

An artificial antenna complex containing four Ru(bpy)₃²⁺-type chromophores as light-harvesting components and a Ru(bpy)(CN)₄²⁻ subunit as the energy trap. A structural motif which resembles the natural photosynthetic systems

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A cyclam subunit bearing four light-harvesting Ru(bpy)₃²⁺-type species is connected to a Ru(II) compound having low-lying excited states (energy trap) by hydrogen bonding: the light absorbed by the light-harvesting elements is funnelled to the energy trap with high efficiency.

The antenna effect is an essential property of the natural photosynthetic processes.¹ It is also foreseen that for several artificial processes driven by light energy, the same effect may be crucial to gain efficiency. For this reason, research on the design of artificial multichromophoric systems capable of performing the antenna effect is at the center of a large degree of interest. Several approaches have been employed to this aim, sometimes quite different one another, and many artificial light-harvesting systems have been reported, which range from light-active dendrimers to non-covalent supramolecular assemblies.²

Within the field of non-covalent assemblies made of photoactive species, [Ru(bpy)(CN)₄]²⁻ (bpy = 2,2'-bipyridine) is a quite interesting species since it possesses four cyanide ligands which are able to link acidic functions by hydrogen bonding.³ By virtue of such a property, this species has been used to prepare multicomponent, hydrogen-bonded systems in which it is connected with [Ru(bpy)₃]²⁺-type chromophores, and where efficient energy transfer from these latter species to the [Ru(bpy)(CN)₄]²⁻ subunit takes place.⁴

We have been inspired from the reported, above mentioned abilities of [Ru(bpy)(CN)₄]²⁻ and by the structure of the light-harvesting antenna systems of some photosynthetic bacteria—like the LH1 and LH2 systems of *Rhodospseudomonas acidophila*,⁵ in which the main chromophores are arranged to form well-defined 'wheels', with the energy trap connecting the reaction center (RC) nested into the LH1 wheel—to design the multichromophoric system shown in Fig. 1.† In this species, the cyclam subunit plays the role of a scaffold, with appended, modified [Ru(bpy)₃]²⁺-type subunits acting as light-harvesting elements (A in Fig. 1). By taking advantage of the two ammonium protons of the cyclam structure, [Ru(bpy)(CN)₄]²⁻ can be coordinated and may act as the energy trap (T in Fig. 1) of the whole assembly, since the excited state of this latter species would be the lowest-lying excited state of the entire array. The system has some resemblance to the LH1-RC system, with the difference that whereas in Nature the structural organization is guaranteed by the proteic architecture, here it is sustained by covalent bonds for the light-harvesting subunits and by hydrogen bonding for the connection between the light-harvesting part of the antenna and the energy trap.

The absorption spectra in air-equilibrated acetonitrile of the separated components, the tetrametallic cyclam-Ru₄ compound **1** and [Ru(bpy)(CN)₄]²⁻ (**2**), are shown in Fig. 2, where also their emission spectra are reported. Compound **1** exhibits absorption and emission properties, dominated by metal-to-

ligand charge-transfer (MLCT) excited states ($\lambda_{\max}(\text{abs}) = 452$ nm ($\epsilon = 46900$ M⁻¹ cm⁻¹); $\lambda_{\max}(\text{em}) = 634$ nm; $\tau = 177$ ns; $\Phi = 0.012$), essentially identical to those of the parent [Ru(bpy)₂(dm-bpy)]²⁺ species (dm-bpy = 4,4'-dimethyl-2,2'-bipyridine),⁷ when the different number of metal centers is considered. Trifluoroacetic acid does not have any effect on the absorption and emission spectra,‡ while the presence of dabco (1,4-diazabicyclo[2.2.2]octane) has a moderate effect on the emission properties, with emission intensity decreased by 10% when one equivalent of dabco is present. No further change is observed upon successive dabco addition, confirming that two amino protons are present on the cyclam moiety. Both MLCT absorption and emission bands of **2** ($\lambda_{\max}(\text{abs}) = 537$ nm ($\epsilon =$

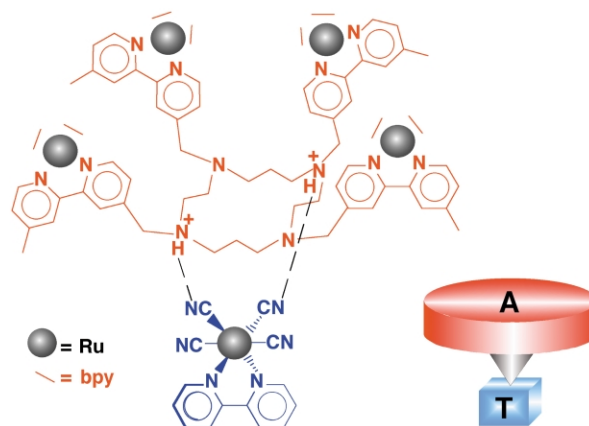


Fig. 1 Structure and schematic representation of the new hydrogen-bonded assembly investigated. The 1 : 1 stoichiometry is inferred from experimental data (see later in the text). The red species (**1**) represents the light-harvesting module and the blue one (**2**) is the energy trap. Charges of the compounds are omitted for the sake of clearness.

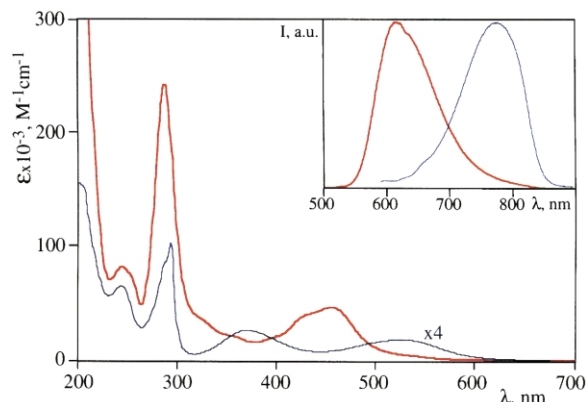


Fig. 2 Absorption and (normalized) uncorrected emission spectra of isolated **1** (red) and **2** (blue) in acetonitrile.

4600 M⁻¹ cm⁻¹); $\lambda_{\text{max}}(\text{em}) = 780 \text{ nm}$; $\tau = 8 \text{ ns}$; $\Phi = 0.0002$) are significantly red-shifted with respect to those of **1**, as a consequence of the electron donor effect of the negatively-charged cyanides which leave more electron density on the metal.³ Emission lifetime and quantum yield are also noticeably lower, as expected on the basis of the energy gap law. As is well-known,^{3,4} the spectroscopic and photophysical properties of **2** are strongly sensitive to the environment, in particular with regard to possible hydrogen bonding/protonation; indeed in the presence of acid, absorption and emission maxima gradually move to higher energies, and lifetime and quantum yield significantly increase. However, luminescence emission maximum of **2** in a possible adduct with **1** is not expected to overcome the limit value of 650 nm, which is the obtained emission maximum (in deoxygenated acetonitrile) of a 1:1 supercomplex between **2** and the polyaza macrocycle [32]ane-N₈H₈⁸⁺, in which all the cyanide ligands of **2** are involved in hydrogen bonding.⁶ This implies that when **2** is coordinated to **1** by hydrogen bonding, although its properties are modified by the environment, it can still play the role of an energy trap.

To investigate the association of **1** and **2** in solution, we examined the changes on the luminescence spectra of **1** ($5 \times 10^{-6} \text{ M}$) upon successive addition of **2** (Fig. 3), until a 1:6 molar ratio was reached. The small concentration of **2** used allows us to neglect the effect of bimolecular quenching. By taking into account the excitation wavelength used (455 nm) and the different absorbance of **1** and **2** at such a wavelength, almost exclusively compound **1** is excited. On considering also the low optical density of the solution, the luminescence titration shown in Fig. 3 definitely indicates that quenching of emission of **1** takes place. The stable spectrum obtained at the end of the titration (*i.e.* for a 1:4 1/2 molecular ratio) suggests that at least two excited states contribute, more or less with the same weight, to the luminescence output. Deconvolution of the final spectrum gives two emission bands, the first one which coincides with that of isolated **1** and the second one peaking at 665 nm. Luminescence decay was fitted by two lifetimes, $\tau(1) = 15 \text{ ns}$ and $\tau(2) = 70 \text{ ns}$, both at 620 and 670 nm, confirming the presence of two contributions. The relative importance of the longer-lived component increases at longer wavelength.

To rationalize the experimental data, it is useful to compare them with those obtained for the assembly of **2** with the complex [(bpy)₂Ru(bpy-cyclamH₂)₄]⁴⁺,⁴ (**Ru-cyclam**; bpy-cyclamH₂ = 1-(2,2'-bipyridin-5-yl-methyl)-1,4,8,11-tetraazacyclotetradecane), which differs from **1** in that it only contains a single metal chromophore appended to the cyclam scaffold. Also in that case, the luminescence of the adduct was fitted by two decays, with lifetimes of 23 and 65 ns, which were assigned to residual emission of **Ru-cyclam** chromophore and to the emission of the hydrogen-bonded **2**, respectively. We suggest that the same assignment also holds for the system studied here. In the present case, the 15 ns decay is therefore assigned to residual emission

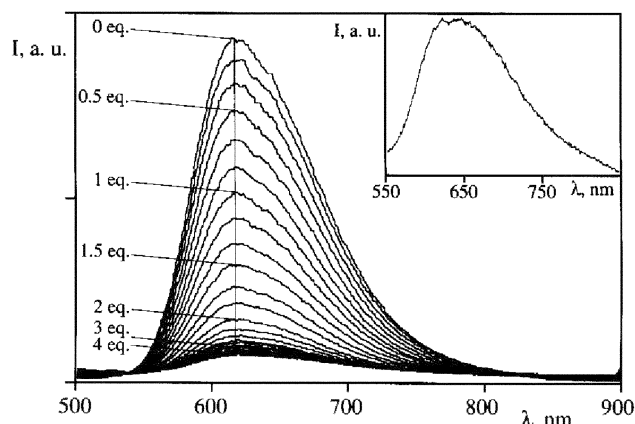


Fig. 3 Titration of the luminescence of **1** in acetonitrile upon successive addition of **2**. Concentration of **1** is $5 \times 10^{-6} \text{ M}$. Equivalents of **2** are shown in figure. Final spectrum is displayed in the inset.

from the [Ru(bpy)₃]²⁺-type chromophores of the light-harvesting subunit **1** and the longer-lived decay is attributed to the coordinated **2** species. § Quenching of **1** luminescence is attributed to energy transfer from **1** to **2**. ¶ the rate constant for this process can be calculated from the lifetime data, yielding a value of $5.1 \times 10^7 \text{ s}^{-1}$, which implies *ca.* 91% efficiency.

Information on stoichiometry and equilibrium constant K_{eq} of the adduct can be inferred by luminescence titration. The non-linear equation developed by Valeur for 1:1 adducts⁹ fits quite well the experimental data ($K_{\text{eq}} = 8.2 \times 10^5 \text{ M}^{-1}$), suggesting that the stoichiometry is 1:1. Interestingly, for the adduct of **Ru-cyclam** and **2**, a 2:1 stoichiometry is reported:⁴ probably a larger steric hindrance (the tetrametallic cyclam species **1** is much larger than the monometallic **Ru-cyclam**) has an important role in governing the stoichiometry of the 1/2 adduct.

In conclusion, a novel multicomponent assembly containing five metal-based chromophores has been prepared. Efficient energy transfer takes place between the hydrogen-bonded counterparts. Consideration of the efficiency of the energy transfer process and the different molar absorptivity of the light-harvesting element and of the energy trap (at their relative MLCT bands), results in the population of the (luminescent) ³MLCT excited state of the latter species in the antenna assembly being enhanced by a factor of 9.3 compared to the population of isolated **2**. Although this figure should not be considered as a quantification of the effective antenna effect in the adduct (which should take into account the integrated absorption spectra of the species in comparison with the solar spectrum), it indicates that the present approach for the design of efficient artificial antennas is quite promising and will be further exploited in the near future.

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Notes and references

† Compound **1** has been prepared as hexafluorophosphate salt. Details will be reported elsewhere. Compound **2**, available from previous work,⁶ has been used as the tetrabutylammonium salt.

‡ This result disagrees with that reported for a very similar species, for which a decrease in luminescence intensity upon acid addition was found.⁸

§ At the end of titration, a significant amount of free Ru(bpy)(CN)₄²⁻ is in solution, however its emission is not detectable since it is very weak and also occurs in a different range.

¶ On the basis of the redox data of the partners,^{6,7} electron transfer could also occur. A proof in favor of energy transfer was obtained by a reference experiment, in which **2** is connected with a species identical to **1** but missing the peripheral Ru(bpy)₂²⁺ subunits. In this case, emission of **2** is observed at 660 nm, and it is significantly lower in intensity than the 650 nm emission of the 1/2 adduct, so indicating that sensitization takes place in the latter species.

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