

Time dependent fluctuations of the non-radiative electronic excitation energy transfer in single nanoassemblies “semiconductor quantum dot – dye molecule”

E. I. Zenkevich¹⁾, C. Von Borczyskowski²⁾

¹⁾ *Belarussian National Technical University, Minsk, Belarus*
e-mail: zenkev@tut.by

²⁾ *Institute of Physics, Technical University, Chemnitz, Germany*
e-mail: borczyskowski@tu-chemnitz.de

It was clearly demonstrated that single object experiments for nanoassemblies based on amine-capped CdSe/ZnS-AM quantum dots and (pyridyl)₂-perilene bisimide molecules (DTPP) may be considered as an unsurpassed tool to investigate subtle conformational changes and the related impact on interchromophoric dynamics. In fact, due to their intrinsic flexibility, DTPP molecules can realise a large variety of conformations on the experimental time scale of seconds to minutes. For this reason, the process of the non-radiative electronic excitation energy transfer QD→DTPP manifests itself in the dynamics the OD photoluminescence blinking, and this process becomes dependent on observation time, which can be followed quite in detail.

Keywords: amine-capped semiconductor quantum dots CdSe/ZnS-AM; (pyridyl)₂-perilene bisimide molecules (DTPP); single molecule detection, photoluminescence intensity blinking, non-radiative electronic excitation energy transfer (FRET).

Зависимые от времени флуктуации безызлучательного переноса энергии электронного возбуждения в одиночных наноквантовых точках «полупроводниковая квантовая точка - молекула красителя»

Э. И. Зенькевич¹⁾, К. фон Борцисковски²⁾

¹⁾ *Белорусский национальный технический университет, Минск, Беларусь*
e-mail: zenkev@tut.by

²⁾ *Институт физики, Технический университет, Хемнитц, Германия*
e-mail: borczyskowski@tu-chemnitz.de

Показано, что эксперименты по детектированию одиночных объектов, выполненные для наноквантовых точек стабилизированных амином (АМ) полупроводниковых квантовых точек (КТ) CdSe/ZnS-AM КТ и молекул (пиридил)₂-перилена-бисимида (DTPP), могут рассматриваться как чувствительный метод исследования тонких конформационных изменений и связанного с ними влияния на межхромофорную динамику взаимодействующих компонент. Благодаря присущей им гибкости, молекулы DTPP способны к различным конформационным перестройкам в экспериментальном масштабе времен от секунд до минут. В силу этих причин в процессе безызлучательного переноса энергии электронного возбуждения КТ→DTPP проявляется динамика мерцаний интенсивности фотолуминесценции КТ, а сам перенос становится зависимым от времени наблюдения и его можно детектировать достаточно подробно.

Ключевые слова: стабилизированные амином полупроводниковые квантовые точки CdSe/ZnS-AM; детектирование одиночных молекул; мерцание интенсивности фотолуминесценции; безызлучательный перенос энергии электронного возбуждения (FRET).

Introduction

Typically, single molecule spectral experiments are usually exploited to investigate the distribution or manifold of conformations and interactions with the environment. It should be noted that number of experiments on the identification of single nanoassemblies is limited [1–3], but even in these cases a complete quantitative determination of the involved quenching and transfer processes is not reported. Here, we will predominantly demonstrate our results being obtained for single nanoobjects, such as semiconductor quantum dots (QDs), dye molecules and nanoassemblies on their basis, showing that this approach may be considered as a tool to precisely identify the interaction of exactly one QD with one dye molecule. In this case it is possible to receive an unique (in some cases) information on a microscopic understanding of the formation (including ligand dynamics) and related QD photoluminescence (PL) quenching dynamics in QD-Dye nanoassemblies. Additionally, a comparison of results being obtained for the same bulk and single nanoassembly allows unraveling the contributions of different quenching mechanisms which are of importance for the identification of dynamic processes for QD-Dye and/or QD-capping ligand systems in general.

Results and Discussion

We have chosen semiconductor CdS/ZnS QDs (diameter $d_{\text{CdSe}} = 3.2$ nm, 2 ZnS monolayers) stabilized by long chain amine (AM) ligands to allow for intercalation of appropriate anchor groups of dye molecules such as (pyridyl)₂-perylene bisimide (DTPP) in toluene at 295 K (Fig. 1). Due to the high quantum yield of fluorescence and large photostability of DTPP molecules it becomes feasible to receive an additional unique information via single QD and single dye molecule detection in an individual nanoassembly [2, 3]. In addition, it has been shown previously in bulk solutions [2, 3] that upon anchoring of perylene bisimide molecules of various types to CdS/ZnS-AM QD surface, the QD photoluminescence (PL) quenching is caused by the non-radiative excitation energy transfer process QD→Dye via Foerster mechanism (FRET) competing with the non-radiative electron tunneling in the conditions of quantum confinement.

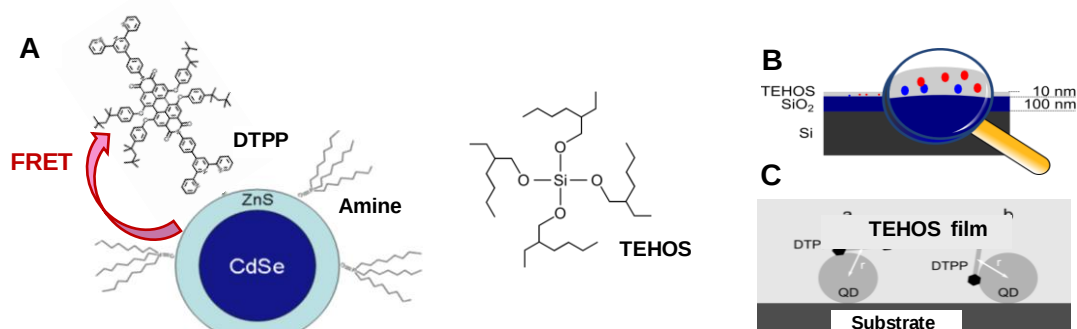


Fig. 1. (A) Schematic presentation of the interaction between surface of amine-capped CdSe/ZnS-AM QD and (pyridyl)₂-perylene bisimide (DTPP). Scheme of sample preparation (B) and two different orientations of the DTPP dye on TOPO-capped CdSe/ZnS QDs (C). For steric reasons DTPP can be attached via the terpyridyl groups at only one end of the dye. DTPP is plotted along the optically active transition dipole moment. In the case DTPP molecules a parallel displacement of the chromophoric part (optical transition dipole moment) on the QD surface is reasonable

Correspondingly, we analyse in more detail what happens with QD PL quenching and competing FRET and non-FRET processes when using a solvent with considerably reduced polarity ($\epsilon < 2.3$) like TEHOS (tetrakis-2-ethylhexoxy-silane having long aliphatic chains, Fig. 1). The focus on polarity is motivated by the finding that blinking processes in single QDs depend strongly on the solvent polarity [3]. Samples were prepared by dipcoating the silicon substrates (with 100 nm thick thermal oxide, Crystec, Berlin) into solutions of 0.3 % TEHOS in hexane with highly diluted TOPO-capped CdSe/ZnS QDs and DTPP molecules (at molar ratio $x = 1$) resulting in 10 nm thick films of TEHOS with nanomolar concentrated CdSe/ZnS QDs and DTPP. Spectra PL blinking were investigated with a home-built laser scanning confocal microscope described in detail elsewhere [2] (Fig. 2).

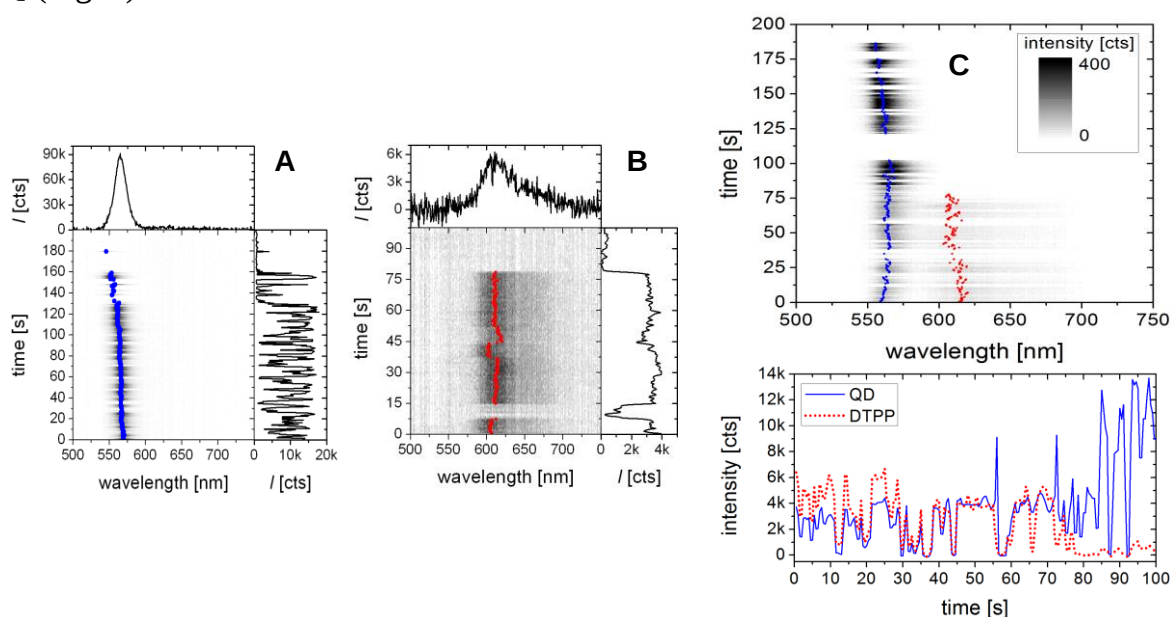


Fig. 2. Typical time dependent emission spectra and intensity blinking of single CdSe/ZnS-AM QD (**A**), (pyridyl)₂-perilene bisimide (**B**) and CdSe/ZnS-AM QD + DTPP (1:1) nanoassembly (**C**) with 1 s integration time (excitation via the 488 nm line of an Ar-ion laser). The respective over the total observation time integrated spectra of QD (**A**) and DTPP (**B**) are shown on top of each spectral trace. **A**, **B**: The integrated luminescence intensity is depicted on the right side of each time trace. **C**: Spectral (top) and intensity (bottom) time traces for CdSe/ZnS-AM QD + DTPP (1:1) nanoassembly at molar ratio $x = 1$ in 10 nm thick films of TEHOS

Intensity fluctuations of the luminescence of single QDs and DTPP molecules as a function of an observation time of several minutes are presented in Fig. 3, A, B. The fluctuating luminescence intensity is shown at the side of each time trace of the series of spectra. CdSe/ZnS QD shows strong intensity fluctuations known as blinking or photoluminescence intermittency [5], while blinking is almost negligible for DTPP. The emission of CdS/ZnS QD and DTPP is bleached after 180 and 77 s, respectively. Bleaching of the QD is in most cases preceded by a strong blue shift of the PL which is tentatively assigned to photooxidation of the CdSe core [6].

It was found that about 10 % of the luminescent spots show spectra of both constituents, QD and dye. Typical example is shown in Fig. 3, C. In general, the time dependent spectral features are quite similar to those shown separately for the QD and the

dye in Fig. 3, A, B, besides the enhanced blinking of DTPP. A closer inspection, however, reveals that the respective luminescence intensities are strongly (positively) correlated, as can be directly seen, when plotting the corresponding intensities on top of each other as shown at the bottom of Fig. 3, C. It is evidently seen that the strong blinking of QDs is imposed on DTPP, which now blinks very often synchronously with the QD. In addition, when DTPP is photobleached (at 77 s) the QD PL increases on average by about a factor of 3. The overall interpretation is that the QD PL is quenched due to FRET CdSe/ZnS-AM QDs $\rightarrow$ DTPP and, correspondingly, DTPP fluorescence is predominantly caused via FRET.

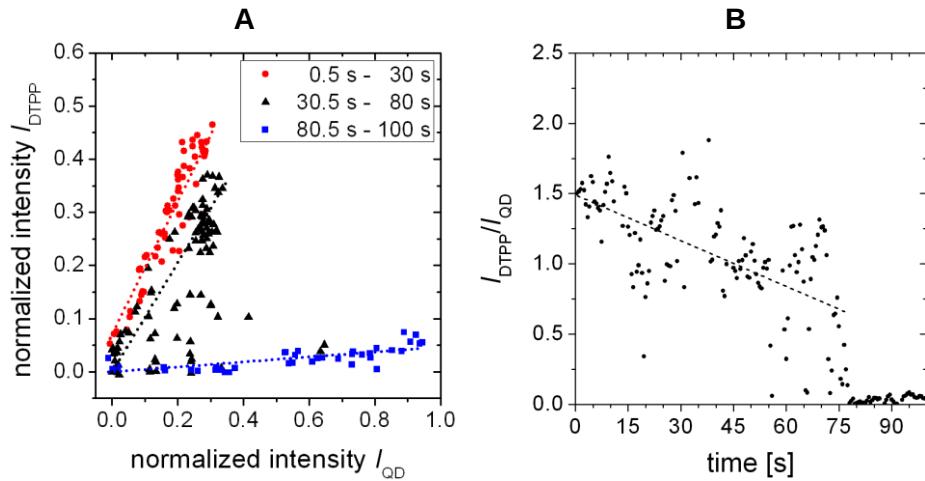


Fig. 3: **A:** Correlation of normalized DTPP and CdSe/ZnS-AM QD emission intensities for selected time ranges related to the time traces for QD-DTPP single nanoassembly A. Intensities have been normalized to the respective maximum of each time trace for each constituent. **B:** Luminescence intensity ratios as a function of observation time

For a single QD-DTPP nanoassembly, the FRET efficiency can be calculated using quenching data for the donor (QD) PL intensity I_{QD} according to following equation [7]:

$$\Phi_{FRET} = 1 - \frac{I_{QD-DTPP}}{I_{QD}}. \quad (1)$$

It is found from Fig. 2, A that DTPP molecule is photobleached for times longer than 77 s. Thus, taking the maximal PL intensity I_{QD} in that range and the maximum of the intensity $I_{QD-DTPP}$ for a QD-DTPP nanoassembly within the time when DTPP is not photobleached (Fig. 2, C, bottom), one can estimate the FRET efficiency to be $\Phi_{FRET} \approx 0.69$ (according to Eq. (1)). This result can be compared to the situation at 57 s and 72 s when DTPP is “off” due to blinking providing I_{QD} and compare it to $I_{QD-DTPP}$ when DTPP is “on” again. According to Eq. (1) this results in $\Phi_{FRET} \approx 0.55$. Both values are in a reasonable agreement with $\Phi_{FRET} \approx 0.85$ calculated for this donor-acceptor pair within the Foerster model [4] not taken into account the existence of some competing non-FRET quenching processes. Nevertheless, it should be noted that obviously, strong variations of Φ_{FRET} are observed for on one and the same assembly, since QD photoluminescence intensity I_{QD} depends on quenching processes other than FRET.

Taking into account previous results obtained for nanoassemblies based on CdSe/ZnS-AM QD and perylene bisimide molecules of various structure [2], the presented single molecule data reveal that for various QD-Dye nanoassemblies, different relative orientations of dye molecules of this type with respect to the QD surface may be realized, for which the acceptor molecule may have different spectral properties. It means that relative efficiencies of FRET QD→Dye may differ significantly for each nanoassembly depending on the conformation of the dye attached to the QD surface. It is clearly seen that FRET transfer parameters related to different QD-Dye nanoassemblies with different PDI conformations may vary essentially.

On the basis of above results some conclusions may be done: i) a nearly perpendicular geometry for perylene bisimide molecules has to be established, ii) the ligand density close to dye molecule has to be low, iii) the identification of perylene bisimide conformations may be used to confirm the surface geometry which is useful for the analysis of FRET calculations and experimental data, and iv) the comparative analysis of the dye conformations distribution serves as probe for the ligand density and dynamics on single quantum dots. Concluding, single molecule data provide more specific information on the structure of the nanoassemblies based on CdSe/ZnS-AM QD and perylene bisimide molecules of various structure.

Conclusions

The presented results clearly demonstrate that single assembly experiments are an unsurpassed tool to investigate subtle conformational changes and the related impact on interchromophoric dynamics. In fact, due to their intrinsic flexibility, DTPP molecules can realise a large variety of conformations on the experimental time scale of seconds to minutes. For this reason, FRET becomes dependent on observation time, which can be followed quite in detail.

Acknowledgements

This work was funded by BPSR program “Photonics and Electronics for Innovations (2021-2025)” and Visiting Scholar Program of TU Chemnitz, Germany (E.Z., 2020-2021).

References

1. A simple and versatile route to stable quantum dot-dye hybrids in nonaqueous and aqueous solutions / T. Ren [et al.] // *J. Am. Chem. Soc.* 2008. Vol. 130, P. 17242–17243.
2. FRET and ligand related non-FRET processes in single quantum dot-perylene bisimide assemblies / D. Kowanko [et al.] // *Phys. Chem. Chem. Phys.* 2010. Vol. 12, P. 4112–4123.
3. *Zenkevich E., Von Borczyskowski C. Self-assembled organic-inorganic nanostructures: optics and dynamics*: Pan Stanford Publishing Pte. Ltd, 2016. 408 p.
4. *Foerster T. Modern Quantum Chemistry* (ed. Sinanoglu O.): Academic Press, New York, 1965.
5. *Cichos F. Power-law intermittency of single emitters* / F. Cichos, C. von Borczyskowski, M. Orrit // *Current Opinion in Colloid & Interface Science*. 2007. Vol. 12, pp. 272–284.
6. Influence of single dye molecules on temperature and time dependent optical properties of CdSe/ZnS quantum dots: ensemble and single nanoassembly detection / E. I. Zenkevich [et al.] // *Chem. Phys.* 2012. Vol. 406, P. 21–29.
7. *Lakowicz J. Principles of Fluorescence Spectroscopy*: Springer, New York, 2006.