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COMMUNICATION

Sevenfold enhancement on porphyrin dye efficiency by coordination of ruthenium polypyridine complexes†‡

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Sevenfold enhancement of photoconversion efficiency was achieved by incorporation of peripheral ruthenium complexes to a porphyrin dye, generating supramolecular effects capable of playing several key roles (*e.g.*, transferring energy to, inhibiting aggregation, and accepting the hole generated in the porphyrin center after electron injection), providing new insights for the design of better DSSC photosensitizers.

Since Grätzel's seminal paper[1] in 1991, research on dye sensitized solar cells (DSSCs) increased explosively all over the world.[2,3] Several classes of molecules have been synthesized[4,5] and tested since then, but the Ru(II) polypyridine complex based dyes were always on the top, showing IPCEs as high as 80% in the visible range and up to 11% overall light-to-electricity conversion efficiency (η).[6] However, increasingly higher values of η have been gradually achieved with new porphyrin dyes[7–9] and, very recently, a special combination of porphyrin dye/[Co(bpy)$_3$] electrolyte system was reported, surpassing the two-decade long 11% efficiency threshold.[10]

Many efforts have been focused on innovative strategies to improve the efficiency of photosensitizers using the supramolecular approach[11–14] since Bignozzi *et al.*,[15,16] demonstrated the concept, using a trinuclear ruthenium polypyridyl complex. Subsequently, many linear, branched and star shaped porphyrin arrays were reported, but exhibiting no significant antenna effect.[17] In fact, porphyrins and ruthenium(II) polypyridine complexes have been successfully employed as building-blocks of supermolecules showing electrocatalytic and photoelectrochemical properties.[18–20] Energy transfer and photoinjection from the ruthenium polypyridine and porphyrin moiety were observed in the photoaction spectra of DSSCs prepared with those dyes, but no significant effect was observed on η probably because they lack TiO$_2$ binding sites.[20–22] Accordingly, here we designed a new supramolecular porphyrin dye encompassing a *meso*-4-carboxyphenyl binding site as well as three [Ru(dmbpy)$_2$Cl]$^+$ complexes (dmbpy = 4,4'-dimethyl-2,2'-bipyridine) coordinated to the *meso*-(4-pyridyl) positions as antennae[23] (Fig. 1A).

The *I–V* curves (Fig. 2) consistently reflect the superior efficiency of the new supramolecular porphyrin dye in comparison with the parent free-base 5-(4-carboxyphenyl)-10,15,20-tri(4-pyridyl)-porphyrin (MCTPyP) and its respective zinc(II) complex (Zn-MCTPyP). In fact, the short-circuit photocurrents measured for the parent porphyrin dyes were 0.5 and 0.8 mA cm^{-2}, while the cells prepared with MCTPyPRu$_3$ and Zn-MCTPyPRu$_3$ showed much higher performance of 3.1 and 4.6 mA cm^{-2}, respectively. Also, the open circuit photovoltage increased from about 0.37 V to 0.41 and 0.50 V suggesting the occupation of higher TiO$_2$ conduction band energy levels as the flux of injected photoelectrons was increased.[16] Since the optical density of the cells were similar for the cells prepared with the conventional and ruthenated porphyrins, a sevenfold enhancement on η (from 0.11 to 0.77 and 0.17 to 1.2%, respectively) was achieved as a consequence of coordination of [Ru(dmbpy)$_2$Cl]$^+$ complexes to the parent MCTPyP and Zn-MCTPyP porphyrin dyes (Fig. 2).

MCTPyP exhibits the Soret band at 416 nm and Q bands at 512, 546, 588 and 643 nm, while Zn-MCTPyP showed bands at 425, 557 and 597 nm, in DMF solution (ESI‡).[23] The coordination of [Ru(dmbpy)$_2$Cl]$^+$ complexes to the peripheral pyridyl N-atoms slightly perturbed the porphyrin energy levels and introduced new absorption bands, characteristic of the ruthenium complexes, at 294 and 505 nm, respectively, assigned to dmbpy pπ–pπ* and Ru^{II}(dπ) → dmbpy(pπ*) charge-transfer transitions.

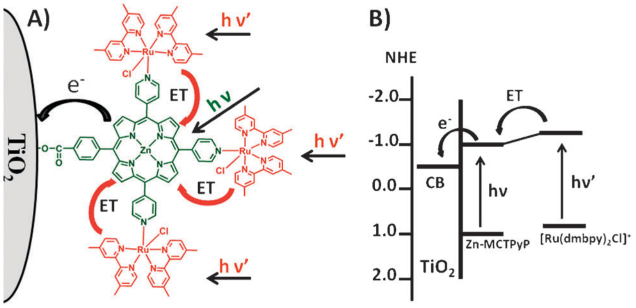

Fig. 1 (A) Scheme showing the supramolecular Zn-MCTPyPRu$_3$ dye anchored on a TiO$_2$ surface. Electron injection takes place after direct excitation of the zinc(II) porphyrin moiety or energy transfer (ET) from the peripheral ruthenium complexes. (B) Energy diagram showing the photo-induced processes at the TiO$_2$/dye interface.

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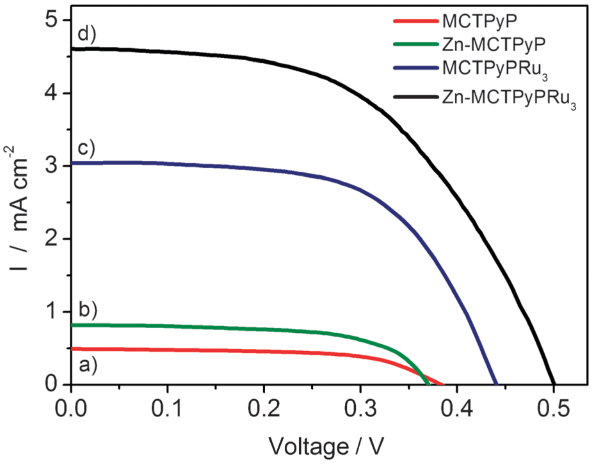

Fig. 2 Current–voltage curves measured for DSSCs sensitized with (a) MCTPyP, (b) Zn-MCTPyP, (c) MCTPyPRu$_3$ and (d) Zn-MCTPyPRu$_3$ porphyrin dyes, under AM 1.5 illumination (100 mW cm^{-2}).

The analysis of the photoaction spectra allowed us to evaluate the contribution of the peripheral ruthenium complexes to the quantum efficiency of the supramolecular dyes. The reflectance spectrum of Zn-MCTPyPRu$_3$ adsorbed on mesoporous TiO$_2$ (Fig. 3) exhibited broadened Soret and Q bands at 430, 563 and 609 nm, as well as the MLCT band characteristic of ruthenium(II) polypyridines at 505 nm. As expected, this band is absent in the parent MCTPyP and Zn-MCTPyP porphyrin dye absorption and photoaction spectra.

Note that the relative intensity of the MLCT band is similar in the photoaction and reflectance spectrum. This is a clear indication that the excited MLCT state to porphyrin energy transfer quantum efficiency is very high, such that the contribution of peripheral ruthenium complex is probably limited by porphyrin injection into TiO$_2$ conduction band. However, the IPCE enhancement around 505 nm alone cannot account for the seven-fold increase of η. This must be a consequence of the enhanced conversion efficiency achieved in the whole visible range, as evidenced by the comparison of the photo-action spectra shown in Fig. 3.

The contribution of the ruthenium complexes can be better understood by considering the energy level diagram shown in Fig. 1B. The singlet excited state potential of Zn-MCTPyP, $E(S^+/S^*) = E(S^+/S) - E^{0-0}$, is 0.45 V above the TiO$_2$ conduction band edge (−0.50 eV) ensuring electron injection into the conduction band. The excited state potentials of MCTPyP and Zn-MCTPyP were estimated from the respective ground state redox potentials, determined by cyclic voltammetry, and the energy of the lowest energy electronic transition (E^{0-0}), as −0.64 and −0.94 eV.

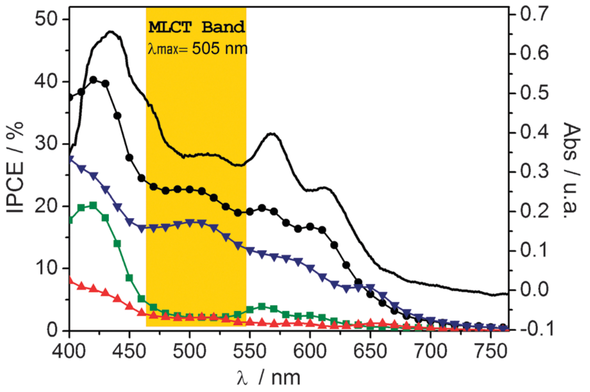

Fig. 3 Photocurrent action spectra of DSSCs using MCTPyP (—▲—), Zn-MCTPyP (—■—), MCTPyPRu$_3$ (—▼—) and Zn-MCTPyPRu$_3$ (—●—) as photosensitizer. The solid black line refers to the absorption spectrum of Zn-MCTPyPRu$_3$ adsorbed on TiO$_2$.

In addition, the excited state energy of the peripheral ruthenium complexes is high enough to transfer energy to the lowest singlet excited state of the porphyrin through Förster or Dexter mechanisms. In contrast, the free-base porphyrin was found to exhibit an excited state potential only about 0.14 eV above the TiO$_2$ conduction band. This small driving force should be responsible for a much slower electron photoinjection kinetics,[24] consistent with their much lower photoconversion efficiency as compared with the respective zinc(II) porphyrin derivatives. In fact, according to Durrant *et al.*,[24] each 0.4 eV increase in ΔE reflects in an order of magnitude enhancement on the electron injection rate. Actually, the best porphyrin photosensitizers were found to be characterized by excited state electron injection potentials higher than −1.3 eV,[24,25] well above the TiO$_2$ conduction band edge.

Our supramolecular porphyrin dye was specially designed pursuing energy transfer to the porphyrin and hole transfer to the peripheral ruthenium complexes (E^0 porphyrin > E^0 ruthenium complexes), thus inhibiting the electron–hole recombination and increasing the overall light harvesting efficiency. In our case, the possibility of direct electron injection from the excited ruthenium complexes to TiO$_2$ cannot be ruled out, since their excited state potential is higher than $E(S^+/S^*)$, generating a potential gradient that may drive electrons directly to the semiconductor conduction band. Finally, the steric and coulombic repulsions should minimize aggregation, a process that is known to decrease the photo-injection efficiency of porphyrin dyes.[20] Therefore, we believe that such supramolecular porphyrins constitute a promising class of DSSC photosensitizers in which the light harvesting efficiency should be further enhanced if porphyrin derivatives possessing higher (more negative) electron injection potentials are used.

In conclusion, more than simply enhancing the light harvesting in the visible spectrum, the peripheral ruthenium complexes promoted a sevenfold enhancement of the energy conversion efficiency (as compared with the parent species) by playing several key roles (inhibiting aggregation, transferring energy to and accepting the hole generated in the porphyrin after electron injection), revealing important new insights for the design of more efficient supramolecular porphyrin dyes.

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