

Switching of Electron- to Energy-Transfer by Selective Excitation of Different Chromophores in Arrays Based on Porphyrins and a Polypyridyl Iridium Complex

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Excitation at 350–355 nm of the dyads **PAu–Ir**, **PH₂–Ir** and of the triads **PH₂–Ir–PAu** and **PZn–Ir–PAu** where **Ir**, iridium(III) bis-terpyridine, is covalently linked to gold (III), free-base and zinc(II) tetraarylporphyrins (**PAu**, **PH₂**, **PZn**), produces to a predominant extent the ligand centered triplet excited state of the iridium complex unit, ³Ir. The processes occurring in the arrays upon UV excitation have been characterized by steady state and time-resolved spectroscopic methods. Energy transfer to the porphyrin triplets dominates the deactivation of ³Ir in **PAu–Ir**, **PH₂–Ir**, and **PH₂–Ir–PAu**, with rates of $2.9 \times 10^{10} \text{ s}^{-1}$ (³Ir → ³PAu) and ca. 10^{11} s^{-1} (³Ir → ³PH₂), in contrast to what has been shown to occur upon selective excitation of the PH₂ unit, which yields electron transfer leading to charge separation. The different outcome is discussed on the basis of the overlap of the HOMO and LUMO orbitals involved in the electron-transfer reaction for the Ir acceptor unit and the PH₂ donor unit, with the aid of semiempirical calculations. Remarkably, the PZn based array **PZn–Ir–PAu** displays efficient electron transfer with the formation of a charge separated state with unitary yield, irrespective of the component which is excited. A very high driving force, $\Delta G^\circ = -1.1 \text{ eV}$, could explain the prevalence of the electron-transfer reaction in the latter case.

Introduction

The demand for “smart” molecular arrays, able to perform useful acts upon external stimuli is rapidly increasing. These arrays are the basis for the construction, with a “bottom up” approach, of nanostructures whose application spans from molecular electronics^{1–3} to storage of information and motion,^{4–6} and from sensing^{7,8} to energy conversion.^{9–12}

Among the possible external stimuli which can be used to operate the arrays, light has a prominent position. The development of modern laser technology offers, in fact, a control over time, space, and type (i.e. wavelength) of the stimulus whose precision is hardly reached by any other external system which could be used to trigger the desired function. Under this respect, the possibility of modulating the type of function by simply modifying the light wavelength input is particularly attractive.

The present report addresses the effect of using excitation with UV light in a series of dyads and triads (Figure 1) based on porphyrins and an Ir(III) terpyridine complex. Excitation of these arrays by light in the visible range excites only the porphyrins and the results, summarized below, have recently been reported by our groups.^{13–15}

Selective excitation of the free base porphyrin in acetonitrile solutions of the arrays **PH₂–Ir** and **PH₂–Ir–PAu** results in an electron-transfer process from the excited state of the free base porphyrin to the metal complex with a rate of $3.3 \times 10^{10} \text{ s}^{-1}$, leading to a charge separated state (CS) characterized by a formally reduced metal complex, where the extra electron is

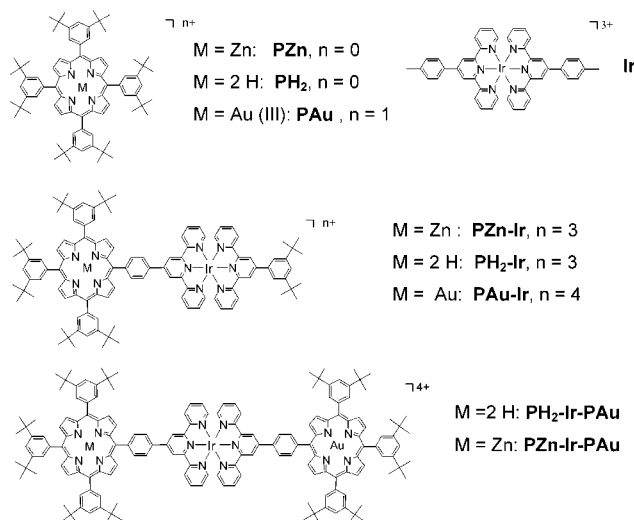


Figure 1. Arrays and related models.

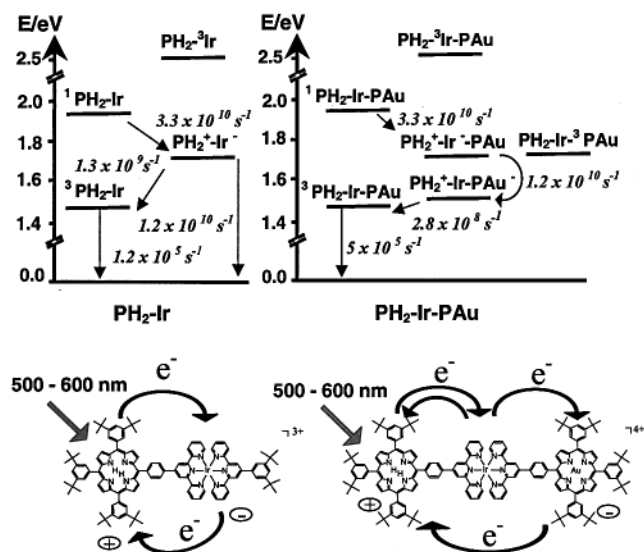
localized on the ligand, and an oxidized free-base porphyrin with a nearly unity yield. In the dyad, the recombination of the CS occurs with a rate of $1.3 \times 10^{10} \text{ s}^{-1}$ (10% to the triplet and 90% to the ground state), whereas in the triad a further electron-transfer step to the gold porphyrin moiety, characterized by a rate of $1.2 \times 10^{10} \text{ s}^{-1}$, can compete with the back electron transfer and gives origin to the fully charge separated state, **PH₂⁺–Ir–PAu[–]**, with a yield of approximately 0.5. This CS recombines to the triplet excited state with a lifetime of 3.5 ns (Scheme 1). As regards to the zinc metalated homologues, excitation of the zinc porphyrin unit in the triad **PZn–Ir–PAu** in toluene, two consecutive electron-transfer steps with rates $> 5 \times 10^{10} \text{ s}^{-1}$ occur and lead to the CS state **PZn⁺–Ir–PAu[–]**

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SCHEME 1: Processes Occurring in the Arrays upon Selective Excitation of the Free-Base Unit and Schematic Energy Diagrams of $\text{PH}_2\text{-Ir}$, PAu-Ir , and $\text{PH}_2\text{-Ir-PAu}$ in Acetonitrile



with a unity yield and a lifetime of 450 ns. For solubility reasons, the corresponding dyads PZn-Ir and PAu-Ir , could not be studied in the same solvent.

Excitation in the visible of the arrays can also lead to the excitation of the gold porphyrin units which very rapidly (less than 20 ps) yields the triplet excited state of the unit. This is not effective during its short lifetime (1.5 ns in acetonitrile, 2.5 ns in toluene) and no energy or electron transfer to the other components is detected.^{16,17}

UV light excitation of the arrays around the 350–355 nm wavelength, produces to a predominant extent the excited state of the metal complex identified as a ligand centered state.¹⁸ In the present report, we show that excitation of this unit gives origin to an energy transfer process in the arrays PAu-Ir , $\text{PH}_2\text{-Ir}$, and $\text{PH}_2\text{-Ir-PAu}$, in contrast with the electron-transfer process observed for excitation of the porphyrin free-base photosensitizer. Switching of the type of process from electron-to energy-transfer by changing the excitation wavelength, does not occur in PZn-Ir-PAu , which exhibits electron-transfer irrespective of the unit which has been photoexcited. The results can be interpreted in a unified view and are discussed within the frame of current theories on energy and electron transfer.

Experimental Section

The synthesis of the arrays has been reported elsewhere.¹⁵ The solvents used are Spectroscopic Grade (C. Erba). Absorption spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer and uncorrected emission spectra were detected by a Spex Fluorolog II spectrofluorimeter. The 77 K phosphorescence spectra of porphyrin triplets were detected by the same spectrofluorimeter equipped with a phosphorimeter accessory (1934D Spex). The acquisition parameters of the phosphorimeter were set to: (i) gate open for 70 ms with 1 ms delay with respect to excitation, for the ^3PZn phosphorescence spectrum and: (ii) gate open for 200 μs with a delay of 20 μs with respect to the excitation, to detect ^3PAu phosphorescence spectrum. Time-resolved luminescence apparatus was based on a Nd:YAG laser (Continuum PY62/10 with a 35 ps pulse duration, 355 nm, 1 mJ) and a Streak Camera.¹⁹ Lifetimes longer than 2 ns were detected with a Time Correlated Single Photon Counting apparatus with 1 ns resolution.

Transient absorbance in the picosecond range made use of a pump and probe system based on a Nd:YAG laser (35 ps pulse, 355 nm, 3–4 mJ) and an OMA detector. Further details can be found elsewhere.²⁰

Yields and lifetime of the absorbing species in the 10 ns–1000 μs range were determined by a laser flash photolysis apparatus with a Nd:YAG laser (JK Lasers, with 18 ns pulse, 355 or 532 nm, 2–4 mJ). Relative yields of triplets localized on the units in the arrays, were determined against the model porphyrin in the same solvent as a standard, by comparing absorbances of the triplets at wavelength longer than ground state absorbance. In such determination, only the photons absorbed by the unit of interest were considered. Relative yields were converted to absolute yields on the basis of the absolute yield value of 0.6, 0.7, and 1 for $^3\text{PH}_2$, ^3PZn , and ^3PAu , respectively.²¹ The yield of the state $\text{PZn}^+\text{-Ir-PAu}^-$ upon excitation at 355 nm was determined against the yield of the same state formed upon excitation at 532 nm ($\phi = 1^{15}$), after correcting for the different absorbance of the sample and the different number of photons delivered by the laser at the two wavelengths. Air-free solutions were bubbled with argon for 5 min and stored in vacuum tight homemade cells. For luminescence experiments at 77 K, quartz capillary tubes were immersed in liquid nitrogen contained in a homemade quartz dewar.

Experimental uncertainties are estimated to be within 8% for lifetime determination, 15% for quantum yields, 20% for molar absorption coefficients and 3 nm for emission and absorption peaks. The temperature was 298 K, unless otherwise stated.

To get a semiquantitative description of the HOMO and LUMO involved in the photophysical processes, semiempirical calculations on the excited states of PH_2 , PZn , and phenyl terpyridine were carried out starting from MM+ optimized geometries and using the ZINDO/S (Zerner intermediate neglect of differential overlap/spectroscopic) program included in the Hyperchem package.²² The CI was fixed to 9×9 singly excited configurations.

Results and Discussion

Ground-State Absorption. The absorption spectra of the dyads PAu-Ir , $\text{PH}_2\text{-Ir}$ and of the triads $\text{PH}_2\text{-Ir-PAu}$ and PZn-Ir-PAu are reported with those of the component models in Figure 2. The spectra of the arrays well agree with a simple superposition of the spectra of the single components and this allows to establish, on the basis of the molar absorption coefficients of the models, the partition of the photons on the different units of the arrays for the selected wavelength. At energies higher than the Soret band, the porphyrins display a poor absorbance, whereas the absorbance of the complex prevails. At 355 nm, a wavelength convenient for laser excitation, the relative amounts of photons absorbed by the different units of each array in acetonitrile solutions are for $\text{PH}_2\text{-Ir}$, 32% on PH_2 unit and 68% on Ir unit; for PAu-Ir , 25% on PAu unit and 75% on Ir unit; for $\text{PH}_2\text{-Ir-PAu}$, 26% on PH_2 unit, 19% on PAu unit and 55% on Ir unit. In the case of PZn-Ir-PAu (toluene) the partition is 20% on PZn unit, 20% on PAu unit and 60% on Ir unit.

Luminescence. Room Temperature. The luminescence of Ir in acetonitrile solution displays a maximum at 506 nm with a broad shoulder extending up to 600 nm; the excited-state responsible for this emission is the ligand centered triplet state (^3LC).¹⁸ This luminescence is totally quenched in acetonitrile solutions of the arrays $\text{PH}_2\text{-Ir}$, PAu-Ir and $\text{PH}_2\text{-Ir-PAu}$, as shown in Figure 3 for concentrations adjusted to have the same number of photons absorbed by the Ir moiety. A similar

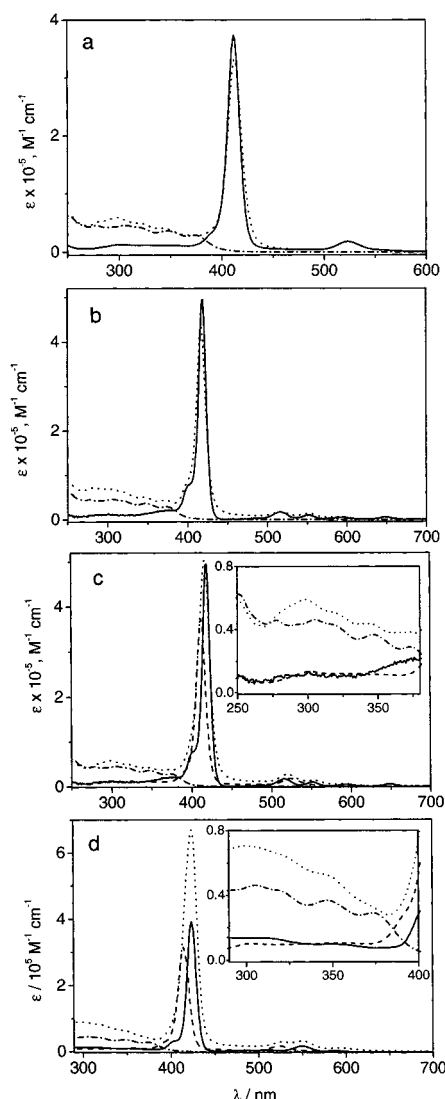


Figure 2. Absorption spectra of: (a) **PAu-Ir** (···), **Ir** (---), **PAu** (—) in acetonitrile; (b) **PH₂-Ir** (···), **Ir** (---), **PH₂** (—) in acetonitrile; (c) **PH₂-Ir-PAu** (···), **Ir** (---), **PH₂** (—), **PAu** (---) in acetonitrile; (d) **PZn-Ir-PAu** (···), **PZn** (—), **PAu** (---), **Ir** (---) in toluene, **Ir** (---) is in acetonitrile.

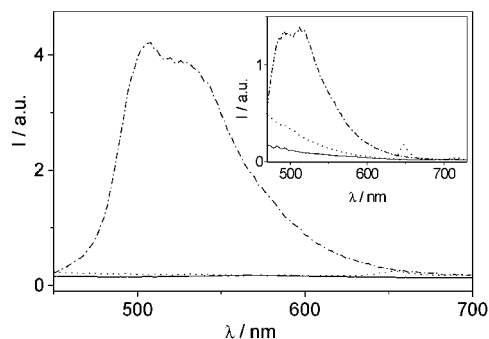


Figure 3. Room-temperature emission spectra in acetonitrile of **Ir** (---), **PH₂-Ir** (···) and **PAu-Ir** (—). Excitation at 355 nm where the absorbances of the solutions are 0.13 for **Ir**, 0.21 for **PH₂-Ir** and 0.19 for **PAu-Ir**, corresponding to the same numbers of photons absorbed by the **Ir** unit (see text). In the inset is the 77 K emission spectra in butyronitrile solutions.

complete quenching of the **Ir** unit occurs also in the array **PZn-Ir-PAu** (data not shown). Time-resolved experiments by a single photon time correlated apparatus indicate that the luminescence lifetime of **Ir**, 2.4 μ s in air-equilibrated acetonitrile

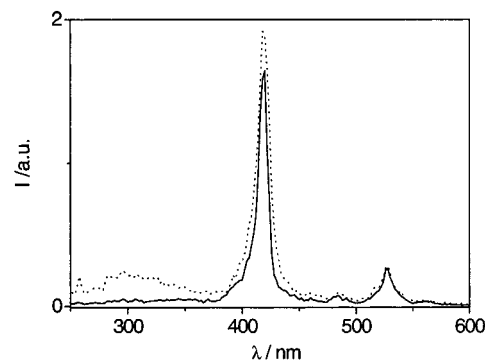


Figure 4. Excitation spectra at $\lambda = 710$ nm of **PAu** (—) and **PH₂-Ir-PAu** (···), butyronitrile glass at 77 K.

solutions (9.5 μ s air free), is quenched to a value shorter than the instrumental resolution (0.5 ns). Further experiments with a 20 ps resolution system do not show any detectable luminescence for the arrays in the range 500–550 nm. The absence of a detectable luminescence signal could be assigned to the low radiative rate constant of **Ir** ($k_{\text{rad}} = 4 \times 10^5 \text{ s}^{-1}$ ¹⁸) which prevents detection by means of luminescence technique based on single pulse experiments, like the present one, rather than to a lifetime shorter than the 20 ps resolution.

77 K Glass. The luminescence of the **Ir** component in the arrays **PAu-Ir**, **PH₂-Ir**, **PH₂-Ir-PAu**, and **PZn-Ir-PAu** is totally quenched also at 77 K in glassy matrixes (Inset of Figure 3). It is worth recalling that the quenching of the luminescence of the free-base porphyrin or of the zinc porphyrin units of the arrays occurs only at room temperature and *not* in a rigid glass at 77 K.¹⁵

Steady-state delayed spectra in butyronitrile glassy solution of **PAu-Ir** and **PH₂-Ir-PAu**, following excitation at 355 nm, allow to detect the phosphorescence of the triplet localized on the gold porphyrin ($\lambda_{\text{max}} = 705\text{--}710$ nm). The phosphorescence of the **PH₂** unit is at 840 nm,²⁰ a region where the instrumental sensitivity is too low to allow quantitative considerations. The excitation spectra of the phosphorescence of the gold porphyrin unit at 710 nm in **PH₂-Ir-PAu**, reported in Figure 4 with the phosphorescence of the model **PAu**, shows the contribution of the **Ir** moiety below 400 nm. This indicates that an energy transfer mechanism from the **Ir** metal complex unit to the gold porphyrin is occurring in **PH₂-Ir-PAu**.

The delayed spectrum of toluene glassy solution of **PZn-Ir-PAu** shows the phosphorescence band of the **PAu** unit at 710 nm, and of the **PZn** unit at 785 nm. The excitation spectrum of **PZn-Ir-PAu** registered at 710 nm, is reported in Figure 5a, with the excitation spectrum of the model **PAu** in the same conditions. In Figure 5b the excitation spectrum detected at 785 nm is shown for **PZn-Ir-PAu** in toluene together with the excitation spectra of the model **PZn** in the same conditions. Unfortunately, the quality of the toluene solid matrix is not as good as the butyronitrile matrix used above for the **PH₂-Ir-PAu** and the conclusions cannot be so firm. Nonetheless, in contrast to the previous case, the contribution of the **Ir** complex band around 350 nm in **PZn-Ir-PAu** is *not* evident either in the emission of the **PAu** unit or in that of the **PZn** unit. Therefore, for **PZn-Ir-PAu** there is no clear indication of energy transfer at 77 K from the **Ir** unit to the porphyrins. It should be noticed that the excitation spectrum of the ³**PZn** unit at 77 K (Figure 5b) displays clear evidence of the contribution of the **PAu** bands, pointing to an energy transfer from the gold-porphyrin localized triplet to the zinc porphyrin localized triplet, separated by a distance of 3 nm. Such a long-range energy

TABLE 1: Luminescence Properties in Acetonitrile^a and Toluene,^b Excitation at 355 nm if Not Otherwise Specified

	state	298 K			77 K		
		λ_{max} (nm)	τ (ns)	Φ_{fluor}	λ_{max} (nm)	τ (μ s)	E (eV) ^e
Ir^a	³ Ir	506	2400 ^c	0.029 ^c	494	39	2.51
PH₂^a	¹ PH ₂	652	8.3	0.15 ^d	647	0.011	1.92
	³ PH ₂				840 ^d	6×10^3 ^d	1.47 ^d
PAu^a	³ PAu				710	10; 100	1.75
PH₂–Ir^a	¹ PH ₂	652	0.03	0.002	648	0.012	1.91
PAu–Ir^a	³ PAu				705	16; 100	1.76
PH₂–Ir–PAu^a	¹ PH ₂	652	0.03	0.001	650	0.011	1.91
	³ PAu				706	20; 150	1.75
PZn^b	¹ PZn	596	2.2	0.08	596	0.0024	2.08
	³ PZn				776	18.9×10^3	1.60
PAu^b	³ PAu				712	n.d.	1.74
	¹ PZn		≤ 0.020	≤ 0.0006	606	0.0024	2.05
PZn–Ir–PAu^b	³ PZn				786	n.d.	1.58
	³ PAu				716	n.d.	1.73

^a Acetonitrile at room temperature except for PH₂, dissolved in a mixture of acetonitrile/butyronitrile (2:1), experiments at 77 K are in butyronitrile.

^b Toluene at room temperature and at 77 K. ^c Air equilibrated. ^d From ref 20, excitation at 532 nm. ^e Energy level from the emission maxima at 77 K.

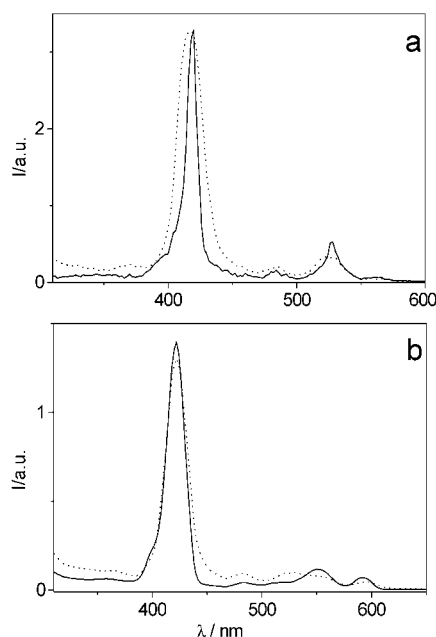


Figure 5. Excitation spectra in toluene glass at 77 K: (a) emission at $\lambda = 710$ nm of **PAu** (—) and **PZn–Ir–PAu** (···); (b) emission at $\lambda = 785$ nm of **PZn** (—) and **PZn–Ir–PAu** (···).

transfer by a Dexter mechanism is rather unusual¹⁷ but it has been demonstrated to occur with a rate of $2.5 \times 10^7 \text{ s}^{-1}$ between the same type of porphyrins separated by a distance of 2.1 nm and with an interposed bis-terpyridine ruthenium complex in rigid glass at 77 K.^{17a} In the present case, the distance is increased from 2.1 to 3 nm, but the lifetime of the ³PAu at 77 K is of the order of 10^{-4} s, which allows for the occurrence of a much lower energy transfer process than the one reported for the system containing the ruthenium complex. In Table 1, are summarized the luminescence properties of the arrays and their models.

Transient Absorbance. The ³LC excited state of **Ir** displays a strong absorption spectrum with a broad maximum around 680 nm (Figure 6a) and a lifetime of $2.4 \mu\text{s}$ ($9.5 \mu\text{s}$ air-free)¹⁸ in agreement with the luminescence lifetime. Transient absorbance technique can therefore be a powerful tool for elucidating the photoinduced processes originating from this state.

PAu–Ir. The spectrum detected at the end of a 35 ps pulse at 355 nm in an acetonitrile solution of the dyad **PAu–Ir** is reported in Figure 6a. In the same figure are also reported the

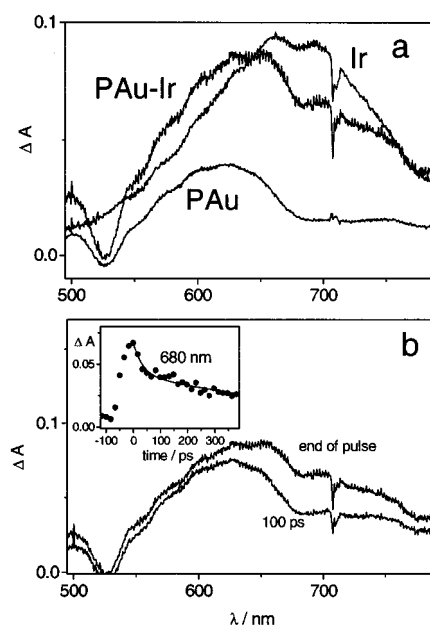


Figure 6. Transient absorbance changes upon excitation at 355 nm (35 ps pulse, 3 mJ). (a) End of pulse in an acetonitrile solution of **Ir**, **PAu** and **PAu–Ir** with ground-state absorbances at 355 nm of 0.24 for **Ir**, 0.07 for **Au** and 0.36 for **PAu–Ir**, respectively (see text for detail). (b) End of pulse and 100 ps after the end of the pulse in the solution of **PAu–Ir**. The inset shows the decay of the absorbance at 680 nm and the fitted biexponential decay according to lifetimes of 35 ps and 1.5 ns.

end of pulse spectra detected for the models **Ir** and **PAu** at concentrations corresponding to the absorbance of the same number of 355 nm photons as those of the individual components in the array. The lifetime of **PAu** is 1.5 ns, whereas the absorbance of **Ir** is essentially stable over the time window of this experiment, 3 ns. The spectrum of the dyad displays an initial broad band around 600–700 nm where the ³Ir unit absorbs, which evolves with a lifetime of 35 ps (inset of Figure 6b) to a spectrum typical of the gold porphyrin triplet (Figure 6b). This species which decays back to zero with a lifetime of 1.5 ns is identified as the gold porphyrin triplet. A comparison of the signal of the ³PAu in the model and in the dyad under identical conditions of absorbed photons, see Figure 6a, indicates that its yield in the dyad is at least twice the one in the model. The above data clearly indicate that an energy transfer process from the ³LC localized on the **Ir** component to the triplet

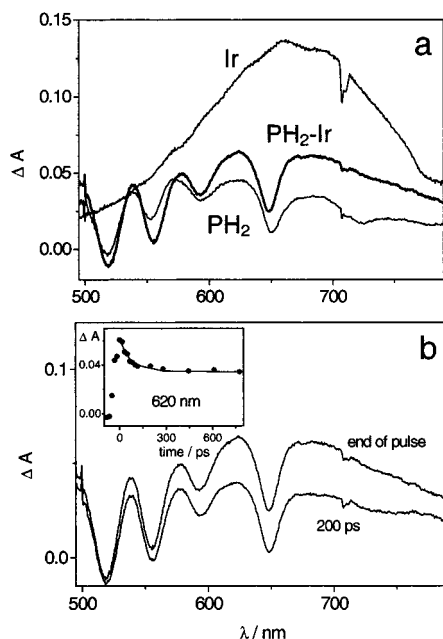


Figure 7. Transient absorbance changes upon excitation at 355 nm (35 ps pulse, 4 mJ). (a) End of pulse in an acetonitrile solution of **Ir**, **PH₂** and **PH₂-Ir** with ground-state absorbances at 355 nm of 0.28 for **Ir**, 0.11 for **PH₂** and 0.54 for **PH₂-Ir**, respectively (see text). (b) End of pulse and 200 ps after the end of the pulse in the **PH₂-Ir** solution. The inset shows the decay of the absorbance at 620 nm and the fitted exponential decay according to a lifetime of 70 ps.

localized on the gold porphyrin occurs with a lifetime of 35 ps, corresponding to a reaction rate of $2.9 \times 10^{10} \text{ s}^{-1}$.

PH₂-Ir. The end of pulse spectrum detected in an acetonitrile solution of **PH₂-Ir** following excitation at 355 nm with a 35 ps pulse is displayed in Figure 7a. In the same figure are reported the end of pulse spectra detected for acetonitrile solutions of **PH₂** and **Ir** at concentrations where the number of 355 nm photons absorbed by the samples is identical to those occurring in the individual components of the dyad. Any trace of the Ir component band is lacking in the initial spectrum detected in **PH₂-Ir** solutions; the end of pulse signal displays an evolution, accounting for a very minor component of the spectrum, to a very similar spectrum with a lifetime of 70 ps, identical over the whole spectral range (Figure 7b). This lifetime is the same, within experimental uncertainty, to the one of the CS state **PH₂⁺-Ir⁻** produced upon selective excitation of the **PH₂** moiety (75 ps);^{13,15} since at 355 nm the **PH₂** unit is also directly excited (see above) the 70 ps decay accounting for a very minor component, is assigned to the processes originating from *direct* excitation of the **PH₂** unit at 355 nm. After the initial spectral change, no further time evolution can be detected in the 3 ns time window which can be probed by this technique. A wider time window can be examined by nanosecond laser flash-photolysis. This allow to establish that the residual absorbance is due to the free-base porphyrin localized triplet, which displays a strong absorption band at 480 nm and a lifetime of 8 μs .¹⁵ Comparison of the absorption signal at 700 nm of the triplet in the dyad and in the model **PH₂**, indicates in the former a 3-fold increase in the triplet yield. The above data indicate that the excited state of the Ir unit is quenched with a rate exceeding our resolution and that the free-base porphyrin triplet is sensitized in the quenching; this clearly points to an energy transfer mechanism for this quenching.

PH₂-Ir-PAu. The system is rather complex, nonetheless with the support of the results derived for the more simple dyads, the processes occurring can be disentangled. The end of pulse

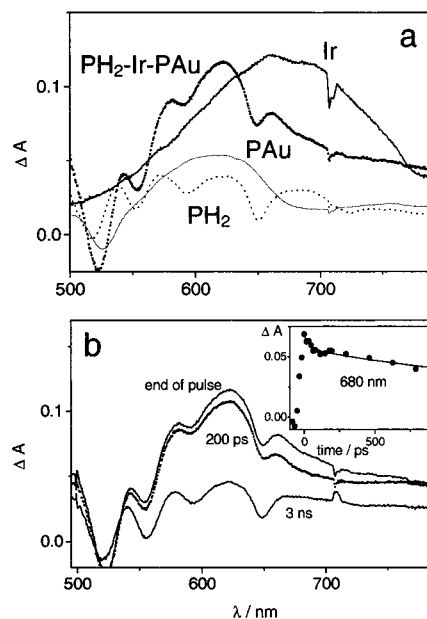


Figure 8. Transient absorbance changes upon excitation at 355 nm (35 ps pulse, 4 mJ): (a) End of pulse in an acetonitrile solution of **Ir**, **PH₂**, **PAu**, and **PH₂-Ir-PAu**. The ground-state absorbances of the solutions at 355 nm are 0.24 for **Ir**, 0.10 for **PH₂**, 0.07 for **PAu** and 0.67 for **PH₂-Ir-PAu**, respectively (see text). (b) End of pulse, 200 ps after and 3 ns after the end of the pulse in the of **PH₂-Ir-PAu** solution. The inset shows the decay of the absorbance at 680 nm and the fitted biexponential decay according to lifetimes of 40 ps and 1.4 ns.

spectrum of an acetonitrile solution of the triad **PH₂-Ir-PAu** is reported in Figure 8a with the absorption spectra of the model component **PH₂**, **PAu**, and **Ir** detected at concentrations corresponding to the absorption of the same number of photons as the individual components in the array. The spectrum of the array does not show contribution from the Ir component, whereas the presence of the triplet localized on the gold porphyrin unit, with the typical maximum at 620 nm is clearly present. Spectra of **PH₂-Ir-PAu** with time delays of zero, 200 ps and 3 ns with respect to the end of pulse, are drawn in Figure 8b. The immediate spectrum displays a rapid time evolution with a lifetime of 40 ps, accounting for a modest amount of the total absorbance followed by a slower decay with a lifetime of 1.4 ns identical, within experimental error, to the lifetime of ³**PAu** (Inset of Figure 8b). The 40 ps component can be identified with the decay of the CS state **PH₂⁺-Ir⁻-PAu** formed by *direct* excitation of the free-base porphyrin moiety (26% of the photons are absorbed by this unit at 355 nm); this state displays a lifetime of 40 ps in **PH₂-Ir-PAu**, as already reported in the previous study related with the selective excitation of the free base porphyrin unit.^{13,15} At the end of the 3 ns time window, a residual absorbance is left. The yield of the gold porphyrin triplet in the triad, once the absorption at 620 nm has been corrected for the residual spectrum at 3 ns, is only slightly higher (ca. 1.2 times), than that of the model **PAu**. This indicates that the sensitization of the gold porphyrin triplet is very little effective in the triad. The identification of the species responsible for the absorbance at 3 ns delay, can be performed by experiments with a nanosecond laser-flash photolysis. The resulting spectrum, with a pronounced band at 480 nm and a lifetime of 2 μs is typical of the triplet localized on the free base porphyrin in the triad, ³**PH₂-Ir-PAu**.¹⁵ The relative yield of this triplet in the array, measured against the photons absorbed by the **PH₂** unit only, is twice that of the model **PH₂**. The results reported indicate that excitation of the Ir unit

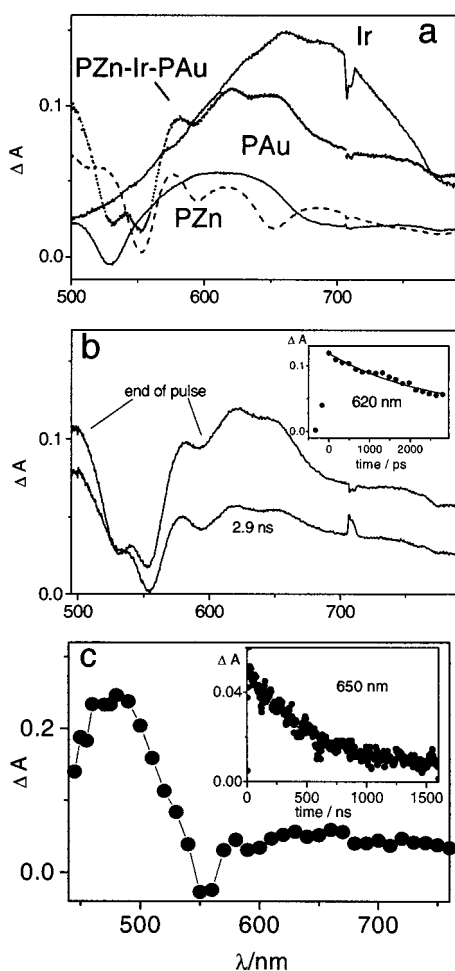


Figure 9. Transient absorbance changes upon excitation at 355 nm: (a) End of pulse in an acetonitrile solution of Ir, and toluene solutions of PZn, PAu, and PZn-Ir-PAu (35 ps pulse, 4 mJ). The ground-state absorbances of the solutions at 355 nm are 0.32 for Ir, 0.07 for PZn, 0.08 for PAu and 0.8 for PZn-Ir-PAu, respectively (see text). (b) End of pulse and 2.9 ns after the end of the pulse in a toluene solution of PZn-Ir-PAu (35 ps pulse, 4 mJ). The inset shows the decay at 620 nm and the fitted exponential decay. (c) End of pulse in a nanosecond laser flash-photolysis experiment (18 ns pulse, 2 mJ) in a toluene solution of PZn-Ir-PAu. In the inset the decay at 650 nm is reported.

in the triad leads to sensitization of the free base-porphyrin and, to a lower extent, of the gold porphyrin triplets. On a qualitative basis, the relative efficiency of the sensitization of the two triplets should reflect the ratio of the rates of the two competing energy transfer steps, which indicate for the sensitization of free-base porphyrin a rate exceeding that of $2.9 \times 10^{10} \text{ s}^{-1}$, determined for the energy transfer process to gold porphyrin. This is in agreement with the results reported above for the dyad **PH₂-Ir** where a rate faster than our resolution ($\geq 5 \times 10^{10} \text{ s}^{-1}$) was indicated.

PZn-Ir-PAu. The spectrum after excitation at 355 nm of a toluene solution of **PZn-Ir-PAu** is reported in Figure 9a together with the spectra detected for the models **Ir** (in acetonitrile), **PAu**, and **PZn** (in toluene) at concentrations adjusted to absorb the same number of photons as those of the corresponding units in the arrays. The spectrum of **PZn-Ir-PAu** shows contribution from ³PAu; its time evolution is consistent with a lifetime of 2.5 ns, typical of the gold porphyrin triplet in toluene (Figure 9b). The residual absorbance, detected by a nanosecond flash-photolysis apparatus (Figure 9c) shows the same spectral shape and time evolution, 450 ns in air-free

TABLE 2: Transient Absorption at Room Temperature in Acetonitrile^a or Toluene^b

	state	excitation on the porphyrins ^c		excitation on metal complex	
		τ (ns)	Φ^d	τ (ns)	Φ^d
Ir^a	³ Ir			2400 ^e	
PH₂^a	³ PH ₂	200 000	0.6 ^f		0.6
PAu^a	³ PAu	1.4	1 ^f		1
PH₂-Ir^a	³ PH ₂	8000	0.1	8000	1.8
	³ Ir			<0.020	
PAu-Ir^a	PH ₂ ⁺ -Ir ⁻	0.075	1		
	³ PAu	1.4	1	1.4	2
	³ Ir			0.035	
PH₂-Ir-PAu^a	³ PH ₂	2000	0.6 ^g		1.2
	³ PAu	1.4	1		1.2
	³ Ir			<0.020	
	PH ₂ ⁺ -Ir ⁻ -PAu	0.04	1		
	PH ₂ ⁺ -Ir-PAu ⁻	3.5	0.5		
PZn^b	³ PZn	300 000	0.7 ^f	300 000	0.7
PAu^b	³ PAu	2.5	1 ^f	2.5	1
PZn-Ir-PAu^b	³ PZn	7000	≤ 0.07	7000	≤ 0.07
	³ PAu	2.5	1	2.5	1
	³ Ir			<0.020	
	PZn ⁺ -Ir ⁻ -PAu	≤ 0.020		≤ 0.020	
	PZn ⁺ -Ir-PAu ⁻	450	1	450	4

^a Acetonitrile except for PH₂, dissolved in a mixture of acetonitrile/butyronitrile (2:1). ^b Toluene. ^c From ref 15. ^d Absolute yields calculated on the basis of the photons absorbed by the PH₂ and PZn (or PAu) unit only, for details see Experimental Section. At 532 nm the partition of photons in PH₂-Ir-PAu is 25% on PH₂, 75% on PAu, in the two dyads only porphyrin moiety absorbs light. For the partition at 355 nm, see text. ^e Air equilibrated. ^f From ref 21. ^g PH₂ in the triad is formed mainly by recombination of the CS state, with a yield of 0.5.¹⁵

solution, as detected following excitation of the PZn unit.¹⁵ In that case, the transient was formed together with a minor yield of PZn triplet excited state ($\Phi \leq 0.07$ and $\tau = 7 \mu\text{s}$) which allowed an unambiguous identification of the transient as the CS state **PZn⁺-Ir-PAu⁻**. Also in the present case a very minor yield of triplet is detected, and the only significant difference with the selective excitation of the porphyrins at 532 nm, is in the yield of the CS species measured with respect to the photons absorbed by the PZn unit, which is four times higher in this case. This clearly indicates that the photons absorbed by the Ir unit in the present experiment (ca. 3 times those absorbed by PZn) leads to charge separation with a unity yield, exactly as those absorbed by the PZn unit. In this array therefore, in contrast with the PH₂ based structures, excitation of both Ir and PZn units leads to the same product, the primary CS state **PZn⁺-Ir-PAu⁻**, which evolves to the final CS state **PZn⁺-Ir-PAu⁻**. In Table 2, are summarized the transient absorption data at ambient temperature for excitation of the different components.

Photoinduced Processes. The processes occurring upon selective excitation of the metal complex in the dyads **PAu-Ir** and **PH₂-Ir** and in the triad **PH₂-Ir-PAu** are reported with the pertinent rates in the schematic energy level diagrams of Figure 10. This has to be compared with Scheme 1 where the result of excitation of the PH₂ unit is summarized. A discussion of the different outcome upon selective excitation of the different units in **PH₂-Ir-PAu** can be performed in the frame of classical treatment for nonadiabatic electron transfer,²³ which predicts a rate of electron transfer (k_{el}) described by the following equation

$$k_{\text{el}} = \sqrt{\frac{\pi}{\hbar^2 \lambda k_{\text{B}} T}} |V|^2 \exp\left(\frac{-(\Delta G^\circ + \lambda)^2}{4\lambda k_{\text{B}} T}\right) \quad (1)$$

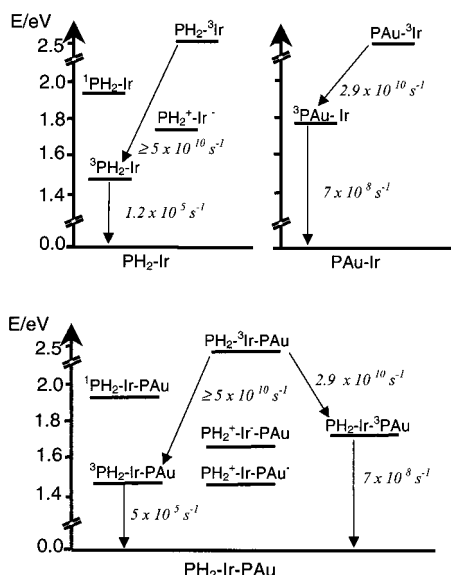
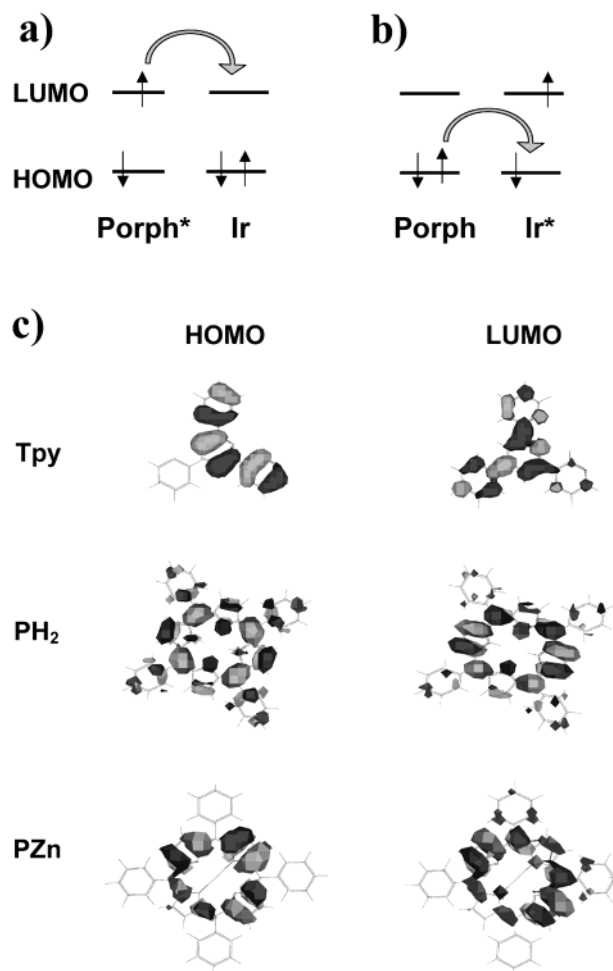


Figure 10. Schematic energy diagrams of $\text{PH}_2\text{-Ir}$, PAu-Ir , and $\text{PH}_2\text{-Ir-PAu}$ in acetonitrile, upon selective excitation of the Ir unit.

where λ is the reorganization energy, k_B is the Boltzmann constant, ΔG° is the standard free energy change of the reaction. In general terms, the preexponential is generally referred to as “electronic factor” and includes the electronic matrix element (V) which depends on the overlap of the electronic wave functions of the donor and acceptor groups, whereas the exponential term is referred to as “nuclear factor” and is correlated to the standard free energy change (ΔG°) and to the reorganization energy of the reaction.

In the discussion of the present data, the intrinsic different nature of the molecular orbitals involved in the electron-transfer process depending on the starting excited state, should be taken into account. In the case of excitation of the porphyrin unit, the primary electron transfer consists of an electron which moves from the LUMO of the porphyrin donor to the LUMO of the complex acceptor (Scheme 2a) localized on the terpy ligand, whereas when the Ir unit is excited, the same CS state would be formed by the transfer of an electron from the HOMO of the porphyrin to the HOMO of the central iridium complex localized on the ligand (Scheme 2b). Therefore, a favorable electronic factor would require a good LUMO–LUMO overlap in the first case, whereas in the second case, a good HOMO–HOMO overlap would be necessary. To get information on the orbitals involved, a simplified approach was used, making use of ZINDO/S²² calculations carried out on the simple porphyrinic components and on the phenyl terpyridine ligand of the complex. Inclusion of the Ir ion in the calculation of the complex molecular orbitals is prevented by the lack of parameters in the current method used. Nonetheless, given the ligand centered nature of the complex excited state,¹⁸ the approach used can be sufficient for the present qualitative purposes. The results indicate (Scheme 2c) that although the electron distribution of both HOMO's and LUMO's of the PH_2 porphyrin are extended, even if to a different extent, to the aryl substituent, in the case of the terpyridine, only the LUMO extends over the aryl substituent. It is quite evident that although the electronic factors for the electron transfer are maximized when the porphyrin is excited due to the *favorable overlap* of the two LUMO's which are delocalized over the bridging phenyl, when the Ir unit is excited the HOMO of the phenyl terpy has no charge density on the bridging phenyl, making the overlap with the HOMO of the PH_2 , close to zero. This would affect the electronic term

SCHEME 2: Pictorial Display of the Probable Electron Jumps in Case of Excitation of the Porphyrin Unit (a) or Ir Unit (b). Calculated HOMO and LUMO Orbital Distributions (dark gray negative, light gray positive) for the Main Fragments Involved (c)



(eq 1) in the reaction rate expression of the electron transfer from the Ir donor excited moiety to the PH_2 acceptor moiety in $\text{PH}_2\text{-}^3\text{Ir-PAu}$ and, despite the high driving force (ΔG° ca. -0.8 eV) it would make the electron transfer reaction not competitive with the other possible deactivation processes, namely the energy transfer to the triplet states of the two porphyrins. One of these rates, the one pertinent to energy transfer from the gold porphyrin triplet, is experimentally determined to be $2.9 \times 10^{10} \text{ s}^{-1}$. The other parallel energy transfer reaction to the free-base porphyrin is experimentally found to exceed our resolution ($5 \times 10^{10} \text{ s}^{-1}$) but can be estimated on the basis of the ratio of the yields of the triplets $^3\text{PH}_2\text{-Ir-PAu}$ and $\text{PH}_2\text{-Ir-}^3\text{PAu}$. Because the yield of the gold porphyrin sensitized by energy transfer is 0.2, i.e., only that exceeding the one directly formed accounting for a yield of 1, and the yield of free-base sensitized porphyrin is ca. 1,²⁴ the rate of energy transfer to free-base porphyrin is evaluated to be ca. 4–5 times faster than the rate of energy transfer to gold porphyrin. This places the rate of energy transfer from the triplet localized on the Ir complex to the triplet localized on PH_2 (ΔG° ca. -1 eV) around 10^{11} s^{-1} , a very fast process which can effectively compete with an electron-transfer characterized by a modest electronic term.

Therefore, the different outcome of the excitation of different moieties in the PH_2 based arrays can be explained on the basis

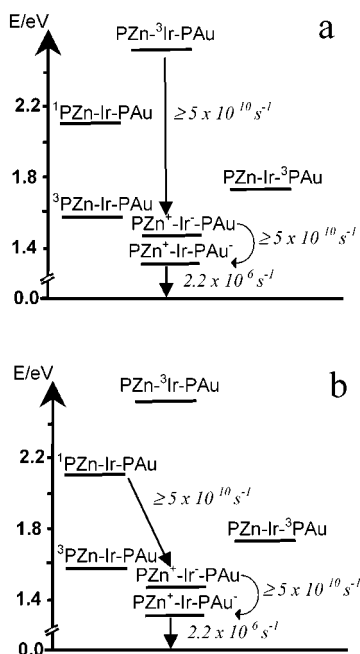


Figure 11. Schematic energy diagrams of **PZn-Ir-PAu** in toluene, upon selective excitation of the Ir unit (a) and of the porphyrin unit (b).

of the nature of the different molecular orbitals involved in the electron transfer processes in the two cases and by the fact that an energy transfer from the excited state of the Ir complex to the two porphyrins can efficiently compete.

In Figure 11, is reported the energy level scheme and the processes occurring upon excitation of either the Ir complex unit (a) or the Zn porphyrin unit (b) in the array **PZn-Ir-PAu**; in both cases the process is an electron transfer leading to the charge separated state **PZn⁺-Ir-PAu⁻**. Also in this case, as previously discussed, electron transfer from the porphyrin excited state requires a good LUMO-LUMO overlap between the Zn porphyrin donor and the Ir complex acceptor, whereas electron transfer from the ligand centered complex excited state requires a good overlap of the HOMO's of the donor and acceptor units. The simplified treatment for the ligand phenyl terpyridine is obviously the same as in the previous case, whereas the phenyl Zn porphyrin HOMO and LUMO, at variance with the case of the phenyl free-base display less delocalization on the phenyl substituents and some degree of asymmetry (Scheme 2c). On such basis, we are unable to clearly explain the behavior of the array based on PZn on mere overlap of electronic wave functions and have to assign a role to the "nuclear term". In particular the high driving force for the primary electron-transfer reaction in **PZn-Ir-PAu**, (ΔG° ca. -1.1 eV), could favor an electron transfer even in the absence of very favorable electronic factor. A con-cause for the electron transfer to occur could be a less exothermic ($\Delta G^\circ = -0.9$ eV), and therefore less competitive, energy transfer reaction from **PZn-³Ir-PAu** to **³PZn-Ir-PAu** in this case compared to the corresponding reaction for the free-base derivative where the driving force of the energy transfer reaction is higher ($\Delta G^\circ = -1$ eV). Remarkably, in **PZn-³Ir-PAu**, the energy transfer step does not seem to compete with the electron transfer even at 77 K in a glassy matrix, there is in fact no evidence of such transfer from the excitation spectra (Figure 5). This is rather surprising because the rigid medium does not appreciably alter the rate of energy transfer processes²⁵ while electron transfer are, in general, slowed or inhibited²⁶ because of the absence of stabilization of the frozen solvent unable to re-polarize. Clearly,

the high driving force for the electron-transfer reaction can make this reaction feasible even in the absence of stabilization of the charge separated state.

Conclusions

The results here reported indicate that in the arrays **PH₂-Ir** and **PH₂-Ir-PAu** it is possible to switch the nature of the photoinduced process between energy and electron transfer by selective excitation of the different component units. Excitation of the Ir complex unit in the ultraviolet leads to energy transfer and sensitization of the triplets of the porphyrins whereas excitation of the free-base porphyrin in the visible wavelength range leads to electron transfer which yields a CS state. The observations can be rationalized on the basis of current classical electron and energy transfer theories. The behavior of the array containing zinc porphyrin, **PZn-Ir-PAu**, which gives origin to a CS state with unity yield irrespective of the excited unit, can be rationalized on the basis of a high driving force for the electron-transfer reaction which would counterbalance a non favorable electronic coupling for the same reaction.

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