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## Charge-transfer excited state in pyrene-1-carboxylic acids adsorbed on titanium dioxide nanoparticles

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### ABSTRACT

The electronic structure of excited photosensitizer adsorbed at the surface of a solid is the key factor in the electron transfer processes that underlie the efficiency of dye-sensitized solar cells and photocatalysts. In this work, Stark effect (electroabsorption) spectroscopy has been used to measure the polarizability and dipole moment changes in electronic transitions of pyrene-1-carboxylic (PCA), -acetic (PAA) and -butyric (PBA) acids in ethanol, both free and adsorbed on colloidal TiO<sub>2</sub>, in glassy ethanol at low temperature. The lack of appreciable increase of dipole moment in the excited state of free and adsorbed PAA and PBA points that two or more single bonds completely prevent the expansion of  $\pi$ -electrons from the aromatic ring towards the carboxylic group, thus excluding the possibility of direct electron injection into TiO<sub>2</sub>. In free PCA, the pyrene's forbidden S<sub>0</sub> → S<sub>1</sub> transition has increased intensity, exhibits a long progression in 1400 cm<sup>-1</sup> A<sub>g</sub> mode and is associated with  $|\Delta\mu|$  of 2 D. Adsorption of PCA on TiO<sub>2</sub> causes a broadening and red shift of the S<sub>0</sub> → S<sub>1</sub> absorption band and an increase in dipole moment change on electronic excitation to  $|\Delta\mu| = 6.5$  D. This value increased further to about 15 D when the content of acetic acid in the colloid was changed from 0.2% to 2%, and this effect is ascribed to the surface electric field. The large increase of  $|\Delta\mu|$  points that the electric field effect can not only change the energetics of electron transfer from the excited sensitizer into the solid, but can also shift the molecular electronic density, thus directly influencing the electronic coupling factor relevant for electron transfer at the molecule-solid interface.

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### 1. Introduction

The light-induced transfer of electrons from the sensitizer to a solid is a widely investigated class of phenomena important for constructing and improving the performance of dye-sensitized solar cells (DSSC) and photocatalysts. In these applications which utilize the energy of absorbed light, the factor of primary importance is the transfer of light energy to the semiconductor electrode (TiO<sub>2</sub>) by an electron from the excited state of the photosensitizer, which is mostly a transition-metal coordination compound of ruthenium [1–3] or a purely organic dye. The photosensitizers are anchored to TiO<sub>2</sub> electrode by binding to the unsaturated valence of surface titanium atoms through the dihydroxy, carboxy, phosphonic, pyridyl, hydroxamate or other polar groups which bind to TiO<sub>2</sub> in the bridging or chelating configuration [4–6].

The absorption spectra of adsorbed photosensitizers usually undergo a red shift and broadening, which are tentatively interpreted as

indicatives of the charge-transfer character of the electronic excited state. In this respect, a combination of two extreme cases can be considered in the context of electron transfer from the excited photosensitizer to the solid. They are (i) an indirect electron injection beginning with the local excitation of the sensitizer molecule, allowing for thermal relaxation, then followed by subsequent electron transfer, and (ii) the direct injection with an electron being shifted into the solid already during the light absorption event. The mixing of both ways, meaning a partial charge-transfer excitation and concomitant thermal relaxation of injected electron are extremely fast processes that have been addressed both experimentally and by computational modelling only recently [7–10]. It is clear that independent determination of the degree of electron delocalization in the excited state just attained provides an important information about the initial state prepared by light absorption, which is the starting point for the complete electron transfer.

Among the photosensitizers based on polycyclic aromatic hydrocarbons, perylene and pyrene were used in conjunction with different spacing and linking groups. The energetics and kinetics of electron transfer (ET) from perylene adsorbed at TiO<sub>2</sub> surface with a carboxylic group attached either directly or through  $-(CH_2)_2-$  or  $-CH=CH-$  spacers, or with  $-CH_2-$  phosphonic acid linker have been extensively characterized [11]. It was found that the adsorbed perylene molecule is

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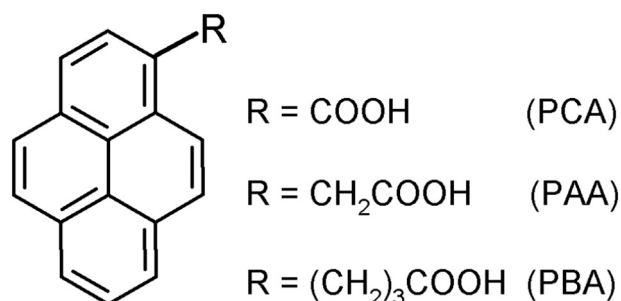
capable of transferring an electron to the solid in 10 to nearly 60 femtoseconds after pulse excitation, with the transfer rate dependent on the spacer present and related to the degree of broadening of the absorption spectra. The broadening of the absorption spectrum was ascribed to extreme lifetime shortening of the perylene excited state [11–13], or to the mixing of the charge-transfer and locally excited states [14,15].

This work deals with carboxylic derivatives of pyrene (Scheme 1) with a carboxy group anchoring them at the TiO<sub>2</sub> surface. Pyrene itself has long been the subject of research interest, mainly because of its ability to form excimers, but also its monomeric form presents peculiar spectroscopic features. They include the very weak S<sub>0</sub> → S<sub>1</sub> electronic transition and characteristic features in fluorescence spectra [16–18], which make pyrene a useful probe of solvent polarity [19] with vibronic coupling-based mechanism [20]. A number of pyrene derivatives have been synthesized with the aim to obtain effective, purely organic light absorbers injecting the excited electron from the pyrene-based chromophore through a bridge towards the TiO<sub>2</sub> electrode [21–23] or with a pyrene bridge [24], with the prospect of their use in DSSC, and for use in organic light emitting diodes, organic field effect transistors and molecular electronics purposes. Carboxylic derivatives of polycyclic aromatic hydrocarbons, in particular pyrene, have also been indicated as a useful reference system for explaining the spectroscopic properties of oxidized graphene, where the localization of excited state orbitals within only a few condensed aromatic rings is induced by polar substitution at graphene's edge [25].

The initial redistribution of the electronic charge on photon absorption is a relevant factor that can influence the forward electron transfer rate. In this work it is probed with the Stark effect (electroabsorption) spectroscopy used to measure the change in permanent dipole moment, |Δμ|, accompanying the excitation of pyrene-1-carboxylic derivatives adsorbed at the surface of TiO<sub>2</sub>. The pyrene derivatives used here contain a carboxylic group separated from the aromatic pyrene moiety by either one (PCA), two (PAA) or four (PBA) single bonds. The charge shift reflected by |Δμ| has been determined together with the change of molecular polarizability, Δα, and other spectral characteristics for the S<sub>0</sub> → S<sub>1</sub> and S<sub>0</sub> → S<sub>2</sub> electronic transitions, and their dependence on the surface electric field has been examined.

## 2. Experimental Section

Pyrene-1 carboxylic derivatives and the solvents were purchased from Fluka and Aldrich and used as received. The slight dissociation of pyrenecarboxylic acids observed in ethanol was prevented by adding acetic acid (0.01%), while in 2-MeTHF and ethylbenzene-toluene no such measures were needed. Colloidal solution of TiO<sub>2</sub> nanoparticles with ≈6 nm diameter in anhydrous ethanol was prepared at 100 mM concentration by slow hydrolysis of titanium tetraisopropoxide [26] in the presence of 0.2% (w/w) acetic acid. Samples with larger acid content were prepared prior to the experiment. Large excess of TiO<sub>2</sub> adsorption sites, as estimated according to published formula [27], was maintained to ensure complete adsorption of pyrene derivatives. Samples used to



Scheme 1.

measure the electroabsorption spectra were colloidal solutions frozen between two conducting glass (ITO) electrodes spaced by 0.08 mm.

Absorption and electroabsorption (Stark) spectra were measured simultaneously using experimental setup and methods described previously [28]. Briefly, the rigid sample solution was subject to a strong sinusoidal electric field and the modulated light intensity was measured on the second harmonic frequency in the transmission mode in order to detect the signal of absorption proportional to the square of electric field intensity. The measured signals were used to determine the absorbance, *A*, and its field-induced component, Δ*A*. According to theory [29], the field-induced shift of the absorption spectrum (Stark effect) results in changes of absorbance that can be described as a linear combination of the first and second derivatives of the absorption spectrum:

$$\Delta A = a_0 A + a_1 \nu \frac{d(A/\nu)}{d\nu} + a_2 \nu \frac{d^2(A/\nu)}{d\nu^2} \quad (1)$$

where  $\nu$  is the wavenumber. By adjusting the above combination to the measured  $\Delta A(\nu)$  with a least squares procedure, the values of the coefficients  $a_1$  and  $a_2$  were obtained and then used to calculate the differences in polarizability tensor, Δα, and permanent dipole moment, |Δμ|, between the electronic excited and ground states. The first term ( $a_0$ ) was neglected due to its very small and uncertain contribution. The following equations [29,30], were used which are applicable to spectra measured with the sample tilted in the linearly polarized light beam so as to establish the magic angle 54.7° between the applied field vector **F** and the electric vector of light:

$$a_1 = \frac{(fF)^2}{6\sqrt{2}hc} \text{Tr}(\Delta\hat{\alpha}), \quad a_2 = \frac{(f \cdot |\Delta\mu|)^2 F^2}{6\sqrt{2}h^2 c^2}. \quad (2)$$

Here  $f$  denotes the local field factor,  $f \approx 1.1$ – $1.3$  for frozen solvents. The data reported in this work represent the values of  $f^2 \cdot \text{Tr}(\Delta\hat{\alpha})$  and  $f \cdot |\Delta\mu|$ .

Description of Δ*A*( $\nu$ ) with Eq. (1) is possible only in the spectral range comprising a single electronic transition. Since some of the spectra measured in this work comprise two overlapping electronic transitions, their deconvolution into individual vibronic bands was performed. A set of log-normal components [31] was used with adjustable asymmetry parameter common to all component bands. A weighted sum of square deviations for the normalized absorption and electroabsorption spectra was minimized.

## 3. Results and Discussion

### 3.1. Free Photosensitizers and Their Adsorption on TiO<sub>2</sub>

#### 3.1.1. PBA and PAA

The absorption and fluorescence spectra of carboxylic derivatives of pyrene were recorded in slightly acidic ethanol in order to prevent the formation of either carboxylate or the doubly protonated forms [32–34]. The absorption and fluorescence spectra of PBA shown in Fig. 1, representative also to PAA, are similar to those of unsubstituted pyrene, where the symmetry allowed S<sub>0</sub> → S<sub>1</sub> transition has very weak intensity in perfectly symmetric molecule [16–20]. The weak perturbation of pyrene in PBA and PAA slightly enhances the S<sub>0</sub> → S<sub>1</sub> absorption features. In PBA, the S<sub>0</sub> → S<sub>1</sub> transition starts with the weak (0–0) band at 375 nm and is accompanied by a composite band around 368 nm and another one at 360 nm, being the false origins of vibrationally induced S<sub>0</sub> → S<sub>1</sub> transitions, which are build on nontotally symmetrical vibrations of 550–700 cm<sup>−1</sup> and 1100 cm<sup>−1</sup> frequency and borrow intensity from the higher energy S<sub>0</sub> → S<sub>2</sub> transition which begins at 342 nm. The 1100 cm<sup>−1</sup> vibration giving rise to the 360 nm band was indicated as particularly important for the mechanism of solvent polarity sensing by the vibronic intensities in pyrene fluorescence spectra [20]. This vibronic structure in PBA and PAA absorption spectra is similar to the relatively weaker S<sub>0</sub> → S<sub>1</sub> absorption and fluorescence of

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