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Energy transfer pathways in pyridylporphyrin metal adducts and side-to-face arrays

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Contents

Abstract

Side-to-facearrays in which a free-base porphyrin is connected by axial coordination of its *meso*-pyridyl groups to one or more ruthenium porphyrin units exhibit interesting photophysical properties. The photophysics is characterized by efficient energy transfer, at the triplet level, from the peripheral ruthenium units to the central free-base. When the central unit is zinc-metalated the triplet energy transfer is reversible, leading to an excited-state equilibrium. In the arrays, the singlet state of the central unit is always quenched relative to the isolated free-base (or zinc) porphyrin, as a consequence of the heavy-atom effect of ruthenium. This general behavior is confirmed by the behavior of a number of adducts between pyridylporphyrins and simple Werner-type ruthenium complexes. Some insight into the mechanisms of the heavy-atom quenching is obtained from the time-resolved spectroscopy of these systems: besides enhanced intersystem crossing within the porphyrin chromophore, singlet–triplet energy transfer to the ruthenium center(s) acts as an additional efficient channel for deactivation of the pyridylporphyrin chromophore. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pyridylporphyrins; Porphyrin arrays; Energy transfer; Heavy-atom effect; Supramolecular photochemistry

1. Introduction

In the rapidly developing field of supramolecular chemistry [1], porphyrins and metallo-porphyrins occupy a relevant place, being frequently used as building blocks for the construction of artificial systems with special built-in properties or functions. Among these, light-induced functions [2], and in particular those inspired by natural photosynthesis, have attracted a great deal of attention. Photoinduced charge separation in the reaction center [3] is mimicked by several types of covalently-linked donor-acceptor systems, including porphyrin-based ‘triads’ and more complex architectures [4]. For the light-harvesting function carried out by a large number of chlorophyll molecules in the ‘antenna’ units [5], several synthetic models have been developed,

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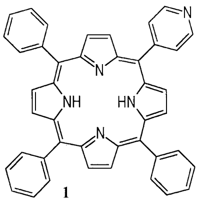
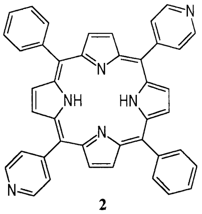
including multi-porphyrin arrays [6]. In most of such porphyrin-based molecular devices, the molecular components are connected by covalent linkages, usually through the *meso* positions of the porphyrin ring. For multi-porphyrin systems, this results in a 'side-to-side' arrangement.

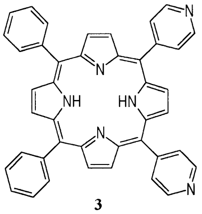
Pyridylporphyrins (PyPs) can be considered as particularly attractive building blocks for the construction of photoactive supramolecular systems. A typical series, carrying a variable number of 4′-pyridyl (*n*) and of phenyl (4-*n*) groups in the *meso* positions of the porphyrin ring, is shown in **1**–**5**. All these molecules are very similar in their useful spectroscopic, redox, and photophysical properties to standard porphyrins (e.g. tetraphenylporphyrin, TPP). In addition, however, the presence of *meso*-pyridyl groups provides a further dimension in synthetic flexibility, as these groups can be coordinated to metal-containing fragments of various coordination number and geometry. Adducts obtained by peripheral coordination of pyridylporphyrins to singly unsaturated metal centers have shown new, interesting photophysical properties [7–9]. On the other hand, when poly-unsaturated metal fragments are used to bridge two (or more) pyridylporphyrin units, supramolecular species of considerable structural and photophysical interest, ranging from discrete supermolecules (molecular squares, 3 × 3 arrays) [10] to solid state arrays (tapes, surfaces) [10e,11] are obtained. Furthermore, if axially-coordinated metal porphyrins are used as adduct-forming fragments, interesting 'side-to-face' porphyrin arrays can be generated [12–16]. This remarkable structural variety can be further enriched if a parallel series of molecules with 3′-pyridyl (instead of 4′-pyridyl) substituents in the *meso* positions is used as the central pyridylporphyrin in the construction of adducts and arrays [12b,12i,17].



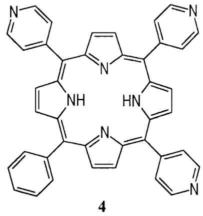
1
MPyP



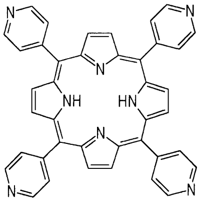
2
t-DPyP



3
c-DPyP



4
TrPyP



5
TPyP

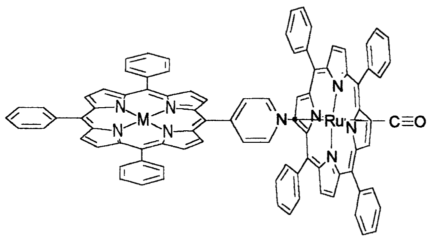
In this review article, we want to summarize the prominent aspects of the photophysical behavior of adducts [9] and arrays [12b] formed between pyridylporphyrins and various ruthenium-containing fragments. For synthetic strategies, structural characterization, and experimental details, the reader is referred to the original papers.

2. Triplet energy transfer in side-to-face porphyrin arrays

In one of our laboratories, a series of stable and inert side-to-face arrays has been produced by axial coordination of a pyridylporphyrin ('side' unit) to one or more peripheral ruthenium porphyrins carrying CO as the sixth ligand ('face' units). A wide variety of arrays arises because of the possibility to vary the number of peripheral units, the state of metalation of the pyridylporphyrin, and the binding geometry [12]. Dimeric and pentameric 'perpendicular' arrays are represented schematically in Fig. 1, along with a dimeric 'canted' structure. The shorthand notation indicates the state of metalation of the side unit (Fb for free-base, Zn for zinc-porphyrin), the positional isomer of the pyridyl group ((4) for 4-pyridyl, (3) for 3′-pyridyl), and the number of peripheral ruthenium porphyrin units. The canted pentameric species **Zn(3)Ru$_4$** is illustrated by the crystal structure (Fig. 2), showing a 'flying saucer' shape with peripheral ruthenium porphyrin units alternately above and below the plane of the central pyridylporphyrin [12c,12d]. The photophysics of all these arrays has been studied [12b] in toluene [18]. In this section, the results will be briefly summarized and discussed.

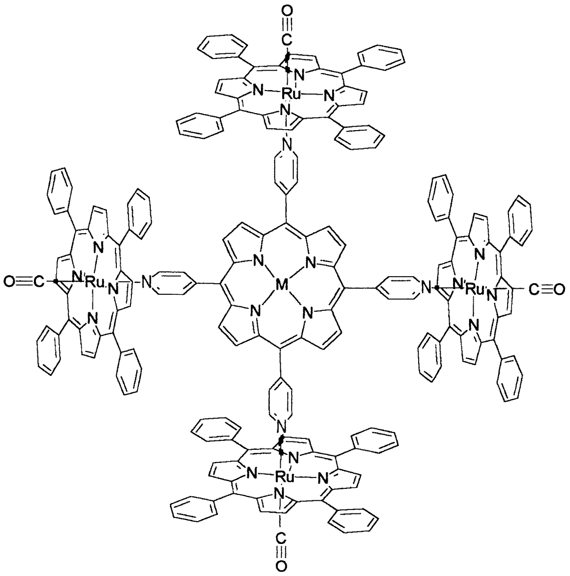
2.1. Perpendicular free-base arrays

The **Fb(4)Ru** and **Fb(4)Ru$_4$** arrays contain two types of molecular components, ruthenium porphyrin units and a free-base porphyrin. Suitable models for these two types of molecular components are Ru(TPP)(CO)py (thereafter indicated as **Ru**) and 4′MPyP (thereafter indicated as **Fb**). The photophysical behavior of **Ru** and **Fb**, is summarized in Fig. 3. Both models have lowest excited states of porphyrin π–π* character. The differences in behavior (in particular, the complete quenching of S_1 by ultrafast intersystem crossing in **Ru**) can be easily explained in terms of the spin–orbit coupling provided by the heavy metal center. The absorption spectra of the arrays are always a nice superposition of those of the molecular components (Fig. 4). Thus, a general energy level diagram for these arrays (Fig. 5) can be easily obtained using the spectroscopic and electro-



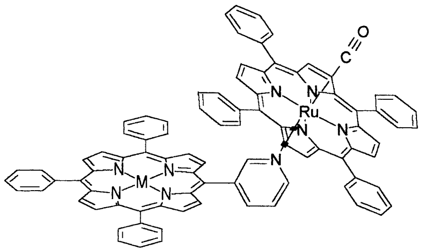
M = $2H^+$, Fb(4)Ru

M = Zn , Zn(4)Ru



M = $2H^+$, Fb(4)Ru_4

M = Zn , Zn(4)Ru_4



M = $2H^+$, Fb(3)Ru

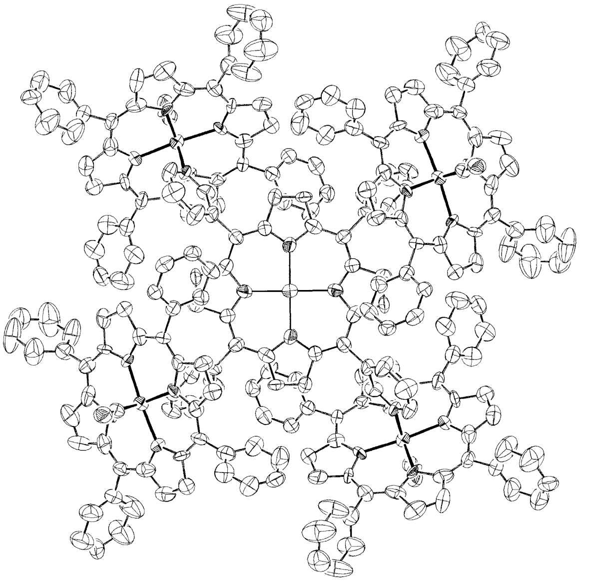
M = Zn , Zn(3)Ru

Fig. 1. Schematic structures of dimeric and pentameric arrays.

chemical data of the model molecules. Predominant excitation of the ruthenium porphyrin units (ca. 80% for **Fb(4)Ru** and ca. 95% for **Fb(4)Ru_4**) can be achieved using 530-nm light (Fig. 4). Various intercomponent processes are thermodynamically allowed following excitation of the Ru-based molecular component (Fig. 5): *singlet energy transfer* (Fb–^{1}*Ru → ^{1}*Fb–Ru), *electron transfer* (Fb–^{1}*Ru → Fb^-–Ru^+),· and · *triplet energy transfer* (Fb–^{3}*Ru → ^{3}*Fb–Ru). Relevant experimental observations, obtained following ruthenium porphyrin excitation are: no Fb fluorescence, complete quenching of the Ru phosphorescence, prompt 100% formation of Fb triplet in nanosecond laser flash photolysis. These results clearly demonstrate that: (i) singlet energy transfer and electron transfer do not occur (presumably because of the exceedingly fast intersystem crossing in the Ru-based unit); (ii) Ru-to-Fb triplet–triplet energy transfer is fast ($k > 10^8$ s^{-1}) and efficient ($\eta \approx 1$) in the arrays. The photophysical behavior is summarized in Fig. 5, with the quantitative figures referring to the **Fb(4)Ru_4** case (those for **Fb(4)Ru** are only slightly different).

2.2. Perpendicular zinc-porphirin arrays

A similar experimental study has been carried out on **Zn(4)Ru** and **Zn(4)Ru_4**. For the zinc porphyrin units, an appropriate model is the tetraphenyl species ZnTPP



Zn(3)Ru$_4$

Fig. 2. Crystal stucture of the canted pentameric species **Zn(3)Ru$_4$** (from ref. [12d]).

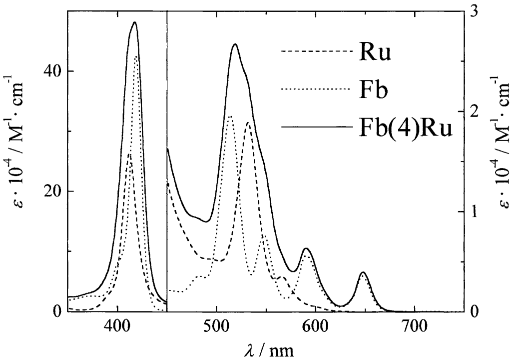


Fig. 4. Absorption spectra of **Fb(4)Ru** and monomeric models in toluene.

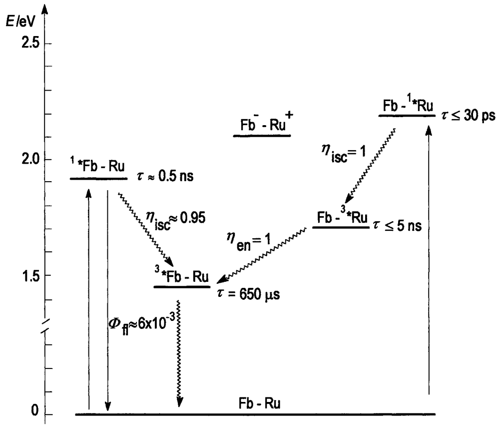


Fig. 5. Energy-level diagram and relevant photophysical parameters for the arrays based on free-base porphyrins.

(**Zn**) [19]. The photophysical behavior of **Zn** is qualitatively similar to that of **Fb**. The main difference between the two models lies in the energies of the S_1 and T_1 states, that are higher by ca. 0.15 eV for **Zn** relative to **Fb**. This difference gives a level diagram for **Zn(4)Ru** and **Zn(4)Ru$_4$** in which the driving force for the intercomponent energy transfer processes is smaller than in the corresponding free-base systems. As a consequence, the photophysical behavior of the Zn-containing systems (Fig. 6) is different: the Ru-to-Zn triplet–triplet energy transfer is now a reversible process, leading to an excited-state equilibrium (as evidenced by the identical lifetimes of the two triplets).

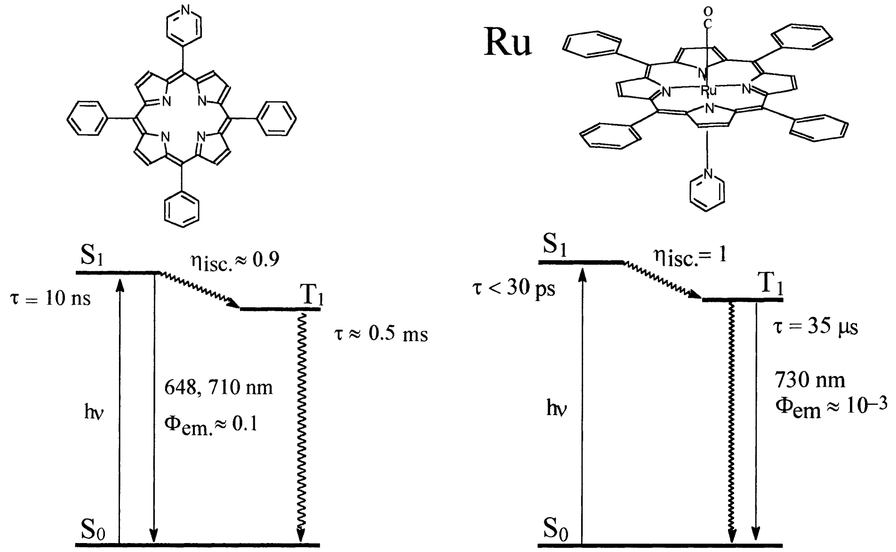


Fig. 3. Energy-level diagrams and summary of photophysical behavior of the monomeric model systems.

2.3. Canted arrays

The change in connecting structural motif (from perpendicular to canted, e.g. from **Fb(4)Ru$_4$** to **Fb(3)Ru$_4$**) does not bring about appreciable differences in photophysical behavior. In all the canted arrays, Ru-to-Fb (or Ru-to-Zn) triplet–triplet energy transfer is 100% efficient and fast ($k > 10^8$ s^{-1}). Within this range, of course, differences in rate constants with respect to the perpendicular case cannot be ruled out.

In conclusion, the photophysical studies reviewed in this section [12b] indicate that all the side-to-face arrays behave as very efficient systems for funneling the light energy absorbed by the peripheral ruthenium porphyrin units, at the triplet level, to the central free-base or zinc porphyrin unit (Fig. 7).

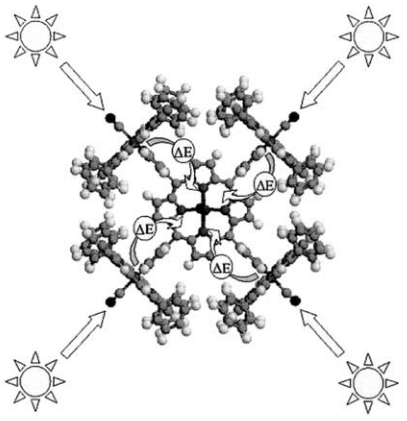


Fig. 7. Pictorial representation of triplet energy transfer in a perpendicular pentameric array.

3. Heavy-atom effects in arrays and metal adducts

In the side-to-face adducts discussed above, the prominent results (triplet energy transfer) are obtained following excitation of the ruthenium porphyrin. Nevertheless, an interesting observation was also made upon [12b] selective excitation of the pyridylporphyrin unit: the singlet excited state of this unit, and the associated fluorescence emission, is always substantially quenched in the array with respect to model pyridylporphyrin (e.g. 3.6 ns in **Fb(4)Ru** and 0.5 ns in **Fb(4)Ru$_4$**, as compared with 9.7 ns for **Fb**) [20]. This result is remarkable, as the classical quenching mechanisms (singlet energy transfer, photoinduced electron transfer) are prohibited on energetic grounds (Figs. 5 and 6). Turning to less obvious mechanisms, a likely explanation of the pyridylporphyrin singlet quenching in the arrays can be identified in the 'heavy-atom effect' of the metal.

The conventional notion of this effect is that heavy-atom substituents introduce spin–orbit coupling into a molecule, thereby relaxing selection rules. In simple molecular systems, the heavy-atom effect quenches the lowest excited singlet state by enhancing $S_1 \rightarrow T_1$ intersystem crossing. The situation is more complex in supramolecular systems of the type we are dealing with. Here, besides intersystem crossing within the pyridylporphyrin chromophore (k_{ISC}), an additional spin-forbidden channel is available for deactivation of the pyridylporphyrin singlet, i.e. singlet–triplet energy transfer to the attached unit (k_{STEn}) (Fig. 8). In principle, both channels are expected to be sensitive to the heavy-atom effect of ruthenium, although their relative importance is difficult to predict: for k_{ISC} the heavy atom is remote, but the process is an intra-component one; for k_{STEn} the heavy metal center is directly involved, but the process is an inter-component one. In principle, the two types of heavy-atom effects could be experimentally discriminated, as they have opposite effects on the population of the polypyridylporphyrin triplet PyP(T_1) (increase in the case of enhanced k_{ISC}, decrease in the case of k_{STEn}). In practice, with the side-to-face arrays discussed above this distinction is impossible, because of the occurrence of efficient intercomponent triplet energy transfer.

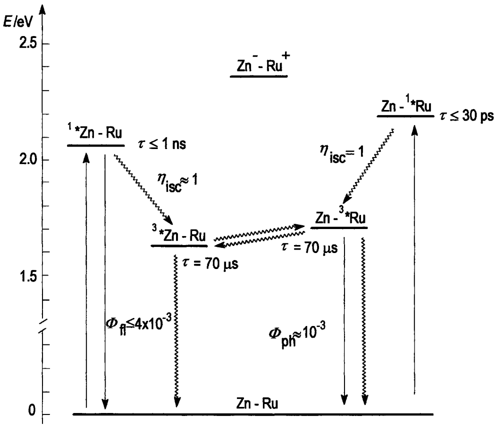


Fig. 6. Energy-level diagram and relevant photophysical parameters for the array based on Zn porphyrins.

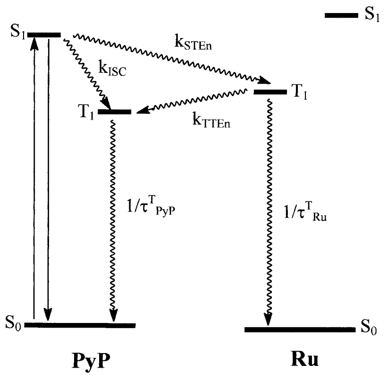


Fig. 8. Available deactivation pathways for the porphyrin singlet in metal adducts.

An attempt to discriminate between the two routes can be made by studying adducts of pyridylporphyrins with simple Ru(II) Werner-type complexes. These units are characterized by very short-lived triplet states [21], that should prevent the occurrence of any intercomponent energy transfer at the triplet level. Adducts **6**–**11**, involving four pyridylporphyrins (**1**, **3**, **4**, **5**) and two octahedral Ru(II) fragments with different ligands and stereochemistry, have been studied [9]. In these adducts, the Ru(II) fragments are non-absorbing in the visible, so that selective excitation of the pyridylporphyrin is easy. Consistently with what observed in the arrays, in all the adducts the emitting singlet excited state is shorter-lived than in the parent pyridylporphyrin molecule. The differences are not very large, but clearly outside the experimental error. The ratios between the lifetimes of parent pyridylporphyrin, τ^0, and adduct, τ, are plotted in Fig. 9 for the various adducts as a function of the number of ruthenium centers attached to each pyridylporphyrin chromophore. The interesting observations are: (i) with the same type of Ru center, there is a nice correlation between the lifetime shortening and the number of metal centers attached to each chromophore; (ii) the magnitude of the effect seems to depend markedly on the nature of the Ru center, being higher for the adducts **10**, **11** than for the series **6**–**9**.

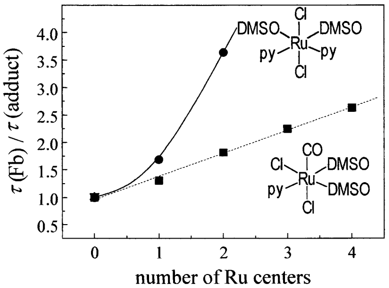
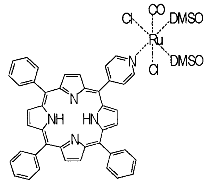
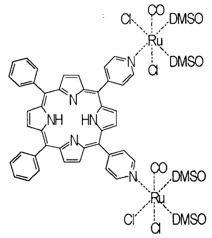


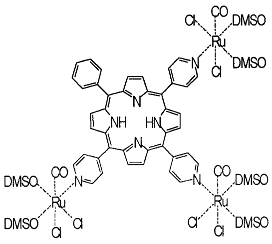
Fig. 9. Singlet quenching as a function of the number of ruthenium centers attached to each pyridylporphyrin (τ, lifetime of the adduct; τ^0, lifetime of the parent pyridylporphyrin).



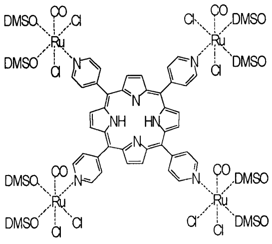
6
$\mathrm{MPyP[RuCl_2(DMSO)_2(CO)]}$



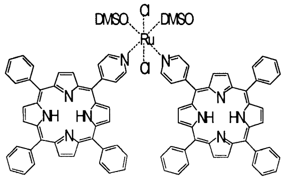
7
c-$\mathrm{DPyP[RuCl_2(DMSO)_2(CO)]_2}$



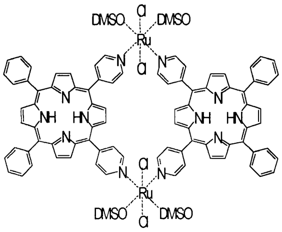
8
$\mathrm{TrPyP[RuCl_2(DMSO)_2(CO)]_3}$



9
$\mathrm{TPyP[RuCl_2(DMSO)_2(CO)]_4}$



10
$\mathrm{(MPyP)_2[RuCl_2(DMSO)_2]}$



11
$\{$*c*-$\mathrm{DPyP[RuCl_2(DMSO)_2]\}_2}$

Transient spectroscopic experiments can be used to discriminate between the two pathways [9]. An acceleration of the ISC process in the PyP–Ru adducts should give a slight increase in the amount of PyP(T_1) formed with respect to the pyridylporphyrin models (where the quantum yield is already ca. 90%) [22]. On the other hand, the yield of formation of PyP(T_1) is expected to be substantially diminished if singlet–triplet energy transfer takes place in the adducts, as the very short lifetime of the Ru(T_1) states [21] precludes any possibility of re-formation of PyP(T_1) by triplet energy transfer. Pyridylporphyrin and adduct transient spectra are compared in Fig. 10 for three relevant cases (adducts **9**–**11**). The results seem to indicate different pathways for adducts with different Ru centers. In particular, for **9** the PyP(T_1) absorption has the same intensity (except for an expected red shift) as for the pyridylporphyrin model **5** TPyP. This supports enhanced intersystem crossing within the porphyrin (k_{ISC} in Fig. 8) upon adduct formation. On the other hand, an evident decrease in triplet formation is observed for **10** and **11**, with the effect paralleling the amount of singlet quenching (Fig. 9). This supports the occurrence, for this type of adducts, of singlet–triplet energy transfer (k_{STEn} in Fig. 8).

In conclusion, both mechanisms seem to be operative in the adducts studied, the choice being dependent on the type of Ru center: enhanced intersystem crossing with centers of the $\mathrm{RuCl_2(DMSO)_2(CO)(4'\text{-}py)}$ type [23], singlet–triplet energy transfer with centers of the $\mathrm{RuCl_2(DMSO)_2(4'\text{-}py)_2}$ type. The most likely explanation for this switch in mechanism lies in the dependence of the energy of the Ru(T_1) state on the coordination environment at the ruthenium center. Although direct spectroscopic information on ligand field triplet energies of this type of Ru(II) complexes is not available, ligand field arguments suggest that the singlet–triplet energy transfer channel may be energetically available only for adducts with centers of the $\mathrm{RuCl_2(DMSO)_2(4'\text{-}py)_2}$ type.

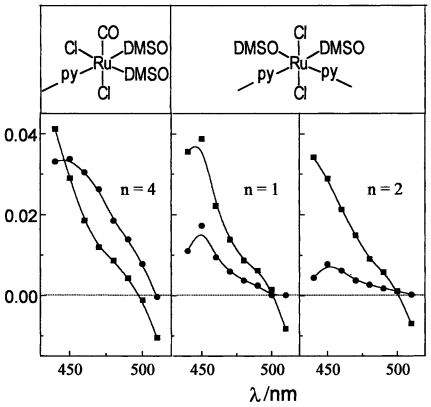


Fig. 10. Quantitative comparison between the triplet absorption spectra of pyridylporphyrins (squares) and adducts (circles): left to right, **5** vs. **9**, **1** vs. **10**, **3** vs. **11**. The type and number of metal fragments in the adduct are also indicated.

In view of these results, it is very likely that the singlet quenching observed in the side-to-face arrays (where this channel is definitely accessible, see Figs. 5 and 6) also proceeds by intercomponent singlet–triplet energy transfer.

4. Conclusions

Coordination of the peripheral groups of pyridylporphyrins to ruthenium metal centers yields a variety of structurally and photophysically interesting systems: adducts with simple Werner-type ruthenium complexes, side-to-face arrays with carbonyl ruthenium porphyrins. In all cases, the ruthenium center quenches by heavy-atom effect the singlet state of the pyridylporphyrin. In addition to conventional enhanced intersystem crossing, however, in these supramolecular systems the heavy-atom effect can proceed by singlet–triplet intercomponent energy transfer. Provided that the intercomponent process is energetically allowed, this mechanism seems to predominate. In the side-to-face arrays, excitation of the ruthenium porphyrin units leads to fast and efficient triplet–triplet energy transfer to the pyridylporphyrin. The process is irreversible when the pyridylporphyrin is a free-base but involves a reversible equilibrium in the case of the Zn-metalated systems.

Acknowledgements

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