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Dendrimers based on photoactive metal complexes. Recent advances

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Abstract

Recent advances in the field of photoactive dendrimers containing metal complexes are reviewed. Dendrimers with $[Ru(bpy)_3]^{2+}$ as a core exhibit the characteristic $[Ru(bpy)_3]^{2+}$-type luminescence that can be (i) protected from external quenchers by the dendrimer branches and (ii) sensitized by chromophoric groups contained in the periphery of the dendrimer (antenna effect). Several examples of dendrimers fully based on transition metal complexes (i.e., containing a metal at each branching point of the dendrimer structure) have been investigated with the purpose of light harvesting. Dendrimers containing one or more free base and metal porphyrin units have been investigated for light harvesting and for a variety of other purposes.

Scattered examples of other types of photoactive dendrimers are also reviewed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Dendrimers; Metal complexes; Photochemistry; Luminescence; Light harvesting

1. Introduction

Dendrimers [1] are well-defined macromolecules exhibiting a tree-like structure (Fig. 1), first derived by the 'cascade molecule' approach [2]. Dendrimer chemistry is a rapidly expanding field for both basic and applicative reasons [3]. Like trees, dendrimers usually exhibit aesthetically pleasant structures. However, as in the case of a tree, the interest in a specific dendrimer does not depend on its beauty, but on the 'fruit' (i.e. the specific function) that it is able to produce [4].

From a topological viewpoint, dendrimers contain three different regions: core, branches, and surface (Fig. 1). Functional groups can be incorporated in each one of these three regions. Because of their proximity, the various functional groups of a dendrimer may easily interact with one another and, in any case, the resulting properties are modulated by the dendrimer as a whole. Therefore, dendrimers incorporating functional units can be considered as supramolecular species.

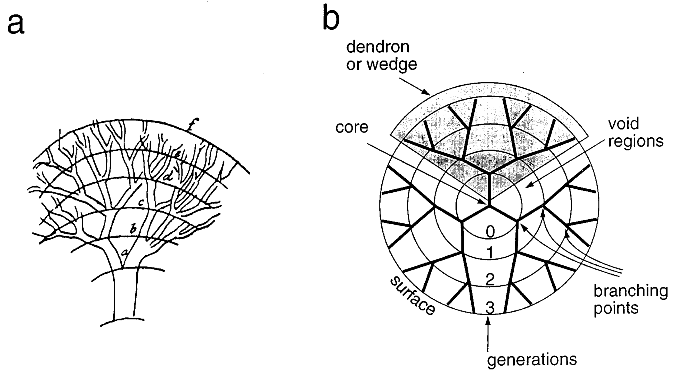


Fig. 1. (a) A sketch by Leonardo da Vinci on tree branching; (b) schematic representation of a dendrimer.

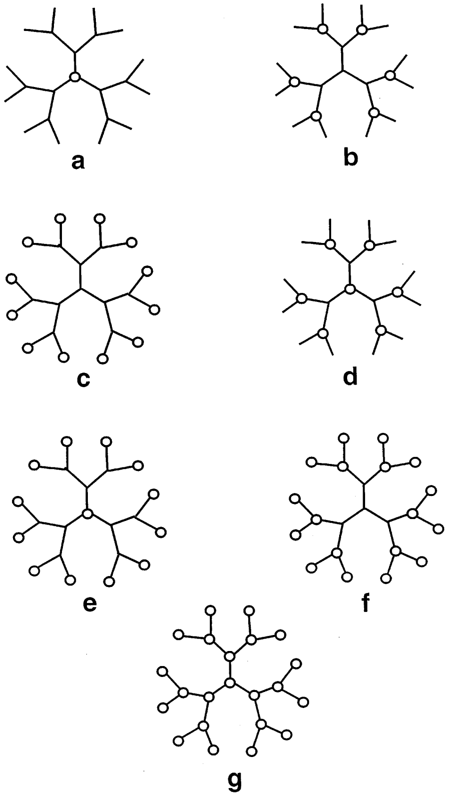


Fig. 2. Schematic representation of dendrimers evidencing the possible positions available to photoactive units (circles).

It is well known that one of the most interesting aspects of the chemistry of supramolecular species is their interaction with light and the great variety of processes that may ensue [5]. For this reason the research on dendrimers carrying photoactive units has rapidly grown in the last few years. Important points of interest in this research field are the following: (i) cooperation among photoactive components can allow the dendrimer to perform useful functions such as light harvesting [6]; (ii) changes in the photophysical properties can be exploited for sensing purposes with signal amplification [7]; (iii) luminescence signals offer a handle to better understand the dendritic structures and superstructures [8].

Photoactive units can be directly incorporated or appended with covalent or coordination bonds in different regions of a dendritic structure [9]. Schematically (Fig. 2), we can envisage the presence of such units (a) in the core, (b) in the branches, (c) in the surface, (d) in the core and in the branches, (e) in the core and in the surface, (f) in the branches and in the surface, and (g) in the core, branches and surface. Furthermore, photoactive units can be non-covalently hosted in the cavities of a dendritic structure [10] or associated on the dendrimer surface [11] (Fig. 3).

In this paper we will review some recent advances in the field of dendrimers containing photoactive units based on metal complexes. Recent advances in the field of dendrimers containing electroactive units based on metal complexes will be reviewed elsewhere [12].

2. Dendrimers with a $[Ru(bpy)_3]^{2+}$-type core

2.1. General properties

The complexes of the $[Ru(bpy)_3]^{2+}$ family (bpy = 2,2′-bipyridine) exhibit a unique combination of photophysical and redox properties [13]. Because of these properties, they are extensively used as photocatalysts [14], reactants in intermolecular [15] and intramolecular [16] energy- and electron-transfer processes, building blocks for the construction of supramolecular species [5,6,17], and systems showing very extensive redox series [18].

2,2′-Bipyridine can be easily functionalized in the 4 and 4′ positions, so that a variety of dendritic wedges can be appended to bpy ligands and dendrimers containing a $[Ru(bpy)_3]^{2+}$-type unit as a core can be prepared. Chart 1 shows the bpy-based dendrons that have been prepared and used as ligands to obtain a variety of dendrimers [19–21] whose luminescence properties are summarized in Table 1.

All these dendrimers exhibit the characteristic luminescence of their $[Ru(bpy)_3]^{2+}$-type core, both in fluid solution at room temperature and in a rigid matrix at 77 K. Looking at the data shown in Table 1, one can notice: (i) small displacements in the wavelength of the emission maximum, that can be assigned to the electronic nature of the groups directly linked to the bpy ligands in the 4,4′ positions; (ii) a decrease in the excited state lifetime (and, when available, in the luminescence quantum yield) in going from deaerated to aerated solutions; this effect, which is caused by the quenching of the luminescent excited state by dioxygen, will be discussed in the next section.

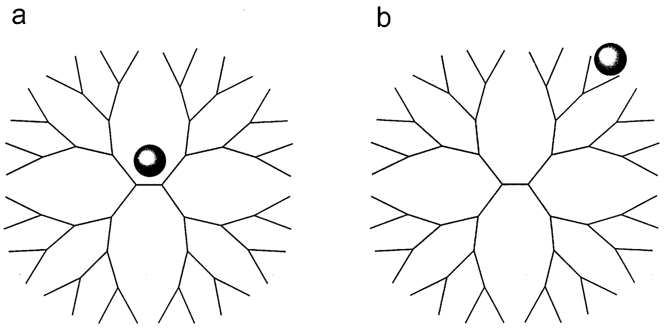
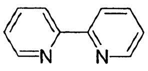
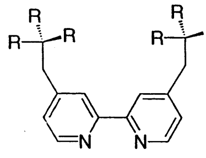


Fig. 3. Dendrimers can host (a) or associate to (b) photoactive units (black spheres).

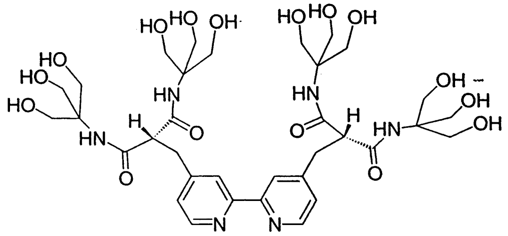


bpy



R=CO$_2$Et

1



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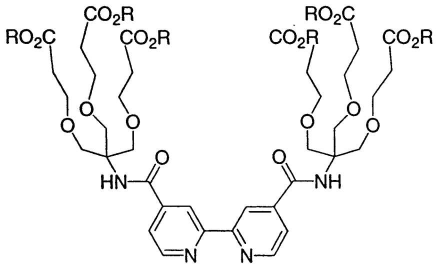
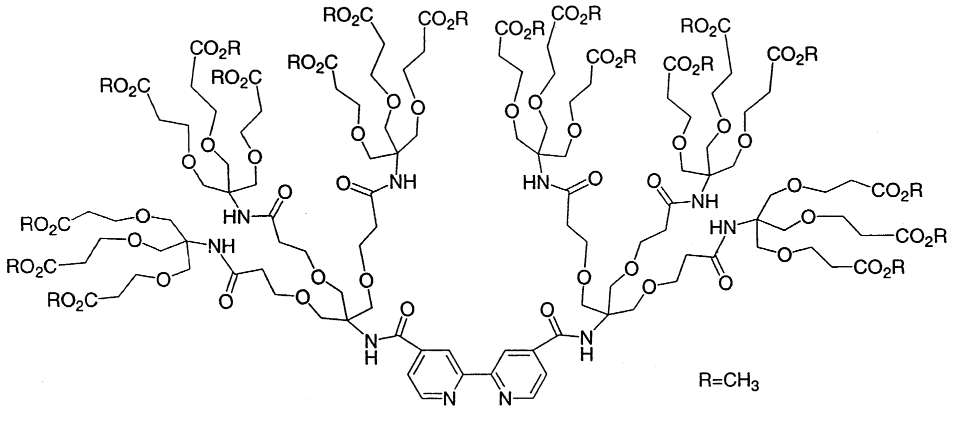


R=CH$_3$

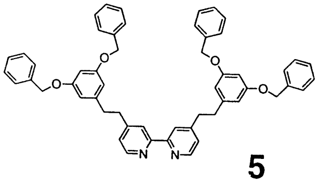
3



R=CH$_3$

4

Chart 1.



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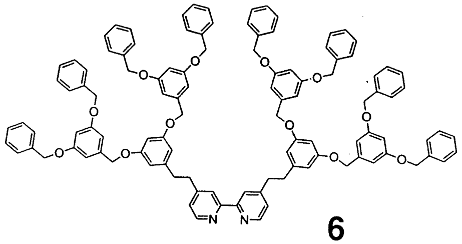

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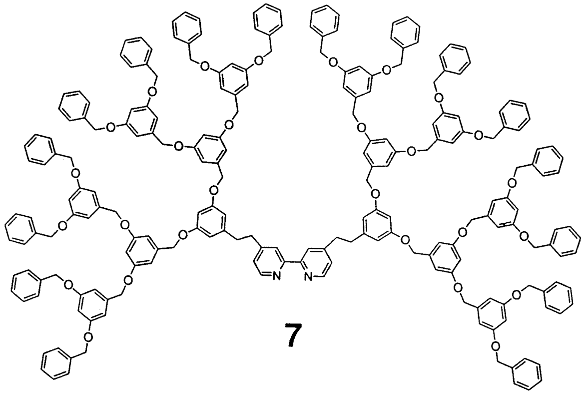

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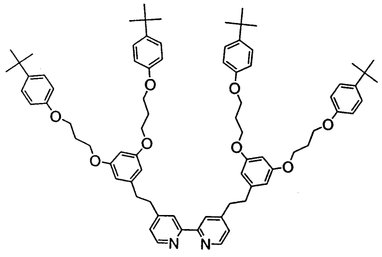

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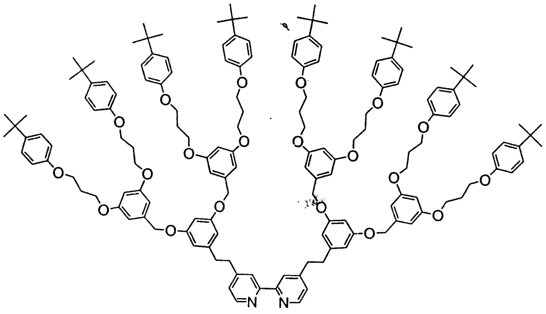

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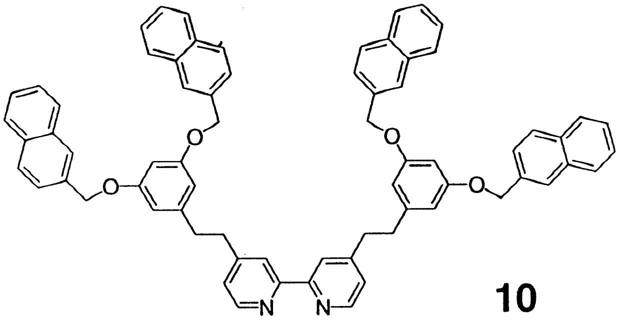

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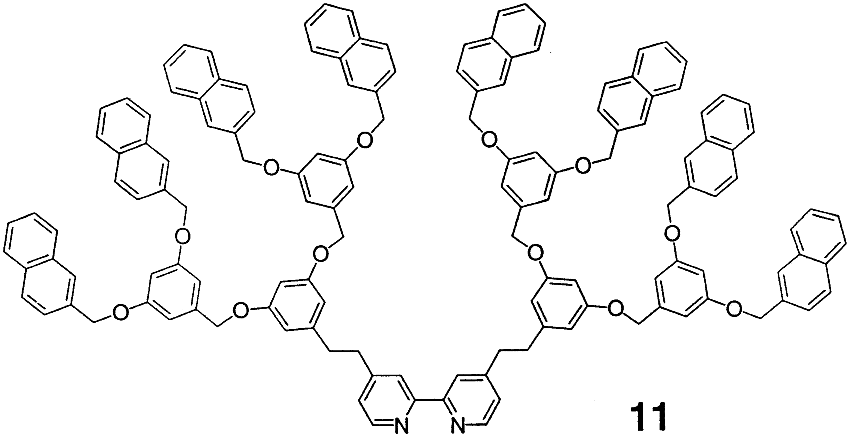

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We would also like to recall the study of the photophysical properties of Ru(II) complexes containing dendritic ligands based on the functionalization of the 4 and 7 positions of 1,10-phenanthroline [22]. The photophysical properties of such compounds are in line with those obtained for the dendrimers containing $[Ru(bpy)_3]^{2+}$-type cores.

2.2. Quenching of the core luminescence

It is well known that electronically excited molecules can be quenched via energy or electron transfer by other molecules [23]. In fluid solution a quenching reaction usually occurs during an encounter between excited molecule and quencher. It follows that only the excited states that exhibit a reasonably long lifetime may undergo quenching processes. The lifetime of the triplet metal-to-ligand charge-transfer (^{3}MLCT) luminescent excited state of Ru(II)-polypyridine complexes is long enough to allow the occurrence of encounters when the quencher concentration is not extremely low [13].

Table 1
Luminescence data

	298 K [a]				77 K [b]	
	λ_{max} (nm)	τ (ns)	$\Phi_{\mathrm{em}} \times 10^2$	k_q (10^9 $\mathrm{M^{-1}\ s^{-1}}$) [c]	λ_{max} (nm)	τ (μs)
$[\mathrm{Ru(bpy)_3}]^{2+}$	611	172 [d], 990 [e]	1.6 [d], 6.2 [e]	2.5	582	4.8
$[\mathrm{Ru}(\mathbf{1})_3]^{2+}$ [f]	611	287 [d], 960 [e]	3.5 [d], 10 [e]	1.3	583	5.4
$[\mathrm{Ru}(\mathbf{2})_3]^{2+}$ [f,g]	618	580 [d], 730 [e]	3.7 [d], 5.1 [e]	1.3	–	–
$[\mathrm{Ru}(\mathbf{3})_3]^{2+}$ [f]	630	760 [d], 1940 [e]	7.0 [d], 12 [e]	0.43	602	5.5
$[\mathrm{Ru}(\mathbf{4})_3]^{2+}$ [f]	638	1010 [d], 1740 [e]	6.2 [d], 13 [e]	0.22	606	5.5
$[\mathrm{Ru}(\mathbf{5})_3]^{2+}$ [h]	614	191 [d], 1160 [e]	1.9 [d]		586	5.3
$[\mathrm{Ru}(\mathbf{6})_3]^{2+}$ [h]	611	316 [d], 990 [e]	2.9 [d]		584	5.0
$[\mathrm{Ru}(\mathbf{7})_3]^{2+}$ [h]	609	562 [d], 1040 [e]	4.8 [d]		579	5.6
$[\mathrm{Ru(bpy)_2}(\mathbf{8})]^{2+}$ [h]	620	170 [d], 1080 [e]	1.8 [d]	3	588	5.2
$[\mathrm{Ru(bpy)_2}(\mathbf{9})]^{2+}$ [h]	616	193 [d], 1050 [e]	1.9 [d]	2	586	5.6
$[\mathrm{Ru}(\mathbf{9})_3]^{2+}$ [h]	611	415 [d], 992 [e]	3.5 [d]	0.7	581	5.5
$[\mathrm{Ru}(\mathbf{10})_3]^{2+}$ [i]	613	240 [d], 1100 [e]	4.6 [d]		585	5.0
$[\mathrm{Ru}(\mathbf{11})_3]^{2+}$ [i]	610	412 [d], 915 [e]	3.8 [d]		582	5.7

[a] Acetonitrile solution.
[b] Butyronitrile solution.
[c] Rate constant for quenching by dioxygen at 298 K.
[d] Aerated solution.
[e] Deaerated solution.
[f] From Ref. [19].
[g] H_2O solution.
[h] From Ref. [21].
[i] From Ref. [20].

When a luminescent unit is buried into the core of a dendrimer, the rate of the quenching reactions is expected to be slower than for the free unit. Despite its potential interest for a variety of applications [24], this effect has been the object of only a few scattered investigations [19–21,25]. More attention has been paid to dendrimers as supramolecular host environment for quenching reactions involving excited Ru polypyridine complexes and a variety of quenchers [11].

The rate constant k_q of a quenching process taking place by a diffusional mechanism can be obtained from the Stern–Volmer equation [23]

$$\tau^\circ/\tau = \Phi^\circ/\Phi = 1 + k_q \tau^\circ [Q] \tag{1}$$

where τ° and Φ° are the excited state lifetime and quantum yield in the absence of quencher, and τ and Φ are the same quantities measured in the presence of a quencher concentration $[Q]$.

2.2.1. Quenching by dioxygen

The quenching of the luminescent ^{3}MLCT level of Ru(II)-polypyridine compounds by dioxygen contained in the solvent is a well documented phenomenon [13,15]. Although some details of the quenching mechanism are still the object of some controversy [26], both energy transfer and electron transfer are involved. Using the lifetime values measured in deaerated and air equilibrated solutions and knowing the concentration of dioxygen in the air equilibrated solutions (1.9×10^{-3} M in acetonitrile and 0.29×10^{-3} M in water at 298 K [27]), the quenching constants shown in Table 1 have been evaluated from Eq. (1).

Comparison between the $[Ru(\mathbf{3})_3]^{2+}$ and $[Ru(\mathbf{4})_3]^{2+}$ dendrimers [19], where the groups directly linked to the bpy ligands are the same, shows that in deaerated solutions the lifetime of $[Ru(\mathbf{4})_3]^{2+}$ is shorter than that of $[Ru(\mathbf{3})_3]^{2+}$, whereas in aerated solutions the situation is reversed. This indicates that the increase in the length of the branches decreases slightly the intrinsic lifetime of the Ru-bpy core, but in aerated solution the excited state of the compound with longer branches, $[Ru(\mathbf{4})_3]^{2+}$, is less quenched by dioxygen than the excited state of the smaller $[Ru(\mathbf{3})_3]^{2+}$ compound. The quenching constant decreases by a factor of about six in going from $[Ru(bpy)_3]^{2+}$ to $[Ru(\mathbf{3})_3]^{2+}$ and further decreases by a factor of two for $[Ru(\mathbf{4})_3]^{2+}$.

In the homogeneous $[Ru(\mathbf{5})_3]^{2+}$, $[Ru(\mathbf{6})_3]^{2+}$ and $[Ru(\mathbf{7})_3]^{2+}$ family [21] the lifetime in aerated solution increases with increasing size of the branches. The lifetime of the largest compound is three times longer than that of the smallest one. An increase in lifetime with increasing size or number of the dendritic branches occurs also for the $[Ru(bpy)_2(\mathbf{8})]^{2+}$, $[Ru(bpy)_2(\mathbf{9})]^{2+}$, and $[Ru(\mathbf{9})_3]^{2+}$ family [21].

The same behavior is shown by other dendrimers. In aerated solution, the luminescence lifetime of $[Ru(\mathbf{10})_3]^{2+}$ is about 40% longer than that of the $[Ru(bpy)_3]^{2+}$ model compound, and that of $[Ru(\mathbf{11})_3]^{2+}$ is more than twice as long [20].

These data show that the dendrimer branches protect the Ru-bpy based core from dioxygen quenching. A long lifetime of the luminescent excited state in aerated solutions is important for immunoassay applications since the signal of the label can be read after the decay of the background fluorescence of the sample, whose lifetime usually is in the nanosecond time scale [28].

The protection of the dendrimer branches on the luminescent ^{3}MLCT level of the Ru(II)-bpy core can be assigned to one or more of the following factors: (i) decrease in the diffusion rate constant with the increasing volume of the compound; (ii) lower solubility of dioxygen in the interior of the dendrimer; (iii) preferential 'solvation' of the metal-complex core by the dendrimer branches, with consequent difficulty to obtain a suitable orbital overlap with dioxygen for energy or electron transfer quenching processes.

2.2.2. Quenching by other species

The only systematic investigation performed in this field [21] is that on the quenching of the luminescent excited state of the $[Ru(bpy)_2(\mathbf{8})]^{2+}$, $[Ru(bpy)_2(\mathbf{9})]^{2+}$, and $[Ru(\mathbf{9})_3]^{2+}$ dendrimers by three compounds that were already known to quench the luminescence of $[Ru(bpy)_3]^{2+}$ [15]: 1,1′-dimethyl-4,4′-bipyridinium dication (MV^{2+}), tetrathiafulvalene (TTF), and anthraquinone-2,6-disulfonate anion (AQ^{2-}). These three quenchers do not possess excited states below the ^{3}MLCT level of the $[Ru(bpy)_3]^{2+}$ chromophoric unit, but are easy to reduce (MV^{2+} and AQ^{2-}) or to oxidize (TTF). The experiments were performed at 298 K in acetonitrile solutions containing $TBAPF_6$ to control the ionic strength.

Electron-transfer quenching reactions may involve the oxidation or the reduction of the excited state:

$$A^* + B \rightarrow A^+ + B^- \text{ oxidative quenching} \tag{2}$$

$$A^* + B \rightarrow A^- + B^+ \text{ reductive quenching} \tag{3}$$

The thermodynamic driving force of the reaction can be estimated from the approximate equations:

$$\Delta G^\circ = -\Delta E^{\circ\circ} + E(A^+/A) - E(B/B^-) \tag{4}$$

$$\Delta G^\circ = -\Delta E^{\circ\circ} - E(A/A^-) + E(B^+/B) \tag{5}$$

where $\Delta E^{\circ\circ}$ is the spectroscopic energy (in eV) of the excited state to be quenched and $E(A^+/A)$, $E(B^+/B)$, $E(A/A^-)$, and $E(B/B^-)$ are the one-electron energies (in eV) corresponding to the reduction processes of the ground states of the two reactants [29]. The $[Ru(bpy)_2(\mathbf{8})]^{2+}$, $[Ru(bpy)_2(\mathbf{9})]^{2+}$, and $[Ru(\mathbf{9})_3]^{2+}$ dendrimers and the $[Ru(bpy)_3]^{2+}$ model compound have practically the same excited-state energy (about 2.12 eV), and the same $E(A^+/A)$ and $E(A/A^-)$ potential values [21]. The values of $E(B/B^-)$ are -0.44 and -0.57 V (versus SCE) for MV^{2+} and AQ^{2-}, respectively, and the value of $E(B^+/B)$ is $+0.33$ V for TTF. Insertion of these values in Eq. (4) or Eq. (5) shows that (i) both oxidative quenching by MV^{2+} and AQ^{2-} and reductive quenching by TTF are thermodynamically allowed processes and (ii) the free energy change is practically the same for the quenching of the three dendrimers by the same quencher.

Measurements of the luminescence lifetimes of the $[Ru(bpy)_2(\mathbf{8})]^{2+}$, $[Ru(bpy)_2(\mathbf{9})]^{2+}$, and $[Ru(\mathbf{9})_3]^{2+}$ dendrimers for at least five different quencher concentrations of the three selected quenchers were found to obey the Stern–Volmer equation (Eq. (1)). The values of the quenching constants are gathered in Table 2 [21]. As one can see, there is an almost generalized decrease of the quenching constant with increasing number and size of the organic branches appended to the $[Ru(bpy)_3]^{2+}$ core. This effect, however, is not the same in all

Table 2
Quenching constants $k_q \times 10^{-9}$ (M^{-1} s^{-1}) [a]

	MV^{2+}	TTF	AQ^{2-}
$[Ru(bpy)_3]^{2+}$	1.4	12	12
$[Ru(bpy)_2(\mathbf{8})]^{2+}$	0.78	9.9	7.3
$[Ru(bpy)_2(\mathbf{9})]^{2+}$	0.58	8.3	8.6
$[Ru(\mathbf{9})_3]^{2+}$	0.10	5.4	2.7

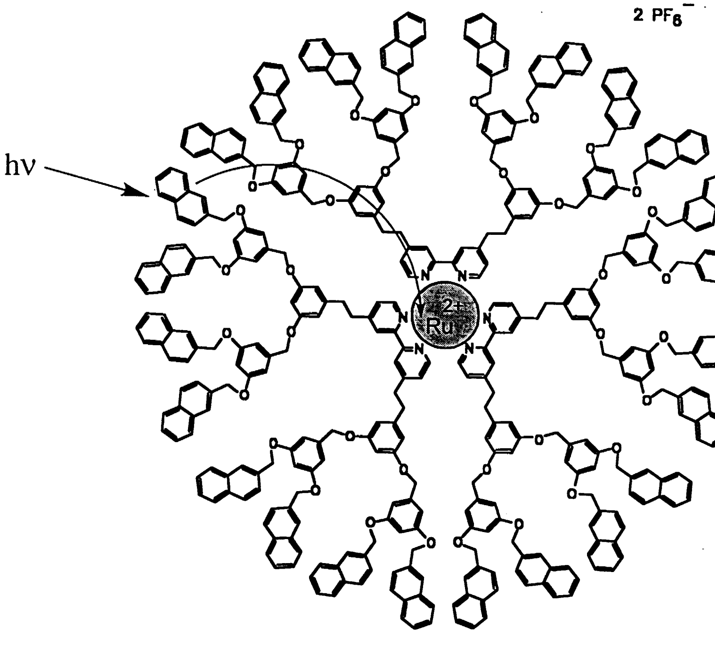
[a] From Ref. [21]; acetonitrile solutions containing 5×10^{-2} M $TBAPF_6$; k_q values obtained from Eq. (1) by using lifetimes from at least five different quencher concentrations.

cases. For the positively charged MV^{2+} quencher, the rate constant decreases by more than one order of magnitude in going from $[Ru(bpy)_3]^{2+}$ to the fully dendritic $[Ru(\mathbf{9})_3]^{2+}$ compound, whereas the effect is smaller for the negatively charged AQ^{2-} quencher and very small (only a factor of two) for the neutral TTF quencher. In going from $[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)_2(\mathbf{8})]^{2+}$, a comparable decrease is observed for MV^{2+} and AQ^{2-}, and practically no effect for TTF. Increasing in the length of the dendritic wedge in the $Ru(bpy)_2$-type species has a small decreasing effect for MV^{2+} and TTF, whereas for AQ^{2-} the rate constant increases slightly. Finally, replacement of the two unsubstituted bpy ligands of $[Ru(bpy)_2(\mathbf{9})]^{2+}$ with dendritic ligands has a much larger effect for AQ^{2-} than for TTF. These results are difficult to rationalize, presumably because the rate constant of the quenching process is affected by several, sometimes contrasting, factors including the following ones: (i) dependence of the diffusion rate constant on the radius of the compound; (ii) protection of the dendrimer branches toward diffusion of the quencher within the dendrimer volume; (iii) competition between solvent and dendrimer branches for the solvation of the core; (iv) coulombic attraction/repulsion between the positively charged core and the charged quenchers; (v) folding of the dendrimer branches of $[Ru(bpy)_2(\mathbf{8})]^{2+}$ and $[Ru(bpy)_2(\mathbf{9})]^{2+}$ around the unsubstituted bpy ligands. Clearly, the dynamic quenching of an excited state situated in the core of a dendrimer is a very complex process that needs further investigations. Anyway, a protection effect by the dendrimer branches is certainly present and can perhaps be exploited for practical applications requiring an increase in the excited state lifetime under particular experimental conditions [24].

2.3. Sensitization of the core luminescence

In the dendritic complexes $[Ru(\mathbf{10})_3]^{2+}$ and $[Ru(\mathbf{11})_3]^{2+}$ (Fig. 4) the 2,2′-bipyridine ligands of the $[Ru(bpy)_3]^{2+}$-type core carry branches containing 1,2-dimethoxybenzene- and 2-naphthyl-type chromophoric units [20]. Since such units (as well as the core) are separated by aliphatic connections, the interchromophoric interactions are weak and the absorption spectra of $[Ru(\mathbf{10})_3]^{2+}$ and $[Ru(\mathbf{11})_3]^{2+}$ dendrimers are substantially equal to the summation of the spectra of the chromophoric groups that are present in their structures (see, e.g. Fig. 5). The three types of chromophoric groups contained in the dendritic complexes $[Ru(\mathbf{10})_3]^{2+}$ and $[Ru(\mathbf{11})_3]^{2+}$, namely, the $[Ru(bpy)_3]^{2+}$, dimethoxybenzene, and naphthalene, are potentially luminescent species.

The luminescence spectrum of the wedge **11** (Fig. 6a) shows an intense emission band in the region of the dimethoxybenzene- and naphthyl-type units. Such a band, however, is almost completely absent in the emission spectrum of dendrimers $[Ru(\mathbf{10})_3]^{2+}$ and $[Ru(\mathbf{11})_3]^{2+}$, which exhibit only the visible emission band characteristic of $[Ru(bpy)_3]^{2+}$-type chromophoric group, regardless of the excitation wavelength (see, e.g. Fig. 6). A quantitative comparison of the emission intensity in the UV region of wedge **11** and the $[Ru(\mathbf{11})_3]^{2+}$ dendrimer upon excitation at 270 nm, which in the dendrimer is mainly absorbed by the dimethoxybenzene- and naphthyl-type units, showed that at least 90% of the emission of the chromophoric



$[Ru(11)_3]^{2+}$

Fig. 4. Formula of dendrimer $[Ru(\mathbf{11})_3]^{2+}$ and schematic representation of the energy transfer processes taking place in this system.

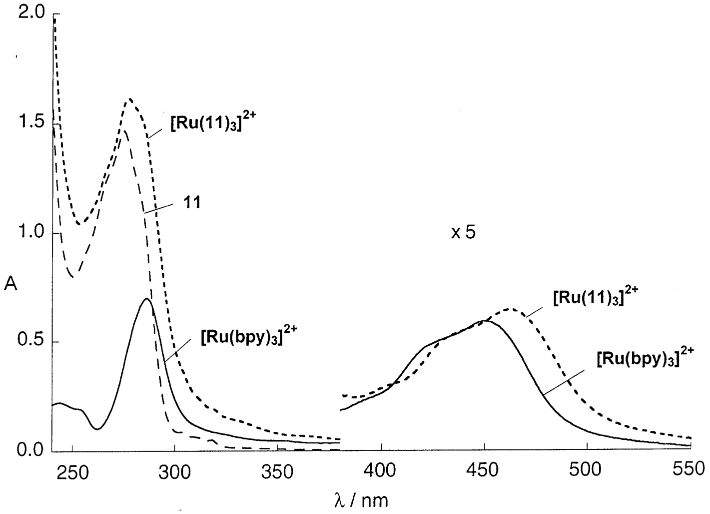
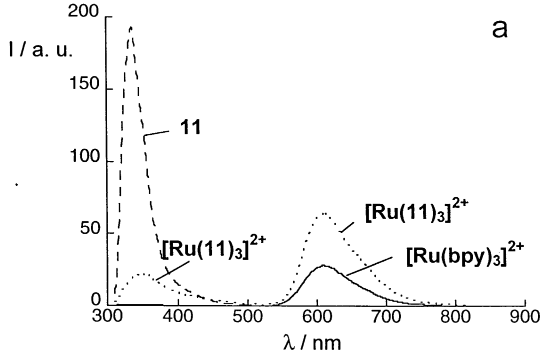


Fig. 5. Absorption spectra (acetonitrile solution, 298 K) of dendrimer $[Ru(\mathbf{11})_3]^{2+}$ (8.0×10^{-6} M), $[Ru(bpy)_3]^{2+}$ (8.0×10^{-6} M), and wedge **11** (4.8×10^{-4} M).

groups of the wedges is quenched in the dendrimer. A quantitative comparison of the emission intensity at 610 nm of $[Ru(bpy)_3]^{2+}$ and the $[Ru(\mathbf{11})_3]^{2+}$ dendrimer upon excitation with 450 nm light, which in $[Ru(\mathbf{11})_3]^{2+}$ is absorbed only by the $[Ru(bpy)_3]^{2+}$-type core (Fig. 6b), and with 270 nm light, which in $[Ru(\mathbf{11})_3]^{2+}$ is mainly absorbed by the wedges (Fig. 6a), showed that the light absorbed by the dimethoxybenzene- and naphthyl-type units of the wedge is almost as efficient as the light absorbed by the core as far as the intensity of the 610 nm band is concerned. These results show that a very efficient energy-transfer process takes place from the potentially fluorescent excited states of the aromatic units of the wedges to the metal-based dendritic core (antenna effect, Fig. 4). The spectra reported in Fig. 6b show that, as discussed above, in aerated solution the luminescence intensity of the dendrimer is more intense than that of the $[Ru(bpy)_3]^{2+}$ model compound because the dendrimer branches protect the Ru-bpy based core from dioxygen quenching.

In conclusion, because of the very high absorbance of the naphthyl groups in the near UV spectral region, the high energy transfer efficiency, and the strong emission



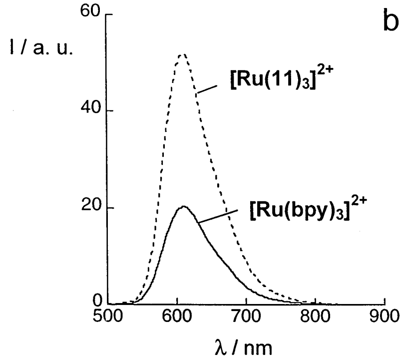


Fig. 6. (a) Luminescence spectra of dendrimer $[Ru(\mathbf{11})_3]^{2+}$, wedge **11**, and $[Ru(bpy)_3]^{2+}$ on excitation at 270 nm. The absorbance of the solution was 0.160 in all cases. (b) Luminescence spectra of dendrimer $[Ru(\mathbf{11})_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ on excitation at 450 nm; the absorbance of the solution was 0.120 in both cases. All the spectra were recorded in air equilibrated acetonitrile solution.

of the $[Ru(bpy)_3]^{2+}$-type core, dendrimer $[Ru(\mathbf{11})_3]^{2+}$ exhibits a strong visible emission upon UV excitation even in very diluted (10^{-7} M) solutions [20].

3. Arrays of Ru(II) and/or Os(II) polypyridine complexes

3.1. General properties

Polypyridine ligands have extensively been used to build up polynuclear complexes with dendritic structures. In such dendrimers, the metal units are linked together by bridging ligands. The choice of suitable bridging ligands is crucial to determine the properties of dendrimers for the following reasons: (i) their coordinating sites (together with those of the 'terminal' ligands) influence the spectroscopic and redox properties of the active metal-based units; (ii) their structure and the orientation of their coordinating sites determine the architecture of the dendrimer; (iii) their chemical nature controls the electronic communication between the metal-based units.

Although a variety of dendrimers containing Ru(II) and, less frequently, Os(II) polypyridine complexes have been reported, only those based on 2,3- and 2,5-bis(2-pyridyl)pyrazine (2,3- and 2,5-dpp) as bridging ligands and 2,2′-bipyridine (bpy) and 2,2′-biquinoline (biq) as terminal ligands (Fig. 7) have been carefully investigated from the photophysical viewpoint [6,30]. The typical strategy used to prepare dendrimers containing the 2,3- and 2,5-dpp bridging ligands is the so-called 'complexes as metals and complexes as ligands' approach [6,31] which has allowed the construction of species containing four, six, ten, 13 and 22 metal-based units.

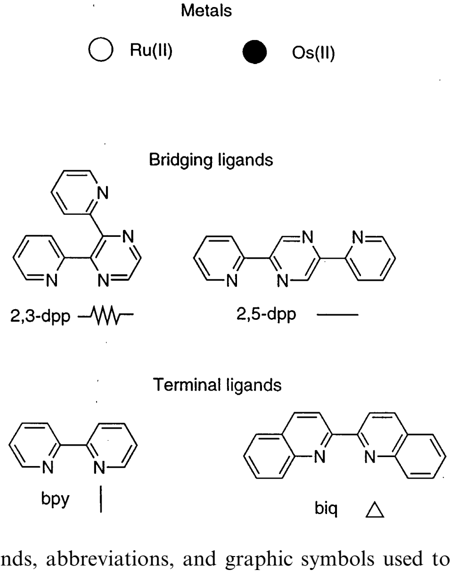


Fig. 7. Formulas of the ligands, abbreviations, and graphic symbols used to represent the components of the dendrimers.

Different representations of a dendrimer made of ten Ru(II)-based units, $[\mathrm{Ru}\{(\mu\text{-}2,3\text{-dpp})\mathrm{Ru}[(\mu\text{-}2,3\text{-dpp})\mathrm{Ru}(\mathrm{bpy})_2]_2\}_3]^{20+}$, are shown in Fig. 8. Fig. 9 shows schematically a docosanuclear dendrimer of that family. The latter compound is a 44+ cationic species made of 1090 atoms, has a molecular weight of 10 890 Da, and an estimated size of 5 nm. Besides the 22 metal atoms, it contains 24 terminal ligands and 21 bridging ligands. In principle, the dendrimers of this type can exist as different isomers because the two coordinating nitrogen atoms of each chelating site

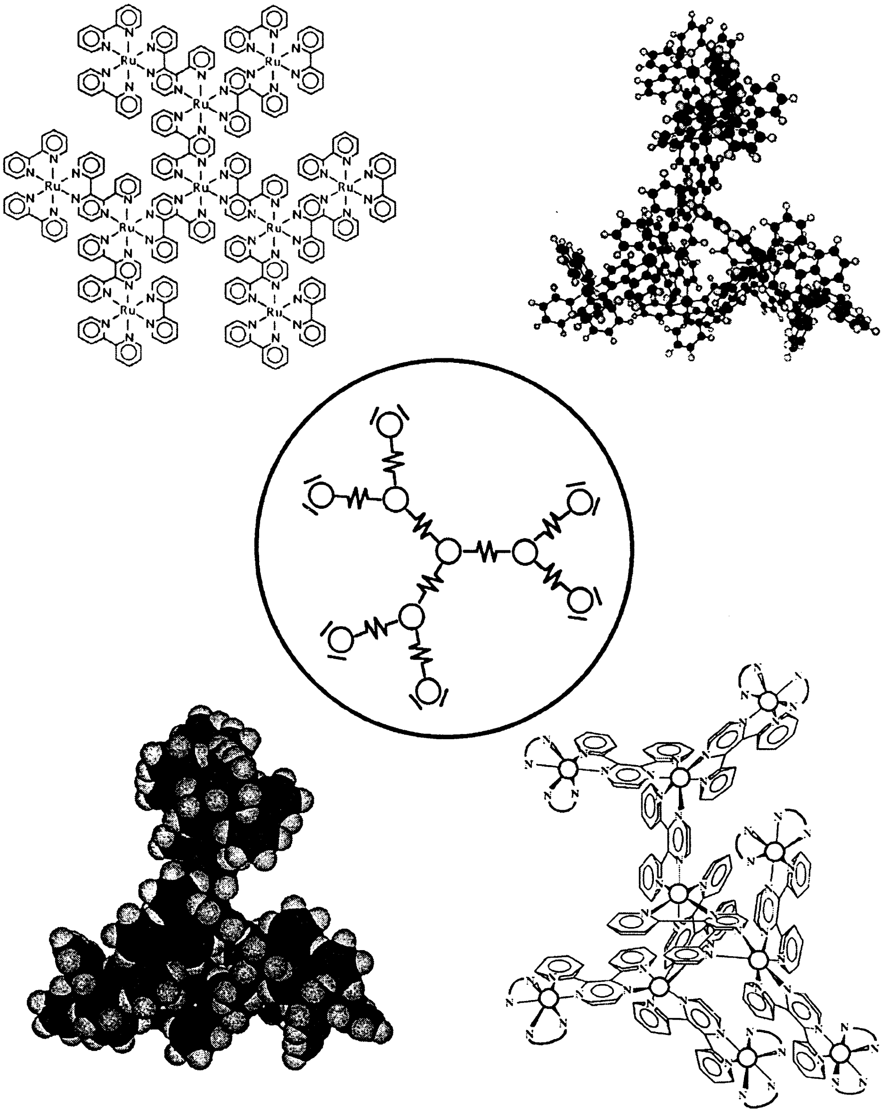


Fig. 8. Different schematic representations of a decanuclear dendrimer.

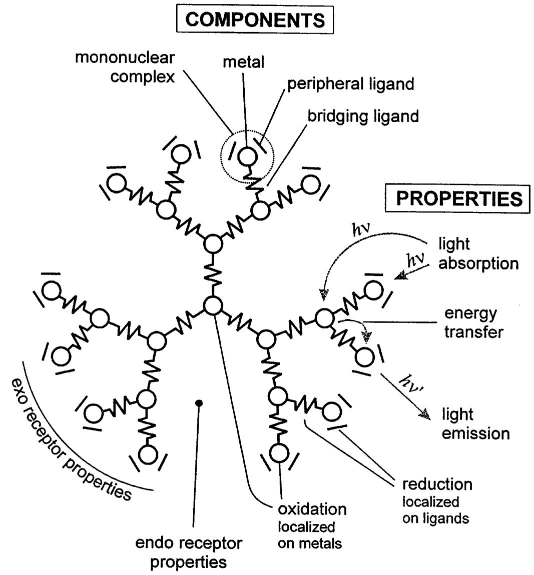


Fig. 9. Schematic representation of a docosanuclear Ru(II) dendrimer with some interesting features evidenced.

of the bridging ligands are not equivalent. Furthermore, they can be a mixture of several diastereoisomeric species since each metal center is also a stereogenic center. Differences arising from the presence of isomeric species, however, do not affect the photochemical and photophysical properties (vide infra).

3.2. Light harvesting and antenna effect

Each dendrimer can be viewed as an ordered ensemble of metal-based $[M(L)_n(BL)_{3-n}]^{2+}$ units (M = Ru(II) or Os(II); L = bpy or biq; BL = 2,3- or 2,5-dpp) which are known [30–32] to exhibit (i) intense ligand-centered (LC) absorption bands in the UV region and moderately intense metal-to-ligand charge-transfer (MLCT) bands in the visible region and (ii) a relatively long-lived luminescence in the red spectral region, due to the lowest ^{3}MLCT level. In the dendrimers, there is only a small electronic interaction between nearby mononuclear units and therefore the absorption spectrum is practically the 'sum' of the spectra of the constituent units. Therefore, in the dendrimers of higher nuclearity, the molar absorption coefficient is huge throughout the entire UV–vis spectral region ($\varepsilon = 202\,000$ $M^{-1}cm^{-1}$ at 542 nm for the Ru(II) docosanuclear dendrimer) [33] so that most of the photochemically active part of sunlight can be absorbed.

In these dendrimers, because of the chemical nature of the bridging ligands, there is a small but not negligible electronic interaction which is sufficient to cause a very fast (exoergonic) energy transfer between nearby units. This leads to the quenching of the potentially luminescent units having higher energy ^{3}MLCT levels and the sensitization of the luminescence of the units having lower energy ^{3}MLCT levels.

The energy of the ^{3}MLCT level excited state of each unit depends on metal and ligands in a predictable way [30]. By the above mentioned modular synthetic strategy, dendrimers can be obtained with a high degree of synthetic control in terms of the nature and position of metal centers, bridging ligands, terminal ligands. Such a synthetic control translates into a high degree of control on the direction of energy flow within the dendritic array. For example, in the tetranuclear compound shown in Fig. 10a the lowest energy excited state is located on the Os-based core, so that energy transfer from the excited peripheral Ru-based units to the core takes place with unitary efficiency. Reversing the positions of the Ru and Os metals (Fig. 10b), center-to-periphery energy transfer can be obtained [34,35]. By using different combinations of metals and ligands, other energy-migration patterns have also been obtained (Fig. 10). On increasing nuclearity, however, a unidirectional gradient (center-to-periphery or vice versa) for energy transfer cannot be obtained with only two types of metals (Ru(II) and Os(II)) and ligands (bpy and μ-2,3-dpp), as illustrated in Fig. 11 for a decanuclear and a docosanuclear dendrimer [6].

Recently, other polypyridine bridging ligands have been used to synthesize stereochemically pure tetra- and deca-nuclear complexes [36]. For the tetranuclear compound displayed in Fig. 12, it has been shown that energy transfer occurs from the central to the peripheral units and that the photophysical and electrochemical properties are the same, within experimental uncertainties, for all stereoisomers.

4. Dendrimers containing porphyrins

Another class of chromophoric units extensively used as photoactive groups in dendrimers are porphyrins. These compounds are particularly appealing because of their similarity to the natural chromophores, their light absorption and redox

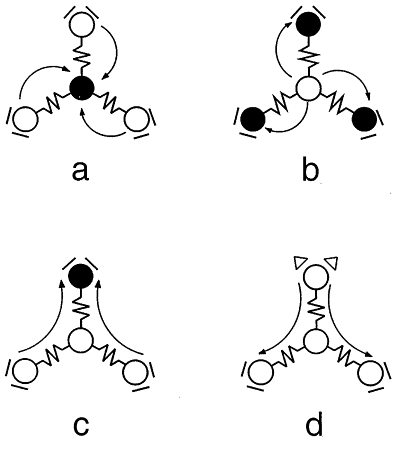


Fig. 10. Energy migration patterns in tetranuclear dendrimers. For the meaning of symbols, see Fig. 7.

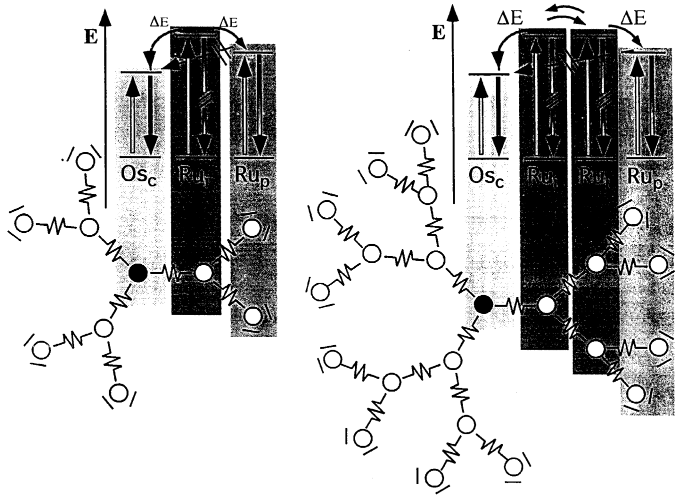


Fig. 11. Energy migration patterns for a decanuclear and a docosanuclear dendrimer. For the meaning of symbols, see Fig. 7.

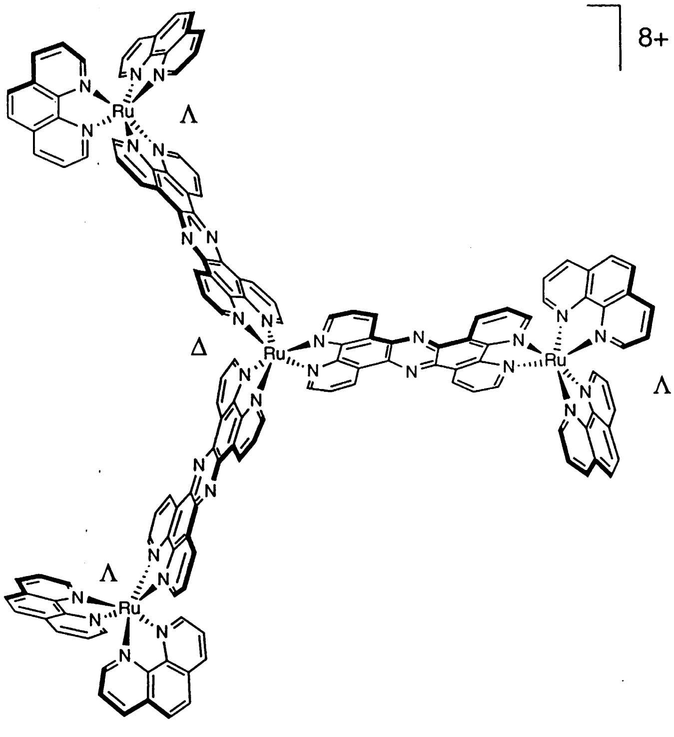


Fig. 12. The $\Delta\Lambda_3$ stereoisomer of a tetranuclear dendrimer.

properties, their stability, their relatively easy synthetic accessibility, and the large number of structural variations that are available [37].

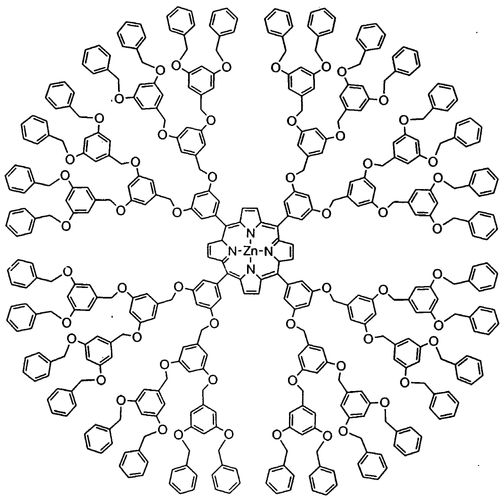
4.1. Dendrimers with a porphyrin-type core

Several dendrimers having a porphyrin or metalloporphyrin core have been investigated. In a recent paper [38], the photophysical and hydrodynamic properties of Fréchet-type dendrimers with zinc porphyrin (PZn) and tetraphenylporphyrin ($TPPH_2$) cores have been reported (Fig. 13). The absorption spectra of the PZn-based dendrimers (generation 1 to 3) exhibited a small red-shift of the Soret band upon increasing generation, which was attributed to an interaction between the dendrons and the core. No shift, however, is observed for the $TPPH_2$-based dendrimers where the additional phenyl groups increases the distance between the branches and the porphyrin moiety. In all cases the fluorescence decay showed a monoexponential profile and the fluorescence quantum yields were identical to those observed for the zinc tetraphenylporphyrin and tetraphenylporphyrin model compounds, respectively. Volume measurements indicated that the extra phenyl spacers present in the $TPPH_2$-based dendrimers allow more flexibility to the structure.

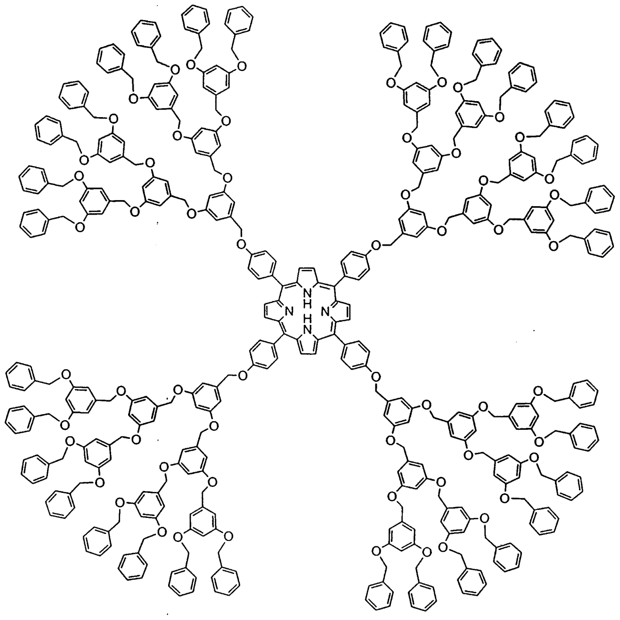
A series of polyglutammic Pd porphyrins with Pd-*meso*-tetra-4-carboxyphenylporphyrin (PdTCPP) core have been reported to exhibit a strong phosphorescence with $\lambda_{max} = 690$ nm and lifetimes in the range 0.5-1.0 ms in deoxygenated solution [39]. Phosphorescence quenching by dioxygen was observed both in DMF and water solutions. In DMF there was almost no difference in the quenching constants for all the investigated compounds, whereas in water the values of the quenching constant decreased significantly as the size of the dendrimer increased. This effect was taken as evidence that, depending on the solvent properties, the polyglutamic branches adopt either open or compact conformations. In the latter case, increasing dendrimer size would imply increasing barrier to oxygen diffusion towards the porphyrin core.

Electrostatic assembly of negatively and positively charged dendrimer porphyrins has been investigated by means of energy transfer measurements [40]. The compounds used were made of zinc (PZn) and free base (PH_2) porphyrin cores surrounded by second generation Fréchet-type dendrons functionalized at the periphery with ammonium and carboxylate units, respectively. The energy transfer rate constant was found to be 3.0×10^9 s^{-1}, in satisfactory agreement with the expected core-to-core distance in the assembly of the positively and negatively charged dendrimers.

In an attempt to mimic natural photosynthetic antenna complexes for light harvesting, up to eight boron-dipyrrin (BDPY) pigments have been appended to a free base or Zn porphyrin core (Fig. 14) [41]. The energy-transfer process occurs with efficiency higher than 85% and time constants 2 and 20 ps. The presence of two excited-state conformers, differing in the planarity of the boron-dipyrrin unit and its orientation with respect to the 5-aryl ring, has been inferred.



PZn-core



$TPPH_2$-core

Fig. 13. Third generation dendrimers with zinc porphyrin (PZn) and tetraphenylporphyrin ($TPPH_2$) cores.

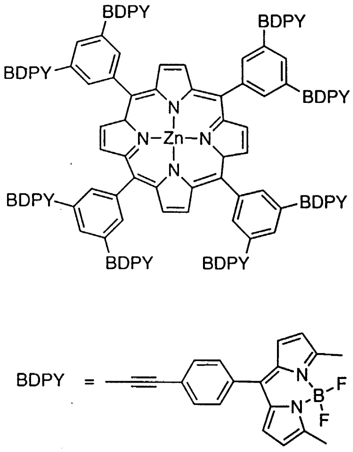


Fig. 14. A dendrimer made of a Zn porphyrin core with appended eight BDPY chromophoric units.

4.2. Multiporphyrin arrays

By using a modular approach, a variety of di-, tri-, tetra- and pentameric (Fig. 15) porphyrin arrays have been obtained and systematic investigations of their properties have been reported [42]. The arrays have been constructed with an ethyne linkage between aryl groups on adjacent tetraarylporphyrin macrocycles, which provides a semirigid architecture that limits direct chromophore interactions. The center-to-center and edge-to-edge distances for the porphyrins in these systems are approximately 20 and 13.5 Å, respectively. The electronic coupling of the porphyrin chromophores is weak. In the star-like array of five porphyrins (Fig. 15) efficient singlet–singlet energy transfer from the peripheral Zn-containing units to the free-base core was observed. A thorough photophysical investigation of this and related compounds [42b] has shown that (i) singlet excited-state energy transfer from the Zn porphyrin to the free-base porphyrin is extremely efficient (95–99%); (ii) competitive electron-transfer reactions are not observed; (iii) the mechanism of energy transfer predominantly involves through-bond communication via the ethyne linker; (iv) energy transfer between two isoenergetic Zn porphyrins is very fast. A successful modeling approach has also been developed [42d] which permits facile calculation of the quantum efficiency of energy-migration processes as well as the antenna effect in a wide assortment of arrays. More recently, energy transfer in trimers made of Mg, Zn, and free base porphyrins and the influence of varying linker attachment sites have been investigated [43]. A study on energy migration in other kinds of Zn porphyrin arrays has also appeared [44]. All these studies demonstrate that extended multiporphyrin arrays can be designed in a rational manner with predictable photophysical features and efficient light-harvesting properties.

As a further step towards artificial photosynthesis, an array consisting of four Zn porphyrins and a free base porphyrin has been linked to a fullerene unit to form the

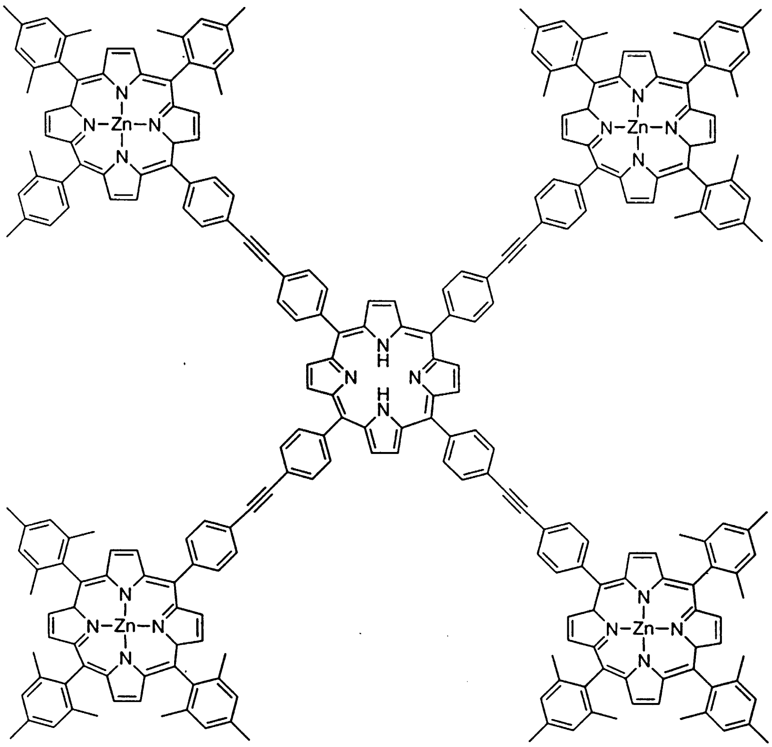


Fig. 15. A pentameric light-harvesting porphyrin array.

$(PZn)_4$–(PH_2)–C_{60} hexad shown in Fig. 16 [45]. In such a system, the four PZn units constitute a light harvesting antenna and the (PH_2)–C_{60} moiety plays the role of a reaction center for charge separation. Efficient singlet–singlet energy transfer from the PZn units to the PH_2 unit is followed by a very fast ($k = 3 \times 10^{11}$ s^{-1}) electron-transfer process which leads to the formation of the $(PZn)_4$–$(PH_2)^+$–C_{60}^- charge separated state with quantum yield 0.70. The charge separated state then goes back to the ground state with time constant 1.1 ns.

Energy transfer in porphyrin arrays made of more than five units has also been reported [46].

4.3. Dendrimers with appended porphyrins

Poly(L-lysine) dendrimers with appended up to 32 free base porphyrins or zinc porphyrins on the branches have been synthesized [47]. From the photophysical viewpoint, an even more interesting system is the dendrimer which carries 16 free base porphyrins in one hemisphere and 16 zinc porphyrins in the other one. In such

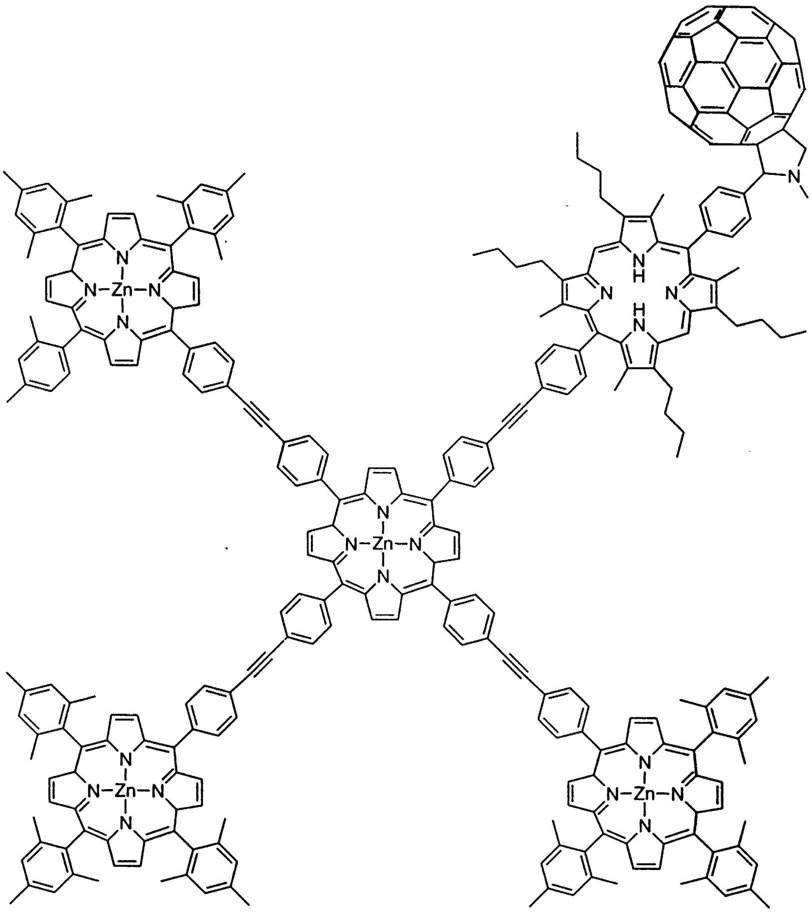


Fig. 16. A $(PZn)_4$–(PH_2)–C_{60} hexad for light harvesting and photoinduced charge separation.

a dendrimer, energy transfer from the free base units to the Zn porphyrin ones has been observed.

Globular dendrimers involving a C_{60} core with appended a zinc tetraphenylporphyrin chromophore and ten Fréchet-type dendrons have been prepared [48]. Their fluorescent properties are quite similar to those of the parent zinc tetraphenylporphyrin unit.

We would also like to recall a thorough investigation, carried out by time-resolved fluorescence anisotropy measurements, of the dynamics of energy transfer in poly(propylene amine) dendrimers of the first, third and fifth generation functionalized in the periphery with free base porphyrins [49].

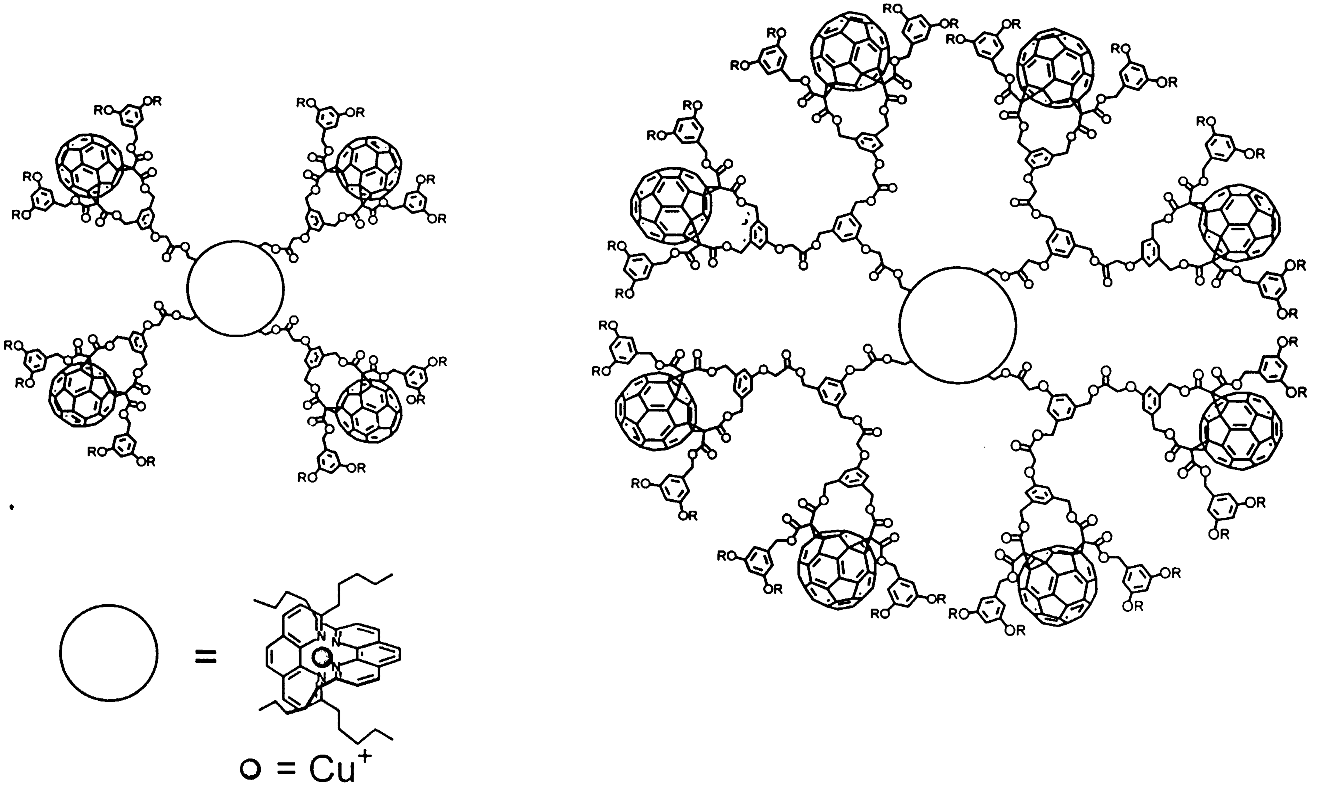


Fig. 17. First and second generation dendrimers with $[Cu(phen)_2]^+$ core and peripheral fullerene units. The third generation dendrimer is shown on the next page.

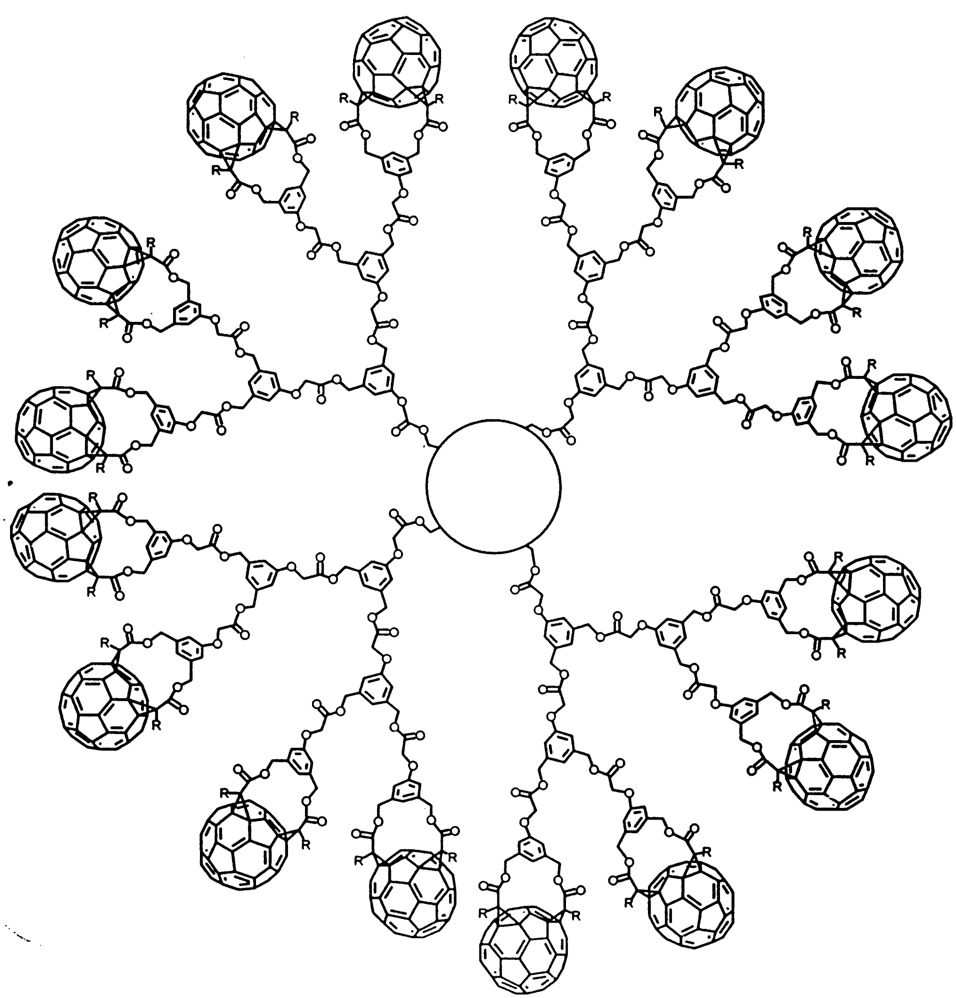


Fig. 17. (*Continued*)

5. Other systems

The photophysical properties of dendrimers with bis(1,10-phenanthroline)-copper(I) ($[Cu(phen)_2]^+$) core and peripheral fullerene units (Fig. 17) have been investigated [50]. The luminescent ^{3}MLCT excited state of the metal complex core is completely quenched in CH_2Cl_2 solution at room temperature. In principle, the quenching process may take place by (i) energy transfer to the fullerene centered singlet, (ii) energy transfer to the fullerene centered triplet, and (iii) electron transfer yielding a fullerene based anion and an oxidized Cu(II) complex. The electron-transfer process, however, does not seem to be the prevailing phenomenon for two reasons: (1) the luminescence quenching takes place also in rigid matrix at 77 K in spite of the low exoergonicity ($\Delta G = -0.17$ eV) of the electron-transfer process; (2) quenching of the fullerene fluorescence, which in principle could occur by electron transfer with a comparable driving force, is not observed.

An organometallic alkynylruthenium dendrimer has been found to exhibit third-order optical nonlinearity and a strongly enhanced two-photon absorption compared with the constituent components [51].

6. Conclusion

Metal complexes, because of their outstanding photochemical and photophysical properties, are among the most interesting photoactive units that can be incorporated in dendrimers. So far, literature in this field mainly deals with photophysical investigations, but some interesting examples of photoinduced electron-transfer processes have also been reported. Particularly important are the advances in the construction of dendrimers capable of harvesting visible light. Some of the systems discussed above show that the presence of photoactive units in dendrimers leads to unusual properties and can be exploited for probing a variety of aspects of dendrimer chemistry. Many facets of the photochemical and photophysical properties of dendrimers remain to be explored.

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References

[1] (a) D.A. Tomalia, H.D. Durst, Top. Curr. Chem. 165 (1993) 193. (b) J.M.J. Fréchet, Science 263 (1994) 1710. (c) N. Ardoin, D. Astruc, Bull. Soc. Chim. Fr. 132 (1995) 875. (d) G.R. Newkome, C. Moorefield, F. Vögtle, Dendritic Molecules: Concepts, Syntheses, Perspectives, VCH, Weinheim, 1996. (e) F. Zeng, S.C. Zimmerman, Chem. Rev. 97 (1997) 1681. (f) J.-P. Majoral, A.-M. Caminade, Top. Curr. Chem. 197 (1998) 79. (g) O.A. Matthews, A.N. Shipway, J.F. Stoddart, Prog. Polym. Sci. 23 (1998) 10. (h) D.K. Smith, F. Diederich, Chem. Eur. J. 4 (1998) 1353. (i) H.-F. Chow, T.K.-K. Mong, M.F. Nongrum, C.-W. Wan, Tetrahedron 54 (1998) 8543. (j) M. Fischer, F. Vögtle, Angew. Chem. Int. Ed. 38 (1999) 884. (k) A.W. Bosman, H.M. Janssen, E.W. Meijer, Chem. Rev. 99 (1999) 1665. (l) G.R. Newkome, E. He, C. Moorefield, Chem. Rev. 99 (1999) 1689.

[2] E. Buhleier, W. Wehner, F. Vögtle, Synthesis (1978) 155.

[3] (a) R. Dagani, Chem. Eng. News, February 8 (1999) 33. (b) M. Freemantle, Chem. Eng. News, November 1 (1999) 27.

[4] A.D. Schlüter, J.P. Rabe, Angew. Chem. Int. Ed. Engl. 39 (2000) 864.

[5] V. Balzani, F. Scandola, Supramolecular Chemistry, Ellis Horwood, New York, 1991.

[6] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, Acc. Chem. Res. 31 (1998) 26.

[7] See, e.g. (a) V. Balzani, P. Ceroni, S. Gestermann, C. Kauffmann, M. Gorka, F. Vögtle, Chem. Commun. (2000) 853. (b) F. Vögtle, S. Gestermann, C. Kauffmann, P. Ceroni, V. Vicinelli, V. Balzani, J. Am. Chem. Soc. 122 (2000) 10398.

[8] See, e.g. (a) J. Hofkens, L. Latterini, G. De Belder, T. Gensch, M. Maus, T. Vosch, Y. Karni, G. Schweitzer, F.C. De Schryver, A. Hermann, K. Müllen, Chem. Phys. Lett. 304 (1999) 1. (b) K. Tsuda, G.C. Dol, T. Gensch, J. Hofkens, L. Latterini, J.W. Weener, E.W. Meijer, F.C. De Schryver, J. Am. Chem. Soc. 122 (2000) 3445.

[9] M. Venturi, S. Serroni, A. Juris, S. Campagna, V. Balzani, Top. Curr. Chem. 197 (1998) 193.

[10] (a) J.F.G.A. Jansen, E.M.M. de Brabander-van den Berg, E.W. Meijer, Science 266 (1994) 1226. (b) A.P.H.J. Schenning, E. Peeters, E.W. Meijer, J. Am.Chem. Soc. 122 (2000) 4489 and references therein. (c) G. Pistolis, A. Malliaris, D. Tsiourvas, C.M. Paleos, Chem. Eur. J. 5 (1999) 1440. (d) V. Chechik, M. Zhao, R.M. Crooks, J. Am. Chem. Soc. 121 (1999) 4910. (e) V. Balzani, P. Ceroni, S. Gestermann, M. Gorka, C. Kauffmann, M. Maestri, F. Vögtle, ChemPhysChem. (2000) 224.

[11] D. ben-Avraham, L.S. Dchulman, S.H. Bossmann, C. Turro, N.J. Turro, J. Phys. Chem. B 102 (1998) 5088.

[12] A. Juris, M. Venturi, P. Ceroni, V. Balzani, S. Campagna, S. Serroni, Collect. Czech. Chem. Commun. 66 (2001) 1.

[13] (a) A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. von Zelewsky, Coord. Chem. Rev. 84 (1988) 85. (b) V. Balzani, A. Juris, Coord. Chem. Rev. 211 (2001) 97.

[14] (a) V. Balzani, F. Barigelletti, L. De Cola, Top. Curr. Chem. 158 (1990) 31. (b) B. O'Regan, M. Grätzel, Nature 353 (1991) 737.

[15] M.Z. Hoffman, F. Bolletta, L. Moggi, G. Hug, J. Phys. Chem. Ref. Data 18 (1989) 219.

[16] V. Balzani, A. Juris, M. Venturi, S. Campgna, S. Serroni, Chem. Rev. 96 (1996) 759.

[17] (a) E.C. Constable, Chem. Commun. (1997) 1073. (b) E.C. Constable, O. Eich, C.E. Housecroft, D.C. Rees, Inorg. Chim. Acta 300–302 (2000) 158.

[18] See, e.g. (a) P. Ceroni, F. Paolucci, C. Paradisi, A. Juris, S. Roffia, S. Serroni, S. Campagna, A.J. Bard, J. Am. Chem. Soc. 120 (1998) 5480. (b) M. Marcaccio, F. Paolucci, C. Paradisi, S. Roffia, C. Fontanesi, L.J. Yellowlees, S. Serroni, S. Campagna, G. Denti, V. Balzani, J. Am. Chem. Soc. 121 (1999) 10081.

[19] J. Issberner, F. Vögtle, L. De Cola, V. Balzani, Chem. Eur. J. 3 (1997) 706.

[20] M. Pleovets, F. Vögtle, L. De Cola, V. Balzani, New J. Chem. (1999) 63.

[21] F. Vögtle, M. Pleovets, M. Nieger, G.C. Azzellini, A. Credi, L. De Cola, V. De Marchis, M. Venturi, V. Balzani, J. Am. Chem. Soc. 121 (1999) 6290.

[22] S. Serroni, S. Campagna, A. Juris, M. Venturi, V. Balzani, G. Denti, Gazz. Chim. Ital. 124 (1994) 423.

[23] A. Gilbert, J. Baggot, Essentials of Molecular Photochemistry, Blackwell Scientific Publications, Oxford, 1991.

[24] C. Gorman, Adv. Mater. 10 (1998) 295.

[25] (a) R.H. Jin, T. Aida, S. Inoue, J. Chem. Soc. Chem. Commun. (1993) 1261. (b) R. Sadamoto, N. Tomioka, T. Aida, J. Am. Chem. Soc. 118 (1996) 3978. (c) M. Kimura, K. Nakada, Y. Yamaguchi, K. Hanabusa, H. Shirai, N. Kobayashi, Chem. Commun. (1997) 1215.

[26] (a) X. Zang, M.A.J. Rodgers, J. Phys. Chem. 99 (1995) 12797. (b) F. Wilkinson, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 22 (1993) 113. (c) C. Tanielian, C. Wolff, M. Esch, J. Phys. Chem. 100 (1996) 6555.

[27] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, Dekker, New York, 1993.

[28] J.-C.G. Bünzli, in: J.-C.G. Bünzli, G.R. Choppin (Eds.), Lanthanides Probes in Life, Chemical and Earth Sciences, Theory and Practice, Elsevier, New York, 1989, p. 219.

[29] V. Balzani, F. Bolletta, M.T. Gandolfi, M. Maestri, Top. Curr. Chem. 75 (1978) 1.

[30] (a) G. Denti, S. Campagna, V. Balzani, In: D. Mendenhall, A. Greensberg, J. Liebman (Eds.), Mesomolecules: from Molecules to Materials, Chapman and Hall, New York, 1995, p. 69. (b) S. Serroni, S. Campagna, G. Denti, A. Juris, M. Venturi, V. Balzani, In: G.R. Newkome (Ed.), Advances in Dendritic Macromolecules, vol. 3, JAI, London, 1996, p. 61.

[31] G. Denti, S. Serroni, S. Campagna, A. Juris, M. Ciano, V. Balzani, in: A.F. Williams, C. Floriani, A.E. Merbach (Eds.), Perspectives in Coordination Chemistry, VCH, Basel, 1992, p. 153.

[32] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, Sol. Energy Mater. Sol. Cells 38 (1995) 159.

[33] (a) S. Serroni, G. Denti, S. Campagna, A. Juris, M. Ciano, V. Balzani, Angew. Chem. Int. Ed. Engl. 31 (1992) 1493. (b) S. Campagna, G. Denti, S. Serroni, A. Juris, M. Venturi, V. Ricevuto, V. Balzani, Chem. Eur. J. 1 (1995) 211.

[34] G. Denti, S. Serroni, S. Campagna, V. Ricevuto, V. Balzani, Coord. Chem. Rev. 111 (1991) 227.

[35] V. Balzani, S. Campagna, G. Denti, S. Serroni, in: E. Kochanski (Ed.), Photoprocesses in Transition Metal Complexes, Biosystems, and Other Molecules, Kluwer, Dordrecht, 1992, p. 233.

[36] (a) S. Campagna, S. Serroni, S. Bodige, F.M. MacDonnel, Inorg. Chem. 38 (1999) 692. (b) M.-J. Kim, F.M. MacDonnell, M.E. Gimon-Kinsel, T. Du Bois, N. Asgharian, J.C. Griener, Angew. Chem. Int. Ed. Engl. 39 (2000) 615.

[37] (a) K. Kalyanasundaram, Photochemistry of Polypyridine and Porphyrin Complexes, Academic Press, London, 1992. (b) D. Gust, T.A. Moore, in: K.M. Kadish, K.M. Smith, R. Guillard (Eds.), The Porphyrin Handbook, vol. 8, Electron Transfer, Academic Press, San Diego, 2000, p. 153.

[38] M.S. Matos, J. Hofkens, W. Verheijen, F.C. De Schryver, S.K. Hecht, W. Pollak, J.M.J. Fréchet, B. Forier, W. Dehaen, Macromolecules 33 (2000) 2967.

[39] S.A. Vinogradov, L.-W. Lo, D.F. Wilson, Chem. Eur. J. 5 (1999) 1338.

[40] N. Tomioka, D. Takasu, T. Takahashi, T. Aida, Angew. Chem. Int. Ed. Engl. 37 (1998) 1531.

[41] F. Li, S.I. Yang, Y. Ciringh, J. Seth, C.H. Martin III, D.L. Singh, D. Kim, R.R. Birge, D.F. Bocian, D. Holten, J.S. Lindsey, J. Am. Chem. Soc. 120 (1998) 10001.

[42] (a) R.W. Wagner, T.E. Johnson, J.S. Lindsey, J. Am. Chem. Soc. 118 (1996) 11166. (b) J.-S. Hsiao, B.P. Krueger, R.W. Wagner, T.E. Johnson, J.K. Delaney, D.C. Mauzerall, G.R. Fleming, J.S. Lindsey, D.F. Bocian, R.J. Donohoe, J. Am. Chem. Soc. 118 (1996) 11181. (c) A.A. Bothner-By, J. Dadok, T.E. Johnson, J.S. Lindsey, J. Phys. Chem. 100 (1996) 17551. (d) P.G. Van Patten, A.P. Shreve, J.S. Lindsey, R.J. Donohoe, J. Phys. Chem. B 102 (1998) 4209.

[43] R.K. Lammi, A. Ambroise, T. Balasubramanian, R.W. Wagner, D.F. Bocian, D. Holten, J.S. Lindsey, J. Am. Chem. Soc. 122 (2000) 7579.

[44] H.S. Cho, N.W. Song, Y.H. Kim, S.C. Jeoung, S. Hahn, D. Kim, S.K. Kim, N. Yoshida, A. Osuka, J. Phys. Chem. A 104 (2000) 3287.

[45] D. Kuciauskas, P.A. Liddell, T.E. Johnson, S.J. Weghorn, J.S. Lindsey, A.L. Moore, T.A. Moore, A. Gust, J. Am. Chem. Soc. 121 (1999) 8604.

[46] C.C. Mak, D. Pomeranc, M. Montalti, L. Prodi, J.K.M. Sanders, Chem. Commun. (1999) 1083.

[47] N. Maruo, M. Uchiyama, T. Kato, T. Arai, H. Akisada, N. Nishino, Chem. Commun. (1999) 2057.

[48] X. Camps, E. Dietel, A. Hirsh, S. Pyo, L. Echegoyen, S. Hackbarth, B. Röder, Chem. Eur. J. 5 (1999) 2362.

[49] E.K.L. Yeow, K.P. Ghiggino, J.N.H. Reek, M.J. Croosley, A.W. Bosman, A.P.H.J. Schenning, E.W. Meijer, J. Phys. Chem. B 104 (2000) 2596.

[50] N. Armaroli, C. Boudon, D. Felder, J.-P. Gisselbrecht, M. Gross, G. Marconi, J.-F. Nicoud, J.-F. Nierengarten, V. Vicinelli, Angew. Chem. Int. Ed. Engl. 38 (1999) 3730.

[51] A.M. McDonagh, M.G. Humphrey, M. Samoc, B. Luther-Davies, Organometallics 18 (1999) 5195.