

CdSe/ZnS Quantum Dots in Solutions with Diarylethenes Showing Photoinduced Fluorescence Modulation

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Introduction

Photochromic compounds, reversibly changing their spectral properties under light irradiation, are attractive compounds that have great potential for development of devices for molecular electronics and photonics, and can be used as various types of photoswitches.

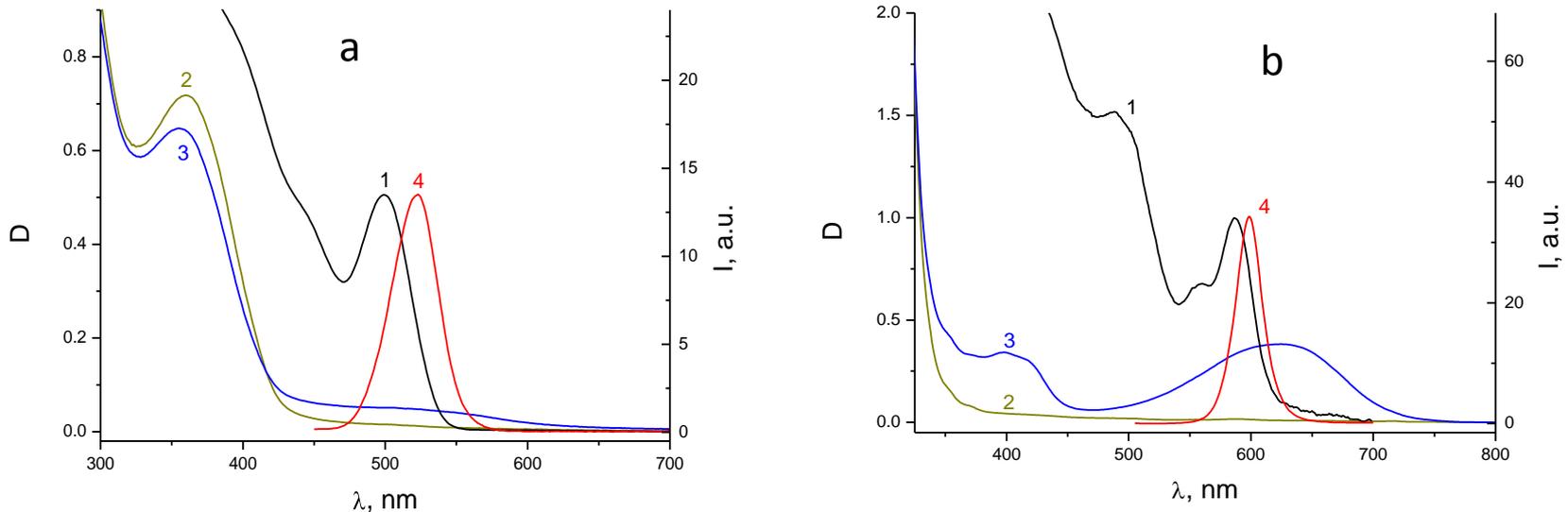
Reversible photoconversions of a photochromic group within bichromophoric molecular systems or complexes containing a fluorophore and the photochromic compound, can lead to fluorescence intensity modulation via 1) alteration of emission quantum yield of the fluorophore as a result of Förster resonance energy transfer (FRET) to the photochromic molecule or 2) due to reabsorption of fluorescence by the photochromic compound (inner filter effect).

In this work we studied toluene solutions of two types of CdSe/ZnS QDs in presence of diarylethenes (DAE), with photoswitchable absorption bands having good overlap with QD fluorescence spectra.

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Spectra QD and DAE

The experimental data show good overlap for the absorption spectrum of the cyclic form B of compound DAE1 with QD525 fluorescence spectrum, and for the absorption spectrum of the cyclic form DAE2(B) with QD600 emission spectrum. Thus, there are two donor-acceptor pairs QD525-DAE1 and QD600-DAE2, which are convenient spectrally for observation of an efficient FRET. Initially, the DAE molecules are in the open form A (lacking absorption band in the range of 450–650 nm) and QDs fluorescence is not expected to be quenched by FRET. UV irradiation of the solution results in formation of the cyclic form B of DAE molecules and probability of quenching of QDs fluorescence by DAE(B) appears, depending on distance between the donor and acceptor.

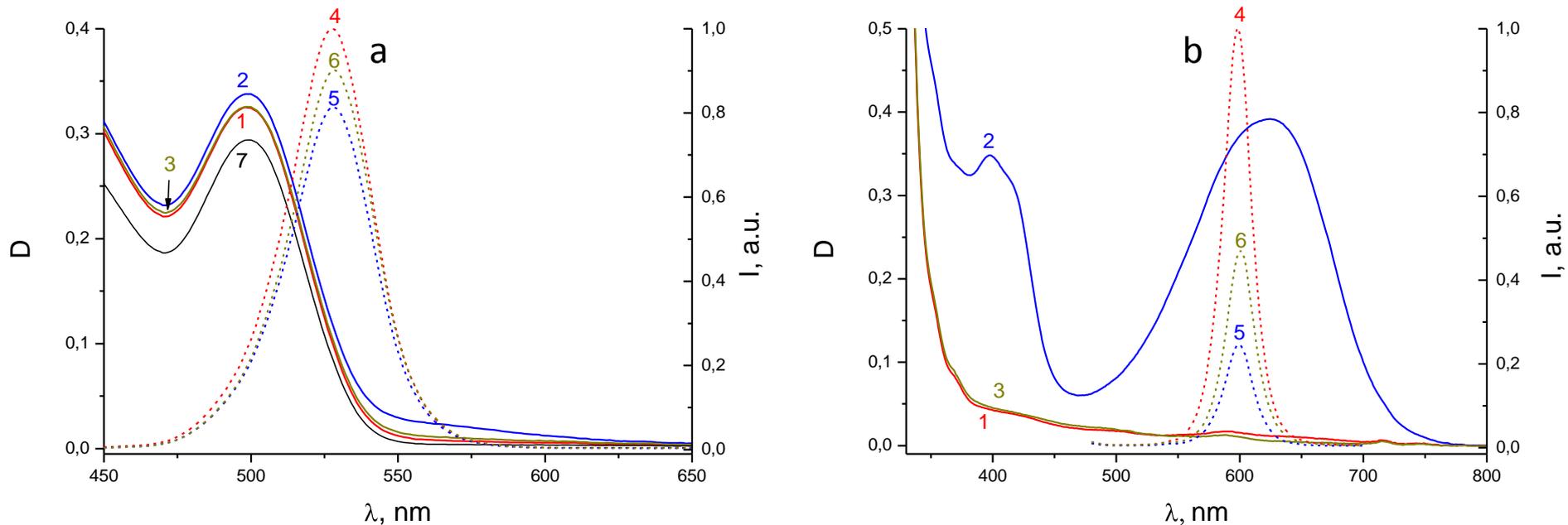


Absorption spectra of QD(1), DAE in the open A (2) and cyclic B (3) forms, and QD fluorescence spectra (4) in toluene for donor-acceptor pairs DAE1-QD525 (a) and DAE2-QD600 (b)

Based on the spectral data, values of Förster critical radii were calculated to be equal to $R_{10} = 4,65$ nm (for QD525-DAE1(B) pair) and $R_{20} = 4,85$ nm (for QD600-DAE2(B) pair).

Spectra of QD+DAE complexes

Fluorescence intensity of QDs decreases after UV irradiation, leading to formation of DAE molecule in the cyclic colored form B. The subsequent irradiation with visible light, which restores the colorless open form A of DAE, leads to an increase in fluorescence intensity of QDs. The observed modulation of QD emission can be explained both by the inner filter effect (reabsorption of QD fluorescence by photochrome in form B) and by a change in the quantum yield of QD fluorescence due to FRET from QD to DAE(B).

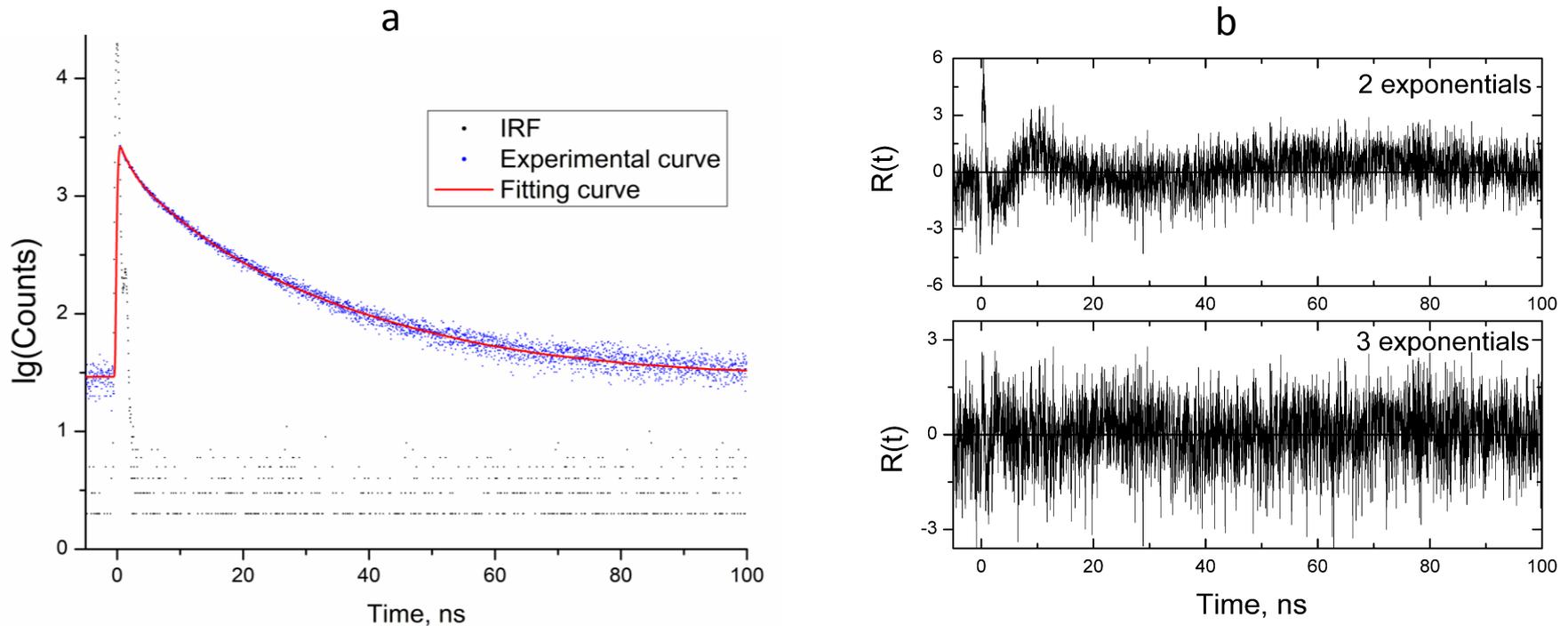


Absorption (1, 2, 3) and fluorescence spectra (4, 5, 6) of QD and DAE mixture in toluene before (1, 4) and after UV radiation (365 nm) during time t_1 (2, 5), subsequent irradiation by visible light with wavelength λ_v during time t_2 (3, 6). Absorption spectrum of QD at the same concentration (without DAE) is shown by curve 7. a Ratio DAE1: QD525 = 10: 1 ($\lambda_v = 514$ nm, $t_1 = 200$ s, $t_2 = 45$ s), b Ratio DAE2: QD600 = 11,000: 1 ($\lambda_v = 627$ nm, $t_1 = 240$ s, $t_2 = 120$ s). c QD525 = 6.1 μ M, C QD600 = 40 nM

Fluorescence kinetics of QD+DAE

To simulate the modulation of fluorescence and the interaction of photochromic DAE molecules with the surface of QDs, the dependence of the mechanism of fluorescence decay of QDs in the initial DAE (A) and photoinduced forms of DAE (B) was studied.

Experimentally measured kinetics of QD emission decay has essentially multiexponential character and, for example, at least 3 exponential components with lifetimes $\tau_1 \sim 1$ ns, $\tau_2 \sim 6$ ns и $\tau_3 \sim 20$ ns are needed to describe fluorescence decay curves for QD525.



Fluorescence decay curve for QD525 in toluene. a – IRF and decay curve are shown with dots, fitting curve – with line. b Plot of weighted residuals $R(t)$ for 2 and 3 exponential fitting

Conclusions

- Photoinduced modulation of QD fluorescence intensity was demonstrated for toluene solutions of photochromic DAE molecules with QDs of two sizes, having fluorescence bands at 525 nm and 600 nm. Change of QD emission intensity was synchronous with the changes in the photoinduced absorption of DAE molecules during their photochromic transformations.
- The observed modulation of fluorescence intensity is mainly associated with fluorescence reabsorption due to the inner filter effect and partially with Forster resonant energy transfer from QD to the photoinduced cyclic form B of DAE molecules. According to our estimations changes in fluorescence intensity related to the reabsorption effect are equal to 4% and 37% for QD525-DAE1 and QD600-DAE2 systems respectively.
- Forster radii for donor-acceptor pairs QD525-DAE1 and QD600-DAE2 were calculated to be 4.65 nm and 4.85 nm correspondingly.
- It was found that fluorescence decay lifetime of QD was sensitive to chemical properties and concentration of DAE in solution. Decrease of fluorescence decay lifetime in presence of DAE was interpreted as evidence of specific interactions of photochromic molecules with QD surface.
- Using emission decay kinetics data the effective dissociation constants were evaluated to be $\sim 40 \mu\text{M}$ for both types of QD-DAE complexes.
- Taking into account different surface areas for QD525 and QD600 (~ 3 times), the higher affinity of DAE1 to QD surface is supposed to be related to presence of chemically active thiol groups in DAE1 molecule.

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