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Charge Separation in a Molecular Triad Consisting of an Iridium(III) – bis-terpy Central Core and Porphyrins as Terminal Electron Donor and Acceptor Groups[**]

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Synthetic multiporphyrin systems represent interesting mimics of the natural photosynthetic reaction centers in green plants[1a] and bacteria.[1b] In photosynthetic bacteria, one of the key reactions is electron transfer from the singlet excited state of the primary donor (special pair of bacteriochlorophylls, P) to a tetrapyrrolic unit (accessory bacteriochlorophyll, B), which is followed by another ultrafast electron transfer to a secondary acceptor (bacteriopheophytin, H). This three-component natural device (triad) is extremely efficient and has triggered the synthesis and study of many triads, designed to function in a similar way.[2]

Until now most of these systems relied on covalent bonds. Recently, alternative strategies were proposed for constructing multiporphyrin assemblies, mostly based on hydrogen bonds,[3a] mechanical bonds,[3b] or coordination bonds.[3c] In particular, ruthenium(II) bis-terpy (terpy = 2,2′:6′,2″-terpyridine) has been used as a central complex[4] that 1) gathers together the various electro- and photoactive groups to be incorporated in the triad, and 2) provides a central electroactive species that participates in the multistep electron-transfer process. This latter function can be complicated by energy-transfer processes, due to the presence of a relatively low lying (ca. 1.9 eV) triplet metal-to-ligand charge transfer (^{3}MLCT) state located on the $[Ru(terpy)_2]^{2+}$ core.[5] To circumvent these potential difficulties we looked for an alternative metal, and iridium(III) appeared to be particularly well suited. The $[Ir(terpy)_2]^{3+}$ unit forms the central complex (A_1) of the present triad (Scheme 1), in which a free-base porphyrin (PH_2) is the primary electron donor (D), and a gold(III) porphyrin (PAu) the secondary electron acceptor (A_2). In the natural photosynthetic reaction center, D, A_1, and A_2 are P, B, and H, respectively. It is noteworthy that the three-component assembly PH_2-[Ir]-PAu (**5**$^{4+}$) has a linear arrangement with very little flexibility and hence good control over the geometry of the ensemble. Given the properties of

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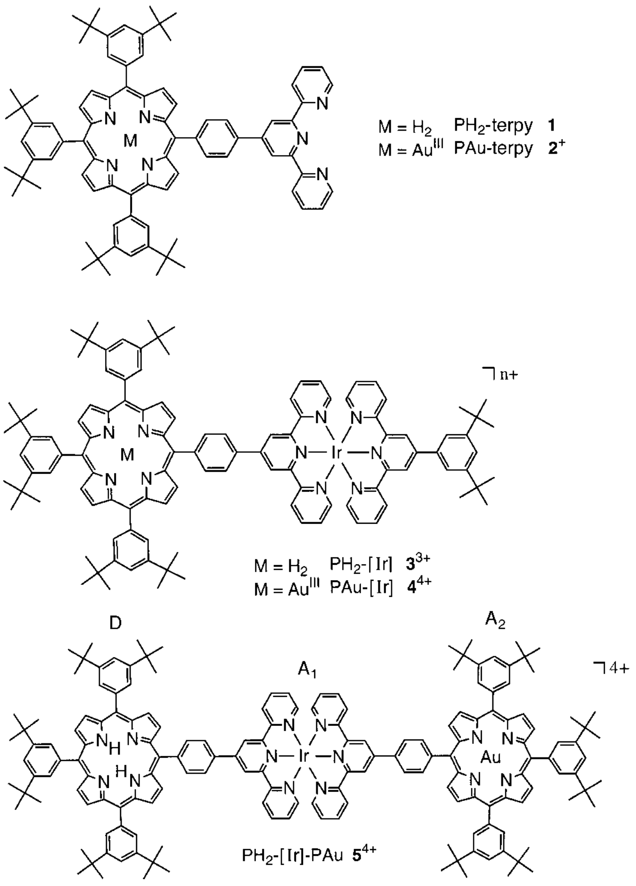

Scheme 1. Components of the triad PH$_2$-[Ir]-PAu **5**$^{4+}$.

the independent D, A$_1$, and A$_2$, the present triad is expected to undergo the sequence of reactions (1)–(3).

$$\text{D-A}_1\text{-A}_2 \xrightarrow{h\nu} \text{D*-A}_1\text{-A}_2 \tag{1}$$

$$\text{D*-A}_1\text{-A}_2 \longrightarrow \text{D}^+\text{-A}_1^-\text{-A}_2 \tag{2}$$

$$\text{D}^+\text{-A}_1^-\text{-A}_2 \longrightarrow \text{D}^+\text{-A}_1\text{-A}_2^- \tag{3}$$

The complex [Ir(terpy)$_2$]$^{3+}$ was described by Demas et al. in 1990.[6] Recently, we reported an efficient synthetic procedure for making related complexes, including asymmetrical compounds containing two different terpy ligands.[7] A detailed electrochemical, spectroscopic, and photochemical study clearly showed that 1) [Ir(terpy)$_2$]$^{3+}$ is a potentially interesting electron relay (Ir^{III}/Ir^{II}: $E^0 \approx -0.7$ V vs. SCE in CH$_3$CN; "Ir^{II}" is in fact an iridium(III)-stabilized radical anion localized on the terpy ligand), 2) no low-lying excited states (<2.5 eV) are present, and 3) the excited state populated by light absorption (mostly of ligand-centered character) is photochemically very promising, especially for complexes of 4′-substituted terpy: it is long lived (>1 μs at 298 K in CH$_3$CN), strongly luminescent, and expected to display a very strong electron-accepting character. To the best of our knowledge, this family of compounds represents the first series of multicomponent iridium(III) complexes of the polyimine type. In fact, it is likely that the expected synthetic difficulties had discouraged other groups from using such complexes.

The synthesis of Ir^{III} complexes containing two different terpy ligands is a key reaction. As in our previous work,[7] we developed a two-step procedure. The most difficult reaction is the coordination of the second terpy ligand. It is carried out under harsh conditions over a short period of time. The use of robust tetraarylporphyrins is essential, since etioporphyrins would not resist the brutal conditions necessary for the complexation of the second ligand.

The unsymmetrical porphyrin **1** (see Scheme 1) can be prepared by Adler's procedure,[4] but we instead chose a Suzuki coupling procedure between a porphyrin bearing a boronic ester (prepared by the method of Lindsey et al.[8]) and 4′-bromo-terpy.[9] Metalation of **1** with gold(III) to afford **2**$^+$ (Scheme 1) was achieved under the usual conditions.[10] Diads **3**$^{3+}$ and **4**$^{4+}$ and triad **5**$^{4+}$ were obtained from the terpy–porphyrin conjugate **1** after appropriate metalation reactions of its coordination sites. Their synthesis and characterization will be reported elsewhere. For the sake of clarity, the names of the compounds are used in the discussion instead of formula numbers.

In the diads and the triad, the presence of phenylene spacers should ensure a certain degree of electronic insulation of the components. Therefore, the redox potentials are expected to remain unchanged on going from individual components to the diads and the triad. In the free-base diad PH$_2$-[Ir], the oxidation of the porphyrin occurs at +0.96 V, and the reduction of the terpy ligands at −0.78 and −0.94 V. In the gold diad PAu-[Ir], the reduction of the porphyrin occurs at −0.59 and −1.11 V, while the reduction of the terpy ligands occurs at −0.75 and −0.91 V.

The absorption spectra of the diads and the triad are in good agreement with the sum of the absorption spectra of the components PH$_2$, [Ir] (standing for the relevant model [Ir(4′-tolylterpy)$_2$]$^{3+}$) and PAu (acetonitrile solutions). This is again indicative of the absence of strong coupling between the different units of the structure.

At 298 K, the luminescence intensity of the free-base porphyrin (λ_{exc} = 592 nm) is strongly quenched in acetonitrile solutions of PH$_2$-[Ir] and of PH$_2$-[Ir]-PAu. Time-resolved emission measurements indicate that the lifetime of the singlet free base is reduced from 8.3 ns to 30 ps in PH$_2$-[Ir] and PH$_2$-[Ir]-PAu. Such quenching does not occur in a butyronitrile glass at 77 K, where the lifetime of the model porphyrin (11 ns) is maintained in both arrays (Table 1). These obser-

Table 1. Emission properties and energy levels of the excited states.[a]

	298 K			77 K		
	λ_{max} [nm]	τ [ns]	Φ_{fluo}	λ_{max} [nm]	τ [μs]	E [eV][b]
PH$_2$[c]	652	8.3	0.15[d]	647	0.011	1.92
				840[d]	6000[d]	1.47[d]
PAu[e]				710	10; 100	1.75
PH$_2$-[Ir][c]	652	0.03	0.002	648	0.012	1.91
PAu-[Ir][e]				705	16; 100	1.76
PH$_2$-[Ir]-Au[c]	652	0.03	0.001	650	0.011	1.91
				706[e]	20; 150[e]	1.75[e]

[a] In CH$_3$CN at 298 K, except for PH$_2$ (CH$_3$CN/BuCN 2/1); in BuCN at 77 K. [b] Energy levels from the emission maxima at 77 K. [c] Excitation at 592 nm for steady-state and at 532 nm for time-resolved experiments. [d] From ref. [11]. [e] Excitation at 405 nm for steady-state and 532 nm for time-resolved experiments.

vations support a quenching of the excited state of PH_2 by electron transfer. Table 1 lists the luminescence properties at 298 K and 77 K for the arrays and the pertinent models.

Transient absorbance measurements at ambient temperature ($\lambda_{exc} = 532$ nm) on acetonitrile solutions of PH_2-[Ir]-PAu and PAu-[Ir] allowed the detection of the triplet state of the gold porphyrin, which is formed with a yield of unity (calculated on the basis of the photons absorbed by this unit only) and has a lifetime of 1.4 ns, both typical of the model PAu. This indicates that the energy absorbed at 532 nm by the free-base moiety in the triad is not funneled to the triplet state of the gold porphyrin and that the triplet state of the gold porphyrin that is directly formed by irradiation at 532 nm is not quenched.

In the absence of any detectable photoproduct and excluding the possibility of an external heavy atom effect, which would be active also at 77 K in a glass, the quenching of the free base porphyrin singlet in PH_2-[Ir] and in PH_2-[Ir]-PAu, which occurs with a rate of $k = 3.3 \times 10^{10}\,s^{-1}$, must be ascribed to electron and/or energy transfer occurring with 100% efficiency.

In the case of PH_2-[Ir], on the basis of the electrochemical and spectroscopic data, electron transfer from the porphyrin to the metal complex can be expected. This is in fact the only thermodynamically allowed process, with $\Delta G \approx -0.2$ eV. A transient absorption experiment with selective excitation of the PH_2 unit of PH_2-[Ir] ($\lambda_{exc} = 532$ nm) allowed the product of the electron transfer process, namely, the charge-separated state PH_2^+-[Ir]$^-$, to be detected (Figure 1). This spectrum, the main features of which are in agreement with those of the free-base porphyrin cation,[2, 4] decays with a lifetime of (75 ± 5) ps that is identical over the whole spectral range. The PH_2-localized triplet, measured with a nanosecond flash-photolysis apparatus ($\lambda_{exc} = 532$ nm), had a lifetime of 8 μs and a yield of 0.1. Therefore the decay of the charge-separated state PH_2^+-[Ir]$^-$ occurs essentially by charge recombination to give the ground state.

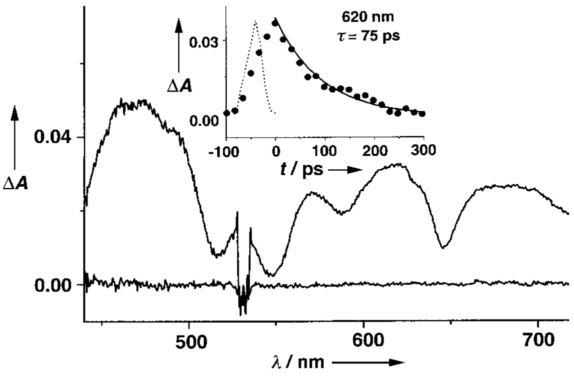

Figure 1. Transient absorption changes detected in a solution of PH_2-[Ir] in acetonitrile after a laser pulse (35 ps FHWM, $\lambda = 532$ nm). In the inset the decay of the absorbance at 620 nm is shown with the fitted decay function and the laser profile (---). A = absorption.

A schematic energy level diagram for PH_2-[Ir]-PAu, drawn by using the excited state energies (Table 1) and the electrochemical data, is shown in Figure 2. In the triad, the decay of the excited singlet state of the free-base porphyrin is identical to that detected in PH_2-[Ir]. Hence, the same process that for the diad was assigned to an electron transfer from the porphyrin excited state to the iridium complex is assumed to also occur in PH_2-[Ir]-PAu at the same rate ($3.3 \times 10^{10}\,s^{-1}$). Selective excitation of the free-base porphyrin moiety at 598 nm yields a transient state very similar to PH_2^+-[Ir]$^-$, which we assign to PH_2^+-[Ir]$^-$-PAu (Figure 3). The time evolution of this species, which decays with a lifetime of (40 ± 5) ps that is shorter than in the diad, leads to a longer-lived species with a rather broad and featureless spectrum. We identify the latter, which has a lifetime of (3.5 ± 0.3) ns, as the fully charge-separated state, PH_2^+-[Ir]-PAu$^-$, formed by a secondary electron-transfer step from the reduced Ir(III) complex to the easily reducible gold porphyrin unit ($\Delta G \approx -0.2$ eV). This assignment is in agreement with previous reports on similar charge-separated states.[4]

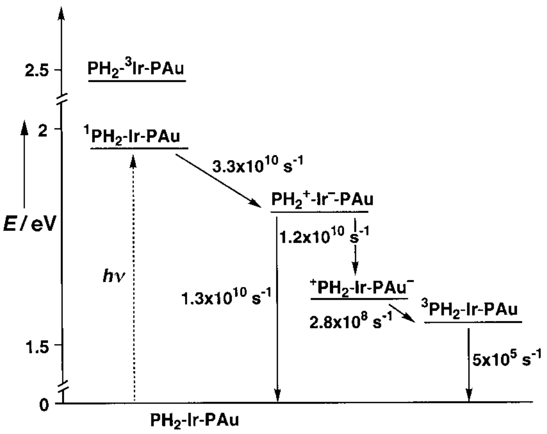

Figure 2. Schematic energy level diagram for the processes taking place in PH_2-[Ir]-PAu.

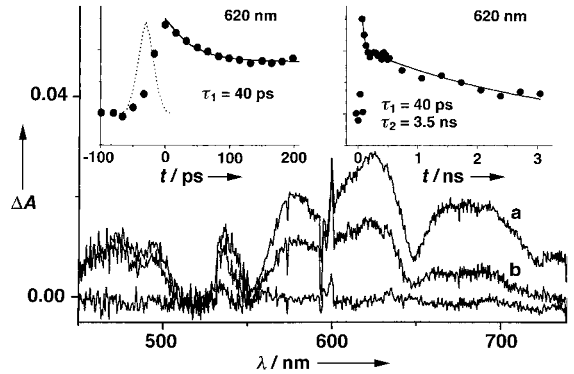

Figure 3. Transient absorption changes detected in a solution of PH_2-[Ir]-PAu in acetonitrile after excitation (35 ps FHWM, $\lambda = 598$ nm) at the end of the pulse (a) and 140 ps after the end of the pulse (b). In the insets the decay at 620 nm in two different time ranges is shown with the fitted functions. The laser profile is also plotted (---). A = absorption.

By comparing the lifetime of the PH_2^+-[Ir]$^-$ state in the diad (75 ps) to the lifetime of the PH_2^+-[Ir]$^-$-PAu state in the triad (40 ps), a rate for the secondary electron transfer (PH_2^+-[Ir]$^-$-PAu $\rightarrow$ PH_2^+-[Ir]-PAu$^-$) of $1.2 \times 10^{10}\,s^{-1}$ and an efficiency of approximately 50% can be derived. The triplet localized on the free-base porphyrin was examined in a nanosecond flash-photolysis experiment ($\lambda_{exc} = 532$ nm). This revealed a lifetime of 2 μs and a yield of 0.6, calculated on the basis of the photons absorbed by the PH_2 unit. The calculated yield allows us to establish that the PH_2^+-[Ir]-PAu^- state, formed by a two-step mechanism from the excited-state singlet of the free base, is essentially deactivated through the triplet state. The presence of this low-lying triplet state clearly facilitates charge recombination. It is expected that longer-lived charge-separated states can be obtained with other metalated porphyrins that do not display such low-lying triplet states.

The present system utilizes an iridium(III) complex as electron relay and central core. This species is particularly well suited to the construction of multicomponent assemblies that can undergo charge separation, as demonstrated, in particular, by the behavior of the triad PH_2-[Ir]-PAu. The fully charge-separated state is formed with a quantum efficiency of 0.5, and recombination is 50 times slower than in the corresponding diad PH_2-[Ir].

Experimental Section

Cyclic voltammetry was carried out in MeCN solution with Bu_4NPF_6 as supporting electrolyte, a Pt working electrode, a Pt counterelectrode, and a saturated calomel electrode (SCE) as reference. The typical sweep rate was 200 mV s^{-1}, and the window used was from -1.4 to $+1.3$ V. All waves were irreversible. 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 phosphorimeter accessory (1934 D). The time-resolved luminescence apparatus was based on an Nd:YAG laser (35 ps FHWM = full width at half maximum) and a Streak Camera. The standard iterative reconvolution procedure with the laser profile was used to measure emission lifetimes shorter than 90 ps. Transient absorbance in the picosecond range was measured with a pump and probe system based on the same laser and an OMA detector. Time zero for these experiments was set at the end of the laser pulse, calibrated by a 3,3′-diethyloxadicorbocyanine iodide (DODCI, $C_{23}H_{23}N_2O_2I$) solution in methanol,[11] and decay analysis was performed after the end of the laser pulse. Under these conditions deconvolution of the signal with the laser profile was unnecessary. For excitation at 598 nm, the second harmonic (532 nm) was Raman-shifted by a cell containing perdeuterated cyclohexane. The PH_2 triplet yields and lifetimes were determined by a laser flash photolysis apparatus with a Nd:YAG laser (20 ns pulse). Triplet yields were measured in oxygen-free solutions with the models PAu and PH_2 as reference, only the photons absorbed by the examined unit were taken into account, and calculations were performed on the basis of the molar absorption coefficients. The error for quantum yield determinations was 20 % and that for lifetime determinations 10 %, unless otherwise specified. Further details on the experimental setup, solvents, sample preparation and experimental procedures can be found elsewhere.[5, 11, 12].

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A Hermaphrodite Molecule: Quantitative Copper(I)-Directed Formation of a Doubly Threaded Assembly from a Ring Attached to a String[**]

M. Consuelo Jiménez, Christiane Dietrich-Buchecker, Jean-Pierre Sauvage,* and André De Cian

Whereas catenanes, rotaxanes, and knots were regarded as laboratory curiosities only 15 years ago,[1] they are now relatively common molecules[2, 3] with a fast growing number of uses regarding electron transfer,[4] polymers,[5] and controlled molecular motions. The last-mentioned field of research is particularly active and has recently produced

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