COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Porphyrin capped TiO_2 nanoclusters, tyrosine methyl ester enhanced electron transfer†

Junhua Yu, Jingrong Chen, Xuesong Wang,* Baowen Zhang* and Yi Cao

Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, P. R. China.
E-mail: g203@ipc.ac.cn; Fax: 86-10-64879375; Tel: 86-10-64888103

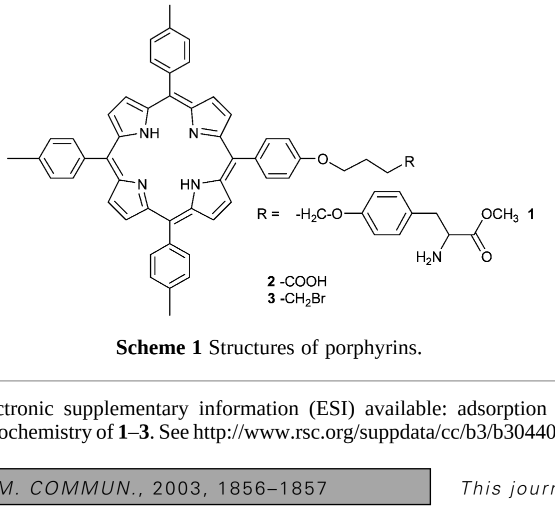
Received (in Cambridge, UK) 24th April 2003, Accepted 28th May 2003
First published as an Advance Article on the web 19th June 2003

The photoinduced electron transfer between neutral titanium dioxide nanoclusters and porphyrin is enhanced by the bridging of tyrosine methyl ester to the two components.

Heterogeneous systems for photoelectron transfer and photoionization have been extensively studied owing to their advantage in light energy storage as well as photodecomposition of toxic wastes.[1–3] Such a system is believed to yield high charge separation and low back-electron transfer. The rates of electron injection for different dyes were reported to be in the femtosecond time domain and those of recombination in the time range from tens of picoseconds up to milliseconds, and these are partly determined by the linkage of the dyes to the semiconductor particles.[4–6] The attaching group is usually carboxy by virtue of the formation of an ester bond and the electron transfer would be weak in alkaline solution because of the hydrolysis of the ester bond, except where there is adsorption on the surface of the semiconductor by electrostatic interaction.[2,7]

Here we use tyrosine methyl ester as a bridge between titanium dioxide‡ nanoclusters and tetratolylporphyrin (TTP) (Scheme 1) in neutral ethanol solution to investigate the photoinduced electron transfer in a heterogeneous system. Tyrosine has attracted much attention for its indispensable function in nature. To act as an electron relay station in Photosystem II (PS II) is one of its contributions to nature, in which tyrosine reduces the originally produced P_{680}^{+} and then is regenerated by retrieving an electron from a manganese cluster.[8] In this communication, the tyrosine bridge in **1** was found to facilitate the electron transfer between TiO_2 nanoclusters and the TTP chromophore, which otherwise was too inefficient to be detected.

The concentrations of porphyrin and TiO_2 were kept at 2.3×10^{-5} mol L^{-1} and 1 g L^{-1}, respectively, for photolysis and fluorescence lifetime measurement (single photon counting), and the samples were degassed with N_2 for at least 30 min. The lifetimes were determined from kinetic analysis of the transient decays, carried out using Levenberg–Marquardt nonlinear fitting programs. For the electron paramagnetic resonance (EPR) experiments, the samples became more concentrated. The above experiments were all excited by Nd^{3+}:YAG laser at 532 nm, and for each kind of measurement, the laser energy is kept constant (1–5 mJ).



Scheme 1 Structures of porphyrins.

The incorporation of the tyrosine methyl ester in the side chain of TTP as end group has little influence on the electronic absorption spectrum of TTP, and **1**, **2** and **3** have the same absorption character in the visible region with a B band at 416 nm and Q band at 515, 550, 592 and 648 nm, respectively. The steady state absorption spectra and fluorescence spectra have no change in the presence of TiO_2, indicating a weak ground-state and singlet excited-state intercoupling between the porphyrins and TiO_2 nanoclusters. The fluorescence lifetime measurement also supports such a statement, *i.e.*, the fluorescence lifetimes of compound **1** at 658 nm in ethanol are 11.8 ns ($\chi^2 = 0.921$) with TiO_2 and 12.2 ns ($\chi^2 = 1.020$) without TiO_2; those of compound **2** are 12.1 ns ($\chi^2 = 1.043$) and 12.2 ns ($\chi^2 = 0.949$), respectively, and those of **3** are 12.5 ns ($\chi^2 = 1.044$ and 1.051, respectively) for both. The little change in fluorescence lifetimes and fluorescence intensities means there is no significant interaction such as electron transfer or energy transfer between the singlet excited states of the porphyrins and TiO_2 nanoclusters.

Nanosecond photolysis of the porphyrins shows the electron transfer between the triplet-excited porphyrin and TiO_2 in compound **1**. Each transient absorption spectrum of the porphyrins measured by laser flash photolysis at 532 nm exhibits a major peak around 440 nm which results from triplet–triplet absorption.[9] The lifetime of the triplet excited state of **1** in ethanol is 21 μs, becoming shorter after the addition of TiO_2 (for the transient absorption decays, see ESI†). The lifetime with TiO_2 can be fitted appropriately to the biexponential law, resulting in a shorter lifetime of 2.9 μs (95%) and a longer one of 23 μs (5%). Considering the fact that the singlet excited state of compound **1** is not affected by the addition of TiO_2, it can be reasonably concluded that the triplet excited state of **1** has been quenched by TiO_2, leading to the short lifetime, and the longer lifetime can be assigned to the porphyrin that has not been quenched efficiently.

Contrary to what we observed with **1**, the addition of TiO_2 to ethanol solutions of **2** and **3** gives no quenching of the triplet excited states of porphyrins. The triplet excited state lifetimes of **2** are 28 μs and 25 μs with and without TiO_2, respectively, and those of **3** are 34 μs and 32 μs, respectively. It is plausible that **1** attaches to the surface of the nanocluster by hydrogen bonds between the amino groups as well as the carbonyl groups of tyrosine and the surface state of TiO_2, and that **2** attaches by its carboxy group since carboxylic acid is very suitable for the attachment of dyes to TiO_2 and the adsorption of carboxy groups on TiO_2 can be stable under our experimental conditions.[10] However the interaction between nanoclusters and **3** would be weak because of the bromo group which is inert to the formation of hydrogen bonds. Due to the long triplet excited-state lifetime of **3** (*ca.* 30 μs) the diffusional quenching of unbound excited dye molecules would be allowed, given that the concentration of TiO_2 is about 1.3×10^{-5} mol L^{-1}.[11] We also tested their adsorption ability on TiO_2 by means of a thin solid TiO_2 film (see ESI†) and found that **2** with carboxy groups adsorbed even more strongly on TiO_2 than **1** did. The small

---

† Electronic supplementary information (ESI) available: adsorption and electrochemistry of **1**–**3**. See http://www.rsc.org/suppdata/cc/b3/b304403c/

DOI: 10.1039/b304403c

This journal is © The Royal Society of Chemistry 2003

influence of TiO_2 on the triplet excited state lifetimes of **2** and **3** means the electron transfer from TTP to TiO_2, responsible for the excited state quenching of porphyrin derivatives by semiconductor nanoclusters in many systems, is not strong enough to be detected in triplet multiplicity, as in their excited singlet states it made no difference whether the porphyrins are attached on TiO_2 surface or not.[12] The cathodic shift of the conduction band potential of TiO_2 nanoclusters (E_{CB}) upon pH increase (0.059 V per unit increase in pH)[13], which restricts electron injection from excited porphyrins to the TiO_2 conduction band by reducing the driving force of ($E_{CB} - E_{OX\text{-(excited-porphyrin)}}$), might partly account for the inertness of neutral TiO_2 to excited singlet or triplet porphyrins **2** and **3**. The lack of strong electronic coupling between excited porphyrins and TiO_2 may also be responsible for the observation of no excited singlet or triplet state quenching of **2** and **3** by TiO_2 *via* electron injection.[14]

The fact that **1** but not **2** and **3** is quenched by the addition of TiO_2 suggests that tyrosine methyl ester in **1** might play a unique role in facilitating the electron transfer between porphyrins and TiO_2. We can exclude the influence of redox differences of **1** to **3** on the energy gap between excited porphyrin and conduction band of TiO_2, and the driving force for the reaction between singlet excited-state porphyrin and tyrosine methyl ester is about 0.1 V and the triplet porphyrin and tyrosine methyl ester is about −0.5 V, thus the direct reaction between the two moieties is not favourable (see ESI†). A possible mechanism is proposed (see ESI†). It is difficult for the excited porphyrin (singlet, $^1P^*$) to inject an electron into TiO_2 due to the short singlet lifetime and the relatively long distance between dye and semiconductor, whereas the triplet excited state porphyrin ($^3P^*$) would have enough time to inject electron into TiO_2, probably through the bending of the side chain. Though it is not efficient in such a process, the injection would be enhanced by the tyrosine group in **1**. Once an electron is injected into the conduction band, the consequent cationic porphyrin radical can be reduced exoenergically by the nearby tyrosine. Such an injection becomes efficient by coupling with an analogous tyrosine-mediated reaction of naturally occurring in PS II now and, accordingly, the triplet-excited state is quenched as we observed. We may have to take the more flexible nature of **1** into account, but all these compounds are not so rigid that they can bend to the surface of the TiO_2, and the influence of side-chain bending might be small.

The enhanced electron-donating ability of TTP by tyrosine methyl ester can be also verified by EPR experiments. We used oxygen as the acceptor to replace TiO_2 and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as spin-trapping agent. When irradiated by 532 nm laser, the aerated ethanol solution of **1** exhibits a typical EPR signal attributed to the adduct of superoxide anion radical with DMPO (DMPO-$O_2^{-\cdot}$) as shown in Fig. 1 (inset). This spectrum is characterized by three coupling constants (α^N = 13 G, $\alpha_\beta{}^H$ = 10 G, and $\alpha_\gamma{}^H$ = 1.5 G), consistent with previously reported values for DMPO-$O_2^{-\cdot}$ radical adduct.[15] In the absence of light, oxygen or porphyrin, no EPR signal is detected, indicating that the formation of the DMPO-$O_2^{-\cdot}$ adduct is dependent on the presence of oxygen and the irradiation of porphyrin. The addition of superoxide dismutase (40 μg mL^{-1}) prior to illumination prevents the formation of DMPO-$O_2^{-\cdot}$ adduct efficiently, confirming its proper identification.

The EPR signal of the DMPO-$O_2^{-\cdot}$ adduct increases along with irradiation of the aerated ethanol solution of porphyrin and DMPO. As shown in Fig. 1, the signal of solution **1** increases more rapidly than that of **3**, indicating that it is more efficient for **1** to generate a superoxide anion radical by the direct electron transfer from TTP to oxygen. A photostationary state can be reached after 2 min of continuous irradiation for both **1** and **3**. The higher EPR signal intensity for **1** at the photostationary state further indicates that the electron transfer from excited TTP chromophore to O_2 competes more efficiently in **1** than other deactivation processes of excited TTP, such as its intrinsic monomolecular decays and its energy transfer to O_2.[16] The enhanced electron transfer from excited **1** to TiO_2 can also be rationalized in the way shown in Fig. 4S (see ESI†) where O_2 plays a similar role to TiO_2

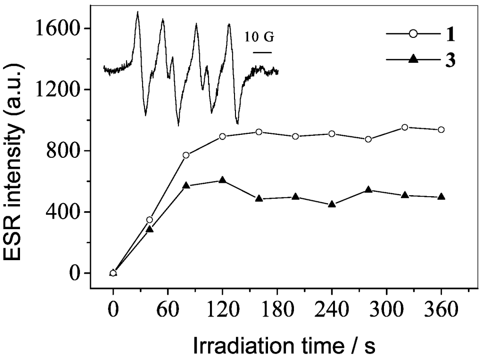


Fig. 1 Signal intensities of the DMPO-$O_2^{-\cdot}$ adduct during illumination of ethanol solutions of porphyrin **1** and **3** (9.2×10^{-5} mol L^{-1}) and DMPO (5×10^{-2} mol L^{-1}). The inset shows the EPR signal of DMPO-$O_2^{-\cdot}$ adduct.

We would like to thank NNSFC and the Ministry of Science and Technology of China for support (grant No. 29971031, 20073050, G2000028204).

Notes and references

‡ The neutral titanium dioxide is prepared by neutralization of the acid ethanol solution of titanium dioxide with solid potassium hydroxide to keep the absorption spectrum of porphyrin same as that of in neutral organic solvent, because the absorption spectrum of porphyrin would change in acid as well as in basic solution.

1 E. Galoppini, W. Guo, W. Zhang, P. G. Hoertz, P. Qu and G. J. Meyer, *J. Am. Chem. Soc.*, 2002, **124**, 7801.
2 K. Kalyanasundaram, N. Vlachopouios, V. Krishnan, A. Monnier and M. Grätzel, *J. Phys. Chem.*, 1987, **91**, 2342.
3 J. Z. Zhang, *J. Phys. Chem. B*, 2000, **104**, 7239.
4 G. Benkö, M. Hilgendorff, A. P. Yartsev and V. Sundström, *J. Phys. Chem. B*, 2001, **105**, 967.
5 Y.-X. Weng, Y.-Q. Wang, J. B. Asbury, H. N. Ghosh and T. Lian, *J. Phys. Chem. B*, 2000, **104**, 93.
6 Y. Tachibana, J. E. Moser, M. Grätzel, D. R. Klug and J. R. Durrant, *J. Phys. Chem.*, 1996, **100**, 20056.
7 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382.
8 B. A. Barry, M. K. El-Deeb, P. O. Sandusky and G. T. Babcock, *J. Biol. Chem.*, 1990, **265**, 20139.
9 H. Gratz and A. Penzkofer, *Chem. Phys.*, 2000, **254**, 363.
10 A. Zaban, S. Ferrere and B. A. Gregg, *J. Phys. Chem. B*, 1998, **102**, 452.
11 N. J. Turro, *Moden Molecular Photochemistry*, Benjamin/Cummings: California, 1978, pp. 296–361.
12 A. Kay and M. Grätzel, *J. Phys. Chem.*, 1993, **97**, 6272; K. Kalyanasundaram, N. Vlachopouios, V. Krishnan, A. Monnier and M. Grätzel, *J. Phys. Chem.*, 1987, **91**, 2342.
13 S. G. Yan and J. T. Hupp, *J. Phys. Chem.*, 1996, **100**, 6867.
14 J. B. Asbury, E. Hao, Y. Wang, H. N. Ghosh and T. Lian, *J. Phys. Chem. B*, 2001, **105**, 4545.
15 E. Finkelstein, G. M. Rosen and E. J. Rauckman, *Arch. Biochem. Biophys.*, 1980, **200**, 1.
16 M. A. Fox, in *Photoinduced Electron Transfer Reaction: Inorgnic Substrate and Applications*. M. A. Fox and M. Chanon, Eds, pp. 1–28, 1988.