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Photophysical properties of TICT molecule adsorbed on semiconductor titania–silica colloids

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Abstract

The effect of semiconductor titania–silica colloids on the fluorescent properties of adsorbed 4-(4′-*N*,*N*-diethylaminophenyl-3,5-dimethyl-1,7-diphenyl-bis-pyrazolo-[3,4-b, 3′-e]-pyridine (DEA-DMPP) has been studied by steady-state and time-resolved fluorescence spectroscopy. 3,5-dimethyl-1,7-diphenyl-bis-pyrazolo-[3,4-b,3′-e]-pyridine (DMPP) in presence of *N*,*N*-dimethylaniline has been employed as the system simulating the separate electron acceptor and electron donor subunits of DEA-DMPP molecule. Silica and titania–silica colloid surfaces inhibited the formation of the intramolecular charge transfer state (ICT) of adsorbed DEA-DMPP due to formation of H-bonds between the amino group of DEA-DMPP and OH-groups localized on the surface.

Keywords: Semiconductor titania–silica colloids; Fluorescence of DEA-DMPP; Charge transfer state

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1. Introduction

utilization of semiconductor titania particulate systems in the colloid and powder forms as reactive heterogeneous media has been and remains intensively studied in carrying out of photochemical transformations of adsorbed organic compounds. Mixed silica–titania compositions can be often more efficient photocatalysts than pure titania. Interfacial photoinduced electron transfer reactions on the surface of disperse solids are governing stages in processes involving storage of the light energy and separation of charges [1,2]. Actually, the electron-transfer dynamic of organic dyes bound to the semiconductor particles (powders, films) have been intensively investigated for nearly two decades [3–5]. Titanium ions in mixed silica–titania compositions are available to the local electron–acceptor interaction with the adsorbed excited organic molecules. It can create a competing deactivation pathway for the excited donor-acceptor pair. Recently, we have studied the photophysics of polyacenes (anthracene, pyrene) adsorbed on photocatalytic silica–titania mixed oxide systems [6,7]. It was shown that electron transfer from excited anthracene to Ti^{4+} ions of silica–titania compositions caused effective fluorescence quenching.

The possibility of intermolecular electron transfer from tertiary amine to excited polyacene on the silica and silica–titania surfaces has been studied [7–12]. Photoinduced electron transfer reactions between adsorbed anthracene (pyrene) and *N*,*N*-dimethylaniline (DMA) in porous silica gel have been examined by fluorescence quenching [7–10] and transient absorption technique [11]. The quenching on silica surfaces is found to be diffusion controlled

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and gives rise to exciplex formation on silica surfaces [8]. Coadsorption of anthracene (An) and DMA on the silica–titania surface caused the decrease on the quenching action of titanium ions on the anthracene fluorescence [12]. Analysis of intermediates formed under laser excitation revealed the absence of the intermolecular electron transfer from tertiary amine to excited anthracene in this case. However in spite of weak electron donor properties of *N*,*N*-dimethylaniline relatively to titania when adsorbed alone, kation-radical $DMA^{+\bullet}$ and ions Ti^{3+} formation has been observed when DMA and An were coadsorbed. We suggested the formation of exciplex $An^{-\bullet}DMA^{+\bullet}$ and electron transfer from this complex (exciplex) to Ti^{4+} ions on the surfaces. In such way the effect of silica–titania surface on the mechanism of bimolecular electron transfer reaction has been revealed. Thus, the inhibition of diffusion-controlled photoreaction in presence of Ti in silica took place.

The photoinduced ICT processes of adsorbed twisted intramolecular charge transfer (TICT) molecules, i.e. *p*-*N*,*N*-dimethylaminobenzonitrile have been studied on the dielectric surfaces: silica gel and zeolite [14,15]. The hydrogen-bonding effect on the ICT process of the adsorbed TICT molecule has been found due to formation of strong Si-O-H. . .NR_3 hydrogen bonds. Similar effect of TiO_2/SiO_2 composites on intramolecular charge transfer has been observed for adsorbed TICT molecules push–pull stilbenes [13]. Investigation of ICT molecules on the semiconductor surfaces can provide the information on the interfacial electron-transfer effect of the TICT molecules containing an electron-acceptor and electron-donor group. The electron transfer processes between CdS or TiO_2 colloids and *p*-*N*,*N*-dimethylaminobenzoic acid (DMABA) have been studied [16]. It has been established that CdS interacts with DMABA in the ICT excited state, while TiO_2 interacts with DMABA in the local excited state. The formation of the ICT state of DMABA was observed to become more favorable for the electron transfer from CdS to DMABA at the DMABA–CdS interface, while the electron transfer at the DMABA–TiO_2 interface inhibited the formation of ICT excited state of DMABA.

Photophysical properties of 4-(4′-*N*,*N*-dimethylaminophenyl-3,5-dimethyl-1,7-diphenyl-bis-pyrazolo-[3,4-b,3′-e]-pyridine (DMA-DMPP), homological with DEA-DMPP, composed of the dimethylaniline electron donor subunit and the bulky electron acceptor one, have been shown to depend on solvent polarity [17]. The molecules with large π-electron donor and acceptor subsystems could be interesting as new promising sensitive probes for heterogeneous photocatalysts.

In this work we report the results of investigation of the effect of semiconductor titania–silica colloids on the fluorescent properties of adsorbed 4-(4′-*N*,*N*-diethylaminophenyl-3,5-dimethyl-1,7-diphenyl-bis-pyrazolo-[3,4-b,3′-e]-pyridine (DEA-DMPP) by steady-state and time-resolved fluorescence spectroscopy. These molecules, composed of bulky π-electron donor and electron acceptor, show high sensitivity on environment due to formation of ICT (most probably TICT) state with relatively high fluorescence quantum yeld. 3,5-Dimethyl-1,7-diphenyl-bis-pyrazolo-[3,4-b,3′-e]-pyridine (DMPP) in presence of *N*,*N*-dimethylaniline has been employed for the comparative purposes as the system simulating separate electron acceptor and electron donor subunits.

2. Experimental

Titania–silica colloids (Ti/Si) with titania content 0–5 wt% were prepared by low temperature sol–gel method with controlled hydrolysis of titanium(IV) *i*-propoxide in stable silica colloid Ludox AS 40 (Aldrich) in presence of HCl, EtOH and water (in proportion 6:1:800,000). The freshly prepared colloid binaries are stable during several days. Ethanol (Aldrich) has been used as received.

DEA-DMPP and 3,5-dimethyl-1,7-diphenyl-bis-pyrazolo-[3,4-b;4′3′-] pyridine (DMPP) has been synthesized in Agricultural University, Cracow, Poland. DEA-DMPP, DMPP and DMA (Aldrich) in ethanol solutions were added to titania–silica colloids. After precipitation of colloid, DEA-DMPP was not found in solution that confirmed DEA-DMPP adsorption on the surface of colloidal particles.

For [4-(3,5-dimethyl-1,7-diphenyl-1,7-dihydro-dipyrazolo[3,4-b;4′,3′-e]pyridine-4-yl)-phenyl]-diethyl-amine (DEA-DMPP) synthesis 0.01 mol of *N*,*N*-diethylbenzaldehyde and 0.02 mol of 5-amino-1-phenyl-3-methylpyrazole were heated together at 250 °C for 3 h in sulfolane (10 ml). After cooling the reaction mixture was digested with ethanol (20 ml) to give a yellow precipitate, which was purified by column chromatography (Merck Silica Gel 60; toluene/ethyl acetate; 3:1). Light yellow crystals (2.4 g, 49%), m.p. 212–215 °C (toluene).

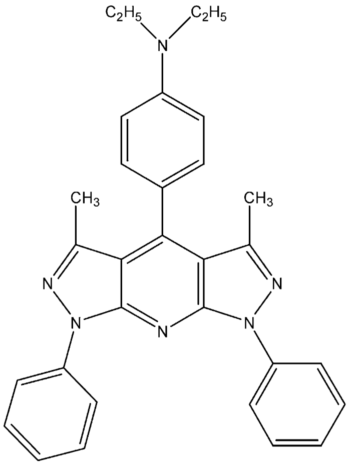
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42(4H, d, $J = 8.7$ Hz, 2,6-$H_{1\text{ and }7\text{-Ph}}$); 7.53(4H, t, $J = 7.4$ Hz, 3,5-$H_{1\text{ and }7\text{-Ph}}$); 7.30–7.18(4H, m, 4-$H_{1\text{ and }7\text{-Ph}}$, BB′, 3,5-$H_{4\text{-Ph}}$); 6.82; 6.75(AA′, 2,6-$H_{4\text{-Ph}}$); 3.46(4H, q, $J = 7$, 1 Hz, $NC\mathbf{H_2}CH_3$); 2.22(6H, s, 2 × Me); 1.25 (6H, t, $J = 7$, 1 Hz, $NCH_2C\mathbf{H_3}$).

Anal. Calcd. for $C_{31}H_{30}N_6$: C 76.52; H 6.21; N 17.27. Found C 76.45; H 6.16; N 17.11.

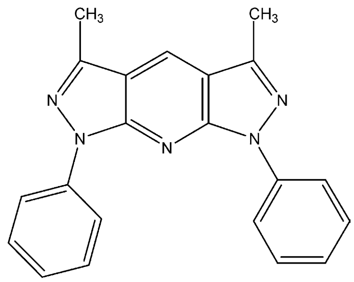
3,5-Dimethyl-1,7-diphenyl-1,7-dihydro-dipyrazolo[3,4-b;3′,4′-e]pyridine was prepared according to Brack [18].

The absorption spectra were measured either with a Shimadzu or Hitachi U3300 spectrophotometer. Fluorescence measurements were performed using Analytical Edinburgh Instruments spectrometer, with FS 900CDT steady-state T-geometry Fluorometer, FL 900 CDT Time-resolved T-geometry Fluorometer (time resolution of the instrument 0.1 ns) supplied with FLA-900 Level 2 Xe 900 Short Arc Lamp CD-900TE.

2.1. Formulae



DEA-DMPP



DMPP

3. Results and discussion

The experimental results of photophysical investigations and theoretical calculations for DMA-DMPP suggest the ICT character of its fluorescing state, most probably the TICT state in polar solvents [17,19]. The same seems to be also for DEA-DMPP, which exhibits the strong similarity of absorption and fluorescence spectra to those of DMA-DMPP. Thus, we can ascribe the fluorescence in non-polar dodecane to the emission from locally (primarily) excited state and to the emission from ICT excited state fluorescence in polar benzonitrile (Fig. 1).

Absorption (curve 1) and normalized fluorescence (curve 2) spectra of DEA-DMPP in ethanol solution are shown in Fig. 1. The short wavelength shoulder of fluorescence spectrum between 400 and 450 nm is seen in addition to the intensive long wavelengths ICT band, peeking at about 520–530 nm, similarly as in the case of DMA-DMPP in alcohols [17]. The short wavelength band of DMA-DMPP was ascribed to the emission from hydrogen-bonded molecules [19–21].

The fluorescence spectra of DEA-DMPP adsorbed on the colloid titania–silica surfaces (Fig. 2) differ dramatically from those in ethanolic solution (Fig. 1, spectra 2) and show only short-wave emission with max 450 nm, similar to the spectra in non-polar environment (Fig. 1 inset, curve 3) or in acidified ethanolic solutions (Fig. 1 inset, curve 5). We suggest that silica and titania–silica colloid surfaces inhibit the formation of the ICT state of adsorbed DEA-DMPP because of H-bonding between of amino groups of DEA-DMPP and OH-groups localized on the surface. Relative intensity of the spectra with max 450 nm increased in presence of titania in the binary colloid (Fig. 2, spectra 2–4). OH-groups of

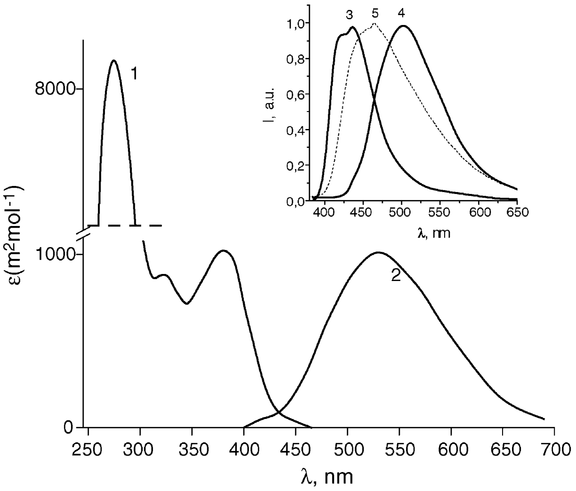


Fig. 1. Absorption (1) and normalized fluorescence (2) spectra ($\lambda_{exc} = 340$ nm) of DEA-DMPP in ethanol solution. *Inset*: fluorescence spectra in dodecane (3), benzonitrile (4) and in acidified ethanol solution (5).

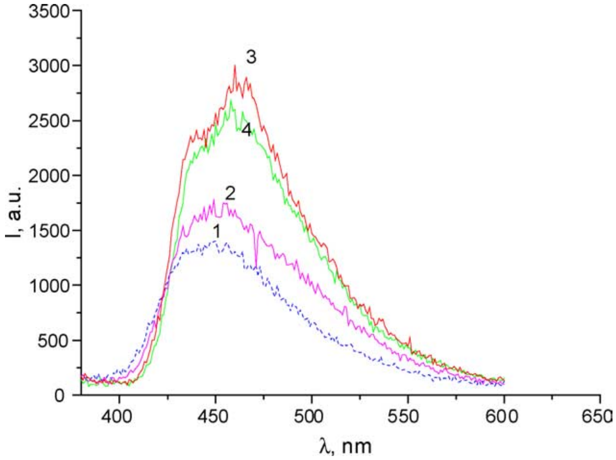


Fig. 2. Fluorescence spectra ($\lambda_{exc} = 340$ nm) of DEA-DMPP in Ti/Si colloids with TiO_2 content in: 0 wt% (1), 0.6 wt% (2), 3 wt% (3), 5 wt% (4); $C_{DEA\text{-}DMPP} = 1.2 \times 10^{-7}$ mol/g SiO_2/TiO_2.

Table 1
Effect of Ti/Si colloids on fluorescence decay time (ns), of DEA-DMPP at monitoring wavelength 457 nm; A_1, A_2—preexponential factors

Environment		τ_1 (ns)	A_1	τ_2 (ns)	A_2
EtOH		4.5	1.0		
EtOH+HCl		1.4	0.97	4	0.02
SiO_2	TiO_2 (wt%)				
	0	3	0.3	11	0.7
	1	3.8	0.15	22.2	0.85
	3	4.	0.15	20.1	0.85
	5	3.2	0.08	17	0.92

silica–titania surface possess high Brönsted activity, because the water molecules can be dissociatively adsorbed on titania [22]. Thus, diethylamino groups of DEA-DMPP molecules should be bonded with acidic OH groups of Ti/Si surface and do not interact with bulky electron acceptor.

The average ratio of adsorbed DEA-DMPP to titania ions (1:2000 for 1% of Ti, and 1:10,000 for 5% of Ti in silica formally calculated per gram of mixed colloids) clearly shows that there are significant proportions of the molecules adsorbed at titania sites, where protonation of DEA electron donor group occurs. In Table 1, the results of DEA-DMPP fluorescence decay times are collected. The lifetime data for DEA-DMPP in neat ethanol was calculated as monoexponential ones; the lifetime data for DEA-DMPP in acidified ethanol $C_{HCl} = 10^{-4}$ M can be fitted better biexponentially with $t_1 = 1.4$ ($A_1 = 97.0$), $t_2 = 4.0$ ($A_2 = 0.2$); $\chi^2 = 1.12$. The data can be compared with the lifetime data for DEA-DMPP adsorbed on SiO_2 surface [23] measured for vacuumed samples: $t_1 = 2.2$ ($A_1 = 58.0$); $t_2 = 11.0$ ($A_2 = 42.0$); $\chi^2 = 1.64$, that can be described as follows: t_1 as lifetime for DEA-DMPP molecules hydrogen-bonded on the silica surface and t_2 as belonging to monocation formed by protonation of aminogroup. Fluorescence spectra with maximum near 450 nm, very close to maximum in acidified ethanol solution at 450 nm confirm this suggestion.

The main component, i.e. the fast one corresponds to the decay of the free molecules, whereas the slow component τ_2 to strongly hydrogen bonded. Fluorescence lifetime of DEA-DMPP increased in presence of Ti in comparison with pure silica colloid (Table 1). The comparison of decay curves in EtOH-HCl solution with the decay curves of the fluorescence of molecules adsorbed on colloids (Fig. 3) testified that acid medium of Ti/Si colloids does not cause the DEA-DMPP fluorescence quenching.

DMPP with coadsorbed *N*,*N*-dimethylaniline (DMPP + DMA) were used as fluorescent probes for comparison of intermolecular charge transfer process with intramolecular one from DMA as donor and DMPP as bulky electron acceptor. DMA-DMPP and DEA-DMPP comprise the example of typical intramolecular charge transfer molecules. DMA acts as quencher of the fluorescence of excited DMPP molecule via intermolecular charge transfer process [24]. The electron-donor abilities of DEA and DMA characterised by the redox potentials E ($D^{+\bullet}$/D) are equal to 0.76 and 0.81 V, respectively [25]. It means that DMA is even slightly weaker electron donor and the fluorescence quencher than DEA. Using this line of reasoning we suggested that the formation of hydrogen bonded amine with surface OH groups is even less favorable that in the case of DEA, and bimolecular reaction resulting in the DMPP emission quenching can favour over strong adsorption of DMA on the surface OH groups.

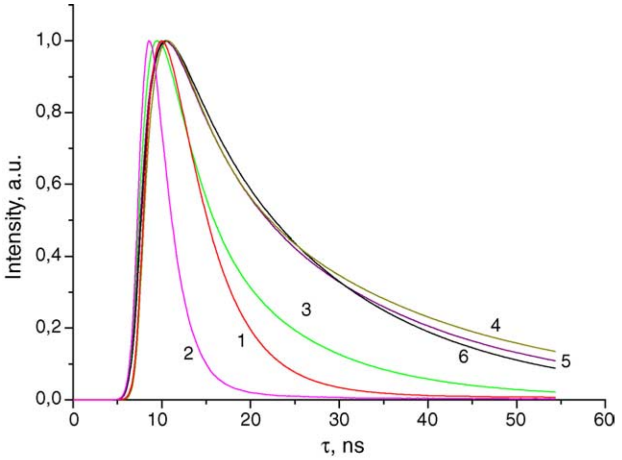


Fig. 3. Fluorescence decay curves ($\lambda_{max} = 457$ nm) of DEA-DMPP in EtOH (1), in EtOH + HCl (2), and adsorbed on SiO_2/TiO_2 colloids with TiO_2 content in wt%: 0 (3), 1 (4), 3 (5), 5 (6); $C_{DEA\text{-}DMPP} = 1.2 \times 10^{-7}$ mol/g.

The fluorescence of DMPP is quenched in presence of titania (Fig. 4, curves 1, 3, 5). This implies that the electron transfer takes place from the singlet excited state of the adsorbed DMPP to the titania colloid particles, by analogy with the interaction between anthracene and silica-titania surface [6]. Co-adsorption of DMA resulted in unexpected essential increase of fluorescence intensity of adsorbed DMPP on titania-contained surfaces (Fig. 4, curves 4 and 6) instead of fluorescence quenching observed for these two species mixed in ethanol solution. Competitive adsorption of DMA

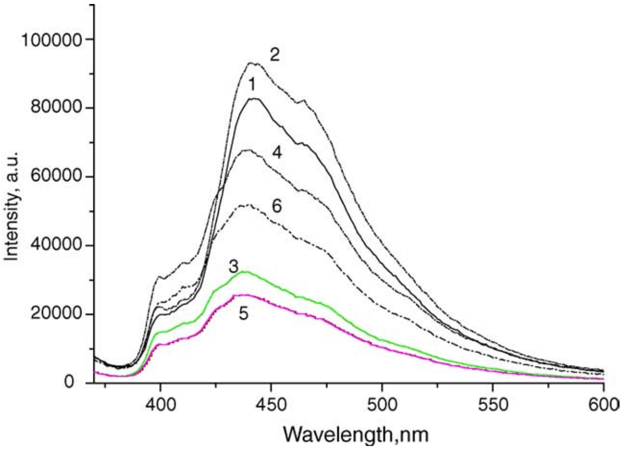


Fig. 4. Fluorescence spectra ($\lambda_{exc} = 340$ nm) of DMPP (curves 1, 3, 5) and DMPP + DMA system (2, 4, 6) on SiO_2/TiO_2 colloids with TiO_2 content in wt %: 0 (curves 1 and 2), 0.6 (3 and 4), 3 (5 and 6); $C_{DMPP} = 5{\cdot}10^{-8}$ mol/g, $C_{DMA} = 5{\cdot}10^{-6}$ mol/g. The values of fluorescence intensities were reproduced with accuracy of ∼1%.

Table 2
Effect of TiO_2 in Ti/Si colloids on fluorescence decay time [ns] of DMPP, monitoring at wavelength 442 nm; A_1, A_2—preexponential factors

Content TiO_2 (wt%)	τ_1 (ns)	A_1	τ_2 (ns)	A_2
0	2.43	0.19	7.24	0.81
1	3.1	0.12	8.7	0.87
5	4.5	0.30	7.9	0.70

molecules on the Ti/Si colloid surface occurred in this case. Most probably DMA molecules occupied more active “titania” sites causing the remove of DMPP molecules to the weaker OH-groups located on the silica part. H-bonded DMA molecules prevent electron transfer from DMPP to the titania particles.

The lifetime of fluorescence of DMPP adsorbed on colloid surface is shorter than even in neat polar solvents (∼30 ns) [26]. It did not demonstrate direct dependence on titania content (Table 2).

Time correlated single photon counting measurements have shown that the fluorescence decay is non-exponential but the fluorescence decay profiles are insignificantly influenced by titania content (Fig. 5). It confirmed the static mechanism of DMPP fluorescence quenching and the implication therefore is that fluorescence is observed from DMPP molecules adsorbed on silica rather than titania sites. Static character of the fluorescence quenching therefore shows that there are a significant amount of DMPP molecules adsorbed on or near titania sites. The most probable quenching mechanism is electron transfer mediated.

The decay of DEA-DMPP is attributed to the emission from the primarily excited non-polar excited state from H-bonded form. The long wavelength ICT emission is totally quenched due to strong adsorption of electron donor (DEA group) on the surface caused by interaction with OH groups. This means that the DEA-DMPP molecules are adsorbed on the Ti/Si and silica colloid surfaces via free electron pair of the nitrogen atom of amino group. An increase of the TiO_2 content in the binaries causes an increase of fluorescence intensity (Fig. 2) due to decrease of the mobility of adsorbed molecules on the acid OH groups, and decrease of non-radiative energy loss from the excited molecule.

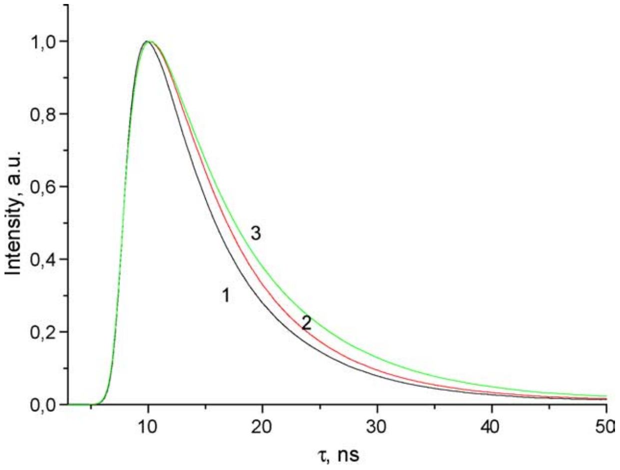


Fig. 5. Fluorescence decay curves of DMPP (monitoring at 442 nm), adsorbed on SiO_2/TiO_2 colloids with TiO_2 content in wt%: 0 (1), 1 (2), 5 (3); $C_{DMPP} = 5 \times 10^{-8}$ mol/g.

In the case of DMPP molecules fluorescence on the colloid surfaces, most probably the electron transfer into titania colloids takes place from the excited state of adsorbed DMPP. Fluorescence intensity of adsorbed DMPP decreased correspondingly to the titania content in the binaries due to ET quenching effect and, in contrary, increased in presence of coadsorbed quencher DMA due to competitive adsorption of DMA on the Ti-OH-centers. In this case, H-bonded DMA prevents ET from DMPP to the titania particles. It should mean that we measured lifetimes of non-quenched DMPP molecules adsorbed on the silica part of colloid binaries.

4. Summary

Electron transfer from DEA-DMPP to TiO_2 colloid particles embedded within silica becomes less favorable due to immobilization of amino groups on the acid surface OH-groups. It should protect direct ET from fluorophore to titania. Thus, silica and titania–silica colloid surfaces inhibited the formation of the ICT state of adsorbed DEA-DMPP because of H-bonding between of amino group of DEA-DMPP and OH-groups localized on the surface. The position of the maximum of the spectrum and the fluorescence lifetime hint to highly emissive non-CT fluorescence. Long-wavelength ICT band did not occur in the spectra. Lifetime of DEA-DMPP and DMPP slightly increased in presence of Ti in comparison with pure silica colloid due to immobilization of adsorbed molecules and the reduce of their mobility and variations.

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