

Charge separation and energy transfer in multicomponent porphyrinic arrays*

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Abstract: An overview of the recent activity of the laboratory in the determination of the photophysical properties of porphyrinic arrays, with emphasis on the theme of photoinduced charge separation, is presented.

INTRODUCTION

The wide use of porphyrins in synthetic molecular arrays for the conversion of light into chemical energy is based on imitation of nature, which uses this and closely related chromophores for the collection of light energy, for its storage, transport, and final utilization in the photosynthetic reaction centers. What has been in nature the result of an evolutionary selection is based on the outstanding properties of these molecules as photo- and electro-active agents. High absorption coefficients in the visible, high-emission yields, and the possibility of tuning the redox properties by simple changes in the molecular structure have been some of the reasons of the success of this class of molecules in the evolutionary competition. A further reason that increases the degree of their appreciation by photochemists is the fact that the intermediates that follow light excitation are characterized by strong spectroscopic diagnostic signals, both as emission and/or as absorption features, in the easily accessible UV–vis range. This allows the rare opportunity to precisely identify the intermediates and their time evolution with the possibility to detect each elementary step and unravel the complex kinetic schemes associated with multicomponent systems. This understanding is the necessary basis for assigning a precise role to each different parameter which can affect the photoreactivity, with the consequent possibility to act at the design level for the improvement of the desired performances.

This report intends to show the contribution of a detailed photophysical characterization to the design of multicomponent systems able to perform light-triggered actions. In particular, the role of energy-transfer processes in systems designed to achieve charge separation will be addressed, and its occurrence, generally regarded as competitive, will be shown to assist electron transfer in selected cases and to contribute to the overall efficiency of charge separation.

CHARGE SEPARATION

Figure 1 schematically illustrates two simple three-component systems (triads) to achieve charge separation over nanometric distance. The active components can be separated by spacers whose role will not be discussed here. The two devices differ in the fact that in Case A, the photoactive component (P) from which the multistep vectorial electron transfer originates is at one extremity of the array, while in Case B, the photoactive primary electron donor is in the center of the array. The electron-transfer sequences in the two cases are different (see numeration) and so are the electrochemical and spectroscopic requirements of the component units. In particular, in Case A, component P in its excited state (P*) should be

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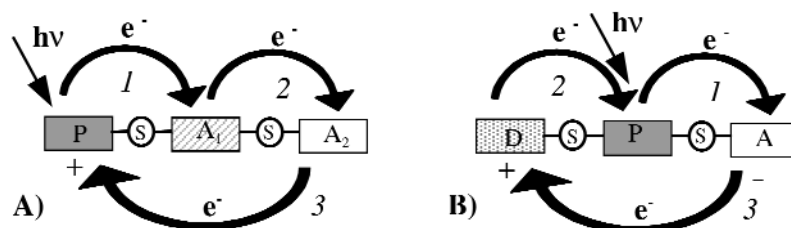


Fig. 1 Two simple types of charge-separation devices.

able to reduce A_1 which, once it has been reduced, should be able to transfer an electron to the final acceptor A_2 ; in Case B, the excited component P^* should be able to reduce A and, once in the oxidized form, it should be reduced by a close-lying electron donor D, to the original P. In the former case, the final charge-separated state is a $P^+-A_1-A_2^-$, in the latter is a D^+-P-A^- , in any case the electron and the hole are located at the extremities, and the final goal is that of keeping them separated as long as possible.

Type A device

In Fig. 2 is reported a general formula of a linear, covalently linked porphyrinic array assembled around a bis-terpyridine metal complex with zinc or free-base tetra-aryl porphyrins as photosensitizer and primary electron donor (P) and gold(III) porphyrin as final electron acceptor.

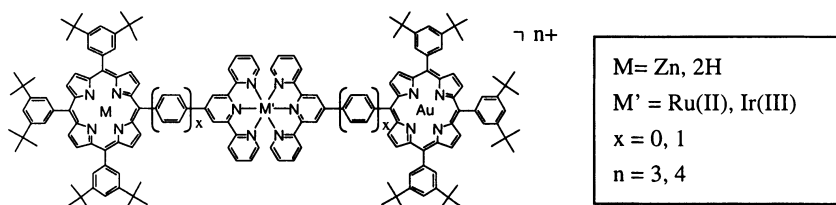


Fig. 2 General scheme of a triad containing a bis-terpyridine complex and porphyrins.

The role of the central metal complex is that of acting as an electron relay, accepting at first electrons by the excited state of the zinc or free-base porphyrin, and transferring them to the final acceptor A_2 , more prone to reduction. Both the photophysical and the electrochemical properties of the central metal complex are crucial. Use of Ru(II) bis-terpyridine complex has proven to: (i) provide insufficient driving force for the primary electron transfer to occur; and (ii) offer a deactivation path by energy transfer since this complex has an excited state ($^3\text{MLCT}$) close in energy to the singlet state of the porphyrin photosensitizer [1]. This unusual quenching process involving the porphyrin singlet excited state and the lowest MLCT of the Ru(II) complex, which is formally a triplet, is made possible by the perturbation brought about by the Ru(II) heavy metal ion. The occurrence of energy-transfer processes from the free-base porphyrin which acts as an energy donor rather than an electron donor, is competitive to the primary electron transfer and prevents charge separation (Fig. 3). A subsequent approach made use of Ir(III) bis-terpyridine, whose properties [2] proved to be promising for the construction of such type of device. Ir(III) bis-terpyridine displayed, in fact, the lowest excited state (^3LC) well above in energy to the excited state of the porphyrin donor, inhibiting an energy-transfer process. The reduction potential of Ir(III) bis-terpyridine is less negative than that of the Ru(II) complex, increasing the driving force for the primary electron transfer. A triad based on Ir(III) bis-terpyridine complex and bearing free-base and

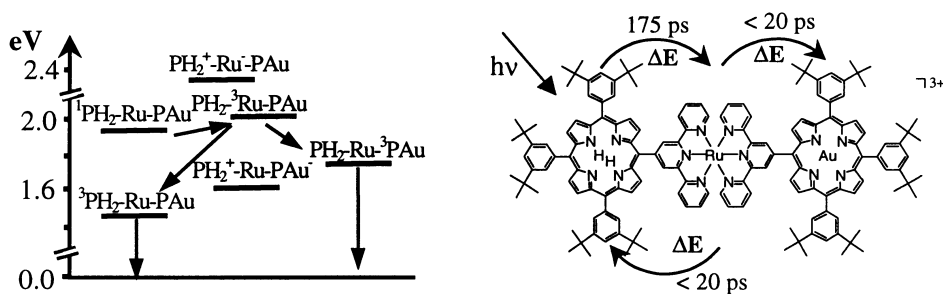


Fig. 3 Energy-level scheme and graphical summary of processes in $\text{PH}_2\text{-Ru-PAu}$.

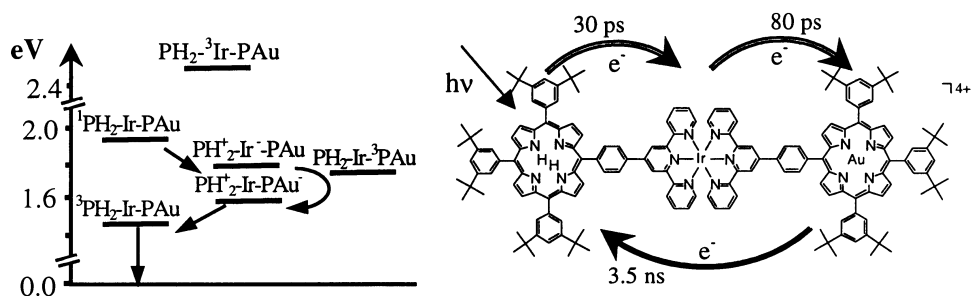


Fig. 4 Energy-level scheme and graphical summary of processes in $\text{PH}_2\text{-Ir-PAu}$.

gold(III) porphyrins as electron donor and electron acceptor, respectively, can efficiently act as a charge-separation device upon excitation of the free-base porphyrin, as summarized in Fig. 4 [3]. A further improvement is being pursued with the use of zinc porphyrin as primary donor, characterized by higher excited state energy and better reducing action.

Type B device

The array of Fig. 5 is similar to the previous one, since zinc and gold(III) porphyrins are present in the structure [4]. Nevertheless, the properties of the Cu(I) complex, which is a poor oxidant, do not permit a primary electron transfer from zinc porphyrin to the copper complex. What is feasible in the present array is: (i) energy transfer from zinc porphyrin singlet to the $^1\text{MLCT}$ excited state of the copper complex and (ii) electron transfer from the excited copper (I) complex to the nearby gold (III) porphyrin. To notice that, because of the bulky porphyrinic substituents on the phenanthroline ligand, the oxidation potential of Cu(I) is dramatically increased with respect to that of substitution with plain phenanthroline, and overcomes that of the zinc porphyrin with the obvious consequence that copper(II) can be reduced by the ground-state zinc porphyrin. Therefore, this assembly meets the conditions for a type B device where, upon excitation of the copper(I) unit, the electronic sequence illustrated above for device B could occur. What appears to be a serious drawback of the system, the fact that the light is absorbed by porphyrins (and not by the copper complex), is overcome by an efficient energy transfer from zinc porphyrin to the copper unit. An efficient charge separation originating from a photoexcited copper complex sensitized by the porphyrin takes place in agreement with the general scheme described for type B. In Fig. 6 a schematic energy level diagram and the elementary steps of the overall reaction are reported [4]. In this case, the occurrence of an energy-transfer process is of key importance for the occurrence of charge separation.

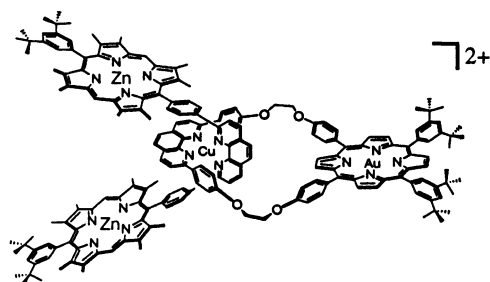


Fig. 5 The Cu(I) rotaxane $Zn_2-Cu-Au$.

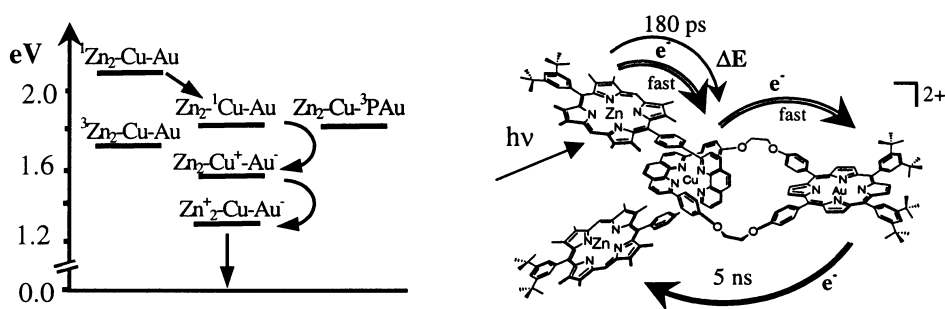


Fig. 6 Energy-level diagram and graphical summary of processes occurring in $Zn_2-Cu-Au$.

CONCLUSIONS

The few examples reported here show that the detailed determination of the elementary steps occurring upon photoexcitation of multicomponent systems of even modest complexity is essential to optimize the design. Energy-transfer processes in charge-separation devices are discussed, and their role in competing or assisting the desired function is illustrated.

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