Photoinduced processes in porphyrin-stoppered [3]-rotaxanes

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Energy and electron transfer processes taking place in [3]-rotaxanes containing various photo- and electro-active metal-complex fragments, such as zinc(II)- and gold(III)-porphyrin stoppers, copper(I)- and silver(I)-bis-phenanthroline complex moieties, were studied by spectroscopic steady state and time resolved techniques. Energy transfer from the zinc porphyrin excited singlet state to the MLCT excited state of the Cu(I) complex fragments was observed in the [3]-rotaxane **[PZnCuCuPZn]$^{2+}$**, with a lifetime of 180 ps. In the rotaxane **[PZnCu-PZn]$^{+}$** energy transfer occurred only from the porphyrin ($\tau = 490$ ps) close to the Cu(I) complex, while the lifetime of the distant zinc porphyrin was unaffected. Quenching of the distant porphyrin was partly restored in **[PZnCuAgPZn]$^{2+}$**, while the one close to the Cu(I) complex displayed a luminescence lifetime of 300 ps. In the case of the free [3]-rotaxane **[PZn--PAu]$^{+}$**, the data suggest that a very slow electron transfer process takes place between the porphyrin stoppers probably through the extended "necklace" spacer.

Introduction

The study of photoinduced electron and energy transfer between porphyrins or their analogues is a topic of high biological relevance, because such processes take place in the membranes of green plants and photosynthetic bacteria.[1] Many bis-porphyrin systems in which the two components are linked *via* covalent spacers,[2] hydrogen bonds,[3] or coordination bonds,[4] have been designed and synthesized, and their intramolecular electron or energy transfer properties examined. We have been interested for several years in the synthesis and study of bis-porphyrin conjugates in which the donor and acceptor porphyrins are covalently linked by chelate species, such as 2,9-diphenyl-1,10-phenanthroline[5] (dpp) or, more recently, 6,6′-diphenyl-2,2′-bipyridine.[6] Zinc(II) porphyrins were used as electron or energy donors and free-base porphyrins as energy acceptors.[5a] Of the trivalent metal-containing porphyrins, gold(III) porphyrins were found to be ideal electron acceptors,[5b,c] the redox processes being ligand localized.[7] Thanks to their chelate bridges, the bis-porphyrin conjugates turned out to be ideal dumbbell species for constructing [2]-rotaxanes[8] using the transition metal-templated strategy developed earlier by our group for making catenanes.[9] Furthermore, the rate of photoinduced electron transfer could be controlled by the metal complexed in the central, bis-dpp tetrahedral coordinating cavity, being accelerated by a factor of 20 when the metal was the Cu(I) template itself.[8b,c]

We recently described the synthesis of porphyrin-stoppered [3]-rotaxanes.[10] These molecules are made from a bis-phenanthroline (bisphen)-based molecular dumbbell onto which two dpp-containing macrocycles are threaded. The schematic structures of the [3]-rotaxanes studied and of the related models, along with the abbreviations used, are reported in Scheme 1. These [3]-rotaxanes contain two types of coordinating sites (porphyrins or bis-phenanthrolines), which can host different metals and will allow for the study of various intramolecular photoinduced processes between the metal complex fragments. The [3]-rotaxane with the zinc porphyrins at both ends, **[PZnCuCuPZn]$^{2+}$**, **[PZnCuAgPZn]$^{2+}$**, and **[PZnCu-PZn]$^{+}$**, are ideal systems to study a genuine energy transfer process between ^{1}PZn and the Cu(I) bisphen components, with the possibility of evidencing proximal and distal effects between the donor and the acceptor. Electron transfer between these units is, in fact, prevented by the fact that both PZn and the Cu(I) complex units tend to donate electrons.[4,8] In the case of the free [3]-rotaxane **[PZn--PAu]$^{+}$**, on the contrary, electron transfer from the zinc- to the gold-porphyrin units can occur while energy transfer from ^{1}PZn to ^{1}PAu is endoergonic.[4,8]

Results and discussion

Electrochemistry

Electrochemical data of the compounds of this study were obtained by cyclic voltammetry and are collected in Table 1. The solvent of choice was butyronitrile, since the spectroscopic and photophysical studies were carried out in this solvent, however in some cases the oxidation processes were better characterized in CH_2Cl_2 solution (see below).

The models. The cyclic voltammogram of the **PZn** model in CH_2Cl_2 shows two quasi-reversible waves at $+0.69$ and $+0.96$ V *vs.* SCE, which are very close to the values obtained by Fuhrhop *et al.*[11] for ZnOEP: in butyronitrile solution, this compound shows two consecutive waves centered at $+0.63$ and $+1.02$ V *vs.* SCE, which can be attributed to the $PZn^{\cdot +}/PZn$ and $PZn^{2+}/PZn^{\cdot +}$ redox couples, respectively. The reduction process in butyronitrile takes place at -1.54 V (-1.61 V for ZnOEP),[11] and is reversible ($\Delta E_p = 75$ mV). The cyclic voltammogram of the other porphyrinic model, **PAu^{+}**, shows two reduction waves, at -0.59 and -1.33 V *vs.* SCE in butyronitrile. As established for other Au(III) porphyrins by Jamin and Iwamoto,[7] these waves correspond to the **PAu^{+}**/**PAu$^{\cdot}$** and **PAu$^{\cdot}$**/**PAu^{-}** redox couples. Therefore, the first reduction potential of **PAu^{+}** is much less cathodic than that corresponding to **PZn**, making the former a suitable electron acceptor. In dichloromethane, these reduction potentials are shifted cathodically by 90 and 40 mV, respectively. Oxidation of **PAu^{+}** to **PAu^{2+}** occurs, of course, at more anodic

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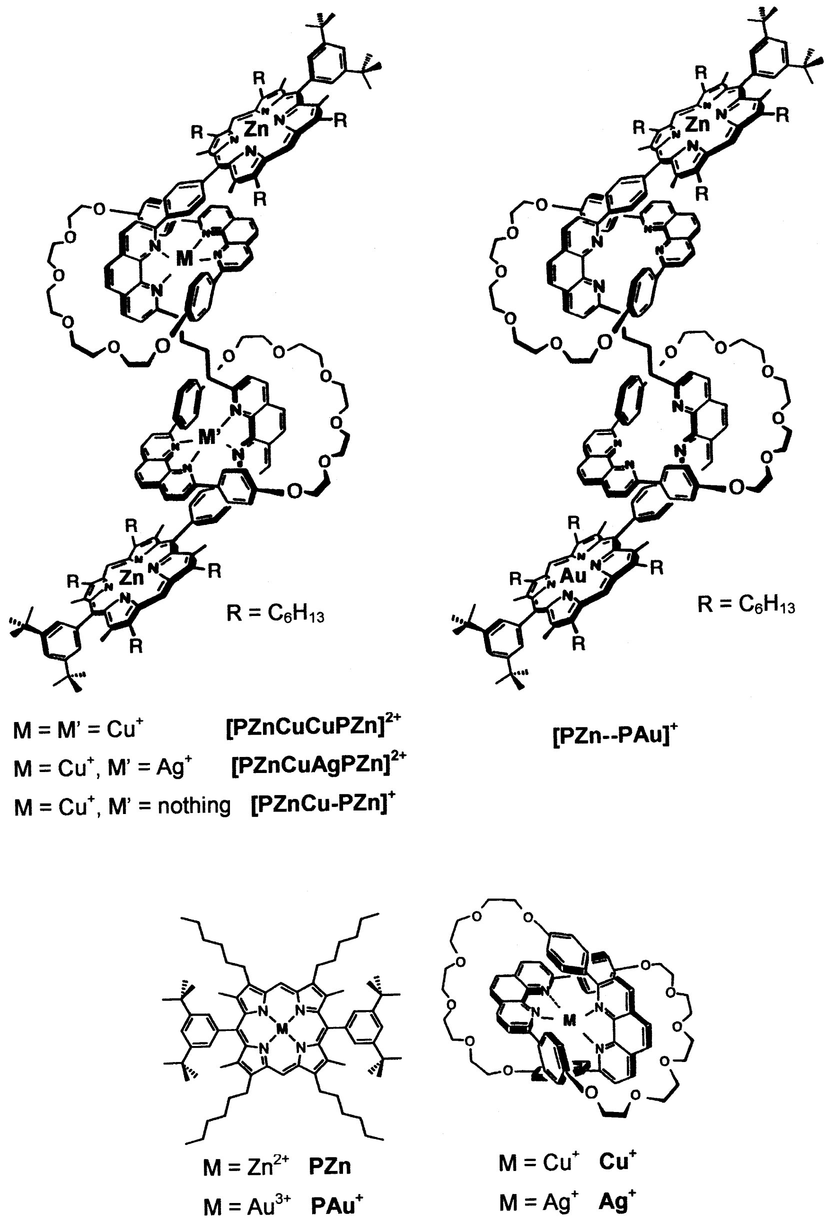

Scheme 1

potentials than oxidation of **PZn**, being observed at +1.55 V in butyronitrile, which is fully consistent with the value of +1.57 V reported by Jamin and Iwamoto in the same solvent.[7]

The models selected for the metal-complexed bis-phenanthroline tetrahedral sites of the [3]-rotaxanes are the Cu(I) and Ag(I) catenates **Cu**$^+$ and **Ag**$^+$.[12] As shown in Table 1, the reduction of **Ag**$^+$ is shifted anodically by *ca.* +0.9 V by comparison to **Cu**$^+$, making the former a much better electron acceptor than the latter. In addition, the reduction process is metal-centered in the case of **Ag**$^+$, whereas it is ligand-centered in the case of **Cu**$^+$.

Table 1 Electrochemical data of the reference compounds and the [3]-rotaxanes[a]

	Oxidation	Reduction
PZn	+0.96(100), +0.69(100)[b]	−1.54(75)[c]
PAu$^+$	+1.55(100)[c]	−0.59(80), −1.33(80)[c]
		−0.68(135), −1.37(125)[b]
Cu$^+$[e]	+0.57[d,e]	−1.61[e,f]
Ag$^+$[e]		−0.70[d,e,g]
[PZnCuCuPZn]$^{2+}$	+1.01(sh), +0.89(85), +0.75(55)[c]	−1.47(60)[c]
	+0.96(80), +0.75(55)[b]	
[PZnCu-PZn]$^+$	+0.97(85), +0.72(80)[b]	−1.50(90)[c]
[PZnCuAgPZn]$^{2+}$	+0.94(120), +0.75(55)[c]	−1.47(55)[c]
		−0.54(irr), −1.49(40)[c,g]
[PZn--PAu]$^+$	+1.32(70), +1.24(sh), +0.87(230), +0.83(sh)[c,h,i]	−0.37(75), −1.03(65), −1.27(55), −1.47(240)[c,h,i]

[a] Unless otherwise noted: V *vs.* SCE at 100 mV s^{-1} (ΔE_p, mV; irr = irreversible, sh = shoulder), 0.1 M TBAB as supporting electrolyte, Pt disk as working electrode. [b] In dichloromethane. [c] In butyronitrile. [d] In acetonitrile. [e] Ref. 12. [f] In DMF. [g] Hanging mercury electrode (HME) as working electrode. [h] V *vs.* Ag/Ag$^+$ reference electrode. [i] In this experiment, SCE is −0.280 V *vs.* Ag/Ag$^+$.

[3]-Rotaxanes. The anodic part of the cyclic voltammogram of the **[PZn--PAu]$^+$** free rotaxane system in butyronitrile shows two main oxidation peaks each accompanied by a shoulder, whereas the cathodic part shows four waves. The first two of these correspond obviously to the **PAu$^+$/PAu$^\cdot$** (-0.37 V *vs.* Ag, -0.65 V *vs.* SCE) and **PAu$^\cdot$/PAu$^-$** (-1.03 V *vs.* Ag, -1.33 V *vs.* SCE) redox couples by comparison with the results obtained with the model Au(III) porphyrin **PAu$^+$**. Whereas the second reduction is virtually unchanged, the first reduction is 60 mV more negative than in the case of **PAu$^+$**. Jamin and Iwamoto[7] reported a third reduction step at -1.67 V *vs.* SCE for Au(TPP)$^+$ in DMSO, 700 mV more cathodic than the second one, and which is absent in the case of Au(Etio)$^+$ (Etio = etioporphyrin). In the case of the model **PAu$^+$**, the region of interest was hidden by the electrolyte. Assuming an intermediate behavior for the Au(III) porphyrin component of the [3]-rotaxane, the last wave at -1.47 V *vs.* Ag (-1.75 V *vs.* SCE), 440 mV from the second reduction wave of the Au(III) porphyrin fragment, could be due to a third reduction step. The other reduction wave observed at -1.27 V *vs.* Ag (-1.55 V *vs.* SCE) is due to the **PZn/PZn$^{\cdot-}$** redox couple, as shown by comparison with the model system. Assuming that the first anodic wave of **[PZn--PAu]$^+$** is due to the **PZn$^{\cdot+}$/PZn** redox couple, the energy level of the charge separated state **[PZn$^+$--PAu$^-$]$^+$** can be estimated as *ca.* 1.24 eV. The determination, which is very rough, does not take into consideration the Coulombic effects which would affect the energy by, at most, 0.1 eV.

Comparison of the cyclic voltammograms of **[PZnCuCuPZn]$^{2+}$** and **[PZnCu-PZn]$^+$** in dichloromethane (Fig. 1) allowed for the determination of the oxidation potential of the complexed Cu(I) in these two [3]-rotaxanes. As for **PZn**, two well-separated waves are observed in the anodic region of the voltammograms, at very similar potentials. The first wave, at *ca.* $+0.75$ V, corresponds to the **PZn$^{\cdot+}$/PZn** redox couple and the second wave, at *ca.* $+0.96$ V, corresponds to the **PZn^{2+}/PZn$^{\cdot+}$** redox couple. Since the intensity of this second wave is decreased in the case of **[PZnCu-PZn]$^+$** by comparison with **[PZnCuCuPZn]$^{2+}$**, it also corresponds to the Cu^{2+}/Cu$^+$ redox couple, which is therefore shifted anodically by *ca.* 400 mV with respect to the value measured for the **Cu$^+$** model.

The cyclic voltammogram of [3]-rotaxane **[PZnCuAgPZn]$^{2+}$** shows two oxidation waves in butyronitrile: the first one, centered at $+0.75$ V *vs.* SCE and with a sharp anodic peak, is due to the **PZn$^{\cdot+}$/PZn** redox couple and the second one, at $+0.94$ V *vs.* SCE, with a relatively broad anodic peak, is probably due to the combination of the Cu^{2+}/Cu$^+$ and **PZn^{2+}/PZn$^{\cdot+}$** redox couples. This is confirmed by the fact that, in butyronitrile, the cyclic voltammogram of **[PZnCuCuPZn]$^{2+}$** shows significant differences to that run in dichloromethane: whereas the first wave is quasi superimposable, the second is sharper, but cathodically shifted to $+0.89$ V *vs.* SCE, and accompanied by a shoulder around 1.01 V *vs.* SCE. We suggest that the maximum is due to Cu^{2+}/Cu$^+$, and the shoulder to the **PZn^{2+}/PZn$^{\cdot+}$** redox couple.

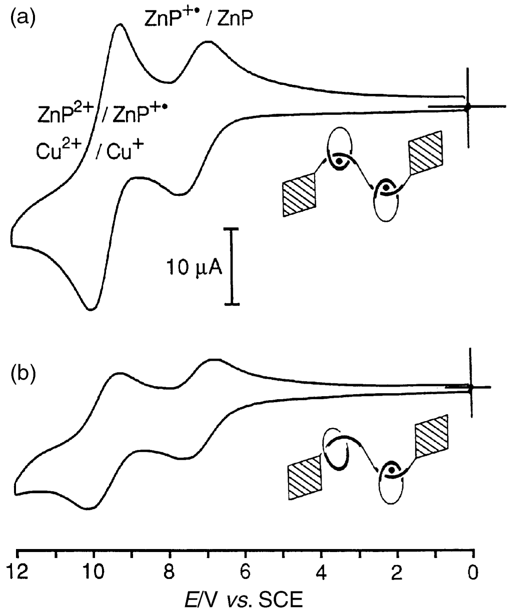

Fig. 1 Cyclic voltammograms of (a) **[PZnCuCuPZn]$^{2+}$** and (b) **[PZnCu-PZn]$^+$**. 0.1 M TBAB in dichloromethane, platinum disk electrode.

The detection of complexed Ag$^+$ in catenates[12] always proved to be very difficult and the present study confirms this fact for threaded systems. Only when a hanging mercury electrode (HME) was used as working electrode, could the reduction of complexed Ag$^+$ be measured.[12] The process is highly irreversible, suggesting that any Ag^0 produced is decomplexed. The value found for [3]-rotaxane **[PZnCuAgPZn]$^{2+}$** was -0.54 V *vs.* SCE in butyrontrile, and confirmed that complexed Ag$^+$ is reduced at higher potentials than complexed Cu$^+$, which is not reduced prior to -1.47 V in **[PZnCuCuPZn]$^{2+}$**, under the same conditions.

From the above electrochemical data the approximate levels of the charge separated states corresponding to the oxidation of the zinc porphyrin and reduction of the Cu(I) complex unit can be derived as *ca.* 2.2 eV and that corresponding to the oxidation of zinc porphyrin and reduction of the Ag(I) unit is calculated as *ca.* 1.3 eV. In view of the approximate treatment no correction for Coulombic effects was made (see above).

Spectroscopy and photophysics

The photophysical study of the models for the arrays, of the bis(zinc porphyrin) stoppered rotaxanes liable to energy transfer processes and of **[PZn--PAu]$^+$**, where electron transfer can occur, are presented below in three separate sections.

The models. Ground state absorption spectra of the two model porphyrins **PAu$^+$** and **PZn** in butyronitrile are shown in Fig. 2 along with the emission at room temperature of **PZn** (inset). No emission can be detected at room temperature for **PAu$^+$**. The absorption displays the usual pattern of a very intense Soret band ($S_0 \rightarrow S_2$) at 416 nm for **PZn** and 401 nm for **PAu$^+$**, the Q bands (a vibronic sequence of $S_0 \rightarrow S_1$) of the zinc porphyrin are located at 544 nm and 578 nm and those of the Au(III) derivative at 519 nm and 554 nm. Both the position of the bands and the oscillator strength of the transitions are in agreement with the corresponding tetraaryl or Etio-derivatives. The luminescence spectra detected in butyronitrile glass at 77 K (Fig. 3 and Table 2), display in the case of **PAu$^+$**

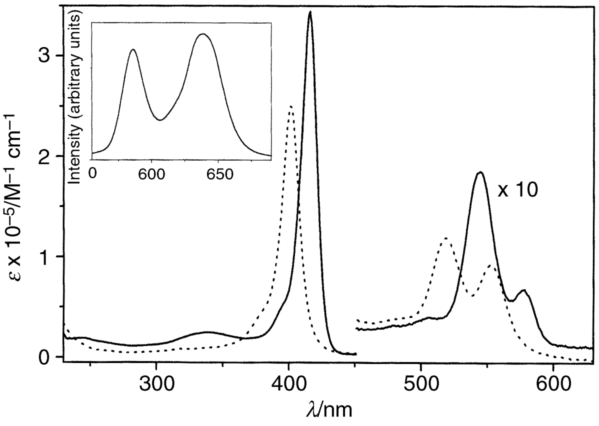

Fig. 2 Absorption spectra in butyronitrile at 298 K: **PZn** (——) and **PAu$^+$** (– – –). In the inset the fluorescence spectrum of **PZn** in butyronitrile at 298 K is shown.

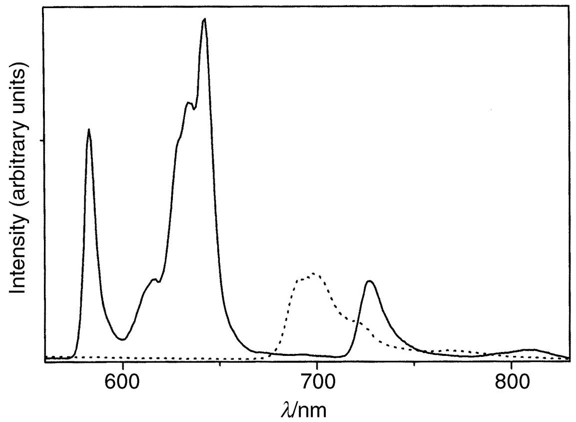

Fig. 3 Luminescence spectra of **PZn** (——), and **PAu⁺** (– – –) in butyronitrile glass at 77 K.

only a structured phosphorescence band (695, 720, 772 nm) whereas for **PZn** both fluorescence (583, 616, 627, 634, 643 nm) and phosphorescence (726, 809 nm) are observed. The appearance of a rather complex structure in the luminescence bands of these porphyrins in the low temperature glass, could be ascribed to the high degree of asymmetry due to the substituents. Of note from these data one can see that the triplet energy of **PZn** is 0.17 eV higher than that of the corresponding tetraaryl derivative in the same solvent (1.54 eV),[13] Table 2.

The decay of ^{3}**PAu**$^+$ in glassy media displays a biexponential behavior with lifetimes of *ca.* 20 and 150 μs, similar to what happens for closely related gold porphyrins.[4d,14] The room temperature lifetime of ^{3}**PAu**$^+$, measured by transient absorption spectroscopy, is *ca.* 400 ps, to be compared with 1.4 ns measured for the tetraaryl derivative; the spectra ($T_1 \rightarrow T_n$) are essentially identical in the two cases, with a strong band around 610–630 nm.[4c]

The fluorescence yield of **PZn**, 0.01, is lower by one order of magnitude with respect to the related tetraaryl compound in the same solvent (0.08) which has a lifetime of 2.00 ns,[13] very similar to that of the present compound, 1.85 ns. This suggests a substantial change of the radiative rate constant of the singlet excited state for the present porphyrin.

Both the singlet and the triplet excited states can be detected by transient absorption spectroscopy; the singlet has a maximum around 460 nm and the triplet at 470 nm. The two states exhibit additional, minor spectral features extending to the near infrared, dominated by the ground state bleaching bands. The lifetime of the triplet is 8 μs in a deaerated butyronitrile solution, to be compared to *ca.* 200 μs for the aryl derivatives.[13] The shortening of the triplet lifetime is in contrast with the expectations based on the increase of the T_1–S_0 energy gap, according to which a longer lifetime is predicted with respect to the tetraaryl derivative, possessing a lower lying triplet state. On the contrary, the energy gap rule is obeyed at 77 K in glassy matrices, where the lifetime of this porphyrin is *ca.* 50 ms, compared to the *ca.* 19 ms[13] of the tetraaryl derivative.

Cu⁺ and **Ag⁺** catenates have been thoroughly investigated in the past.[15,16] The photophysical properties of these complexes can be summarized as follows. **Cu⁺** emission at room temperature is from an MLCT excited state, peaking around 730 nm and characterized by a lifetime of 175 ns in deaerated CH_2Cl_2 (125 ns in aerated conditions). In aerated butyronitrile the lifetime is 60 ns. The emission at room temperature has been demonstrated to occur from a singlet MLCT state, in thermal equilibrium with a lower lying triplet MLCT excited state.[17] This fact can account for the drastic reduction in emission intensity at 77 K, where no thermal equilibrium is possible.[17] **Ag⁺** does not emit at room temperature; in frozen CH_2Cl_2 a very strong ligand centered phosphorescence can be detected peaking at 498 nm, with a lifetime of 12 ms.[15] The luminescence properties of the models are summarized in Table 2 along with those of the investigated [3]-rotaxanes; the triplet state yields and lifetimes of the porphyrin models and of the rotaxanes are collected in Table 3.

Bis(zinc-porphyrin) stoppered [3]-rotaxanes. Energy transfer. The absorption spectra of **[PZnCuCuPZn]²⁺**, **[PZnCu-PZn]⁺** and **[PZnCuAgPZn]²⁺** are displayed in Fig. 4. The position of the bands is as expected from the plain superposition of the individual components, but a broadening of the Soret band with a consequent decrease of molar absorption coefficients on the maxima can be detected for all the [3]-rotaxanes. These spectroscopic results are consistent with a weak coupling between the components. The absorption in the visible region is substantially ascribable to the zinc porphyrins, with a small contribution from the Cu⁺ chromophore which, on the maximum of its MLCT absorption band in butyronitrile (424 nm), has a molar absorption coefficient of *ca.* 2200 M^{-1} cm^{-1}.

Upon excitation of the porphyrin, the steady state luminescence of the zinc porphyrin moiety is quenched in the rotaxanes by 93%, 82% and 55% for **[PZnCuCuPZn]²⁺**, **[PZnCuAgPZn]²⁺** and **[PZnCu-PZn]⁺** respectively. Further

Table 2 Emission properties of the reference compounds and [3]-rotaxanes[a]

	298 K			77 K		
	λ_{max}/nm	τ/ns	Φ_{em}	λ_{max}/nm	τ/μs	E^b/eV
PZn	586, 693	1.85	0.01	583, 643	0.0025	2.13
				726[c]	53 000[c]	1.71
PAu⁺	—	—	—	695[d]	20; 150[d]	1.78
Cu⁺[e]	730	175	0.0011	685	1.1	1.85
Ag⁺[e]	—	—	—	498	12 000	2.49
[PZnCuCuPZn]²⁺	586, 640	0.18	0.0007[f]	582, 642	[h]	2.13
				724[c]	49 000[c]	1.71
[PZnCu-PZn]⁺	586, 640	0.49(47%)[g]	0.0045[f]	582, 642	[i]	2.13
		1.8(53%)[g]		724[c]	51 000[c]	1.71
[PZnCuAgPZn]	586, 640	0.30(50%)[g]	0.0018[f]	582, 642	[j]	2.13
		1.3(50%)[g]		724[c]	51 000[c]	1.71
[PZn—PAu]⁺	586, 640	1.32	0.0055[f]	582, 641	0.0021	2.13
				724[c]	52[c]	1.71
				692[d]	15; 120[d]	1.79

[a] In butyronitrile, unless otherwise noted. [b] Energy level from the emission maxima at 77 K. [c] ^{3}PZn phosphorescence. [d] ^{3}PAu phosphorescence. [e] In CH_2Cl_2, from ref. 15. [f] Yield of PZn fluorescence calculated on the basis of the photons absorbed by this moiety only. [g] Relative weight of the component with the reported lifetime. [h] 0.460 ns (70%) and 1.8 ns (30%). [i] 0.63 ns (70%) and 2.4 ns (30%). [j] 0.63 ns (45%) and 2.6 ns (55%). For more details see text.

Table 3 Porphyrin triplet state properties in the reference compounds and in the [3]-rotaxanes[a]

		τ/ns	Φ^b
PZn	^{3}PZn	8000	1
PAu$^+$	^{3}PAu	0.370	1
[PZnCuCuPZn]$^{2+}$	^{3}PZn	5800	1.5
[PZnCu-PZn]$^+$	^{3}PZn	6500	1.3
[PZnCuAgPZn]$^{2+}$	^{3}PZn	6300	1.2
[PZn--PAu]$^+$	^{3}PZn	4600	0.85
	^{3}PAu	0.390	1

[a] Ambient temperature in butyronitrile. [b] Relative ^{3}PAu and ^{3}PZn triplet yields calculated on the basis of the photons absorbed by the mojety only. Excitation at 532 nm, see Experimental section for details.

insight on the luminescence quenching process comes from the time resolved experiments. The luminescence decay of the porphyrin, derived from a streak camera image, can be fitted by a single exponential only in the case of **[ZnCuCuPZn]$^{2+}$** (180 ps). The decays of the other rotaxanes can be satisfactorily fitted only by the sum of two exponentials with equivalent preexponential factors: 490 ps (47% of the total count) and 1.8 ns (53%) for **[PZnCu-PZn]$^+$** and 300 ps (50%) and 1.3 ns (50%) for **[PZnCuAgPZn]**. The luminescence properties at ambient temperature are collected in Table 2. Any attempt to detect the weak luminescence of the copper(I) units in the rotaxanes, both in steady-state and in time resolved regimes, was unsuccessful due to the stronger emission, albeit quenched, of the zinc porphyrin unit in the spectral region of interest.

PZn singlet and triplet states are the species which dominate the transient absorption spectra and again there is no possibility of detecting the fate of the directly formed, or of the sensitized, MLCT excited state localized on the copper complex (at the excitation wavelength, 532 nm, ε of **Cu$^+$** is 1500 M^{-1} cm^{-1}, so only 10% of the light, at most, goes on the Cu(I) complex). No species other than ^{1}PZn or ^{3}PZn are detected by this technique. On a microsecond scale, the yield and decay lifetime of the triplet PZn excited state can be measured and they are reported in Table 3. It is clear that the formation of triplet porphyrin is increased in the copper containing [3]-rotaxanes with respect to the model **PZn**.

The quenching of the zinc porphyrin fluorescence takes place also at 77 K in the rotaxanes; time resolved experiments show that the luminescence of the moiety in all the rotaxanes can be fitted by two exponentials (Table 2). In the glass the ^{3}PZn phosphorescence is also detected, which displays spectra and lifetimes essentially identical to the model. The excitation spectra read on the phosporescence at 725 nm of the ^{3}PZn unit in the rotaxanes, shows the contribution around 450 nm from the MLCT band of the Cu(I) complex, as can be seen in Fig. 5.

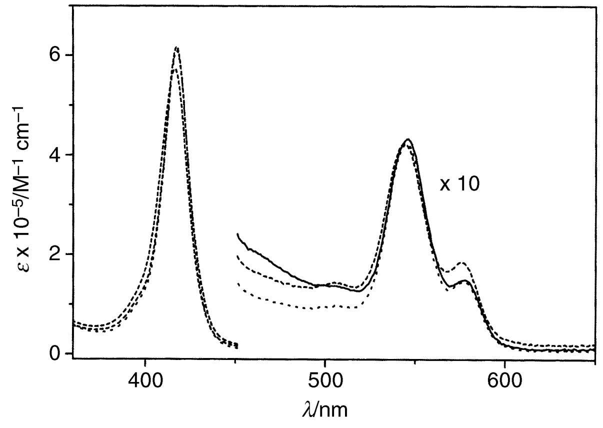

Fig. 4 Absorption spectra of the [3]-rotaxanes in butyronitrile, 298 K: **[PZnCuCuPZn]$^{2+}$** (——), **[PZnCuAgPZn]$^{2+}$** (···), **[PZnCu-PZn]$^+$** (– – –).

The interpretation of the data above can be attempted by considering the occurrence of photoinduced energy transfer (Forster[18a] or Dexter type[18b]) or electron transfer processes. The thermodynamically allowed processes will be briefly discussed and to this aim a schematic energy level diagram of the excited states (see Table 2) and of the charge separated states involved (see electrochemistry section) is reported in Fig. 6(a). The singlet excited state localized on zinc porphyrin has an energy content of 2.13 eV; therefore energy transfer to the copper complex moiety, *ca.* 1.85 eV, is energetically allowed. Spin selection rules allow this energy transfer , in fact as mentioned above, mixing of singlet and triplet states is likely to occur in the lowest excited state of **Cu$^+$**. On the contrary, the energy transfer from zinc porphyrin to the silver complex moiety which has its lowest excited state at 2.49 eV, cannot occur. The excited copper-complex unit could also be a candidate to transfer energy to the triplet localized on the zinc

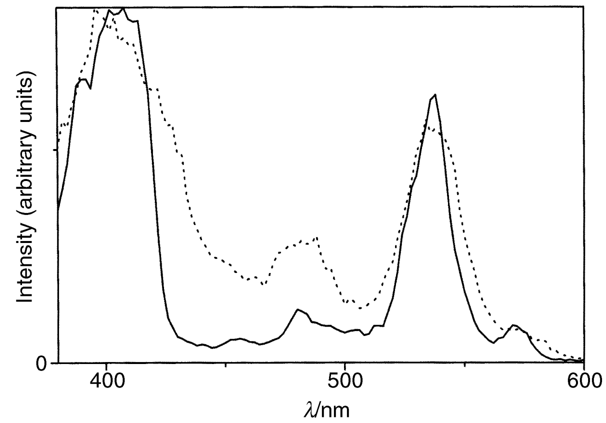

Fig. 5 Excitation spectra detected at λ_{em} = 725 nm in butyronitrile glass at 77 K: **[PZnCuCuPZn]$^{2+}$** (– – –), **PZn** (——).

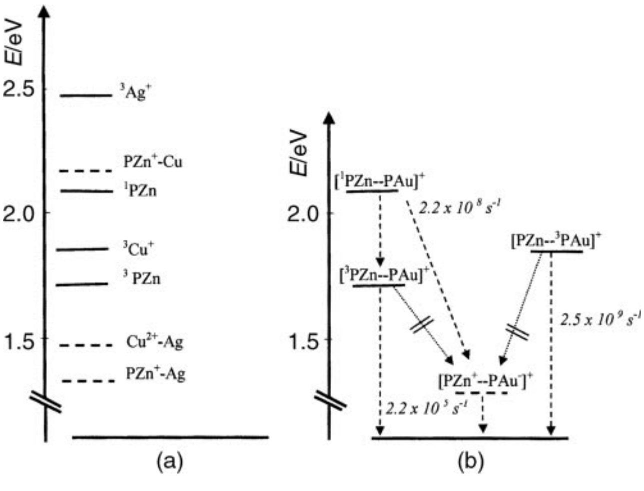

Fig. 6 Schematic energy level diagrams of: (a) the bis(zinc porphyrin) derivatives; (b) **[PZn--PAu]$^+$**.

porphyrin moiety (1.71 eV). As far as electron transfer is concerned, by inspection of Fig. 6(a), it is evident that electron transfer from the excited PZn unit to the copper complex moiety is endoergonic, the corresponding charge separated state being at an energy of *ca.* 2.2 eV. On the contrary, electron transfer would be feasible from the excited singlet of zinc porphyrin to the silver complex moiety, $\Delta G \cong -0.85$ eV, since the corresponding charge separated state is calculated to lie at *ca.* 1.3 eV. Based on energetic considerations, an electron transfer step from the Cu-complex excited state (1.85 eV) to the silver complex center (the corresponding charge separated state is approximately at a level of 1.5 eV), would be allowed ($\Delta G \cong -0.35$ eV). However we will disregard this case since the excitation at 532 nm predominantly excites the porphyrin unit.

In the **[PZnCuCuPZn]**$^{2+}$ system where, upon PZn excitation, the only allowed process is energy transfer to the MLCT excited state localized on the Cu-complex, a quenching rate constant[19] of 5×10^9 s^{-1} can be derived at ambient temperature. In the less rigid **[PZnCu-PZn]**$^+$ system we detected at ambient temperature two lifetimes for the zinc porphyrin decay, 1.8 ns and 490 ps with the same contribution. The former lifetime is coincident with that of the model, therefore we assign it to the unquenched PZn moiety distant from the copper complexed phenanthrolines. As for the 490 ps lifetime we assign it to the quenching of the PZn unit by energy transfer to the nearby Cu(I) moiety. This quenching rate, $k = 1.5 \times 10^9$ s^{-1}, is lower than that found for the fully complexed **[PZnCuCuPZn]**$^{2+}$, and this is probably due to the different molecular rigidity. Actually in the previous case, the second copper center leads to a rigid conformation of the [3]-rotaxane inducing, perhaps, an extended electronic coupling all over the structure.

In **[PZnCuAgPZn]**$^{2+}$, as discussed above and evidenced in the energy level diagram of Fig. 6(a), ^{1}PZn could, in addition to the energy transfer previously considered, transfer an electron to the silver containing unit. This would produce the charge separated state with the electron localized on the Ag complex and a hole on the zinc porphyrin. We determined for this system at ambient temperature, two decay lifetimes, 300 ps and 1.3 ns with equivalent preexponential factors. This suggests that the two extreme porphyrins are quenched in different ways depending on their distance from the copper complex. The rigidity and geometry of this system is similar to that of **[PZnCuCuPZn]**$^{2+}$, since the steric and electronic properties of the silver(I) ion are very similar to those of copper(I), however, given the larger radius of Ag(I) ion, some distortion has to be expected. On this basis the shorter lifetime, 300 ps, could be ascribable to the energy quenching of the ^{1}PZn moiety by the proximal Cu$^+$ complex, being of the same order of magnitude as the 180 ps and 490 ps values determined for the same process for **[PZnCuCuPZn]**$^{2+}$ and **[PZnCu-PZn]**$^+$. The longer lifetime, 1.3 ns could be explained either by a very inefficient ($k = 2.2 \times 10^8$ s^{-1}) electron transfer from the ^{1}PZn center to the nearby Ag(I) unit or by energy transfer from a porphyrin to the distant copper complex, made possible in this case by the better electronic coupling of the partners brought about by the occupation of the "empty" space by the silver ion. The latter hypothesis is in agreement with the absence of detection of charge separated states in transient absorption experiments. The energy transfer steps discussed above are very likely occurring by an electron exchange mechanism,[18b] as the effect of the interposed Ag(I) complex on the quenching of the distant porphyrin seems to suggest.

The ^{3}PZn yield in the above rotaxanes *increases* with respect to the model; we identify an energy transfer step from the ^{3}MLCT of the Cu$^+$ complex (either directly formed or sensitized) as responsible for the observed increase. A more detailed analysis of the meaning of these yields is not possible, because of the large intrinsic error associated with this type of determination. The lifetime of the triplet of the zinc porphyrin unit is only slightly shortened in the rotaxanes with respect to the model, Table 3, and this indicates that ^{3}PZn is not active toward intramolecular processes.

Quenching of the zinc porphyrin luminescence also occurs at 77 K, supporting the energy transfer nature of the process. Actually, electron transfer is, in general, less favored in the glass because of the destabilization of the charge separated state, due to the decreased solvation by the rigid solvent.[20] Double exponential decays are found for **[PZnCu-PZn]**$^+$ and **[PZnCuAgPZn]**$^{2+}$ which have lifetimes of 630 ps and *ca.* 2.5 ns (see footnotes to Table 2). The latter lifetime, coincident with the one of the model **PZn** at this temperature, indicates that the quenching of the distant PZn unit by the copper complex is no longer efficient in the glass. At odds with the 298 K data, a double exponential decay is found also for **[PZnCuCuPZn]**$^{2+}$, with lifetimes of 460 ps (70%) and 1.8 ns (30%). We do not have an explanation for the dual nature of the decay, but this apparent inconsistency with our interpretation based on the room temperature data, could be the consequence of association phenomena. These have been noticed in nitrile solutions also at room temperature and could become important in the low temperature medium even at the spectroscopic concentrations used.[10] The sensitization of the zinc porphyrin triplet by the copper complex unit is efficient also at 77 K; in fact the excitation spectrum of PZn phosphorescence in the rotaxanes is consistent with the contribution of the copper complex MLCT excited states, as can be seen in Fig. 5.

Zinc-gold-porphyrin stoppered rotaxane. Electron transfer. The absorption spectrum of **[PZn--PAu]**$^+$ is reported in Fig. 7, superimposed with the sum of the two component porphyrins. The phenanthrolines absorb in the UV region and are not included in the figure. Regarding the Soret band region, the two well separated peaks in the model compounds merge into a single band in the rotaxane. Because of the absence of coordinating metals a more floppy structural frame is expected for **[PZn--PAu]**$^+$ with respect to the rotaxanes examined above; in some cases the two porphyrins could be very close with a consequent increase of the interactions, as testified by the absorption spectrum.

The removal of the metal ions, which we have shown to be responsible for the deactivation of the ^{1}PZn by energy transfer, and the substitution of the second PZn with the easily reducible PAu, could in principle promote the conditions for a genuine electron transfer between the two extreme porphyrins. The charge separated state corresponding to the oxidized zinc porphyrin unit and to the reduced gold porphyrin **[PZn**$^+$**--PAu**$^-$**]**$^+$ is located at *ca.* 1.25 eV, as derived from the electro-

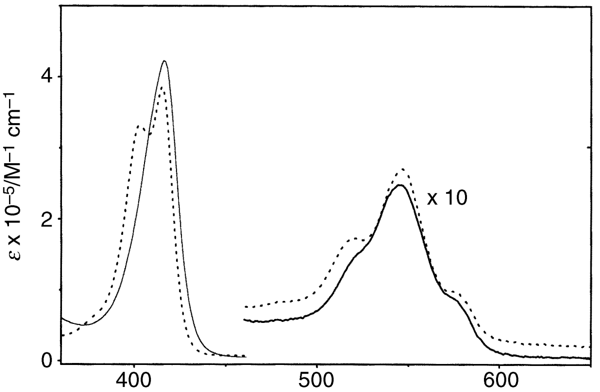

Fig. 7 Absorption spectra in butyronitrile, 298 K: **[PZn--PAu]**$^+$ (——), sum of the absorption spectra of **PZn** and **PAu**$^+$ (- - -).

chemical data (Table 1). A schematic energy level diagram of the states of this system is reported in Fig. 6(b).

The steady state luminescence quenching of the intensity of the model porphyrin in **[PZn--PAu]$^+$** is 45%, while the quenching of the lifetime (which is strictly mono-exponential) is only 28%, from 1.85 ns of the model to 1.32 ns, see Table 2. This is an indication of the existence of, at least, two conformers in this [3]-rotaxane; one of these might exhibit a bent conformation where the two porphyrins are close, resulting in an immediate ("static") quenching which can only be detected by steady-state methods. The other limit could correspond to an extended conformation, where the two partners are kept apart and the electron transfer occurs slowly, through the linking chain. The latter is the conformation where we can detect the quenching by time resolved methods. The efficiency of electron transfer for this conformation is rather low, 28%, this in fact occurs with a rate of 2.2×10^8 s^{-1} compared to a rate of 5×10^8 s^{-1} for the intrinsic deactivation of the donor. With such a low yield we do not expect to be able to detect the charge separated state **[PZn$^+$--PAu$^-$]$^+$** which, in addition, is characterized by spectral features rather similar to the excited states of the two porphyrins.[5b] Accordingly, the time resolved transient absorbance spectra with 35 picosecond resolution show the bands of ^{1}PZn($\lambda_{max} = 460$ nm) and ^{3}PAu($\lambda_{max} = 625$ nm) decaying respectively with lifetimes of 1.3 and 390 ps. The ^{1}PZn lifetime is in agreement with that detected by luminescence in the same sample and the ^{3}PAu lifetime matches the determination performed on the model, indicating that this state is not actively participating in any process.

In spite of the uncertainty affecting this determination, the relative porphyrin triplet yield, ^{3}PZn, in **[PZn--PAu]$^+$** indicates a loss of triplet with respect to the model; this is consistent with the parent ^{1}PZn being conveyed in part to a different path which we identify with the electron transfer. The detection of the so formed charge separated state eludes measurement also because of the modest yield of formation. In addition its lifetime could be short and determined by the rapid exchange of conformations rather than by the back electron transfer along the flexible bridge, *i.e.* the back electron transfer could occur in a different conformation (with the terminal porphyrins very close) than the direct electron transfer.

In the glass at low temperature only a small change of the Zn porphyrin lifetime in **[PZn--PAu]$^+$** occurs, compared to the model **PZn**, indicating the very poor contribution of the electron transfer to the decay. The expected destabilization of the charge separated state in the solid glass, caused by the absence of the solvent reorientation upon charge transfer,[20] can account for a drastic reduction in the driving force for this process.

Conclusions

In this study, we have described the different photoinduced, energy and electron transfer processes taking place in [3]-rotaxanes containing various photo- and electro-active metal complex components. For the system **[PZnCuCuPZn]$^+$**, in which the stoppers are zinc(II) porphyrins and the macrocycles are fastened to the thread through coordination to Cu(I), only energy transfer from the PZn excited state to the central metal complex fragments can take place. The data obtained for **[PZnCu-PZn]$^+$**, in which one macrocycle is free, show that the Cu(I) complex fragment quenches only the excited state of the proximal Zn(II) porphyrin stopper. When the excitation is localized on the distal zinc porphyrin, this decays unquenched, the interposed dumbbell portion being sufficient to prevent interaction with the Cu(I) complex acceptor. In [3]-rotaxane **[PZnCuAgPZn]$^{2+}$**, the quenching of the PZn fragment distal to the Cu(I) center is partly reestablished, suggesting that the Ag(I) bis-phen moiety is mediating the necessary electronic coupling between the partners. In the [3]-rotaxane system **[PZn--PAu]$^+$**, the macrocycles are only mechanically bound to the dumbbell, and the stoppers can act as an electron donor/acceptor pair. Quenching of the zinc porphyrin luminescence, assigned to electron transfer, was 45% by intensity determination and 28% by lifetime measurements. This led us to assume the existence of two different conformers in this rotaxane. The detected lifetime quenching was assigned to an extended conformation, where the electron transfer occurs slowly, through the linking "necklace".

Experimental

Synthesis

The preparation of **PZn** and the [3]-rotaxanes of this study was conducted as described in ref. 10. **PAu$^+$** was prepared as its $BF_4{}^-$ salt from the corresponding free-base porphyrin,[10] using the method of ref. 21, and purified on alumina (activity III), eluting with CH_2Cl_2/0.25–0.5% MeOH. Yield: 62%. ^{1}H NMR (200 MHz, CD_2Cl_2, ppm downfield from $SiMe_4$): δ 10.67 (s, 2H, H_{meso}), 8.00 (t, 2H, H_p), 7.89 (d, 4H, H_o), 4.11 (t, 8H, $J = 7.9$ Hz, CH_{2a}), 2.61 (s, 12H, CH_3), 2.25 (quint., 12H, CH_{2b}), 1.79 (quint., 12H, CH_{2c}), 1.54 (s, 36H, ^{t}Bu), 1.50 (m, 16H, $CH_{2(d+e)}$), 0.94 (t, 12H, $J = 7.2$ Hz, CH_{3f}). UV-Vis (CH_2Cl_2; λ_{max}/nm; ε/L mol^{-1} cm^{-1}) : 402 (315 000), 518 (15 000), 551 (12 500).

Electrochemistry

Butyronitrile[22] was treated with concentrated HCl, then dried with K_2CO_3, distilled over CaH_2 under argon, and stored under argon. Dichloromethane (Carlo Erba, analytical grade, stabilised with 0.2% EtOH) was used as received. Tetra-*n*-butylammonium tetrafluoroborate (TBAB) was recrystallized twice in a mixture of H_2O/MeOH and dried for 48 h at 60 °C under vacuum.

Cyclic voltammetry measurements were performed on an EG&G Princeton Applied Research Potentiostat/Galvanostat model 273A equipped with an Ifelec IF 3802 recorder. A saturated calomel electrode (SCE) separated from the test solution by an auxiliary compartment filled with the electrolyte, or a silver wire (Ag/Ag^+) served as the reference electrode. A hanging mercury electrode (HME, Metrohm EA 290), and a platinum disk elecrode were used as working electrodes. All of the experiments were carried out under an argon atmosphere in a Metrohm universal recipient, in a three-electrode configuration.

Spectroscopic and photophysical measurements

The solvent used was butyronitrile (Fluka). Absorption spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer. Uncorrected emission spectra were detected by a Spex Fluorolog II spectrofluorimeter, equipped with a Hamamatsu R-928 photomultiplier tube. The same spectrofluorimeter equipped with a phosphorimeter accessory (1934D Spex) was used to register phosphorescence spectra of porphyrin triplets. Experiments at 77 K were conducted on samples contained in quartz capillary tubes immersed in a home made quartz dewar, filled with liquid nitrogen. The fluorescence quantum yield of **ZnP** was determined by the method of Demas and Crosby[23] using [Ru(bpy)$_3$]Cl$_2$ in aerated water as standard ($\Phi = 2.8 \times 10^{-2}$).[24]

A system based on a Nd : YAG laser (20 ns pulse) and a detection system consisting of an Hamamatsu R936 photomultiplier were used to detect emission lifetimes in the range from micro- to milli-seconds. The light emitted was collected at right angles with respect to the excitation (1–2 mJ at 532 nm), selected by a series of filters, then directly fed into the photomultiplier. An Hamamatsu C1587 streak camera coupled to a PY-62 Nd : YAG laser by Continuum ($\lambda_{exc} = 532$

nm, 0.2–0.5 mJ, 35 ps pulse) was used to detect fluorescence lifetimes from 20 ps to 2.5 ns. Time and spectral profiles were derived from the streak image, resulting from the average of several hundred shots. The time profiles were analyzed by standard iterative methods according to a single or a double exponential fitting. Further experimental details on this apparatus are reported elsewhere.[25]

Nanosecond flash photolysis studies were made with a Nd : YAG laser (532 nm, 1–2 mJ per pulse). Samples were deaerated by bubbling argon in home modified quartz cuvettes. Details of the experimental set-up were reported previously.[26] Transient absorption spectra in the picosecond time domain were measured by a pump and probe system. The second harmonic (532 nm) of a Nd : YAG laser (Continuum PY62-10) with a 35 ps pulse was used to excite the samples with energy ranging from 2 to 5 mJ. 50 mJ of the fundamental wavelength of the same laser (1064 nm) were used to produce a white continuum from a D_2O–D_3PO_4 solution, which was used as probe. Further details on this experimental set-up and the treatment of data are reported elsewhere.[13]

Yields of formation of the porphyrin triplets (Φ_t) in the rotaxanes were determined by comparing the transient absorbances at 620–650 nm, the wavelength region away from the ground state absorption, with the corresponding values of the model compounds **PZn** and **PAu$^+$**, making corrections for the fraction of light absorbed at 532 nm by the moiety of interest in the sample. The depletion of the ground state was limited to *ca.* 10–20%. It was assumed that the molar absorption coefficients of triplets are unaffected in passing from models to the arrays. The molar absorption coefficient for **PAu$^+$**, **PZn** and **Cu$^+$** units at 532 nm are 7200 M^{-1} cm^{-1}, 10 750 M^{-1} cm^{-1} and 1500 M^{-1} cm^{-1} respectively. The spectroscopic energies of the electronic levels of the various compounds were derived from the maxima of the luminescence bands at 77 K. Experimental uncertainties are estimated to be 8% for lifetime determination, 15% for quantum yields, 20% for molar absorption coefficients and 2 nm for emission and absorption peaks. The working temperature was 298 K, unless otherwise stated.

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