Supramolecular Chemistry

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Self-Assembly of a Light-Harvesting Antenna Formed by a Dendrimer, a Ru^{II} Complex, and a Nd^{III} Ion**

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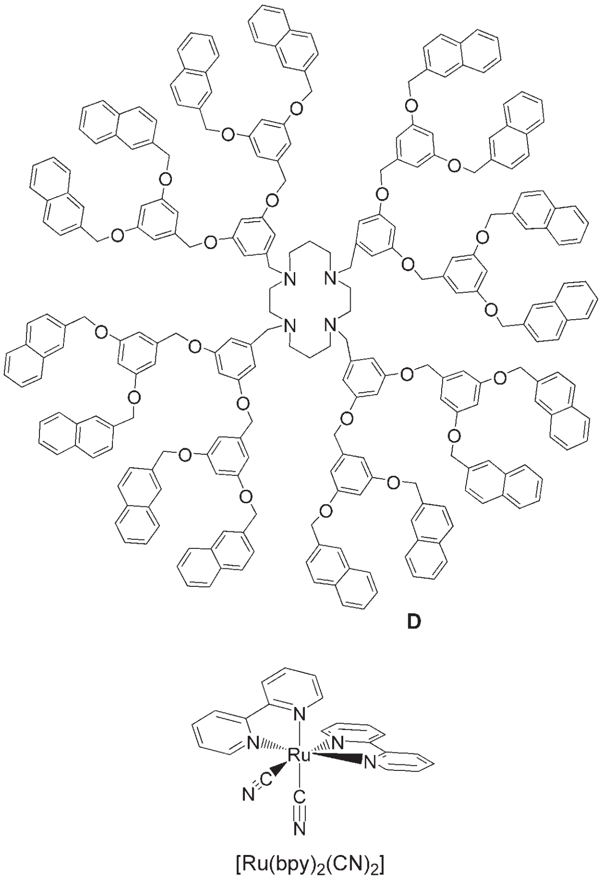
Self-assembly of molecular components by weak, non-covalent interactions is widespread in nature's forms and functions[1] and is attracting increasing interest in artificial systems.[2] The study of light-induced processes in artificial molecular assemblies is a very promising approach to control mechanical movements, process information, and harvest sunlight.[3]

Lanthanide metal ions exhibit long-lived and line-like luminescence, but direct excitation of lanthanide metal ions is inefficient because of the forbidden nature of their electronic transitions. Therefore, coordinating organic or inorganic chromophores are usually exploited to sensitize the luminescence of the ions (antenna effect).[4] A particularly interesting class of ligands are dendrimers because they can collect excitation light and encapsulate chemical species in predetermined sites.[5] We report herein on a three-component self-assembled light-harvesting antenna formed by a dendrimer, a Ru^{II} complex, and a luminescent Nd^{III} ion.

Dendrimer **D** (Scheme 1), consisting of a 1,4,8,11-tetraazacyclotetradecane (cyclam) core with appended 12 dimethoxybenzene and 16 naphthyl units[6] encapsulates Nd^{III} ions, but, when photoexcited, it is unable to transfer energy to the metal ion.[7] We have now found that when Nd^{III} is added, as trifluoromethanesulfonate salt, to a CH_3CN:CH_2Cl_2 solution containing **D** and [Ru(bpy)$_2$(CN)$_2$] in a 1:1 molar ratio, self-assembly leads to a three-component system, {**D**·Nd^{III}·[Ru(bpy)$_2$(CN)$_2$]}, in which the luminescence of both **D** and [Ru(bpy)$_2$(CN)$_2$] is quenched and the luminescence of Nd^{III} is sensitized. In this three-component system excitation of the dendrimer in the UV and of the Ru^{II} complex in the Vis and UV spectral regions is indeed followed by efficient energy transfer to the lanthanide metal ion which emits NIR light, and plays the role of a light harvesting unit. For comparison purposes, we have also investigated the systems in which Gd^{III} replaces Nd^{III}.



Scheme 1. Formulae of dendrimer **D** and the [Ru(bpy)$_2$(CN)$_2$] complex.

Dendrimer **D** has a single and strongly coordinating site, that is, its cyclam core. In CH_3CN:CH_2Cl_2 1:1 (v/v) solution, **D** forms stable **D**$_2$M complexes,[8] where M = Nd^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III} (see Supporting Information).

Complexes of Ru^{II} containing 2,2′-bipyridine (bpy) and cyanide ligands, [Ru(bpy)$_2$(CN)$_2$] and [Ru(bpy)(CN)$_4$]$^{2-}$, are particularly interesting because they are luminescent and can play the role of ligands giving rise to supercomplexes.[9,10] In particular, [Ru(bpy)$_2$(CN)$_2$] has low-energy absorption bands and a luminescence band in the visible region which are related to metal-to-ligand (bpy) charge-transfer (MLCT) excited states (spin-allowed states for the absorption bands; the lowest spin-forbidden state for the emission band).[9b,c,11] The energies of these excited states are strongly dependent on the interaction of the cyanide ligands with solvent molecules,[9,11] proton,[12] or metal ions.[13] In particular, the lowest energy band maximum shifts toward the blue when cyanide ligands are linked to a cation because of the lower electron

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density on the Ru^{II} metal center. Titration of a $CH_3CN:CH_2Cl_2$ 1:1 (v/v) solution of $[Ru(bpy)_2(CN)_2]$ with Nd^{III} causes changes in the absorption spectrum and quenching of the $[Ru(bpy)_2(CN)_2]$ emission, accompanied by sensitized Nd^{III} emission. When the absorption and emission titration plots are superimposed they show a linear trend which reaches a plateau at ca. 0.5 equivalent of Nd^{III} per Ru^{II} complex (see Supporting Information).

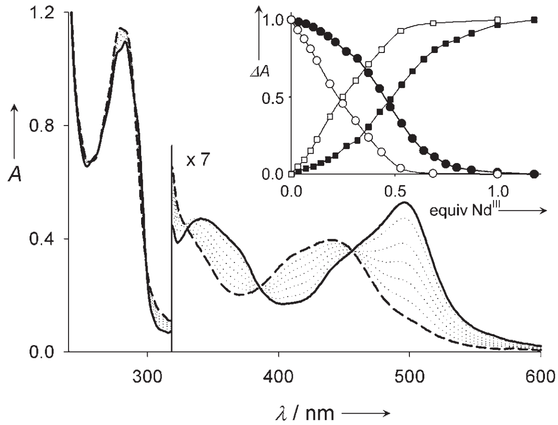

Figure 1. Changes in the absorption spectrum of a 1:1 mixture of dendrimer **D** and $[Ru(bpy)_2(CN)_2]$ ($c = 7.7\times10^{-6}$ M) in $CH_3CN:CH_2Cl_2$ 1:1 (v/v) solution at 298 K upon titration with 1 mM $Nd(CF_3SO_3)_3$. The bold dashed and solid lines are the spectra upon addition of 0 and 1.0 equivalents of $Nd(CF_3SO_3)_3$, respectively. Inset shows the normalized absorbance changes at 402 (squares) and 496 nm (circles) in the presence (solid symbols) and absence (empty symbols) of dendrimer **D**.

The absorption and emission spectra of a 1:1 mixture of dendrimer **D** and $[Ru(bpy)_2(CN)_2]$ in $CH_3CN:CH_2Cl_2$ 1:1 (Figure 1 and 2, solid lines) are equal to the sum of the absorption and emission spectra of the two separated components, showing that there is no interaction. Upon titration of this solution with $Nd(CF_3SO_3)_3$, the lowest energy absorption band is blue-shifted (Figure 1), as observed for the titration of $[Ru(bpy)_2(CN)_2]$ with $Nd(CF_3SO_3)_3$ in the absence of dendrimer. On a quantitative basis, however, the plots of the absorption changes at 402 and 496 nm (inset of Figure 1) are substantially different from the plots obtained in the absence of dendrimer **D**. Instead of linear plots that reach a plateau at approximately 0.5 equivalents of Nd^{III} per Ru^{II} complex (empty symbols in Figure 1, inset), in the presence of dendrimer **D**, two mirror-image like sigmoid plots are observed with a plateau at approximately 1.0 equivalent (solid symbols in Figure 1, inset).

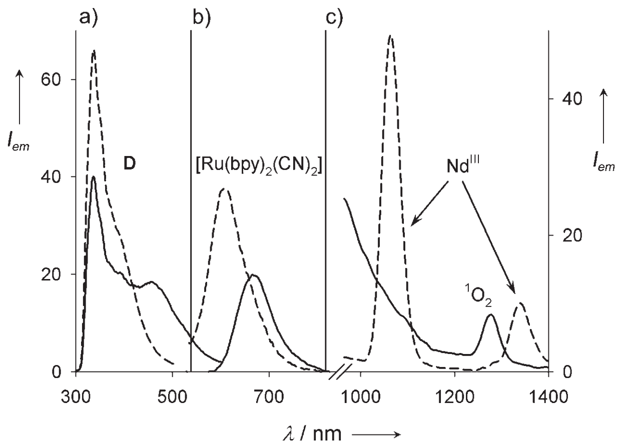

Figure 2. Emission spectra in the a) 300–550 nm ($\lambda_{ex} = 260$ nm), b) 550–800 nm ($\lambda_{ex} = 450$ nm), and c) NIR spectral region ($\lambda_{ex} = 450$ nm) of a 1:1 mixture of dendrimer **D** and $[Ru(bpy)_2(CN)_2]$ (7.7×10^{-6} M) in $CH_3CN:CH_2Cl_2$ 1:1 (v/v) solution at 298 K before (——) and after (– – –) addition of 1.0 equivalent of $Nd(CF_3SO_3)_3$.

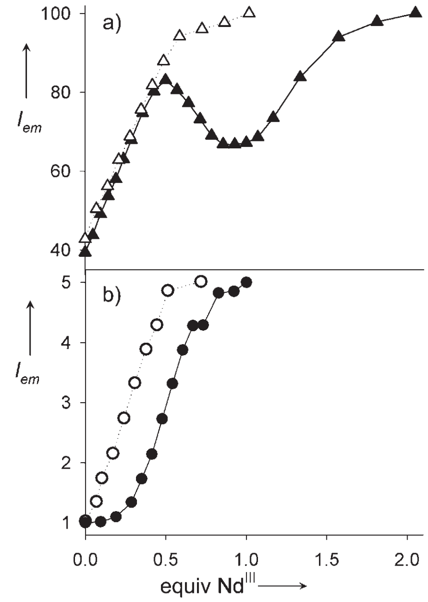

Figure 3. a) Emission intensity changes at 337 nm ($\lambda_{ex} = 260$ nm) of dendrimer **D** (7.7×10^{-6} M) in $CH_3CN:CH_2Cl_2$ 1:1 (v/v) solution at 298 K upon titration with Nd^{III} in the presence (▲) or in the absence (△) of $[Ru(bpy)_2(CN)_2]$ (7.7×10^{-6} M). b) Emission intensity changes at 1064 nm ($\lambda_{ex} = 450$ nm) upon titration with Nd^{III} of $[Ru(bpy)_2(CN)_2]$ (7.7×10^{-6} M) in $CH_3CN:CH_2Cl_2$ 1:1 (v/v) solution at 298 K in the presence (●) or in the absence (○) of dendrimer **D** (7.7×10^{-6} M).

As far as emission is concerned, the changes in the shape and position of the naphthyl-based (Figure 2a) and $[Ru(bpy)_2(CN)_2]$ emission bands (Figure 2b) are apparently similar to those observed for the titration of the two separate components (see Supporting Information). However, a closer look at the data reveals substantial differences. Upon excitation at 260 nm, where most of the light is absorbed by the **D** component, the intensity of the naphthyl-monomer emission at 337 nm (Figure 3a, solid triangles) does not show a continuous increase, as observed in the absence of the $[Ru(bpy)_2(CN)_2]$ complex (Figure 3a, empty triangles), but reaches a maximum at 0.5 equivalents and then decreases up to about 1.0 equivalent of Nd^{III} to rise again for higher metal-ion concentrations. The emission intensity at 1.0 equivalent is lower than that observed in the absence of $[Ru(bpy)_2(CN)_2]$ (Figure 3a, empty triangles). These results show that a three-component system $\{\mathbf{D}\cdot Nd^{III}\cdot[Ru(bpy)_2(CN)_2]\}$ is formed in which the dendrimer emission is quenched. Further addition of Nd^{III} (> 1.0 equiv) revives the dendrimer emission up to the value obtained in the absence of the Ru^{II} complex, as expected, because excess of Nd^{III} disassembles the three-component system into dendrimer–neodymium and [Ru(bpy)$_2$(CN)$_2$]–neodymium two-component species. The three-component system can also be disassembled by addition of **D**, [Ru(bpy)$_2$(CN)$_2$], or cyclam. When Nd^{III} is replaced by Gd^{III}, which exhibits the same coordinating properties of Nd^{III} but has no low-energy excited state, the titration plot of the dendrimer emission intensity at 337 nm resembles that obtained with Nd^{III}, suggesting that, also in this case, a three-component system {**D**·Gd^{III}·[Ru(bpy)$_2$(CN)$_2$]} is formed, in which the dendrimer emission is quenched by the Ru^{II} complex.

Upon excitation of the {**D**·M^{III}·[Ru(bpy)$_2$(CN)$_2$]} systems at 450 nm, at which wavelength the light is absorbed only by the [Ru(bpy)$_2$(CN)$_2$] component, the MLCT emission intensity at 607 nm is much weaker for M^{III} = Nd^{III} than for M^{III} = Gd^{III} (see Supporting Information). Such a quenching effect can be assigned to energy transfer from the [Ru(bpy)$_2$(CN)$_2$] excited state to Nd^{III}, as confirmed by the appearance of Nd^{III} characteristic emission bands (Figure 2c). On a quantitative basis, again, the plot of emission intensity at 1064 nm for the three-component system is substantially different from the plot obtained in the absence of dendrimer **D**. Instead of a linear plot that reaches a plateau at approximately 0.5 equivalent of Nd^{III} per [Ru(bpy)$_2$(CN)$_2$], a sigmoid plot with a plateau at approximately 1.0 equivalents is observed in presence of dendrimer **D** (Figure 3b). The sensitized intensity maximizes for 1:1:1 ratio of the three components confirming the formation of a {**D**·Nd^{III}·[Ru(bpy)$_2$(CN)$_2$]} species.

Excitation of [Ru(bpy)$_2$(CN)$_2$] both in the absence and in the presence of **D** leads to $^1O_2$ emission (solid line in Figure 2c). In both cases, the titration with Nd^{III} leads to the disappearance of the $^1O_2$ emission and the appearance of the Nd^{III} characteristic emission bands. The $^1O_2$ emission, however, does not disappear upon titration with Gd^{III}.

The main photophysical processes of the {**D**·Nd^{III}·[Ru(bpy)$_2$(CN)$_2$]} adduct are summarized in Figure 4 which shows the energy levels of the three components. In the two-component dendrimer–Nd^{III} system, energy transfer from either the lowest singlet (S$_1$) or triplet (T$_1$) excited state of the naphthyl units of the dendrimer to the lanthanide ion does not occur. Sensitization of the Nd^{III} emission upon dendrimer excitation in the three component system is mediated by the [Ru(bpy)$_2$(CN)$_2$] component. Comparison between the emission quantum yield of [Ru(bpy)$_2$(CN)$_2$] upon excitation at 260 nm (dendrimer absorption) and 450 nm ([Ru(bpy)$_2$(CN)$_2$] absorption) has allowed us to estimate that the energy-transfer efficiency from the S$_1$ excited state of the naphthyl groups to the ^{1}MLCT excited state of [Ru(bpy)$_2$(CN)$_2$] is about 60 % (Figure 4). The energy-transfer efficiency from the ^{3}MLCT excited state of [Ru(bpy)$_2$(CN)$_2$] to Nd^{III} can be assumed to be equal to the efficiency of the quenching of the [Ru(bpy)$_2$(CN)$_2$] emission (ca. 90 %) because quenching by electron transfer can be ruled out in view of the Nd^{III} redox properties. No evidence of energy transfer in the adduct from the naphthyl-localized T$_1$ excited state of the dendrimer to the lowest ^{3}MLCT state of [Ru(bpy)$_2$(CN)$_2$] has been found since no change in the T$_1$ lifetime at 77 K has been observed.

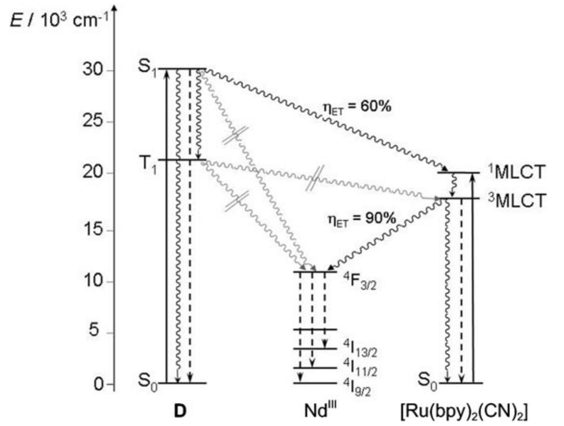

Figure 4. Energy-level diagram showing the excited states involved in the main photophysical processes (absorption: solid lines; radiative deactivation: dashed lines; non-radiative deactivation processes: wavy lines) of the {**D**·Nd^{III}·[Ru(bpy)$_2$(CN)$_2$]} three-component system. For the sake of clarity, naphthyl excimer energy level has been omitted.

In conclusion, the reversible self-assembly of a {**D**·Nd^{III}·[Ru(bpy)$_2$(CN)$_2$]} three-component system has been demonstrated. Because of the complementary properties of the three components, new functions emerge from their assembly. Dendrimer **D** has a very high molar absorption coefficient in the UV spectral region because of 12 dimethoxybenzene and 16 naphthyl units, but it is unable to sensitize the emission of a Nd^{III} ion placed in its cyclam core. The [Ru(bpy)$_2$(CN)$_2$] complex can coordinate (by the cyanide ligands) and sensitize the emission of Nd^{III} ions. Self-assembly of the three species leads to a quite unusual Nd^{III} complex which exploits a dendrimer and a Ru^{II} complex as ligands. Such a system behaves as an antenna that can harvest UV to Vis light absorbed by both the Ru^{II} complex and the dendrimer and emit in the NIR region with line-like bands. In principle, the emission wavelength can be tuned by replacing Nd^{III} with other lanthanide ions having low-lying excited states. Useful applications can be envisaged in the field of biosensors, imaging,[4,14] and photonics.[15]

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