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Shape-Persistent Macrocycles as Ligands and Sensitisers of Nd^{3+} Ions

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Two shape-persistent macrocycles with a hexagonal backbone incorporating two bpy units and two nonchromophoric methoxytetrahydropyran units (**M**), or two coumarin 2 dyes (**C2**–**M**–**C2**) are highly absorbing and emitting species in dichloromethane solution (ε_{max} = 1.90×10^5 $M^{-1}cm^{-1}$ at 308 nm and 1.92×10^5 $M^{-1}cm^{-1}$ at 309 nm; ϕ_{em} = 0.60 and 0.73, τ = 0.76 and 3.6 ns for **M** and **C2**–**M**–**C2**, respectively). Time-resolved fluorescence anisotropy measurements of **M** in dichloromethane has given information on the hydrodynamic volume of the free macrocycle in solution, which is close to the molecular volume measured by X-ray crystallographic analysis. **M** and **C2**–**M**–**C2** are very good ligands for lanthanide ions (Nd^{3+} and Gd^{3+}): they form complexes with 1:2, 1:1 and 2:1 (clearly evident only in the case of **M**) metal to ligand stoichiometry. These complexes are characterised by very high association constants in dichloromethane solution, as demonstrated by significant changes to the photophysical properties of the macrocycles. In the 1:2 and 1:1 complexes, the lanthanide ion is likely sandwiched between two macrocycles and coordinated by two bpy units. The efficiency of energy transfer from the ligand to the lanthanide ion is quite high (73 % in the case of the $[Nd_2\mathbf{M}]^{6+}$ complex), and it is not sensitive to the presence of oxygen. For the Nd^{3+} complexes with the **C2**–**M**–**C2** macrocycle, sensitisation of the lanthanide NIR emission takes place with lower efficiency (ca. 50 %), due to a competitive electron transfer process from the coumarin to the complexed macrocycle. Lastly, upon addition of an excess of a competitive ligand, all the absorption and emission spectroscopic changes are completely reversible.

Introduction

Trivalent lanthanide metal ions possess 4*f* open-shell electronic configurations with forbidden intra-configurational *f*–*f* transitions, which results in very low extinction coefficients (ε typically from ca. 1 to 10 $M^{-1}cm^{-1}$), characteristic narrow line-like emission bands, mostly in the visible and near infrared regions, and long-lived luminescence.[1] A drawback of lanthanide luminescence is nonradiative quenching of the emitting excited state by energy loss to high frequency vibrational modes of the ligand or of coordinated solvent molecules,[1,2] a phenomenon that can at least in part be prevented by encapsulation of the metal ion.[3] Because direct excitation of lanthanide ions is inefficient, coordinating chromophores are usually exploited to sensitise their luminescence (antenna effect).[4,5] The mechanism of energy transfer from coordinating ligand to lanthanide ions is currently the subject of several studies. The most frequently reported mechanism involves the lowest triplet excited state (T_1) of the ligand[4,5] but, evidence for efficient energy transfer from the lowest singlet exited state (S_1) of the ligand, first proposed by Kleinerman[6] and then by Horrocks,[7] has recently been provided both for Eu^{3+}[8] and Nd^{3+}.[9] In the case of Yb^{3+}, characterised by a low reduction potential, sensitisation can also be mediated by a photoinduced electron transfer process.[10,11]

The unique photophysical and magnetic properties of these metals have attracted great interest over the past few years, and useful applications can be envisaged in the field of medical diagnostics,[12] as biosensors,[13] for luminescent imaging,[4b,4c,14,15] and in photonic applications,[16] such as waveguide amplifiers, plastic lasers, and light-emitting diodes.

One of the first multidentate ligands developed for lanthanide ions with encapsulation properties was a cage constructed with three 2,2′-bipyridyne (bpy) units.[17] This ligand was designed to provide: (a) kinetically stable complexes, (b) protection towards deactivating interactions of the lanthanide ion with the solvent and (c) efficient energy transfer from the strongly absorbing ligand to the coordinated lanthanide ion. The resultant cryptate was reported to be an excellent luminescent probe and light harvester by an efficient antenna effect, and it has been commercially developed by CisBio. Since then, many bpy derivatives have been employed as ligands for lanthanide ions.[3d,8]

Herein, we report on lanthanide complexes with bpy containing macrocycles as an extension of our previous work.[19,20] These macrocycles are shape-persistent with a hexagonal backbone incorporating two bpy units on opposite sides. The exocyclic peripheries are decorated with either nonchromophoric methoxytetrahydropyran units (**M**,

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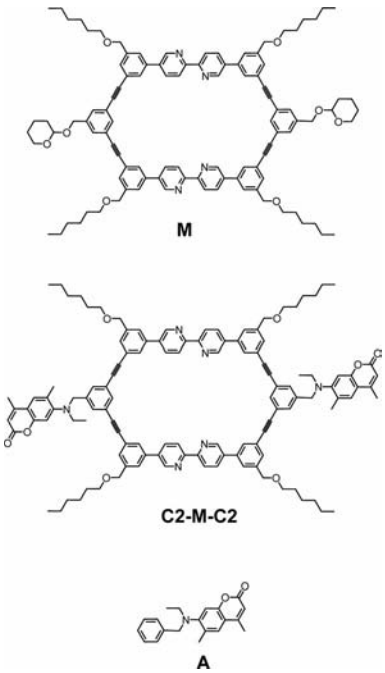
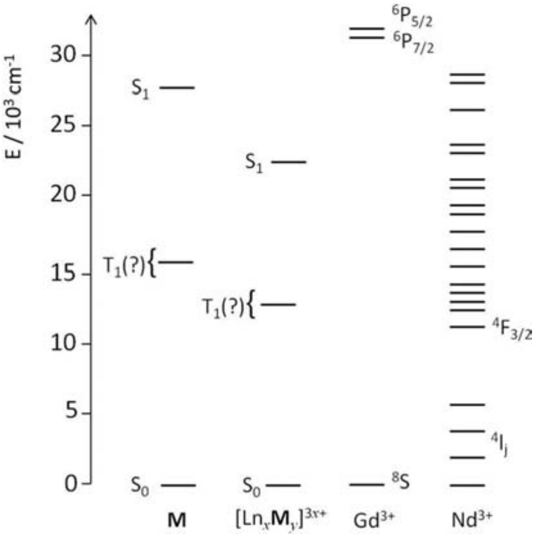
Scheme 1) or two coumarin 2 dyes (**C2**–**M**–**C2**, Scheme 1) at the opposite corners of the structure, and four hexyloxymethyl chains at the remaining four corners for solubility reasons.[21] Owing to its rigid backbone, macrocycle **M** has the capacity to form supramolecular structures, as ordered tubular channels or 2D nanopatterns on surfaces.[18a] They can also act as scaffolds for placing functional units at predetermined spatial positions and to tune the luminescence properties of the appended chromophores by external chemical inputs, such as protons[19a,19b] and/or metal ions.



Scheme 1. Structural formulae of the shape-persistent macrocycle **M**, of the coumarin-functionalised shape-persistent macrocycle **C2**–**M**–**C2** and of the coumarin model compound **A**.



Scheme 2. Schematic energy level diagram of macrocycle **M**, its complex with lanthanide ions [Ln**M**]$^{3+}$ as well as Gd^{3+} and Nd^{3+} ions. [Ln$_x$**M**$_y$]$^{3x+}$ represents 1:2, 1:1 and 2:1 (metal to ligand) complexes, since the excited state properties are not dependent on the stoichiometry of the complex. The position of the triplet excited state of **M** either free or bound to lanthanide ions is uncertain because no phosphorescence emission can be observed.

In the present work, we have investigated the coordinating properties of macrocycles **M** and **C2**–**M**–**C2** towards Nd^{3+} ion and their ability to sensitize its near-infrared luminescence, a spectral region useful for bioimaging, optical amplifiers, telecommunication and laser devices.[4b,22,23] The results have been compared with those obtained upon additions of Gd^{3+} since these two ions have identical charge and very similar ionic radii, and Gd^{3+} cannot be involved in energy (on the contrary of Nd^{3+}) or electron transfer processes with the investigated chromophores because it does not possess low-energy excited states (see Scheme 2) and it is not easy to reduce or oxidise.[1]

Results and Discussion

All experiments were performed in dichloromethane solution at 298 K. The number of equivalents of metal ion was calculated per macrocycle. The most relevant photophysical data of the investigated compounds are reported in Table 1.

Table 1. Photophysical parameters of the investigated shape-persistent macrocycles, **M** and **C2**–**M**–**C2**, and of the model compound **A** in air-equilibrated dichloromethane solution at 298 K.

	λ_{max} [nm]	ε_{max} [M^{-1} cm^{-1}]	λ_{em} [nm]	Φ_{em}	τ [ns]	θ [ns][a]
M	308	190000	381	0.60	0.76	0.19
A	346	15300	436	0.79	3.2	
C2–**M**–**C2**	309	191770	428	0.73	3.6	

[a] θ is the rotational relaxation time derived by Equation (2).

Photophysical Properties of M and C2–M–C2

Macrocycle **M** shows a strong structured absorption band in the UV region with λ_{max} = 308 nm (ε_{308nm} = 1.90×10^5 M^{-1} cm^{-1}) and a very intense blue emission with λ_{max} = 381 nm (black lines in Figure 1). The emission quantum yield (ϕ_{em} = 0.60) is somewhat smaller than those ex-

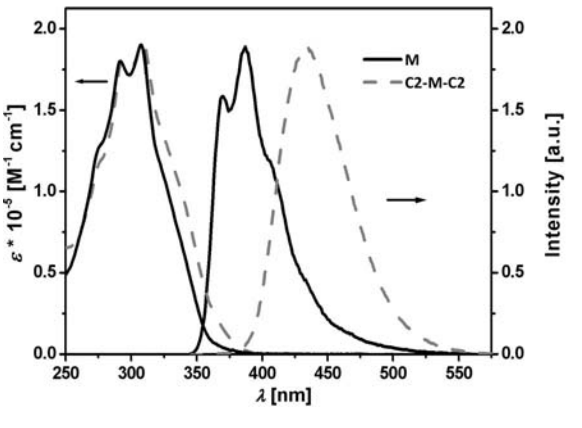


Figure 1. Absorption end emission spectra of **M** (black lines) and C2–M–C2 (grey lines) in air-equilibrated CH$_2$Cl$_2$ solution at 298 K.

hibited by analogous previously investigated macrocycles,[19b,21b] while the luminescent excited state lifetime (τ = 0.76 ns) is unperturbed. No evidence of phosphorescence was obtained in dichloromethane/chloroform, 1:1 (v/v) rigid matrix at 77 K.

Measurements of fluorescence anisotropy were performed to obtain information on the dimension of the molecule in solution. In fact, **M** has a high emission quantum yield and quite a short lifetime, ideal features for these kinds of experiments. Fluorescence anisotropy r is defined in Equation (1).

$$r = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp}) \tag{1}$$

$I_{\parallel}$ and $I_{\perp}$ are the emission intensities measured when the emission and excitation polarisers are oriented parallel or perpendicular, respectively. For randomly oriented molecules containing a single fluorophore, directly after excitation (t = 0), the anisotropy r_0 should be 0.4 if the absorption and emission transition dipole moments have the same orientation. This value decreases if they are not collinear and/or when the molecule undergoes a change in orientation during the excited state lifetime.[24] For a spherical rotor, the fluorescence anisotropy decay is monoexponential and can be fitted using the following model shown in Equation (2).

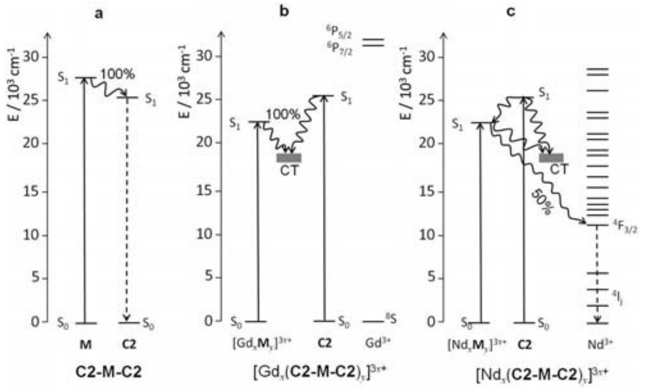
$$r(t) = r_0 e^{-t/\theta} \tag{2}$$

where θ is the rotational relaxation time. The value of θ can be related to the hydrodynamic volume V_h by the Stokes–Einstein–Debye equation (3), which describes the rotational diffusion of a solute molecule in a solvent consisting of molecules with much smaller dimensions, where η is the viscosity of the neat solvent, k_B the Boltzmann constant and T the absolute temperature.

$$\theta = V_h\, \eta / k_B\, T \tag{3}$$

In the present case, time-resolved measurements can be fitted according to Equation (2) with r_0 = 0.37 and θ = 0.19 ns, which gives a hydrodynamic volume V_h = 1880 Å^3. This result is in agreement with the molecular volume measured by X-ray crystallographic analysis of an analogous macrocycle (2218 Å^3)[19a] and estimated by molecular modelling calculations (2120 Å^3).[25]

The absorption spectrum (Figure 1, grey line) of macrocycle **C2–M–C2** coincides with that of a 1:2 mixture of the unsubstituted macrocycle **M** and *N*-benzyl-coumarin 2 (compound **A** in Scheme 1, λ_{max} = 346 nm; ε = 1.53×10^4 M^{-1} cm^{-1}), demonstrating that no ground-state interaction takes place between the two chromophores. Upon excitation of **C2–M–C2** with 278-nm light, which is absorbed almost exclusively by the macrocyclic component **M**, only one emission band with maximum at 428 nm, Φ = 0.73, and τ = 3.6 ns is observed (Figure 1, grey line; Table 1), which we assigned to the **C2** moieties on the basis of the emission properties of the model compound **A** (λ_{em} = 436 nm; Φ = 0.79; τ = 3.2 ns). This result is clear evidence that an energy transfer process from the excited state of the macrocyclic component to **C2** occurs with an almost unitary efficiency (Scheme 3, a). No phosphorescence was observed for **C2–M–C2** in a dichloromethane/chloroform 1:1 (v/v) rigid matrix. Fluorescence anisotropy measurements were been performed on this compound because the lifetime of its fluorescent excited state is longer than that of **M**, so that complete depolarisation takes place by rotational motions of the fluorophore in the time-window available with our equipment.



Scheme 3. Energy level diagram of (a) **C2–M–C2**, (b) [Gd**C2–M–C2**]$^{3+}$, and (c) [Nd**C2–M–C2**]$^{3+}$. Solid and dashed arrows represents absorption and emission processes, respectively, and wavy lines represent nonradiative deactivation processes. CT is a charge transfer state (the corresponding energy is uncertain). Triplet state energies of the **C2** and **M** moieties in **C2–M–C2** and [Ln$_x$(**C2–M–C2**)$_y$]$^{3x+}$ are not reported since no triplet emission in a rigid dichloromethane/chloroform 1:1 (v/v) matrix at 77 K was observed. The reported energy level diagram is valid for the complexes of different stoichiometries that can be formed, since the excited state properties are not dependent on the complex stoichiometry.

Complexation of Nd^{3+} Ions by Macrocycle M

Association Constants and Stoichiometry

Upon titration of a 2.0 μM solution of **M** in dichloromethane with Nd(CF$_3$SO$_3$)$_3$, strong changes in the macrocycle absorption and emission spectra are observed (Figure 2). The absorption spectrum shows a decrease in the band at 308 nm and the appearance of a new band at ca. 350 nm, similar to that observed for the diprotonated macrocycle.[21b] By plotting the intensity changes of these two bands at selected wavelengths, a non-mirror like trend may be observed (Figure 3). The increase of the absorbance at 377 nm is indeed less steep (solid squares in Figure 3, plateau reached at 2.0 equiv. of Nd^{3+}) than the corresponding decrease at 307 nm (solid circles in Figure 3, plateau reached at 1.2 equiv. of Nd^{3+}). This result suggests that more than one complex is formed, characterised by different molar absorption coefficients in the lowest energy band. Further evidence of this hypothesis is the presence of two families of isosbestic points: one between 0.0 and 1.0 equiv. (340 nm) and the other one between 1.0 and 2.0 equiv. (335 nm) (Figure 4). Indeed, by global fitting analysis of these spectra (see experimental section for details), complexes with 1:2, 1:1, and 2:1 metal to ligand stoichiometries are evident, with very high formation constants of $\log\beta_{1:1} = 8.1$, $\log\beta_{1:2} = 14.2$ and $\log\beta_{2:1} = 13.9$. At the beginning of the titration, when an excess of **M** is present, the $[Nd\mathbf{M}_2]^{3+}$ complex is formed, where each lanthanide ion is coordinated by two bpy units of two different macrocycles (Scheme 4, a). Upon increasing the metal ion concentration, the 1:1 complex is formed, in which two Nd^{3+} ions are likely sandwiched by two macrocycles (Scheme 4, b). A structure in which a Nd^{3+} ion is coordinated by two bpy units of a single macrocycle can be ruled out because of the rigidity of the backbone and the excessively large cavity of the macrocycle. In the presence of excess Nd^{3+} ions, the $[Nd_2\mathbf{M}]^{6+}$ complex is formed (Scheme 4, c), in which each metal ion is coordinated by one bpy unit with the remainder of the coordination sphere likely completed by counterions and/or solvent molecules. Part b of Figure 2 one can observe that the emission spectrum shows the complete disappearance of the macrocycle emission at 381 nm and the appearance of a very weak and broad band at 500 nm, clearly visible at the end of the titration and reminiscent of that observed upon protonation of the macrocycle bpy units.[21b]

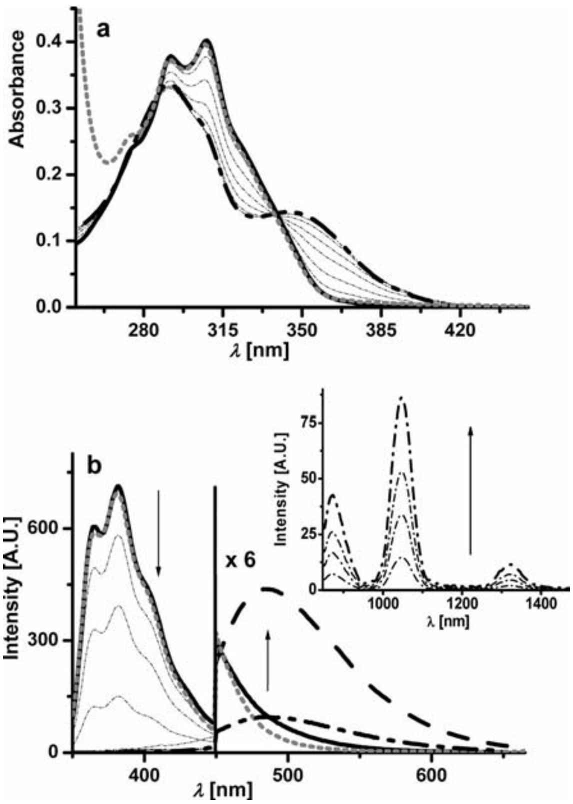


Figure 2. Absorption (a) and emission spectra (b, λ_{ex} = 337 nm) of a 2.0 μM air-equilibrated solution of **M** in dichloromethane at 298 K upon titration with $Nd(CF_3SO_3)_3$: 0.0 (bold solid line), 3.3 (bold dashed dotted line) equiv. of $Nd(CF_3SO_3)_3$, and successive additions of an excess of 1,4,8,11-tetraazacyclotetradecane (cyclam) (bold dotted grey line). For comparative purposes, the emission band obtained after the addition of 3.3 equiv. of $Gd(CF_3SO_3)_3$ is reported (dashed line). In the inset of panel b: emission spectra in the NIR region during the titration with $Nd(CF_3SO_3)_3$ are reported (λ_{ex} = 337 nm).

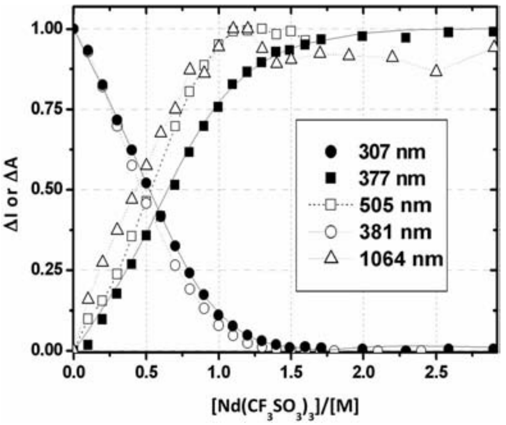


Figure 3. Normalised absorption (solid symbols) and emission (open symbols) titration curves obtained for **M** upon addition of $Nd(CF_3SO_3)_3$ (dichloromethane solution, 298 K, λ_{ex} = 337 nm). Solid lines show the results obtained from the Global Fitting Analysis; dotted lines are reported as a guide for the eyes.

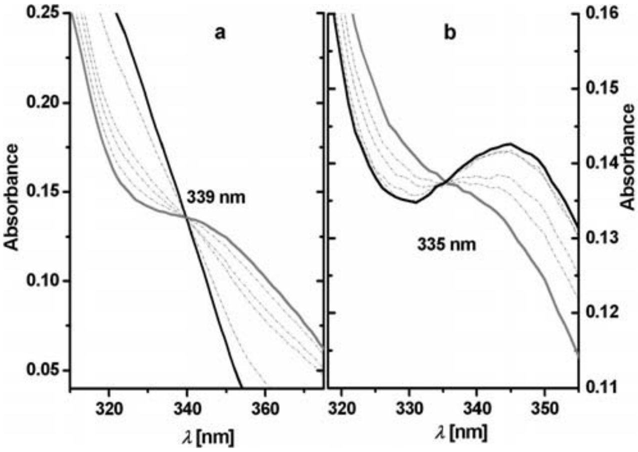
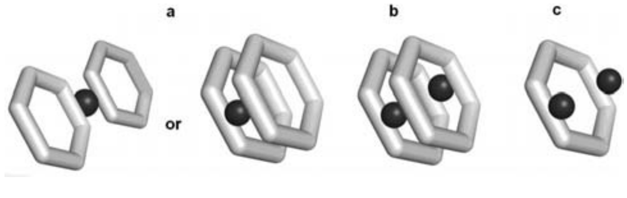


Figure 4. Enlarged view of the absorption spectra of a 2.0 μM air-equilibrated solution of **M** in dichloromethane at 298 K observed during the titration with $Nd(CF_3SO_3)_3$ in the following ranges: (a) 0.0 (bold black line) – 1.0 (bold grey line), and (b) 1.0 (bold grey line) – 2.0 (bold black line) equiv. of $Nd(CF_3SO_3)_3$.



Scheme 4. Schematic representation of Ln^{3+}/**M** complexes with different metal to ligand stoichiometries: (a) 1:2, (b) 1:1, and (c) 2:1.

The normalised emission intensity changes at 381 and 505 nm show a mirror-like trend with a plateau at 1.0 equiv. of Nd^{3+} (open symbols in Figure 3). This emission intensity decrease at 381 nm is practically coincident with the corresponding decrease in the absorbance at 307 nm. Notably, upon addition of 0.5 equiv. of Nd^{3+} ions, we observed a 50% decrease in emission intensity such that in the $[Nd\mathbf{M}_2]^{3+}$ complex, only the emission of the bpy unit directly coordinated by the lanthanide ion is quenched. Furthermore, upon excitation at 337 nm, where the absorbance is practically constant throughout the titration, the characteristic Nd^{3+} emission in the near infrared (NIR) region, reported in the inset of Figure 2 (c), can be observed with a maximum intensity reached after addition of 1.0 equiv. of metal ions (open triangles in Figure 3). This result demonstrates that the macrocycle can sensitise the lanthanide luminescence because the light at 337 nm is not directly absorbed by Nd^{3+}.

As reported in Figure 2 (grey dotted lines), the absorption and emission spectroscopic changes are completely reversible upon addition of an excess of competitive ligand for lanthanide ions, namely 1,4,8,11-tetraazacyclotetradecane (cyclam), which does not absorb at $\lambda > 280$ nm or emit in the investigated spectroscopic region.

Efficiency of Nd^{3+} Sensitisation and Emission Quantum Yield

To obtain quantitative information on the quenching/sensitisation efficiency, a comparison with the behaviour observed upon titration of **M** with $Gd(CF_3SO_3)_3$ was made. The absorption and emission spectra in the UV/Vis region are very similar to those discussed previously for the Nd^{3+} case, apart from a higher intensity corresponding to the complexed macrocycle emission at 500 nm (see the dashed line in the inset of Figure 2, b). No sensitised luminescence of Gd^{3+} could be observed, as expected on the basis of the energy of its emissive excited state (Scheme 2). The best fit of a global analysis of the absorption spectra was obtained by formation of complexes with 1:2, 1:1, and 2:1 metal to ligand stoichiometries, with association constants of $\log\beta_{1:1} = 8.0$, $\log\beta_{1:2} = 13.6$ and $\log\beta_{2:1} = 15.1$, which are very similar to those observed for the Nd^{3+} titration. To compare the emission quantum yield of the complexed macrocycle emitting at ca. 500 nm for $[Nd_2\mathbf{M}]^{6+}$ and $[Gd_2\mathbf{M}]^{6+}$, addition of 3.3 equiv. of Nd^{3+} or Gd^{3+} to a solution of **M** with the same concentration was performed. The experimental data shows that the $[Nd_2\mathbf{M}]^{6+}$ emission is quenched by 73% compared with that of $[Gd_2\mathbf{M}]^{6+}$ (inset of Figure 2, b). This quenching process cannot be ascribed to a stronger heavy atom effect for the intersystem crossing process $S_1 \rightarrow T_1$ in the case of $[Nd_2\mathbf{M}]^{6+}$ compared with $[Gd_2\mathbf{M}]^{6+}$ because Nd^{3+} ($Z = 60$) has a lower atomic number than Gd^{3+} ($Z = 64$). Moreover, no phosphorescence of the ligand was observed in the presence of either Gd^{3+} or Nd^{3+} in a dichloromethane/chloroform rigid matrix at 77 K. Therefore, we can attribute this effect to the energy transfer from S_1 to a manifold of isoenergetic excited states of the Nd^{3+} ion (Scheme 2). The mechanism of Nd^{3+} sensitisation via the singlet excited state of the complexed macrocycle can also be confirmed by the experimental observation that the efficiency of sensitised Nd^{3+} emission is not affected by the presence of dioxygen in solution.

The quenching of the S_1 state can also be observed by monitoring the emission intensity decays at 500 nm under the same conditions: a biexponential decay was observed, with τ values higher for complexes with Gd^{3+} ($\tau_1 = 7.9$ and $\tau_2 = 17.8$ ns) that those with Nd^{3+} ($\tau_1 = 2.7$ and $\tau_2 = 10.4$ ns), and we attribute the shorter lifetime component to the $[Ln_2\mathbf{M}]^{6+}$ (Ln = Gd or Nd) complexes because its relative contribution increases upon increasing the lanthanide ion concentration and a stronger heavy-atom effect is expected in the presence of two metal ions per macrocycle.

The emission quantum yield of $[Nd_2\mathbf{M}]^{6+}$ was obtained by comparing the area underneath the emission spectrum in the range 850–1400 nm of two isoabsorbing solutions at the excitation wavelength of 337 nm of $[Nd_2\mathbf{M}]^{6+}$ in air-equilibrated dichloromethane solution and a reference complex, tris(1,1,1,5,5-hexafluoroacetylacetonato)neodymium(III), dissolved in degassed and deuterated tetrahydrofuran ($\phi_{em} = 0.30\%$, see experimental section).[26] The resultant emission quantum yield of $[Nd_2\mathbf{M}]^{6+}$ is 0.13%, i.e. of the same order of magnitude of that reported for the reference complex.[26] The emission quantum yield (ϕ_{em}) can be expressed as the product of the energy transfer efficiency (η_{et}) and the intrinsic Nd^{3+} emission efficiency (ϕ_{Nd}), see Equation (4).

$$\phi_{em} = \eta_{et} \times \phi_{Nd} \qquad (4)$$

The value of ϕ_{Nd} is typically lowered by energy loss to high frequency vibrational modes of coordinated molecules (ligands or solvent molecules). For this reason, the reference neodymium complex contains C–F instead of C–H bonds in the ligand and a deuterated solvent was used (upon excitation in the ligand-centred bands $\eta_{et} = 20\%$, and $\phi_{Nd} = 1.5\%$).[26] In the present case, we calculated the sensitisation efficiency to be $\eta_{et} = 73\%$ from the difference between the $[Nd_2\mathbf{M}]^{6+}$ and $[Gd_2\mathbf{M}]^{6+}$ emission (see above), so that $\phi_{Nd} = 0.2\%$. The value of ϕ_{Nd} is much lower because of the presence of groups (e.g. C–H) in the ligand, which have high energy vibrations.

In order to investigate the ability of the macrocycle to encapsulate the metal ion and shield it from the bulk solvent, we measured the Nd^{3+} emission intensity in a dichloromethane or [D$_2$]dichloromethane solution of **M** upon addition of 0.5 equiv. of Nd^{3+} (experimental conditions in which only the $[Nd\mathbf{M}]^{3+}$ and $[Nd\mathbf{M}_2]^{3+}$ complexes are present at roughly the same concentration). In dichloromethane, the emission intensity is roughly 80% of that observed in deuterated solvent, demonstrating that the complexes are still sensitive to changes in the bulk solvent and that the metal ions are most likely not fully encapsulated.

Complexation of Nd^{3+} Ions by Macrocycle C2–M–C2

Association Constants and Stoichiometry

Strong changes are observed in the **C2**–**M**–**C2** absorption and emission spectra upon titration with $Nd(CF_3SO_3)_3$ (Figure 5). Similar to that observed for **M**, the absorption spectrum shows a decrease in the band at 309 nm and the appearance of a new band at 350 nm. The absorption increases and decreases are mirror-like, and reach a plateau after the addition of 1.0 equiv. of metal ions (Figure 6). These experimental results can be globally fitted by the formation of complexes with 1:1 and 1:2 metal to ligand stoichiometries, with very high association constants of $\log\beta_{1:1} = 9.1$ and $\log\beta_{1:2} = 15.3$. Although no evidence for the formation of a 2:1 (metal to ligand) complex was given by the fit for this macrocyclic ligand, it is likely to be formed when an excess of lanthanide ion is added, as previously observed in the case of **M**. Additionally, at the end of the titration, the observed absorption spectrum (Figure 5, a) is very similar to the sum of those of the model compound **A** and the complexed macrocycle **M**, confirming that the coumarin is not directly involved in the metal coordination.

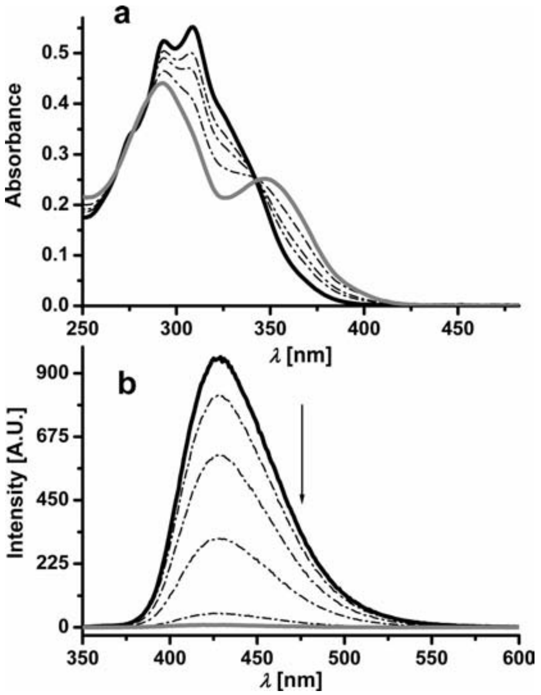


Figure 5. Absorption (a) and emission spectra (b) (λ_{ex} = 342 nm) of a 2.9 μM air-equilibrated solution of **C2**–**M**–**C2** in dichloromethane at 298 K upon titration with $Nd(CF_3SO_3)_3$: 0.0 (bold black line), 2.4 equiv. of $Nd(CF_3SO_3)_3$ (bold grey line).

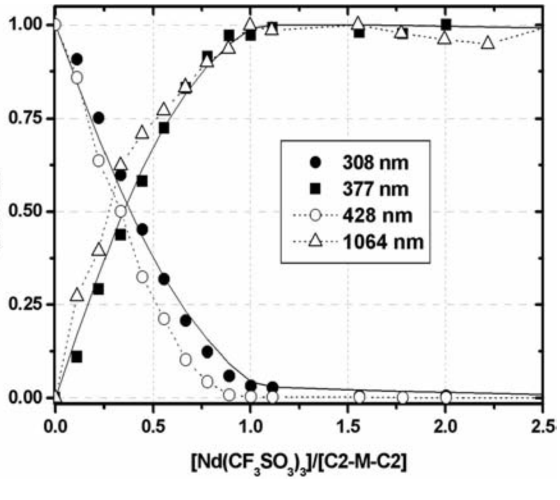


Figure 6. Normalised absorption (solid symbols) and emission (open symbols) titration curves obtained for **C2**–**M**–**C2** upon addition of $Nd(CF_3SO_3)_3$ (dichloromethane solution, 298 K, λ_{ex} = 337 nm). Solid lines show the results obtained from the Global Fitting Analysis; dotted lines are printed as a guide for the eyes.

Indeed, upon titration of a 3.6×10^{-5} M dichloromethane solution of **A**, very small changes in the absorption and emission spectra can be observed with up to 10 equiv. of metal ions added. If the coumarin dye were coordinated to a trivalent metal ion, a strong change in the absorption and emission spectra would be expected, since the lowest lying electronic transition has charge transfer character from the amine unit to the aromatic system.[27]

Upon excitation at 342 nm, where the absorption is constant throughout the titration and the percentage of light absorbed by the two coumarin chromophores is ca. 30%, the emission intensity at 428 nm, characteristic of the coumarin unit, decreases and practically disappears (residual emission intensity < 1%) upon addition of 1.0 equiv. (Figure 5, b). Concomitantly, an increase in the Nd^{3+} emission at 1064 nm can be observed with up to 1.0 equiv. of metal ions added (open triangles in Figure 6), while no emission band at 500 nm is visible even in the presence of a large excess of metal ions, in contrast with the previous case.

The absorption and emission spectroscopic changes are completely reversible upon addition of an excess of cyclam.

Efficiency of Nd^{3+} Sensitisation and Emission Quantum Yield

To compare the observed behaviour with that of a reference system in which the lanthanide ion cannot be involved in photoinduced energy and/or electron transfer processes, we performed a titration of **C2**–**M**–**C2** with $Gd(CF_3SO_3)_3$. The absorption and emission spectroscopic changes are practically coincident with those observed upon addition of Nd^{3+}, apart from in the NIR region. In particular, the emission spectrum after excitation at 342 nm shows the complete disappearance (quenching > 99%) of the coumarin emission, and no emission could be observed from the complexed macrocycle at 500 nm, which is significantly different to the behaviour previously observed for **M** complexes with Gd^{3+}. Indeed, at the end of the titration, excitation at 342 nm of the complexed macrocycle (70%) and the coumarin dyes (30%) does not result in either of the two expected emissions. The quenching of both complexed macrocycle and coumarin emissions is likely the result of an electron transfer process (Scheme 3, b). Indeed, upon bpy coordination with a trivalent metal ion, the macrocycle reduction becomes easier so that excitation of either the coumarin or the complexed macrocycle leads to a photoinduced electron transfer from the coumarin units to the macrocycle, behaviour similar to that previously observed upon diprotonation of the **C2**–**M**–**C2** macrocycle.[21b]

The Nd^{3+} emission quantum yield, determined with a large excess of metal ions, is lower (0.086%) for the complex with **C2**–**M**–**C2** compared to that with **M**. By assuming that the quantum yield of the intrinsic Nd^{3+} emission (ϕ_{Nd}) is the same for the two complexes and by using Equation (4), we can estimate an efficiency of ca. 50% for the energy transfer process, which is lower than that obtained for the **M** complex (73%). This decrease is in agreement with the presence of a competitive electron transfer deactivation process for the complexed S_1 excited state (Scheme 3, c). Analogously to the results observed for macrocycle **M**, no change of the Nd^{3+} emission intensity was obtained in deaerated solution: this result may suggest that sensitisation of the lanthanide ion takes place by the S_1 excited state, taking advantage of the high density of Nd^{3+} excited states which have energy comparable to that of the fluorescent excited state (Scheme 2), or that the quenching of the T_1 excited state by the Nd^{3+} ion is so fast that dioxygen quenching cannot compete.[3c,28] Since we have not observed phosphorescence in a rigid matrix of either the coumarin 2 or the macrocyclic moieties of **C2**–**M**–**C2**, even in the presence of Gd^{3+}, the former hypothesis is apparently the most likely one.

A comparison between the absorption and excitation spectra of the **C2**–**M**–**C2** complex with Nd^{3+} (λ_{em} = 1064 nm) shows that the **C2** units do sensitise the Nd^{3+} emission, even if a quantitative analysis of their contribution with respect to the macrocyclic unit cannot be performed because of the small molar absorption coefficient of the **C2** units compared to macrocycle **M**.

Conclusions

Macrocycles **M** and **C2**–**M**–**C2** are composed of a shape-persistent hexagonal backbone, appended with two nonchromophoric methoxytetrahydropyran units or two coumarin 2 dyes, respectively. These macrocycles, which contain bpy coordinating units on opposite sides, are very good ligands for Nd^{3+} and Gd^{3+} lanthanide ions in dichloromethane solution. Both macrocycles form complexes with 1:2 and 1:1 metal to ligand stoichiometries, characterised by high association constants. In these complexes, each lanthanide ion is likely sandwiched between two macrocycles and coordinated by two bpy units. In the case of **M**, clear evidence for the formation of a $[Ln_2\mathbf{M}]^{6+}$ complex (Ln^{3+} = Nd^{3+} or Gd^{3+}) is also obtained by absorption spectroscopic changes, whereas in the case of **C2**–**M**–**C2**, although the complex with 2:1 metal to ligand stoichiometry is also likely to be formed, all absorption changes reach a plateau at 1.0 equiv. of metal ion.

A good ligand for photoactive applications of lanthanide ions should not only coordinate them with high association constants, but also sensitise their emission (direct excitation is inefficient), and protect them from quenching by means of energy loss to high frequency vibrational modes of the solvent. The two presently investigated macrocycles fulfil these requisites, and behave as very good antenna because of their (a) very high molar absorption coefficients in the UV region (ε = 1.75×10^5 and 1.59×10^5 at 291 nm for Nd^{3+} complexes of **M** and **C2**–**M**–**C2**, respectively) and (b) high to moderate energy transfer efficiencies (73 % and ca. 50 % for Nd^{3+} complexes of **M** and **C2**–**M**–**C2**, respectively). As a consequence, the resultant brightness ($\varepsilon\times\phi_{em}$ ca. 230 and 140 for Nd^{3+} complexes of **M** and **C2**–**M**–**C2**, respectively) is quite good compared with those of other lanthanide complexes.[29] In the case of Nd^{3+} complexes with **C2**–**M**–**C2**, the energy transfer efficiency is lower because of the competitive quenching of the sensitising excited state by photoinduced electron transfer involving the coumarin dyes. For both macrocycles, the Nd^{3+} emission quantum yields are not sensitive to the presence of dioxygen, which demonstrates that the process of energy transfer from the organic ligands to the lanthanide ion is fast with respect to dioxygen quenching.

The investigated Nd^{3+} complexes of macrocycle **M** and **C2**–**M**–**C2** are good candidates as light-converting materials[30] for optical communication systems and as luminescent probes with potential applications in the field of sensors and photonics.

Experimental Section

Materials: $Nd(CF_3SO_3)_3$, $Gd(CF_3SO_3)_3$ and 1,4,8,11-tetraazacyclotetradecane (cyclam) were high purity reagents. Macrocycles **M** and **C2**–**M**–**C2** were synthesised according to previously published procedures.[21c]

Photophysical Experiments: Photophysical experiments were performed in dichloromethane solution, either in air-equilibrated conditions or degassed by several pump-freeze-thaw cycles. Titration with lanthanide ions were performed by addition of an acetonitrile solution of the corresponding triflate salt. UV/Vis absorption spectra were recorded with a Perkin–Elmer λ40 spectrophotometer. Fluorescence spectra were obtained with a Perkin–Elmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube for the UV/Vis range. Luminescence spectra in the NIR region were recorded by using a home-made apparatus based on an Edinburgh FLS920 spectrometer, which uses a xenon lamp as the excitation source, a NIR emission monochromator M300 with a 600 lines/mm grating, and a liquid-nitrogen-cooled hyperpure germanium crystal as detector. Fluorescence quantum yields were measured following the method of Demas and Crosby[31] using tris(1,1,1,5,5-hexafluoroacetyl-acetonato)neodymium(III) in deuterated tetrahydrofuran as a reference, kindly supplied by Prof. S. Yanagida.[26] Global fitting of absorption or emission spectra was performed using Specfit software.[32]

Fluorescence lifetime measurements were performed 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 and a LDH-P-C-405 pulsed diode laser.

The estimated experimental errors are: 2 nm on the band maximum, 5 % on the molar absorption coefficient, emission intensity in the UV/Vis spectral region, fluorescence lifetime, and log *K* values, 10 % on the fluorescence quantum yield, and emission intensity in the NIR spectral region.

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[1] a) R. Reisfeld, C. H. Jørgensen, in: *Lasers and Excited States of Rare Earths*, Springer, Berlin, **1977**; b) K. A. Gschneider Jr.,

L. Eyring, in: *Handbook on the Physics and Chemistry of Rare Earths*, North Holland, Amsterdam, **1979**, vol. 3 and 15.

[2] a) A. Beeby, S. Faulkner, *Chem. Phys. Lett.* **1997**, *266*, 116–122; b) A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. de Sousa, J. A. G. Williams, M. Woods, *J. Chem. Soc. Perkin Trans. 2* **1999**, 493–503; c) G. A. Hebbink, D. N. Reinhoudt, F. C. J. M. van Veggel, *Eur. J. Org. Chem.* **2001**, 4101–4106.

[3] a) V. Balzani, J. van de Vandeloosdrecht, A. Mecati, N. Sabbatini, J.-M. Lehn, R. Ziessel, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 190–191; b) N. Sato, S. Shinkai, *J. Chem. Soc. Perkin Trans. 2* **1993**, 621–624; c) C. Galaup, C. Picard, L. Cazaux, P. Tisnes, D. Aspe, H. Autiero, *New J. Chem.* **1996**, *20*, 997–999; d) S. I. Klink, L. Grave, D. N. Reinhoudt, F. C. J. M. van Veggel, *J. Phys. Chem. A* **2000**, *104*, 5457–5468; e) S. I. Klink, G. Hebbink, L. Grave, G. B. O. Alink, F. C. J. M. van Veggel, *J. Phys. Chem. A* **2002**, *106*, 3681–3689.

[4] a) D. Parker, *Coord. Chem. Rev.* **2000**, *205*, 109–130; b) J.-C. G. Bünzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *34*, 1048–1077; c) S. Faulkner, L. S. Natrajan, W. S. Perry, D. Sykes, *Dalton Trans.* **2009**, 3890–3899.

[5] J. P. Leonard, C. B. Nolan, F. Stomeo, T. Gunnlaugsson, in: *Top. Curr. Chem.* (Eds.: V. Balzani, S. Campagna), Springer, New York, **2007**, vol. 281, pp. 1.

[6] M. J. Kleinerman, *J. Chem. Phys.* **1969**, *51*, 2370–2375.

[7] a) W. D. Horrocks Jr., W. E. Collier, *J. Am. Chem. Soc.* **1981**, *103*, 2856–2862; b) J. Bruno, W. D. Horrocks Jr., R. J. Zauhar, *Biochemistry* **1992**, *31*, 7016–7026.

[8] a) C. Yang, L.-M. Fu, Y. Wang, J.-P. Zhang, W.-T. Wong, X.-C. Ai, Y.-F. Qiao, B.-S. Zou, L.-L. Gui, *Angew. Chem. Int. Ed.* **2004**, *43*, 5010–5013; b) M.-H. Ha-Thi, J. A. Delaire, V. Michelet, I. Leray, *J. Phys. Chem. A* **2010**, *114*, 3264–3269.

[9] a) G. A. Hebbink, S. I. Klink, L. Grave, P. G. B. O. Alink, F. C. J. M. van Veggel, *ChemPhysChem* **2002**, *3*, 1014–1018; b) L. Yang, Z. Gong, D. Nie, B. Lou, Z. Bian, M. Guan, C. Huang, H. J. Leeb, W. P. Baikb, *New J. Chem.* **2006**, *30*, 791–796; c) W.-K. Lo, W.-K. Wong, W.-Y. Wong, J. Guo, K.-T. Yeung, Y.-K. Cheng, X. Yang, R. A. Jones, *Inorg. Chem.* **2006**, *45*, 9315–9325.

[10] T. Lazarides, N. M. Tart, D. Sykes, S. Faulkner, A. Barbieri, M. D. Ward, *Dalton Trans.* **2009**, 3971–3979.

[11] W. D. Horrocks Jr., J. P. Bolender, W. D. Smith, R. M. Supowski, *J. Am. Chem. Soc.* **1997**, *119*, 5972–5973.

[12] a) S. Aime, M. Fasano, E. Terreno, *Chem. Soc. Rev.* **1998**, *27*, 19–29; b) E. Tóth, L. Burai, A. E. Merback, *Coord. Chem. Rev.* **2001**, *216*, 363–382; c) D. Parker, *Chem. Soc. Rev.* **2004**, *33*, 156–165; d) T. Koullourou, L. S. Natrajan, H. Bhavsar, S. J. A. Pope, J. Feng, J. Narvainen, R. Shaw, E. Scales, R. Kauppinen, A. M. Kenwright, S. Faulkner, *J. Am. Chem. Soc.* **2008**, *130*, 2178–2179; e) E. G. Moore, A. P. S. Samuel, K. N. Raymond, *Acc. Chem. Res.* **2009**, *42*, 542–552.

[13] E. J. New, D. Parker, D. G. Smith, J. W. Walton, *Curr. Opin. Chem. Biol.* **2010**, *14*, 238–246.

[14] a) R. A. Poole, G. Bobba, M. J. Cann, J.-C. Frias, D. Parker, R. Pecacock, *Org. Biomol. Chem.* **2005**, *3*, 1013–1024; b) P. Escribano, B. Julian-Lopez, J. Planelles-Arago, E. Cordoncillo, B. Viana, C. Sanchez, *J. Mater. Chem.* **2008**, *18*, 23–40; c) A. S. Chauvin, S. Comby, B. Song, C. D. B. Vandevyver, J.-C. G. Bünzli, *Chem. Eur. J.* **2008**, *14*, 1726–1739.

[15] J.-C. G. Bünzli, A.-S Chauvin, C. D. B. Vandevyver; S. Bo, S. Comby, in: *Fluorescence Methods and Applications: Spectroscopy, Imaging, and Probes*, Book Series: *Annals of the New Academy of Science*, Blackwell Publishing, Oxford, **2008**, vol. 1130, pp. 97–105.

[16] a) K. Kuriki, Y. Koike, Y. Okamoto, *Chem. Rev.* **2002**, *102*, 2347–2356; b) J.-C. G. Bünzli, *Acc. Chem. Res.* **2006**, *39*, 53–61; c) A. de Bettencourt-Dias, *Dalton Trans.* **2007**, 2229–2241.

[17] a) B. Alpha, V. Balzani, J.-M. Lehn, S. Perathoner, N. Sabbatini, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1266–1267; b) B. Alpha, J.-M. Lehn, G. Mathis, *Angew. Chem.* **1987**, *99*, 266–267.

[18] a) V. Balzani, E. Berghmans, J.-M. Lehn, N. Sabbatini, R. Terorde, R. Ziessel, *Helv. Chim. Acta* **1990**, *73*, 2083–2089; b) C. Bazzicalupi, A. Bencini, A. Bianchi, C. Giorgi, A. Masotti, B. Valtancoli, V. Fusi, A. Roque, F. Pina, *Chem. Commun.* **2000**, 561–562; c) L. J. Charbonnière, R. Ziessel, M. Montalti, L. Prodi, Z. Nelsi, B. Christian, G. Wipff, *J. Am. Chem. Soc.* **2002**, *124*, 7779–7788; d) L. N. Puntus, *Helv. Chim. Acta* **2009**, *92*, 2552–2563; e) H.-B. Xu, L.-Y. Zhang, X.-M. Chen, X.-L. Li, Z.-N. Chen, *Cryst. Growth Des.* **2009**, *9*, 569–576; f) H. Li, N. Lin, Y. Wang, Y. Feng, Q. Gan, H. Zhang, Q. Dong, Y. Chen, *Eur. J. Org. Chem.* **2009**, 519–523.

[19] 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, F. Marchioni, B. F. Ribera, V. Balzani, D. M. Opris, A. D. Schlüter, *ChemPhysChem* **2006**, *7*, 229–239.

[20] 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.

[21] a) J. Sakamoto, A. D. Schlüter, *Eur. J. Org. Chem.* **2007**, 2700–2712; b) C. Giansante, V. Balzani, P. Ceroni, M. Venturi, J. Sakamoto, A. D. Schlüter, *Chem. Eur. J.* **2008**, *14*, 10772–10781; c) C. Giansante, P. Ceroni, M. Venturi, J. Sakamoto, A. D. Schlüter, *ChemPhysChem* **2009**, *10*, 495–498.

[22] a) W. D. Horrocks Jr., N. Albin, in: *Progress in Inorganic Chemistry* (Ed.: S. J. Lippard), John Wiley & Sons, New York, **1984**; vol. 31, pp. 1; b) W. T. Carnall in *Handbook on The Physics and Chemistry of Rare Earths* (Eds.: K. A. Gschneider Jr., L. Eyring), Elsevier, Amsterdam, **1987**, vol. 3, pp. 171; c) S. Faulkner, J. L. Matthews, in: *Comprehensive Coordination Chemistry*, 2nd ed. (Ed.: M. D. Ward), Elsevier, **2004**, vol. 9, pp. 913–944; d) S. Comby, J.-C. G. Bünzli in *Handbook of the Chemistry and the Physics of Rare Earths* (Eds.: K. A. Gschneider Jr., J.-C. G. Bünzli, V. K. Pecharsky), Elsevier, **2007**, vol. 37, pp. 217–470.

[23] a) M. P. O. Wolbers, F. C. J. M. van Veggel, F. G. A. Peters, S. E. Eric van Beelen, J. W. Hofstraat, F. A. J. Geurt, D. N. Reinhoudt, *Chem. Eur. J.* **1998**, *4*, 772–780.

[24] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 3rd ed., Springer, New York, **2006**.

[25] The structure of **M** was optimised using ChemSketch 12.

[26] M. Iwamuro, Y. Wada, T. Kitamura, N. Nakashima, S. Yanagida, *Phys. Chem. Chem. Phys.* **2000**, *2*, 2291–2296.

[27] A. V. Deshpande, R. R. Panhalkar, *J. Lumin.* **2002**, *96*, 185–193.

[28] See, for instance: N. S. Baek, M. K. Nah, Y. H. Kim, H. K. Kim, *J. Lumin.* **2007**, *127*, 707–712.

[29] a) M. H. V. Werts, R. H. Woudenberg, P. G. Emmerink, R. van Gassel, J. W. Hofstraat, J. W. Verhoeven, *Angew. Chem. Int. Ed.* **2000**, *39*, 4542–4544; b) M. H. V. Werts, *Sci. Prog.* **2005**, *88*, 101–131.

[30] See, for example: a) D. An, Z. Yue, R. T. Chen, *Appl. Phys. Lett.* **1998**, *72*, 2806–2807; b) J. W. Hofstraat, M. P. O. Wolbers, F. C. J. M. van Veggel, D. N. Reinhoudt, M. H. V. Werts, J. W. Verhoeven, *J. Fluorine Chem.* **1998**, *8*, 301–308; c) V. Balzani, P. Ceroni, M. Maestri, V. Vicinelli, *Curr. Opin. Chem. Biol.* **2003**, *7*, 657–665.

[31] J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991–1024.

[32] a) R. A. Binstead, *SPECFIT*, Spectrum Software Associates, Chapell Hill, NC, **1996**; b) H. Gampp, M. Maeder, C. J. Meyer, A. D. Zuberbühler, *Talanta* **1985**, *32*, 251–264.

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