Asian Journal of Chemistry Vol. 19, No. 2 (2007), 897-911

Photosensitization of Colloidal TiO_2 Semiconductor with Zinc Phthalocynine

RAED GHANEM
Department of Chemistry, University of Al al-Bayt, P.O. Box-130040
Mafraq 25113, Jordan
E-mail: readsa@yahoo.com

Zinc-phtalocyanine with tyrosine substituents (ZnPcTyr) was attached to the surface of the colloidal nanocrystalline TiO_2 *via* carboxylic acid group. The interaction of ZnPctyro with colloidal was studied by absorption and fluorescence spectroscopy. The apparent association constant for the association between ZnPcTyr and TiO_2 is about 4.5×10^4 M^{-1} with a degree of association up to 90%. Presence of the tyrosine group in ZnPcTyr enhances the solubility of the dye in ethanol and decrease the aggregation behavior. Anchoring of the dye complex to the nanocrystalline TiO_2 enables ultrafast injection of electrons from the excited state into the conduction band of TiO_2 (completed in *ca.* 500 fs) which results in strong quenching of the singlet state of the ZnPcTyr and a maximum of incident photon to current efficiency (IPCE) is *ca.* 24% at 690 nm, the low IPCE is due to the surface aggregation and fast charge recombination. Photophysical properties of the zinc phthalocyanine and the transient spectra were also determined.

Key Words: Zinc-phthalocyanine, Tyrosine, Colloidal TiO_2, Ultrafast spectroscopy.

INTRODUCTION

Recently, metallophthalocyanine complexes have been extensively studied and attracted attention because of their application on different areas such as in display devices, data storage, solar cell, photo reduction of water to dihydrogen and other UV-Visible light driven process[1,2], as well as their role in the photodynamic therapy of the cancer[3,4].

Phthalocyanines represent a chemical system with many possibilities since all the metallic elements having the possibility to be inserted into the cycle[5]. Moreover, phathalocyanines can undergo photooxidation or photoreduction depending on the presence of electron donor or accepter. Photoreduction of the phthalocyanines was reported to be occured in the presence of electron donors such as organic amine (triethylamine, triethanoloamine, *etc.*) and azaferrocene[6-9].

On the other hand, metallophthalocyanines such as, zinc phthalocyanines complexes are wildely used in dye-sensitized photo electrochemical solar cell which is considered as one of the promising devices for harvesting solar energy by converting it into electricity, the main component of this cell is the photo anode based on the nanoporous nanocrystalline[10-12]. In such cell, light absorption of the dye was followed by electron injection from the excited absorbed dye into the conduction band of the semiconductor; the electrons are brought back to the oxidized dye through an external way using a counter electrode (Pt) and a redox system.

Theoretically, for a dye to be used as a sensitizer, two conditions should be applied[13], the dye should absorb in the whole solar spectrum with energy of its lowest unoccupied molecular orbital (LUMO) higher than the conduction band edge of the semiconductor. The dye also should be attached strongly to the semiconductor surface to allow the fast electron injection into the conduction band with a quantum yield of unity.

Up to date, ruthenium polypyridyl complexes proven to be the best sensitizer for the dye-sensitized with nanostructured TiO_2 solar cell as well as a promising system to mimic the important parts of the light driven process in photosystem II. Gratzel and co-workers[10,11] succeeded in using the nanostructured TiO_2 film together with $Ru(dcbpy)_2(NCS)_2$, (dcbpy = 4,4-dicarboxy-2-2-bipyridine) (RuN_3-system) to achieve an overall conversion efficiency (solar energy into electricity) of *ca.* 10 %. Despite their proven functionality, ruthenium compounds suffered from the lack of absorption in the far-red/near IR region of the solar spectrum[13]. Phthalocyanine complexes known to have an intensive absorption in the far-red/near IR region, they prove to be chemically and thermally stable and posses the appropriate redox properties for sensitizing a large band gape semiconductors like TiO_2 which make them a promising candidates for dye-sensitized photo electrochemical solar cell.

Through dye-sensitization of a wide gap semiconductors, *i.e.* TiO_2, electron can be injected from the excited state of the dye into the semiconductors[14-22]. Recently, zinc phthalocyanine with tyrosine substituted were synthesized, a constructed solar cell based on the ZnPcTy-sensitized-TiO_2 electrode succeeded to achieve an overall conversion efficiency of 0.54% with a highest monochromatic incident photo-to-current conversion efficiency of around 24% with electron injection from the excited state of the dye into the conduction band completed in about 500 fs and a recombination rate of about 300 ps between the injected electron and oxidized dye[23]. Attachment of the dye to the surface of the semiconductors and the surface aggregation is consider as a crucial factors controlling the performance of the solar cell based on the zinc phthalocyanine.

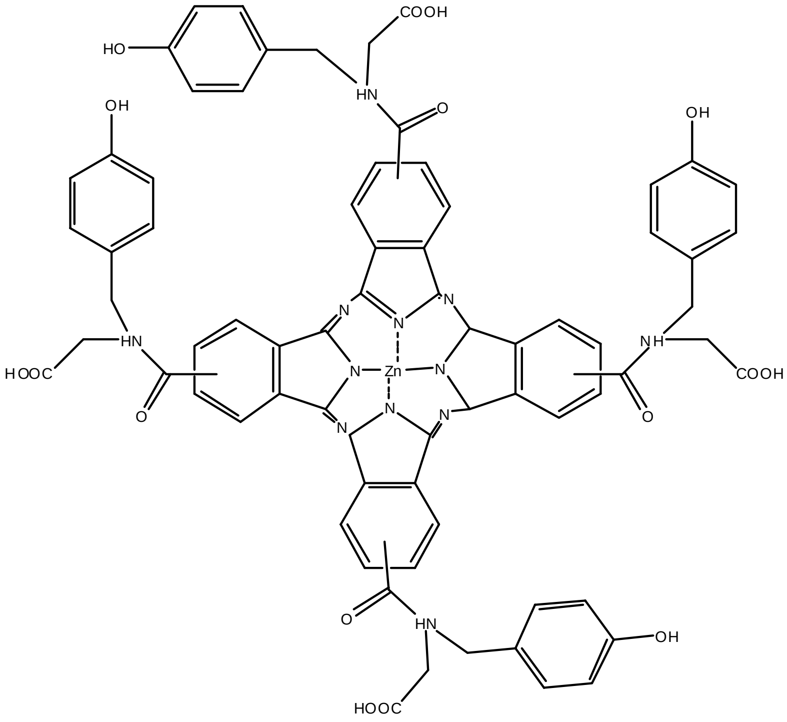
To investigate the reactivity of the photoexcited of zinc-phthalocyanine toward the semiconductors TiO_2 and the origin of the strong attachment between the zinc-phthalocyanine and the semiconductors, we decided to study in more details the photophysical properties and the quenching process of the zinc-phthalocyanine by the colloidal nanostructured TiO_2. In this study, zinc-phthalocyanine with a tyrosine group (**1**) and zinc-phthalocyanine with glycine (**1a**) as a reference compound were studied, Fig. 1. The incorporation of tyrosine group into the macrocycle of zinc-phthalocyanine (**1**) could improve the solubility in ethanol and reduce the surface aggregation due to the steric effect, moreover, tyrosine is known to play an important role in the photosynthetic water oxidation into molecular oxygen in a photosystem (II).

EXPERIMENTAL

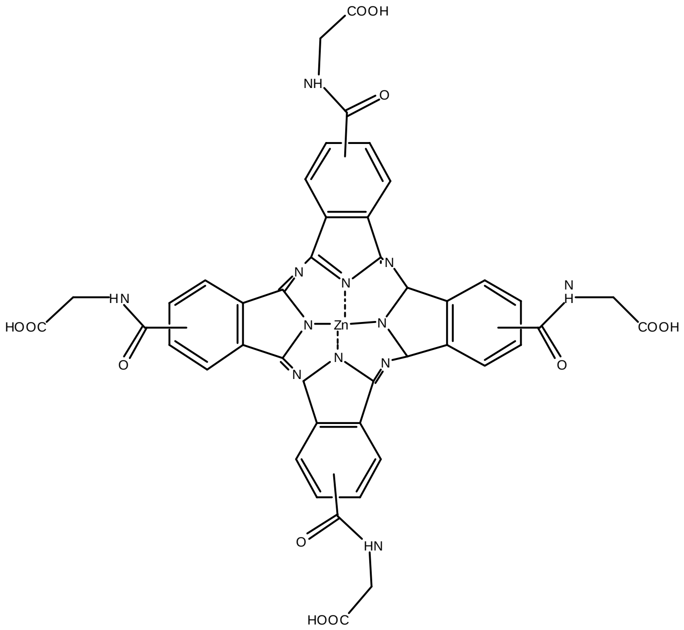
Synthesis and characterization of ZnPcTyr (**1**) and ZnPcGly (**1a**) has been described elsewhere[23]. The solution pH was adjusted with HCl or NaOH and the pH was measured with a Metrohm pH-meter.

Preparation of nanocrystalline colloidal TiO_2: Nanocrystalline colloidal TiO_2 particles were prepared by a controlled hydrolysis of $TiCl_4$ as proposed by Kormann *et al*[24]. $TiCl_4$ (1 mL) cooled to -20°C was added slowly to 257 mL of vigorously stirred distilled water at 1°C. After stirring for 0.5 h at this temperature, the reaction mixture was dialyzed for 1 h (Spectropor membrane) using 500 mL of distilled water. The dialysis procedure was repeated 4 times to change the pH of the solution from 1 to 2.4. The dialysis also improved stability of the colloid and facilitated the formation of TiO_2 crystals. Evaporating the solvent by a rotary evaporator at 30°C and 25 mbar led to the formation of a white-yellowish crystal, which was dissolved in distilled water to obtain a perfectly transparent colloidal TiO_2 suspension. The quality of the obtained particles was tested by analyzing the UV-Vis absorption spectrum, according to the method suggested by Kormann[24]. The plot of the natural logarithm of the absorption coefficient against the photon energy yields the band gap energy (E_{gap}) of 3.0 eV, which is comparable to the value obtained by Kormann[24], E_{gap} = 3.2 eV, for an average particle diameter of 2.4 nm.

Spectroscopic measurements: Luminescence spectra were recorded using a SPEX Flurolog fluorimeter by exciting the sample at 600 nm. Absorption spectra were recorded on a Jasco-V-530 spectrophotometer in a 1 cm quartz cell. Transient absorption experiments were conducted with a nanosecond laser flash photolysis setup. The excitation pulse at 600 nm was obtained from a Quanta-ray master optical parametric oscillator (MOPO) pumped by a Quanta-ray 230 Nd:YAG laser, having a pulse energy of 1-2 mJ and duration of *ca*. 7 ns. The probe light from a xenon arc lamp (75 W) was focused to a 1 mm diameter spot overlapping with the



(1)



(1a)

Fig. 1. Structures of ZnPcTyro (**1**) and its analogous ZnPcGly (**1a**)

unfocused pump beam of 2.5 mm diameter. After the 1 cm quartz cell containing the sample, the probe light was passed through two single grating monochromators and detected by a photomultiplier tube Hamamatsu R 928.

The stock solutions of ZnPcTyr (**1**) and ZnPcGly (**1a**) were prepared in ethanol and stored in the dark. Since ZnPcGly is insoluble in pure ethanol; solutions were prepared with the aid of DMSO (2% v/v). A transparent colloidal TiO_2 solution was prepared by dissolving the TiO_2 crystals in distilled water. The sample solution was prepared by adding a few microliters of TiO_2 solution to freshly prepared solutions of **1** or **1a** to obtain the desired concentration and the pH value was measured with a standard pH meter.

Absorption spectra were measured before and after flash photolysis measurements to check whether photochemical changes occurred during the experiment. No sample degradation was observed during the flash photolysis experiment. The transient spectra at different delay times were constructed from average kinetic traces measured at different wavelengths. All kinetic traces and spectral profiles were fitted using data-analysis package microcal origin.

RESULTS AND DISCUSSION

Absorption and emission spectra of the dye

The π-conjugated system in the zinc phthalocyanines result in a very intense absorption band in the visible region with high molar absorption coefficient *ca.* 10^5 M^{-1} cm^{-1}.

Metallophthalocyanines has a low solubility in aqueous solution with high tendency to aggregate[25-27]. However, the substituents at peripheral position can improve the solubility of the metallophthalocyanines complexes with a better resolution of Q-band; the peripheral substituents increase the distance between the planar macrocycle ring carrying the π-electrons thereby making solvation easier, on the other hand, solvation of zinc phthalocyanine complex in aqueous solvent result in highly aggregate of the complex with broadening of Q bands[28]. However, the presence of tyrosine group in ZnPcTyro (**1**) is not only enhanced the solubility of this compound in ethanol compared with ZnPcGly (**1a**) complex, but also reduces its ability to aggregate.

The steady state absorption spectra are shown in Fig. 2, where the absorption spectra are recorded in ethanol. The maximum values of the absorption and emission are represented in Table-1.

The absorption spectra of the diluted solution of ZnPCTyr show the characteristics absorption band of metallophthalocyanine with D_{4h} symmetry[29]. The sharp and strong absorption band in the Q-band region (*ca.* 680 nm) corresponding to [$S_1(0) \leftarrow S_0(0)$], the weak Soret band in the 350 nm [$S_2 \leftarrow S_0$] and the weak Q-band *ca.* 630 nm [$S_1(1) \leftarrow S_0(0)$] which could be attributed to the characteristic Q-band of the ZnPCTyr face-to-face dimmer or higher aggregate (H-aggregate).

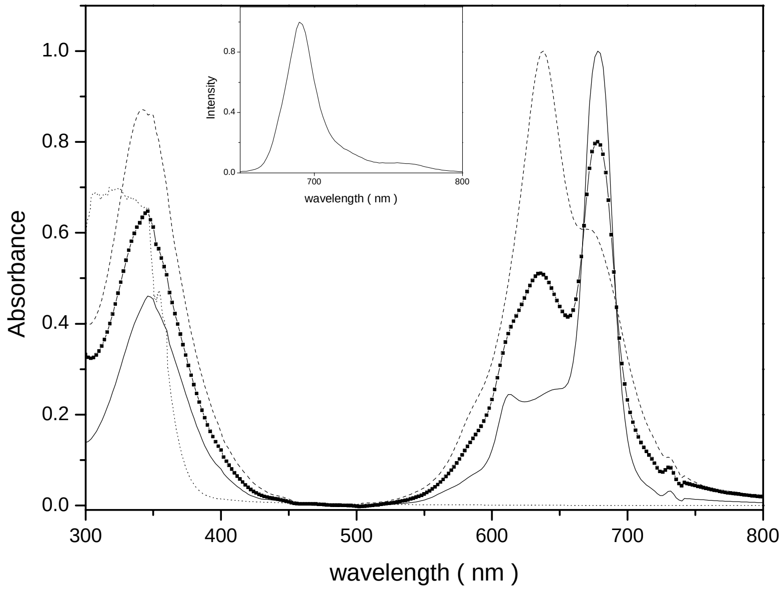


Fig. 2. Normalized absorption spectra of compound **1** in ethanol at different concentration (–) 3.0×10^{-6} M; (---) 5×10^{-5} M. Normalized absorption of colloidal TiO_2 (**---**) in ethanol and the normalized absorption spectra of compound **1a** (–■–) in ethanol at 3×10^{-5} M. The inserted figure is the emission spectra of ZnPcTyro excited at Q-band nm

TABLE-1
WAVELENGTH (nm) OF THE CHARACTERISTICS BAND OF PHTHALOCYANINE COMPLEXES

Complex	Absorption			Emission	
	Soret band	Q-band	Q-band	Q-band	Q-band
	[$S_2 \leftarrow S_0$]	$(0) \leftarrow (1)$	$(0) \leftarrow (0)$	$(0) \leftarrow (0)$	$(1) \leftarrow (0)$
ZnPcTyr (1)	347	612	680	690	755
ZnPcGly(1a)	345	635	678	690	755

The dilute solution contains mainly the monomeric phthalocyanine, as the concentration of the dye increases the order of aggregation increase (appearance of the Q-band around 640 nm). On the other hand, the emission spectra (Fig. 2) are characterized by the appearance of a strong fluorescence band concentrated at 690 nm originated from the S_1 state [$S_1(0) \leftarrow S_0(0)$] and a weak band at *ca.* 755 nm originated also from S_1 state [$S_1(0) \leftarrow S_0(1)$]. Fig. 3 shows the energy level scheme with corresponding transition.

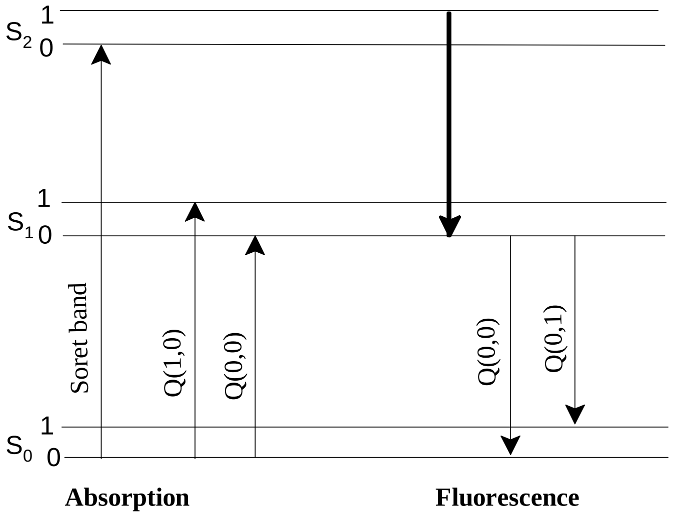


Fig. 3. Energy level scheme with corresponding transition

For both complexes **1** and **1a** the characteristics bands (Q and Soret bands) seem to be not affected on substituents peripheral ring, except for a better resolution of the Q-band (*ca.* 635 nm) which may be due to higher aggregation in the case of **1a**.

Its interesting to note that the Q-band is red shifted by 10 nm from 629 to 639 nm upon increasing the pH of the solution from 3 to 11, meanwhile the sort band is not affected upon changing the pH.

Determination of pK_a Values

pK_a value reveals the electrostatic properties of the dye, since the adsorption of the dye molecules to the TiO_2 surface depends on the electrostatic attraction between the dye and the TiO_2, determination of the pK_a value becomes an important step. The pK_a values of complex **1** were determined by UV-Vis and emission measurements over the pH range 1 to 11. A stock solution of 5×10^{-6} M was prepared in 20 % H_2O/ethanol mixture containing 0.1 M NaCl. The initial pH of the solution was adjusted to 11 by adding 0.1 M NaOH solution. The pH of the solution was lowered by the addition of HCl solution. The acid was added in such a way that throughout the entire measurements the total volume of added acid was negligible and the ionic strength of the solution remained constant thorough the whole solutions. The luminescence spectrum of each solution was obtained after the solutions were equilibrate for 5 min. ZnPcTyro (**1**) at pH 11 showd a visible Q-band band at 638 nm and soret band 340, moreover, buffer solution increases the aggregation resulting in a low resolution of the Q-band at 680 nm. Upon lowering the pH from 11 to 4.5, the Q-band at 638 nm is shifted to a higher energy by 10 nm from 638 to 628 nm with two isosbestic points at 388 and 570 nm. Further lowering of the pH from 4 to

1 lead to an opposite situation, where the Q-band at 628 nm was shifted to lower energy, from 628 to 638 nm with two isosbestic points at 418 and 511 nm (Fig. 4). The ground-state pK_a values can be determined from the relationship between the changes in the optical density or the peak maximum with the pH for a given wavelength. A plot of the λ_{max} of the Q-band transition as a function of pH shows a sigmoidal shape with a pH at the inflection point assigned to the pK_a value. In a pH range of 11 to 4.5 the pH at inflection point giving the ground-state pK_a value of 6.0 ± 0.2. On the other hand, in a pH range of 4.0 to 1 the pK_a value was found to be 2.6 ± 0.1. The fact two separate equilibria were obtained in complex **1** (two pK_a value) suggests that the carboxylic acid groups are non-equivalent. **Scheme-1** shows two-step equilibrium of **1** and **1a**.

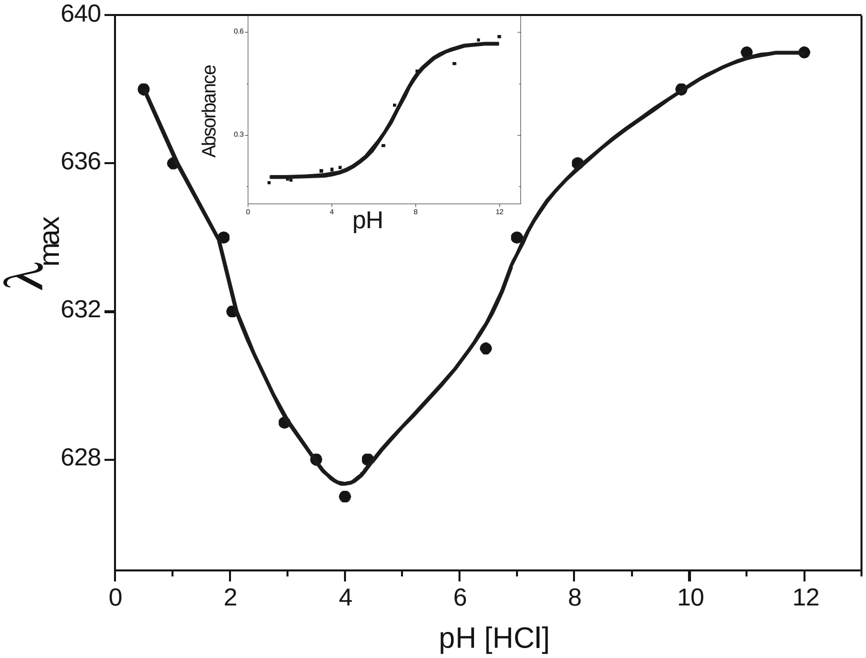


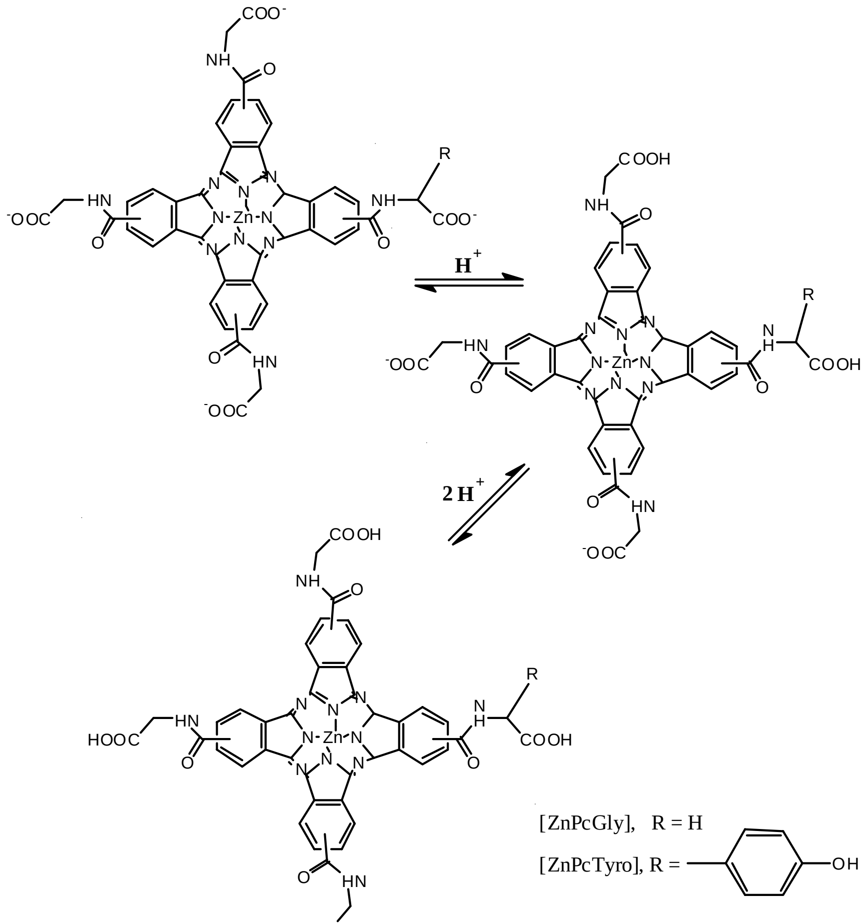
Fig. 4. Maximum wavelength changes of the absorption spectral of ZnPcTyro ([**1**] = 5 × 10^{-5} M) as a function of pH, pH changes from 11 to 1

Zinc phthalocynine-TiO_2 system

Addition of TiO_2 colloidal to **1** or **1a** solution affects both the absorption and emission spectra of the phthalocayanine dye. Figs. 5 and 6 show the spectral changes of solution of compound **1** in ethanol upon increasing the concentration of TiO_2 colloidal. Upon addition of TiO_2 colloidal the absorption of compound (**1a**) decreases with tow isobestic points at 680 and 560 nm. The adsorption of compound (**1a**) on the surface of TiO_2 modify the electron density of compound (**1a**) and a new absorption band at 438 nm appears which is attributed to the adsorbed dye on the surface of TiO_2. The equilibriums between the adsorbed and unadsorbed molecule of ZnPc are expressed in eqns. 1 and 2.

$$\mathrm{Dye-COO^{-}+TiOH}\ \underset{}{\overset{\mathbf{Ka}}{\rightleftharpoons}}\ \mathrm{[Dye-COO-Ti\equiv]} \qquad (1)$$

$$K_a = \mathrm{[Dye-COO-Ti\equiv]/[Dye-COO^{-}]\cdot[TiOH^{+}]} \qquad (2)$$



Scheme-1

The apparent association constant could be evaluated using the method described by Bensi and Hildebrand[30]. Eqn. 3 could be obtained from eqns. 1 and 2.

$$\frac{[\mathrm{ZnPc}]_0}{D} = \frac{1}{\varepsilon} + \frac{1}{[\mathrm{TiO_2}]_0 K_a \varepsilon} \qquad (3)$$

where $[\mathrm{ZnPc}]_0$ and $[\mathrm{TiO_2}]_0$ refers to the total concentration of ZnPc and TiO_2, respectively. D refers to the absorption of [(**1**)…TiO_2] and ε is the molar absorption coefficient.

According to eqn. 3, plot of [ZnPc]/D against the reciprocal concentration of colloidal TiO_2 is linear with slop equal to $1/K_a$ and intercept equal to 1/ε. Indeed, a straight line was observed, Fig. 5, the apparent association constant K_a was found to be $3.9 \times 10^4\ M^{-1}$.

Fluorescence quenching of 1 or 1a by colloidal TiO_2

As it's shown in Fig. 5, the fluorescence intensity of **1** (or **1a**) is quenched strongly in the presence of the colloidal TiO_2.

The observed quenching of the (Q band) excited state could be attributed to energy or electron transfer to the semiconductor[13,20]. Since, the absorption spectrum of colloidal TiO_2 and the emission spectrum of **1** do not overlap, the energy transfer mechanism can be excluded[17,23]. The quenching behavior observed here is similar to the quenching by TiO_2 observed for different dye. Ruthenium dyes[20,21] and zinc phthalocyanines[32] attributed to electron injection from the excited state of the dye to the conduction band of TiO_2[15]. The electron injection from the excited state of the dye into the conduction band of TiO_2 is thermodynamically allowed since the excited state energy of the dye is at 1.82 eV and the energy level of the singlet excited state (LUMO) of **1a** and **1** were determined to be at -1.35 eV and -1.27 V, respectively and the energy level of the conduction band of the TiO_2 is at *ca.* -0.74 eV.

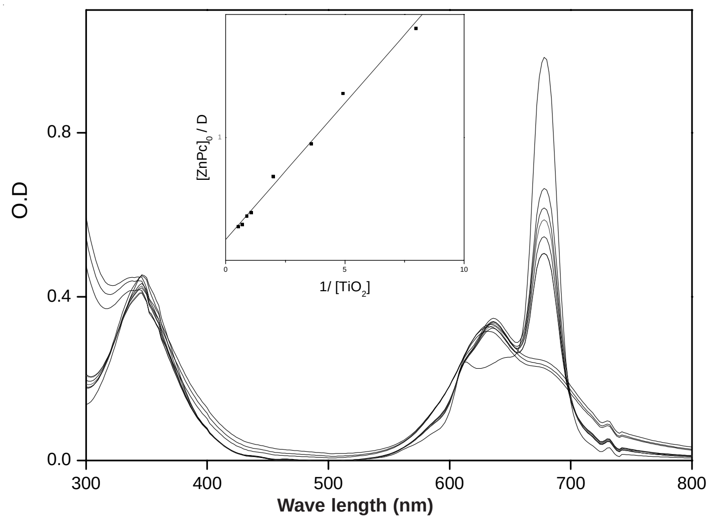


Fig. 5. Absorption spectra of compound **1** in presence of various concentrations of TiO_2 colloidal solution (0.00 - 2.0 × 10^{-4} M) [**1**] = 15 µM. The insert curve is the dependence of $[ZnPcTyr]_0/D$ on the reciprocal concentration of TiO_2 colloidal

Adsorption of the dye on the surface of TiO_2

TiO_2 has an isoelectric point[33] at pH = 5, *i.e.*, below pH 5 the TiO_2 is positively charged [$TiOH^+$] and at pH > 5 is negatively charged. Thus, at pH < 5 we have the desired situation of negatively charged dye and positively charged TiO_2 surface, providing favorable electrostatic attraction for adsorption of complexes **1** and **1a** to the semiconductor surface. Moreover, at low pH the stability of the TiO_2 colloid is improved[17] due to the accumulation of charge at low pH and thus a condition of strong electrostatic interaction between the dye and TiO_2 is achieved. Attachment of the complexes to the TiO_2 surface in this pH interval was examined by observing the quenching of luminescence by TiO_2.

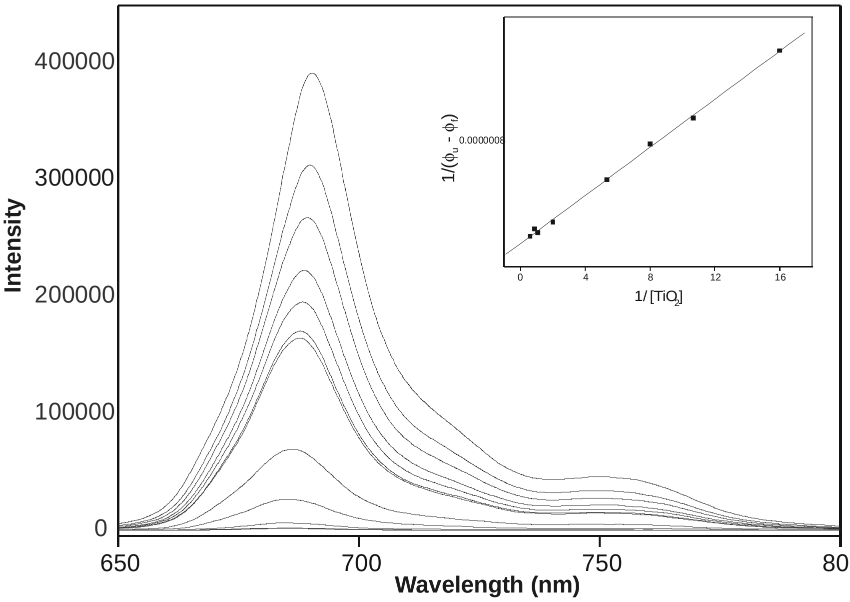


Fig. 6 Fluorescence emission spectra of compound **1** upon titration with TiO_2 colloidal solution (0.00 - 2.0 × 10^{-4} M) [**1**] = 3 μM. The insert curve is the relation between $1/(\phi_u-\phi_f)$ with $1/[TiO_2]$

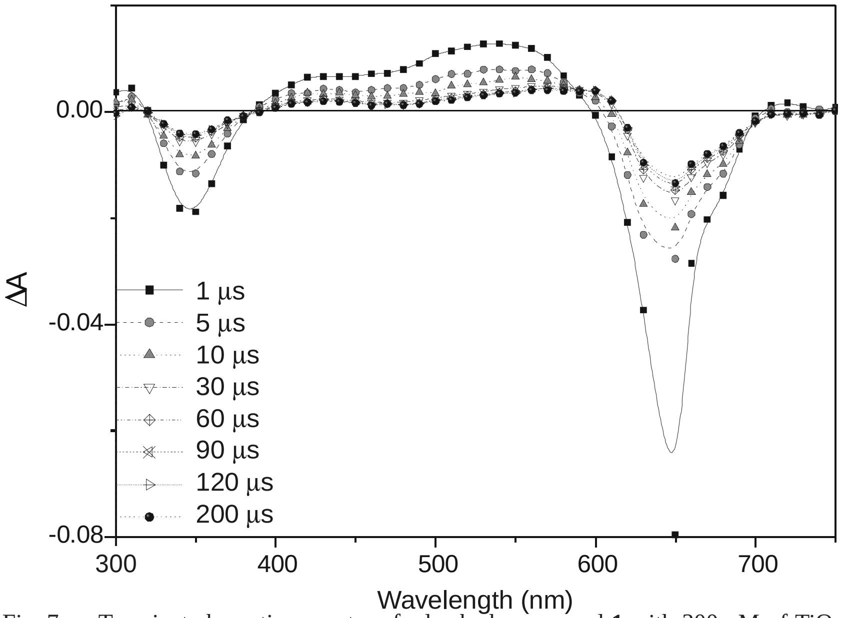


Fig. 7. Transient absorption spectra of adsorbed compound **1** with 300 μM of TiO_2 at different delay times after excitation at 640 nm

As shown in Fig. 6, the luminescence intensity of **1** is decreased with the increase of TiO_2 concentration until it reaches a constant value at concentrations of about 300 µM. The dye adsorption to TiO_2 also causes a small blue shift of the emission maximum (*ca.* 5 nm) at high concentration TiO_2. The similarity of the quenching pattern observed for both complexes shows that the presence of the tyrosyl in compound **1** does not affect the functionality of the carboxylic acid group, which makes the following analysis valid for both compounds **1** and **1a**.

According to Kamat *et al*[19,34] the quenching of luminescence by the TiO_2 colloidal particle reflects the amount of chemisorbed dye on the surface of the TiO_2 particle. In order to obtain an association constant (K_a) for the dye-TiO_2 interaction, quenching of the luminescence intensity of compounds **1** and **1a** by TiO_2 was analyzed by considering an equilibrium between the adsorbed and unadsorbed dye molecules (eqn. 1).

The observed emission quantum yield ϕ_f of the dye in the presence of colloid is related to the emission quantum yield of the unadsorbed dye ϕ_u and the emission quantum yield of the adsorbed molecule, ϕ_f', by the following equation (4).

$$\phi_f = (1 - \alpha)\,\phi_u + \alpha\phi_f' \tag{4}$$

where α is the degree of association between the TiO_2 particles and compound **1**. Under the condition of high TiO_2 concentration ($[TiO_2] >> [dye]$), α can be expressed as

$$\alpha = \frac{K_a[TiO_2]}{1 + K_a[TiO_2]} \tag{5}$$

By substituting equation (5) into equation (4), the quenching of luminescence emission of compounds **1** or **1a** by TiO_2 can be represented as:

$$\frac{1}{(\phi_u - \phi_f)} = \frac{1}{\phi_u - \phi_f'} + \frac{1}{K_a(\phi_u - \phi_f')[TiO_2]} \tag{6}$$

The experimental data were fitted using equation (6), Fig.6 and an apparent association constant K_a of 5.3×10^4 M^{-1}. This result is in a good agreement with the result obtained from absorption method, the emission quantum yield of adsorbed molecule (ϕ_f') is very small so the ZnPc…TiO_2 has no fluorescence. The same quenching pattern was observed for the reference compound **1a**, with a similar association constant as for compound **1**. This shows that under our experimental conditions *ca.* 90 % of compounds **1** or **1a** is adsorbed to the surface of TiO_2.

Transient absorption spectroscopy

The absorption spectrum of the complex **1**-TiO_2 electrode exhibits the characteristics absorption of the monomer **1** with a small shift by 4 nm (from 346 to 342 nm). Comparing with the absorption spectrum of the

TiO_2-electrode, complex **1**-TiO_2 electrode extends the optical absorption spectrum into visible region, so higher energy conversion efficiency could be obtained. For a cell based on complex **1**-TiO_2, the incident-photon-to-current-conversion efficiency (IPCE) was previously determined[23] and a maximum of *ca.* 24 % of IPCE was obtained at 690 nm with an overall conversion efficiency of 0.54 %. The performance of the complex **1**-TiO_2 based cell is still lower that the cell invented by Grarzel (*i.e.* RuN_3 system shows a quantum efficiency of *ca.* 100 % and overall conversion efficiency of *ca.* 100 %). The difference in the performance between the two systems could be clarified by examining the main factors affecting the overall conversion efficiency *i.e.*, the time constant of electron injection and charge recombination. In order to clarify this point, the photoinduced electron transfer was investigated.

The photoinduced electron transfer processes were initiated when a pulse of visible light (λ = 640 nm) excites the Q-band of the monomer species of compound **1** where an electron can be injected into the conduction band of TiO_2. As a result, the oxidized dye is formed and the ground state absorption is bleached.

Once the oxidized dye is formed, there are two possible ways for the photogenerated dye to return back to the ground state: either by back electron transfer from the nanocrystalline TiO_2 (charge recombination), or by a second intramolecular electron transfer process from the linked tyrosine moiety. Both reactions will result in repopulation of the ground state and thus recovery of the ground state bleaching. Fig. 7 shows the transient spectra of complex **1**-TiO_2. The transient spectrum does not exhibit any distinct spectral band corresponding to the formation of the tyrosyl radical, (which has a characteristic band at 410 nm) which excludes the intramolecular electron transfer process. In fact the comparison of the transient absorption spectra of the complex **1**-TiO_2 and its analogous complex **1a**-TiO_2 shows a comparable transient spectra.

The electron injection for the complex **1**-TiO_2 system occurs in *ca.* 500 fs[23], while for the RuN_3-system it is completed only after *ca.* 100 ps[35]. However, even that ZnPcTyr is slightly better than RuN_3 from the electron injection point of view, the recombination in complex **1**-TiO_2 is considerably faster than it is in RuN_3-TiO_2 (*i.e.* the injected electrons recombine with the oxidized dye in *ca.* 300 ps for the complex **1**-TiO_2 system[23] compared to a longer recombination time for RuN_3-TiO_2. In fact there is no recombination in 300 ps) which could explain the low performance of the complex **1**-TiO_2 compared to the RuN_3-TiO_2 system.

Conclusion

In this work, we reported the photophysical properties of two zinc-phthalocyanine and quenching of the fluorescence of the excited state as well as the adsorption behavior of the dye on the surface of the TiO_2.

The absorption spectra of the ZnPc was observed due to the transition of Q(0-0) and Q(0-1) which is responsible for the appearance of the absorption band at 780 nm. The transition of the soret band (0-0) is the origin of the absorption band appearing at 350 nm, on the other hand the emission radiation for the ZnPc was originated from the S_1.

The presence of the tyrosine group enhances the solubility of the dye in ethanol and decreases the aggregation behaviour. The aggregation behaviour of the ZnPc compound can be directly observed through the monitoring of the appearance of the Q-band at 640 nm .

The presence of the carboxylic acid groups enables anchoring of the complex to nanocrystalline TiO_2 with a good degree of association (up to 90 % with an apparent association constant K_a of 4.5×10^4 M^{-1}). Anchoring of the dye complex to the nanocrystalline TiO_2 enables ultrafast injection of electrons from the excited state into the conduction band of TiO_2 (completed in *ca*. 500 fs) which result in strong quenching of the singlet state of the ZnPc.

The low ICPE percentage (*ca*. 24 % at 690 nm) obtained could be attributed to the surface aggregation and fast charge recombination.

ACKNOWLEDGEMENTS

The author thanks Dr. Fatima Delmani and Dr. Musa Barguthi for critical reading of this manuscript. Financial support from the following agencies is gratefully acknowledged: Knut and Alice Wallenberg Foundation, Delegationen för Energiförsörjning i Sydsverige (DESS), the Swedish National Energy Administration, the Swedish Natural Science Research Council (NFR) and the Swedish Research Council for Engineering Sciences (TFR).

REFERENCES

1. G. Ferraudi, in eds: C.C. Leznoff and A.B.P. Lever, Phthalocyanines: Properties and Applications, VCH, New York, Vol. 1, pp. 293-340 (1989).
2. J.R. Darwent, P. Duglas, A. Harrimann, G. Poter and M.C. Richoux, *Coord. Chem. Rev.*, **44**, 83 (1982).
3. I. Rosenthal and E. Ben-Hur, in eds: C.C. Leznoff and A.B.P. Lever, Phthalocyanines: Properties and Applications, VCH, New York, Vol. 1, pp. 39, 7-427 (1989).
4. R. Bonnet, *Chem. Soc. Rev.*, **24**, 19 (1995).
5. T. Ohm. S. Kato and T. Tanno, *J. Phys. Chem.*, **87**, 775 (1983).
6. M. De Baker, P. Jacquot, F.X. Sauvage, B. Van Vlierberege and G. Lepoutre, *J. Chim. Phys.*, **84**, 429 (1987).
7. Y. Kaneko, Y. Nishimura, Y. Arao, H. Sakuragei, K. Tokumaru and D. Mastsunaga, *J. Photochem. Photobiol. A Chem.*, **89**, 37 (1995).
8. J, Delaire. C, Giannotti and J. Zakrzewski, *J. Photochem. Photobiol. A Chem.*, **112**, 2005 (1998).
9. K. Bayo, J.C. Mossoyan and G.V. Quedraogo, *Spectrochim. Acta A*, **60**, 653 (2004).
10. B. O'Regan and M. Grätzel, *Nature*, **353**, 737 (1991).

11. M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, **115**, 6382 (1993).
12. A. Hagfeldt and M. Grätzel, *Chem. Rev.*, **95**, 49 (1995).
13. M.K. Nazeeruddin, P. Pe´chy, T. Renouard, S.M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi and M. Grätzel, *J. Am. Chem. Soc.*, **123**, 1613 (2001).
14. M.K. Nazeeruddin, E. Muller, R. Humphry-Baker, N. Vlachopoulos and M. Grätzel, *J. Chem. Soc. Dalton Trans.*, 4571 (1997).
15. A. Thomspon, M. Smailes, J. Jeffery and M. Ward, *J. Chem. Soc. Dalton Trans.*, 737 (1997).
16. M.K. Nazeeruddin, S.M. Zakeeruddin, R. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C.H. Fischer and M. Grätzel, *Inorg. Chem.*, **38**, 6298 (1999).
17. C. Chen, X. Qi and B. Zhou, *J. Photochem. Photobiol. A*, **109**, 155 (1997).
18. E. Ghenne, F. Dumont and C. Buss-Herman, *Colloid Surf. A*, **131**, 63 (1998).
19. V. Kamat, *J. Phys. Chem.*, **93**, 859 (1989).
20. Y. Tachibana, S. Haque, I. Mercer, J. Durrant and D. Klug, *J. Phys. Chem. B*, **104**, 1198 (2000).
21. J. Asbury, E. Hao, Y. Wang, H. Ghosh and T. Lian, *J. Phys. Chem. B*, **105**, 4545 (2001).
22. R. Argazzi, C. Bignozzi, T. Heimer, F. Castellano and G. Meyer, *J. Phys. Chem. B*, **101**, 2591 (1997).
23. J.H.G. Benko, F. Korodi, T. Polivka, R. Lomoth, B. Åkermark, L. Sun, A. Hagfeldt and V. Sundstrom, *J. Am. Chem. Soc.*, **124**, 4923 (2002).
24. C. Kormann, W. Bahnemann and R. Hoffmann, *J. Phys. Chem.*, **92**, 5196 (1988).
25. V. Iliev, V. Alexiev and L. Bilyarska, *J. Mol. Catal. A. Chem.*, **137**, 15 (1999).
26. P.C. Martin, M. Gouterman, B.V. Pepich, G.E. Renzeoni and D.C. Schindele, *Inorg. Chem.*, **30**, 3305 (1991).
27. K. Lang, D.M. Wagnerova and J. Brodilova, *J. Photochem. Photobiol. A: Chem.*, **72**, 9 (1993).
28. A. Ferencz, D. Neher, M. Schulze, G. Wegner, L. Viaene and F.C. Schryver, *Chem. Phys. Lett.*, **245**, 23 (1995).
29. M.J. Stillman, T.Nyokong, in edn: C.C. Leznoff and A.B.P. Lever, Phtahlocyanines: Properties and Applications, VCH, New York, Vol. 1 (1989).
30. H.A. Bensi and J.H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2701 (1949).
31. J. Moser and M. Grätzel, *J. Am. Chem. Soc.*, **106**, 6557 (1984).
32. H. Mao, H. Deng, H. Li, Y. Shen, Z. Lu and H. Xu, *J. Photochem. Photobiol. A: Chem.*, **114**, 209 (1998).
33. G. Sprintschnik, H.W. Sprintschnik, P.P. Kirsch and D.G. Whitten, *J. Am. Chem. Soc.*, **99**, 4947 (1977).
34. (a) J. Xiang, C. Chen, B. Zhou and G. Xu, *Chem. Phys. Lett.*, **315**, 371 (1999); (b) P. Kamat, *Chem. Rev.*, **93**, 267 (1993).
35. S.A. Haque, Y. Tachibana, R.L. Willis, J.E. Moser, M. Grätzel, D.R. Klug and J.R. Durrant, *J. Phys. Chem. B*, **104**, 538 (2000).

(*Received*: 12 May 2005; *Accepted*: 30 June 2006) AJC-5031