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Sensitization of TiO_2 by Supramolecules Containing Zinc Porphyrins and Ruthenium–Polypyridyl Complexes

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Modification of wide band gap semiconductor surfaces by a new generation of supramolecular sensitizers combining porphyrin and ruthenium–polypyridyl complexes leads to versatile molecular interfaces, allowing the exploitation of photoinduced charge transfer in photoelectrochemical devices.

Since the announcement of 10% efficiency, dye sensitized photoelectrochemical cells (DSSC) based on a nanoporous TiO_2 have been attracting widespread attention because of their relatively low energetic cost, easy preparation, and great potential.[1] Up to the present time, metal polypyridyl complexes, particularly Ru(II), are so far the most investigated sensitizers for DSSC applications.[1−3] In these complexes, the MLCT transitions account for nearly all the visible light absorption. To increase the light harvesting capability, several approaches have been employed, and the use of supramolecular species remains as an elegant and scientifically interesting alternative. Bignozzi et al. were the first ones to exploit the photoinduced charge separation and antenna properties of supramolecular polypyridyl metal complexes.[4]

Porphyrins, phthalocyanines, and related macrocycles such as *meso*-tetrapyridylporphyrins and *meso*-tetraphenylporphyrins have been extensively employed as building blocks for assembling supramolecular systems, stimulated by their photochemical, electrochemical, and catalytic properties.[5−9] These organic dyes are also well-known TiO_2 sensitizers due to their strong absorption at 400−450 nm (B or Soret band) and 500−700 nm (Q bands).[2,10−12]

In the past decade we focused our efforts on the preparation and characterization of tetrapyridylporphyrins (TPyP) coordinated to four $[Ru(bipy)_2Cl]^+$ and $[Ru(phen)_2Cl]^+$ complexes (bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline), in solution and as thin molecular films.[13,14] We have shown energy transfer from the peripheral groups to the porphyrin ring in *meso*-tetrapyridylporphyrins containing four $[Ru(bipy)_2Cl]^+$.[15] This supramolecule was initially tested as sensitizer,[16] but it adsorbed too weakly to yield significant photoeffects. In contrast, the zinc porphyrins (ZnTPyP) coordinated to four $[Ru(phen)_2Cl]^+$ and four $[Ru(bipy)_2Cl]^+$ (TRu$\underline{\text{phen}}$ZnTPyP and TRu$\underline{\text{bipy}}$ZnTPyP, Figure 1a,b) adsorbed rather strongly, producing photoelectrochemically active red-brown films. It is important to notice that the dye remains strongly adsorbed onto the oxide films after the photoelectrochemical measurements, even without using typical anchoring groups such as hydroxyl, carboxyl, or phosphonate. In addition, dye desorption induced by solvent or electrolyte has not been observed, as deduced from the identical absorption spectra obtained before and after the experiments. In this work we focus on the characterization of the novel molecular interfaces with TiO_2 and their corresponding photoaction response. To our knowledge, the photoelectrochemical behavior of such a supramolecular tetraruthenated metalloporphyrin has never been reported before.

The energy diagram for the supramolecular species is shown in Figure 1c. In this diagram, the redox potentials in the ground (HOMO) and excited states (LUMO) estimated

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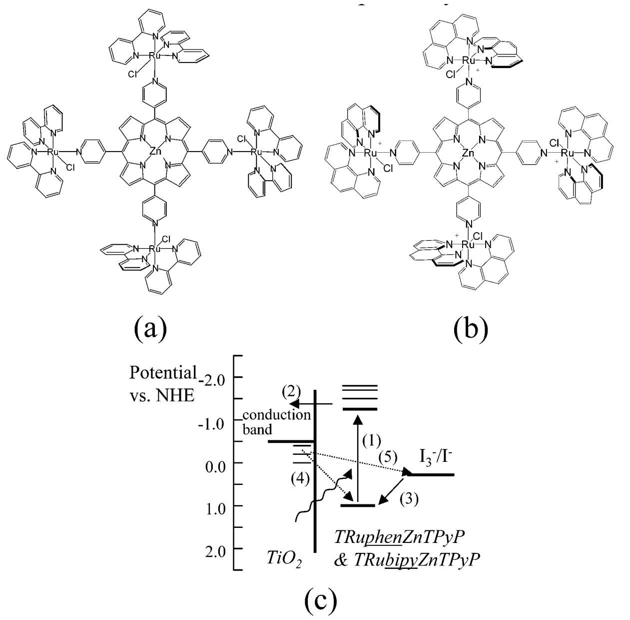

Figure 1. Molecular structure of the supramolecular species constituted by *meso*-tetrapyridylporphyrin coordinated to (**a**) four $[Ru(bipy)_2Cl]^+$ (bipy = bipyridine) (TRubipyZnTPyP); (**b**) four $[Ru(phen)_2Cl]^+$ (phen = phenanthroline) (TRuphenZnTPyP). (**c**) Schematic representation of the energy diagram for the DSCC and the most important kinetic processes: (1) dye absorption; (2) electron injection into TiO_2; (3) dye regeneration; (4) charge recombination; (5) dark current.

using the electrochemical and fluorescence spectral data are, respectively, 0.96 and −1.2 V vs NHE for both species. The potential of the conduction band of the TiO_2 electrode is −0.5 V, and the redox potential of the I_3^-/I^- couple is 0.4 V vs NHE.[2,17] According to the energy diagram, the electron injection and the regeneration processes are energetically favorable. (The free energies calculated for processes 2 and 3 are $-\Delta G = 0.7$ eV and $-\Delta G = 0.6$ eV, respectively.) The energy levels were calculated from the ground state Ru(II)/Ru(III) potential and E_{0-0} value, considering that, after dye excitation (1) and electron injection to TiO_2 (2), the hole is localized on one of the ruthenium moieties of the supramolecular porphyrin in agreement with electrochemical[13,15] and theoretical data.

Typical photoaction spectra (IPCE curve vs λ) of the photoelectrochemical devices assembled with TiO_2/TRuphenZnTPyP films prepared from different solutions are shown in Figure 2. The electronic spectrum of the TRuphenZnTPyP species in ethanol solution, whose pattern was essentially unchanged in other solvents, was included for comparison purposes. Except for the strong photoaction response observed at 350 nm from the direct excitation of the TiO_2, the IPCE curves resemble the spectrum of the supramolecular dye, displaying the characteristic Soret, MLCT, and two Q bands at 440−450, 480−530, 575, and 620 nm, respectively.

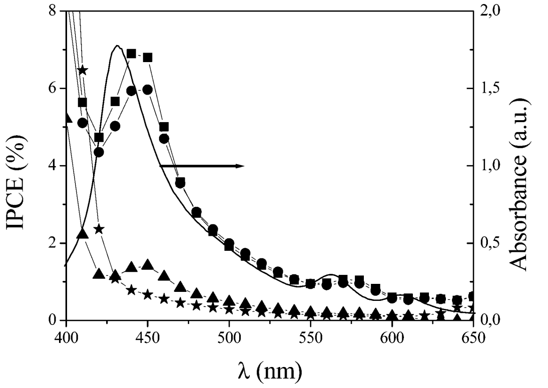

Figure 2. IPCE curves for the DSSC assembled with TiO_2/TRuphenZnTPyP films prepared from different solutions: (−●−) ethanol; (−■−) ethanol/acetonitrile (2:1); (−▲−) 2,2,2-trifluorethanol; and (−★−) bare TiO_2. The solid line refers to the absorption spectrum in ethanol.

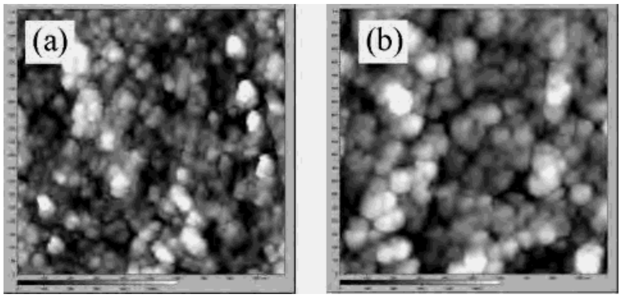

Figure 3. MAC mode AFM micrographs of TiO_2 nanoporous films (a) before and (b) after the coating with TRuphenZnTPyP prepared from ethanol solution.

Different photocurrent responses were obtained for the devices using films prepared from trifluoroethanol, ethanol, and acetonitrile solutions, as can be seen in Figure 2. In fact, films prepared from trifluoroethanol solution exhibited OD < 0.04, while the films prepared from ethanol/acetonitrile and ethanol solutions showed OD = 0.04 and 0.4, respectively, at 615 nm. Accordingly, we would expect that the films generated from ethanol, would give rise to the highest IPCE values. However, the IPCE measured at 440−450 nm was lower than that of the film obtained from ethanol/acetonitrile (2:1) solution, suggesting that, in that case, the supramolecular species are present as aggregates onto the TiO_2 surface. It is well-known that aggregation of porphyrins is a drawback for high efficient photoenergy conversion, promoting excited state quenching via fast energy transfer. The insulating nature of the thick dye layers can also contribute to lower the electron transfer efficiency. Possibly, from our results, the combination of solubility and aggregation should be optimized, to improve the efficiency of the devices. This is an important aspect, usually neglected in the study of porphyrin sensitized TiO_2 films. In fact, it may be, in part, responsible for the wide range of IPCE values obtained from different porphyrin assemblies.[10,11,18−20]

Typical MAC mode AFM micrographs of TiO_2 and TiO_2/TRuphenZnTPyP films generated from ethanol solution are shown in Figure 3. The films show a rather uniform distribution of nanosized TiO_2 particles. The presence of the supramolecular films leads to an apparent increase in the average particle size, from 20−50 nm to 50−100 nm. This

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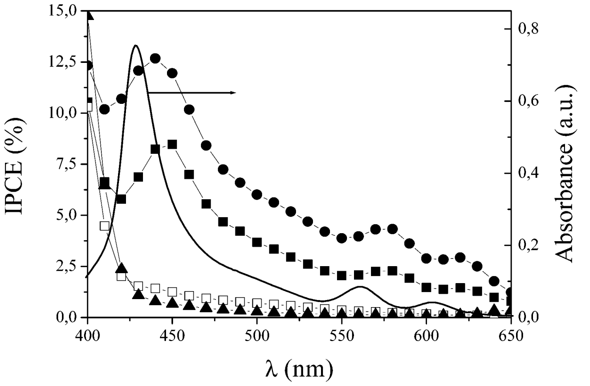

Figure 4. IPCE curves for the DSSC assembled with TiO$_2$/TRubipyZnTPyP (−●−); TiO$_2$/TRuphenZnTPyP (−■−); free base TRubipyTPyP (−▲−); bare TiO$_2$ (−□−). All films were prepared from acetonitrile solution. The solid line refers to the absorption spectrum of the TRubipyZnTPyP in acetonitrile.

can be related to the agglomeration of the supramolecules, masking the TiO$_2$ particle boundaries.

Based on the previous results, the photoaction spectra of the TRuphenZnTPyP and TRubipyZnTPyP species were obtained for the films prepared from acetonitrile solution (Figure 4). For comparison we have included the spectra of bare TiO$_2$ and free base TRubipyTPyP (without Zn), showing, in both cases, a rather poor photoaction response. The response for the TRuphenTPyP is identically poor. In contrast, analogously to the TRuphenZnTPyP species, TRubipyZnTPyP exhibited much higher IPCE values, reaching 13% at maximum absorption of the supramolecule (Soret band).

In the IPCE curves for TRubipyZnTPyP and TRuphenZnTPyP, we can observe contributions from porphyrin bands (440, 580, and 620 nm) and Ru(II) complexes (broad band centered at 510 nm). In all photoaction spectra (Figures 2 and 4), the porphyrin bands are red-shifted with respect to the species in solution, indicating that the supramolecular species can interact with the TiO$_2$ surface via porphyrin core. The free base supramolecules, TRubipyTPyP and TRuphenTPyP, did not adsorb onto TiO$_2$; as a consequence no photoeffect could be detected. This result is clear evidence that the attachment of our supramolecules containing metalloporphyrins should involve a binding between the central Zn(II) ion and the hydroxyl groups of the TiO$_2$ surface as previously reported in the literature for another zinc porphyrin system.[21]

The remarkable similarity between the absorption and photoaction spectra shown in Figures 2 and 4 indicates that all the chromophore groups, porphyrin and peripheral ruthenium complexes are contributing to the photocurrent. To get more information about the electron transfer processes, we performed some theoretical calculations using the ZINDO/S method (for more details, see the Supporting Information) for the TRuphenZnTPyP species. A remarkable point is the strong mixing of the porphyrin and ruthenium molecular orbitals in the HOMO level (MO413 = 38.3% Ru, 8.1% phen, 11.6% py, 40.5% porphyrin), while the LUMO level (MO414 = 0.9% Ru, 11.0% py, 87.5% porphyrin) exhibits essentially porphyrin character. These observations imply that, in fact, the porphyrin and ruthenium complexes cannot be considered as isolated groups. The theoretical calculations also revealed that MO(401,413) → MO(414,415) transitions are responsible for the vibronic Q$_{(0-0)}$ and Q$_{(0-1)}$ bands at 606 and 563 nm, respectively and that the MO(400,401) → MO(414,415) transitions are responsible for the observed Soret band at 430 nm. Since both MO400 and MO413 involve significant ruthenium−porphyrin mixing, we can conclude that, in the supramolecular species, the porphyrin Soret and Q bands are also influenced by the ruthenium complexes. According to the calculations, the Ru ($d\pi$) → phen($p\pi$) charge-transfer transitions in the [Ru(phen)$_2$Cl]$^+$ groups are expected to occur in the 434−550 nm range, contributing to the broad shoulder observed in this region. Interestingly, in the 400−430 nm range, the electronic transitions involve excitation from the HOMO levels, with predominant Ru(II) contribution, to excited levels essentially localized on the porphyrin ring. Thus, in this particular spectral range, coinciding with the Soret band, the electronic transitions exhibit a large charge-transfer character, from the peripheral Ru(II) complexes to the porphyrin center.

In the case of porphyrin systems, there is an agreement that electron injection occurs from the lowest singlet excited state.[11,22] For the tetraruthenated porphyrins, the mechanisms involved in electron transfer are more complex, since both components are responsible for photocurrent generation. As already discussed, from the HOMO and LUMO compositions, the peripheral ruthenium complexes can effectively transfer electronic charge to the porphyrin center via Ru ($d\pi$) → porphyrin MLCT transitions. Finally, we have also shown that the direct interaction between the ZnTPyP core and TiO$_2$ plays an important role in the photoresponse efficiency. Because of the several aspects involved, efforts are being directed in our laboratory to improve the photon energy conversion, particularly, to find a better commitment between solubility and aggregation of the different modifiers.

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Supporting Information Available: Preparation of the TiO$_2$ films, assembling the DSSC, theoretical calculations, and photoelectrochemical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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