Hybrid organic-inorganic nanostructures combining semiconductor quantum dots and J-aggregates

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Abstract

We report on optical properties of a novel type of hybrid nanostructures that combine CdTe colloidal quantum dots (QDs) with organic dye molecules (1,1′-Diethyl-2,2′-cyanine iodide (PIC)) in J-aggregate state. CdTe quantum dots capped with thioglycolic acid (thus, carrying a negative charge) were synthesized in aqueous medium as described elsewhere [1]. Aqueous colloidal solution of QDs with photo-luminescence (PL) maximum at 539 nm (Fig. 1a) and PL quantum efficiency of 17% at room temperature were used in experiments. In order to develop an efficient hybrid material we carefully selected emission properties of the QDs to be optically coupled to the dye absorption. Selected CdTe QDs emit light in the spectral region of maximum of PIC absorption, providing the best conditions for Förster resonant energy transfer (FRET). Immediately upon injection of 0.43µM solution of CdTe QDs into 31.2µM of PIC aqueous solution, we have observed the formation of well pronounced J-band in the absorption spectra of hybrid nano-system centered at 578 nm (Fig. 1b).

Band deconvolution analysis of the absorption spectra yields 8 nm as fwhm value of the J-band, whereas corresponding value for the absorption peak of the monomer (centred at 523 nm) is 36 nm. With these values we were able to estimate the number of aggregated dye molecules across which the exciton is delocalized [2] to be N_c=20.

Direct evidence of FRET can be seen in Fig. 2a where PL spectra of non-aggregated and J-aggregated PIC/QDs (curves 1 and 2, respectively) are shown. These spectra were recorded when excited with λ=400 nm, which is the wavelength of minimum in PIC absorption (Fig. 1b). Almost complete quenching of QDs emission and appearance of prononced PL band (15 nm fwhm) at the wavelengths of J-aggregates are key signatures of FRET. It is noteworthy that the estimated value of Stokes shift is less then 1 nm (3.7 meV) indicating high degree of order in formed J-aggregates. Changes in the CdTe QDs PL lifetime as a result of FRET were monitored by time-resolved PL measurements recorded in spectral region of the QDs PL (Fig.2b). Strong shortening of PL lifetime upon conjugation with J-aggregates is another signature of FRET.

Measured PL decays were reconvoluted using non-linear least squares method according to equation:

$$I(t) = \Sigma\alpha_i \exp(-t/\tau_i), \tag{1}$$

where τ_i are the PL decay times (Fig.2b). The pre-exponential factors α_i, were taken into account by normalisation of the initial point in the decay to unity. The average lifetimes were calculated as follows:

$$\tau_{av}= \Sigma\alpha_i\tau i/\Sigma\alpha_i. \tag{2}$$

The FRET efficiency (η) and corresponding rate of energy (Γ) transfer can be estimated by the following equation:

$$\eta = 1 - \tau_{DA}/\tau_D = \Gamma/(1/\tau_D + \Gamma), \tag{3}$$

where τ_{DA} and τ_D are the donor PL lifetimes in the presence and absence of the acceptor.

Table 1. Parameters obtained from the fitting of PL decay curves.

	τ_1 (ns)	α_1	τ_2 (ns)	α_2	τ_3 (ns)	α_3	τ_{av} (ns)
QDs	2.997	0.407	16.664	0.593	-	-	11.1
QDs/PIC	0.171	0.857	1.166	0.089	14.905	0.054	1.05

Using averaged PL lifetimes, obtained from the fitting of the multi-exponential decays to measured data (Table 1), we find that the FRET efficiency is 91% and correspondingly, that the FRET rate is at least 91 times faster than the QDs average PL lifetime.

In conclusion, we used CdTe QDs as templates for aggregation of cyanine dye to J-aggregate state in aqueous solution at room temperature. We also demonstrated highly efficient and extremely fast excitation energy transfer from QDs to J-aggregates.

References

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Figures

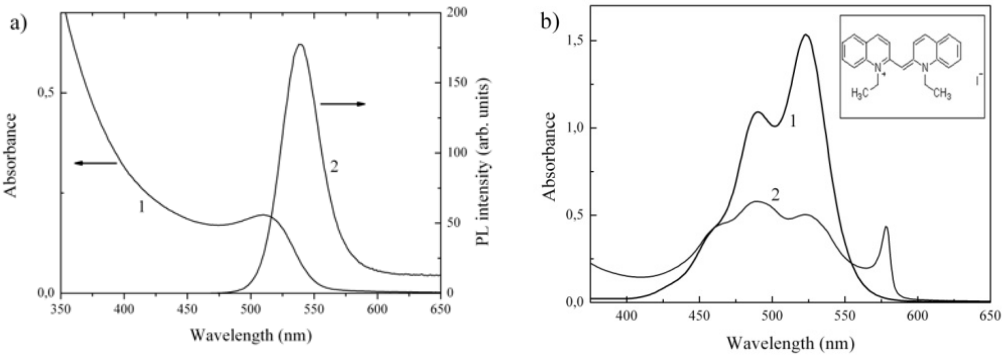

Figure 1. a) Absorption (1) and PL spectra of CdTe QDs, b) Absorption spectra of PIC (1) and PIC aggregated in the presence of QDs (2). Insert shows the molecular structure of PIC.

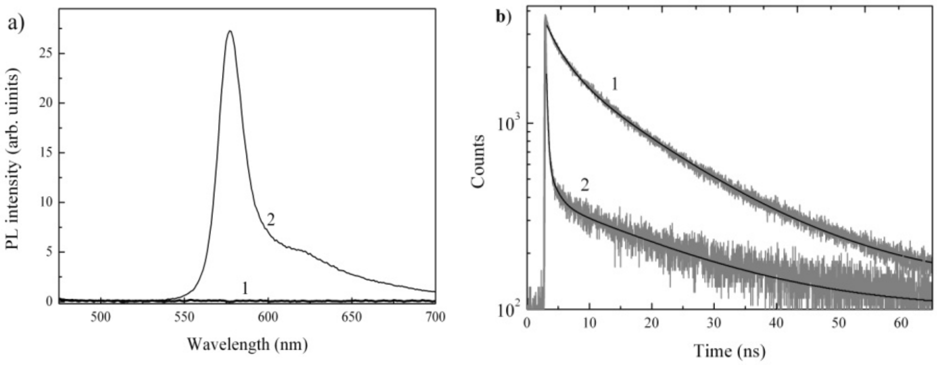

Figure 2. a) PL spectra recorded using excitation at 400 nm. 1 – without QDs, 2 – after injection of QDs, b) Comparison of PL decays for the QDs (1) and QDs injected in PIC (2). Results of multi-exponential analysis of decay curves are shown by thick lines.