Photoinduced modulation of emission of CdSe/ZnS quantum dots with photochromic diarylethenes in solid-state films

G. T. Vasilyuk[1*], P. V. Karpach[1], A. A. Scherbovich[2], V. I. Stsiapura[1], A. A. Maskevich[1], M. V. Artemyev[3], A. O. Ayt[4], V. A. Barachevsky[4], S. A. Maskevich[2]

1 – Yanka Kupala State University of Grodno, Grodno, Belarus

2 – Belarusian State University, ISEI BSU, Minsk, Belarus

3 – Research Institute for Physical Chemical Problems of the Belarusian State University, Minsk, Belarus

4 – Photochemistry Center, Federal Scientific Research Centre "Crystallography and Photonics", RAS, Moscow, Russia

** vasilyuk@grsu.by*

Introduction

Currently, the area of molecular electronics and photonics is actively developing, associated with the development and study of devices that are promising for use in photocontrolled switches, memory elements and multifunctional displays.

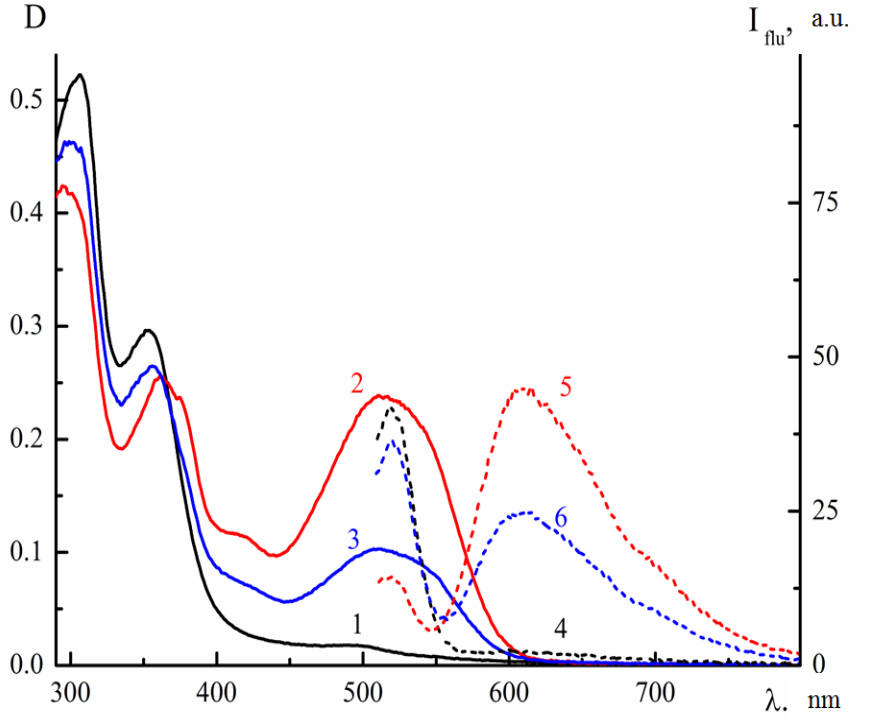
Photocontrol of them is often based on the effect of photochromism.

It is important for practical applications to study the properties of such objects in the solid state - in amorphous solid-phase films or in polymer films (matrices).

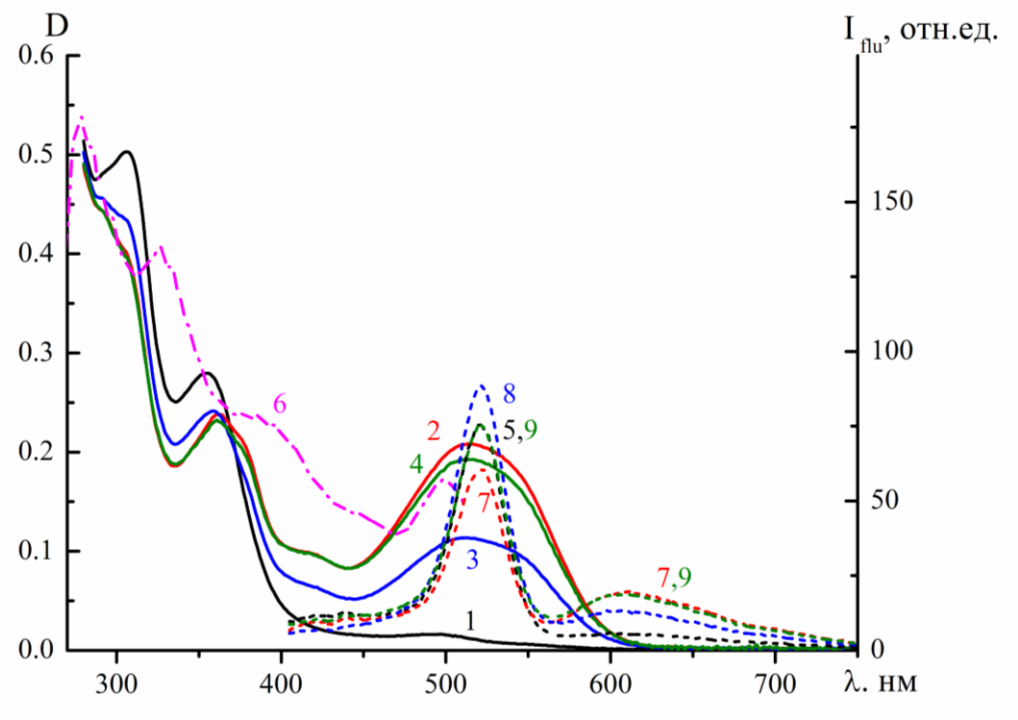
In this work we studied solid-state photoswitchable systems containing CdSe/ZnS quantum dots (QDs) in presence of photochromic diarylethenes (DAE), with photoswitchable absorption bands having good overlap with QD fluorescence spectra.

- 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.
- Barachevsky, V.A. Optical polymer materials with photocontrolled fluorescence / V.A. Barachevsky [et al.] // Opt. Mater. – 2013. – Vol. 35. – P. 1805–1809.

Spectra of QD + DAE in polymeric films

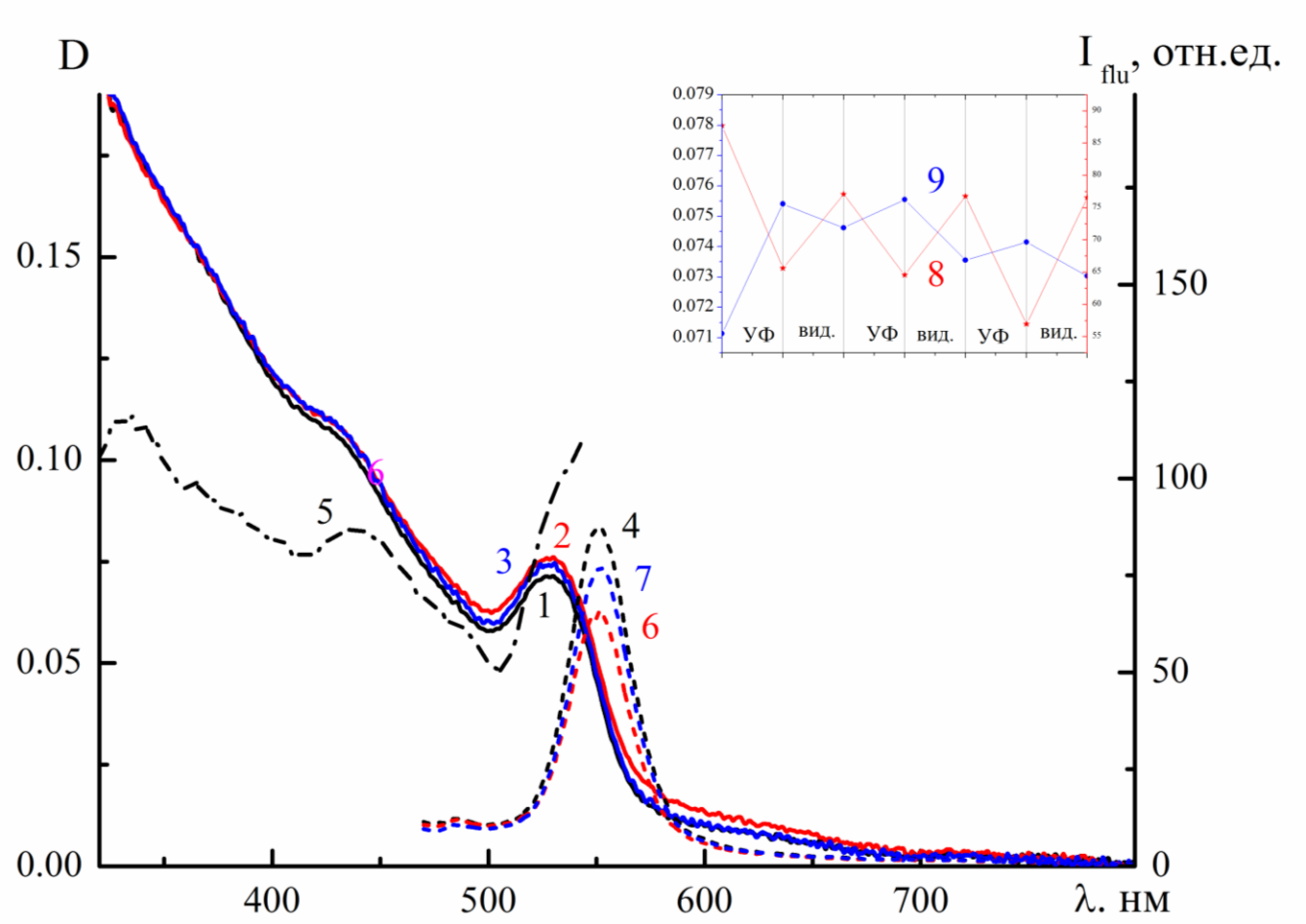


Absorption (1-3) and fluorescence (4-6) spectra at an excitation wavelength of 500 nm of the SH1402/QD in 10% AC polymer composition on quartz glass before (1,4), after UV irradiation (2,5) and visible (3,6) light



Spectra of absorption (1-4), fluorescence excitation in the registration at the wavelength 516 nm (6) and fluorescence at an excitation wavelength of 395 nm (5,7-9) of SH1402/QD in 10% PMMA polymer composition on quartz glass before (1,5,6), after UV irradiation (2, 7) and visible (3,8) light and after repeated UV irradiation (4,9)

Spectra of nanospheres QD + DAE containing (in polymeric films)



Spectra of absorption (1-3), fluorescence excitation in the registration at the wavelength 553 nm (5) and fluorescence at an excitation wavelength of 440 nm (4,6-7) polymeric films from a solution of N3 nanospheres in water before (1,4,5), after UV irradiation (2, 6) and visible (3,7) light

Fluorescence kinetics of QD+DAE (in polymeric films)

BL	a_1	t_1, ns	S_1, %	a_2	t_2, ns	S_2, %	a_3	t_3, ns	S_3, %	Real Mean Tau <t>, ns	Amplitude Averaged Tau t, ns	χ^2
Bl3 before irradiation	0,460 +/- 0,009	3,82 +/- 0,07	21,7	0,485 +/- 0,009	10,00 +/- 0,11	59,9	0,055 +/- 0,003	27,22 +/- 0,63	18,4	11,84 +/- 0,35	8,10	1,06
Bl4 45 s after UV irradiation	0,436 +/- 0,007	2,13 +/- 0,05	14,0	0,489 +/- 0,007	7,79 +/- 0,09	57,5	0,075 +/- 0,003	25,22 +/- 0,42	28,5	11,96 +/- 0,29	6,63	1,10
Bl6 30 s after visible (514nm) light	0,399 +/- 0,010	4,44 +/- 0,08	20,1	0,515 +/- 0,010	9,65 +/- 0,10	56,4	0,086 +/- 0,003	23,98 +/- 0,37	23,5	11,96 +/- 0,23	8,80	1,09

Conclusions

As solid-state photochromic systems, we used both polymer films based on AC or PMMA polymers with complexes of CdSe / ZnS QDs and photochromic DAE molecules, and solid-phase films on quartz obtained from toluene solutions of QDs in the presence of DAE molecules. In addition, we studied films based on PVA polymer containing hybrid nanostructures consisting of CdSe / ZnS QDs with rigid bonds, between which photochromic DAE molecules are located, and covered with a polymer shell.

In the studied solid-state systems, in addition to photoinduced modulation of absorption, photoinduced modulation of fluorescence is observed. It can be caused both by inductive-resonant energy transfer from QDs to the photoinduced cyclic form of DAE molecules (FRET), and by the effect of fluorescence reabsorption by photochromic molecules.

This work was supported by BRFFR (Pr. F18R-074), RFBR (Pr. 18-33-00010 Bel_a), Ministry of Education of Belarus (pr. 1.5 of "Photonics and electronics for innovation") and the Russian Ministry of Science and Higher Education within the State assignment FSRC «Crystallography and Photonics» RAS.