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Spectral Properties and Deactivation Processes of Anionic Porphyrin Coupled with TiO_2 Nanostructure

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Abstract *Meso*-tetrakis (4-sulphonatophenyl)porphyrin (TSPP) and its complex with TiO_2 were studied by absorption, fluorescence, and steady-state and time-resolved photothermal spectroscopy. A TiO_2–TSPP complex was obtained by covalent bonding of anionic porphyrin with the nanostructural form of TiO_2. The TiO_2 colloidal carriers modifying the thermal energy distribution and considerably influencing the photophysical processes were found to lead to changes in the population of the porphyrin singlet and triplet states, resulting in singlet oxygen generation and/or electron transfer.

Keywords Optical and photothermal spectroscopy · Porphyrin · Singlet oxygen · TiO_2 nanostructure

1 Introduction

Nanotechnology is much promising in a wide gamut of applications including medical science offering new methods for cancer imaging and treatment with the use of novel diagnostic or therapeutic agents synthesized using nanoparticles [1,2]. The most interesting is the development of nanomaterials, i.e., organic solids associated with organic photoactive compounds interacting at the molecular level [3]. Nanoscale titania (TiO_2) is of great interest mainly because of its unique properties, such as high photocatalic

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activity and size-dependent optical properties [4]. However, TiO_2 absorbs light only in the UV-region (bandgap of around 3.2 eV); therefore, various materials like dyes have been used as sensitizers to extend the photoactivity of TiO_2 to the visible range [5].

Porphyrins are the most widespread of all prosthetic groups found in nature and have found a large number of applications (e.g., for electron transfer, oxygen transport and storage, photosynthetic processes and catalytic substrate oxidation, laser technology, as photoconverters in solar cell devices, as sensitizers in medical applications, etc.) [6,7]. To obtain a full description of light-induced molecular processes and to achieve a better understanding of photophysical features of both singlet and triplet states, free *meso*-tetrakis (4-sulphonatophenyl)porphyrin (TSPP) and TSPP coupled with TiO_2 were studied by applying optical and photothermal methods. The radiative as well as fast and slow non-radiative deactivation processes of the dyes followed by absorption of light energy were studied. The light-activated sensitizers can thermally deactivate the absorbed energy from the singlet state via internal conversion or intersystem crossing, and from the triplet state (involving dioxygen) by energy transfer, electron transfer, or thermal deactivation.

The results have provided information on the influence of heterogeneous organic compounds-semiconductor nanosized assemblies (TiO_2 covalently bonded to TSPP), especially about the photophysical processes taking place on a molecular level and leading to changes in the absorbed energy distribution as well as in the decay of the porphyrin singlet and triplet states.

2 Measurements

The preparation of a TiO_2–TSPP complex (Fig. 1) made of anionic porphyrin covalently bound to colloidal semiconductor nanocrystals was described earlier [8]. The average TiO_2 and TiO_2–TSPP nanoparticle size was estimated to be around 32 nm and 37 nm, respectively [8]. TSPP was purchased from Sigma-Aldrich.

The absorbance and fluorescence spectra were measured on a UV/vis spectrophotometer (Cary 4000) and fluorometer (Hitachi F4500). The fluorescence reference dyes (chlorophyll *a* and TSPP) used for estimation of the fluorescence yield (Φ_F) for TSPP and for TSPP bound TiO_2, respectively, were in an ethanol solution. The heat generated as a result of light energy absorption was measured by steady-state and time-resolved photothermal techniques. Using photoacoustic (PAS) spectroscopy [9], the heat produced by TiO_2 and TiO_2–TSPP powdered samples were recorded. To record the time-resolved photothermal signals, the laser-induced optoacoustic spectroscopy (LIOAS) method [10,11] was applied. The excitation source was the nitrogen-dye laser (Photon Technology Int., GL-3300/GL301), and the detection system was operated using a piezoelectric transducer (Panametric Inc.,V1030). Measurements were carried out in an air atmosphere at ambient temperature. To analyze the LIOAS signals, the Sound Analysis 1.50 D program was used.

For measurements, the samples were suspended in ethanol (99.8 % purchased from POCH, Poland). For LIOAS experiments, as calorimetric references, bromocresol purple (BCP) and ferrocen (FC) purchased from Sigma-Aldrich were chosen. These dyes absorbed in the same spectral range as the porphyrin investigated, and they did

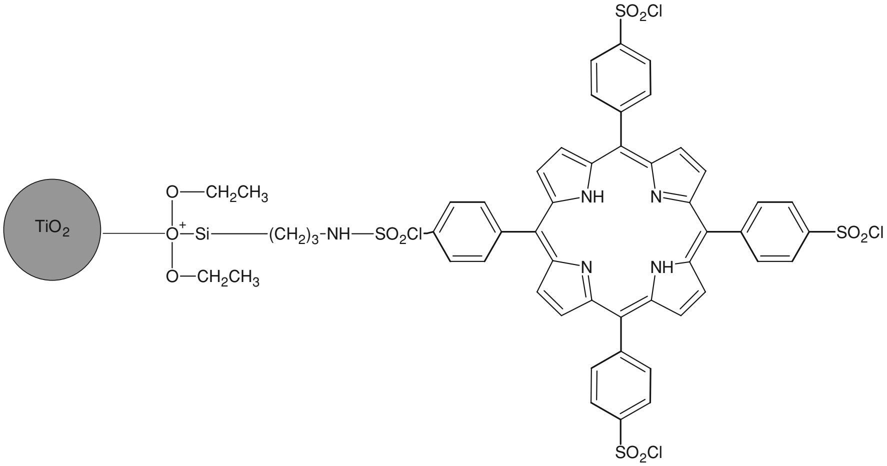

Fig. 1 Molecular structure of TiO_2–porphyrin complex

not emit fluorescence, but promptly exchanged total excitation energy into heat (in time range shorter than 0.5 μs estimated as a time resolution of experimental setup). LIOAS signals were measured in the time range up to 5 μs.

3 Results

Figure 2 shows the absorption spectra of porphyrin free and covalently bound with TiO_2. The absorption spectrum of free TSPP is typical of the high symmetry (D_{4h}) porphyrin group. The main intense band at 414 nm is the characteristic so-called Soret (B) band, whereas the four bands at around 512 nm, 546 nm, 590 nm, and 645 nm are assigned as Q bands. Comparison of this spectrum with that of the TiO_2–TSPP complex shows that the Soret band is apparently shifted (about 9 nm) to the red; additionally a batochromic shift of the Q bands is also observed. The changes in the TiO_2–TSPP absorption spectrum are related to chemical (SO_2–NH) bonding between the porphyrin and TiO_2. At high concentrations of TiO_2 nanoparticles, a similar spectrum was observed for anionic TSPP adsorbed on the semiconductor surface by a porphyrin anchoring group (SO_3^-) [12]. The photoacoustic spectrum of the complex investigated (Fig. 2) resembles its absorption spectrum, which permits conclusions about the whole thermal deactivation processes. The spectra of the dye involved in the complex suggest that TSPP in an organic solvent as well as in powder exists in the monomeric form, and it can exchange the absorbed energy into heat with S_1 more efficiently than with the S_2 singlet as well as with triplet states participation (see also Table 1). It seems that the decay of the S_1 state involves competing non-radiative processes.

The fluorescence emission and excitation spectra of the samples investigated are shown in Fig. 3. For the sake of illustration, the spectra excited and observed at two wavelengths characteristic of free (414 nm and around 650 nm) and bound (423 nm and 603 nm) porphyrin are presented. As expected, for TSPP typical emission spectra

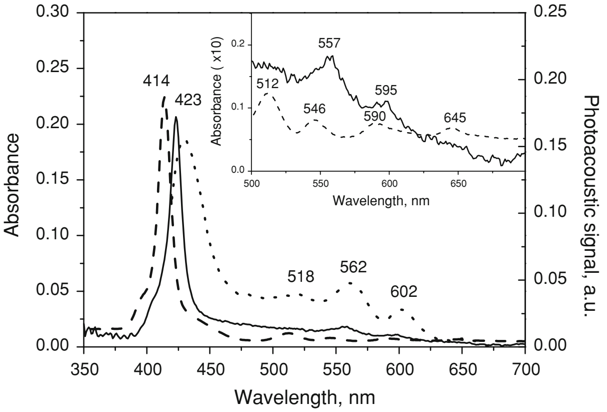

Fig. 2 Absorption (*solid line*) and photoacoustic (*dotted line*) spectra of covalently bounded TSPP with TiO_2 nanostructure and absorption spectrum of free TSPP (*dashed line*); insert—10 times multiply absorption of Q bands for free (*dashed line*) and involved in complex (*solid line*) TSPP

Table 1 Some photophysical parameters estimated for free TSPP and its complex with TiO_2

Sample	Φ_F^a	$k_1(\alpha)^{b,c}$	k_2^b	k_3^b	Σk_i	$\tau_2^d(\mu s)$	$k_T \times 10^{9e}(Ms)^{-1}$	Φ_Δ^f	E_S^g(eV)
TSPP	0.065	0.34	0.32	0.33	0.99	7.90	0.06	0.80	1.92
TSPP-TiO_2	0.011	0.94	0.04	0.02	1.00	0.67	0.82	0.13	2.06

[a] Φ_F: fluorescence yield, $\Phi_F = \Phi_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2}$, where Φ_R is the fluorescence quantum yield of the reference, I, I_R; OD, OD_R; and n, n_R are the areas under the fluorescence curves, the absorption intensities, and refractive indices of the sample and reference, respectively

[b] k_i: pre-exponential factors (the fractions of thermal energy released in i-th lifetime)

[c] α: a fraction of excitation energy exchange into heat promptly (in shorter time than time resolution of apparatus)

[d] τ_2: decay time

[e] k_T: rate constant of triplet state depletion

[f] Φ_Δ: yield of singlet molecular oxygen production estimated based on $\Phi_\Delta = [(1-\alpha)E_{h\nu} - \Phi_F E_S - E_{h\nu}k_2]/E_\Delta$, where $E_{h\nu}$ is the molar energy of the incident photons, E_S is the energy of singlet state in $[\mathrm{kJ \cdot mol^{-1}}]$, and E_Δ is the energy of oxygen singlet state ($E_\Delta = 94\,\mathrm{kJ \cdot mol^{-1}}$)

[g] E_S: the energy of singlet state

of the monomeric form of the dye were observed with the Q(0,0) and Q(0,1) bands at 645 nm and around 707 nm. At both excitations the same peak ratios (645 nm to 707 nm) of around 2.6 were obtained (Fig. 3a). The estimated yield of fluorescence (Table 1) is in agreement with the 0.058 and 0.080 values reported in the literature [13,14]. The emission peaks of TSPP bound to TiO_2 are blue shifted to 601 nm and 650 nm, respectively. The peak ratios (601 nm to 650 nm) varied from 0.89 to 1.24, but the fluorescence yields calculated for bound TSPP at both excitation wavelengths are the same (Table 1).

The excitation fluorescence spectra observed at 603 nm show the peaks corresponding to the absorption spectrum of bound porphyrin and do not reveal any contribution from free TSPP. At 650 nm observation wavelengths, the emission bands (Fig. 4b) correspond well to the respective absorption spectra of free or bound TSPP (Fig. 2).

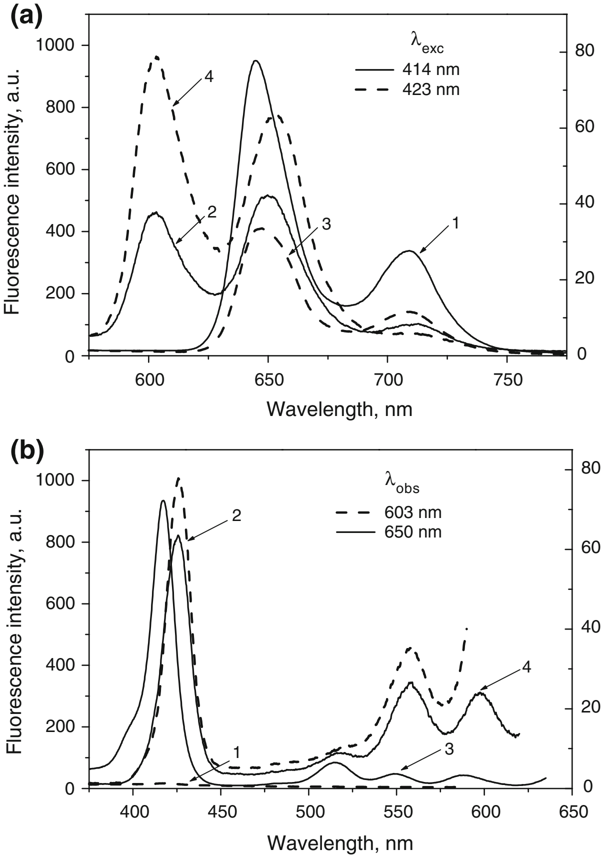

Fig. 3 Fluorescence (**a**) emission and (**b**) excitation spectra for porphyrin (curves 1 and 3, left scale) and TSPP–TiO_2 complex (curves 2 and 4, right scale) in ethanol

As the spectra of the TiO_2–TSPP sample do not show any evidence of any other form of porphyrin which can be anchored to the TiO_2 surface, it can be concluded that all porphyrins are chemically bound to the nanostructures. The new 601 nm maximum appearing in the fluorescence spectra is clearly related to the TiO_2–TSPP complex. It should be noted also that the fluorescence intensity of porphyrin in complexes is significantly lowered. The yield of the fluorescence estimated for TSPP bound to TiO_2 is about 1/6 of that for free TSPP (Table 1). The fluorescence quenching as reported in [12] could be attributable mainly to electron transfer from the excited singlet state porphyrins to the conduction band of colloidal TiO_2. The presence of charge anchoring groups in porphyrin molecular structure plays a major role in the electron transfer processes. It seems that TiO_2–TSPP sensitization can be achieved by excitation of the dye molecules covalently bound to a semiconductor. The interaction between a heterogeneous semiconductor–organic compound and the close distance between them allow the TSPP singlet depopulation by the subsequent electron injection into a conductive

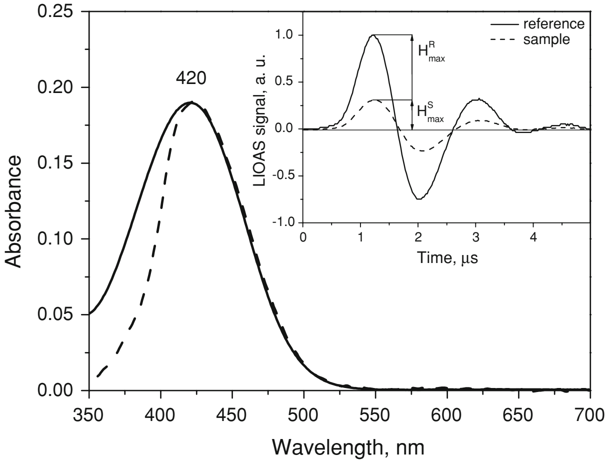

Fig. 4 Absorption spectra of BCP with (*dashed line*) and without (*solid line*) TiO_2 presence in ethanol; inset LIOAS signals for TSPP (*dashed line*) and BCP (*solid line*) as a reference sample

band of semiconductor or/and by competing processes such as intersystem crossing transition ($S_1 \rightarrow T_1$).

To obtain information about the efficiency of dye triplet state quenching for free TSPP and that covalently bound to the semiconductor structure, the LIOAS method was used. It was checked also whether the TiO_2 nanoparticles were able to interact with BCP (or FC) in ethanol (Fig. 4). The lack of charged groups in the dye's molecular structure as well as the additivity of their absorption spectra (Fig. 4) allows their application as a calorimetric reference in LIOAS measurements.

Analysis of the photothermal signal was performed by means of two methods proposed by Marti et al. [15] and by Small et al. [16]. The Marti et al. [15] method is based on comparison of the maximal amplitudes ($H_{\max}$) of the LIOAS signal (describe by Eq. 1) recorded for the sample (S) and the reference (R) (Fig. 4)

$$H_{\max} = K\alpha E_{\text{las}}(1 - 10^{-A}) \tag{1}$$

where A is the absorbance, E_{las} is the laser pulse energy, and K is the coefficient related to the optical geometry, electronic impedance, and thermoelastic properties of the sample solution. With this equation it is possible to estimate the α parameter describing the fraction of energy that is promptly thermally deactivated by singlet states of the dye.

Analysis of the LIOAS signal (Table 1) gives the information on the non-radiative fast deactivation of excited singlet states, on depopulation of the long-lived states of the dye and on the dye ability to generate reactive oxygen species.

As follows from Table 1, for TSPP coupled with the nanostructure, the appreciable fraction (α) of the whole energy adsorbed is exchanged into heat with involvement of the singlet state. It has been estimated that independent of the dye reference used, in prompt radiationless processes (in time shorter than 0.5 μs), the porphyrin coupled with TiO_2 is able to exchange into heat around three times more of the energy absorbed than TSPP. To obtain a more precise description of the fate of the energy absorbed by the porphyrin studied and its loss through non-radiative channels, the deconvolution method [16] was applied. The sample signals were convoluted with those of the reference using a sum of single exponentials (Eq. 2) for the time evolution of the pressure wave in the sample,

$$H \sim \sum_i k_i \exp\left(\frac{-t}{\tau_i}\right) \tag{2}$$

where τ_i is the lifetime of the i-th thermal deactivation process and k_i is a pre-exponential factor (related in i-th lifetime). Applying the α parameter as k_1 and τ_Δ ($= 13\,\mu\text{s}$)—the time decay of singlet oxygen in ethanol as τ_3—the analysis of the LIOAS signal recorded for samples in an air atmosphere was performed and the yield of singlet oxygen generation (Φ_Δ) was calculated (Table 1).

For the porphyrin in complex with TiO_2, not so much energy is consumed for dye triplet state generation (low k_2 value). The estimated Φ_Δ value for TSPP (Table 1) is slightly larger than that reported in the literature [17], but it is comparable with the yield of triplet state formation (Φ_T) [13]. A consequence of chemical bonding of TSPP to the nanosized TiO_2 was a significant decrease in the quantum yield of singlet oxygen from 80 % to 13 % for the bound and the free porphyrin. Furthermore, the time τ_2 decreased from $7.90\,\mu\text{s}$ to $0.67\,\mu\text{s}$ for free and bound porphyrins. This decrease can suggest that the fast process, e.g., the electron transfer from the excited triplet state of TSPP into the TiO_2 conduction band might occur in competition with the triplet–triplet energy transfer between the dye and dioxygen. The rate constant of triplet-state depletion (k_T), calculated as $k_T = 1/\tau_2[O_2]$ (where $[O_2]$—concentration of oxygen in air-saturated solvent), is quite high for porphyrin involved in the complex with TiO_2. This value is comparable with the electron transfer rate constant estimated for TSPP adsorbed on the TiO_2 surface [12].

It was observed [12] that the presence of anchoring groups improved the efficiency of electron injection from porphyrins into the semiconductor. The ability to inject the electrons into the conduction band of TiO_2 is determined by the energy difference between the conduction and valence bands of TiO_2 and the electron-donating energy levels of porphyrins. In the opinion of some authors [18,19], the excited singlet state and the triplet state could contribute to the charge separation process and be involved in the photocurrent generation in the photoelectrochemical cell based on porphyrin dyes. The high population of the porphyrin triplet state and its long-lifetime allow the process of charge separation to occur. The energy of $S_1 \rightarrow S_0$ transitions (calculated from fluorescence spectrum) is nearly 1.92 eV for the free and 2.06 eV for bound TSPP (Table 1). The energetic distance of the $T_1 \rightarrow S_0$ transitions for this porphyrin is 1.43 eV [13]. It has been shown that the conduction band potential of the TiO_2 semiconductor is -0.5 V versus anatase (NHE), and the ground oxidation potential of TSPP porphyrin is 0.98 V in N,N′-dimethylformamide [11]. Hence, from simple calculations it is possible to conclude that for TSPP coupled with TiO_2 both singlet and triplet states lie above the conduction band of TiO_2, which suggests the electron transfer is energetically favorable from singlet and triplet states of TSPP involved in the complex, assuming that the singlet–triplet energy gap is the same as for TSPP (0.48 eV).

The interaction with charge transfer from the sensitizer molecule to molecular oxygen has been considered as one of the reasons for the decrease in the quantum yield of photosensitized formation of singlet oxygen due to the realization of an additional competing quenching channel [13]. It seems possible that the anion–cation interaction has some influence on the quenching processes of the excited single and triplet states of TSPP coupled with TiO_2.

Xu et al. [20] have found for the hypocrellin B (HB)–TiO_2 composite that both electron and energy transfer processes are possible. They claim the possibility of electron transfer from the excited HB–TiO_2 complex to the conduction band of TiO_2 and energy transfer between the excited triplet state of the HB–TiO_2 complex and ground-state oxygen. We can adopt the scheme proposed be Xu et al. [20] and propose that the photosensitization of the TiO_2–TSPP complex could be attributed to two sources of active oxygen species, i.e., singlet oxygen ($^1O_2$) and superoxide radical anion ($O_2^{\bullet -}$):

$$\mathrm{TiO_2{-}TSPP} \overset{h\nu}{\rightarrow} \mathrm{TiO_2} -{}^1\mathrm{TSPP}^* \rightarrow \mathrm{TSPP}^+ + e^-_{cb}\,(\mathrm{TiO_2}) \tag{3}$$

or

$$\mathrm{TiO_2{-}TSPP} \overset{h\nu}{\rightarrow} \mathrm{TiO_2} -{}^1\mathrm{TSPP}^* \overset{ISC}{\rightarrow} \mathrm{TiO_2} -{}^3\mathrm{TSPP}^* \rightarrow \mathrm{TSPP}^+ + e^-_{cb}\,(\mathrm{TiO_2}) \tag{4}$$

$$e^-_{cb}\,(\mathrm{TiO_2}) \rightarrow O_2^{\bullet -} \tag{5}$$

and

$$\mathrm{TiO_2{-}TSPP} \overset{h\nu}{\rightarrow} \mathrm{TiO_2} -{}^1\mathrm{TSPP}^* \overset{ISC}{\rightarrow} \mathrm{TiO_2} -{}^3\mathrm{TSPP}^* \tag{6}$$

$$\mathrm{TiO_2} -{}^3\mathrm{TSPP}^* \rightarrow {}^1O_2 \tag{7}$$

We could propose that the S_1 TSPP state depopulation is realized by two pathways of two competing processes: charge transfer (Eq. 3) or/and intersystem crossing transition (Eq. 4). The decay of the T_1 TSPP state also takes place by two non-radiative deactivation channels, i.e., electron injection to the conduction band (cb) of TiO_2 (Eq. 4) or/and energy transfer to dioxygen (Eq. 6).

The photodynamic effect was observed after injection of TiO_2–TSPP solution into tumor tissue of skin mice [3]. After exposure of the tumor and it irradiation, the antineoplastic effect was obtained. It was suggested that the singlet oxygen might be involved in the cytotoxic effect of TiO_2–TSPP. In the light of the above-performed investigation and discussion, it seems that the effect will be rather related to the toxicity mediated by $O_2^{\bullet -}$ (5) than $^1O_2$ (7).

4 Conclusions

The results presented show that the appearance of a new fluorescence band at 601 nm and a batochromic shift (about 5 nm to 9 nm) of the absorption bands with respect to those of free TSPP testify to the formation of the supramolecular complex of TSPP with TiO_2. The anionic porphyrin covalently bound to TiO_2 nanostructure affects the distribution of energy exchanged into heat with participation of singlet and triplet states. The chemical bond of TSPP modifies the radiation and photothermal processes of the dye by decreasing the yield of fluorescence by a factor of six and the ability to generate singlet oxygen from 80 % to 13 %. It was estimated that in fast radiationless processes (in time shorter than $0.5\,\mu$s) of porphyrin coupled with TiO_2 three times more of the energy absorbed is exchanged into heat than with TSPP. It was suggested the presence of charge transfer as a competing channel of the singlet and triplet states quenching could be responsible for the decrease in the efficiency of emission and in the photosensitized formation of singlet molecular oxygen. To confirm for TSPP coupled with TiO_2, the participation of the triplet state and singlet state in charge separation processes and radical formation for this complex, the electron paramagnetic resonance and time-resolved fluorescence measurements are necessary.

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References

1. J. Gao, B. Xu, Nano Today **4**, 37 (2009)
2. S. Wang, R. Gao, F. Zhou, M. Selke, J. Mater. Chem. **14**, 487 (2004)
3. R.-M. Ion, D.-V. Brezoi, Solid State Phenom. **106**, 79 (2005)
4. A. Fujishima, K. Honda, Nature **238**, 37 (1972)
5. H.-Y. Si, Z.-H. Sun, H.-L. Zhang, Colloid. Surf. A **313–314**, 604 (2008)
6. D. Wróbel, A. Dudkowiak, Mol. Cryst. Liq. Cryst., **448**, 15 (2006)
7. H. Scheer, *Chlorophylls* (CRC Press, Boca Raton, FL, 1991)
8. S. Agirtas, R.-M. Ion, O. Bekarogulu, Sci. Eng. **C**, 396 (1999)
9. A. Rosencwaig, *Photoacoustics and Photoacoustic Spectroscopy* (Wiley & Sons, New York, 1980)
10. S.E. Braslavsky, G.E. Heibel, Chem. Rev. **92**, 1381 (1992)
11. G.O. Andres, V. Martinez-Junza, L. Crovetto, S.E. Braslavsky, J. Phys. Chem. A **110**, 10185 (2006)
12. A. Kathiravan, R.Renganathan, J. Colloid Interf. Sci. **331**, 40 (2009)
13. K. Kalyanasudaram, M. Neumann-Spallart, J. Phys. Chem. **86**, 5163 (1982)
14. T. Gensch, S.E. Braslavsky, J. Phys. Chem. **101**, 101 (1997)
15. C. Marti, S. Nonell, M. Nicolaus, T. Torres, Photochem. Photobiol.**71**, 53 (2000)
16. J.R. Small, L.J. Libertini, E.W. Small, Biophys. Chem. **42**, 29 (1992)
17. F. Wilkinson, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data **22**, 113 (1993)
18. H. Ohtani, T. Kobayashi, T. Tanno, A. Yamada, D. Wöhrle, T. Ohno, Photochem. Photobiol. **44**, 125 (1986)
19. E.G. Azenha, A.C. Serra, M. Pineiro, M.M. Pereira, J.S. de Melo, L.G. Arnaut, Chem. Phys. **280**, 177 (2002)
20. S. Xu, J. Shen, S. Chen, M. Zhang, T. Shen, J. Photochem. Photobiol. B **67**, 64 (2002)