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Light-harvesting metal dendrimers appended with additional organic chromophores: a tetranuclear heterometallic first-generation dendrimer exhibiting unusual absorption features†

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A new tetranuclear heterometallic complex carrying six pyrenyl chromophores at the periphery has been prepared: this species is an example of a new class of light-harvesting metal dendrimer, in which multinuclear metal dendrimers are surrounded by additional purely organic chromophores.

Dendrimers based on Ru(II) and Os(II) polypyridine complexes have recently attracted a great deal of interest because they can play the role of light-harvesting antenna systems in artificial solar energy conversion schemes.[1–4] Most of the light-harvesting metal-based dendrimers reported so far essentially belong to two general categories: (i) species in which the metal-based chromophores are present in all the positions of the dendrimeric array[1,5] and (ii) species in which a single metal-based chromophore is located at the core of the dendrimer, surrounded by purely organic wedges bearing chromophores at the periphery (Fig. 1).[2,5] In the latter case (ii), the light energy absorbed by the peripheral organic chromophores is transferred to the central metal-based chromophore by energy transfer processes which can be mediated either (a) by the organic dendritic framework by superexchange pathways or (b) by direct coulombic interactions allowed *via* dendritic folding. In the former case (i), both center-to-periphery or periphery-to-center energy transfer processes have been reported, the efficiency of which depends on the energy gradient within the dendritic metal branches. In both cases, strict requirements must be fulfilled for efficient energy transfer, for example the correct energy gradient within the multimetal array [for (i)-type dendrimers] or suitable distance and nature of the dendritic framework [for (ii)-type dendrimers].

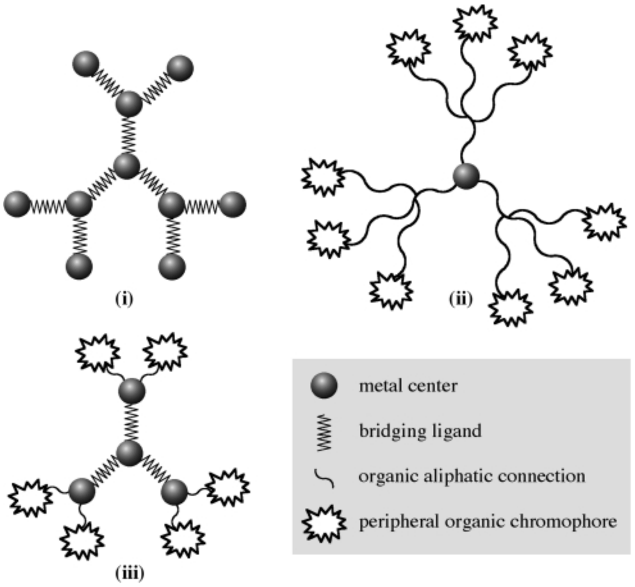

Fig. 1 Representation of metal-based light-harvesting dendrimers.

Here we report the synthesis and the absorption spectra and luminescence properties of a new tetranuclear mixed-metal dendrimeric complex **1** bearing six pyrenyl chromophores at the periphery (Fig. 2). Compound **1** belongs to the first-generation of a large class of luminescent and redox-active metal dendrimers based on the 2,3-dpp bridging ligand [2,3-dpp = 2,3-bis(2′-pyridyl)pyrazine],[1,5,6] and can also be regarded as a new type of light-harvesting dendrimer [(iii) in Fig. 1], coupling some properties of the two types of dendrimers (i) and (ii) discussed above. The four metal-based subunits constitute a (i)-type dendrimer, and the six appended pyrenyl chromophores resemble the peripheral subunits of (ii)-type dendrimers. This new approach allows us to obtain a dendrimer containing three 'layers' of chromophores (from the outer layer to the inner one: six pyrenyl units, three Ru-based chromophores and one Os-based one) in fewer synthetic steps.[6]

The synthesis of **1** is an application of the 'complexes as ligands/complexes as metals' synthetic approach.[7] The procedure is identical to that used for the synthesis of $[Os\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2\}_3]^{8+}$ **2** (bpy = 2,2′-bipyridine).[8] Apparently, the presence of the pyrenyl subunits does not affect the reactivity of the complex-metal species, giving similar yields under analogous reaction conditions.

The absorption spectrum of **1** is shown in Fig. 3, where the spectrum of **2** is also reported for comparison purposes. As expected, at longer wavelengths than 550 nm the spectra of **1** and **2** are almost coincident, with the absorption feature at about 550 nm receiving contributions from spin-allowed metal-to-ligand charge-transfer (MLCT) transitions (namely, Ru→μ-2,3-dpp and Os→μ-2,3-dpp CT) and the long tail which extends towards the IR region assigned to spin-forbidden MLCT transitions involving the Os(II) chromophore.[1,8] In **1**, the intense

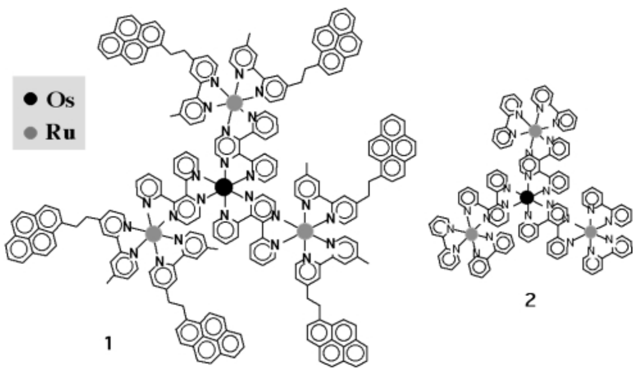

Fig. 2 Structural formula of **1** and of the tetranuclear compound **2**, used as a reference. For simplicity, the charges of the complexes are omitted.

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† Electronic supplementary information (ESI) available: synthesis of 4-methyl-4′-[2-(1-pyrenyl)ethyl]-2,2′-bipyridine and synthetic scheme for **1**. See http://www.rsc.org/suppdata/cc/b1/b109068b

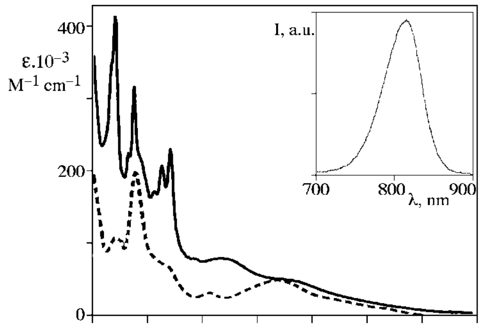

Fig. 3 Absorption spectra in acetonitrile of **1** (——) and **2** (- - - -). In the inset, the luminescence spectrum of **1** is shown.

and structured absorption peaks in the 310–350 nm region and at 239 nm can be mainly assigned to pyrene-centered transitions, 1La and 1Bb, respectively.[9,10] The broad absorption band around 320 nm which is present in **2**, assigned to 2,3-dpp centered (π–π*) transitions[1,8] is obscured in **1** by the more intense pyrene-centered ^{1}La bands. Finally, the band peaking at 279 nm in **1** receives contributions from both the peripheral pyrenyl chromophores and the four metal subunits of the tetranuclear structure, containing the bpy-centered π–π* absorption feature, already present in **2**.[6,8]

From the above discussion it appears that **1** significantly absorbs more than **2** in the UV region, confirming our expectations. However, Fig. 3 also shows that **1** absorbs significantly more than **2** in the region 400–550 nm. Indeed the absorption spectrum of **1** exhibits an intense broad band in that region (molar absorption of the band maximum, 8 × 104 M^{-1} cm^{-1}), which includes the Ru→bpy charge-transfer (CT) band peaking at 420 nm in **2**, but that clearly receives additional contributions from other transitions. To rationalize this behavior it should be considered that the pyrene subunits of **1** are good electron donor groups, in that they can be oxidized at about +1.2 V *vs.* SCE,[11] whereas the polypyridine ligand bpy and expecially the bridged 2,3-dpp are very good electron acceptors (reversible reduction process for 2,3-dpp is around −0.60 V *vs.* SCE).[6,8] The ethylene chains connecting bpy and pyrenyl subunits are flexible enough to allow direct interactions between the pyrenyl subunits with bpy and 2,3-dpp (for 2,3-dpp, CPK models suggest that conformations in which this latter ligand and pyrene can lie in almost parallel planes separated by < 360 pm are possible[12]). Therefore, intramolecular pyrene-to-bpy and/or pyrene-to-μ-2,3-dpp CT transitions (with the latter at lower energy) are possible. The intensity of such transitions can be relatively high: for example, CT transitions in [3,3]paracyclophane–quinhydrones lead to a molar absorbance of between 10^3 and 10^4 M^{-1} cm^{-1} depending on solvent polarity.[13] Significant charge transfer transitions from pyrenyl subunits to polypyridine ligands coordinated to Pt(II) have been recently reported, although in this latter case the pyrene and the polypyridine ligands were directly connected.[14] Similar transitions were also found in the adducts of dibenzyl ether dendrimers with fullerenes.[15] Since the number of such CT transitions in **1** can be high, the relatively intense broad band in the 400–550 nm region is tentatively assigned to these type of transitions (together with contributions from Ru→bpy CT transitions). This somewhat unexpected result is very interesting: the light-harvesting properties of **1** compared to **2** are improved by the presence of the additional peripheral chromophores much more than initially foreseen, due to the coming into play of visible absorption bands which arise from new intercomponent (supramolecular) CT transitions.

The luminescence properties of **1** (deoxygenated acetonitrile at room temperature: $\lambda_{\max} = 860$ nm; $\tau = 16$ ns; $\Phi = 5 \times 10^{-4}$. The uncorrected luminescence spectrum is shown in the inset of Fig. 3) are practically identical to those of **2** ($\lambda_{\max} = 860$ nm; $\tau = 18$ ns; $\Phi = 5 \times 10^{-4}$).[8] Therefore, the emission of **1** is assigned to the same excited state responsible for emission of **2**, that is the triplet Os→μ-2,3-dpp CT level.[8] The constancy of the luminescence lifetime and quantum yield on passing from **2** to **1** indicates that the pyrenyl subunits do not affect the luminescence properties of the Os core. Interestingly, the excitation spectrum closely matches the absorption spectrum, demonstrating that the light energy absorbed by the Ru-based chromophores and the peripheral pyrene subunits is quantitatively channelled to the Os core, which plays the role of the energy trap. Taken together, the absorption properties and the energy transfer processes occurring in **1** and the comparison of these data with those of the parent complex **2**, it appears that the presence of suitable peripheral organic chromophores can lead to metal dendrimers which would be better artificial antenna systems compared to the species reported so far.

In conclusion, we have prepared a new type of light-harvesting metal dendrimer, **1**, which couples the structural properties of former studied metal dendrimers. The new compound **1** exhibits better properties compared to the species previously reported, as far as the antenna properties are concerned, owing to the absorption of the additional organic chromophores and also to new absorption features originating from the interaction of the pyrene peripheral subunits with the tetranuclear metal-based core. Work is in progress to study in further detail the photophysical processes and to prepare larger and more complex systems of this type.

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