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COMMUNICATION

A multichromophoric dendrimer: from synthesis to energy up-conversion in a rigid matrix[†]

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A dendrimer with a $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) complex as a core and four diphenylanthracene units at the periphery was prepared from a scaffold based on a bipyridyl ligand bearing four terminal alkyne groups. Upon green light excitation, the dendrimer shows blue luminescence even in a rigid matrix at 77 K thanks to the dendritic multichromophoric structure.

Dendrimers are repeatedly branched macromolecules with a well-defined and tree-like structure.¹ They are ideal scaffolds to arrange multiple and different functional units within a nanoobject according to a predetermined pattern. Several examples of dendrimers containing photoactive units have been investigated in the last decade² and photoinduced electron and energy transfer processes have been investigated for sensing with signal amplification and light-harvesting purposes.

In the present communication, a dendritic structure (7 in Scheme 1) consisting of a $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine) complex as a core and four diphenylanthracene (hereafter called DPA) units at the periphery has been synthesized. These chromophoric units have been selected because in fluid solution they are known³ to exhibit energy up-conversion by low-power excitation, the process in which incident photons of a given energy are converted into photons of higher energy.⁴ The novelty of the present approach is the use of a multichromophoric system in which energy up-conversion works even in a rigid matrix at 77 K since it does not rely on bimolecular processes. To the best of our knowledge, dendrimers have never been used for this application, apart from one example reported by us,⁵ based on chromophores absorbing and emitting in the UV region.

We have recently developed a "click" approach to triazole disubstituted bipyridyl compounds.⁶ In this work we expand the number of triazole substituents per bpy moiety by the synthesis of a scaffold (compound **4**) bearing four terminal alkyne groups

that can be reacted in a Copper Catalyzed Azide–Alkyne Cycloaddition (CuAAC).⁷ This scaffold is highly versatile and can be decorated at the periphery with four long chains, compound **5**, or four diphenylanthracene units, compound **6** (Scheme 1). The crucial step of the synthesis is the alkylation of the dianion of 4,4'-dimethyl-[2,2']bipyridine (**2**) with benzyl bromide **1** to afford **3** (see ESI†). The use of LDA/CsOAc⁸ (unprecedented in the literature) was mandatory to obtain acceptable yields in the alkylation process since the use of simple LDA⁹ or LDA/tBuOK¹⁰ (both at -60 °C and -80 °C) gave complex reaction mixtures which afforded lower yields of **3**. The CuAAC reaction of **4**, after desilylation of **3**, with *n*-dodecyl azide gave compound **5** while the same reaction with 9-(4-azidomethyl-phenyl)-10-phenyl-anthracene gave **6**. Dendrimer **7** was prepared by reacting compound **6** with [Ru(bpy)₂Cl₂].

The absorption spectrum of dendrimer 7 (Fig. 1) compared to that of model compounds shows that the lowest energy band at 459 nm is the characteristic metal-to-ligand charge transfer band (MLCT) of Ru(II) polypyridine complexes.¹¹ A slight red shift is observed compared to pristine [Ru(bpy)₃]²⁺ ($\lambda_{max} = 451$ nm) and it is likely due to the substituents on one of the bpy ligands which lower the energy of the corresponding MLCT transition. The vibrationally structured band in the range between 330–410 nm is mainly due to the DPA chromophores (S₀ \rightarrow S₁(π,π^*)) with almost no shift compared to pristine 9,10-diphenylanthracene.¹² The band at 290 nm is centered on the bpy ligand, as evident by the comparison with the well-known spectrum of [Ru(bpy)₃]²⁺.

Upon excitation at 373 nm, where most of the light (ca. 85%)is absorbed by DPA, two emission bands are observed (Fig. 1, inset) due to the fluorescence of DPA¹² at 410 nm and the phosphorescence of the Ru(II) complex at 617 nm with a slight red shift compared to $[Ru(bpy)_3]^{2+}$.¹¹ The luminescence results show that the $S_1(\pi,\pi^*)$ excited state of peripheral DPA units of dendrimer 7 is quenched 40 times compared to the model compound, and that of the Ru(II) complex is quenched 10 times (η_q in Table 1). For more details on the quenching efficiency, see the ESI.† As reported in Fig. 2, both energy and electron transfer to the $[Ru(bpy)_3]^{2+}$ core are thermodynamically allowed. In the case of electron transfer, ΔG° (~-0.5 eV) can be estimated by the energy of S₁(π,π^*) and the redox potentials of 9,10-diphenyl anthracene and $[Ru(bpy)_3]^{2+}$ model compounds.¹³ The efficiency of the energy transfer process is very low, as demonstrated by the excitation spectrum performed with $\lambda_{em} = 620$ nm, in which the characteristic bands of DPA chromophores in the range 330-410 nm are barely visible.

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Scheme 1 Synthetic procedure for compounds 5 and 6 (eqn (1)) and 7 (eqn (2)).



Fig. 1 Absorption spectra of a 1.6×10^{-5} M solution of 7 (red line) in CH₃CN at 298 K. For comparison purposes, normalized absorption spectra of 9,10-diphenylanthracene (green line) and [Ru(bpy)₃](ClO₄)₂ (blue line) are reported. Inset shows the emission spectrum upon excitation at 373 nm. For the sake of clarity, in the range between 530–780 nm the emission spectra have been normalized.

 Table 1
 Emission data for dendrimer 7 compared to model compounds in CH₃CN at 298 K in air-equilibrated solution

	λ_{em}/nm	τ/ns	$\Phi_{ m em}$	η_{q}
7	410	< 0.5	0.023 ^a	0.99
	617	15.2	0.003^{b}	0.90
$[Ru(bpy)_3]^{2+}$	610	157	0.028^{c}	
DPA	410	5.4	0.90^{c}	

^{*a*} $\lambda_{ex} = 373$ nm. Emission quantum yield is estimated by taking into account the percentage of light absorbed by the core chromophore at the excitation wavelength. ^{*b*} $\lambda_{ex} = 460$ nm. ^{*c*} From ref. 13.

The quenching of $[Ru(bpy)_3]^{2+}$ phosphorescence is due to energy transfer from ³MLCT to populate the T₁(π,π^*) excited state of the DPA units with 90% efficiency (Table 1).



Fig. 2 Schematic energy level diagram showing the absorption (dashed grey lines), emission (solid black lines), and non-radiative processes (wavy lines) occurring in dendrimer 7 at 298 K. CT is a charge transfer state corresponding to photoinduced oxidation of DPA and reduction of $[Ru(bpy)_3]^{2+}$ moieties.

At 77 K in C₂H₅OH/CH₂Cl₂ 1 : 1 (v/v) rigid matrix, fluorescence of DPA and phosphorescence of Ru(II) complex can be observed upon excitation at 373 nm. At variance with the experimental results in fluid solution, quenching of an S₁(π,π^*) excited state of peripheral DPA units is less efficient and takes place by energy transfer, as estimated by the excitation spectrum. Indeed, electron transfer is precluded as a result of the destabilization of the CT level at 77 K due to the lack of solvent repolarization.¹⁴

Upon laser excitation of a 4.2×10^{-5} M deaerated solution of dendrimer 7 at 532 nm, fluorescence of DPA at 410 nm is observed both at 298 K in CH₃CN and at 77 K in C₂H₅OH/ CH₂Cl₂ 1:1 (v/v) rigid matrix (Fig. 3 and S1, ESI†). The corresponding decay time is much longer (µs-time scale in both cases) than that reported in Table 1. This is due to delayed fluorescence of DPA obtained by an energy up-conversion mechanism. This process is based on sensitized triplet–triplet annihilation of DPA chromophores, as described by the following equations:

$$\operatorname{Ru}(S_0) + h\nu \to \operatorname{*Ru}(S_1) \tag{1}$$



Fig. 3 Emission intensity decay at 425 nm as a function of excitation power of a 4.2×10^{-5} M solution of 7 in a C₂H₅OH/CH₂Cl₂1:1 (v/v) rigid matrix at 77 K. $\lambda_{ex} = 532$ nm. Inset shows the emission intensity at 3 µs as a function of the normalized laser power.

$$*Ru(S_1) \rightarrow *Ru(T_1) \tag{2}$$

$$*Ru(T_1) + DPA(S_0) \rightarrow Ru(S_0) + *DPA(T_1)$$
(3)

$$*DPA(T_1) + *DPA(T_1) \rightarrow *DPA(S_1) + DPA(S_0) \quad (4)$$

*DPA(S₁)
$$\rightarrow$$
 DPA(S₀) + $h\nu'$ (5)

where Ru stands for $[Ru(bpy)_3]^{2+}$. This mechanism is consistent with the energy level diagram shown in Fig. 2.

It takes advantage of the unitary efficiency of process (2) for $Ru(\Pi)$ polypyridine complexes,¹¹ and of the presence of multiple DPA units in close proximity at the periphery of the dendrimer.

For an equimolar solution $(4.2 \times 10^{-5} \text{ M})$ of the two model compounds under the same experimental conditions, the emission intensity of DPA delayed fluorescence is higher at 298 K compared to dendrimer 7, while it is not observed at all at 77 K. The higher intensity observed for the separated components at 298 K is due to the fact that quenching of the S_1 state of 9,10-diphenylanthracene by energy and electron transfer processes to the Ru(II) complex core is precluded. Dynamic quenching processes cannot compete with the intrinsic deactivation of the S1 state of 9,10-diphenylanthracene since its lifetime is too short and the concentration of $[Ru(bpy)_3]^{2+}$ is too low.¹⁴ Processes (3) and (4) can occur intermolecularly in fluid solution thanks to the longer lifetime of the triplet excited states of both chromophores.[†] but are precluded in rigid matrix. Therefore, at 77 K up-converted emission is observed only for the multichromophoric dendrimer 7 in which processes (3) and (4) occur intramolecularly. A further proof of the intramolecular nature of process (4) is given by the plot of the delayed luminescence intensity as a function of the excitation power (Fig. 3, inset). This plot is not quadratic, but linear at low power and reaches a plateau at higher value due to excitation of all the $[Ru(bpy)_3]^{2+}$ chromophores of the solution within the laser pulse.

The advantage of the present multichromophoric dendritic structure, compared to the previously reported examples based on the two separated chromophores,^{3,4,15} is that energy up-conversion can be observed also in rigid media, a very important step toward solid-state devices. Moreover, at 77 K quenching of DPA fluorescence is less efficient than at 298 K since the photoinduced electron transfer is precluded.

In conclusion, we have synthesized a dendrimer constituted by a $[Ru(bpy)_3]^{2+}$ core and four DPA units at the periphery. The photophysical processes show a quite complex pattern of energy and electron transfer processes. The most interesting result is the observation of the blue emission of DPA chromophores upon green-laser light excitation at 532 nm of the Ru(II) core both in fluid CH₃CN solution and in a C₂H₅OH/ CH₂Cl₂ 1:1 (v/v) rigid matrix at 77 K. This result is very important in view of a potential application of energy up-conversion in a solid state device for wavelength shifting in spectroscopy. By proper choice of the chromophoric units and based on previously reported examples in fluid solution,¹⁶ these dendritic systems may be applied to the sensitization of photovoltaics by harvesting the red and near infrared region of the solar spectrum.

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Notes and references

 \ddagger In deaerated solutions at 298 K, the lifetimes of the lowest triplet excited states are: 0.89 μs and 8000 μs for $[Ru(bpy)_3]^{2+}$ and 9,10-diphenylanthracene. 13

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