Photoinduced Enhancement in the Luminescence of Hydrophilic Quantum Dots Coated with Photocleavable Ligands

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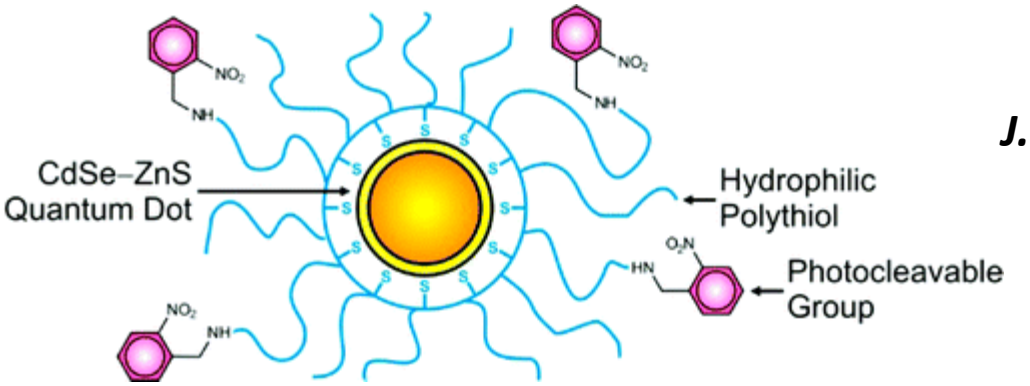

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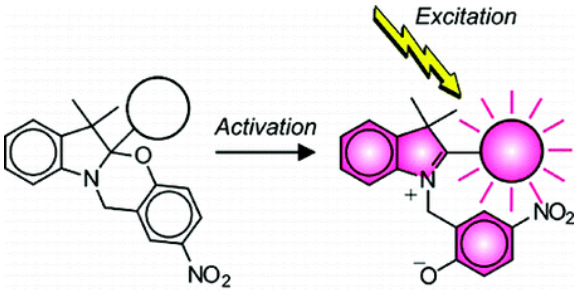
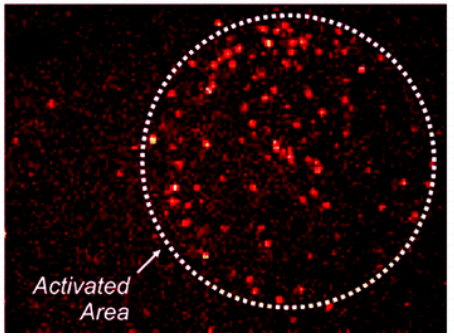
Introduction

❖ **Photoactivation of luminescence of a fluorophore**

- switch from a nonemissive to an emissive state upon illumination at an appropriate wavelength - valuable analytical tool in biological samples.

- local activation of fluorescence under optical control.



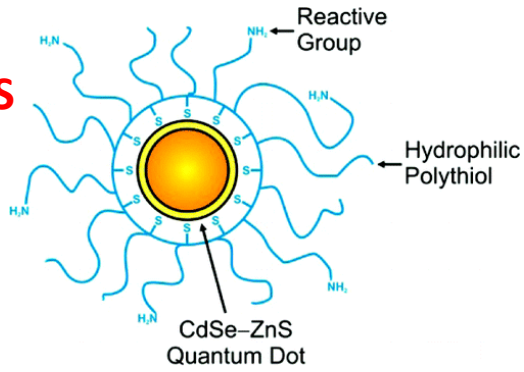


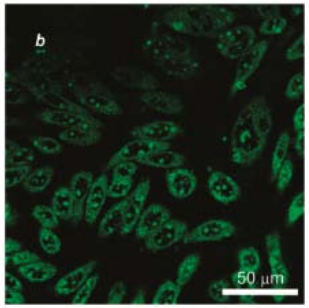
J. Phys. Chem. C, 2012, 116 (10), pp 6058–6068

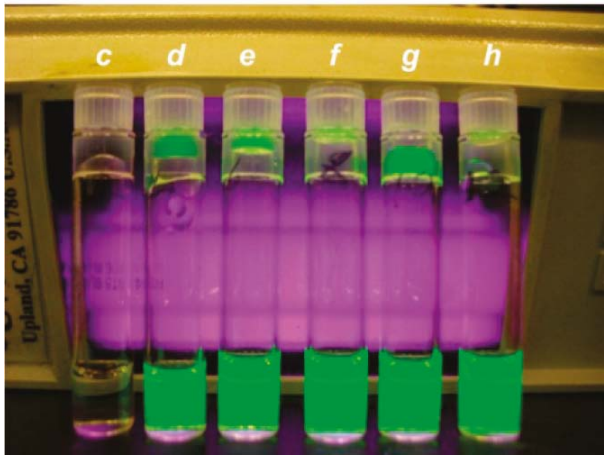
❖ **Semiconductor Quantum dots**

long luminescence lifetimes, excellent photobleaching resistances compared to most organic dyes and fluorescent proteins, narrow and symmetric emission bands, tunable luminescence across the visible region etc.

Amphiphilic CdSe-ZnS Core-Shell Quantum Dots





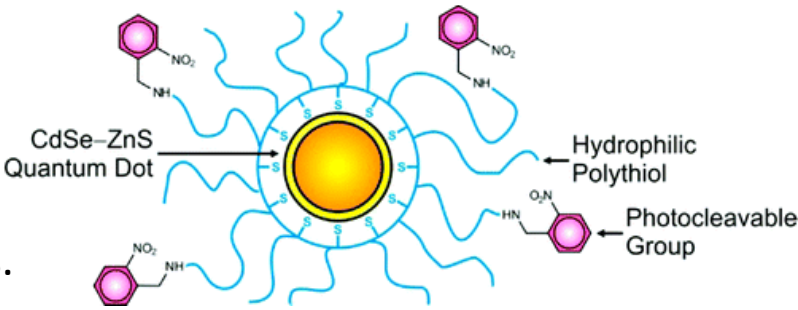


❖ Identification of mechanisms to photoactivate the luminescence of quantum dots can translate into the development of photocaged probes with improved performance.

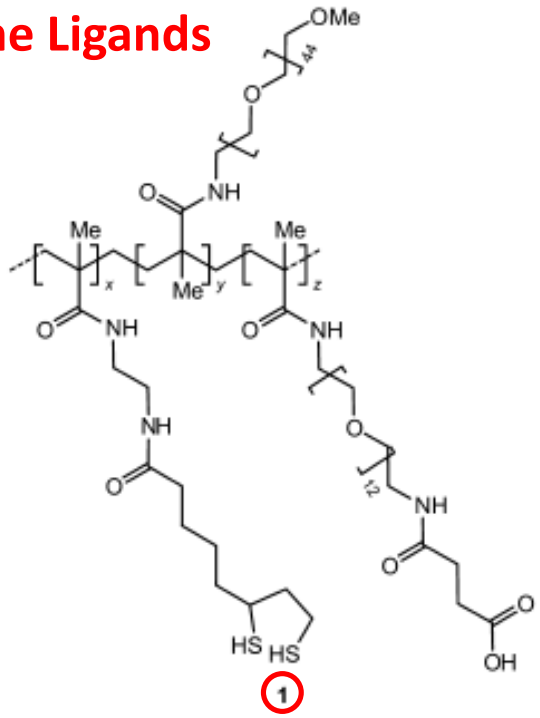
Langmuir 2010, 26(13), 11503–11511

In this paper

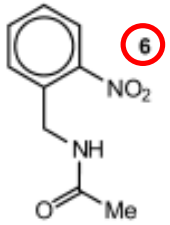
- Coupling of 2-nitrobenzyl groups to polymer-coated CdSe–ZnS core–shell quantum dots.
- Use of appropriate model systems to study the photochemical and photophysical properties of the resulting photoresponsive nanostructured assemblies.



Design of the Ligands

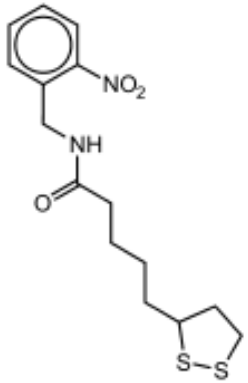


1



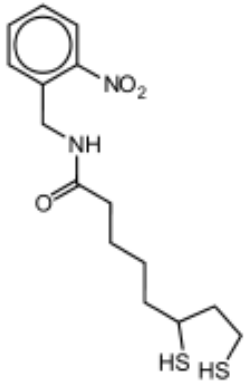
6

amide



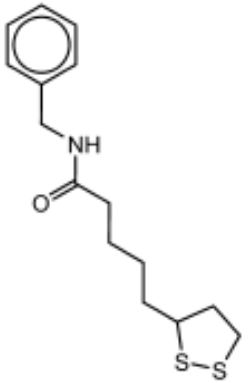
2

dithiolane



3

bisthiol



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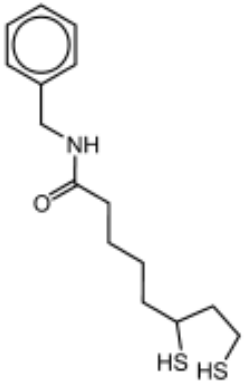


5

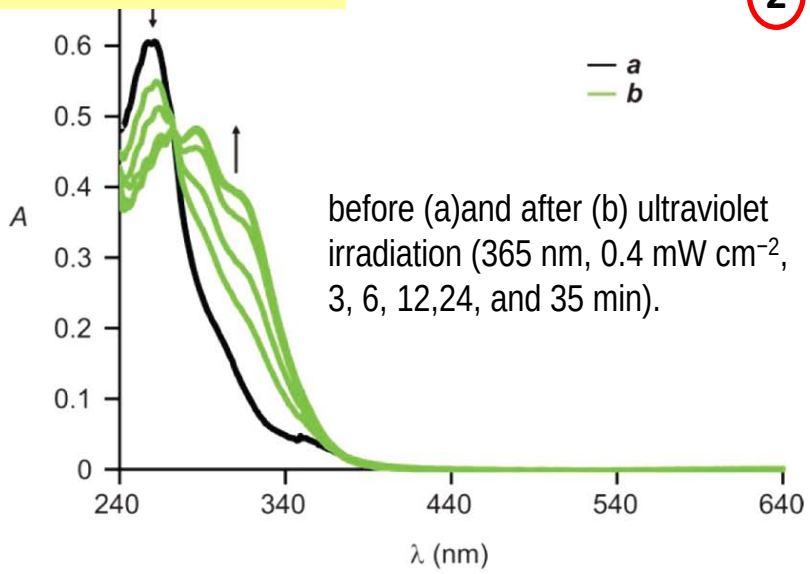
(1) Copolymer: achoring thiol groups, hydrophilic PEG chains and connecting carboxylic acids

(2)-(6) model compounds

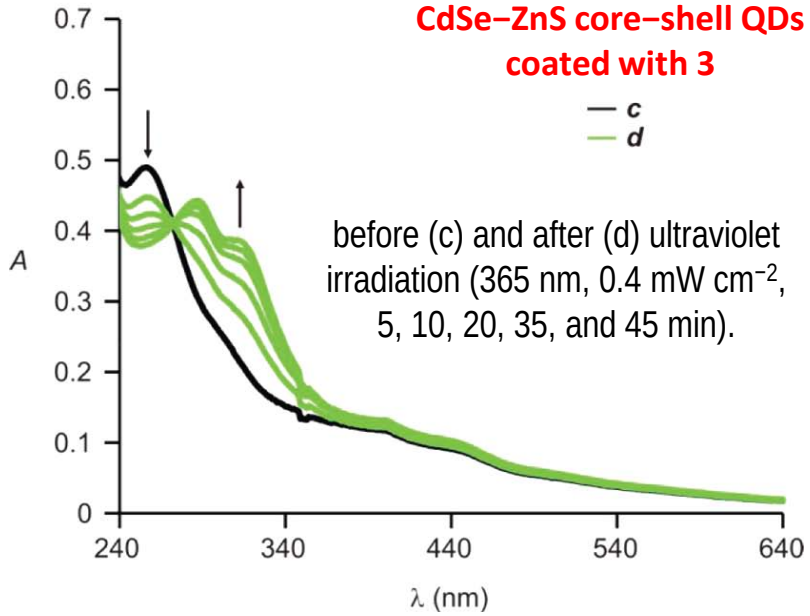
Spectroscopy of the Models

Absorption spectra

2



before (a)and after (b) ultraviolet irradiation (365 nm, 0.4 mW cm^{-2}, 3, 6, 12,24, and 35 min).

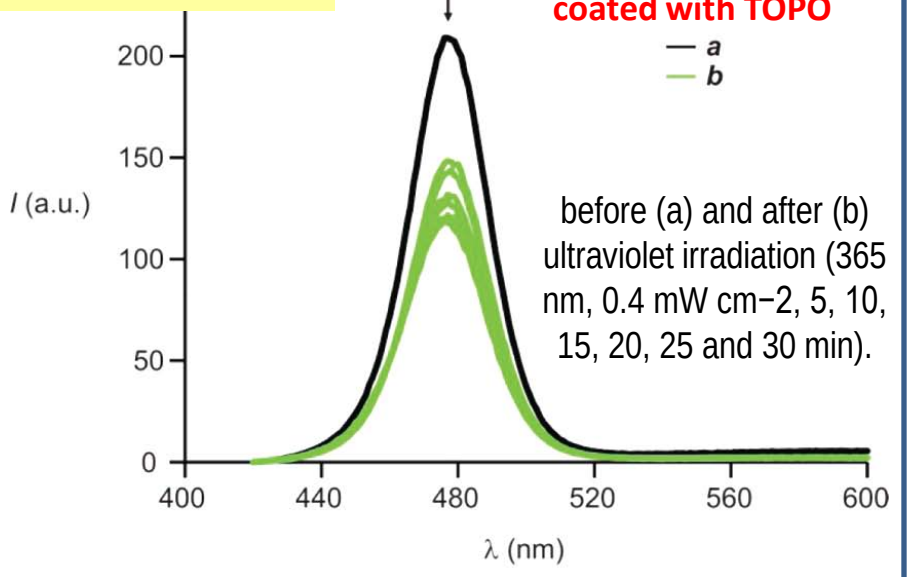


CdSe–ZnS core–shell QDs coated with 3

before (c) and after (d) ultraviolet irradiation (365 nm, 0.4 mW cm^{-2}, 5, 10, 20, 35, and 45 min).

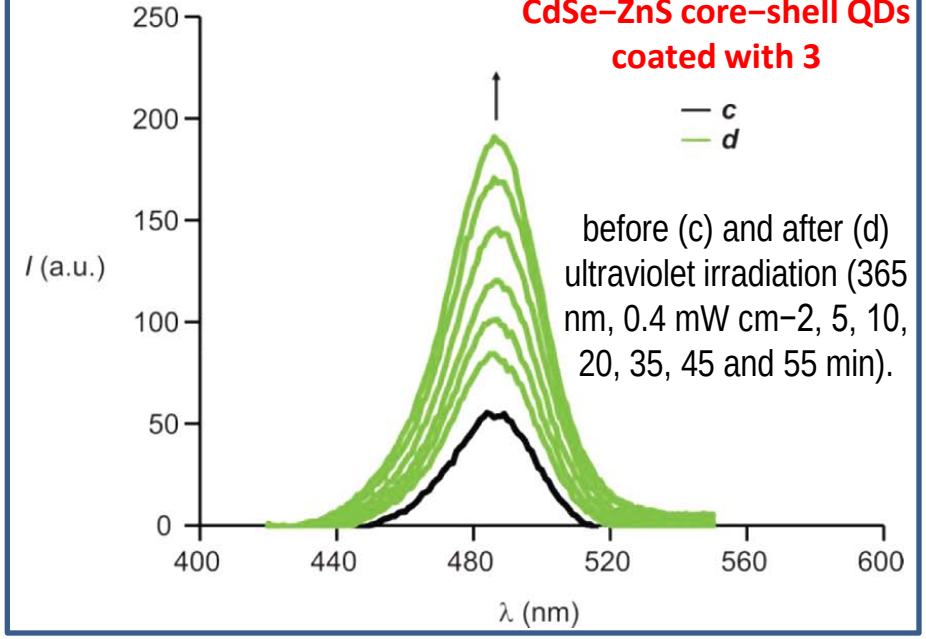
Emission spectra

CdSe–ZnS core–shell QDs coated with TOPO



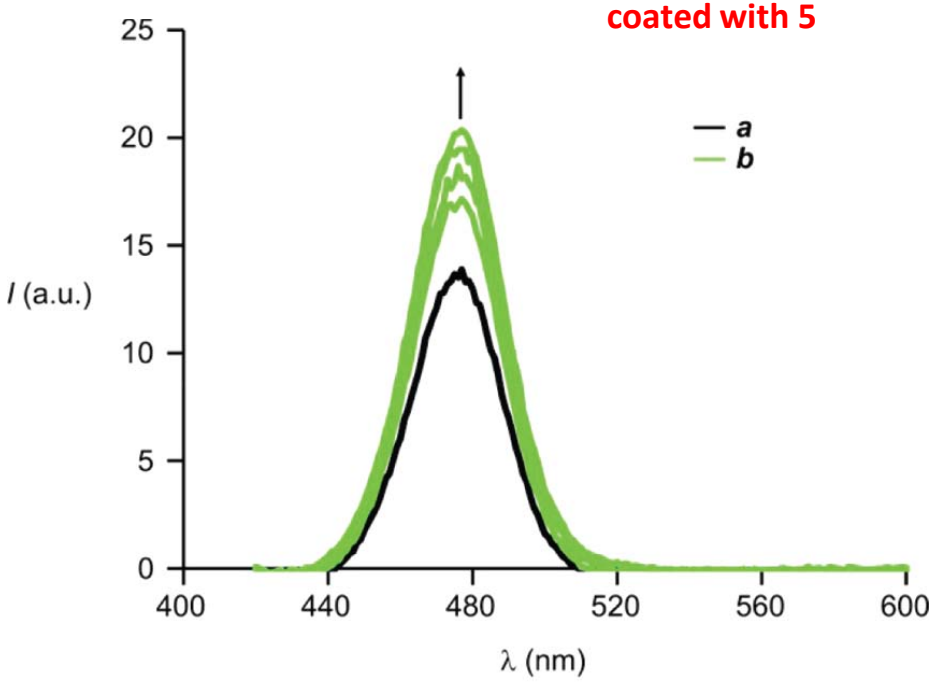
before (a) and after (b) ultraviolet irradiation (365 nm, 0.4 mW cm−2, 5, 10, 15, 20, 25 and 30 min).

CdSe–ZnS core–shell QDs coated with 3



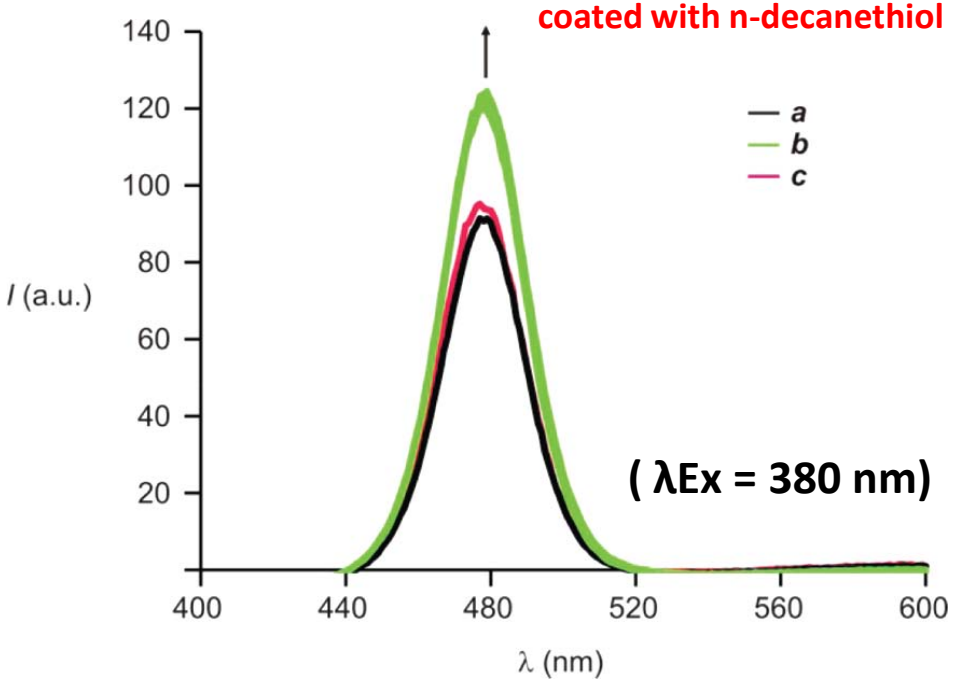
before (c) and after (d) ultraviolet irradiation (365 nm, 0.4 mW cm−2, 5, 10, 20, 35, 45 and 55 min).

CdSe–ZnS core–shell QDs coated with 5



before (a) and after (b) ultraviolet irradiation (365 nm, 0.4 mW cm−2, 5, 10, 15, and 20 min).

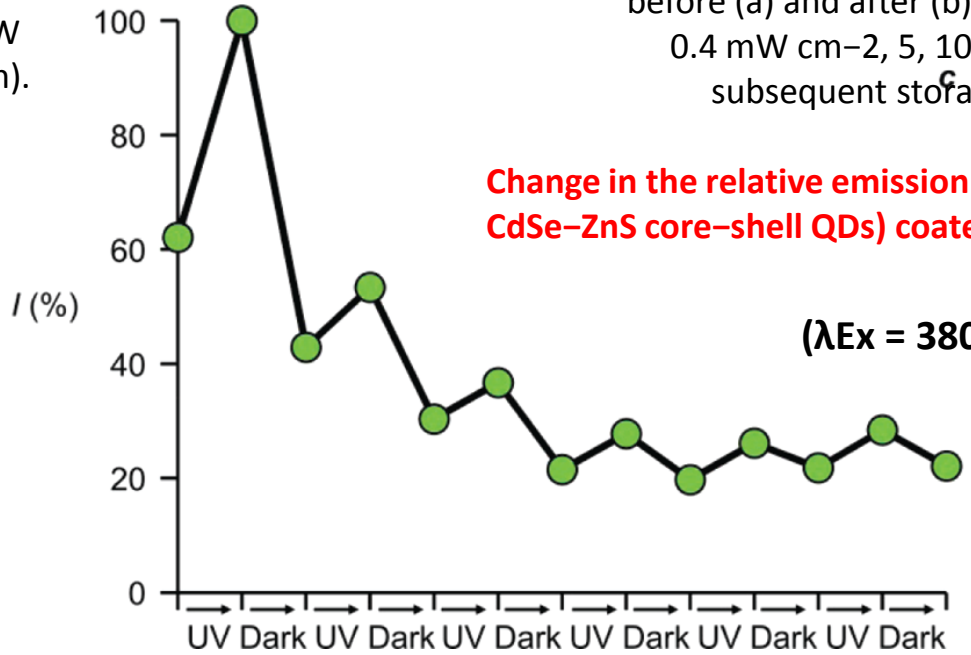
CdSe–ZnS core–shell QDs coated with n-decanethiol



before (a) and after (b) ultraviolet irradiation (365 nm, 0.4 mW cm−2, 5, 10, 15, 20, 25, and 30 min) and subsequent storage in the dark for 48 h (c).

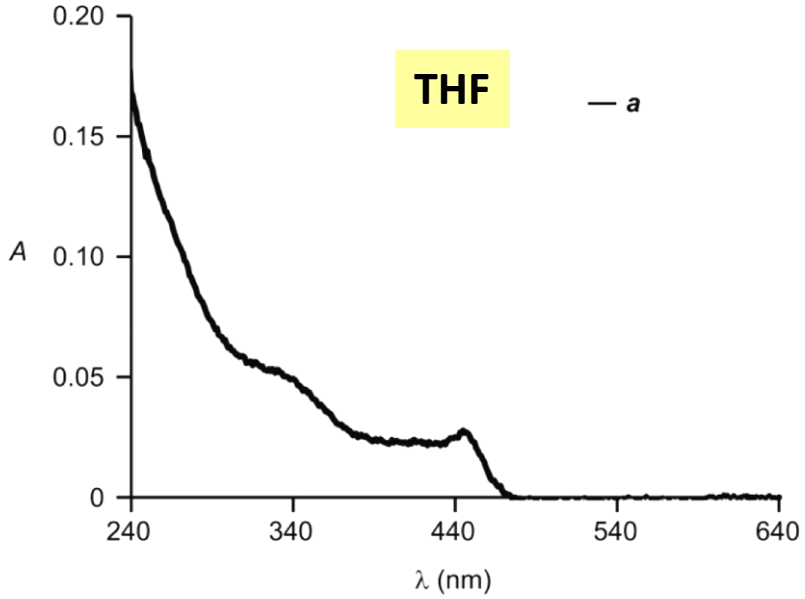
Change in the relative emission intensity of CdSe–ZnS core–shell QDs) coated with 5

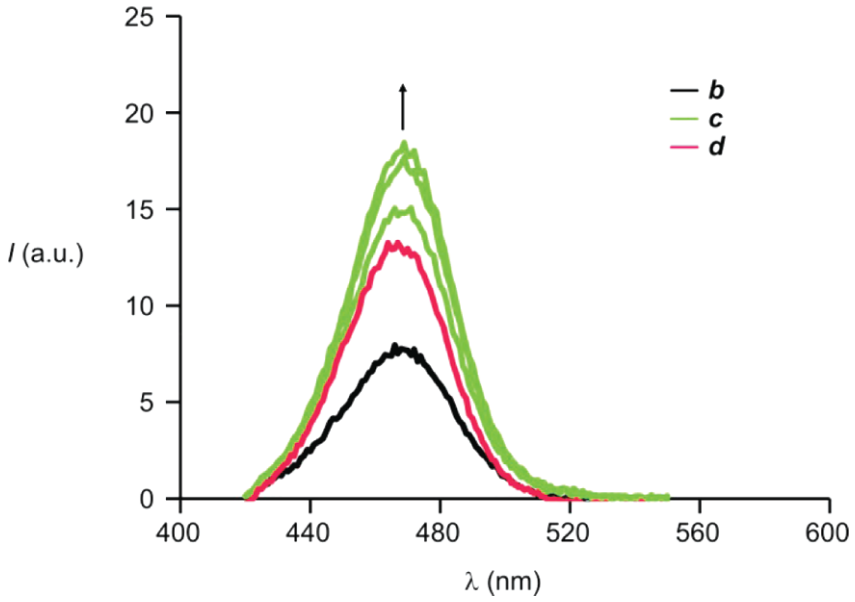
(λEx = 380 nm, λEm = 476 nm

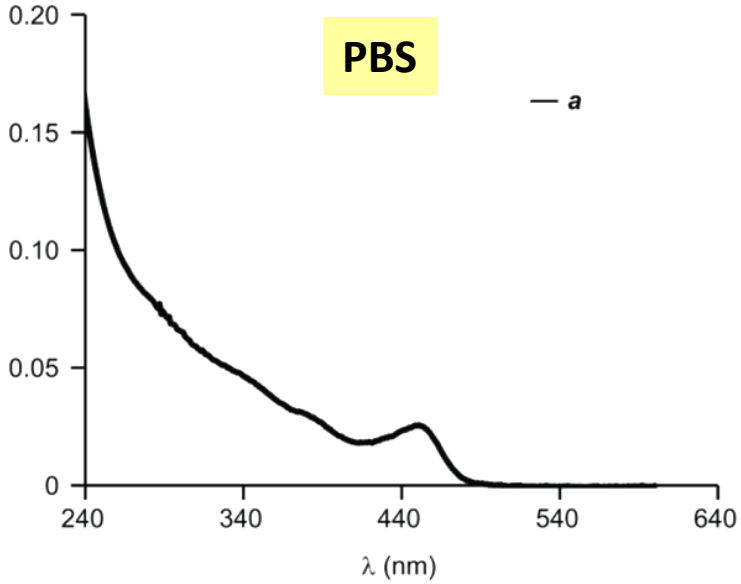


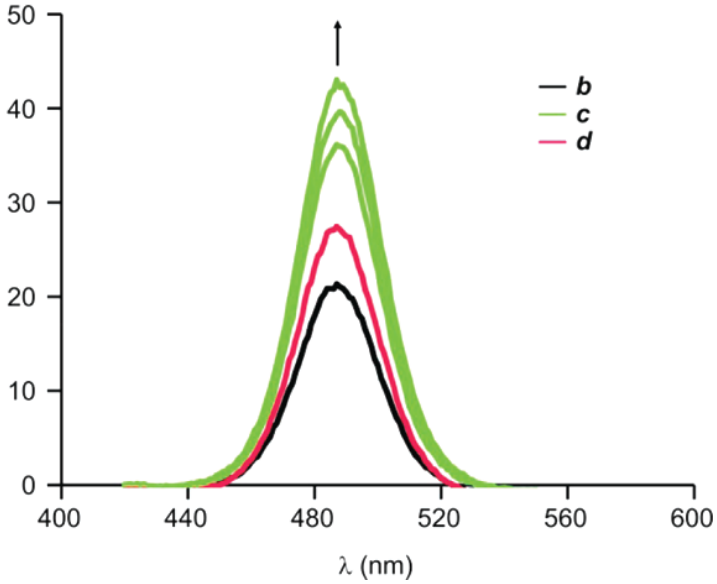
upon ultraviolet irradiation (365 nm, 0.4 mW cm−2, 10 min) and storage in the dark (24 h).

With copolymer 1: different solvents

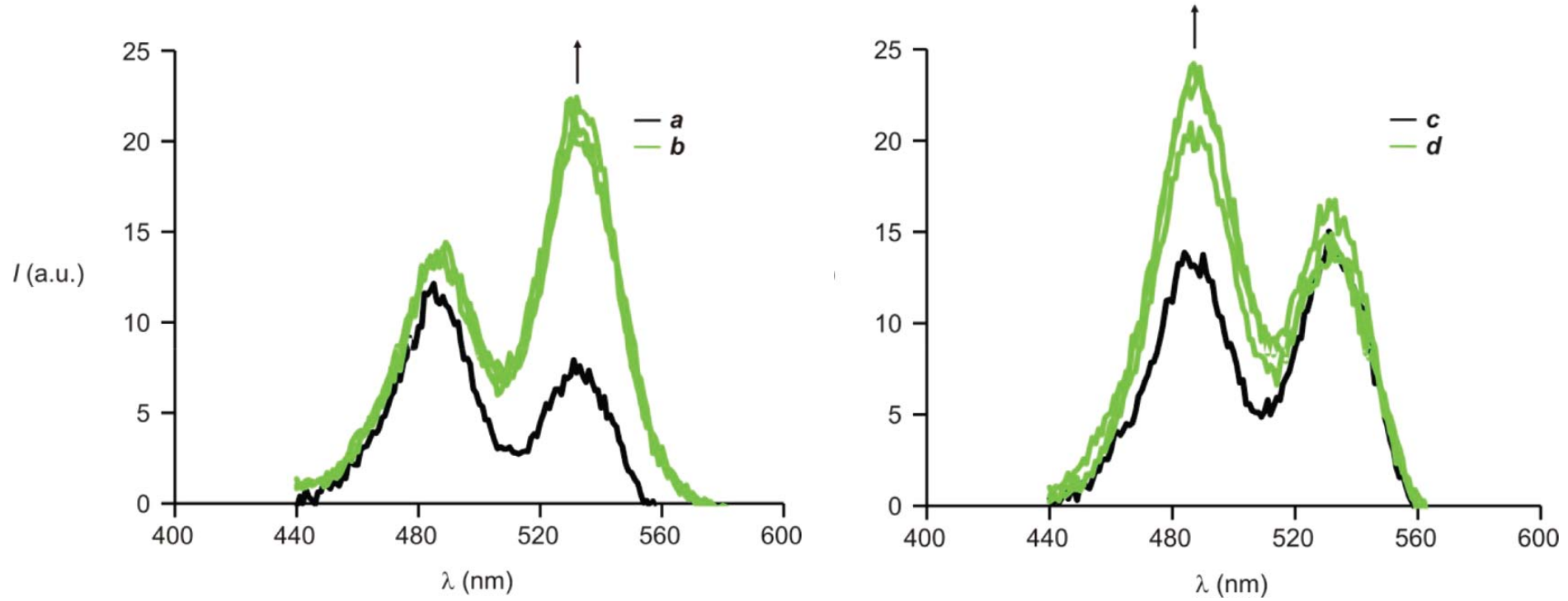




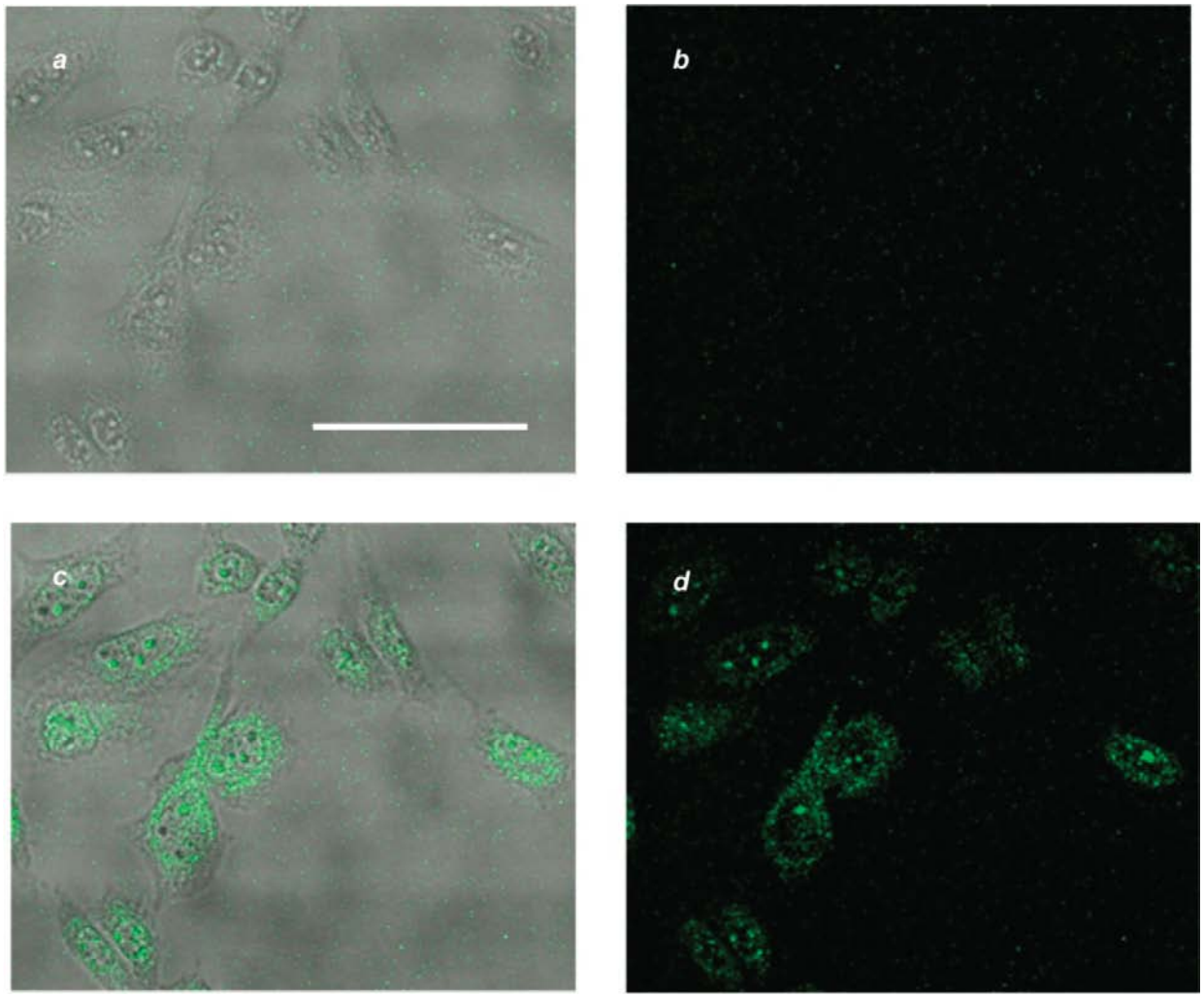




Emission spectra of mixtures (PBS, pH = 7.4, 25 °C, λEx = 420 nm) of two sets of CdSe−ZnS core−shell quantum dots, both coated with 1 but differing in core diameter, recorded after ultraviolet irradiation for 30 min (365 nm, 0.4 mW cm−2) and conjugation of 2- nitrobenzylamine to the set emitting at long (a) or short (c) wavelengths and after further ultraviolet irradiation for 5, 10, and 15 min (b and d). The concentrations of the quantum dots emitting at short wavelengths are 0.1 (a and b) and 1.8 µM (c an



Intracellular Luminescence Photoactivation.



Phase-contrast (a and c) and luminescence (b and d) images (λEx = 800 nm, scale bar = 50 μm), recorded before (a and b) and after (c and d) irradiation (365 nm, 0.4 mW cm−2, 30 min), of CHO cells incubated with CdSe−ZnS core−shell quantum dots (30 nM), coated with 1 and conjugated to 2-nitrobenzylamine, for 3 h.

Conclusions

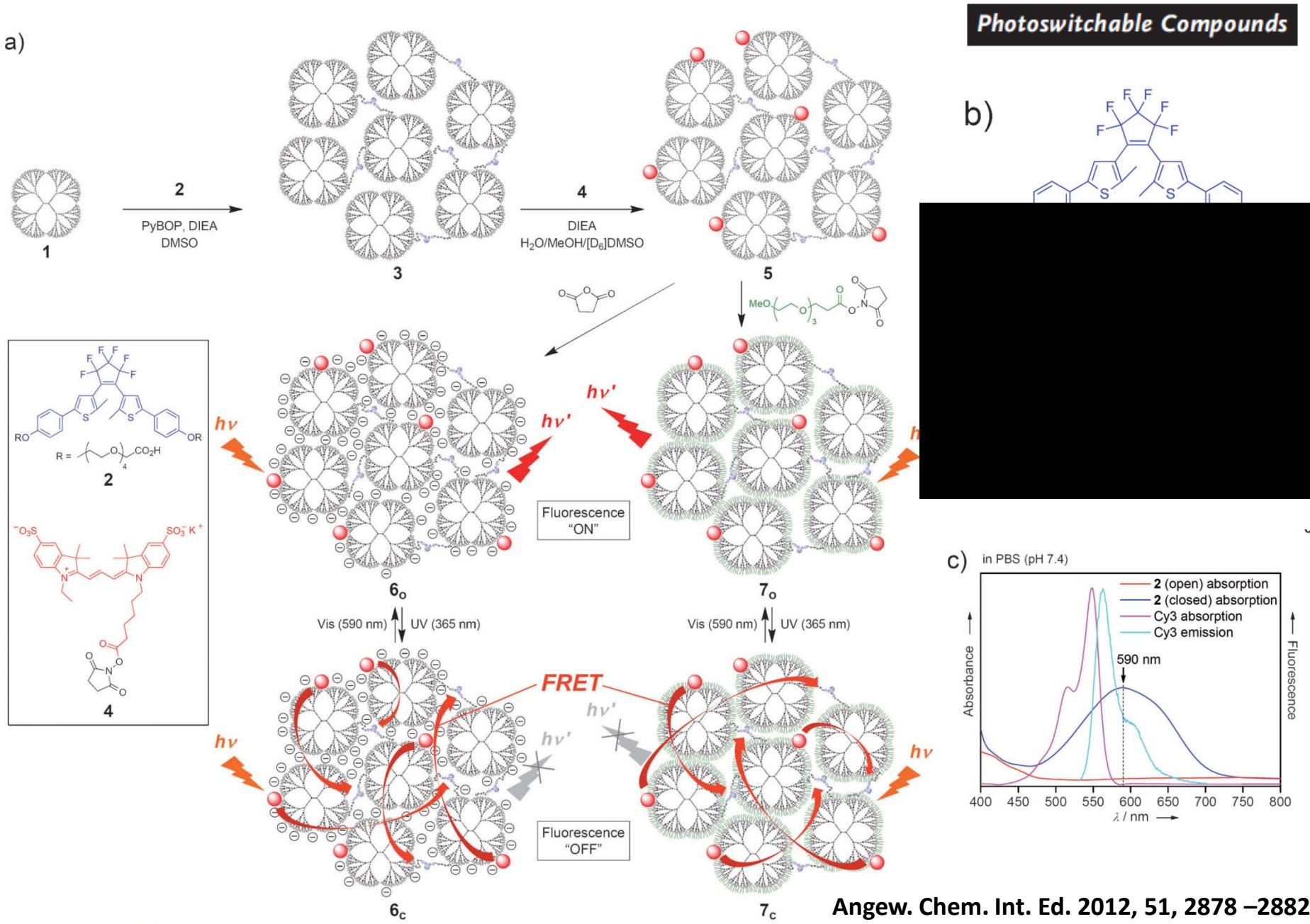
• Photocleavable 2-nitrobenzyl groups attached covalently to the polymeric coating of hydrophilic CdSe−ZnS core−shell QDs can be cleaved by UV illumination leading to significant luminescence enhancement.

• Control experiments with model systems suggest that the 2-nitrobenzylchromophores can quench luminescence of the QDs. Therefore, the photoinduced removal of the 2-nitrobenzyl quenchers suppresses this particular electron-transfer pathway and enhances the nanoparticle luminescence.

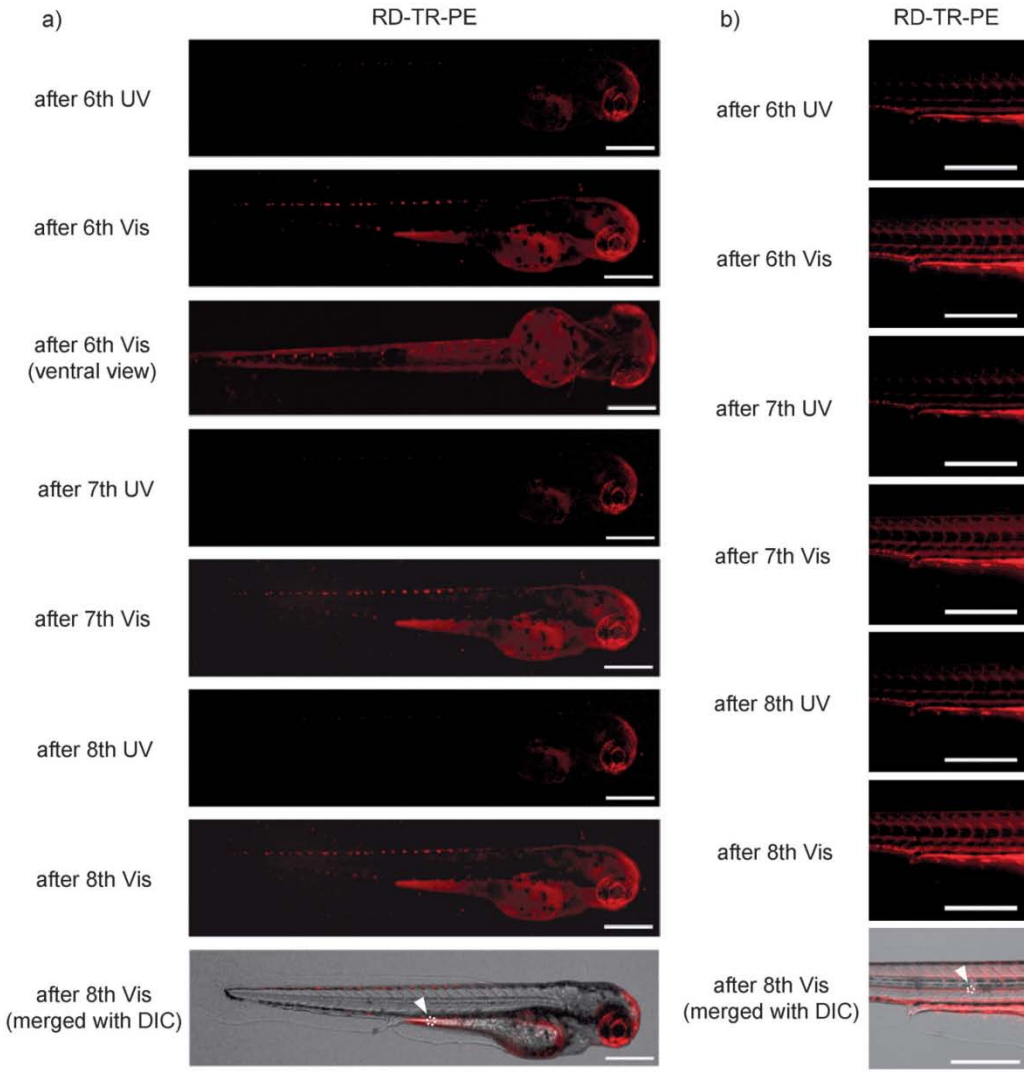
• In addition to the 2-nitrobenzyl chromophores, the thiol groups responsible for the adsorption of the polymeric coating on the ZnS shell of the quantum dots affect the excitation dynamics of these nanostructured constructs. Luminescence enhancement caused by the thiol groups are reversible and is not affected by the presence of molecular oxygen as well as by the nature of the solvent.

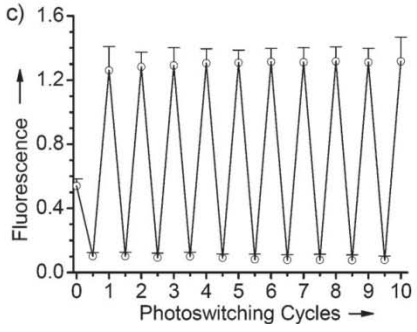
• The polymeric coating around theinorganic core encourages the internalization of these photoswitchable constructs in model cells. Ultraviolet illumination ofstained cells results in the intracellular cleavage of the 2-nitrobenzyl quenchers with a luminescent enhancementapproaching 80%.

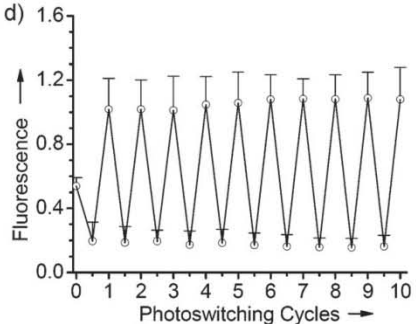
High-Contrast Reversible Fluorescence Photoswitching of Dye- Crosslinked Dendritic Nanoclusters in Living Vertebrates



Angew. Chem. Int. Ed. 2012, 51, 2878 –2882


a)
RD-TR-PE
after 6th UV
after 6th Vis
after 6th Vis
(ventral view)
after 7th UV
after 7th Vis
after 8th UV
after 8th Vis
after 8th Vis
(merged with DIC)
b)
RD-TR-PE
after 6th UV
after 6th Vis
after 7th UV
after 7th Vis
after 8th UV
after 8th Vis
after 8th Vis
(merged with DIC)


c)
Fluorescence
0.0
0.4
0.8
1.2
1.6
0 1 2 3 4 5 6 7 8 9 10
Photoswitching Cycles


d)
Fluorescence
0.0
0.4
0.8
1.2
1.6
0 1 2 3 4 5 6 7 8 9 10
Photoswitching Cycles

Thank you