

# TEMPORAL ENERGY TRANSFER IN SINGLE NANOASSEMBLIES “QUANTUM DOT – DYE MOLECULE”

E. Zenkevich<sup>1</sup>, F. Gerlach<sup>2</sup>, C. von Borczyskowski<sup>2</sup>

<sup>1</sup>National Technical University of Belarus, Minsk, Belarus

<sup>2</sup>Technische Universität Chemnitz, Chemnitz, Germany

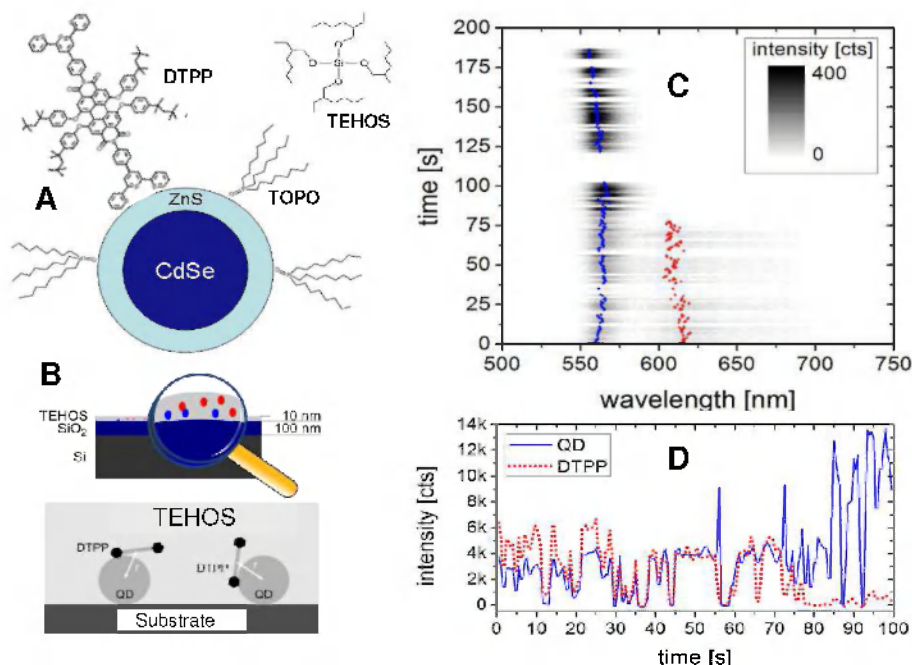
E-mail: [zenkev@tut.by](mailto:zenkev@tut.by)

Typically, single molecule spectral experiments are usually exploited to investigate the distribution or manifold of conformations and interactions with the environment for dye molecules and semiconductor quantum dots (QD). In addition, photoluminescence (PL) quenching for QDs is also detected in single nanoassembly experiments. Especially blinking statistics are valuable tool to investigate various aspects of excited state dynamics in nanoassemblies of various nature and composition [1].

In this report, for nanoassemblies based on TOPO-capped CdSe/ZnS QDs and (pyridyl)<sub>2</sub>-dialkyl-perylene diimide molecule (DTPP) we demonstrate spectral-kinetic observations on the single assembly level which give specific information concerning nanoassembly geometries, conformational mobility and time-dependent non-radiative energy transfer (FRET) QD→DTPP molecules attached to the QD surface (Fig. 1). Samples were prepared by dipcoating the silicon substrates into solutions of 0.3% TEHOS in hexane with highly diluted TOPO-capped CdSe/ZnS QDs and DTPP molecules (at molar ratio 1:1) resulting in 10 nm thick films with nanomolar concentrated CdSe/ZnS QDs and DTPP (Fig.1). Spectral-kinetic measurements have been carried out with a home-built laser scanning confocal microscope described in [2].

Data presented in Fig. 1, *c* and Fig. 1, *d* show that the respective luminescence intensities from QD and DTPP are strongly (positively) correlated: the strong blinking of QDs is imposed on DTPP, which now blinks very often synchronously with the QD. In addition, when DTPP is photobleached (or detached) from the QD (after 77 s irradiation) the QD PL increases on average by about a factor of 3. The overall interpretation is that the PL of the QD is quenched due to FRET QD→DTPP and that DTPP fluorescence is predominantly caused via FRET. It should be noted, that the photoinduced electron transfer from the QD to DTPP can be excluded in this case as far as the formation of charged QD DTPP counterpart in nanoassembly should result to complete quenching of DTPP which is not observed in the given experiments. Contrary to this, DTPP fluorescence is strongly decreased namely when the QD does not emit. The detailed quantitative consideration of FRET in single QD-DTPP nanoassemblies has been described by us recently [1]. The main ideas may be presented as follows. The correlation of normalized DTPP and QD

PL intensities (ratio  $R = I_{\text{DTTP}}/I_{\text{QD}}$ ) depends on the observation time: the linear correlation is quite constant during the first 30 s, but changes in the course of time. This can be interpreted as being due to time dependent changes of the geometry of the nanoassembly or the conformation of the DTTP molecule attached to the QD surface.



**A:** Chemical structures of dye molecule [(pyridyl)<sub>2</sub>-dialkyl-perylene diimide, DTTP], non-polar solvent (tetrakis-2-ethylhexoxy-silane, TEHOS) and schematic presentation of nanoassemblies based on TOPO-capped CdSe/ZnS QD and dye (1:1); **B:** Scheme of sample preparation (spin coating) and orientations of DTTP on QD; **(C)** Spectral and **(D)** intensity time traces for QD-DTTP nanoassemblies in 10 nm TEHOS ( $\lambda_{\text{exc}}=488$  nm).

*Fig. 1.* Structural, spectral and temporal properties of single CdSe/ZnS QD-DTTP nanoassemblies upon laser excitation

Estimated FRET efficiency  $\Phi_{\text{FRET}} \approx 0.55\text{--}0.69$  is in a good agreement with calculations within the Foerster model. Variations of  $\Phi_{\text{FRET}}$  are observed for on one and the same assembly, since  $I_{\text{QD}}$  depends on quenching processes other than FRET (temporal formation of surface trap states).

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2. Krause S., Aramendia P.F., Täuber D., von Borczyskowski C. // Phys. Chem. Chem. Phys. 2011. V. 13, Pp. 1754–1761.