Supporting Information

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"Porphyrin capped TiO_2 nanocluster, tyrosine methyl ester enhanced electron transfer"

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1. The Adsorption of 1 to 3 on the Thin solid TiO_2 Film

The neutral ethanol solution of TiO_2 (1 g/L) was concentrated from 15 mL to 1 mL at room temperature. The resulting concentrated TiO_2 solution was deposited onto the quartz slice whose surface was treated to hydrophilic, and then the quartz was calcinated to 500°C in a furnace (Thermolyne, 48000). The slices at 80 °C were immersed into the chloroform solutions of porphyrins (2×10^{-4} mol L^{-1}) overnight and then rinsed with chloroform until the absorption of the slices has no change. The absorption spectra of 1 to 3 adsorbed on TiO_2 thin films are shown in Fig. 1S, where **2** has the highest absorbance, suggesting that **2** with carboxy group is the best one for attaching on the TiO_2 surface among the compounds. This means that **2** can associate with neutral TiO_2 particles as well as **1**.

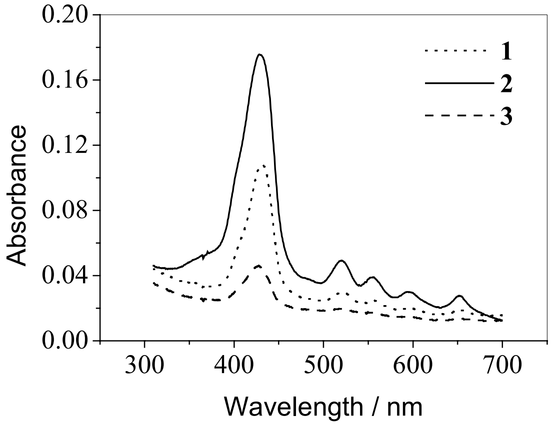

Fig. 1S The absorption spectra of **1** to **3** on thin solid TiO_2 film.

2. The Electrochemistry of 1 to 3

The cyclic voltammograms recorded on EG&G Potentiostat/Galvanostat 283 for **1** to **3** are shown in Fig. 2S. **2** and **3** are in line with the reported E^0 of TPP, *i.e.*, both have the E^0 of 1.03

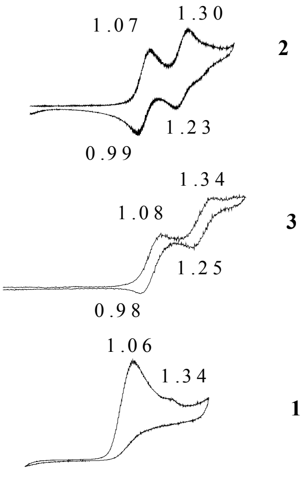

Fig. 2S Cyclic voltammograms recorded for **1** to **3** in CH_2Cl_2, with Pt as working electrode and counter electrode, and SCE as reference.

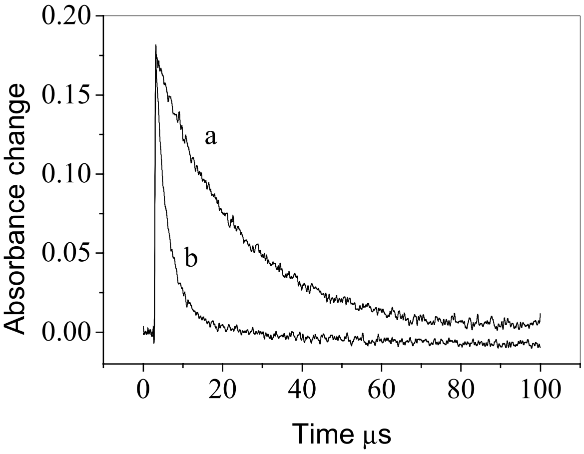

Fig. 3S Triplet-state decays of **1** (2.3×10^{-5} mol L^{-1}) at 440 nm in ethanol (a) and after the addition of 1 g L^{-1} titanium dioxide (b) following a 10-ns 532-nm laser pulse. The signals were normalized to the same initial absorbance change for better comparison of the relative decay rates..

V (vs. SCE)[1] and the difference in terminating groups does not give rise to any change on the E^0 of porphyrins. But **1** becomes irreversible because of the involvement of tyrosine methyl ester which will be oxidized before porphyrin skeleton, and the oxidation peaks of tyrosine and the porphyrin skeleton combine. The first oxidation peak is higher than the second oxidation peak of porphyrin skeleton further supports such a conclusion. Furthermore, tyrosine methyl ester might reduce the oxidized porphyrin thus the reduction peak of porphyrin could not be detected. While the position of oxidation peaks of porphyrin skeleton keep unchanged with respect to the corresponding potentials of **2** and **3**, strongly suggesting that the tyrosine methyl ester moiety of **1** does not influence the oxidative potentials of porphyrin moiety.

3. Comparison of Triplet Excited-state Decay of 1

The typical triplet excited-state decay of **1** is shown in Fig. 3S.

4. The possible mechanism

The possible mechanism is shown in Fig. 4S.

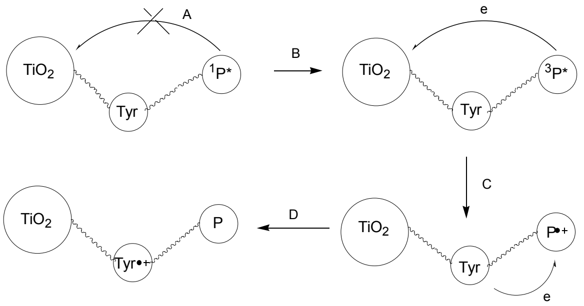

Fig. 4S A possible mechanism for the electron transfer between TiO_2 and tyrosine-methyl-ester-bridged TTP.

Reference

1. G. R. Seely, *Photochem. Photobiol.*, 1978, **27**, 639.