Polymeric Nanospheres Containing CdSe/ZnS Quantum Dots and Photochromic Diarylethene, with Photoswitchable Luminescence

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Introduction

Currently, a new direction of nanotechnology is being formed - nanophotochromism, associated with the development and study of photochromic composite systems, including molecules of photochromic organic compounds (in particular, from the class of diarylethenes) and nanoparticles of noble metals (Ag, Au) or inorganic semiconductors (quantum dots).

Such systems are promising for use as elements of optical integrated circuits, as various types of photo switches, as well as sensors.

In this work, we experimentally developed a new method to produce photoactive nanospheres containing luminescence inorganic CdSe/ZnS quantum dots capped with the amphiphilic polymeric shell, which provides good stability to the nanospheres in aqueous colloidal solutions and the ability to incorporate hydrophobic photochromic diarylethene.

•Feringa, Ed.B.L. Molecular switches / Ed.B.L. Feringa. // Weinheim: Wiley – 2001.

•Klajn, R. Nanoparticles functionalized with reversible molecular and supramolecular switches / R. Klajn, J.F. Stoddart, B.A. Grzybowski // Chem. Soc. Rev. – 2010. –Vol. 39. – P. 2203–2237.

• Scherbovich, A. A. Reversible Photoinduced Luminescence Modulation from Nanospheres Containing CdSe/ZnS Quantum Dots and Photochromic Diarylethene / A. A. Scherbovich [et al.] // The Journal of Physical Chemistry C. – 2020. – Vol. 124. – № 49. – P. 27064–27070.

Research objects

excitation   emission   UV   excitation   FRET   VIS
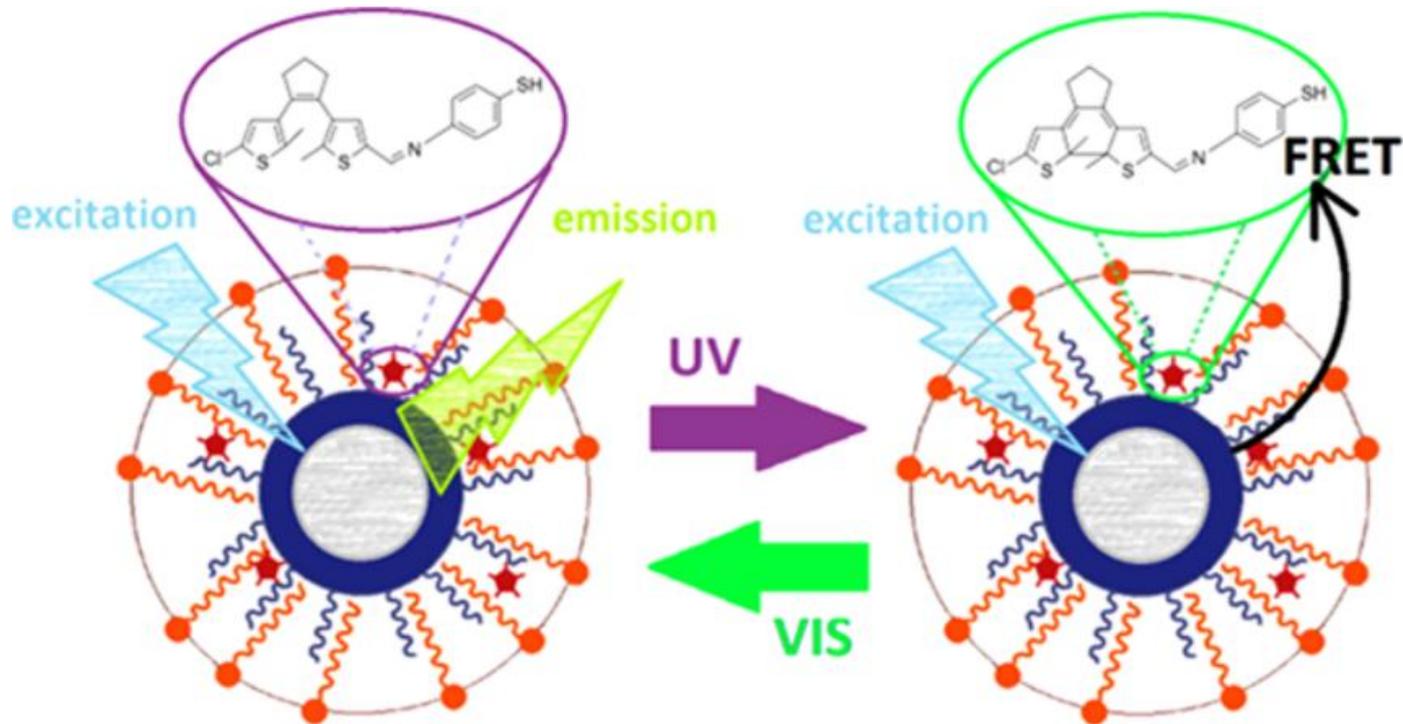
Photoswitchable FRET in synthesized optically active colloidal nanospheres consisting of hydrophobic CdSe/ZnS core-shell quantum dots encapsulated in the amphiphilic PMAT polymeric shell containing photochromic diarylethene DAE1

Spectra of DAE, QD, NS
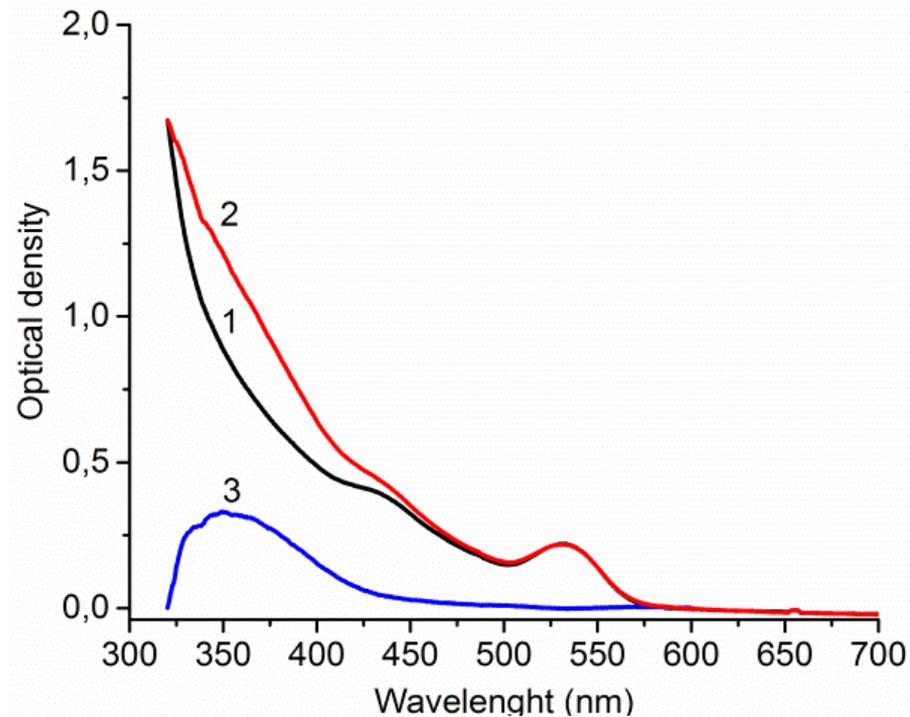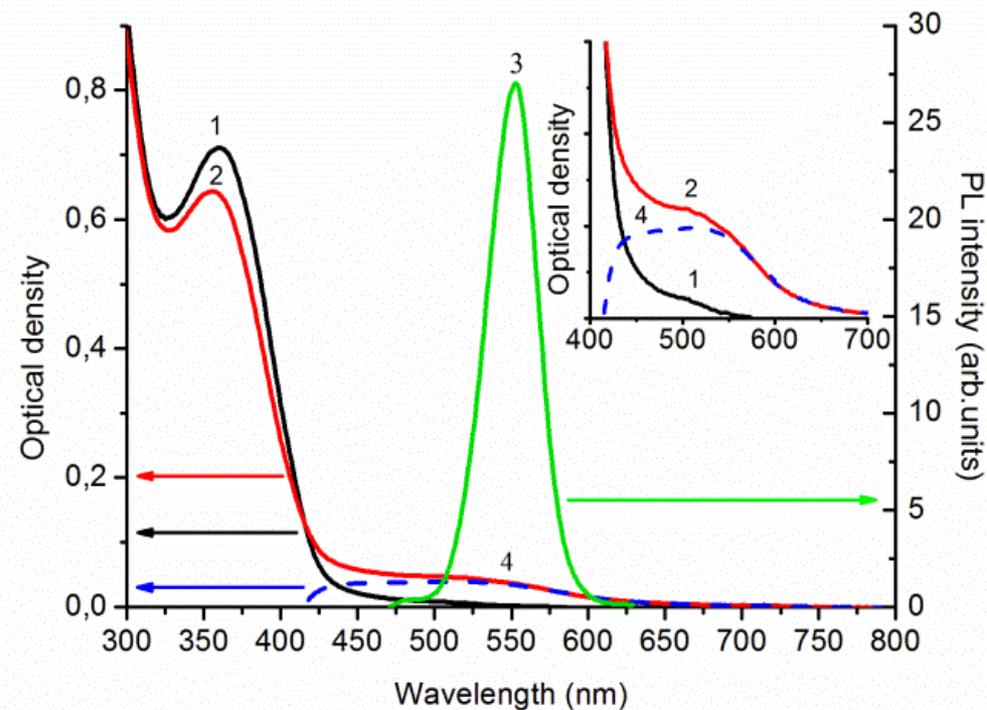
The optical absorption spectra of DAE1 in toluene (the initial open (1) and photoisomerized cyclic (2) forms) together with a representative PL spectrum (3) of encapsulated QDs differential spectrum (4) of curves 2 and 1.

Absorption spectra of aqueous colloidal solutions of NSs without (1) and with DAE1 before photoisomerization (2). Curve 3 – the differential spectrum of 2-1 demonstrating contribution from DAE1 open form

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FRET simulation

Deactivation rate for a single D located at the distance r_1 from single A can be expressed as.

$$\frac{1}{\tau_{DA1}} = \frac{1}{\tau_D} + \frac{1}{\tau_D} \cdot \left(\frac{R_0}{r_1}\right)^6 = \frac{1}{\tau_D} \cdot \left(1 + \left(\frac{R_0}{r_1}\right)^6\right)$$

Presence of more than one A per single D results in additional decrease indecay lifetime and for n molecules of A per single D:

$$\frac{1}{\tau_{DAn}} = \frac{1}{\tau_D} \prod_{i=1}^{n} \left(1 + \left(\frac{R_0}{r_1}\right)^6\right)$$

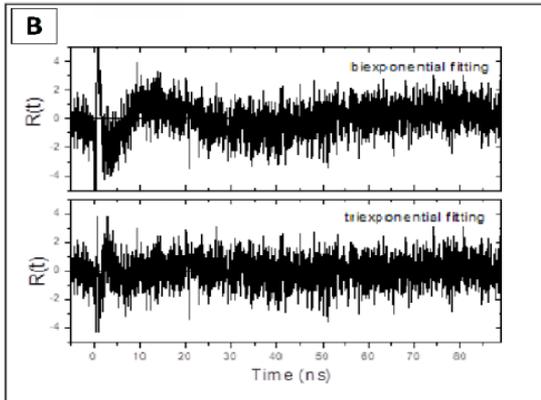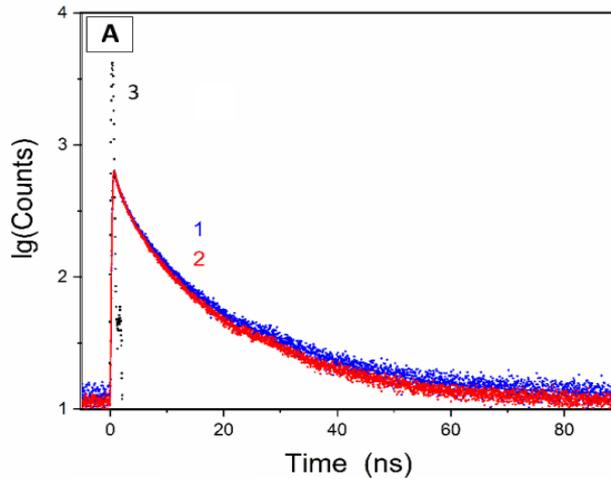Förster radii were calculated in angstroms (Å) according to the eq.:

$$R_0 = 0.211 \left[\kappa^2 n^{-4} Q_D J \lambda\right]^{1/6}$$

where κ^2 – the orientation factor taken as 2/3; n – refractive index; Q_D – PL quantum yield of D in the absence of A, $J(\lambda)$ – overlap integral

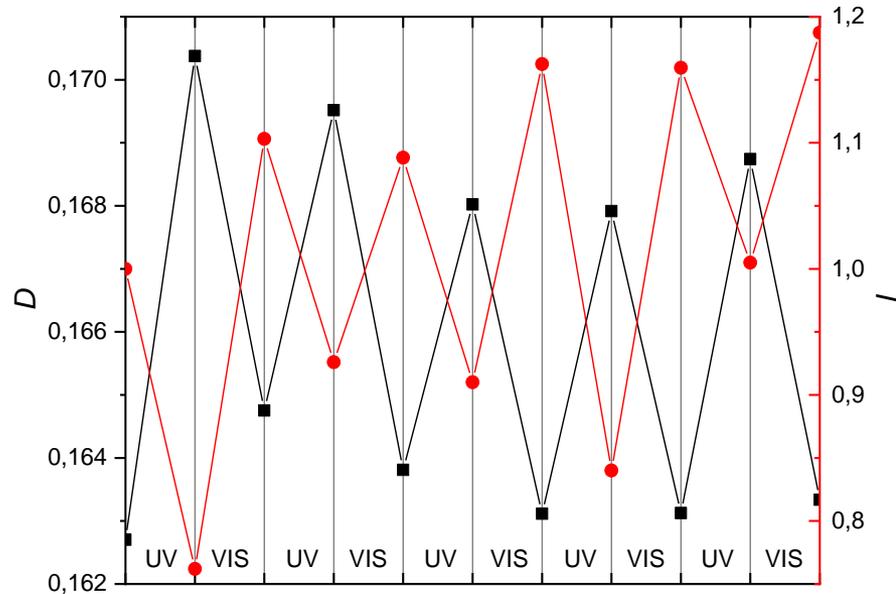$$J(\lambda) = \int_0^\infty F_d(\lambda) \varepsilon_a(\lambda) \lambda^4 d\lambda$$

where $F_d(\lambda)$ – area normalized fluorescence spectrum of the donor; $\varepsilon_a(\lambda)$ – molar extinction coefficient of the acceptor.

Fluorescence kinetics of QD + DAE in nanospheres

α_1	τ_1, ns	S_1, %	α_2	τ_2, ns	S_2, %	α_3	τ_3, ns	S_3, %	$\langle\tau\rangle$, ns	χ^2
before UV irradiation										
0,423	0,74	6,8	0,422	4,61	41,9	0,155	15,39	51,4	9,89	1,12
after UV irradiation										
0,394	0,76	6,7	0,443	4,19	41,9	0,163	13,97	51,4	8,98	1,16
After UV and subsequent Vis irradiation										
0,368	0,92	6,7	0,464	4,70	43,5	0,168	14,80	49,7	9,47	1,07

PL decay parameters for NSs before and after subsequent UV and Vis irradiation. λ_{exc}=467 nm, λ_{em}=525 nm, $S_i \sim \alpha_i\tau_i$ (i=1-3)

PL decay curves for NSs before (1) and after (2) UV irradiation, (3) – instrumental response function). (B) -Plots of weighted residuals R(t) for bi- and triexponential fitting of decay curve 1

Changes in optical density at λ = 557 nm (black) and PL intensity (red) for NSs under cyclic UV (λ = 365 nm, t = 150 s) and VIS (λ = 514 nm, t = 150 s) irradiation

Conclusions

- We prepared for the first time optically active colloidal nanospheres consisting of hydrophobic CdSe/ZnS core-shell quantum dots encapsulated in the amphiphilic PMAT polymeric shell containing photochromic diarylethene DAE1 with stoichiometry ~ 6 dye molecules per single quantum dot. UV-induced cyclic photoisomerization of DAE1molecules results in partial quenching of quantum dot emission due to FRET from the quantum dot to DAE1 photo-isomer with its absorption band spectrally overlapped with quantum dot emission. Modulation of quantum dot emission is reversible under cyclic UV↔VIS induced OPEN↔CLOSED photoisomerization of DAE1.

- We believe that our method is universal and can be applied to a variety of hydrophobic dyes and luminescent nanoparticles, including nanorods, nanoplatelets, etc. Further optimization of our method will include the variation in the hydrophobic bilayer thickness and structure using different surface ligands (aliphatic and aromatic thiols) and chemical modifications of the amphiphilic polymer to increase the amount of incorporated photochromic molecules and adjust their average distance to the surface of the emitting core.

- Likewise, such aqueous colloidal nanospheres having photocontrollable emission properties can be integrated into large-area thin transparent polymeric films suitable for practical applications as rewritable luminescence panels, optically addressable fluorescence markers, etc.