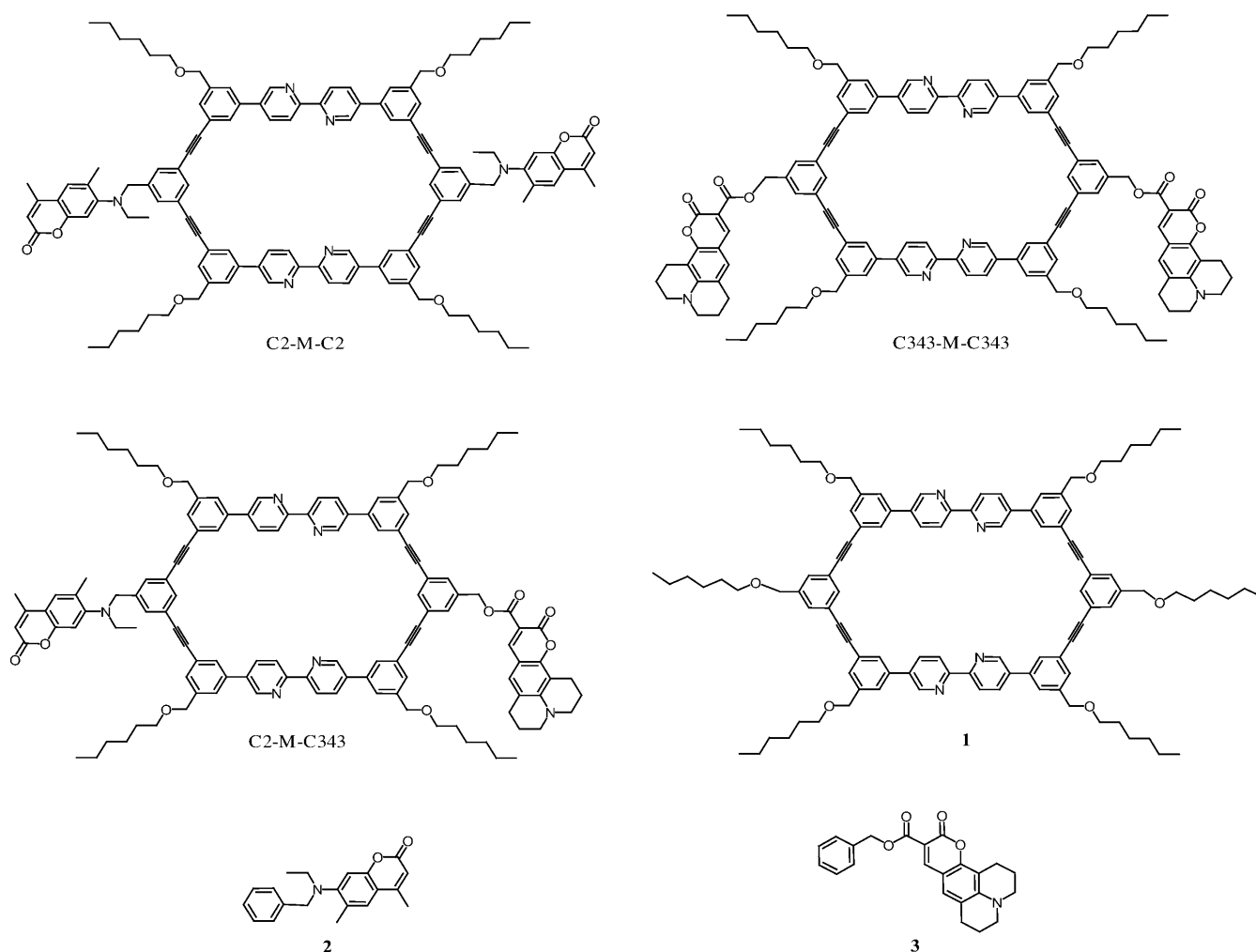
Upon addition of triflic acid, strong spectral changes are observed that can be attributed to monoprotection of the bpy units. The absorption changes are complete when 3.2 equivalents of acid are added and the final spectrum (Figure 1a, ---) with $\lambda_{\max}=360$ nm and $\epsilon_{360}=67000\text{ M}^{-1}\text{ cm}^{-1}$ is assigned to the diprotonated macrocycle. The presence of clean isosbestic points shows that the two bpy units, maintained far apart by the rigid structure of the macrocycle, behave independently. This consideration is supported by the linear changes, observed up to 3.2 equivalents of acid, of the absorbance at 308 (Figure 2, ○) and 360 nm (Figure 2, □), which correspond to the absorption maxima of the unprotonated and diprotonated macrocycle, respectively.

Acid addition induces strong changes in the emission spectrum, monitored by exciting at the 278 nm isosbestic point (Figure 1b): the disappearance of the intense emission with $\lambda_{\max}=381$ nm, characteristic of the unprotonated macrocycle, is accompanied by the appearance of a broad and weak emission at $\lambda_{\max}=514$ nm, which reaches its maximum intensity ($\Phi=0.12$) when 3.2 equivalents of acid are added (Figure 1b, ---; Table 1) and can be attributed to the diprotonated macrocycle.

As shown in Figure 2, the decrease of the emission intensity at 381 nm (●) does not parallel the decrease in the absorption at 308 nm (○). When half of the acid equivalents needed to diprotonate the macrocycle is added, the absorption is that expected for a 1:1 mixture of the unprotonated (○) and diprotonated (□) species, whereas the emission at 381 nm (●) is quenched to about 25% of the initial value. This finding corresponds to a statistic distribution, that is, 25% of the macrocycle is present as the unprotonated species, 25% as the diprotonated species and 50% as the monoprotected species, in which the emission at 381 nm of the unprotonated bpy unit is quenched by the monoprotected one.

Figure 2 also shows that the changes of the emission intensity at 514 nm (■) upon excitation with light at 278 nm (absorbed by the macrocycle regardless of its protonation state) are similar to those observed for the absorption at 360 nm (□). This result indicates that 1) the emission spectra of the mono- and diprotonated species have the same shape and the same quantum yield, and that 2) in the monoprotected macrocycle the quenching of the unprotonated bpy unit emission does not occur by energy transfer to the protonated bpy unit. Energy transfer, which could seem the most obvious kind of quenching process by considering that the protonated species lies at a lower energy than the unprotonated one, can be, indeed, ruled out because, in such a case, the emission increase at 514 nm would be the mirror image of the emission decrease at 381 nm (■).

It is likely that the quenching occurs by photoinduced electron transfer from the excited state of the unprotonated to the protonated bpy because it is easier to reduce the pro-



Scheme 1. Structural formulae of the triads investigated, unsubstituted macrocycle **1**, *N*-benzyl-coumarin **2** and the benzyl ester of coumarin 343 (**3**).

tonated bpy than the unprotonated one.^[8] Unfortunately such hypothesis cannot be verified experimentally because in argon-purged CH_2Cl_2 or in purified tetrahydrofuran (under vacuum conditions) the protonated macrocycle shows irreversible reduction processes and the unprotonated macrocycle does not exhibit oxidation processes in the accessible potential window (+1.7/−1.7 V for CH_2Cl_2 , and +1/−3 V for THF versus SCE).

Time-resolved fluorescence experiments: Time-resolved fluorescence experiments, with excitation at 278 nm, have shown that the excited states of the unprotonated and the diprotonated forms of macrocycle **1** have lifetimes of 750 ps and 11.5 ns (Table 1), respectively, and that during acid titration only two such lifetimes are present. These results enable us to conclude that 1) the mono- and diprotonated species of **1** have the same lifetime and 2) in the monoprotinated macrocycle the quenching of the excited state of the unprotonated bpy unit by the protonated one is a very fast process because only the unquenched lifetime of the unprotonated bpy is observed. Upon addition of increasing amounts of acid

(from 0 to 3.2 equiv), the pre-exponential factor of the unprotonated macrocycle decay (monitored in the isoemitting point at 472 nm) changes as expected for statistical protonation.

Reversibility of the acid-controlled luminescence changes: The switch off of the intense emission of the unprotonated macrocycle and the switch on of the emission of its diprotonated species obtained upon the addition of 3.2 equivalents of triflic acid can be completely reversed by adding a stoichiometric amount of tributylamine. We have verified that the acid–base cycle can be repeated at least ten times without loss of absorption and emission intensities (Figure 3).

Triad C2-M-C2

Acid-controlled absorption and emission spectra: The absorption spectrum (Figure 4, —) of triad C2-M-C2 (Scheme 1) coincides with that of a 1:2 mixture of **1** and **2** (Scheme 1; $\lambda_{\text{max}} = 346 \text{ nm}$; $\epsilon_{346} = 15300 \text{ M}^{-1} \text{ cm}^{-1}$), used as model compounds of macrocyclic backbone M and of the

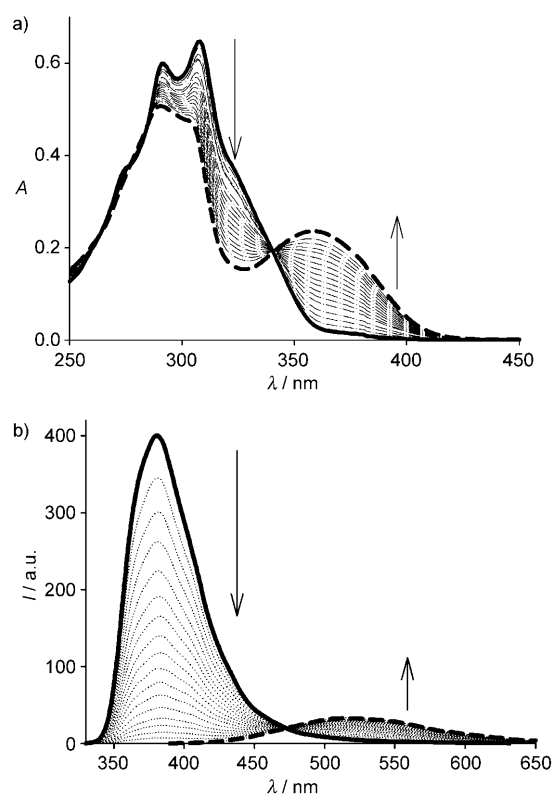


Figure 1. Changes in a) absorption and b) emission ($\lambda_{\text{exc}}=278$ nm) observed in CH_2Cl_2 air-equilibrated solution of **1** (3.4×10^{-6} M) at 298 K during the titration with triflic acid. —: starting spectrum; ---: after the addition of 3.2 equivalents of acid.

Table 1. Photophysical parameters of the investigated triads and model compounds.^[a]

	λ_{em} [nm]	Φ ^[b]	τ [ns]
1	381	0.90	0.75
1 ·2H ⁺	514	0.12	11.5
C2-M-C2	427	0.73	3.6
2	436	0.79	3.2
C343-M-C343	471	0.92	3.0
3	470	0.93	3.0
C2-M-C343	471	0.82	3.0

[a] Air-equilibrated solutions in CH_2Cl_2 at 298 K. [b] Calculated by using a solution of 9,10-diphenylanthracene in deoxygenated ethanol ($\Phi=0.88$) as the standard.

appended C2 moieties, respectively. This finding indicates that the component units of the triad do not interact in the ground state. The situation is, however, completely different as far as the emission properties are concerned. Upon excitation of the triad with 278 nm light, absorbed almost exclusively by the macrocyclic component M, only an emission with a maximum at 427 nm and $\Phi=0.73$ is observed (Figure 5: —; Table 1) that can be straightforwardly assigned to the C2 moieties on the basis of the emission properties of the model compound **2** ($\lambda_{\text{em}}=436$ nm; $\Phi=0.79$; Table 1). This result clearly evidences that an energy-transfer process from the excited state of the unprotonated mac-

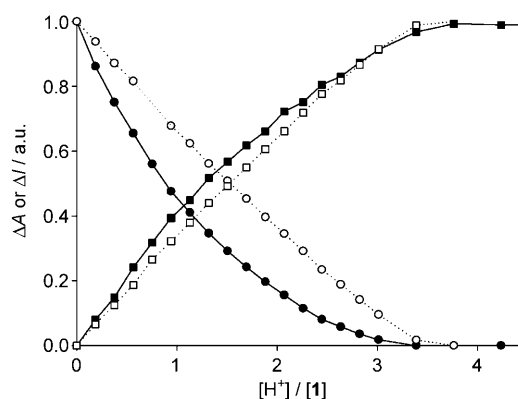


Figure 2. Normalised absorption (308 nm: ○; 360 nm: □) and emission (381 nm: ●; 514 nm: ■; $\lambda_{\text{exc}}=278$ nm) changes in an air-equilibrated solution of **1** (3.4×10^{-6} M) in CH_2Cl_2 at 298 K as a function of the number of equivalents of triflic acid added.

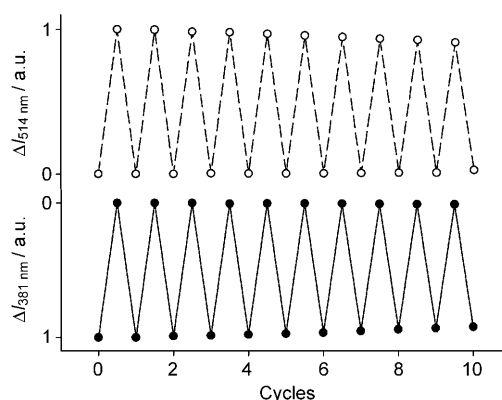


Figure 3. Normalised emission intensities ($\lambda_{\text{exc}}=278$ nm; $\lambda_{\text{em}}=381$ nm: ●; $\lambda_{\text{em}}=514$ nm: ○) of a solution of **1** (3.2×10^{-6} M) in CH_2Cl_2 at 298 K observed during protonation ($\text{CF}_3\text{SO}_3\text{H}$)/deprotonation (Bu_3N) cycles.

rocyclic component to C2 (Figure 6a) occurs with an almost unitary efficiency.

During the titration with triflic acid, strong changes in the absorption and emission spectra are observed (Figures 4 and 5, respectively).

Upon addition of up to 3.2 equivalents of acid, the absorption changes are consistent with the protonation of the bpy units contained in the macrocyclic component, and the final spectrum (Figure 4, ---) shows that diprotonation of the macrocyclic component has occurred.

The absorption decrease at 308 and increase at 352 nm, characteristic of the unprotonated and protonated forms of the macrocyclic component (Figure 7: ○ and □, respectively), are equal to those found for macrocycle **1**.

These changes in the absorption spectrum are accompanied by a decrease in the intensity of the C2-based emission, which disappears almost completely when 3.2 equivalents of acid are added (Figure 5, ---). Such a decrease (Figure 7, ●) can be interpreted by considering that during the statistic protonation of the macrocycle the exciting light is distributed between the unprotonated species, which transfers

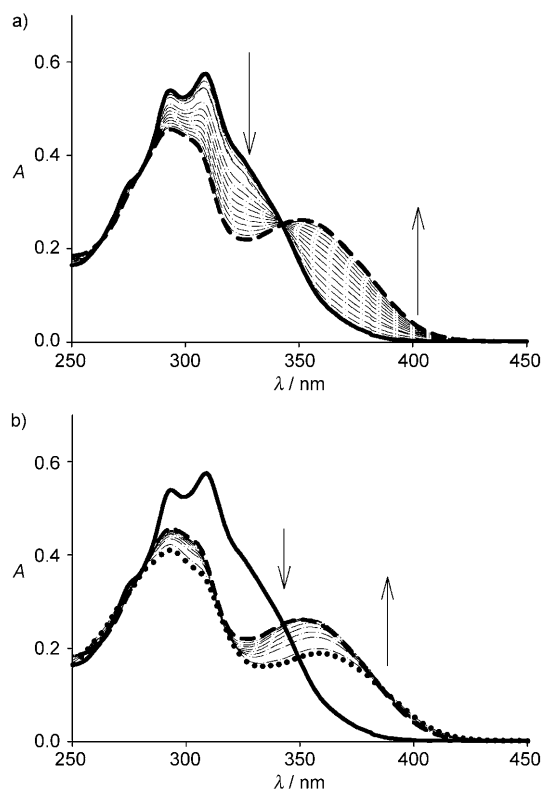


Figure 4. Absorption changes of an air-equilibrated solution of triad C2-M-C2 (3.0×10^{-6} M) in CH_2Cl_2 at 298 K upon addition of triflic acid: a) 0–3.2 equivalents; b) 3.2–10 equivalents. —: starting spectrum; ---: after the addition of 3.2 equivalents of acid;: after the addition of 10 equivalents of acid.

energy to the C2 moiety, and the protonated species, the excited state of which lies below that of C2. The lack of protonated macrocycle emission can be explained by the occurrence of an electron transfer involving the C2 moiety and the excited state of the protonated macrocycle, as schematically shown in Figure 6b.

Upon further addition of acid (from 3.2 to 10 equiv), the C2 moieties are transformed into their non-emissive protonated form (Figure 4,), as established by protonating model compound **4**. Under such conditions the emission with a maximum at around 500 nm appears, characteristic of the diprotonated macrocycle (Figure 5,; Figure 6c). This finding is consistent with the fact that protonated C2 is no longer able to reduce the excited state of the diprotonated macrocycle. As expected, the increase in emission of the diprotonated macrocycle at 500 nm (Figure 7, ■) mirrors the decrease in absorption of the unprotonated C2 moieties at 352 nm (Figure 7, □).

Time-resolved fluorescence experiments: Time-resolved fluorescence experiments were performed by exciting with 278 nm light, which is almost exclusively absorbed by the macrocyclic component regardless of its protonation state. Triad C2-M-C2 exhibits only one mono-exponential decay with a τ value of 3.6 ns (Table 1). This decay can be attribut-

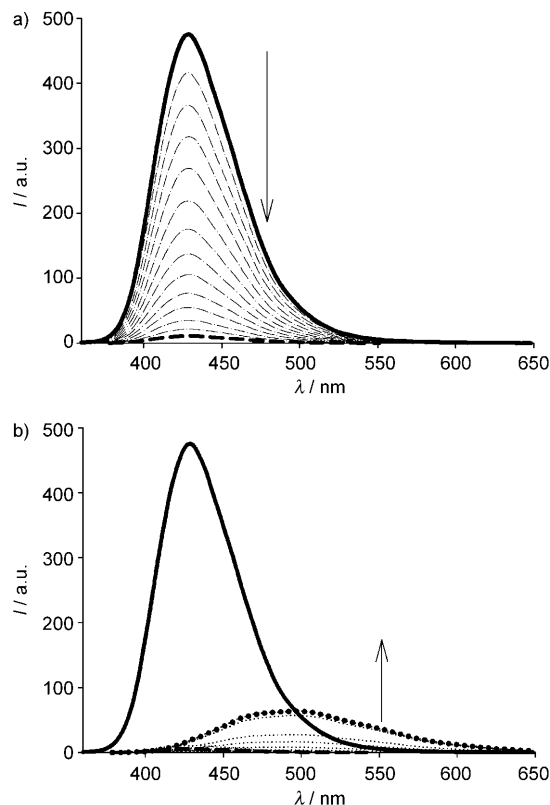


Figure 5. Emission changes ($\lambda_{\text{exc}} = 278$ nm) of an air-equilibrated solution of triad C2-M-C2 (3.0×10^{-6} M) in CH_2Cl_2 at 298 K upon addition of triflic acid: a) 0–3.2 equivalents; b) 3.2–10 equivalents. —: starting emission; ---: after the addition of 3.2 equivalents of acid;: after the addition of 10 equivalents of acid.

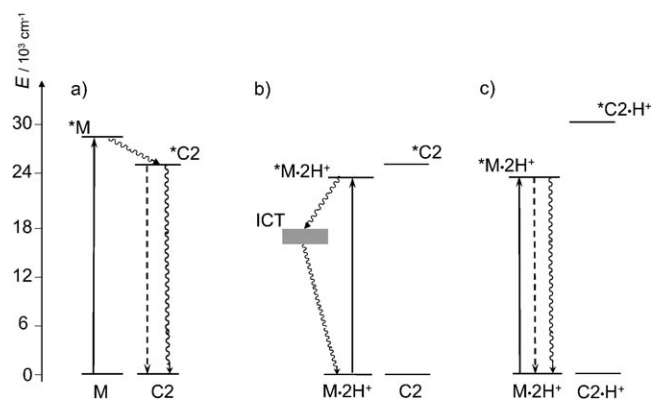


Figure 6. Energy-level diagram of the excited states involved in the energy- and electron-transfer processes occurring in triad C2-M-C2 and its protonated forms. Solid line: selective excitation, dashed line: radiative decay; wavy line: non-radiative decay; ICT (intercomponent charge transfer): the energy of this state is uncertain.

ed, for comparison with model compound **2** ($\tau = 3.2$ ns; Table 1), to the C2 moieties and confirms the occurrence of a fast energy transfer from the excited state of the macrocyclic component to appended C2. This lifetime is observed until complete protonation of M is achieved. For further ad-

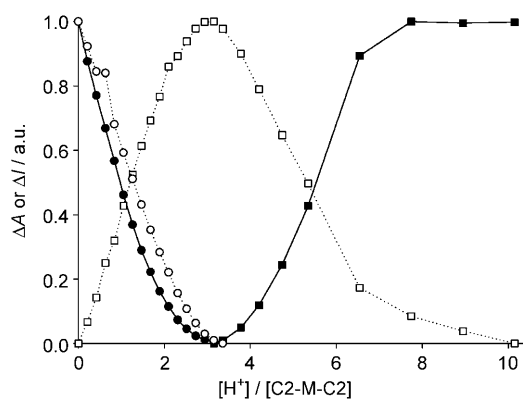


Figure 7. Normalised absorption (308 nm: ○; 352 nm: □) and emission (427 nm: ●; 500 nm: ■; $\lambda_{\text{exc}}=278$ nm) changes of an air-equilibrated solution of triad C2-M-C2 (3.0×10^{-6} M) in CH_2Cl_2 at 298 K upon addition of triflic acid.

dition of acid, a longer lifetime component with $\tau=11$ ns appears, similar to that of $1\cdot 2\text{H}^+$, which indicates that protonation of the C2 prevents electron-transfer quenching of the excited state of the diprotonated macrocycle.

Reversibility of acid-controlled luminescence changes: The reversibility of the switching off of the C2-based luminescence and the switching on of the diprotonated macrocycle-based luminescence has been proven by repetitive (at least ten times) addition of 10 equivalents of triflic acid followed by an equivalent addition of tributylamine.

Triad C343-M-C343

Acid-controlled absorption and emission spectra: The absorption and emission properties of triad C343-M-C343 (Scheme 1) can be substantially interpreted on the basis of the considerations drawn for the previously described triad C2-M-C2. Its absorption spectrum (Figure 8a, —) is coincident with the sum of the spectra of the components, in particular for $\lambda < 350$ nm it is dominated by absorption of the macrocyclic component, whereas the band at $\lambda_{\text{max}}=440$ nm and $\epsilon_{440} = 88000 \text{ M}^{-1} \text{ cm}^{-1}$ can be straightforwardly assigned to the C343 moieties for comparison with the absorption spectrum of the benzyl ester of coumarin 343 (**3** in Scheme 1; $\lambda_{\text{max}}=438$ nm; $\epsilon_{438}=40000 \text{ M}^{-1} \text{ cm}^{-1}$) taken as a model compound.

Selective excitation of the macrocyclic component ($\lambda_{\text{exc}}=278$ nm) leads to an emission with a maximum at 471 nm and $\Phi=0.92$ (Figure 8b, —; Table 1) that can be assigned to the C343 moieties, on the basis of the emission properties of model compound **3** ($\lambda_{\text{em}}=470$ nm, $\Phi=0.93$; Table 1). This result evidences that energy transfer from the excited state of the macrocyclic component to the peripheral moieties occurs (Figure 9a) with an almost unitary efficiency, as we have also found for triad C2-M-C2. In the case of C343-M-C343, this conclusion is further supported by the fact that the same emission quantum yield is obtained by selective excitation of the C343 moiety with 440 nm light.

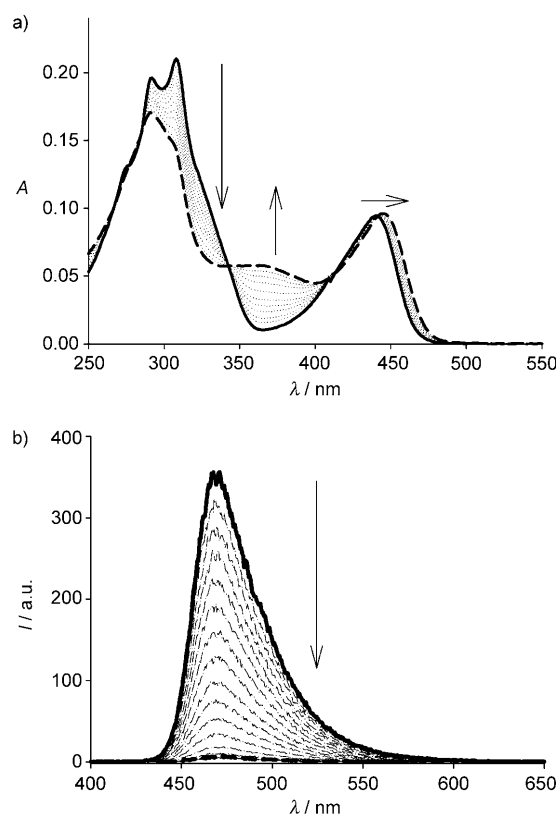


Figure 8. Changes in a) absorption and b) emission ($\lambda_{\text{exc}}=278$ nm) observed of an air-equilibrated solution of triad C343-M-C343 (1.1×10^{-6} M) in CH_2Cl_2 at 298 K upon addition of triflic acid. —: starting spectrum; ---: after the addition of 3.2 equivalents of acid.

As observed for C2-M-C2, addition of 3.2 equivalents of acid (Figure 8a, ---) causes absorption changes for $\lambda < 400$ nm that are consistent with the protonation of the two bpy units contained in the macrocyclic component and a small shift of the C343-based band towards lower energy. During protonation of the macrocycle, almost complete dis-

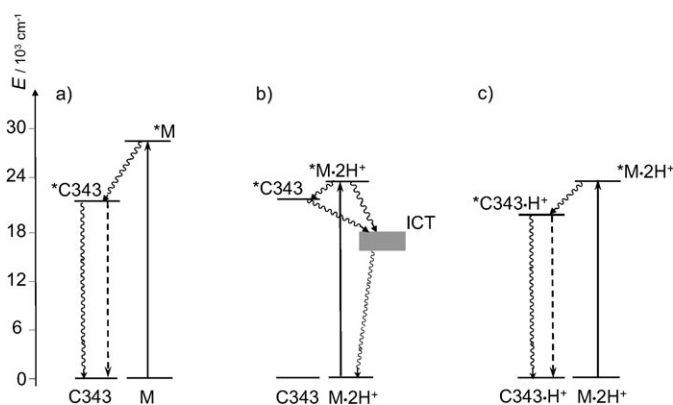


Figure 9. Energy-level diagram of the excited states involved in the energy- and electron-transfer processes occurring in triad C343-M-C343 and its protonated forms. Solid line: selective excitation, dashed line: radiative decay; wavy line: non-radiative decay; ICT (intercomponent charge transfer): the energy of this state is uncertain.

appearance of the C343-based emission is observed (Figure 8b, ---). Because, as established by the absorption spectra, the excited state of C343 lies at a lower energy than the diprotonated macrocycle, the emission disappearance is not due to a lack of population of the coumarin-based excited state, as previously observed for C2-M-C2, but to an electron-transfer quenching process (Figure 9b). Two paths are possible: electron-transfer quenching of the $*M\cdot 2H^+$ excited state by C343, or energy transfer from $*M\cdot 2H^+$ to C343 followed by electron transfer from the excited $*C343$ moiety to the protonated species of the macrocycle. The latter possibility is consistent with the fact that the quenching of the C343 emission is observed when such a unit is directly excited.

From a quantitative viewpoint (Figure 10), 1) the decrease of the absorption band of the unprotonated macrocycle at $\lambda_{\max}=308$ nm (\square), 2) the increase of the absorption band of

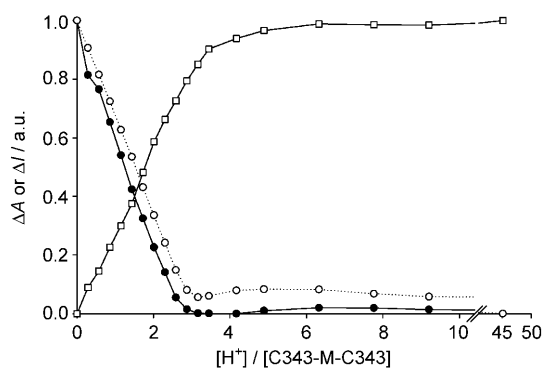


Figure 10. Normalised absorption (308 nm: \square ; 360 nm: \square) and emission (471 nm: \bullet ; $\lambda_{\text{exc}}=278$ nm) changes of an air-equilibrated solution of triad C343-M-C343 (1.1×10^{-6} M) in CH_2Cl_2 at 298 K upon addition of triflic acid.

the protonated macrocycle at $\lambda_{\max}=360$ nm (\circ), and 3) the decrease of the C343-based emission with $\lambda_{\max}=471$ nm (\bullet) show trends similar to those observed for triad C2-M-C2.

Upon further addition of acid, the observed changes in absorption (Figure 11a) and emission (Figure 11b) indicate, on the basis of results obtained for the model compound, that protonation of C343 moieties occurs. This process, however, is incomplete even when 50 equivalents of acid are added, evidencing that C343 is a weaker base than C2.

When C343 is protonated, its emission is sensitised by energy transfer from the protonated macrocyclic component (Figure 9c). This finding suggests that, as expected, protonation of the C343 moiety prevents its involvement in electron-transfer quenching. Incidentally, this result shows that the system is also stable in the presence of a large amount of acid (50 equiv), that is, under conditions in which cleavage of the ester bond connecting the C343 moieties and the macrocyclic component could be expected to occur.

Time-resolved fluorescence experiments: Time-resolved fluorescence experiments performed at 278 nm, which is ab-

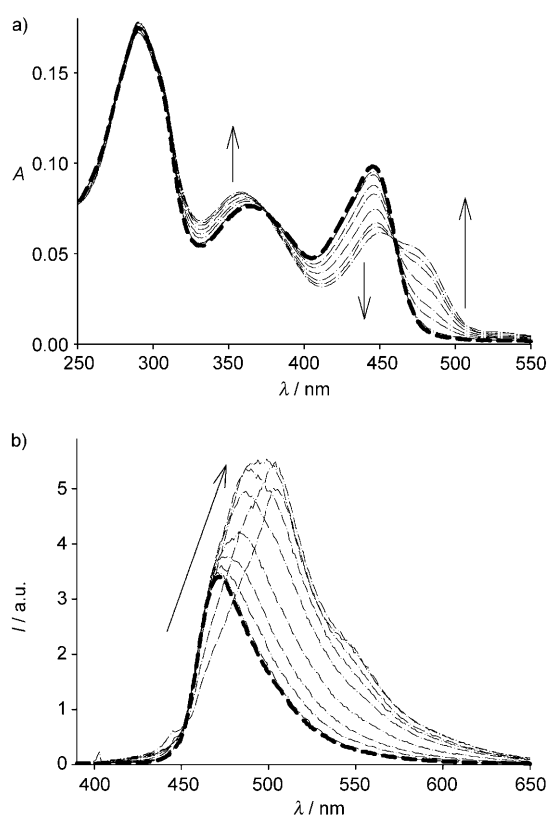


Figure 11. Changes in a) absorption and b) emission ($\lambda_{\text{exc}}=278$ nm) observed for an air-equilibrated solution of triad C343-M-C343 (1.1×10^{-6} M) in CH_2Cl_2 at 298 K upon addition of triflic acid: from 3.2 (---) to 50 (-.-.-) equivalents.

sorbed almost exclusively by the macrocyclic component regardless of its protonation state, have shown that triad C343-M-C343 exhibits only one mono-exponential decay with $\tau=3.0$ ns (Table 1). This decay can be attributed, for comparison with model compound **3** ($\tau=3.0$ ns, Table 1), to the C343 moieties and confirms the occurrence of a fast energy transfer from the excited state of the macrocyclic component to the appended C343 moieties.

During the addition of up to 3.2 equivalents of acid, only the lifetime of the unquenched C343 moiety is observed, which indicates that the quenching electron-transfer processes in the C343-M $\cdot 2H^+$ -C343 species are very fast.

Reversibility of the acid-controlled luminescence changes:

Because C343 is a very weak base, only the reversibility of the protonation/deprotonation process involving the macrocyclic component and thereby the reversibility of the off/on switching of the C343-based luminescence has been investigated. We have found that addition of 3.2 equivalents of triflic acid followed by adding an equivalent amount of tributylamine can be repeated at least ten times with very small changes in the starting absorption and emission spectra. This result shows that the C343 peripheral units do not modify the acid/base properties of the central macrocycle, whereas the protonation state of the macrocycle affects the

C343-based emission that is reversibly switched off/on through electron transfer.

Triad C2-M-C343

Acid-controlled absorption and emission spectra: The absorption spectrum of the triad C2-M-C343 (Scheme 1) coincides with the sum of the absorption of its components, in the same way as the symmetrically substituted compounds; in particular, its spectrum is exactly the sum of half of the absorption spectra of triads C2-M-C2 and C343-M-C343 (Figure 12a, —).

Upon excitation of M in the C2-M-C343 triad no emission from the macrocycle is observed, whereas the C343- and C2-based emissions ($\lambda_{\text{em}} = 471 \text{ nm}$ and 430 nm , respectively) are sensitised with 90 and 5% efficiencies, respectively (Figure 12b, —; Table 1). These values could reflect the different rates of *M to C343 or *M to C2 energy-transfer processes, but population of the *C343 excited state via *C2 cannot be excluded. An estimation of the rate constant of energy transfer from *C2 to C343, based on the Förster equation,^[9] shows that this process can compete with the intrinsic decay of C2.^[10]

Upon addition of 3.2 equivalents of triflic acid, triad C2-M-C343 behaves like triad C343-M-C343: protonation of

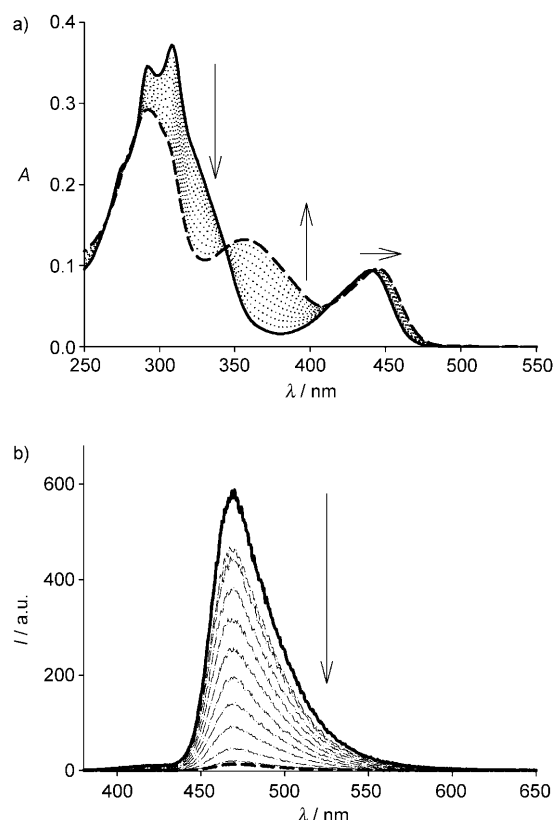


Figure 12. Changes in a) absorption and b) emission ($\lambda_{\text{exc}} = 278 \text{ nm}$) observed for an air-equilibrated solution of triad C2-M-C343 ($2.0 \times 10^{-6} \text{ M}$) in CH_2Cl_2 at 298 K upon addition of triflic acid. —: starting spectrum; ---: after the addition of 3.2 equivalents of acid.

the two bpy units of the macrocyclic component takes place (Figure 11a, ---) with the concomitant, almost complete disappearance of the C343-based emission (Figure 12b, ---).

Further acid addition (up to 25 equiv) causes protonation first of the C2 and then of the C343 moieties without recovery of the emission of the diprotonated macrocycle, as already observed for triad C343-M-C343.

It is important to notice that triad C2-M-C343, although its behaviour matches, particularly in emission, that of C343-M-C343, is characterised by a more complex pattern of energy- and electron-transfer processes.

As schematically shown in the energy-level diagram of Figure 13, this multicomponent system undergoes efficient energy-transfer processes that lead to the appearance of the

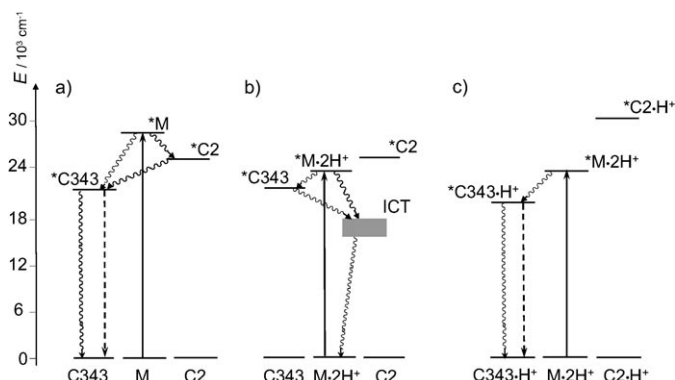


Figure 13. Energy-level diagram of the excited states involved in the energy- and electron-transfer processes occurring in triad C2-M-C343 and its protonated forms. Solid line: selective excitation, dashed line: radiative decay; wavy line: non-radiative decay; ICT (intercomponent charge transfer): the energy of this state is uncertain.

emission characteristic of the C343 moiety (Figure 13a). Upon protonation of the bpy units of M, such an emission is quenched by the occurrence of an electron-transfer process (Figure 13b), that is prevented upon successive protonation of the amine units of C2 and C343. An energy transfer from the excited state of the protonated macrocycle to protonated C343 occurs (Figure 13c), which results in the appearance of the characteristic emission of this latter moiety.

Time-resolved fluorescence experiments: Time-resolved fluorescence experiments performed by selective excitation of the macrocyclic component at 278 nm confirms almost complete energy transfer from the excited states of the macrocycle and appended C2 moiety to the C343 moiety. Indeed, only one mono-exponential decay with $\tau = 3.0 \text{ ns}$ (Table 1) was observed that could be assigned to the C343 moiety, in comparison with the data obtained for model compound **3** and triad C343-M-C343.

Upon acid addition, the changes observed are practically identical to those obtained for triad C343-M-C343, showing once again that the behaviour of triad C2-M-C343 is almost exclusively determined by the C343 moiety.

Reversibility of the acid-controlled luminescence changes: As in the case of triad C343-M-C343, and for the same reasons, only the reversibility of the protonation/deprotonation process involving the macrocyclic component M and thereby of the off/on switching of the C343-based luminescence has been investigated.

In agreement with the results obtained for triad C343-M-C343, we have found that the addition of 3.2 equivalents of triflic acid followed by adding an equivalent amount of tributylamine can be repeated at least ten times with relatively small changes in the absorption and emission spectra of the triad C2-M-C343 (Figure 14). This result shows that the

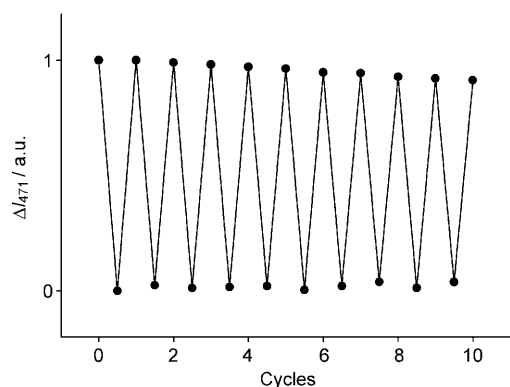


Figure 14. Normalised emission intensities at 471 nm ($\lambda_{\text{exc}}=278$ nm) of an air-equilibrated solution of triad C2-M-C343 (3.0×10^{-6} M) in CH_2Cl_2 at 298 K during reversible protonation ($\text{CF}_3\text{SO}_3\text{H}$)/deprotonation (Bu_3N) cycles.

C343 and C2 peripheral units do not modify the acid/base properties of the central macrocycle and that the emission characteristics of the C343 moiety are reversibly switched off/on upon acid/base addition.

The slight decrease in the C343-based emission observed by increasing the number of the protonation/deprotonation cycles could be due to a very small percentage of photodecomposition that occurs upon long irradiation.

Conclusion

Suitably designed multicomponent systems can play interesting functions upon chemical, electrochemical, and photochemical stimulation.^[11]

Starting with the shape-persistent macrocyclic hexagonal backbone M, which contains two bpy units, and the well-known coumarin 2 (C2) and coumarin 343 (C343) dyes, we have designed and synthesised three novel triads (C2-M-C2, C343-M-C343 and C2-M-C343), the outstanding spectroscopic properties of which (in particular, very strong fluorescence signals) can be profoundly and reversibly modified by chemical inputs (acids and bases). Comparison with the behaviour of model compounds of the component units M, C2 and C343, has allowed us to understand the reasons for the

observed changes. Each of the investigated triads is, indeed, involved in protonation equilibria among five species; taking C2-M-C343 as an example they are C2-M-C343, C2-M·H⁺-C343, C2-M·2H⁺-C343, C2·H⁺-M·2H⁺-C343 and C2·H⁺-M·2H⁺-C343·H⁺.

In the unprotonated triads, excitation of M leads to almost quantitative energy transfer to the lowest coumarin-localised excited state. Protonation of the bpy units of M and of the amine units of C2 and C343 causes inversion of the excited-state order and/or the occurrence of electron-transfer quenching processes in these multicomponent systems.

The possibility of manipulating the absorption spectra and the very strong fluorescence signals by successive acid/base inputs suggests that these compounds could be profitably used for molecular logic purposes.^[3g,h]

Experimental Section

Materials: Tributylamine (Bu_3N , Fluka, $\geq 99.5\%$) and triflic acid ($\text{CF}_3\text{SO}_3\text{H}$, Fluka, $> 99.8\%$) were used as received. The solvent dichloromethane used was purchased from Merck (Uvasol) for the photophysical experiments and from Romil (Hi-dry) for the electrochemical experiments.

Syntheses: Triads C2-M-C2, C343-M-C343, C2-M-C343, and unsubstituted macrocycle **1** were synthesised as described in the literature.^[5]

Photophysical experiments: All the experiments were carried out at 298 K on air-equilibrated solutions that were kept and manipulated in the dark because the compounds investigated, particularly compounds **2** and **3**, are slightly photodecomposed upon long irradiation. UV/Vis absorption spectra were recorded with a Perkin-Elmer $\lambda 40$ spectrophotometer, using quartz cells with a path length of 1.0 cm. Fluorescence spectra were performed with a Perkin-Elmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube, using spectrofluorimetric quartz cells with a path length of 1.0 cm. 9,10-Diphenylanthracene in deoxygenated ethanol ($\phi=0.88$)^[12] was used as the standard for evaluation of the luminescence quantum yield. Fluorescence lifetime measurements were performed by using an Edinburgh FLS920 spectrofluorimeter equipped with a TCC900 card for data acquisition in time-correlated single-photon counting experiments (0.5 ns time resolution) with a D_2 lamp.

Titration experiments: Titrations were performed by adding small aliquots (typically 5 μL) of a concentrated (1.0×10^{-3} M) solution of either acid or base to a dilute (1×10^{-6} – 4×10^{-6} M) solution of the sample (3 mL) by using a microsyringe. UV/Vis absorption and luminescence changes were monitored during the titration. Whenever possible, excitation was performed at an isosbestic point and corrections for inner filter effects^[13] were carried out if necessary.

Electrochemical experiments: The electrochemical investigation of macrocycle **1** and its protonated species was carried out by using the equipment and procedure previously described.^[2b]

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[1] See, for example, the following reviews: a) C. Grave, A. D. Schlüter, *Eur. J. Org. Chem.* **2002**, 3075–3098; b) Y. Yamaguchi, Z. Yoshida,

- Chem. Eur. J.* **2003**, *9*, 5430–5440; c) D. Zhao, J. S. Moore, *Chem. Commun.* **2003**, 807–818; d) S. Höger, *Chem. Eur. J.* **2004**, *10*, 1320–1329; e) S. Höger, *Angew. Chem.* **2005**, *117*, 3872–3875; *Angew. Chem. Int. Ed.* **2005**, *44*, 3806–3808; f) W. Zhang, J. S. Moore, *Angew. Chem.* **2006**, *118*, 4524–4548; *Angew. Chem. Int. Ed.* **2006**, *45*, 4416–4439.
- [2] a) O. Henze, D. Lentz, A. Schäfer, P. Franke, A. D. Schlüter, *Chem. Eur. J.* **2002**, *8*, 357–365; b) M. Venturi, F. Marchioni, V. Balzani, D. M. Opris, O. Henze, A. D. Schlüter, *Eur. J. Org. Chem.* **2003**, *21*, 4227–4233; c) M. Venturi, V. Balzani, F. Marchioni, D. M. Opris, P. Franke, A. D. Schlüter in *Macrocyclic Chemistry—Current Trends and Future Perspectives* (Ed.: K. Gloe), Springer, Dordrecht, **2005**, pp. 219–234; d) M. Venturi, F. Marchioni, B. F. Ribera, V. Balzani, D. M. Opris, A. D. Schlüter, *ChemPhysChem* **2006**, *7*, 229–239.
- [3] a) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **2000**, *112*, 3484–3530; *Angew. Chem. Int. Ed.* **2000**, *39*, 3348–3391; b) Special volume on molecular wires: *Top. Curr. Chem.* **2005**, *257*; c) Special volume on molecular machines: *Top. Curr. Chem.* **2005**, *262*; d) W. R. Browne, B. L. Feringa, *Nat. Nanotechnol.* **2006**, *1*, 25–35; e) B. Champin, P. Mobian, J.-P. Sauvage, *Chem. Soc. Rev.* **2007**, *36*, 358–366; f) E. R. Kay, D. A. Leigh, F. Zerbetto, *Angew. Chem.* **2007**, *119*, 72–196; *Angew. Chem. Int. Ed.* **2007**, *46*, 72–191; g) A. P. De Silva, S. Uchiyama, *Nat. Nanotechnol.* **2007**, *2*, 399–410; h) V. Balzani, A. Credi, M. Venturi, *Molecular Devices and Machines—Concepts and Perspectives for the Nanoworld*, Wiley-VCH, Weinheim, **2008**.
- [4] For some recent examples, see: a) A. P. De Silva, M. R. James, B. O. F. McKinney, P. A. Pears, S. M. Weir, *Nat. Mater.* **2006**, *5*, 787–790; b) V. Balzani, M. Clemente-León, A. Credi, B. Ferrer, M. Venturi, A. H. Flood, J. F. Stoddart, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 1178–1183; c) M. T. Indelli, C. Chiorboli, L. Flamigni, L. De Cola, F. Scandola, *Inorg. Chem.* **2007**, *46*, 5630–5641; d) K. Becker, P. C. Lagoudakis, G. Gaefke, S. Höger, J. M. Lupton, *Angew. Chem.* **2007**, *119*, 3520–3525; *Angew. Chem. Int. Ed.* **2007**, *46*, 3450–3455; e) V. Serreli, C.-F. Lee, E. R. Kay, D. A. Leigh, *Nature* **2007**, *445*, 523–527; f) G. Rogez, B. Ferrer Ribeira, A. Credi, R. Ballardini, M. T. Gandolfi, V. Balzani, Y. Liu, J. F. Stoddart, *J. Am. Chem. Soc.* **2007**, *129*, 4633–4642; g) C. Giansante, P. Ceroni, V. Balzani, F. Vögtle, *Angew. Chem.* **2008**, *120*, 5502; *Angew. Chem. Int. Ed.* **2008**, *47*, 5422–5425; h) S. D. Straight, G. Kodis, Y. Terazono, M. Hambourger, T. A. Moore, A. L. Moore, D. Gust, *Nat. Nanotechnol.* **2008**, *3*, 280–283.
- [5] J. Sakamoto, A. D. Schlüter, *Eur. J. Org. Chem.* **2007**, 2700–2712.
- [6] For example, see: a) G. Jones II, W. R. Jackson, C. Chol, W. R. Bergmark, *J. Phys. Chem.* **1985**, *89*, 294–300; b) T. Gustavsson, L. Casara, V. Gulbinas, G. Gurzadyan, J.-C. Mialocq, S. Pommeret, M. Sorgius, P. van der Meulen, *J. Phys. Chem. A* **1998**, *102*, 4229–4245; c) A. Samanta, R. W. Fessenden, *J. Phys. Chem. A* **2000**, *104*, 8577–8582, and references therein.
- [7] For some specific examples, see: a) A. Adronov, S. L. Gilat, J. M. J. Fréchet, K. Ohta, F. V. R. Neuwahl, G. R. Fleming, *J. Am. Chem. Soc.* **2000**, *122*, 1175–1185; b) L. A. J. Christoffels, A. Adronov, J. M. J. Fréchet, *Angew. Chem.* **2000**, *112*, 2247–2251; *Angew. Chem. Int. Ed.* **2000**, *39*, 2163–2167; c) R. K. Castellano, S. L. Craig, C. Nuckolls, J. Rebek, Jr., *J. Am. Chem. Soc.* **2000**, *122*, 7876–7882; d) X. Schultze, J. Serin, A. Adronov, J. M. J. Fréchet, *Chem. Commun.* **2001**, 1160–1161; e) L. Fabbrizzi, N. Marcotte, F. Stomeo, A. Taglietti, *Angew. Chem.* **2002**, *114*, 3965–3968; *Angew. Chem. Int. Ed.* **2002**, *41*, 3811–3814; f) A. Kishimoto, T. Mutai, K. Araki, *Chem. Commun.* **2003**, 742–743; g) H. Zhang, D. M. Rudkevich, *Chem. Commun.* **2007**, 1238–1239.
- [8] C. V. Krishnan, C. Creutz, H. A. Schwarz, N. Sutin, *J. Am. Chem. Soc.* **1983**, *105*, 5617–5623.
- [9] a) F. Barigelletti, L. Flamigni, *Chem. Soc. Rev.* **2000**, *29*, 1–12; b) G. D. Scholes, *Annu. Rev. Phys. Chem.* **2003**, *54*, 57–87.
- [10] According to Förster theory, the critical radius R_0 , for which 50% of the populated *C2 excited states transfer their electronic energy to $C343$, is estimated to be 4 nm. Since the distance between $C2$ and $C343$ in the triad is ≤ 3 nm, energy transfer from *C2 to $C343$ is expected to be very efficient.
- [11] V. Balzani, A. Credi, M. Venturi, *Chem. Eur. J.* **2008**, *14*, 26–39.
- [12] *Handbook of Photochemistry*, 3rd ed. (Eds.: M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi), CRC, Boca Raton, **2006**.
- [13] A. Credi, L. Prodi, *Spectrochim. Acta Part A* **1998**, *54*, 159–170.

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