

## Effect of titania - silica colloids on photoinduced intramolecular charge-transfer processes of adsorbed DEA-DMPP

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The utilization of semiconductor particulate systems in the colloid and powders forms as a reactive heterogeneous media has been and remains very popular in carrying out of photochemical transformations of organic compounds. Efforts have also made to the preparation of ultrasmall isolated semiconductor particles (SP) in various heterogeneous environments by the fast-developing method of low-temperature synthesis known as sol-gel process. The method of arrested precipitation can be employed to prepare small SP in silica medium, with the homogeneous distribution of the matrix isolated nanoparticles and its protection against aggregation. The photoinduced intramolecular charge transfer (ICT) processes of adsorbed TICT molecules have been studied on the dielectric surfaces: silica gel (Ottolenghi et al., Chem.Phys. Lett., 1985) and zeolite (Yoon et al. *ibid.* 1998). The electron-transfer dynamics of non-ICT organic dyes bound to the semiconductor particles have been increasingly investigated for nearly two decades. Investigation of ICT molecules on the semiconductor surfaces will shed light on the interfacial electron-transfer effect of the TICT molecules containing an electron-acceptor and electron-donor group.

On these ground, we investigate in this work 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. 3,5-dimethyl-1, 7-diphenyl-bis-pyrazolo- [3,4-b, 3'-e]-pyridine (BPP) in presence of N,Ndimethylaniline has been employed as separate electron acceptor and electron donor subunits of DEA-DMPP molecule, for the comparative purposes. Titania-silica colloids 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 in presence of HCl, EtOH and water.

Silica and silica-titania colloidal surface 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. Electron transfer from DEA-DMPP to TiO<sub>2</sub> colloid particles embedded within silica becomes less favorable also. The position of the maximum of the spectrum and the radiative lifetime show highly emissive non-CT fluorescence. Long-wave ICT band did not occur in the spectra. Time life of DEA-DMPP increased in presence of Ti in comparison with pure silica colloid. Excitation spectra of adsorbed fluorophore are slightly red-shifted due to strong adsorption by the colloid surface. This conclusion has been supported with the study of BPP and DMA fluorescence on Ti/Si binaries. Fluorescence intensity of adsorbed BPP decreased depend on 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-centers. In this case, H-bonded DMA prevents ET from BPP to the titania particles. Time life of BPP did not demonstrate direct dependence on titania content.