# A Zn(II) porphyrin–Ir(III) bis-terpyridine–Au(III) porphyrin triad with a charge-separated state in the microsecond range

**Lucia Flamigni,*[a] Isabelle M. Dixon,[b] Jean-Paul Collin*[b] and Jean-Pierre Sauvage*[b]**

[a] *Istituto FRAE-CNR, Via P. Gobetti 101, 40129 Bologna, Italy. E-mail: flamigni@frae.bo.cnr.it*
[b] *Laboratoire de Chimie Organo-Minérale, UMR 7513 CNRS, Université Louis Pasteur, Institut Le Bel, 4 rue Blaise Pascal, 67070 Strasbourg, France. E-mail: sauvage@chimie.u-strasbg.fr*

*Received (in Cambridge, UK) 25th September 2000, Accepted 7th November 2000*
*First published as an Advance Article on the web*

**A photoinduced, multistep electron transfer in a triad containing a zinc porphyrin (electron donor) and a gold(III) porphyrin (electron acceptor) appended to an Ir(III) bis-terpyridine complex produces a charge separated state with a close to unity yield and a lifetime of 450 ns.**

Photoinduced charge separation over nanometer distances in artificial arrays is a topic of high relevance both to fundamental[1] and to applied chemical sciences.[2] This function is achieved by molecular triads and higher analogues, able to undergo stepwise electron transfer under the action of light. It is essential that the multicomponent systems be rigid so as to insure good geometrical control and to favor long-lived charge separated (CS) states. In recent years, we have reported rigid triads based on ruthenium(II) bis-terpy complexes (terpy = 2,2′:6′,2″-terpyridine) and differently metallated porphyrins as electron donor and electron acceptor groups.[3,4] In this type of array, energy transfer processes from the porphyrin photosensitizer to the Ru(II) complex could efficiently compete with the desired electron transfer.[4] Ir(III) bis-terpy revealed itself to be particularly well adapted as a component unit, since it displayed a higher ligand centered excited state and remarkable redox properties.[5] Therefore Ru(II) was replaced by Ir(III) as the assembling metal ion in the synthesis of the rigid molecular triads.[6] In the previous Ir(III) bis-terpy based triad the electron donor was a free-base porphyrin ($PH_2$) and the terminal acceptor was a gold(III) porphyrin (PAu). Clear evidence for the formation of the fully charge-separated state ($PH_2^+$–Ir–$PAu^-$) was obtained by transient absorption spectroscopy.[6] However, charge recombination turned out to be fast (*ca.* 3.5 ns at room temperature in nitriles) due to the presence of a low-lying triplet state localized on $PH_2$. Substitution of the $PH_2$ unit with zinc porphyrin in this triad is expected to result in an increase in the triplet level; this should leave the CS state as the lowest state with the only possibility to deactivate to the ground state. Since the latter reaction is strongly exergonic ($\Delta G$ *ca.* −1.3 eV) we expect it to be placed in the Marcus inverted region[1] in a moderately polar or apolar solvent, and therefore to be slow so allowing for a long-lived CS state.

We now report the detection, upon excitation in the visible region of a toluene solution of **PZn–Ir–PAu** (Fig. 1), of a CS state with a lifetime of 450 ns. The triad **PZn–Ir–PAu**[†] was prepared by metallation of its free-base analogue[6] with zinc acetate in refluxing MeCN–MeOH (1:1 v/v). The absorption spectrum of this triad in toluene is very little perturbed with respect to the superposition of the spectra of the model components **PAu**, **PZn** (in toluene) and **Ir** (in acetonitrile) indicating little electronic coupling between the components. Similar indications are given by electrochemical determinations in dichloromethane where the oxidation of the PZn unit in the dyad PZn–Ir occurs at the same potential as the model **PZn**, +0.68 V (*vs.* SCE) while the PAu unit, which is reduced at −0.66 V (*vs.* SCE) in PAu–Ir *cf.* −0.70 V (*vs.* SCE) of **PAu**, is somehow affected by the presence of the substituent. Reduction of the Ir complex occurs at −0.71 V in the model dyad PZn–Ir. These data place the energy levels of the CS states $PZn^+$–$Ir^-$–PAu and $PZn^+$–Ir–$PAu^-$ in dichloromethane at *ca.* 1.39 and 1.34 eV, respectively. The excited state properties determined by transient absorption and luminescence experiments[‡] at 295 K both for the models and the array are reported in Table 1 with the pertinent energy levels, as derived by the maxima of emissions at 77 K. The emission of zinc porphyrin in the array is quenched with a rate exceeding our resolution time, while the only detectable excited state of the gold porphyrin, the lowest triplet, remains unchanged with respect to the model. The Ir moiety absorbs at higher energies, $\lambda < 400$ nm, therefore this unit is not excited in the present experiment. Upon laser excitation at 532 nm, after the decay of the gold porphyrin triplet ($\tau = 2.5$ ns), a longer lived absorption is left the spectrum of which is displayed in Fig. 2. The decay is monoexponential, identical over the whole spectral region and in air-free solution the lifetime is 450 ns (inset of Fig. 2). Air equilibration of the solution results in a decrease of the exponential lifetime to 310 ns, which allows us to derive a reaction rate with oxygen of *ca.* $5 \times 10^8$ $M^{-1}$ $s^{-1}$. The lifetime was unaffected by changes in the concentration of the array and in the energy of the laser pulse. The spectrum, in full agreement with the bands typical of the zinc porphyrin cation and the reduced gold porphyrin radical, is assigned to the CS state $PZn^+$–Ir–$PAu^-$. In oxygen free solutions a very weak absorption ascribable to the triplet localized on the zinc porphyrin, formed with a very low yield and a lifetime of 7 µs, is left after the decay of the CS state. An estimate of the efficiency of the charge separation process with respect to the photons absorbed by the zinc porphyrin moiety only, calculated on the basis of the molar absorption coefficient of $1 \times 10^4$ $M^{-1}$ $cm^{-1}$ for the cation of tetraphenyl zinc porphyrin at 680 nm,[7] yields a value very close to unity (1.2 ±

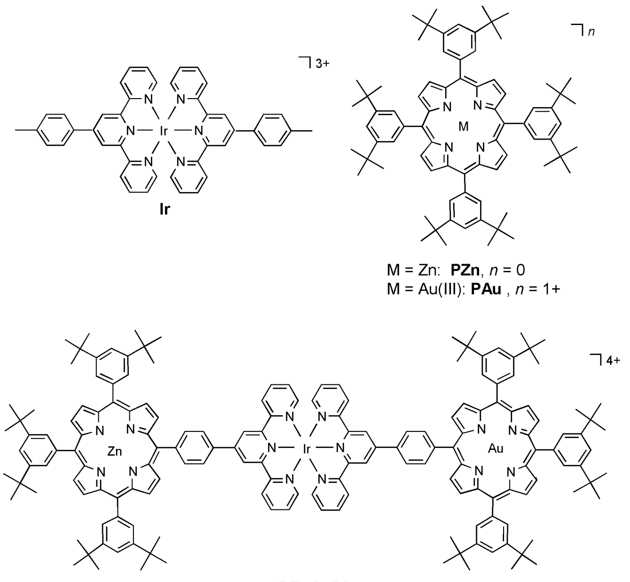

**Fig. 1** Chemical formula of the triad and models.

DOI: 10.1039/b007778j

**Table 1** Excited state properties from luminescence and transient absorbance[a] data in toluene solutions

| | | 295 K | | | 77 K | |
|---|---|---|---|---|---|---|
| | | $\lambda_{max}$/nm | $\tau$/ns | $\Phi_{fluo}$ | $\lambda_{max}$/nm | $E$/eV |
| **PZn** | $^1$PZn | 596 | 2.2 | 0.08 | 606 | 2.05 |
| | $^3$PZn | 470[a] | $300 \times 10^3$[a] | | 770 | 1.61 |
| **PAu** | $^3$PA | 630[a] | 2.5[a] | | 712 | 1.74 |
| **PZn–Ir–PAu** | $^1$PZn | 598 | $\leqslant$0.020 | 0.0006 | 606 | 2.05 |
| | $^3$PZn | 470[a,b] | $7 \times 10^3$[a,b] | | 786 | 1.58 |
| | $^3$PAu | 630[a] | 2.5[a] | | 716 | 1.73 |

[a] From transient absorbance. [b] Extremely low yield.

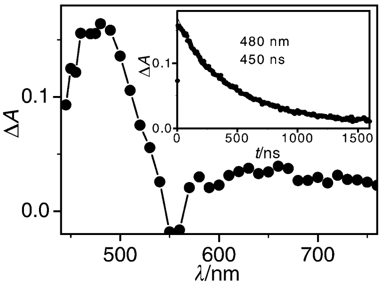

**Fig. 2** Transient absorption changes detected in an air free toluene solution of **PZn–Ir–PAu** upon excitation at 532 nm. In the inset the decay at 480 nm and the fitted exponential function corresponding to a lifetime of 450 ns is shown.

0.3). Such high efficiency in the charge separation process requires a very fast primary (from the excited PZn moiety to the Ir complex) and secondary (from the reduced Ir moiety to the gold porphyrin unit) electron transfer, to prevent competition with the back reactions. The detected quenching of the luminescence is faster than 20 ps in agreement with this requirement, so is also the rise of the absorbance assigned to the CS state which cannot be resolved from the excitation profile in an experiment with 20 ps resolution. Any investigation on the model dyad PZn–Ir which could give further information on the elementary steps of the electron transfer sequence is prevented by the insolubility of the dyad in toluene. Fig. 3 shows a schematic energy level diagram for the system along with the processes and the pertinent rates. The energy levels of the CS states are derived from electrochemical data in dichloromethane and this causes some uncertainty in their location in a toluene solution.

We have shown that highly efficient formation of a long lived charge separated state occurs in this triad in toluene solution upon excitation in the visible range.

This work was supported by the French CNRS and the Italian CNR. We thank European Commission COST programme D11/0004/98 and the French Ministry of Education, Research and Technology for a fellowship to I. M. D. We are also grateful to Johnson Matthey for a generous loan of $IrCl_3$.

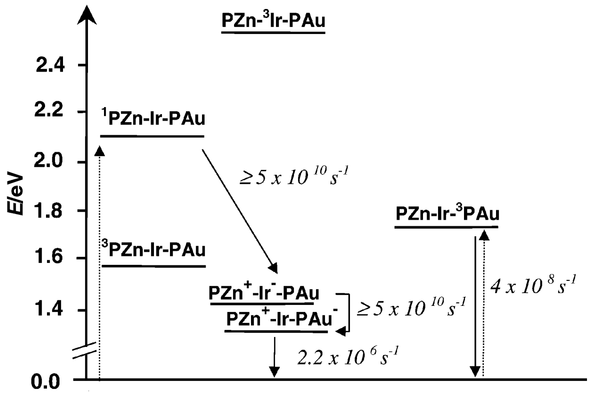

**Fig. 3** Schematic energy level diagrams for **PZn–Ir–PAu**. The charge separated state energies are calculated from electrochemical data in dichloromethane.

## Notes and references

† $^1$H NMR (400 MHz, $CD_3CN$), $\delta$ 9.49–9.42 (m, 8H, pyrroles-PAu), 9.37 (s, 4H, $H_{3'} + H_{5'}$), 8.99 (m, 4H, pyrroles-PZn), 8.93 (d, 4H, $H_6$, $^3J$ 8.2 Hz), 8.90 (s, 4H, pyrroles-PZn), 8.80–8.70 (m, 8H, $H_1 + H_2$), 8.36 (dd, 4H, $H_4$, $^3J$ 7.8 Hz), 8.18 (d, 4H, $H_o$-PAu, $^4J$ 1.7 Hz); 8.16 (d, 2H, $H_{o'}$-PAu, $^4J$ 1.7 Hz), 8.15 (d, 4H, $H_o$-PZn, $^4J$ 2.0 Hz), 8.11 (d, 2H, $H_{o'}$-PZn, $^4J$ 1.9 Hz), 8.09–8.06 (m, 3H, $H_p + H_{p'}$-PAu), 7.95–7.90 (m, 7H, $H_p + H_{p'}$-PZn + $H_3$), 7.68–7.62 (m, 4H, $H_5$), 1.58 (s, 36H, $Bu^t$-PAu), 1.57 (s, 36H, $Bu^t$-PZn), 1.56 (s, 18H, $Bu^{t'}$-PAu), 1.55 (s, 18H, $Bu^{t'}$-PZn). MS (FAB$^+$): *m/z* 3249.3 ($[M + H - PF_6]^+$), 3105.2 ($[M - 2PF_6]^+$), 2960.2 ($[M - 3PF_6]^+$), 2813.1 ($[M - 4PF_6]^+$), 1552.1 ($[M - 2PF_6]^{2+}$), 1479.1 ($[M - 3PF_6]^{2+}$), 1408.1 ($[M - 4PF_6]^{2+}$), 1376.1 ($[M - 4PF_6 - Zn + 3H - \text{terpyPAu}]^+$, *i.e.* $[PH_3 - Ph - \text{terpy} - Ir]^+$, 100%).

‡ Time resolved luminescence was determined with an apparatus based on a Nd-YAG laser (35 ps, 1 mJ at 532 nm) and a streak camera (overall resolution: 20 ps). Transient absorbance changes with 20 ps resolution were determined with a pump and probe system based on a Nd-YAG laser (35 ps, 3 mJ at 532 nm) and an OMA detector. For ns to μs time domains a laser flash photolysis based on a Nd-YAG laser (18 ns pulse, 3 mJ at 532 nm), a pulsed xenon lamp and a photomultiplier Hamamatsu R936, was used. For further details on the experimental set-up see refs. 4–6.

1 R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265 and references therein; G. L. Closs and J. R. Miller, *Science*, 1988, **240**, 440.

2 *Energy Resources through Photochemistry and Catalysis*, ed. M. Grätzel, Academic Press, New York, 1983; C. J. Kleverlaan, M. T. Indelli, C. A. Bignozzi, L. Pavanin, F. Scandola, G. Hasselman and G. J. Meyer, *J. Am. Chem. Soc.*, 2000, **122**, 2840 and references therein.

3 A. Harriman, F. Obodel and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1995, **117**, 9461.

4 L. Flamigni, N. Armaroli, F. Barigelletti, V. Balzani, J.-P. Collin, J.-O. Dalbavie, V. Heitz and J.-P. Sauvage, *J. Phys. Chem.*, 1997, **101**, 5936; L. Flamigni, F. Barigelletti, N. Armaroli, J.-P. Collin, J.-P. Sauvage and J. A. G. Williams, *Chem. Eur. J.*, 1998, **4**, 1744.

5 J.-P. Collin, I. M. Dixon, J.-P. Sauvage, J. A. G. Williams, F. Barigelletti and L. Flamigni, *J. Am. Chem. Soc.*, 1999, **121**, 5009.

6 I. M. Dixon, J.-P. Collin, J.-P. Sauvage, F. Barigelletti and L. Flamigni, *Angew. Chem., Int. Ed.*, 2000, **39**, 1292.

7 J. Fajer, D. C. Borg, A. Forman, D. Dolphin and R. H. Felton, *J. Am. Chem. Soc.*, 1970, **92**, 3451.