

Investigation of fluorescence energy transfer in complexes quantum dots/azo dyes in track membranes

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ABSTRACT

Fluorescence resonant energy transfer in complexes of semiconductor CdSe/ZnS quantum dots with molecules of heterocyclic azo-dyes, 1-(2-pyridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo) resorcinol (PAR) formed at high concentration in the pore track membranes were studied. Evident effect of interaction between the complexes and free quantum dots on the efficiency of the fluorescence energy transfer is presented.

1. INTRODUCTION

During last two decades, photophysical properties of complexes of semiconductor nanocrystals, or quantum dots (QDs) with organic molecules are of great interest (Frasco and Chaniotakis 2009). Creation of different types of structures based on quantum dots allows to expand significantly area of quantum dots applications. These QDs complexes are employed in sensors, catalysis, electronic devices, biology and medical studies (Li, Son et al. 2007; Frasco and Chaniotakis 2009; Kniprath, Rabe et al. 2009; Yun, Feng et al. 2009).

Quantum dots are commonly used as energy donors (Gorbatsevich, Kaputskaya et al. 2004; Yun, Feng et al. 2009; Weaver, Dasari et al. 2010; Artemyev 2012). They have high extinction coefficient in a broad spectral range and a high luminescence quantum yield. Moreover, their optical transition wavelengths depend on the nanocrystal size. Therefore it is very easy to match the luminescence spectra of QDs and absorption spectra of chosen energy acceptor needed for efficient energy transfer. Additionally, QDs have high photostability and chemical resistance compare with organic molecules (Resch-Genger, Grabolle et al. 2008).

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Plenty studies elucidate formation of complexes of quantum dots and organic molecules (Gorbatsevich, Kaputskaya et al. 2004; Artemyev, Ustinovich et al. 2009), which demonstrate effective QD/molecule energy transfer. The fluorescence resonant energy transfer (FRET) is common for such systems.

As a rule, FRET in individual complexes was under consideration but effects of interaction between the complexes on the energy transfer, which may take place at a high complex concentration, were not well analyzed. The high QDs/molecules complex concentration can be realized, e.g. in porous matrices like Poly-(ethylene terephthalate) pore track membrane (PET TM) (Apel 2001). This matrix allows embedding the QDs in loosened layer of the track pore (Orlova, Gromova et al. 2011). Another remarkable feature of the track membrane is possibility to create the complexes by subsequent incorporation of QDs and molecules into the track membrane (Orlova, Gromova et al. 2013).

In present work FRET in complexes of semiconductor CdSe/ZnS quantum dots and molecules of heterocyclic azo-dyes 1-(2-pyridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo) resorcinol (PAR) formed at high concentration in the PET track membranes were studied. We demonstrate evident effect of interaction between the complexes on the efficiency of the QD/molecule FRET.

2. MATERIALS AND METHODS

PET TM were obtained from Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research (Dubna, Russia). The membrane characteristics are shown in Table 1.

Table 1. Parameters of TM

Pore diameter, d	0.5 μm
Thickness, l	12 μm
Pore density, n	$2.9 \cdot 10^7 \text{ cm}^{-2}$
Pore direction (relative to the foil surface), ϕ	90°

Hydrophobic colloidal CdSe/ZnS QDs with 2.5-nm core diameter were synthesized according to Ref. (Talopin, Rogach et al. 2001). The membranes were immersed in the QD colloidal toluene solution with QD concentration of 10^{-6} mol/L for five days. Then, the membranes with embedded QDs were removed from the solutions, rinsed thoroughly by toluene and dried before the measurements. Concentration of QDs embedded in the wall layer along pores was estimated from the absorption spectrum taking into account the TM parameters shown in Table 1 and assumption that thickness of the layer with quantum dots is not exceed 200 nm (Orlova, Gromova et al. 2011).

Azo-dyes 1-(2-pyridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo) resorcinol (PAR) were purchased from Sigma Aldrich and used without further purification. QD/azo-dyes complexes were produced both in solutions and in track membranes. QD/PAN complexes in the toluene solutions were prepared by adding PAN solutions with various concentrations (C_{PAN}) to QD solution with concentration (C_{QD}) of about $5 \cdot 10^{-7}$ mol/L. The $C_{\text{QD}}:C_{\text{PAN}}$ ratio in the solutions varied from 5:1 to 1:10. The QD/PAR

complexes were created similarly. For creation QD/azo-dyes complexes in the track membranes, the TMs with embedded QDs were immersed into toluene PAN or aqueous PAR solutions with different concentration ($10^{-8} \div 10^{-6}$ mol/L). Samples were immersed in the solutions for a week while chemical equilibrium was established. After impregnation of azo-dyes, the membranes were thoroughly rinsed in toluene and dry under the ambient condition.

A spectrofluorometer, Cary Eclipse (Varian), and a spectrophotometer, UV-Probe 3600 (Shimadzu), were used for measuring the steady-state photoluminescence (PL) and absorption spectra of the samples. PL was excited by a 405 nm radiation. Time-resolved PL measurements in back-scattering geometry were performed by a MicroTime 100 laser scanning luminescent microscope (Pico Quant, Germany), with 100 ps time resolution and a 405 nm radiation from a 5 MHz pulsed diode laser was used for PL excitation. Spectral selection of the PL was performed using a set of interference filters with a FWHM of 10 nm in the spectral range 480-590 nm. The

average PL decay time was calculated using the formula: $\langle \tau \rangle = \sum A_i \tau_i^2 / \sum A_i \tau_i$, where A_i and τ_i are the amplitude and decay time of the i -th component, respectively.

3. RESULTS AND DISCUSSION

3.1 Investigation of quantum dots interaction in the track membranes

Impregnation of poly-(ethylene terephthalate) track membranes with hydrophobic quantum dots solution leads to QDs embedding in the loosened layer along the track pore.

The absorption spectrum of QDs in the track membrane coincides with that in toluene (Fig.1) At the same time, a 10 nm red shift of the maximum of QD luminescence is observed for the TM samples after its treatment in the QD toluene solution.

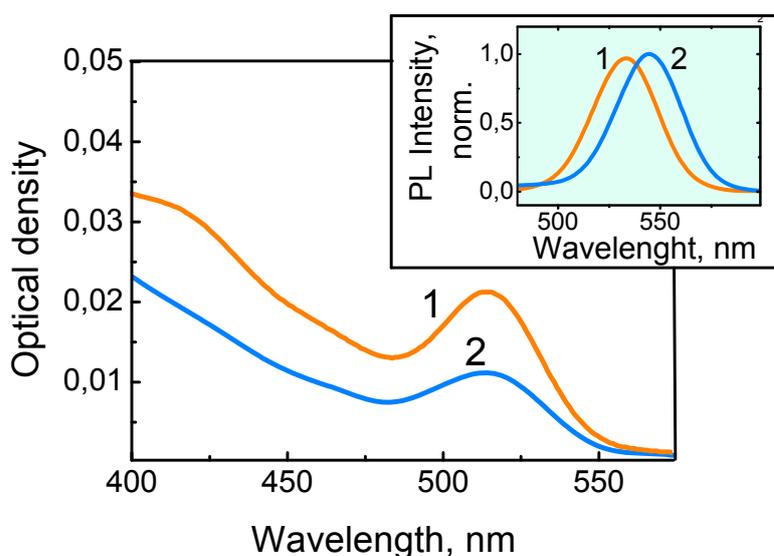


Fig. 1 Absorption and luminescence spectra (insert) of CdSe/ZnS quantum dot toluene solution (1) and the track membranes with embedded QDs (2).

Local concentration of QDs in the wall layer of the TM pores of 10^{-3} mol/L estimated from the TM absorption spectrum is much higher than in the QD toluene solutions ($C_{\text{QD}} = 10^{-6}$ mol/L). Simple estimation, in an assumption that quantum dots uniformly distributed within cylindrical layer around empty track pore gives average distance between QD centers of about 10 nm that make possible an interdot FRET. It is known (Kagan, Murray et al. 1996) that FRET between neighboring QDs in ensemble of the nanocrystals with slightly different sizes results the red shift of the PL peak. Additionally, the PL decay time becomes shorter at the higher energy side of the inhomogeneously broadened QD PL band as compared with the lower energy side. The red shift of the QD PL peak is observed by us. We also compared decay times for PL of QDs in the toluene solution and in the TM sample at different detection wavelengths by using a set of narrow band interference filters. In both cases, the PL decay can be well fitted by a biexponential function. The average luminescence decay time, $\langle \tau \rangle$, for QDs in toluene is same for all detection wavelengths (Fig.2b, curve 1). However, in the track membranes the PL decay time reduces in three times at the higher energy side of the QD PL band as compared with the lower energy side. These facts indicate FRET between QDs in ensemble of the nanocrystals embedded in the wall layer of the TM pores.

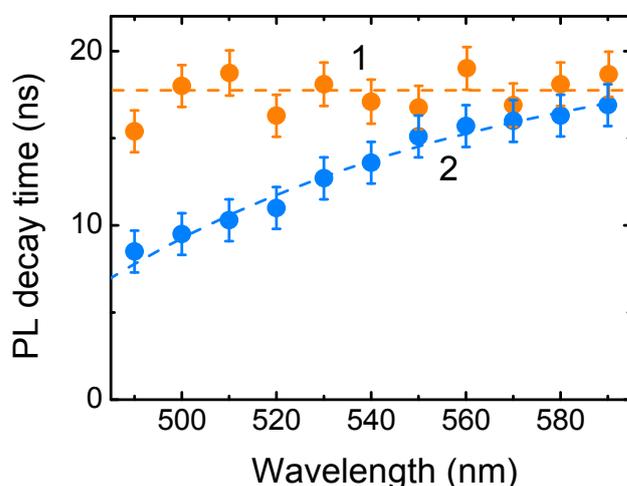


Fig. 2. Quantum dot photoluminescence average decay time $\langle \tau \rangle$ as a function of detection wavelength for QDs in toluene solution (1) and in track membrane (2).

3.2 QD/azo-dyes complexes formation

We used samples of the track membrane demonstrating the interdot energy transfer for creation of complexes of CdSe/ZnS QDs with azo-dyes. The azo-dyes can bind with

Zn ions (Abu-Zuhri 1987) and the PAN and PAR molecules form QD/molecule complex by coordination onto zinc atoms on the QD ZnS shell. Absorption and PL spectra of track membranes with embedded CdSe/ZnS quantum dots before and after QD/PAN and QD/PAR complexes formation are shown in Fig.3a and 3b, respectively. Appearance of a new absorption band at 560 nm, which is characteristic band for PAN/Zn bonding (Maslov, Orlova et al. 2012), indicates the QD/PAN complex formation. Unlike PAN, the PAR is the hydrophilic molecules. Therefore, creation its complexes with hydrophobic QDs in solution is nontrivial task. Fortunately, the PET track membranes allow combining the hydrophobic QDs and hydrophilic PAR (AO Orlova , Gromova et al. 2013) and a new characteristic absorption band at 520 nm in the absorption spectrum of TM treated by QDs and PAR manifests formation of the QD/PAR complexes (Fig. 3b).

In both cases formation of the QD/PAN and QD/PAR complexes are accompanied by QDs luminescence quenching (Figs. 3a and 3b). The QD luminescence quenching due to the QD/PAN complex formation has been reported in Ref. (Baranov, Orlova et al. 2010). It is not surprise, since because of strong overlapping of the QD PL band with both QD/PAN and QD/PAR absorption spectra, the FRET between QDs and molecules is expected.

The photoexcitation energy transfer in the QD/PAN and QD/PAR complexes in the TM and an influence of the interaction between the complexes on the energy transfer efficiency were studied in detail by steady-state and transient PL spectroscopy.

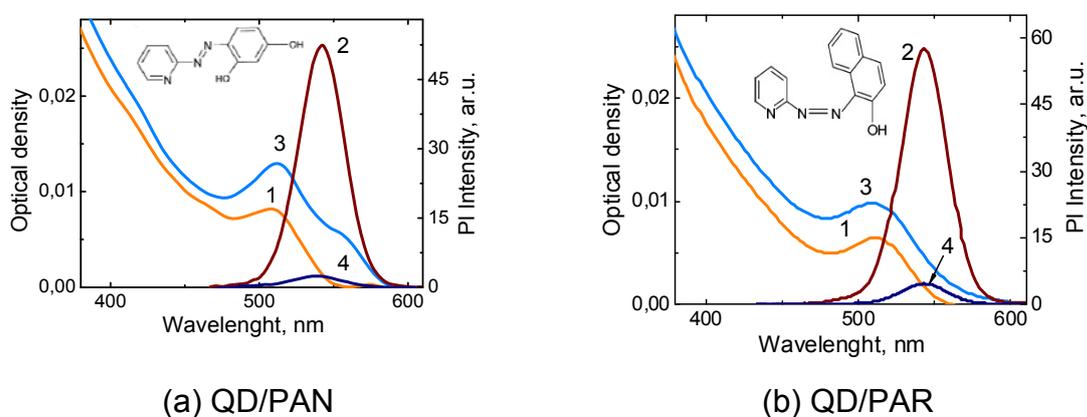


Fig. 3. Absorption and luminescence spectra of CdSe/ZnS quantum dots embedded in track membranes before and after QD/PAN complex formation: 1 is the absorbance of QD embedded in track membrane; 2 is the luminescence of QD in track membrane; 3 and 4 are the absorbance and the luminescence, respectively, of track membranes samples with quantum dots after impregnation with azo-dyes solution.

Dependencies of the QD PL intensity on ratio of quantum dots and azo-dyes concentrations, $n=C_{PAN}/C_{QD}$ are presented in

Fig.4. It is seen that in solution QDs luminescence decay does not depend on the azo-dyes concentration. Therefore, only unbound quantum dots luminesce and binding at least one PAN or PAR molecule with the quantum dot surface leads to total quenching of QD luminescence.

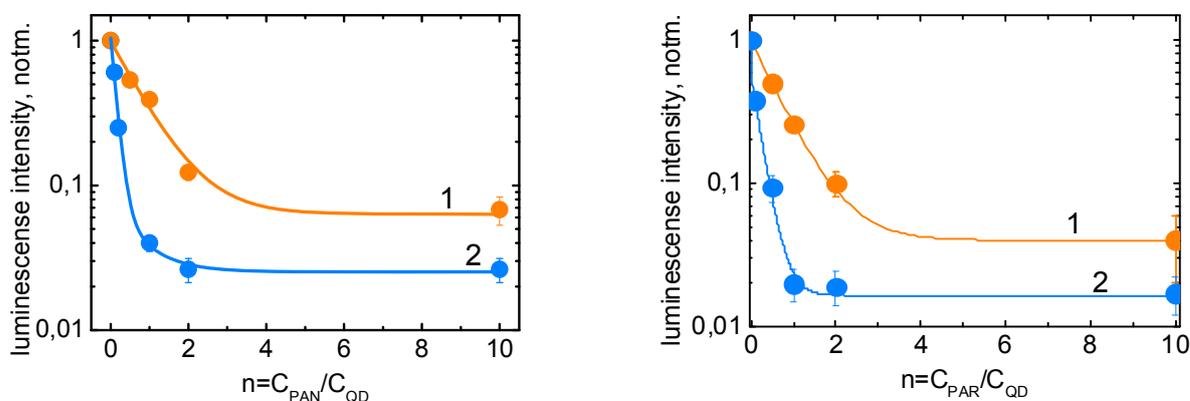
Let us assume that number of azo-dyes molecules bound to quantum dots surface obeys a Poisson statistic. The Poisson distribution fits well number of quencher molecules per micelle in the experiments of luminescence quenching in aqueous micellar solution (Infelta 1979). Then, if all azo-dye molecules are adsorbed on the quantum dot surface, the experimental data presented in Fig. 4 should be described by the following equation:

$$\frac{I}{I_0} = A e^{-\frac{C_{AD}}{C_{QD}} B} + (1 - A), \quad (1)$$

where: I_0 is the initial intensity of sample luminescence, I is the intensity of the luminescence of sample after QD/azo-dyes complexes formation, A ($0 < A < 1$) is the fraction of QDs involved in complex formation, $1-A$ is the fraction of QDs unbound with molecules, C_{AD} is the concentration of azo-dye molecules, C_{QD} is the concentration of quantum dots.

It was found that the function $y=0.92 \cdot \exp(-0.9n)+0.08$ fits well the experimental data of QD luminescence quenching in QD/PAN toluene solution shown in Fig.4a (curve 1). For QD/PAR solution experimental data fits well by function $y=0.94 \cdot \exp(-1.2n)+0.06$ as it is shown in Fig.4b (curve 1). This proves that binding one azo-dye molecule on the QD surface leads to total quenching of the QD luminescence.

Quantum dots luminescence quenching in the track membrane is well fitted by functions $y=0.95 \exp(-3.7n)+0.05$ and $y=0.96 \exp(-5.6n)+0.04$ for PAN and PAR, respectively. It means, that formation of one surface complex QD/PAN leads to quenching of luminescence of host quantum dot and three neighbor QDs and complex QD/PAR result in quenching 5 neighbor QDs. This situation could not be explained by QDs spontaneous aggregation, because position of QDs in the TM is fixed. More real explanation is the FRET between neighboring QD/azo-dye complexes and free QDs contributes to the PL quenching.



(a) QD/PAN

(b) QD/PAR

Fig. 4. Dependence of QDs luminescence intensity on quantum dots and azo-dyes concentration relations in toluene (1) and track membranes (2).

Existence of free QDs in the TM is supported by data on QD luminescence decay time in TM with complexes as a function of ratio of azo-dyes and quantum dots and concentrations, $n=C_{AD}/C_{QD}$. Dependencies of normalized QD luminescence average decay time on ratio of azo-dyes and QDs concentration in solution and in track membrane are given in Fig. 5. Despite of QDs in solution, the QD luminescence decay time in the track membranes decreases with increasing number of molecules per one QD. This is evidence of partial quenching of QD luminescence.

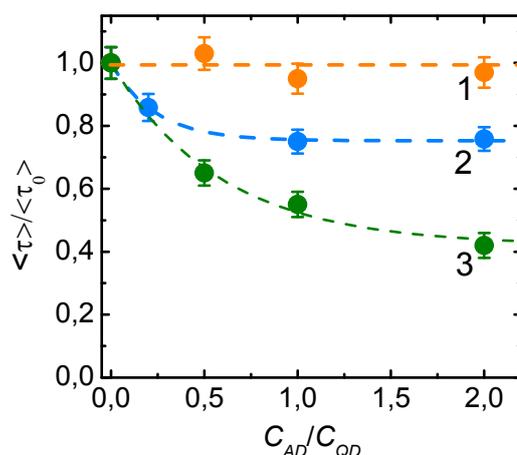


Fig. 5 Dependences of normalized QDs luminescence average decay time on ratio of azo-dyes and QDs concentration in solution (1) and in track membrane for QD/PAN complexes (2) and QD/PAR complexes (3).

It is obvious from experimental data that the formation of QD/PAR complexes quenches luminescence of QDs more efficiently than in PAN case. Our simple estimations show that it comes from different values of corresponding overlap integral. Indeed, if concentration and distance between QDs and QD/azo-dyes complexes are same for both cases, difference in FRET efficiency will determine by overlap integral:

$$J = \int I_D^H(\nu) \cdot \varepsilon_A(\nu) \cdot \nu^{-4} \cdot d\nu, \quad (2)$$

where; $I_D^H(\nu)$ is the normalized luminescence spectrum of the energy donor (QDs); $\varepsilon_A(\nu)$ is the absorption spectrum of the acceptor (QD/azo-dyes complex); ν is wavenumber. Then the overlap integral defines the critical radius (the distance between the donor and acceptor in which energy transfer efficiency is 50%) as:

$$R_0^6 = \frac{9000 \cdot \ln 10 \cdot \Phi^2 \cdot q_{0D}}{128 \cdot \pi^5 \cdot n^4 \cdot N_A} \cdot J, \quad (3)$$

where: Φ is the orientation factor; q_{0D} is the quantum yield of the donor in the absence of quencher; n is the refractive index of the environment; N_A is the Avogadro number.

Using (3) and (4) we can calculate the overlap integrals and critical radii for the PAN and PAR complexes: $J_{PAN} = 5 \cdot 10^{-14} \text{ M}^{-1}\text{sm}^4$ ($R_{0(PAN)} = 31 \text{ \AA}$) and $J_{PAR} = 7 \cdot 10^{-13} \text{ M}^{-1}\text{sm}^4$ ($R_{0(PAR)} = 48 \text{ \AA}$), respectively.

4. CONCLUSION

The creation of QD/azo-dyes complexes in the samples with interdot FRET condition provide opportunity for effective quenching of luminescence of QD ensemble even at low complex concentration. Formation QD/azo-dye complex quenches entirely luminescence of host QD and results in partially quenching of neighbor QDs. Using different azo-dyes allow to control value of overlap integral and to manage the efficiency of QDs luminescence quenching.

Present result could be used for designing different type of micro fluidic devices. Dissociative sensors developing based on track membranes and QD/azo-dyes complexes are promising. In this system elimination of one quencher molecules will lead to recovering luminescence signal from several QDs at once that shall significant increase sensor sensitivity.

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REFERENCES

- Abu-Zuhri A.Z. (1987). "Pyridylazo compounds as analytical reagents." *An-Najah University Journal for Research - Natural Sciences* **4**: 30-40.
- Orlova A.O, Gromova Yu.A, et al. (2013). "Formation of structures based on semiconductor quantum dots and organic molecules in track pore membranes." *Journal of Applied Physics* **113**: 214305.
- Apel P. (2001). "Track etching technique in membrane technology." *Radiation Measurements* **34**(1–6): 559-566.
- Artemyev M.V. (2012). "Resonance energy transfer in conjugates of semiconductor nanocrystals and organic dye molecules." *Journal of Nanophotonics* **6**(1): 061705-061705.
- Artemyev M., E. Ustinovich, et al. (2009). "Efficiency of Energy Transfer from Organic Dye Molecules to CdSe–ZnS Nanocrystals: Nanorods versus Nanodots." *Journal of the American Chemical Society* **131**(23): 8061-8065.
- Baranov, A. V., Orlova A. O., et al. (2010). "Dissociative CdSe/ZnS quantum dot-molecule complex for luminescent sensing of metal ions in aqueous solutions." *Journal of Applied Physics* **108**(7): 074306-074305.
- Frasco M. and Chaniotakis N. (2009). "Semiconductor Quantum Dots in Chemical Sensors and Biosensors." *Sensors* **9**(9): 7266-7286.

- Gorbatsevich S. K., Kaputskaya I. A., et al. (2004). "Fluorescence of CdSe/ZnS quantum dots in solid solutions in the presence of organic molecules DODCl." *Journal of Luminescence* **110**(1–2): 23-29.
- Infelta P. P. (1979). "Fluorescence quenching in micellar solutions and its application to the determination of aggregation numbers." *Chemical Physics Letters* **61**(1): 88-91.
- Kagan C. R., Murray C. B., et al. (1996). "Long-range resonance transfer of electronic excitations in close-packed CdSe quantum-dot solids." *Physical Review B* **54**(12): 8633-8643.
- Kniprath R., Rabe J. P., et al. (2009). "Hybrid photovoltaic cells with II–VI quantum dot sensitizers fabricated by layer-by-layer deposition of water-soluble components." *Thin Solid Films* **518**(1): 295-298.
- Li F., Son D.-I., et al. (2007). "Memory effect of CdSe/ZnS nanoparticles embedded in a conducting poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene] polymer layer." *Applied Physics Letters* **90**(22): 222109-222103.
- Maslov V., Orlova A., et al. (2012). *Combination Therapy: Complexing of QDs with Tetrapyrroles and Other Dyes. Photosensitizers in Medicine, Environment, and Security*. T. Nyokong and V. Ahsen, Springer Netherlands: 351-389.
- Orlova A. O., Gromova Yu A., et al. (2011). "Track membranes with embedded semiconductor nanocrystals: structural and optical examinations." *Nanotechnology* **22**(45): 455201.
- Resch-Genger U., Grabolle M., et al. (2008). "Quantum dots versus organic dyes as fluorescent labels." *Nat Meth* **5**(9): 763-775.
- Talapin D. V., Rogach A. L., et al. (2001). "Highly Luminescent Monodisperse CdSe and CdSe/ZnS Nanocrystals Synthesized in a Hexadecylamine– Trioctylphosphine Oxide– Trioctylphosphine Mixture." *Nano Letters* **1**(4): 207-211.
- Weaver J. E., Dasari M. R., et al. (2010). "Investigating Photoinduced Charge Transfer in Carbon Nanotube–Perylene–Quantum Dot Hybrid Nanocomposites." *ACS Nano* **4**(11): 6883-6893.
- Yun D., Feng W., et al. (2009). "Efficient conjugated polymer-ZnSe and -PbSe nanocrystals hybrid photovoltaic cells through full solar spectrum utilization." *Solar Energy Materials and Solar Cells* **93**(8): 1208-1213.