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A pH-Responsive, TiO₂-Attached Porphyrin for Singlet Oxygen Production in Aqueous Solution

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Abstract

A pH-responsive, TiO₂-attached sensitizer was prepared based on the adsorption of 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (TCPP) onto TiO₂ nanoparticles. This colloiddally dispersed TiO₂-attached TCPP behaves as a single-phase colloidal sensitizer at pH 1.0–3.3 with quantum yields of singlet oxygen production (Φ_{Δ}) between 0.20 and 0.25, as a heterogeneous particle sensitizer at pH 3.5–6.0 with Φ_{Δ} between 0.25 and 0.50, and as homogeneous free TCPP molecules in alkaline solutions with Φ_{Δ} = 0.53. The changes in Φ_{Δ} are fully consistent with pH dependent adsorption of TCPP on TiO₂ surface. Recovery yields of 99.8% for TCPP and 98.8% for TiO₂ were obtained from 1.4 mM TiO₂-attached TCPP. We attribute its photosensitization ability to retain TCPP solubility on TiO₂ surface and hence activity. This novel system shows a potential to bridge the gap between easily recoverable and highly efficient sensitizers.

Keywords

Singlet oxygen; TiO₂-attached porphyrin; pH-responsive and recoverable sensitizer

1. Introduction

The use of heterogeneous sensitizers for singlet oxygen (¹O₂) photooxidation in a solution facilitates product separation and analysis. The first heterogeneous sensitizer was a polymer-attached rose Bengal synthesized by Neckers, Schaap, and their co-workers,^{1,2} which was followed by a series of immobilized dyes on polymers and metal oxides.^{3–9} The adsorption of dye molecules on metal oxides has been well characterized, e.g., in the field of dye-sensitized nanocrystalline TiO₂ solar cells.^{10–13} It is known that a homogeneous sensitizer is more efficient than its heterogeneous counterpart,² and far less affected by limitations due to short lifetime of ¹O₂, and slow transport of reactants and products.¹⁴ Similar awareness existed for the use of catalysts in chemical reactions, in which strategies were developed to facilitate the recovery and recycling of homogeneous catalysts.^{15–22} Understanding the dependence of ¹O₂ production on dye adsorption on support materials may bridge the gap between easily recoverable and highly efficient sensitizers, and benefit areas of ¹O₂-based organic synthesis and water purification. However, such information has been limited.

In present work, 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (TCPP) adsorbed on TiO₂ surface was examined for its ability of ¹O₂ photosensitization. The selection of TiO₂-attached TCPP was based on its pH-responsive stability and photoactivity, as indicated in the following.

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(1) The substantial interaction between TiO_2 and deprotonated carboxyl groups in TCPP has been evidenced by femtosecond electron injection,²³ variation in TCPP fluorescence intensity with pH in a colloid TiO_2 solution,²⁴ X-ray photoelectron spectroscopy, resonance Raman spectroscopy and the red-shift in TCPP Q-band.²⁵ Due to the strong anchoring of TCPP on TiO_2 surface, the electrostatic attraction between $-\text{COO}^-$ groups in TCPP and positively charged TiO_2 nanoparticles prevails at $\text{pH} < 5$. In alkaline solution where the surface charge of TiO_2 is negative, the adsorption of anionic TCPP on TiO_2 surface is inhibited. (2) The solubility of TCPP in acidic solution is very low but can be greatly enhanced by adsorbing on colloidal TiO_2 surface. Due to pH-responsive stability and irreversible formation of TiO_2 -attached TCPP, the recovery of both TCPP and TiO_2 can be simply achieved by centrifugation at certain pHs. (3) Similar to other porphyrin sensitizers, TCPP possesses the ability to produce $^1\text{O}_2$ in organic solvents (toluene, methanol, acetone),²⁶ in neutral water (from TCPP-cyclodextrin supramolecular complexes),²⁷ and in pH 13 aqueous solution.²⁸ Therefore, in present work we characterize in detail the preparation and recovery of TiO_2 -attached TCPP sensitizer, and examine their photosensitization ability in a wide pH range.

2. Results and discussion

2.1. Formation and spectroscopic properties of TiO_2 -attached TCPP sensitizer

The stability of colloidal TiO_2 nanoparticles is pH dependent and can be measured by zeta potential. A higher zeta potential favors the formation of a stable suspension resulted from electrostatic repulsion among nanoparticles. It is well recognized that the surface of TiO_2 in an aqueous environment takes electric charges that are dependent on pH. The positive charge occurred at acidic conditions ($\text{pH} < 5$) due to the presence of $\equiv\text{TiOH}_2^+$ groups where the zeta potentials were sufficiently large to form stable colloids, near neutral charge at zero zeta potential around pH 5–7,^{29,30} and negative charge at basic conditions ($\text{pH} > 7$) owing to $\equiv\text{TiO}^-$ groups³¹ where TiO_2 precipitation from the solution was observed. Carboxylic acid functionality was the most commonly used anchoring group for dye-sensitized solar cells. These carboxylic acid groups, while ensuring efficient adsorption of dyes on TiO_2 surface also promoted electronic coupling between the donor levels of the excited chromophore and the acceptor levels of the TiO_2 semiconductor. Some of the possible modes of chelation/derivatization ranged from chemical bonding (chelating or bridging mode) to H-bonding.¹² Our results showed that TiO_2 -attached TCPP colloids were extremely stable in a pH range of 1.0–3.3 (d in scheme 1) but aggregate at $\text{pH} > 3.5$ (e in scheme 1). The desorption of TCPP from TiO_2 surface was largely enhanced in basic solutions due to fair solubility of TCPP and electrostatic repulsion between negatively charged TiO_2 and TCPP anions (f in scheme 1).

The quantitative adsorption of TCPP onto TiO_2 surface was examined by two experiments. First, an experiment was carried out in order to determine whether a decrease in pH in colloidal solution coincides with the adsorption of TCPP onto TiO_2 surface. A concurrent decrease in pH of the aqueous solution was found, which related to the deprotonation of carboxylic acid groups in TCPP upon its binding on TiO_2 surface. The adsorption of TC over 7 days corresponded to a pH reduction from 2.06 to 1.99. Due to the similar sizes of TiO_2 nanoparticles (1 nm) and TCPP molecules (1.5 nm), it was reasonable to assume that a TCPP molecule could bind vertically on the surface of one TiO_2 nanoparticle through one of the four carboxylic acid anchoring groups. The molar ratio of $[\text{H}^+]_{\text{dissociated}}/\text{TiO}_2$ particles was found to be increased from initial zero to 1.1, which revealed that an average of *ca.* one TCPP molecule per colloidal TiO_2 nanoparticle. Second, the extinction coefficient of TCPP molecules chemisorbed on colloidal TiO_2 surface in pH 2.3 aqueous solution, $\epsilon = 6.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 420 nm was determined from the slope of a calibration curve relating TCPP concentration to absorption (figure 4). The amount of TCPP chemisorbed on TiO_2 surface was measured at 420 nm according to Lambert-Beer's law. Typically an average of 0.7 TCPP molecules loaded on per

TiO₂ particle was obtained. The loading amounts of TCPP on TiO₂ surface from both experiments were comparable with each other. A little bit higher value (compare 1.1 to 0.7) obtained based on pH measurements for the ratio of TCPP molecules over TiO₂ particles might result from partial presence of two carboxylic acid anchor groups on one TiO₂ particle and/or the inconsequential decomposition of TCPP molecules during preparation.

As shown in figure 1, the absorption spectrum of TCPP in pH 2.3 HCl-NaOH solution was characterized by a quite broad Soret band between 405 and 436 nm, and Q band at 524 nm, 560 nm, 597 nm and 650 nm, respectively. The protonation of the nitrogen atoms of the central macrocycle of porphyrins has been well studied. The longer wavelength Q band becomes the most intense upon protonation with the band diminishing in intensity in the order of decreasing wavelength.^{32–34} The longest-wavelength band is the typical for dictations and metal complexes of porphyrins Q band, which is reflected in the spectra of colloidal TiO₂-attached TCPP (black line in figure 1). TCPP was sparingly soluble in acidic solution (blue line in figure 1). Its solubility however could be improved at a low limit of *ca.* 6×10^{-6} M in the presence of sodium salt (red line in figure 1). The lowest intensity Q band at the longest wavelength of 650 nm for TCPP in pH 2.3 HCl-NaOH solution indicates its deprotonated spectral feature, which is probably due to the competition of sodium cations with protons for the central nitrogen atoms. In neutral and alkaline solutions, the presence of TiO₂ had hardly any effect on Q band (table 1). While in acidic solution, a small but reproducible red shift at 650 nm of the Q band ($650 + 8 = 658$ nm) was observed. One possible mechanism for this shift was a charge transfer band. Coupling between the wave functions of excited electronic state of TCPP and the charge separated state could give mixed states.^{35,36} Such strong interaction was accomplished through a chemical bonding between TCPP central macrocycle and TiO₂. The adsorption was also evident by the pronounced effect of pH on Φ_{Δ} (see discussion below.). A sharp change in Φ_{Δ} was observed when pH closed to the point of zero charge (pH $\sim$ 5.0 for TiO₂),³⁷ where the transition from free to surface-bound TCPP occurred. These spectral features clearly indicated the adsorption of TCPP onto TiO₂ surface at acidic pHs and were consistent with the literature reports using various techniques including femtosecond electron injection,²³ fluorescence,²⁴ X-ray photoelectron spectroscopy, resonance Raman spectroscopy and UV/Vis.²⁵ The change in driving force for the electron transfer might also result in an inefficient interaction between TiO₂ and TCPP molecules at higher pH. It was reasonable to suppose that the oxidation potential of porphyrin ring based dyes adsorbed on TiO₂ surface was weakly pH-dependent or pH-independent, especially in the neutral and alkaline solutions. While in TiO₂ with increasing pH, the valence and conduction band edges move to more cathodic potentials. This would reduce considerably the driving force for charge separation.³⁸ Therefore, we concluded that TCPP was strongly adsorbed on TiO₂ surface through chemical bonding at acidic pH but released in neutral and alkaline pH region. The spectroscopic data is summarized in table 1.

2.2. TCPP and TiO₂ recovery

TiO₂-attached TCPP remains as a homogeneous colloid at pH 1.0–3.3, a heterogeneous aggregate at pH 3.5–6.0 and free soluble TCPP molecules at pH > 7. Formation and conversions among these forms are shown in scheme 1. Due to pH-responsive stability and irreversible formation of TiO₂-attached TCPP, the recovery of both TCPP and TiO₂ were simply achieved by centrifugation at certain pHs. To test the recovery yields, a homogeneous solution of TiO₂-attached TCPP at pH between 1.0 and 3.3 was first alkalinized with NaOH to destroy colloids, then followed by centrifugation. The supernatant was analyzed at pH 2.3 to quantify remaining TCPP and TiO₂ concentrations by monitoring TiO₂ at 215 nm using $\epsilon = 6050$ M⁻¹ cm⁻¹ and TCPP at 408 nm using $\epsilon = 9.5 \times 10^4$ M⁻¹ cm⁻¹, respectively (see Experimental Section). The best recovery yields of 99.8% for TCPP and 98.8% for TiO₂ were obtained from 1.4 mM TiO₂-attached TCPP by centrifugation at pH between 4 and 5.

2.3. $^1\text{O}_2$ production and Φ_Δ measurement

$^1\text{O}_2$ luminescence was detected at 1270 nm upon irradiation of TiO_2 -attached TCPP at 532 nm. The data shown in figure 2 was assigned to $^1\text{O}_2$ phosphorescence because both kinetics and intensity of the signals were sensitive to the concentrations of oxygen and azide ions that quenches $^1\text{O}_2$ at a rate constant of $5.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in H_2O .³⁹ Figure 2 also indicated that azide ions quenches not only the lifetime of $^1\text{O}_2$ but also the initial intensity of $^1\text{O}_2$ luminescence, which can be explained by its reactions with both $^1\text{O}_2$ and excited states of a sensitizer.⁴⁰ The kinetic decay was exponential with rate constants (k_d) of $^1\text{O}_2$ in 80% D_2O between 1.2×10^5 and $4.4 \times 10^4 \text{ s}^{-1}$ for a pH range of 1 to 10, respectively. For all calculations in this work, kinetic traces have been corrected for the interference from other rapid events synchronized with laser pulses (i.e., scattered light and fluorescence), using a same but N_2 -saturated sample as a control. Recently we reported $^1\text{O}_2$ production upon two-photon excitation of TiO_2 in CHCl_3 at 532 nm.⁴¹ Compared to TCPP ($\Phi_\Delta = 0.53$ for free TCPP molecules, measured in the work), $^1\text{O}_2$ production from TiO_2 was much less efficient, and could be disregarded. The generation of $^1\text{O}_2$ is based on a bimolecular sensitization reaction, represented by predominantly a triplet quenching process of a sensitizer in the presence of $^3\text{O}_2$ (equation 1 and 2).

$^1\text{O}_2$ production upon visible irradiation of TiO_2 -attached TCPP was also evidenced by steady-state experiments using [2-dicyclohexylphosphino)ethyl]trimethylammonium chloride as a chemical trap of $^1\text{O}_2$. The loss of phosphine was monitored by ^{31}P NMR. Our results indicated that 100% conversion yields of phosphonate were obtained upon 20 minutes visible irradiation of 0.6 μmol phosphine in the presence of $1.0 \times 10^{-5} \text{ M}$ TiO_2 -attached TCPP at pH 2.3, wherein a homogeneous TiO_2 -attached TCPP colloids were formed. We attribute photosensitizing ability to retain TCPP solubility on TiO_2 surface and hence activity.

Φ_Δ is an important measure of the efficacy of $^1\text{O}_2$ photosensitization. The determination of Φ_Δ from a colloidal solution was not very precise because of light scattering by suspended nanoparticles. However, Φ_Δ could be approximated according to equation (4) by comparing the initial $^1\text{O}_2$ intensities with those from a well developed reference sensitizer meso-tetrasulphonatophenyl porphyrin (TSPP) using Φ_Δ 0.63 in D_2O .⁴² TiO_2 -attached TCPP remained as a homogeneous colloidal sensitizer at pH between 1 and 3.3 but aggregated in a pH range of 3.5 to 6. In neutral and basic solutions, $^1\text{O}_2$ was mainly resulted from free TCPP molecules. Φ_Δ exhibited in the sigmoidal curve was pH-dependent and fully consistent with pH dependent TCPP adsorption on TiO_2 surface (figure 3). Observed sharp change in Φ_Δ took place when the pH was close to the point of zero charge (pH ~ 5.0 for TiO_2),³⁷ where the transition from free to surface-bound TCPP occurred. The higher Φ_Δ obtained in neutral and alkaline solutions (0.54 from figure 3) were perfectly in agreements with both of our value 0.53 for free TCPP measured in pH 10 NaOH solution and literature value 0.47 determined at pH 13.²⁸ Similar observations were reported for weak fluorescence quenching at higher pH performed by Hartland for anthracene dyes bound to TiO_2 ,⁴³ and for weak electron transfer in alkaline solutions studied by Gratzel for Zn porphyrin in colloidal TiO_2 solution.⁴⁴ We therefore concluded that efficient energy transfer from triplet TCPP to $^3\text{O}_2$ in neutral and alkaline conditions was due to the lack of the adsorption of anionic TCPP on negatively charged

TiO₂ surface. The electron transfer between TiO₂ and TCPP could compete favorably with the energy transfer process in acidic conditions, subsequently resulting in lower Φ_{Δ} .

2.4. Effects of TiO₂ surface coverage on quenching rates of ¹O₂

To quantify apparent quenching of ¹O₂, total rate constants of ¹O₂ removal (k_T) by free TCPP and TiO₂-attached TCPP were determined by Stern-Volmer analysis using TSPP as a sensitizer. k_T $(1.1 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ measured from TiO₂-attached TCPP in pH 2.3 HCl solution was comparable to those from other porphyrin sensitizers, e.g., $6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for TPP in C₆D₆,⁴⁵ and $< 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for free- and metallo-TSPP in D₂O.⁴⁶ A higher value of $(1.1 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for TiO₂-attached TCPP than that of $(5.0 \pm 0.1) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for free TCPP measured in pH 10 NaOH solution might result from fast quenching of ¹O₂ by TiO₂ nanoparticles.⁴¹

3. Conclusion

TiO₂-attached TCPP retained photosensitization ability in a wide pH range, e.g., as a homogeneous colloid at pH between 1.0 and 3.3, a heterogeneous aggregate in a pH range of 3.5 to 6.0 and free soluble TCPP molecules at pH > 7. Both TCPP and TiO₂ could be easily separated from solutions by centrifugation at pH between 3.5 and 5 with satisfied recovery yields. This pH-responsive, TiO₂-attached TCPP has advantages of high dispersion and subsequent efficient ¹O₂ production. The novel system shows a potential to bridge the gap between easily recoverable and highly efficient sensitizers. Also, it provides a general methodology for the separation of dyes based on their interaction with inorganic metal oxides. The recoverable sensitizers can be of great significance to aqueous phase organic synthesis, water detoxification and disinfection. Due to the photocatalytic activity of TiO₂ under UV illumination, the application of TiO₂-attached TCPP should be restricted to visible light. A challenge for future development is to tailor recoverable sensitizers with the aim of using a wide range of light energy for photosensitization.

4. Materials and Methods

Materials and Instrumentation

Reagents and solvents were obtained commercially and used without further purification. *meso*-Tetra(4-carboxylphenyl) porphine (TCPP) and *meso*-Tetra(4-sulfonatophenyl)porphine dihydrochloride (TSPP) were purchased from Frontier Scientific, Inc., [2-(dicyclohexyl phosphino) ethyl]trimethyl ammonium chloride (> 98%) from Strem Chemicals, Inc., 1.005-0.995 M standard NaOH solution from Fisher Scientific, D₂O (99% atom) from Sigma-Aldrich and sodium azide (99%) from Acros Organics. Deionized water was obtained from a Nanopure Water (Barnsted System, USA). A Q-switched Nd:YAG laser with pulse duration of 3–4 ns and a maximum energy of 30 mJ at 532 nm (Polaris II-20, New Wave Research Merchantek Products), and a liquid N₂-cooled germanium photodetector (Applied Detector Corporation) were used for time-resolved ¹O₂ luminescence measurements. Steady-state photooxidation was conducted in oxygen-saturated solution using a 300 W mercury lamp (Newport Oriel Instruments, 68911 ARC Lamp Power Supply, 200–500 watts Xe/HgXe) equipped with a water filter and a 500 nm cutoff filter. Other instruments employed in this research include a BioMate 3 UV-Vis spectrophotometer (Thermo Scientific) or a Cary 300 UV-Vis spectrophotometer (Varian, Inc.) for taking absorbance and spectra, and a centrifuge (Fisher Scientific, Inc, Centrifuge Model 228) for heterogeneous separation. The determinations of photooxidation products were done with a 300 MHz Bruker Spectrospin FT-NMR and/or a 400 MHz JEOL Eclipse FT-NMR. All measurements were carried out at ambient temperature.

Colloidal TiO₂ preparation and concentration determination

Colloidal TiO₂ solutions were prepared by hydrolysis of TiCl₄ as previously described.^{47,48} Briefly 2.5 mL TiCl₄ at 0°C was introduced under a stream of nitrogen and vigorous stirring into 70 mL water/ice solution of 0.1 M HCl. After 30 min stirring at 0°C, the solution was dialyzed against aqueous HCl of pH 2.3 using Spectrapor membrane tubing (Spectrum Medical Industries) with MW 6000–8000 cutoff pores. A transparent solution containing *ca.* 20 g/L TiO₂ at pH 2.3 was obtained. Molecular TiO₂ concentration was determined by spectrophotometric measurements at 215 nm using molar extinction coefficient 6050 M⁻¹ cm⁻¹.⁴⁷ The solution was kept in refrigerator at 2–5°C and used within 3 months. Colloidal TiO₂ nanoparticles such prepared had an average diameter 1.0 nm with 90% of the diameters in the range 0.8–1.3 nm.⁴⁸ TiO₂ concentrations were reported in terms of TiO₂ particles (C_{TiO₂ particles, molarity}) to better reflect experimental conditions. The particle concentration was calculated according to equation 1 using a TiO₂ density (d_{TiO₂, g/cm³}) of 4 g/cm³ and an average diameter (φ_{TiO₂, nm}) of 1.0 nm.

$$C_{\text{TiO}_2 \text{ particles, molarity}} = \frac{\left(\frac{C_{\text{TiO}_2, \text{g/L}}}{d_{\text{TiO}_2, \text{g/cm}^3}} \right) / \left[\frac{4}{3} \pi \left(\frac{\phi}{2} \times 1 \times 10^7 \right)^3 \right]}{6.02 \times 10^{23}} \quad (3)$$

Preparation of TiO₂-attached TCPP colloids and concentration determination

TiO₂ nanoparticles modified with TCPP molecules were prepared by mixing 0.0063 g TCPP with 20.00 mL pH 2.3 1.7 g/L colloidal TiO₂ solution for 7 days under stirring. The mixture was kept in dark during preparation to avoid photocatalytic decomposition of TCPP. The excessive TiO₂ particles and TCPP molecules were then separated from aqueous phase by centrifugation. TiO₂-attached TCPP colloids such prepared were extremely stable in the pH range of 1.0–3.3 with an extinction coefficient ε = 6.8 × 10⁴ M⁻¹ cm⁻¹ at 420 nm measured at pH 2.3. For extinction coefficient measurement, 100% adsorption of TCPP on TiO₂ surface was required. We therefore used a minimum 10 fold excess of TiO₂ particles relative to the TCPP molecular concentrations. The remaining TiO₂ particles were removed from the solution by centrifugation. The absorption spectra and calibration curve are shown in figure 4. All spectra were measured against pH 2.3 aqueous HCl solution. The amount of TCPP chemisorbed on TiO₂ surface was therefore determined at 420 nm according to Lambert-Beer's law using ε_{420 nm} = 6.8 × 10⁴ M⁻¹ cm⁻¹. Typically, an average load of one TCPP molecules per TiO₂ particle was obtained.

Determination of remaining TCPP concentration in solution

TCPP was nearly insoluble in acidic solution (blue line in figure 1). Its solubility however could be improved at a low limit of *ca.* 6 × 10⁻⁶ M in the presence of sodium salt. A series of standard TCPP solutions at pH 2.3 were therefore prepared by first dissolving TCPP in pH 10 NaOH water, then followed by acidifying the solution to pH 2.3 with HCl. The recovery of TiO₂-attached TCPP aggregates was achieved by centrifugation at pH between 4 and 5. The remaining TCPP concentrations were therefore calculated according to Lambert-Beer's law using ε = 9.5 × 10⁴ M⁻¹ cm⁻¹ measured at 408 nm in pH 2.3 acidic solution as shown in figure 5.

Φ_Δ measurement

Φ_Δ were determined in aerated solutions by comparing the intensity of ¹O₂ phosphorescence at 1270 nm from TiO₂-attached TCPP with that from a reference sensitizer TSPP in D₂O using

a known $\Phi_{\Delta, \text{TSPP}}$ 0.63.⁴² $^1\text{O}_2$ phosphorescence at 1270 nm was monitored as previously described.⁴⁹ The initial $^1\text{O}_2$ intensity was extrapolated to time zero and corrected by using a same but N_2 -saturated sample as a control. The data points of the initial 3–5 ns were not used due to electronic interference signals from the detector. The absorbances of TiO_2 -attached TCPP and TSPP were matched to be the same at excitation wavelength of 532 nm. Φ_{Δ} were calculated according to equation (2).

$$\frac{\Phi_{\Delta, \text{TiO}_2\text{-attached TCPP}}}{\Phi_{\Delta, \text{TSPP}}} = \frac{I_{\Delta, \text{TiO}_2\text{-attached TCPP}}}{I_{\Delta, \text{TSPP}}} \quad (4)$$

Here $\Phi_{\Delta, \text{TiO}_2\text{-attached TCPP}}$ and $\Phi_{\Delta, \text{TSPP}}$ are the Φ_{Δ} from TiO_2 -attached TCPP and TSPP, respectively; and $I_{\Delta, \text{TiO}_2\text{-attached TCPP}}$ and $I_{\Delta, \text{TSPP}}$ the $^1\text{O}_2$ intensities from TiO_2 -attached TCPP and TSPP, respectively.

Determination of total quenching rate constants of $^1\text{O}_2$ removal by Stern-Volmer analysis

Many sensitizers also quench $^1\text{O}_2$ via chemical and/or physical reactions. In order to quantify the apparent strong quenching of $^1\text{O}_2$ by TiO_2 -attached TCPP, we determined the total quenching rate constant of $^1\text{O}_2$ removal (k_T) for both of colloidal TiO_2 particles and TiO_2 -attached TCPP by Stern-Volmer analysis. The quenching rate constants were calculated in terms of TiO_2 particle concentrations. Measurements were carried out at 532 nm excitation using TSPP in pH 2.3 D_2O as a sensitizer. Considering relatively low concentrations of TiO_2 -attached TCPP used in quenching experiments and high Φ_{Δ} from TSPP,⁴² $^1\text{O}_2$ signals resulted from TCPP could be disregarded if comparing to these from TSPP. Our data indicated that the kinetics of $^1\text{O}_2$ luminescence decay at 1270 nm followed Stern-Volmer equation.

$$k = k_d + k_T [Q] \quad (5)$$

Where k is the observed 1st-order rate constant of $^1\text{O}_2$ decay after laser pulse, k_d the 1st-order rate constant of $^1\text{O}_2$ decay in the absence of quencher, k_T the 2nd-order rate constant for bimolecular quenching of $^1\text{O}_2$, or total quenching rate constant of $^1\text{O}_2$ removal. Changes in $^1\text{O}_2$ lifetimes were observed by the addition of TiO_2 particles or TiO_2 -attached TCPP into the solutions. Stern-Volmer plots gave a good linear correlation between k and quencher concentrations $[Q]$. k_T values then can be derived from the slopes of the straight lines.

Photooxidation of [2-dicyclohexylphosphino)ethyl]trimethylammonium chloride

$^1\text{O}_2$ photooxidation of phosphines led to the formation of either phosphonate or a mixture of phosphonate and phosphinate.⁵⁰⁻⁵¹ A water soluble phosphine, [2-(dicyclohexylphosphino)ethyl]trimethylammonium chloride was employed as a $^1\text{O}_2$ trap in steady-state photolysis experiments. Photooxidation products were determined by ^{31}P NMR as previously reported.^{50,51} The reactions were carried out in the presence of 1.00×10^{-5} M TiO_2 -attached TCPP in an O_2 -saturated 90% D_2O solution at pH 2.3. $^1\text{O}_2$ photooxygenation led to a formation of a sole product, phosphonate (figure 6). The percent yields were calculated by comparison of the integrated ^{31}P peaks of phosphine with those of phosphonate in ^{31}P NMR spectra. Control experiments were carried out in order to correct phosphine oxidation by ground state oxygen molecules (line 2 in figure 6). Examples of ^{31}P NMR spectra shown in figure 6 indicated peaks of phosphine δ -6.75 (s, 1P) and phosphonate δ 60.47 (s, 1P).

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References

1. Blosey EC, Neckers DC, Thayer AL, Schaap AP. *J Am Chem Soc* 1973;95:5820.
2. Schaap AP, Thayer AL, Blosey EC, Neckers DC. *J Am Chem Soc* 1975;97:3741.
3. Griesbeck AG, Bartoschek A, Neudorfl J, Miara C. *Photochem Photobiol* 2006;82:1233. [PubMed: 16674271]
4. Wahlen, Joos; De Vos, Dirk E.; Jacobs, Pierre A.; Alsters, PL. *Adv Synth Catal* 2004;346:152.
5. Aebischer D, Azar NS, Zamadar M, Gandra N, Gafney HD, Gao R, Greer A. *J Phys Chem B* 2008;112:1913. [PubMed: 18225891]
6. Schaap AP, Thayer AL, Zaklika KA, Valenti PC. *J Am Chem Soc* 1979;101:4016.
7. Nowakowska M, Kepczynski M, Szczubialka K. *Pure Appl Chem* 2001;73:491.
8. Tamagaki S, Liesner CE, Neckers DC. *J Org Chem* 1980;45:1573.
9. Guarini A, Tundo P. *J Org Chem* 1987;52:3501.
10. O'Regan B, Gratzel M. *Nature* 1991;353:737.
11. Durrant JR, Haque SA, Palomares E. *Coord Chem Rev* 2004;248:1247.
12. Campbell WM, Burrell AK, Officer DL, Jolley KW. *Coord Chem Rev* 2004;248:1363.
13. A small sample of references on TCPP or metallo-TCPP sensitized TiO_2 solar cells are Kroeze JE, Savenije TJ, Warman JM. *J Am Chem Soc* 2004;126:7608. [PubMed: 15198609] Clifford JN, Palomares E, Nazeeruddin MdK, Gratzel M, Nelson J, Li X, Long NJ, Durrant JR. *J Am Chem Soc* 2004;126:5225. [PubMed: 15099107] Walter MG, Wamser CC, Ruwitch J, Zhao Y, Braden D, Stevens M, Denman A, Pi R, Rudine A, Pessiki PJ. *J Porphyrins and Phthalocyanines* 2007;11:601. Jasieniak J, Johnston M, Wacławik ER. *J Phys Chem B* 2004;108:12962. Kroeze JE, Savenije TJ, Warman JM. *Proceedings of SPIE-The International Society for Optical Engineering*. 2003;4801:67. (Organic Photovoltaics III). Ma T, Inoue K, Yao K, Noma H, Shuji T, Abe E, Yu J, Wang X, Zhang B. *J Electroanal Chem* 2002;537:31. Ma T, Inoue K, Noma H, Yao K, Abe E. *J Mat Sci Lett* 2002;21:1013.
14. Zebger I, Poulsen L, Gao Z, Andersen LK, Ogilby PR. *Langmuir* 2003;19:8927.
15. Zheng P, Zhang W. *Journal of Catalysis* 2007;250:324.
16. Palioura D, Armes SP, Anastasiadis SH, Vamvakaki M. *Langmuir* 2007;23:5761. [PubMed: 17408293]
17. Fernandez-Ibanez P, Blanco J, Malato S, Nieves FJdl. *Water Res* 2003;37:3180. [PubMed: 14509705]
18. Zuwei X, Ning Z, Yu S, Li K. *Science* 2001;292:1139. [PubMed: 11349143]
19. Hourdin G, Germain A, Moreau C, Fajula F. *J Catal* 2002;209:217.
20. Dioumaev VK, Bullock RM. *Nature* 2003;424:530. [PubMed: 12891351]
21. Wende M, Meier R, Gladysz JA. *J Am Chem Soc* 2001;123:11490. [PubMed: 11707132]
22. Ishihara K, Hasegawa A, Yamamoto H. *Synlett* 2002:1299.
23. Tachibana Y, Haque SA, Mercer LP, Durrant JR, Klug DR. *J Phys Chem B* 2000;104:1198.
24. Park H, Bae H, Lee JJ, Park J, Choi W. *J Phys Chem B* 2006;110:8740. [PubMed: 16640430]
25. Cherian S, Wamser CC. *J Phys Chem B* 2000;104:3624.
26. Figueiredo TLC, Johnstone RAW, Sorensen AMPS, Burget D, Jacques P. *Photochem Photobiol* 1999;69:517.
27. Mosinger J, Kliment V, Sejbál J, Kubat P, Lang K. *Porphyrins Phthalocyanines* 2002;6:514.
28. Gerdes R, Wöhrle D, Spiller W, Schneider G, Schnurpfeil G, Schulz-Ekloff G. *J Photochem Photobiol A: Chemistry* 1997;111:65.
29. Park H, Choi W. *J Phys Chem B* 2004;108:4086.
30. Dunn WW, Aikawa Y, Bard AJ. *J Am Chem Soc* 1981;103:3456.

31. Hoffmann MR, Martin ST, Choi W, Bahnemann DW. *Chem Rev* 1995;95:69.
32. Knyukshto VN, Solovyov KN, Egorova GD. *Biospectroscopy* 1998;4:121. [PubMed: 9557907]
33. Valanciunaite J, Bagdonas S, Streckyte G, Rotomskis R. *Photochem Photobiol Sci* 2006;5:381. [PubMed: 16583018]
34. Choi MY, Pollard JA, Webb MA, McHale JL. *J Am Chem Soc* 2003;125:810. [PubMed: 12526682]
35. Cohen-Tannoudji, C. *Quantum Mechanics*. Wiley; New York: 1977.
36. Ma T, Inoue K, Noma H, Yao K, Abe E. *J Photochem Photobiol A: Chemistry* 2002;152:207.
37. Colombo DP, Roussel KA, Saeh J, Skinner D, Cavaleri JJ, Bowman R. *Chem Phys Lett* 1995;232:207.
38. Zaban A, Ferrere S, Gregg BA. *J Phys Chem B* 1998;102:452.
39. Haag WR, Mill T. *Photochem Photobiol* 1987;45:317.
40. Hall RD, Chignell CF. *Photochem Photobiol* 1987;45:459. [PubMed: 3575442]
41. Li W, Gandra N, Courtney SN, Gao R. *ChemPhysChem*. 2009 in press.
42. Tanielian C, Wolff C, Esch M. *J Phys Chem* 1996;100:6555.
43. Martini I, Hodak JH, Hartland GV. *J Phys Chem B* 1998;102:9508.
44. Kalyanasundaram K, Vlachopoulos N, Krishnan V, Monnier A, Gratzel M. *J Phys Chem* 1987;91:2342.
45. Ogilby PR, Foote CS. *J Am Chem Soc* 1983;105:3423.
46. Davila J, Harriman A. *Photochem Photobiol* 1990;51:9. [PubMed: 2304981]
47. Gao R, Safrany A, Rabani J. *Radiat Phys Chem* 2002;65:599.
48. Gao R, Safrany A, Rabani J. *Radiat Phys Chem* 2003;67:25.
49. Gandra N, Frank AT, Gendre OL, Sawwan N, Aebischer D, Liebman JF, Houk KN, Greer A, Gao R. *Tetrahedron* 2006;62:10771.
50. Gao R, Ho DG, Dong T, Khuu D, Franco N, Sezer O, Selke M. *Org Lett* 2001;3:3719. [PubMed: 11700121]
51. Ho DG, Gao R, Celaje J, Chung HY, Selke M. *Science* 2003;302:259. [PubMed: 14551430]

Figure 1.

Absorption spectra of TiO_2 , TCPP and TiO_2 -attached TCPP in pH 2.3 aqueous solutions. Black line: 5.1×10^{-5} M TCPP on 1.35×10^{-3} M TiO_2 in pH 2.3 HCl, red line: 3.7×10^{-6} M TCPP in pH 2.3 HCl-NaOH, purple line: 1.35×10^{-3} M TiO_2 , and blue line: TCPP supernatant from pH 2.3 HCl saturated TCPP solution.

Figure 2. Time-resolved $^1\text{O}_2$ emission signals at 1270 nm recorded upon 532 nm irradiation of 1.5×10^{-3} M TiO_2 -attached TCPP in air-saturated 80% D_2O aqueous solutions, black line, at pH7; red line, at pH 3 and blue line, at pH 3 in the presence of 80 mM NaN_3

Figure 3.
Variation in Φ_{Δ} from TiO_2 -attached TCPP with pH using TSPP as a reference

Figure 4.

Absorption spectra and calibration curve of different amount of TCPP on TiO₂ surface in pH 2.3 aqueous solutions. 1, supernatant from saturated TCPP; 2, 2.7×10^{-4} M TiO₂; 3–7, 2.5×10^{-6} , 5.1×10^{-6} , 1.0×10^{-6} , 1.3×10^{-5} , 1.5×10^{-5} M TCPP mixed with 2.7×10^{-4} M TiO₂, respectively; insertion, calibration curve of absorbance at 420 nm vs. 2.5×10^{-6} – 2.5×10^{-5} M TCPP chemisorbed on 2.7×10^{-4} M colloidal TiO₂ nanoparticles at pH 2.3.

Figure 5.

Absorption spectra and calibration curve of TCPP in pH 2.3 HCl-NaOH solutions. All spectra were measured against pH 2.3 aqueous HCl solution. 1–6, 1.1×10^{-6} , 1.5×10^{-6} , 2.2×10^{-6} , 3.2×10^{-6} , 3.7×10^{-6} and 5.6×10^{-6} M TCPP, respectively; insertion, calibration curve of absorbance at 408 nm vs. 1.1×10^{-6} – 5.6×10^{-6} M TCPP at pH 2.3.

Figure 6.

^{31}P NMR spectra of 0.6 μmol phosphine before and after visible light irradiation in the absence and presence of 1.00×10^{-5} M TiO_2 -attached TCPP in an O_2 -saturated 90% D_2O solution at pH 2.3. 1. phosphine before irradiation; 2. 1 after 20 min irradiation; 3. phosphine and TiO_2 -attached porphyrin before irradiation; 4. 3 after 10 min irradiation; 5. 3 after 20 min irradiation

Scheme 1.

Formation and recovery of TiO₂-attached TCPP.

a–d, sensitizer preparation at pH 2.3: a, TiO₂ colloids before adding TCPP; b, TCPP added, not yet mixed; c, mixed for 6 hours under stirring; d, mixed for 7 days under stirring, excess TCPP and TiO₂ removed by centrifugation. e, TCPP and TiO₂ recovered at pH 3.5–5; f, TCPP dissolved in base

Table 1Absorption maxima of TCP in the presence and absence of TiO₂ nanoparticles

Solution	Soret, nm	Q-bands, nm
TCP in pH 2.3 HCl/NaOH	405–436	524 560 597 650
TCP in pH 10 NaOH	414	517 554 580 635
TiO ₂ -attached TCP in pH 2.3 HCl	420	525 560 597 658
TiO ₂ -attached TCP in pH 10 NaOH	414	517 554 580 635