

PHOTONICS AND RELAXATION PATHWAYS FOR SELF-ASSEMBLED NANOSTRUCTURES: MULTIPORPHYRIN COMPLEXES AND NANOCOMPOSITES «SEMICONDUCTOR CdSe/ZnS QUANTUM DOT - ORGANIC DYE»

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At the moment, it is well-documented that *photonics* is playing a pivotal role in advancing Nano/Bio/Info technology by creating new interfaces between multiple disciplines. In this respect, *nanophotonics* provides opportunities for high-density integration in information technology and for efficient harvesting of solar energy, as well as offers real opportunities for fundamental research and various applications to produce novel nanoprobe for biomedical imaging, biosensing and therapy for cancer as well for other major medical needs to advance human health. Correspondingly, nanostructured materials with tuneable morphology have attracted exceptional interest over the past decades because of their unique architectures, tailored physicochemical properties, central roles in fabricating nanoelectronics, and potential applications in bionanotechnology [1-3].

Recently, great efforts have been devoted to bottom-up self-assembled nanostructures. Self-assembly is the fundamental phenomenon that generates structural organization on all scales *in vivo* and *in vitro* [4-6]. In fact, this direction is the supramolecular organic/inorganic chemistry/photochemistry in solutions or at solid/liquid interfaces, a highly interdisciplinary field of science covering the chemical, physical, and biological features of chemical species held together and organized by means of intermolecular binding interactions of various natures. However, many fundamental issues still need to be in-depth investigated in order to have full understanding of mechanisms that drive the properties of such nanocomposites.

Recently, based on ideas of the self-assembly mentioned above, we have succeeded to form multicomponent organic and organic/inorganic nanoassemblies using the combination of covalent and non-covalent binding interactions, that is the preparation of multiporphyrin complexes, and the anchoring of functional organic molecules (including tetrapyrrolic compounds and perylene bisimides) to the surface of semiconductor CdSe/ZnS quantum dots (QD) in solutions and polymeric films (Fig. 1) [7-10]. These nanoassemblies are of considerable scientific and a wide practical interest including material science and biomedical applications.

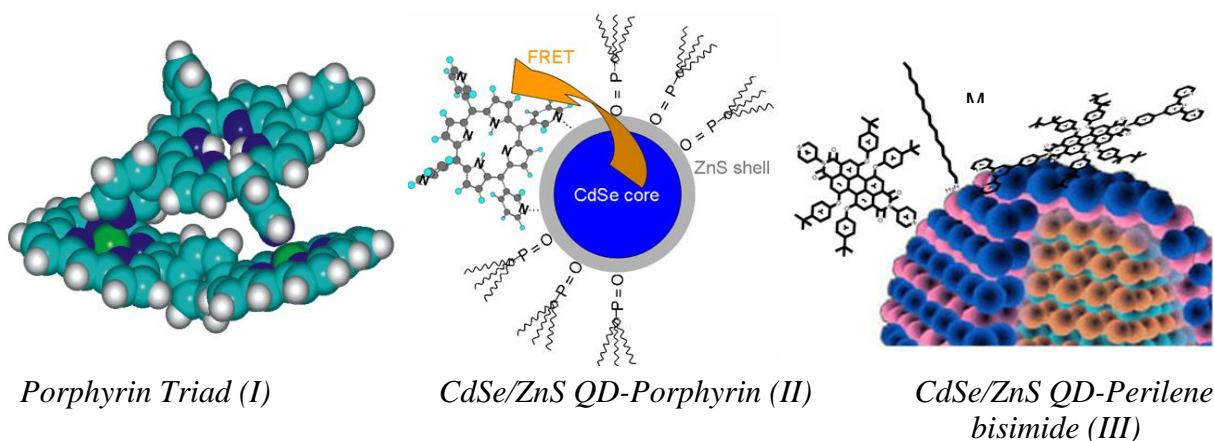


Figure 1. Structures and mutual arrangement of interacting subunits in nanoassemblies

In this paper, we are willing to discuss the formation principles, spectroscopy and mechanisms of excitation energy relaxation being obtained for multiporphyrin complexes (triads) as well for nanocomposites based on trioctylphosphine oxide (TOPO) or long-chain amine (AM) capped core/shell CdSe/ZnS QDs exhibiting size-dependent photophysical properties and surfacely activated by *meso*-pyridyl substituted porphyrins, H₂P, or perilene bisimide dyes, PBI, in solutions and polymer matrixes at 295 K (steady-state, picosecond time-resolved luminescence spectroscopy and single molecule spectroscopy).

Typically, at 295 K triad complexes (Structure I in fig. 1) are formed during a titration of the chemical dimer (ZnOEP)₂Ph solution by the extra-ligand solution or by one-step mixing of the two solutions at appropriate concentrations. In these triads, main fluorescent features are as follows. 1) The dimer fluorescence does show strong quenching (fluorescence decay is shorten from $\tau_{SD}^0=1.15$ ns down to $\tau_{SD} \leq 1.7$ ps), and fluorescence spectra of the triads mainly consist of the porphyrin extra-ligand fluorescence bands. 2) In nonpolar toluene at 295 K, the extra-ligand fluorescence quantum efficiency is also reduced by 1.5-2 times as compared to the individual extra-ligand L [H₂P(m[^]PyR)₂-(iso-PrPh)₂]. 2) The L fluorescence intensity is decreased upon temperature lowering (278-160 K). 3) The increase of the solvent polarity leads to the decrease of the L fluorescence intensity. 4) In polar conditions, the sensitization effect due to the singlet-singlet energy migration (S-S EM) process is absent, though usually through-space S-S EM process in multiporphyrin arrays is hardly dependent on the solvent polarity. 5) Time-correlated single photon counting (TCSPC) fluorescence measurements show that the emission decays of extra-ligand in the triads are reduced noticeably with respect to those for individual uncomplexed porphyrin (fig. 2). Femtosecond pump-probe data for the triad I in toluene at 295 K reveal that the non-radiative relaxation of the dimer S₁-state in the triads realizes within ~1.7 ps.

In the result, on the basis of the detailed experimental data in the combination with theoretical calculations (Foerster resonant energy transfer model and the generalized Haken-Strobl-Reineker formalism) the whole scheme of the dynamics of locally excited S₁-states for components in triad I has been evaluated (fig. 3). The

main quantitative conclusion is that in these complexes, the competition of the energy migration (EM) and photoinduced electron transfer (PET) processes takes place which may be selectively driven by the triad composition, solvent polarity and temperature.

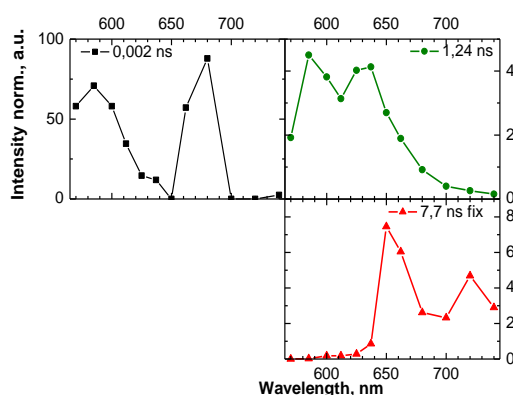


Figure 2. Decay-associated spectra of the triad $(ZnOEP)_2Ph\otimes H_2P(m^{\wedge}Pyr)_2$ (toluene, 293 K, $\lambda_{ex}=546$ nm) derived from a global analysis of 12 TCSPC measurements

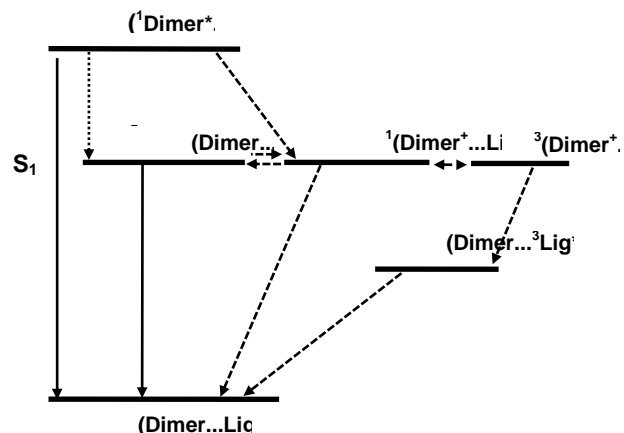


Figure 3. Schematic energy diagram for excited singlet, triplet and radical ion pair CT states and corresponding rate constants in the triad

In the case of organic/inorganic self-assembled nanocomposites, we have shown that dye molecules with pyridyl side substituents (porphyrins and heterocyclic perylene bisimides) coordinatively attached to the surface of CdSe/ZnS QDs form quasi-stable “QD-Dye” nanoassemblies of various geometry in the competition with capping molecules (tri-*n*-octyl phosphine oxide or long chain amines) exchange (structures II and III, Fig. 1). In this case, QD-porphyrin interaction may be described by a Poisson distribution

$$P(n) = x^n \exp(-x) / n! \quad (1)$$

where x is the average number of chromophores per one QD (estimated from a molar ratio ($x = [C_{porphyrin}] / [C_{QD}]$), n is the number of attached chromophores on a given QD. Upon formation of “QD-Dye” nanocomposites the QD photoluminescence (PL) is quenched as can be detected both via single particle detection and time-resolved PL ensemble experiments in solution. PL quenching has been numerically assigned to i) Foerster resonant energy transfer (FRET) and 2) the formation of non-radiative surface states under conditions of quantum confinement in QDs. With respect to non-FRET PL quenching, it was shown for the first time that the quenching rate k_q scales inversely with the QD diameter and can be understood in terms of a tunnelling of the electron (of the excited electron-hole pair). Correspondingly, the QD photoluminescence quenching (as intensity ratio $I(x)/I_0$) may be written as

$$I(x)/I_0 = e^{-x} \sum_{n=0}^{\infty} x^n / n! (1 + nk_Q/k_D) \quad \text{or} \quad \frac{I(x)}{I_0} = \sum_{n=0}^{\infty} \frac{k_D}{k_D + nk_Q} x^n \frac{\exp(-x)}{n!} \quad (2)$$

where k_D is the total QD PL intrinsic decay rate and k_Q the QD PL quenching rate. Using this approach, it was found that the estimated values of complexation constant K_C for “QD-Porphyrin” nanocomposites lie in the region from $\sim 10^5 \text{ M}^{-1}$ to $\sim 10^7 \text{ M}^{-1}$. Notably, the exciton relaxation dynamics in QD initiated by a single titration step is not only due to the added H_2P molecules themselves, but also to a local change in the capping ligand shell on QD surface upon nanocomposite formation as well as to a local replacement of TOPO by H_2P molecules. This argumentation is in line with the finding that dilution of a QD solution reduces the average coverage of the QDs with TOPO, giving rise to both an intrinsic reduction of QD PL as well as to increased accessibility of the QD surface to the quencher molecules.

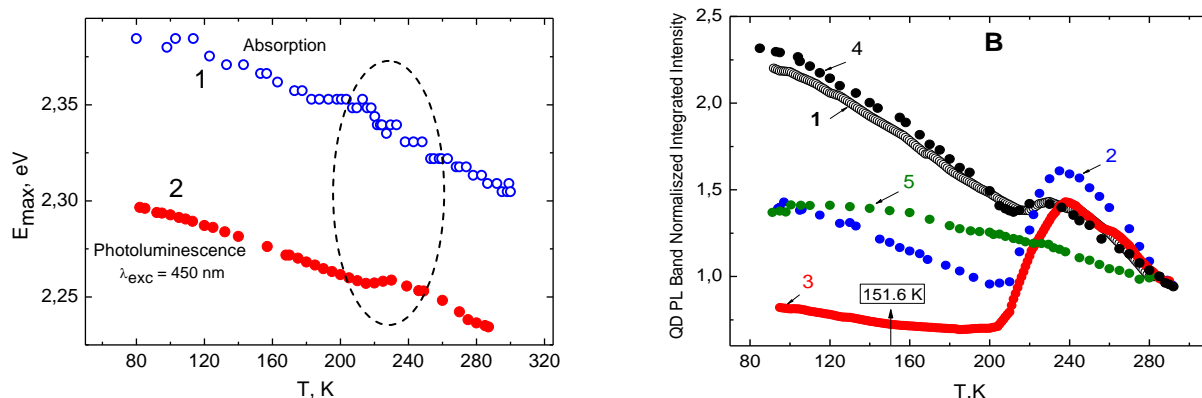


Figure 4. Temperature dependence of absorption peak (1A) and PL band (1B) for alone QDs and “QD-Dye” nanocomposites (B) in methylcyclohexane/toluene (6:1) mixture. (A): Dashed ellipse indicates temperature range at which optical properties change. (B): Temperature dependence of the normalized PL maximum intensity for the same type of CdSe/ZnS QD under various conditions and attached porphyrins: (1) alone QDs; (2) QD+ $\text{H}_2\text{P}(\text{m-Pyr})_4$; (3) QD+ $\text{CuP}(\text{m-Pyr})_4$; (4) QD+tetraphenylporphyrin; (5) QD in dried PMMA film on a quartz plate

Upon temperature lowering it was found for alone QDs, that in a range of 220÷240 K related changes in QD absorption and emission reveal a phase transition of the capping shell (tri-*n*-octyl phosphine oxide and amine). In “QD-Dye” nanocomposites, this phase transition is enhanced considerably by only a few attached dye molecules and has impact on the QD core structure followed by changes of PL quenching and exciton-phonon coupling (fig. 4). This phase transition observed for TOPO-capped CdSe/ZnS QDs between 200 and 240 K, is far from the glass transition temperatures for the solvents. We have demonstrated, that dye molecules (porphyrins or perylene bisimids) noticeably influence the optical properties at ligand controlled phase transitions. Our findings highlight that single functionalized heterocyclic molecules can be considered as extremely sensitive probes for the complex interface physics and dynamics of colloidal semiconductor QDs.

Detecting the PL spectra on each single luminescent spot reveals three types of spectroscopic fingerprints emerge (Fig. 5): (i) PP fluorescence spectra; (ii) QD-AM PL spectra and (iii) simultaneous QD-AM and PP spectra belonging to a nanocomposite. The detection of these three types of emission is an experimental background of the distribution of dye molecules on QDs which may be described by

Poisson approach. In addition, PL band of single QD is blue shifted upon the observation time increase. Average decay time for single uncomplexed QD-AM was measured to be $\langle\tau_D\rangle\approx 20$, while for QD in single nanocomposite (QD-AM)-PP $\langle\tau_{DA}\rangle\approx 16$ ns. The shortening of the decay time is clearly related to the observed decrease of the QD PL intensity upon nanocomposite formation. This proves that QD PL quenching is also observed on a single nanoassembly level and reflects directly the existence of an additional non-radiative channel for QD exciton relaxation in this nanocomposite.

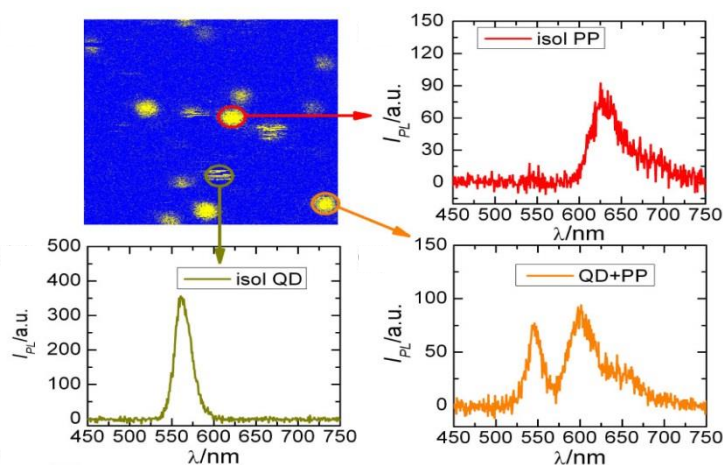


Figure 5. $5\times 5\ \mu\text{m}^2$ confocal scan ($\lambda_{exc}=465\ \text{nm}$; $P=0.6\ \text{kW}\cdot\text{cm}^{-2}$) of PL for single objects based on long-chain amines capped quantum dot (QD-AM) and perylene bisimide (PP) molecules at $x=1$ (see Fig.1, structure III). Because of Poisson distribution of dye molecules on QDs it was possible to detect PL spectra (1 s binning time) of single PP (B), single QD-AM (C) and single nanocomposite with colocalized PP and QD-AM (D)

Finally we like to point out, that properties of QD-Dye nanocomposites are interesting in itself, but also provide a valuable tool to study surface related phenomena in QDs on an extremely low level of the surface modification. Instead of investigating the exchange ligand dynamics directly e. g. by NMR, we suggest to make use of QD PL quenching in combination with appropriately functionalized dye molecules. In contrast to NMR, this approach allows to investigate ligand dynamics at extremely low concentrations of concurrent ligand-type dyes. At last, our data show also, that “QD-Porphyrin” nanocomposites may be considered as potential photosensitizers of a novel type in the photodynamic therapy of cancer.

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References

1. Muraoka T., Kinbara K. *J. Photochem. Photobiol. C: Photochem. Rev.* 2012; 13: 136–147.
2. Mocatta D., Cohen G., Schattner J., Millo O., Rabani E., Banin U. *Science* 2011; 332: 77-81.
3. Cheng H-M. *Chem. Commun.* 2011; 47: 6763-6783.
4. *Handbook of Molecular Self-Assembly: Principles, Fabrication and Devices*, Peinemann K-V and Barboiu M. (Eds.) Pan Stanford Publishing Co. Pte. Ltd.: Singapore, 2012.

5. Nicolini C. In *Nanotechnology and Nanobiosciences*, Vol. 1, Chapter 1 “Nanoscale Materials”, Pan Stanford Series on Nanobiotechnology, 2010.
6. Zenkevich E.I., von Borczyskowski C. In *Handbook of Porphyrin Science with Application to Chemistry, Physics, Materials Science, Engineering, Biology and Medicine*, Vol. 22, Kadish KM, Smith KM and Guillard R. (Eds) World Scientific Publishing Co. Pte. Ltd.: Singapore, 2012; Ch. 104, pp 68-159.
7. Zenkevich E.I., Sagun E.I., Knyukshto V.N., Stasheuski A.S., Galievsky V.A., Stupak A.P., Blaudeck T., von Borczyskowski C. *J. Phys. Chem. C*. 2011; 115: 21535-21545.
8. Blaudeck T., Zenkevich E., Abdel-Mottaleb M., Szwaykowska K., Kowerko D., Cichos F., von Borczyskowski C. *ChemPhysChem*. 2012; 13: 959-972.
9. Zenkevich E.I., Stupak A.P., Kowerko D., von Borczyskowski C. *Chem. Phys.* 2012; 406: 21
10. Zenkevich E.I., von Borczyskowski C. *J. Porphyrins Phthalocyanines*. 2013;. 17: 1–19.