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**SURFACE EFFECTS AND PHOTOINDUCED RELAXATION
PROCESSES IN NANOCOMPOSITES BASED ON
SEMICONDUCTOR QUANTUM DOTS CdSe/ZnS
AND ORGANIC DYE MOLECULES**

At the moment, organic-inorganic nanocomposites are of special interest caused by their applications in nanodevices, sensorics, photovoltaics and biomedicine [1]. A prominent class of such nanocomposites is based on colloidal semiconductor quantum dots (QDs) with attached organic dye molecules [2]. Typically, the development of such functional nanostructures aims for the formation of efficient donor-acceptor organic-inorganic nanoassemblies possessing either the non-radiative Foerster-type fluorescence resonant excitation energy (FRET) or charge transfer (CT) processes. In addition, the self-assembly process is accompanied by not only the intended FRET but also by hitherto unidentified (Non-FRET) PL quenching processes, governed by various surface effects realized upon the attachment of dye molecules on QD surface via various binding interactions.

In this report, we are analyzing the nature of Non-FRET lining up new results on FRET and Non-FRET processes in order to identify intrinsic electronic states such as trap and intra-gap states ascribed to participate in Non-FRET quenching. Here, we are focusing on nanoassemblies based on semiconductor CdSe/ZnS QDs (capped by tri-*n*-octyl phosphine oxide, TOPO, or amine, AM, $d_{\text{CdSe}} \approx 2,6-4,7$ nm) and surfacely attached by non-

covalent binding interactions with (5, 10, 15, 20)-meta-pyridyl-porphyrin, H₂P, or perylene diimide, PDI, molecules in solutions at 77-295 K (Figure 1).

Measurements at 77-300 K were carried out in methylcyclohexane/toluene mixture (6:1). Single QD and QD-Dye samples were prepared in a solvent with considerably reduced polarity ($\epsilon < 2,3$) like TEHOS (tetrakis-2-ethylhexoxy-silane).

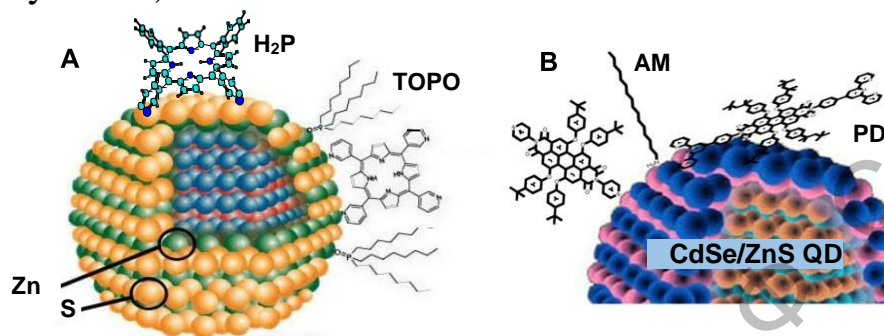


Figure 1 – Schematic presentation of “QD-H₂P” (A) and “QD-PDI” (B) nanoassemblies with corresponding displacement of dye molecules on QD surface

Our findings have shown that surface-mediated processes dictate the probability of several of the most interesting and potentially useful photo-physical phenomena observed for colloidal QDs. The principal aspects are the following [3,4]:

It has been quantitatively clarified that the major part of the observed QD photoluminescence (PL) quenching in QD-Dye nanoassemblies (Figure 2), namely non-FRET processes can be understood on one hand, in terms of electron tunneling beyond the CdSe core under conditions of quantum confinement (Figure 3), and on the other hand, by the influence of ligand dynamics.

FRET QD→Dye often plays a minor role in the QD PL overall quenching. The competition between FRET and non-FRET quenching processes drastically depends on the solvent and ligand properties. Quenching by non-FRET in QD-Dye nanoassemblies is effectively enhanced already in slightly polar solvents.

For QD-PDI nanoassemblies dissolved in strongly non-polar TEHOS, QD PL quenching caused by non-FRET processes is effectively suppressed, and Φ_{FRET} efficiency rises up to 55%. In this case, using single molecule detection with a home-built laser scanning confocal microscope, a pronounced PL intensity intermittency in combination with spectral fluctuations was observed for QD and DPI molecules.

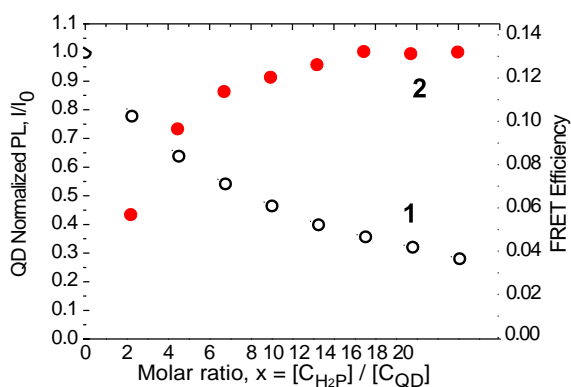


Figure 2 – Comparison of QD PL quenching I/I_0 (1, left scale) and FRET efficiency Φ_{FRET} (2, right scale) for QD-Porphyrin nanoassemblies. In toluene at 295 K, Φ_{FRET} efficiency is $\sim 15\%$ of QD PL quenching

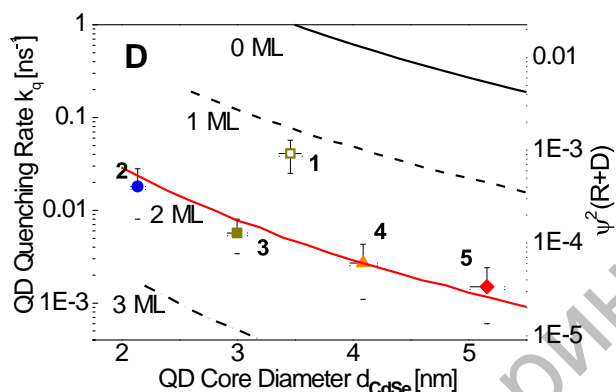


Figure 3 – Comparison experimentally determined quenching rate constants k_q (points, left axis) and calculated probability density functions $\psi^2(r=R+D)$ (lines, right axis) of $1s$ electron tunneling through ZnS shell

It was shown for the first time that the respective PL intensities for QD and DPI in a single nanoassembly are strongly (positively) correlated: the strong blinking of QDs is imposed on DTPP, which blinks very often synchronously with the QD (Figure 4).

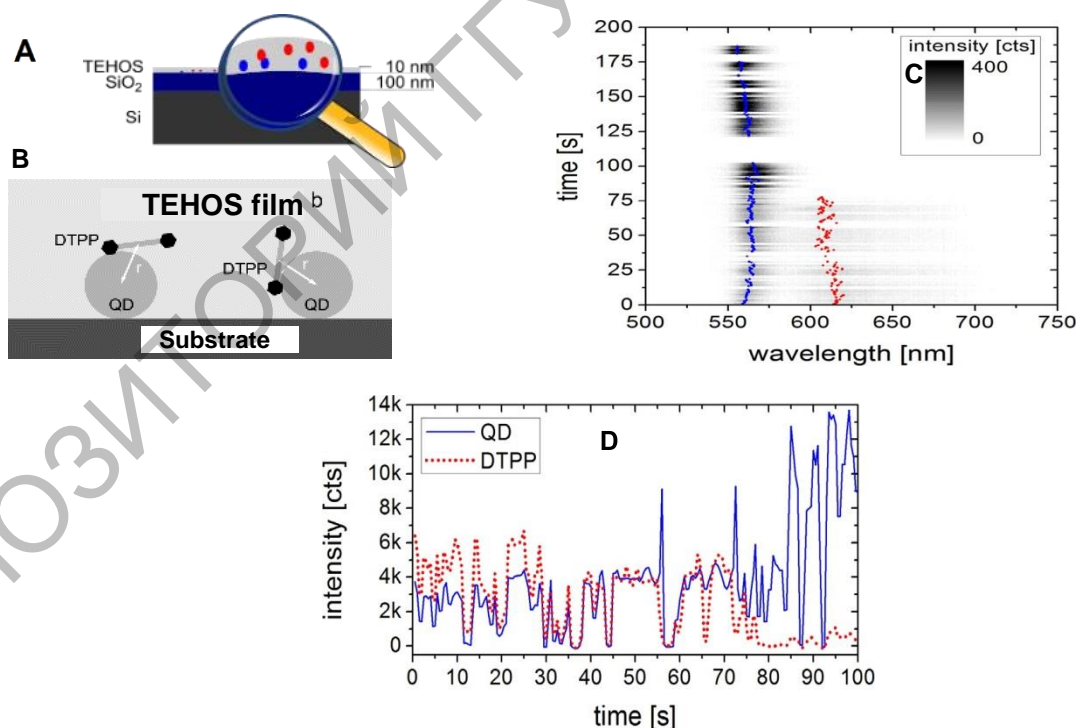


Figure 4 – Scheme of sample preparation (A, B) spectral (C) and intensity (D) time traces for QD-PDI nanoassemblies at molar ratio $x = 1$ in 10 nm thick films of TEHOS

Nevertheless, we have shown quantitatively that even low FRET efficiencies (experimentally found for QD-Porphyrin nanoassemblies in toluene at ambient temperature) may increase significantly the photochemical activity of these complexes. A good quantitative coincidence of experimental FRET efficiencies Φ_{FRET} (found from the acceptor fluorescence sensitization) and $\Phi_{\Delta}^{\text{FRET}}$ values (evaluated via independent measurements of singlet oxygen generation) reveals that namely FRET process QD→porphyrin is the only reason of the essential increase of singlet oxygen generation by nanoassemblies in comparison to QDs without assembly formation.

We have argued that the observed non-FRET quenching of QD PL induced by attachment of only one dye molecule (or incorporation in the ligand shell) can be explained by the presence of a limited number of empty or easily accessible sites on the QD surface followed by ligand competitive exchange (TOPO, amines and dyes) on various time scales. In addition, the efficiency of non-FRET quenching depends on various factors, including QD size (electron tunneling in conditions of quantum confinement), the number of attachment sites, the microscopic nature of these sites, which might be additionally influenced by solvent properties, crystal structure (facets) and QD surface geometry. Moreover, that non-FRET quenching is related to depletion of capping ligands by the respective dye molecules followed-up by creating more and even new quenching states according to the amplitude of the tunnelling (“leaking”) excitonic wave function.

It was found experimentally that temperature variation (77÷295 K) and related changes in QD absorption and emission reveal drastic changes of the ligand shell structure in a narrow temperature range for organic (TOPO and amine) ligands (so-called low-temperatures „phase transition” of capping layer). The effects on QD PL intensities, energies and dynamics at this transition become considerably pronounced upon attachment of only one or a few dye molecules (porphyrin or perylene diimide) to the QD surface (Figure 5).

It follows from these experiments, that the ligand phase transition has impact even on the QD core structure and the corresponding exciton-phonon coupling in QDs. The comparison of averaged and deconvoluted spectral PL properties (such as band energies E_g , spectral widths (FWHM) and relative integrated band intensities I_{Σ}) of only CdSe/ZnS QDs and QDs in QD-Dye nanoassemblies in a wide temperature range proofs that already one attached dye molecule causes not only PL quenching but also changes the energy landscape of the QD PL noticeably. Temperature controls the

energetic ordering of electronic states. Especially below the “phase transition” of TOPO ligands, PL energies depend critically on the type of the surface-attached porphyrin molecule nearly independent on the type of ligand.

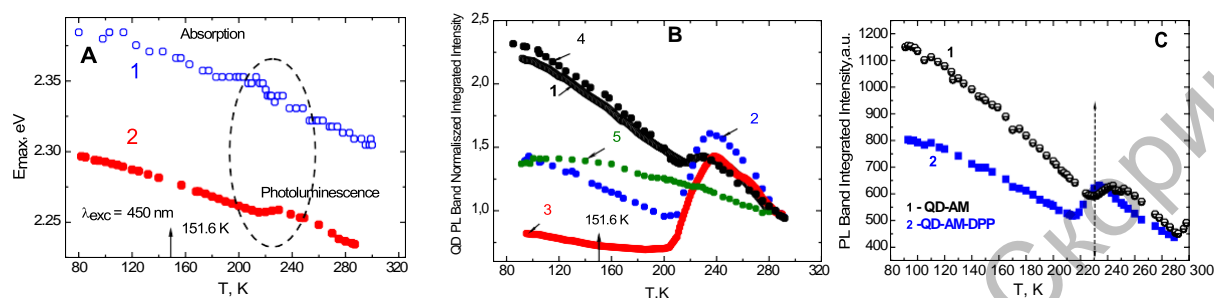


Figure 5 – Temperature dependence of spectral properties (absorption and PL) for TOPO (A, B) – and AM (C) - capped CdSe/ZnS QDs and their nanoassemblies with porphyrins (A, B) and PDI (C) molecules at molar ratio $x = [C_{Dye}]/[C_{QD}] = 1$ in methylcyclo-hexane/toluene (6:1) mixture. The glass transition temperature (151.6 K) of the solvent mixture is indicated by solid arrow. Dashed ellipse indicates temperature range at which optical properties change (showing “kink”)

Concluding, based on a combination of ensemble measurements and single molecule spectroscopy of nanoassemblies, we have shown that single functionalized dye molecules can be considered as extremely sensitive probes for studying the complex interface physics and exciton relaxation processes in QDs. Herein we focused on a quantitative experimental analysis of QD PL properties as well as the observed QD PL quenching in QD-Dye nanoassemblies.

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