Evidence on dye clustering in the sensitization of TiO$_2$ by aluminum phthalocyanine

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As previous studies have shown, the photocatalytic reduction of Cr(VI) to Cr(III) in the presence of 4-chlorophenol can be carried out efficiently under visible irradiation using TiO$_2$ modified with hydroxo-aluminum-tricarboxymonoamide phthalocyanine (AlTCPc) in spite of the high aggregation tendency of the dye. In the present work, photocurrent and absorption spectra of AlTCPc modified TiO$_2$ films are studied together with absorption and fluorescence of the dye in solution as a function of the concentration of the dye to clarify (a) the role of aggregates and the nature of the species responsible for electron injection into the semiconductor and (b) the reasons why, as reported earlier, the photocatalytic activity is nearly independent of dye loading at constant TiO$_2$ mass. Results are consistent with the presence of AlTCPc clusters with similar properties both on the TiO$_2$ surface and in H$_2$O–DMSO solution. The actual photoactive species is the monomeric dye electronically coupled to the semiconductor. Monomer concentration depends only slightly on AlTCPc analytical concentration, in a way similar to surfactant monomers in micellar equilibrium, thus explaining the independence of photocatalytic activity on dye concentration.

Introduction

Metallophthalocyanines (MPc) are a family of compounds showing high absorption coefficients in the far-red and near IR, excellent photostability, chemical and thermal stability and interesting magnetic, electrical and optical properties.[1] In general, MPc triplet states yield efficiently singlet molecular oxygen *via* energy transfer to ground state triplet molecular oxygen. For that reason, they have been extensively considered as type II photosensitizers for the degradation of environmental pollutants and in the photodynamic therapy of cancer.[2] When deposited on the surface of semiconductors, they are able to inject electrons into the conduction band after light excitation.[3] Thus, MPcs have been tested as sensitizers for wide band-gap semiconductors[4–7] and dye-sensitized solar cells.[8] However, owing to their planar conjugated structure and the occurrence of π–π interactions among adjacent molecules they are prone to aggregate strongly.[9] The stacking tendency, with the consequent formation of H-type or columnar aggregates,[10] leads to rapid non-radiative deactivation of exciton states by internal conversion and may render the sensitization processes inefficient if electron injection is not fast enough.

Several strategies have been devised to reduce aggregation of phthalocyanines. The incorporation of different substituents into the molecular structure allows a relative control over dye–dye and dye–solvent interactions, leading to derivatives with tuned properties for different applications. For example, Reddy *et al.*[11] synthesized an unsymmetrical zinc phthalocyanine containing three *tert*-butyl and two carboxylic acid groups for the sensitization of TiO$_2$ films. The carboxylic groups allow grafting of the dye onto the surface and intimate electronic coupling between the excited-state wave function and the conduction band of the semiconductor, while the *tert*-butyl groups enhance solubility in organic solvents, prevent aggregation and tune the LUMO level of the phthalocyanine. In another example, Mori *et al.*[12] synthesized zinc phthalocyanines containing three or six 2,6-diphenylphenoxy groups that prevent aggregation almost completely, allowing a relatively high energy conversion efficiency (4.6%). According to the authors, this is the highest energy conversion efficiency obtained for dye-sensitized solar cells using phthalocyanines.

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Another strategy to reduce dye aggregation on surfaces is co-adsorption. Amao et al.[13] reduced dye aggregation of an aluminum phthalocyanine and improved TiO_2 sensitization efficiency by co-adsorption with myristic acid. Previously, Nazeeruddin et al.[14] obtained good sensitization efficiencies for zinc and aluminum phthalocyanines using cholic acid (cheno) as a co-adsorbate and 4-tert-butylpyridine as a ligand in the axial coordination position of the phthalocyanine metal, thus avoiding stacking. Further examples can be found in the literature.[8,15]

Even when dye aggregation has been recognized as a major factor in reducing the sensitization efficiency, the participation of aggregates in electron injection into semiconductors, in principle, should not be discarded. There are several examples in the literature, where dye aggregation was found to be beneficial to the TiO_2 sensitization efficiency[16,17] or at least the participation of aggregates in the electron injection process was demonstrated.[18,19] Moreover, dye aggregation is generally accompanied by spectral broadening, allowing enhancement in light collection efficiency. In the case of strong electronic coupling between aggregates and the semiconductor, electron injection dynamics may be competitive with exciton intrinsic deactivation pathways, and coherent transport may lead to light harvesting action of the aggregates.[20] For that reason, self-assembled dye aggregates have been considered for the development of highly efficient dye-sensitized solar cells, mimicking the role of light harvesting aggregates in natural photosynthesis.[21]

Evidence on the participation of phthalocyanine aggregates in electron injection into TiO_2 can be found in the literature. For example, He et al.[22] studied metal-free and zinc butoxy-carbonyl phthalocyanines incorporated into TiO_2 films and found that the photocurrent action spectra were very similar to the absorption spectra of the aggregated dyes. Similar results were found for tyrosine and glycine-substituted zinc phthalocyanines on TiO_2.[23] However, Chevaleevski et al.[24] have found that Zn and Cu phthalocyanines get aggregated when adsorbed on TiO_2 but the photocurrent action spectra resemble the absorption spectra of the monomer in solution, demonstrating that the aggregates do not participate in electron injection into the semiconductor or, at least, that they are quite inefficient. Deng et al.[25] found similar results for different tetrasulfonated MPcs. Thus, the participation of aggregates in electron injection probably depends on the nature of the phthalocyanine.

Some time ago, we tested the capability of hydroxyaluminum-tricarboxymonoamide phthalocyanine (AlTCPc) adsorbed on TiO_2 for the photocatalytic reduction of Cr(VI) under visible irradiation in the presence of 4-chlorophenol as a sacrificial electron donor.[26] Though the absorption spectrum of the modified photocatalyst in the solid state and in aqueous suspensions showed clearly that the dye is aggregated on the surface of TiO_2, it was demonstrated that a rapid reduction to Cr(III) was possible. Rather surprisingly, dye loading had no effect on the shape of the absorption spectrum. This is possible only if a single aggregated species prevails or, in other words, if stepwise aggregation with the formation of dimers,

trimers, tetramers and so on is excluded. Furthermore, no effect of dye loading was found on the Cr(VI) reduction rate at constant TiO_2 mass, pointing to the occurrence of a constant concentration of the species responsible for electron injection into the semiconductor. In order to clarify (a) the nature of this species and the role of aggregates in the photosensitization process and (b) the reason for the independence of the photocatalytic activity on dye loading, in the present work photocurrent action spectra of AlTCPc-sensitized TiO_2 films are studied together with the photophysical characterization of the dye in the films and in solution.

Experimental

Chemicals

Commercial TiO_2 powder (Evonik P25, AG Germany, specific surface area 50 m^2 g^{-1}) was used. Hydroxoaluminum-tricarboxy-monoamide phthalocyanine (AlTCPc) was synthesized as previously described.[27] Transparent conducting glass slides (In_2O_3/SnO_2 – ITO, Aldrich), 75 mm × 25 mm × 1.1 mm, surface resistivity 15–25 Ω per square, transmittance >83%, cut to 25 mm × 25 mm, were used for the construction of working electrodes. Graphite–SnO_2 counter-electrodes were obtained by spreading a small amount of graphite powder (Aldrich, <20 μM) over a SnO_2 conducting glass slide. Dimethylsulfoxide (DMSO) was from Anedra, analytical reagent, and water was deionized and 0.22 μM-filtered in a Millipore-Q system.

Film preparation and dye adsorption

Nanocrystalline TiO_2 films were prepared as described elsewhere.[28] Briefly, TiO_2 powder (3 g) was mixed with water (3 mL), adding acetylacetone (0.1 mL) as a particle stabilizer. The homogeneous paste obtained by grinding was diluted with water (0.5 mL) adding Tween 80 (0.05 mL) as a wetting agent. A drop of the diluted paste was placed near the end of an ITO glass. Using an adhesive tape as a spacer, a thin uniform film was obtained on the surface of the conductive substrate by raking off the excess with a cutter blade. The film was dried for 2 h at 100 °C and sinterized in air at 500 °C for 30 min. AlTCPc was adsorbed by dipping the film in a solution of the dye in DMSO for 15 min and dried at 60 °C for 2 h. The concentrations of the dye in the dipping solutions were 3.5, 35 and 92 μM (electrodes A, B and C, respectively).

Optical measurements

Prepared films are semi-transparent and light-scattering. The fraction of incident radiation absorbed by the film and absorbance spectra were calculated as $\alpha = 1 - T_d - R_t$ and $A = -\log(1 - \alpha)$, respectively, where T_d is the diffuse transmittance and R_t the total reflectance of the sample. Measurements were performed using a Shimadzu UV-3101 spectrophotometer equipped with an integrating sphere, using $BaSO_4$ as a standard for the 100% reflectance level. A low absorbance of the unloaded support, almost constant between 500 and 800 nm, was subtracted. In order to ensure the same scattering

properties, the film without the dye was used as a blank. A method for the determination of absorbance spectra of suspensions, similar to the one used here, is described elsewhere.[29]

AlTCPc solutions in DMSO and H_2O–DMSO (90 : 10 v/v) of different dye concentrations in the range from 1.0 to 11 μM were characterized by absorption and steady-state emission measurements. H_2O–DMSO solutions were prepared by pouring into water a solution of the dye in DMSO. Solutions were stable in spite of the low solubility of the dye. Absorption measurements were performed in the same spectrophotometer, used in the transmittance mode. Fluorescence was determined using a PTI model QM-1 spectrofluorometer.

Photoelectrochemical measurements

Photocurrent spectra of working electrodes were measured with a sandwich-type cell (see Scheme 1). The working electrode (WE) – dye-coated film on the ITO glass – was gently squeezed together with a graphite–SnO_2 counter electrode (CE) using a homemade cell holder, consisting of two Plexiglas® plates (H) joined together with plastic screws. The electrical contact was afforded by copper terminals (C) pressed between the electrodes and holder plates. Square 2.5 cm electrodes were used. The electrolyte, 0.5 M KI + 0.05 M I_2 in ethylene glycol, was incorporated between the electrodes by capillarity and the cell edge was sealed with Parafilm®. One of the plates had a 1.5 cm high and 2.0 cm wide window (W) to allow direct illumination through the working electrode. A 450 W xenon lamp with a monochromator (PTI model 01-001, bandpass 4 nm mm^{-1}, slit width 2 mm) was used as a light source. The illuminated area was typically 0.4 cm^2.

Very low photocurrents, in the order of tens of nA, were obtained under irradiation at 700 nm (~1 mW cm^{-2}).
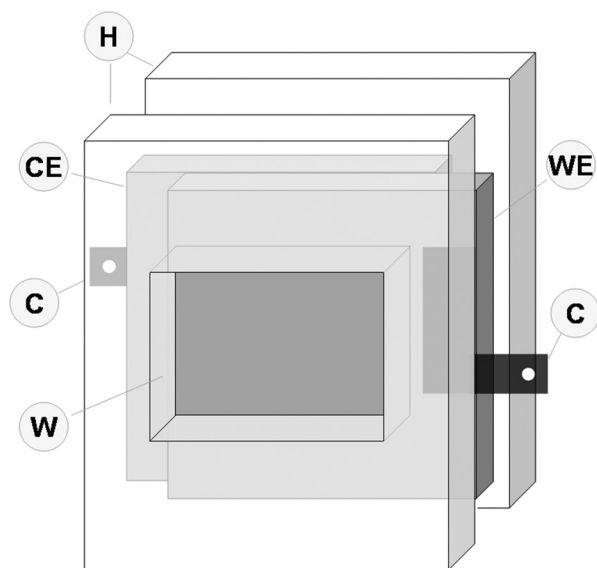
Preliminary experiments were performed under chopped illumination and lock-in amplification of the measured signal. However, it was observed that preirradiation with UV, ~80 μW cm^{-2} at 350 nm (open circuit), increased dramatically the photocurrent, allowing a direct measurement of photocurrent under visible irradiation. Irradiance was measured using a Coherent Fieldmaster power meter with a photodiode model SR45 for the visible and SA62 for the UV. Accordingly, photocurrent measurements at 600–800 nm were performed after excitation of the electrode with UV radiation until maximum photocurrent was obtained. A water filter was set in front of the lamp to avoid IR radiation and a cut-off filter (Schott GG455, 2 mm thickness) was used to prevent UV excitation during irradiation in the visible region. A potentiostat (TEQ-02) was used to measure the current at a constant potential applied between the electrodes. The counter electrode and the reference electrode terminals were short-circuited.

Results and discussion

Spectroscopic characterization of the electrodes

Normalized absorbance spectra of working electrodes with different dye loadings are shown in Fig. 1. They are compared with the remission function spectrum, $F(R) = (1 - R_d)^2/(2R_d)$, where R_d is the diffuse reflectance of a solid microparticulate sample containing 16.1 μmol AlTCPc (g TiO_2)$^{-1}$ (sample I in ref. 26). Within the experimental error, the same shape was found in all cases, the spectrum on P25 powder being nearly 5 nm red-shifted. Spectral shapes for electrodes A, B and C show no systematic variation with dye concentration. The inset shows the linear correlation between the absorbance at the
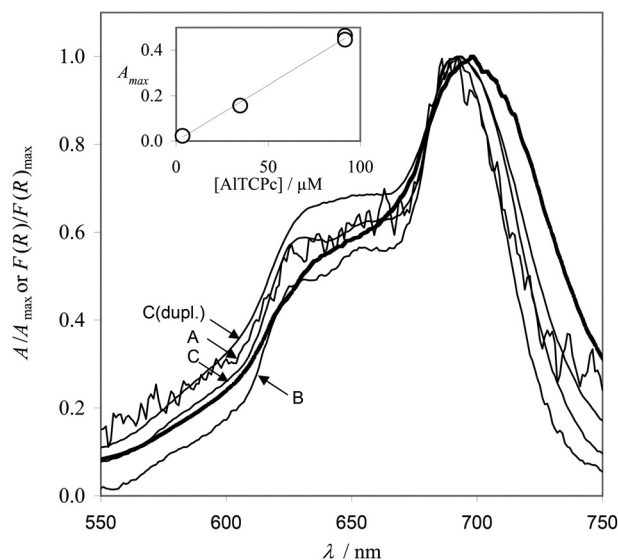

Scheme 1 Cell used for the photoelectrochemical measurements (H: holder plates; W: window; WE: working electrode; CE: counter electrode; C: electrical contacts).

Fig. 1 Normalized absorbance spectra of nanostructured TiO_2 electrodes with different dye loadings (thin lines) and remission function spectrum of AlTCPc adsorbed on P25 (16.1 μmol g^{-1}, thick line). Inset: absorbance of electrodes at maximum (692–693 nm) vs. dye concentration in the dipping solution, electrodes A, B, C and C-duplicate (see text).

maximum and the concentration of the dye in the dipping solution (see the Experimental section); the concordance between sample C and its duplicate shows that the reproducibility is excellent. As the electrode preparation assures a constant film thickness, results show that adsorption is in the linear regime within the concentration range used in this work. This behavior can be explained taking into account that DMSO is a good solvent for the phthalocyanine under study. The high intensity of the satellite around 650 nm, as compared with the main band around 680 nm, and the width of the spectrum suggest a high aggregation degree,[30] independent of dye loading. Similar results were obtained for AlTCPc adsorbed at different concentrations on P25 and in aqueous suspensions of the same samples.[26]

Action spectra

Fig. 2 shows the photocurrent density obtained at 700 nm measured by shortly interrupting the UV irradiation and polarizing the electrode at 100 mV. A marked increment of photocurrent is obtained after illumination at 350 nm, reaching a plateau under the conditions of the experiment at nearly 200 min. Photocurrent decreases slowly when the electrode is kept in the dark between photocurrent measurements (data not shown). The effect is completely reversible when the measurement cell is disassembled and reassembled (data not shown).

Enhancement of photocurrent under visible light by UV preirradiation was already observed in dye-sensitized nanocrystalline TiO$_2$ films.[31–33] In the absence of strongly adsorbed cations, after UV illumination of the semiconductor surface states are reversibly produced at the electrolyte interface. These states reach a high enough density to build up a

continuous percolation pathway, leading to enhanced charge transport and reducing recombination.[34] The adsorption of cations on the TiO$_2$ surface shifts the band edge to positive potentials, thus increasing the photocurrent,[31] but reduces the effect of UV illumination. Li$^+$ is known to adsorb strongly on the surface and intercalate into TiO$_2$ films, thereby increasing the photocurrent but preventing UV effects.[35] In contrast, bulky cations like tetra-n-butylammonium (TBA$^+$) do not adsorb on the TiO$_2$ surface. The effect of K$^+$ is similar to that of TBA$^+$.[31] The important photocurrent UV-enhancement found in our case may be accounted for by the weak adsorption of K$^+$ ions.

The higher photocurrents obtained after UV illumination allowed direct measurement without the need of modulated excitation and lock-in amplification, used in preliminary experiments, improving the quality in the determination of the action spectra. For that reason, action spectra in the visible region were obtained maintaining the photocurrent at the plateau by UV preirradiation between measurements. Results were independent of the applied electrode potential between −100 and +500 mV. In order to discard any systematic effect, spectra were obtained at increasing and decreasing wavelengths. The same photocurrent was measured at each wavelength irrespective of the scanning direction. Action spectra were corrected for the wavelength dependence of the excitation beam intensity and the transmittance spectrum of the ITO substrate. Results are shown in Fig. 3. Photocurrent action spectra are independent of the film concentration and applied potential, and resemble the absorption spectrum of the monomeric dye in DMSO, shifted 9 nm to the red, rather than the absorption spectrum of the electrode (Fig. 1). A similar red
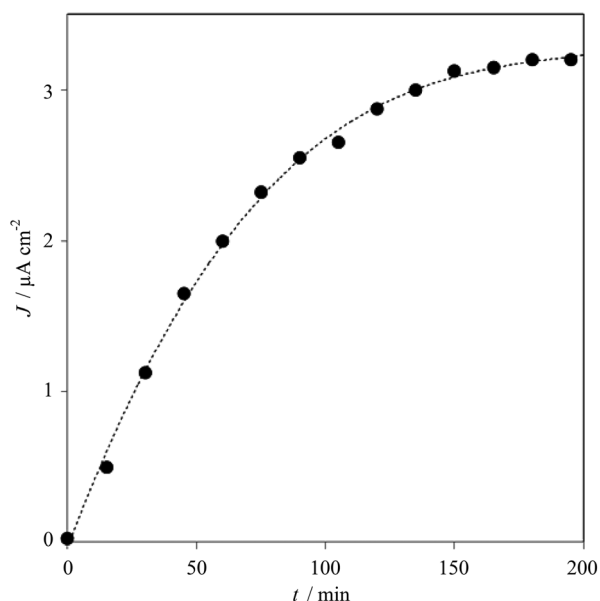
Fig. 2 Photocurrent density at electrode B as a function of time. The electrode is irradiated at 350 nm (~80 μW cm^{-2}), open circuit, between photocurrent measurements with visible light at 700 nm (~1 mW cm^{-2}) at +100 mV vs. counter electrode. The dotted line represents a tendency, not a fitting.
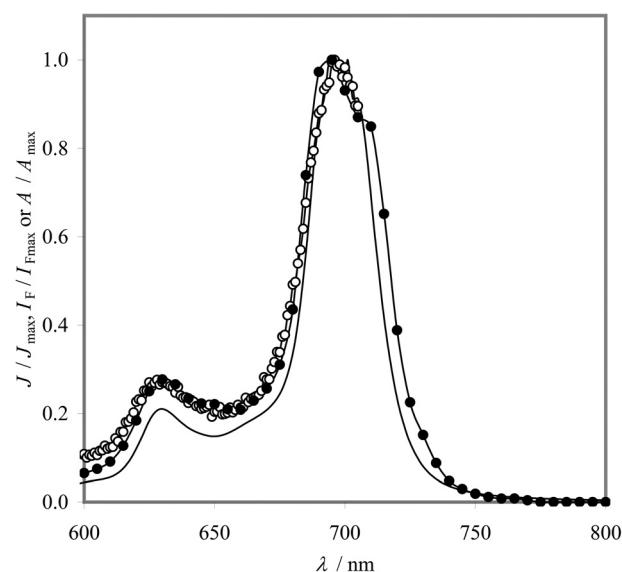
Fig. 3 Normalized photocurrent action spectrum of electrode C (J/J_{max}, line + solid circles), fluorescence excitation spectrum of AlTCPc in 7.6 μM H$_2$O–DMSO 90 : 10 v/v, emission wavelength: 715 nm (I_F/I_{Fmax}, line + open circles) and absorption spectrum of AlTCPc in 1.0 μM DMSO shifted 9 nm to the red (A/A_{max}, full line).

shift observed earlier for a carboxy substituted Zn phthalocyanine was attributed to the creation of electron withdrawing Ti^{4+} centers by the action of the carboxy groups on the semiconductor.[36] This fact suggests that the monomeric dye is the species responsible for electron injection into the semiconductor.

Evaluation of the extent of aggregation in the films through the correlation of photocurrent intensities with dye concentration, under the assumption that the monomeric dye is the active species, is not possible because electrode preparation is not reproducible enough for that purpose. Therefore, other strategies were followed, as the determination of absorption and emission properties of the dye in solution, as described in the next section.

AlTCPc in H$_2$O–DMSO solution

Most phthalocyanines have quite low solubility in water and tend to produce non-fluorescent aggregates.[37] This is the case of AlTCPc, which is soluble only in alkaline aqueous solution or when predissolved in DMSO.[27] Aggregation is demonstrated by absorption spectroscopy through broadening of the absorption spectrum and enhancement of the first satellite (as may be observed by comparing Fig. 1 and 3).[30] Fig. 4 shows normalized absorption spectra of AlTCPc in H$_2$O–DMSO (90 : 10 v/v) for dye concentrations spanning one order of magnitude. Though somewhat different in shape and in the position of the maximum, it is clear that spectra resemble those shown for the electrodes and on suspended TiO$_2$ rather than the spectrum of monomeric phthalocyanine in neat DMSO (Fig. 3). Quite unexpectedly, however, the shape is concentration independent and the absorbance maximum depends linearly on dye concentration, suggesting that the dye is highly aggregated in H$_2$O–DMSO and aggregate properties remain
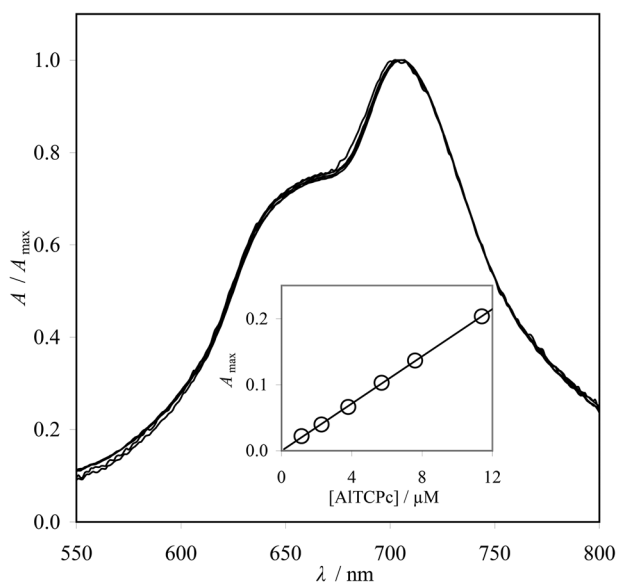
constant as concentration increases. This behavior points to the formation of high-order aggregates or clusters in H$_2$O–DMSO. The similarity found with electrode spectra (Fig. 1) suggests that AlTCPc is also clustered on TiO$_2$. The hypothesis of a simple oligomerization equilibrium may be thus discarded, since in that case a concentration-dependent spectral shape and deviations from the linear dependence of absorbance with concentration would be expected.

Emission results are shown in Fig. 5. Spectral shapes do not depend on concentration and are similar to that found for the same dye in DMSO[27] but shifted around 15 nm to the red. The emission intensity is reproducible and, remarkably, it depends only slightly on concentration, showing that the concentration of the monomer, the only emitting species, is almost constant. Again, this behavior may be expected if the dye is highly aggregated and aggregation is governed by the formation of high-order aggregates or clusters, rather than by a simple oligomerization equilibrium.[37]

The fluorescence intensity in H$_2$O–DMSO solutions is in all cases not greater than 3% of the intensity measured for the same dye concentration in neat DMSO. Assuming the same fluorescence quantum yield for the monomeric dye in DMSO and in H$_2$O–DMSO, it is concluded that more than 97% of the dye is clustered.

The excitation spectrum of AlTCPc in H$_2$O–DMSO was independent of the concentration of the dye and resembles in shape and position the photocurrent action spectrum found for TiO$_2$ films (Fig. 3). This shows clearly that the species responsible for the emission in H$_2$O–DMSO, namely the monomeric form of AlTCPc, is also responsible for electron injection into TiO$_2$ films. Moreover, these results show that the dye
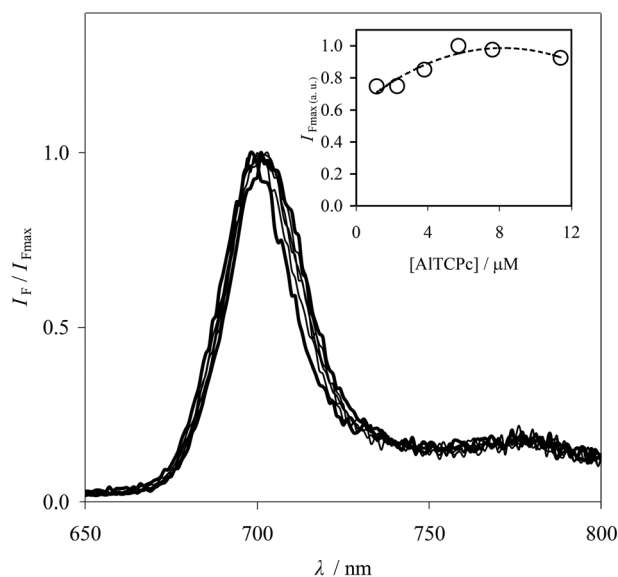

Fig. 4 Normalized absorption spectra of AlTCPc in H$_2$O–DMSO (90 : 10 v/v) at different dye concentrations. Inset: absorbance maxima as a function of AlTCPc concentration.

Fig. 5 Normalized fluorescence spectra of AlTCPc in H$_2$O–DMSO (90 : 10 v/v) at different dye concentrations. Inset: fluorescence intensity against dye concentration. The dashed line represents a tendency and not a fitting. Excitation wavelength: 620 nm.

perceives a similar environment in H_2O–DMSO solution and in the TiO_2 surface.

Results are consistent with the presence of AlTCPc clusters with similar properties on the TiO_2 surface and in H_2O–DMSO solution. Clusters are not able to inject electrons into the semiconductor and act as internal filters for the exciting radiation. Cluster properties do not depend on dye concentration. Most probably, only their number grows on increasing dye concentration both on electrodes and in solution. Notice that films were not prepared from H_2O–DMSO solutions but from AlTCPc in neat DMSO, where the dye is soluble and monomeric, meaning that clusters are not preformed in the dipping solution. All evidence indicates that monomers adsorbed on the semiconductor are the actual electron injecting species.

The present results explain the apparent independence on dye loading of the photocatalytic reduction rate of Cr(VI) by AlTCPc sensitized TiO_2 under visible irradiation.[26] Though phthalocyanine clusters are photocatalytically inactive, a rapid reduction of Cr(VI) was observed, pointing to a high efficiency of electron capture by the oxidized metal related to the formation of a Cr(VI) complex on the TiO_2 surface.[38] If the Cr(VI) complex is highly efficient in the capture of conduction band electrons, it may be expected that almost all electrons photoinjected by the monomeric dye will be captured, reducing thereby the recombination rate.

Conclusions

AlTCPc forms higher-order aggregates or clusters when adsorbed on TiO_2. On excitation, clusters are inefficient for electron injection into the semiconductor. The actual photoactive species are monomeric dye molecules electronically coupled to the semiconductor. This explains the independence of photocatalytic activity on dye loading found in previous work,[26] as in these conditions monomer concentration depends slightly on the analytical concentration of the dye, in a similar way to micellar equilibrium. Even when a low absorbed photon to electron injection efficiency is expected for the AlTCPc–TiO_2 photocatalyst irradiated with visible light, the key point for its efficiency in the reduction of Cr(VI) is the highly efficient capture of conduction band electrons by Cr(VI)–TiO_2 complexes.[38]

Acknowledgements

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