

Identification and assignment of porphyrin–CdSe hetero-nanoassemblies

E.I. Zenkevich^a, T. Blaudeck^b, A.M. Shulga^a, F. Cichos^{b,d}, C. von Borczyskowski^{c,d,*}

^aNational Academy of Science, F. Skaryna Avenue, 220072 Minsk, Belarus

^bPhotonics and Optical Materials, TU Chemnitz, Germany

^cOptical Spectroscopy and Molecular Physics, TU Chemnitz, Germany

^dCenter for Nanostructured Materials and Analytics (NanoMA), Chemnitz University of Technology, 09107 Chemnitz, Germany

Available online 14 March 2006

Abstract

Hetero-nanoassemblies in toluene solution are formed via anchoring pyridyl substituted free base porphyrin molecules on the colloidal core-shell semiconductor nanocrystals CdSe/ZnS. The formation can be identified via quenching of semiconductor photoluminescence and followed via spectral changes of porphyrin spectral properties such as fluorescence, fluorescence decay and absorption. Interpreting these changes we estimate that even at high molar ratios on average only one molecule is anchored on one nanocrystal. Experimentally determined complexation constants are comparable to those observed for multi-porphyrin complexes.

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Keywords: Quantum dots; Nanoassemblies; Porphyrin; CdSe; Fluorescence; Photoluminescence

1. Introduction

Formation of nanostructures from semiconductors and organic dye molecules results in a class of new materials which will be important for photovoltaic [1] and fluorescence markers in biological or medical applications [2]. Especially, II/VI colloidal semiconductor nanocrystals (NC) are promising candidates since they can be prepared by wet chemistry providing well defined sizes [3] and are thus due to quantum confinement quantum dots (QD) with tuneable colour and redox properties [4]. Several experiments have been reported for such systems [5–7]. In most of these cases, the number of dye molecules per QD is not known (besides see Ref. [7]), since they are in organic solvents in the presence of aliphatic capping molecules formed in a statistical manner (for instance, trioctylphosphine oxide, TOPO, or trioctylphosphine, TOP). To elucidate the formation, identification and stability of such

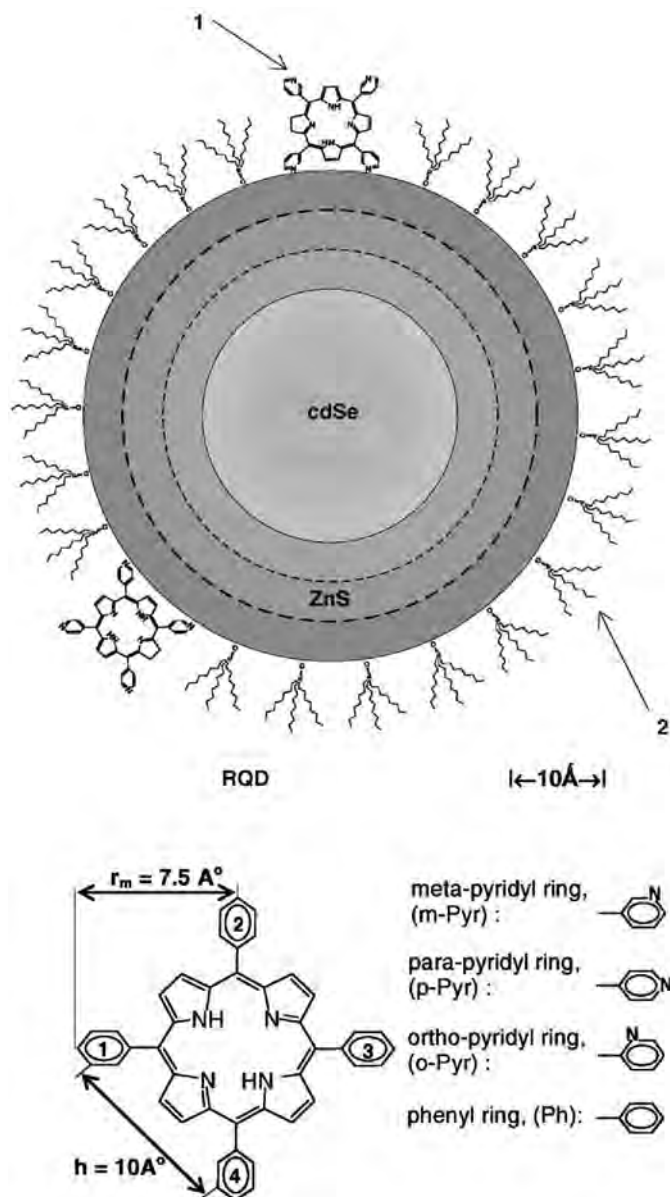
hetero-nanoassemblies we present in this contribution results on the optical spectroscopy of CdSe/ZnS core-shell NC, which can be complexed with porphyrin free-base molecules via substituted pyridyl groups, which make the complexation on the QD surface feasible [8,9]. Experiments have been performed on CdSe/ZnS core-shell NC with two diameters, “yellow” quantum dots, YQD (diameter $d = 2.5$ nm, 2 ZnS monolayers) and “red” quantum dots, RQD ($d = 3.2$ nm, 3 ZnS monolayers) capped with TOPO in toluene solution at room temperature and ambient conditions. Details of the experimental procedure have been reported elsewhere [8].

2. Results and discussion

Recently, we have reported on the influence of various porphyrins on the photoluminescence (PL) of CdSe/ZnS NC [8]. Pyridyl substituted tetraphenyl-free-base molecules $(\text{Pyr})_n\text{H}_2\text{P}$ (see Scheme 1) gave rise to quenching of the CdSe/ZnS PL when titrating a toluene solution containing 5×10^{-7} mol CdSe/ZnS with a comparable amount of $(\text{Pyr})_n\text{H}_2\text{P}$. This has been interpreted as being due to the formation of nanoassemblies via anchoring $(\text{Pyr})_n\text{H}_2\text{P}$ on the ZnS surface. Comparing the influence of the specifically

*Corresponding author. Institute of Physics, Chemnitz University of Technology, Optical Spectroscopy and Molecular Physics, D-09107 Chemnitz, Germany. Tel.: +49 371 531 3035; fax: +49 371 531 3060.

E-mail address: borczyskowski@physik.tu-chemnitz.de (C. von Borczyskowski).



Scheme 1. The Scheme shows on scale (corresponding to the relative sizes of interacting moieties and structural elements) the most probable displacement of anchored porphyrin (m-Pyr)₄H₂P (1) and TOPO (2) molecules on RQD surface (top). The bottom part shows the structures of pyridyl substituted porphyrin free-bases, (Pyr)_nH₂P, with various number (from 1 to 4) of meso-pyridyl rings differing by their relative positions with respect to the porphyrin macrocycle (opposite “–” or adjacent “+”) and to the position (*ortho*-, *meta*-, *para*-) of the pyridyl nitrogen within the pyridyl ring.

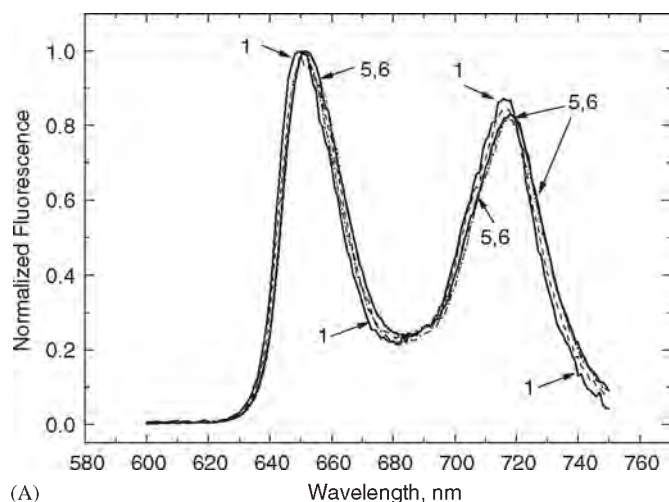
substituted (Pyr)_nH₂P molecules allowed us to rationalise the structure of the nanoassemblies as is also shown in Scheme 1. However, it remained an open question, how many (Pyr)_nH₂P molecules were attached to the surface at a given molar ratio x . Although at sufficient high concentrations in principle several (Pyr)_nH₂P might be attached, one has, however, to consider that the CdSe/ZnS surface has been stabilised by capping TOPO molecules at surface coverage ratios of 25% and larger. This will reduce the probability to decorate independently the CdSe/ZnS

surface with (Pyr)_nH₂P molecules. Moreover, the relative volume ratio of (Pyr)_nH₂P to TOPO is in the order of about 3. This needs (without rearrangement of capping TOPO) at least a free volume corresponding to 3 TOPO molecules to anchor one (Pyr)_nH₂P. As we have shown separately [10] formation of nanoassemblies takes place in a time less than 60s, while (free) TOPO is additionally present in the toluene solution at abundant concentration. At longer waiting times (>15min) the PL quenching further increases [10]. Thus the working hypothesis is, that in a first step free and suitable (not with TOPO covered) surface positions can be occupied by (Pyr)_nH₂P according to a process, which is only controlled by the probability, that a (Pyr)_nH₂P molecule approaches the QD surface with a suitable orientation. The number of pyridyl rings, as has been discussed in detail recently [8], will determine the anchoring probability. The PL quenching process itself might be due to fluorescence resonant energy transfer (FRET), but, as has been outlined recently for YQD and RQD [8], the observed PL quenching and expected (Pyr)_nH₂P fluorescence built-up are experimentally too small to be explained only by this mechanism (though present). We therefore assumed in Ref. [8] that less (Pyr)_nH₂P molecules are attached than predicted from the given molar ratios. Since this assumption could at that time not been proven unambiguously, we have re-examined this question and will report the result in the present contribution.

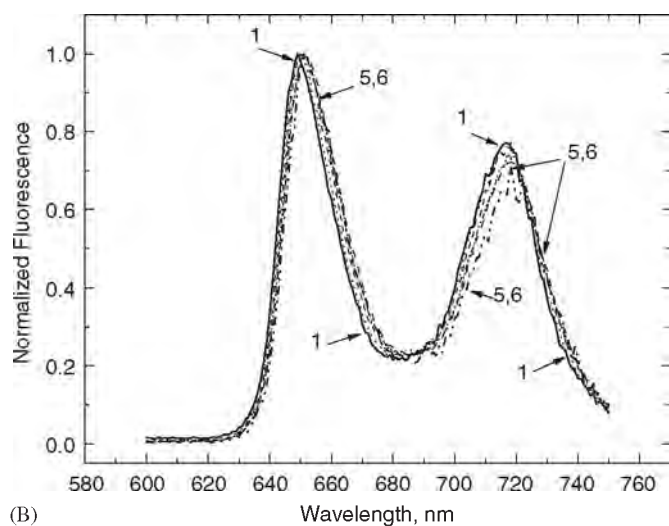
As can be seen in Fig. 1 for two different (Pyr)_nH₂P molecules, the corresponding H₂P fluorescence is shifted to the red as a function of increasing x . Moreover, also line width and Frank–Condon envelopes change. Since this effect is only in the order of a few nm, it is difficult to determine accurately the concentration-dependent spectral shifts, but they approach the spectra of free (Pyr)_nH₂P with increasing x .

Much more precise information can be obtained—as shown in Fig. 2—when inspecting the Soret band absorption of (Pyr)_nH₂P. In this case we observe a spectral blue shift with increasing x . The spectra at above $x = 2$ can be approach to the free Soret band absorption of H₂P in toluene [11]. Changes in the PL spectrum of CdSe/ZnS upon titration are not observed unambiguously. For the origin of the Q-band absorption see (Fig. 2) we could detect only very small spectral (red) shifts. As is additionally shown in Table 1 the (Pyr)_nH₂P fluorescence life times change from a mono-exponential behaviour with $\tau = 11.6 \text{ ns}$ at $x = 1$ to $\tau = 9.5 \text{ ns}$ at molar ratios above $x = 4$. At these concentrations the decay is also mono-exponential and approaches the experimentally observed intrinsic (Pyr)₂H₂P fluorescence lifetime in toluene solutions [11]. In the intermediate range the fluorescence decay is at least bi-exponential.

According to these observations we conclude, that at concentrations well below about $x < 1$ only spectral properties of on the ZnS surface complexed (Pyr)_nH₂P are observed, which implies, that at low concentrations all



(A)



(B)

Fig. 1. Porphyrin fluorescence spectra (normalised to the maximum) in the presence of YQD as a function of the molar ratio x (toluene, 295 K, $\lambda_{exc} = 420$ nm): (A) (m-Pyr)₄H₂P: 1 ($x = 0.52$, $\lambda_{max} = 650$ nm), 2 ($x = 1.03$, $\lambda_{max} = 650$ nm), 3 ($x = 2.04$, $\lambda_{max} = 651$ nm), 4 ($x = 4.02$, $\lambda_{max} = 651$ nm), 5 ($x = 7.5$, $\lambda_{max} = 652$ nm), 6 (m-Pyr)₄H₂P ($x = 0$), $\lambda_{max} = 651$ nm). (B) (m-Pyr)₂H₂P: 1 ($x = 0.55$, $\lambda_{max} = 649$ nm), 2 ($x = 1.09$, $\lambda_{max} = 650$ nm), 3 ($x = 2.16$, $\lambda_{max} = 650$ nm), 4 ($x = 4.25$, $\lambda_{max} = 651$ nm), 5 ($x = 8.30$, $\lambda_{max} = 651$ nm), 6 (m-Pyr)₂H₂P ($x = 0$), $\lambda_{max} = 651$ nm).

those (Pyr) _{n} H₂P with at least 4 pyridyl rings are attached to the CdSe/ZnS surface. (Four pyridyl groups provide the highest probability to anchor a (Pyr)₂H₂P molecule with two of the pyridyl rings on the surface thus providing the strongest complexation [8].)

The increase of fluorescence attributed to “free” (Pyr) _{n} H₂P at $x > 1$ indicates, that about only one accessible “free volume” is on average available in order to attach a (Pyr)₂H₂P molecule on one CdSe/ZnS NC. However, we like to emphasize that at long waiting times after the initial titration step PL quenching is further increased [10], as it also does, when depleting the toluene solution from TOPO. This might in principle indicate an increase of (Pyr) _{n} H₂P on the surface but see the discussion at the end.

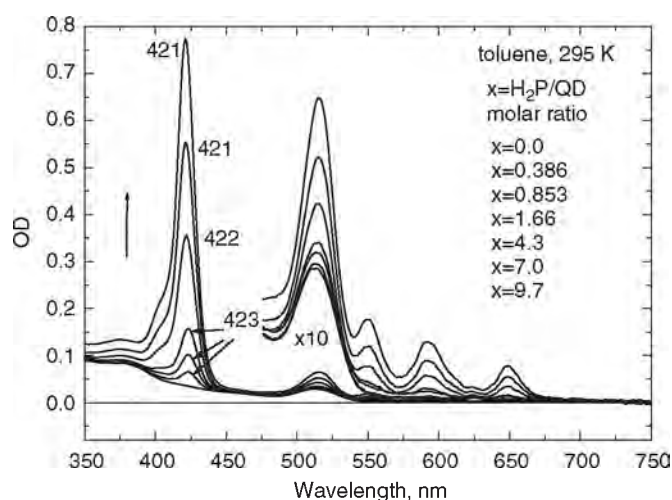


Fig. 2. Absorption spectra of YQD and (m-Pyr)₃H₂P as a function of the molar ratio x . The arrow close to the Soret band shows the increase of absorption with increasing x . Wavelengths are indicated to mark the Soret band shift with molar ratio x .

Table 1
(Pyr)₄H₂P fluorescence lifetime τ as a function of molar ratio x in toluene at 295 K

QD	X	τ /ns
RQD	1	~10
	4	~8
	SO ^a	
SO ^a	1.0	11.6
	2.0	10.5
	4	9.5
	7.0	7.8
	9.7	7.8

^aCdSe QD “SO” is a quantum dot “Snapdragon Orange” ($d = 3.74$ nm) from Evident Technologies, USA.

The observed changes in the (Pyr) _{n} H₂P fluorescence and absorption properties can be discussed as follows. The increase of fluorescence lifetime upon complexation indicates a decrease of non-radiative components which might be rationalised by a more rigid environment surface fixation and partly ordered TOPO shells, as has been argued for some similar systems recently [12]. Further on, since spectral shifts are opposite for Soret band absorption and Q-band emission, these two states are less separated in energy in complexed molecules as with respect to free (Pyr) _{n} H₂P. Since we could not detect a noticeable shift in Q-band absorption, this implies, that the Stokes shift usually observed for H₂P is reduced, making this optically forbidden state more allowed. This points towards a reduction of (Pyr) _{n} H₂P symmetry upon complexation onto the surface which is also supported by the change in the Soret band structure. The observed red shift of the Soret band absorption upon complexation indicates either an extension of the π -electron system into the pyridyl rings attached to the surface or a change in the dielectric

Table 2
Equilibrium constant K_c^a for a $C_{\text{QD}} = 5 \times 10^{-7}$ molar solution of YQD as a function of various $(\text{Pyr})_n\text{H}_2\text{P}$ molecules in toluene at 295 K

H_2P molecule ^b	$K_c C_{\text{QD}}$
(m-Pyr) ₄	1.32
(m-Pyr) ₃	0.39
(m \wedge Pyr) ₂	0.17
(m-Pyr) ₁	0.07
(m \wedge Pyr) ₂ ^c	5.0
(p \wedge Pyr) ₂ ^d	24
(Pyr) ^e	0.005

^aDetermined at $x = 1$.

^bSee Scheme 1.

^cFor comparison: complexation of Zinc-tetraphenylporphyrin dimer (ZnPD) with (m \wedge Pyr)₂ H₂P [11].

^dFor comparison: complexation of ZnPD with (p \wedge Pyr)₂ H₂P [11].

^eFor comparison: complexation of ZnPD with pyridine [11].

environment, since NC have a considerably larger dielectric constant as compared to the toluene solvent and TOPO.

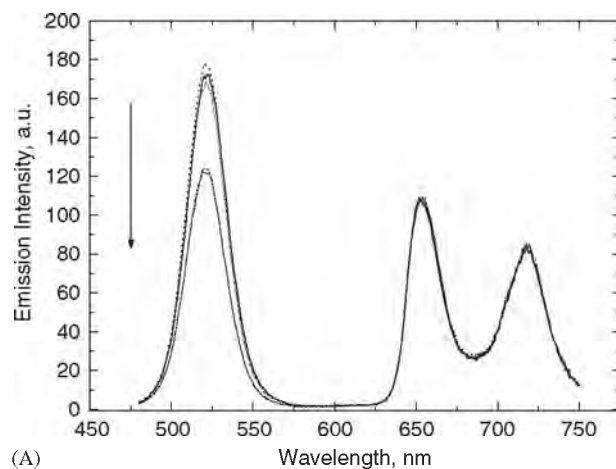
Since the well defined PL quenching effects occur at molar ratios $x < 1$, we can neglect -following statistical arguments—at low concentrations nanoassemblies with more than one $(\text{Pyr})_n\text{H}_2\text{P}$ per QD. We thus can discuss the experimental data using a bi-molecular reaction scheme valid for a dynamic equilibrium between complexed and free constituents as has been applied in many previously reported experiments on the formation of multi-porphyrin assemblies [11]. In this situation the following equation holds for the complexation constant K_c :

$$K_c = \frac{1 - I/I_0}{C_{\text{NC}}I/I_0(x - 1 + I/I_0)}, \quad (1)$$

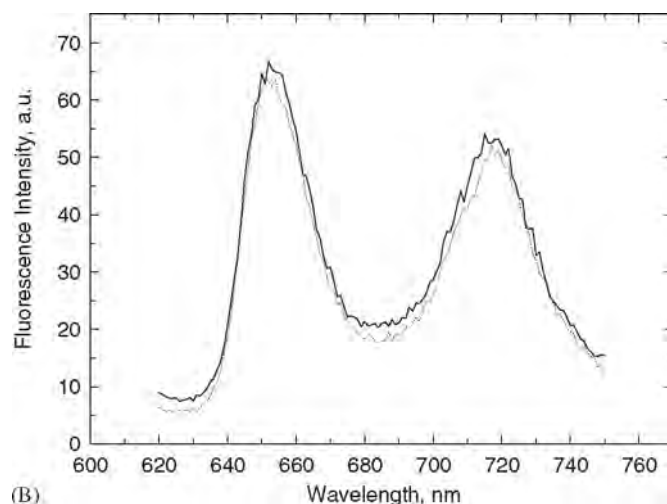
where I/I_0 corresponds to the CdSe/ZnS PL ratio as a function of the molar concentration ratios x and $x = 0$, respectively, and C_{NC} to the initial CdSe/ZnS concentration. Evaluating I/I_0 as a function of x results in an equilibrium constant K_c for the given concentration of CdSe/ZnS of $C_{\text{NC}} = 5 \times 10^{-7}$ M. K_c values for various $(\text{Pyr})_n\text{H}_2\text{P}$ molecules are given in Table 2.

The results clearly show a dependence of K_c on the number of pyridyl rings as it is expected for a dynamic equilibrium. Comparing absolute values with those obtained for various multi-porphyrin complexes [11] shows that they are in a comparable range as with respect to two-fold multi-porphyrin coordination but that they are much larger as compared to one-fold coordination. With respect to the number n of pyridyl rings K_c increases with n , but less dramatic as compared when comparing two- or one-fold multi-porphyrin coordination [11]. This comparison excludes allosteric effects in the present case, which played a dominant role in multi-porphyrin complexes [11].

An interesting observation is made when inspecting as a function of time $(\text{Pyr})_n\text{H}_2\text{P}$ spectra at molar ratios of about $x = 11$. As has been reported recently [10] CdSe/ZnS PL is in the presence of $(\text{Pyr})_n\text{H}_2\text{P}$ continuously decreasing as a



(A)



(B)

Fig. 3. (A) CdSe/ZnS photoluminescence and $(\text{m-Pyr})_4\text{H}_2\text{P}$ fluorescence spectra as a function of waiting time in the dark after the initial titration step with $x = 11$. The shortest waiting time is 15 min, the longest one 3.5 h. During this time CdSe/ZnS PL has decreased from the intensity after the initial titration by about additional 30%. The arrow points towards increasing waiting time. (B) Normalised $(\text{m-Pyr})_4\text{H}_2\text{P}$ fluorescence spectra as a function of waiting time in the dark after the initial titration step with $x = 11$. The full line corresponds to 15 min and the dotted line to 3.5 h waiting time.

function of waiting time after the first initial titration step. This decrease amounts in the example of $(\text{Pyr})_n\text{H}_2\text{P}$ fluorescence shown in Fig. 3 to about a 30% decrease. However, corresponding (“free”) $(\text{Pyr})_2\text{H}_2\text{P}$ fluorescence does hardly show any spectral shifts which implies, that the amount of complexed $(\text{Pyr})_n\text{H}_2\text{P}$ is not increased and stays at the initial ratio of nearly one $(\text{Pyr})_n\text{H}_2\text{P}$ per NC, that is all $(\text{Pyr})_n\text{H}_2\text{P}$ are already attached to the surface shortly after the initial titration step. Correcting for the remaining CdSe/ZnS PL in the spectral range of $(\text{Pyr})_n\text{H}_2\text{P}$, even the corresponding $(\text{Pyr})_n\text{H}_2\text{P}$ fluorescence intensity remains nearly constant. If, however, more $(\text{Pyr})_n\text{H}_2\text{P}$ would be attached to the NC during the waiting time this should result in an increased PL quenching (vide infra), but should also be accompanied by a blue shift of the “complex” $(\text{Pyr})_n\text{H}_2\text{P}$ fluorescence (more complexes). This is obviously

not the case which supports the previous arguments [10] that PL quenching is only partly due to FRET. Additionally, if FRET would be the only quenching mechanism, $(\text{Pyr})_n\text{H}_2\text{P}$ fluorescence should further increase while PL is decreasing during the waiting time. Increase of quenching following a waiting time (in the dark) is thus probably due to the increase of other but still $(\text{Pyr})_n\text{H}_2\text{P}$ induced quenching processes, which most likely resembles a $(\text{Pyr})_n\text{H}_2\text{P}$ induced surface reorganisation thereby inducing new or more efficient surface traps.

3. Conclusions

In this publication, we have shown that nanoassemblies of CdSe/ZnS and suitable porphyrin dye molecules $(\text{Pyr})_n\text{H}_2\text{P}$ are formed at about a 1:1 ratio at low molar ratios x . There is strong evidence that there is only a rather limited number of accessible complexation sites present at least at the beginning of the experiment (namely in the order of one). This allows for an estimation of the complexation constant K_c , which depends in a nearly statistical manner on the number of pyridyl rings. The initially formed nanoassemblies are only metastable and rearrange on time scales longer than 15 min which results in additional PL quenching. However, though PL quenching is increased on this time scale this does not correspond to an increase of the number of complexed $(\text{Pyr})_n\text{H}_2\text{P}$ molecules but more likely to an interface rearrangement induced by $(\text{Pyr})_n\text{H}_2\text{P}$ creating new (or more effective) quenching surface or defect states. Thus dye molecules serve at the same time as initiators and monitors for QD interface dynamics, which will be studied in detail by future single molecule/single particle experiments. Changes observed in the optical spectra of $(\text{Pyr})_n\text{H}_2\text{P}$ can be tentatively interpreted as being due to a more rigid environment upon surface complexation. Further experiments such as Raman spectroscopy will give more precise identification of the corresponding molecular structures.

Acknowledgements

CdSe/ZnS QDs have been obtained from Dr. A. Rogach (Ludwig-Maximilians-University Munich, Germany) and

Dr. D. Talapin (Hamburg University, Germany), which is gratefully acknowledged. Financial support has been provided by the VW foundation within the research program “Physics, Chemistry and Biology with Single Molecules” and the DFG-Graduate College 829 (T. Blaudeck), INTAS Grant No. 03-50-4540 “Optical active assemblies of colloid QD and tetrapyrrole compounds”, and Belarus National Program for Basic and Oriented Research (Spectr 06, Nanotechnology 5.317) and the National Foundation for Basic Research of Belarus, Grant No. Ph05MS-036 (E. Zenkevich and A. Shulga).

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