

# ELECTRONIC STATES TUNING FOR CdSe/ZnS QUANTUM DOTS UPON SELF-ASSEMBLY WITH ONLY ONE FUNCTIONAL DYE MOLECULE

**E. Zenkevich<sup>a</sup>, A. Stupak<sup>b</sup>, C. Göhler<sup>c</sup>, C. Krasselt<sup>c</sup>, and C. von Borczyskowski<sup>c</sup>**

<sup>a</sup>National Technical University of Belarus, Minsk 220013, Belarus

<sup>b</sup>B.I. Stepanov Institute of Physics, 220072 Minsk, Belarus

<sup>c</sup>Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany

It is known that capping organic shell (including surfactants and ligands) have considerable impact on the semiconductor quantum dot (QD) surface structure and optical properties of QDs (hot carrier relaxation, quantum efficiency and photoluminescence, PL energy). Recent progress in quantum chemical calculations of structures and electronic properties of QDs has set new milestones in the understanding of QD surfaces and the capping ligand role. However, detailed and specific experimental studies on the influence of only one (or at least a few) ligand or surface attached dye molecules on surface states are difficult to conceive.

Here, we present spectral and time resolved PL data (from temperature dependent ensemble experiments) for CdSe/ZnS QD-porphyrin nanoassemblies (at molar ratio 1:1) in solvent giving rigid glassy matrix at low temperature. We have succeeded to detect the sensitivity of QD PL parameters to the chemical nature of the respective porphyrin molecules and the impact of the competing ligand layer. In addition, the results of such an elaborated investigation on an ensemble of QD-porphyrin nanoassemblies have been compared with those obtained by a newly designed and complementary (time and spectrally resolved) spectroscopy on single QDs [1]. We concluded that electronic states of different nature with varying PL energies and decay dynamic are subsequently explored on slow time scales typical for blinking phenomena which are buried but nevertheless present in ensemble experiments. Upon temperature variation the ordering of at least 2 energetically deconvoluted PL states is abruptly changed at the “phase transition”. The temperature dependence of the PL observables reveals both the influence of electron-phonon coupling between 77 K and 290 K and a “phase transition” of the capping TOPO shell at  $T_{\text{crit}} \approx 220$  K. According to time resolved experiments we found at least 3 basically different types of emissive states. The specific selectivity of QD PL properties to the surface-attached only one dye molecule provides new and not yet reported experimental insights into QD surface properties. Modifications of PL properties of nanoassemblies are assigned to dye induced ligand removal accompanied by spectral blue shifts and formation of surface trap states in the band gap, and the temperature controls the energetic ordering of electronic states. The basic conclusion is that a dye molecule removes ligands from (specific) surface sites thus acting as a new “ligand” creating a modified set of new surface responsible for “Non-FRET” PL quenching upon QD-dye nanoassembly formation but not leading to FRET or charge transfer events. Such dye molecule may be considered as single molecular surface probe.

*Keywords:* Semiconductor quantum dots, Porphyrins, Perilene-bisimids, Ligand dynamics, Photoluminescence, Surface traps, Temperature surface “phase” transition, Blinking.

## References

[1] E. Zenkevich, A. Stupak, C. Göhler, C. Krasselt, C. von Borczyskowski, ACS NANO 9 (2015) 2886

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 *Poster*

Modifications of PL properties of nanoassemblies are assigned to dye induced ligand removal accompanied by spectral blue shifts and formation of surface trap states in the band gap. Both, the comparison of averaged and deconvoluted spectral PL properties of CdSe/ZnS and QDs in nanoassemblies proves that already one attached porphyrin 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. Also CdSe/ZnS-diimide assemblies with amine ligands show qualitatively similar phenomena.<sup>50</sup>

This specific selectivity to the surface-attached dye molecule provides new and not yet reported experimental insights into QD surface properties. In this respect, a qualitative comparison with calculations on the basis of a TD DFT approach, which takes the number, position and chemical nature of ligands and their specific removal into account, explains qualitatively the observed modifications of PL energies and dynamic. The basic conclusion is that a dye molecules removes ligands from (specific) surface sites thus acting as a new “ligand” creating a modified set of new surface states.<sup>17-24</sup> This explains specifically why (“Non-FRET”) PL quenching upon QD-dye nanoassembly formation is often not exclusively related to energy (FRET) or charge transfer.<sup>30,31,35-39,48</sup> In a certain way we use dye molecules as single molecular surface probes.

In future, increasing knowledge of specific interactions at the QD surface will add to the control of the complex interplay of QD core and surface properties and will allow for a guided tailoring of optical features of semiconductors with respect to applications in photovoltaic and especially nanosensoric.