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ARTICLE TYPE

Light Harvesting of CdSe/CdS quantum dots coated with β -cyclodextrin based host-guests through Resonant Energy Transfer from the nitrobenzoxadiazole guests.

Francesca Villafiorita-Monteoleone,^{*a} Valentina Daita,^b Claudio Quarti,^c Dario Perdicchia,^b Paola Del Buttero,^b Guido Scavia,^a Mirella del Zoppo,^c and Chiara Botta^{*a}

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Films of nano-hybrids based on red emitting CdSe/CdS QDs functionalized with perthiolated β -cyclodextrin hosting a green emitting nitrobenzoxadiazole derivative, show emission harvested by the host-guest organic system through resonant energy transfer from the organic host-guest to the QD.

1. Introduction

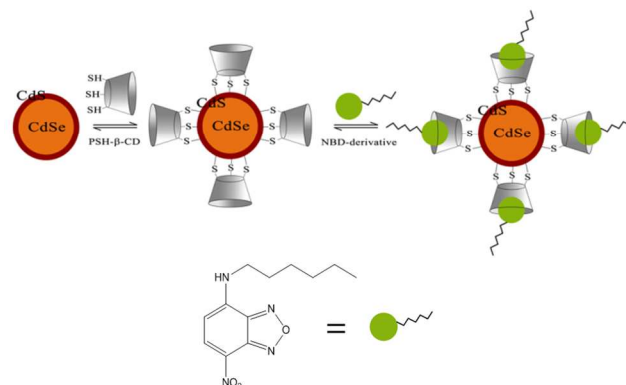
Core-shell semiconductor Quantum Dots (QDs) are becoming valuable alternatives to organic dyes for many fluorescence-based applications, owing to their unique photochemical and photophysical properties, which include high photoluminescence (PL) Quantum Yields (QY), long PL lifetimes, large extinction coefficients, good chemical and photostability, broad absorption spectra with large Stokes shifts, and size-tunable PL emission spectra.^{1,2} Moreover, the possibility to add functionality to the QD surface, through the realization of a coating layer formed by host molecules, makes these materials ideal for the realization of hybrid host-guest systems.^{3,4}

β -cyclodextrin (CD) is an organic host well known for its ability to form inclusion complexes with various guest molecules of hydrophobic nature and suitable size thanks to its special molecular structure, composed by a hydrophobic internal cavity and a hydrophilic external surface.^{5,6} CD modified QDs (CD-QDs) have received much attention as fluorescence sensors. In fact CD-QDs emission properties are strongly modified by the non-covalent interactions between the surface-anchored CD host and the molecular guest, providing a powerful molecular recognition system.^{3,7,8}

QD emission properties are modified either by Resonant Energy Transfer (RET) or by charge transfer (CT) processes occurring with molecules or with other QDs.^{8,9} While RET processes are extremely efficient in the down-conversion of the excitation,^{10,11} providing a color change in the emission, CT prevents radiative recombination of the e-h pair in the QD by inducing its dissociation and therefore act as an efficient PL quencher.¹²⁻¹⁴ Electron and energy transfer processes can therefore be designed to switch the luminescence of QDs in response to molecular recognition events, providing extremely sensitive probes¹⁵ or to efficiently sensitize the electrodes for solar cell applications.¹⁶ QDs can serve both as donors or acceptors when engaged in RET processes with chromophores.¹⁰

However, the need of good and stable emitters in the red or NIR region combined with the broad absorption spectra and high extinction coefficient of the QDs make them ideal as acceptors. Nevertheless, so far, while numerous papers report the use of QDs (mainly CdSe/CdS or CdSe/ZnS) as donors,^{11,17-19} few studies have demonstrated the use of QDs (mainly CdSe/CdZn) as acceptors.²⁰⁻²² Thanks to their strong and size-dependent photoluminescence CdSe/CdS core/shell QDs have recently been shown to be ideal candidates for the fabrication of photoswitchable and electroluminescent devices.^{23,24} Therefore the design of donor-acceptor nano-hybrids where CdSe/CdS QDs have the function of acceptors are highly desirable for optoelectronic applications.

Here we present a new host-guest hybrid system **QD/CD(3)/NBD(1)**, see Scheme 1, based on red emitting CdSe/CdS core/shell QDs functionalized with perthiolated β -cyclodextrin **CD(3)**. A green emitting nitrobenzoxadiazole derivative **NBD(1)** molecule has been inserted in the CD cavity.



Scheme 1 Schematic illustration of the synthesis of the hybrid donor-acceptor system **QD/CD(3)/NBD(1)** (top) and structure of **NBD(1)** (bottom).

We show that this hybrid system realizes an ideal nanoscale RET donor-acceptor dyad, where the organic molecule and the

QD act as donor and acceptor, respectively. The CD host, besides stabilizing the QDs and avoiding their aggregation, has the important function to keep the donor molecules at a fixed distance from the QDs, optimal for efficient RET.

2. Experiment

2.1 General

Starting materials and solvents of analytical grade were obtained from commercial sources and used without further purification. All reagents were purchased from Sigma-Aldrich. Cyclodextrin was dried under vacuum over P₂O₅ prior use. CdSe/CdS core shell QDs ($\lambda_{\text{em}}=625$ nm) dispersed in hexane were obtained from Strem Chemicals.

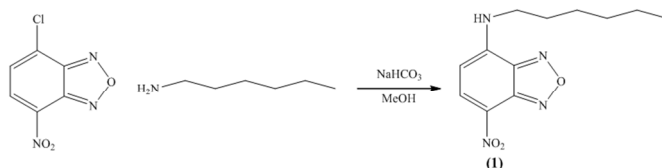
¹H NMR (300 MHz) was taken with a Bruker AMX 300 instrument. Chemical shifts are given as parts per million from tetramethylsilane. Coupling constants (*J*) values are given in hertz and are quoted to ± 0.1 Hz, consistently with NMR machine accuracy.

2.2 Synthesis

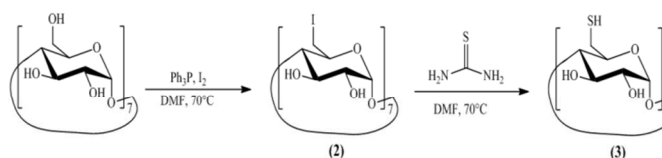
2.2.1 Synthesis of N-hexyl-4-amino-7-nitro-2,1,3-benzoxadiazoles.

4-Chloro-7-nitro-2,1,3-benzoxadiazole (NBD-Cl) (400 mg, 2 mmol) was dissolved in methanol (12 mL) and NaHCO₃ (505 mg, 6 mmol) was added. After the subsequent addition of hexylamine (0.26 mL, 2 mmol), the solution was stirred for 8 hours at room temperature. The reaction mixture was then evaporated to dryness under reduced pressure and the resulting residue chromatographed on silica gel (dichloromethane) to obtain N-hexyl-4-amino-7-nitro-2,1,3-benzoxadiazoles (or NBD-NH(CH₂)₅CH₃) (**1**) in 70% yield (melting point = 105°C).

¹H NMR (300 MHz, DMSO-*d*₆) δ 0,8 (t, 3H, CH₃), 1,25-1,5 (m, 6H), 1,8 (m, 2H), 3,5 (q, 2H), 6,1 (d, *J* = 8,7 MHz, 2H), 6,3 (s, NH), 8,5 (d, *J* = 8,7 MHz, 2H).



Scheme 2 Schematic illustration of the synthesis of the NBD-derivative compound NBD(1).



Scheme 3 Schematic illustration of the synthesis of CD(3).

The symmetric derivatization of the β -CD is made through the synthesis of the intermediate per-6-iodo- β -cyclodextrin (**2**),²⁵ by reaction with iodine and triphenylphosphine in DMF at 70°C. The latter, in the presence of thiourea at 80°C, originates the

corresponding isothiuronium salt, which, following basic hydrolysis, forms the final per-6-deoxy-6-thio- β -cyclodextrin (**3**).²⁶

2.2.2 Synthesis of per-6-iodo- β -cyclodextrin (2).

Ph₃P (3.5 g, 13.2 mmol) was dissolved in 14 mL of dry DMF through stirring. I₂ (3.5 g, 13,8 mmol) was carefully added to the solution over 10 min with the evolution of heat, until reaching approximately 50°C. Dry β -cyclodextrin (1 g, 0.88 mmol) was then added to the resulting dark brown solution, and the temperature was raised to 70°C. The resulting solution was subsequently stirred in a nitrogen atmosphere for 18 h. Heating was then discontinued and the solution concentrated under reduced pressure by removing DMF (~9 mL). NaOMe in methanol (3 M, 5.2 mL) was, therefore, added to the reaction vessel with cooling, and the reaction mixture was stirred for 30 min. It was then poured into methanol (70 mL) to form a precipitate, which was washed with methanol. Compound (**2**) (1.1 g, 70%) was finally recovered as a white powder.

¹H NMR (300 MHz, DMSO-*d*₆) δ 3.28 (t, *J* = 9 Hz, 7H), 3.34–3.48 (m, 14H), 3.54–3.68 (m, 14H), 3.80 (d, *J* = 9 Hz, 7H), 4.99 (d, *J* = 3 Hz, 7H), 5.94 (d, *J* = 2 Hz, 7H), 6.05 (d, *J* = 6.5 Hz, 7H).

2.2.3 Synthesis of per-6-deoxy-6-thio- β -cyclodextrin (3).

Thiourea (0.311 g, 4.0 mmol) was added to a stirred solution of β -cyclodextrin (1 g, 0.52 mmol) in DMF (10 mL) under nitrogen, and heated to 70°C. After 19 h, the solution was concentrated under vacuum to obtain a yellow oil, which was dissolved by addition of NaOH (50 mL, 0.12 M). After 90 min, the product was precipitated by addition of KHSO₄ (1.5 M). The precipitate was finally collected by filtration to obtain a white solid powder (**3**). (550 mg, 84 %).

¹H NMR (300 MHz, DMSO-*d*₆): δ 2,1 (t, *J*=6 Hz, 8 H, SH), 2,7 (m, 7H, H-6a), 3,2 (m, 7H, H-6b), 3,4 (m, 14H, H-2, H-4), 3,6-3,7 (m, 14H, H-3, H-5), 4,9 (d, *J*=2,8 Hz, 7H, H-1), 5,8 (s, 7H, 3-OH), 5,9 (d, *J*=6,7 Hz, 7H, 2-OH).

2.2.4 Synthesis of N-hexyl-4-amino-7-nitro-2,1,3-benzoxadiazoles/per-6-iodo- β -cyclodextrin/QDs system.

Per-6-thio- β -cyclodextrin was dissolved in 2 mL of dry DMF (50 mg, 0.04 mmol), under a nitrogen flow. 0.2 mL of the as-received solution of CdSe/CdS in hexane was quickly injected into the reaction flask, and then stirred for 2 days at room temperature. Subsequently, the mixture was evaporated to dryness under reduced pressure, and the residue washed with methanol, to remove the stabilizers of the quantum dots.

The so-obtained solid was dried in a pump and re-dissolved in DMF (50 mg in 2 mL, approximately 0.02M). Molecule (**1**) (5 mg, 0.02 mmol) was then added and the solution was stirred for one day at room temperature. The reaction mixture was evaporated to dryness under reduced pressure, and the residue (QD/CD(3)/NBD(1)) washed with THF to remove non-included molecules.

2.3 Preparation of films of nano-hybrids in PVA matrix.

Solutions of QD/CD(3)/NBD(1) and polyvinylalcohol (PVA) in water were prepared at concentrations of 90 and 10 wt%, respectively. Each solution was then sonicated for 10 min, in order to obtain a uniform and stable dispersion of nano-hybrids in PVA. Films were eventually prepared by casting 200 μ L of the

as-prepared solutions on quartz substrates.

2.4 Morphological and Optical Characterization.

AFM investigations were performed using a NT-MDT NTEGRA apparatus in tapping mode under ambient conditions with cantilevers with a resonant frequency of 80-200kHz. HRTEM measurements performed with a ZEISS HRTEM LIBRA200.

Optical absorption measurements were performed using a Perkin-Elmer Lambda-9 spectrometer. NBD molar extinction coefficient of $2.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 455 nm has been measured in THF solution, while for QDs a value of $1.2 \times 10^6 \text{ M}^{-1} \text{ cm}^{-1}$ at 500 nm in hexane is obtained.

Photoluminescence (PL) spectra were recorded by using a 270M SPEX spectrometer equipped with a N₂ cooled SPEX Jobin Yvon CCD (charge-coupled device) detector, and by exciting with a Xenon lamp connected to a Jobin Yvon Gemini monochromator for the wavelength selection. The spectra were corrected for the instrument response.

The PL quantum yields (QY) on solid-state materials were obtained using a homemade integration sphere, following the procedure reported elsewhere,²⁷ and a monochromated Xenon lamp. Photoluminescence excitation profiles (PLE) of the different systems were obtained by integrating the emission of the molecule while sweeping the excitation wavelengths. The integrations are then corrected with respect to the change in intensity of the lamp at different wavelengths by using a Rhodamine B solution as reference.

2.5 Computational Methods

As an initial guess for the TD-DFT calculations of the CD/NBD(1) complex we used the molecular geometry of the NBD molecule (optimized at the CAM-B3LYP/6-31G** level) and the structure of β -CD derived from the X-ray diffraction pattern.²⁸ The NBD(1) dye has been placed inside the β -CD cavity, with a distance between the NO₂ group of the dye and one OH group of the β -CD shorter than 3 Å. At first a coarse optimization at MP3 level has been carried out, followed by a more accurate CAM-B3LYP/6-31G** optimization with the Gaussian 09 package.²⁹ Optimizations have been carried out without geometrical constrains and with standard convergence criteria.

A few other relative configurations have been tested all of which yielded less stable structures. In particular, by pulling out, by a sizeable amount, the head of the NBD(1) molecule and re-optimizing the geometry of the complex, we always end up with a stable geometry in which the NBD(1) molecule is inside the cavity. We can thus conclude that, provided the molecule enters the cavity a stable situation is found with the head forming hydrogen bonds with the β -CD OH groups and this causes a red shift of the excitation to the first excited state.

3. Results and discussion

The NBD-NH(CH₂)₅CH₃ compound, hereafter NBD(1), has been synthesized by adding hexylamine to the starting NBD-Cl complex and exploiting the nucleophilic substitution of NBD-Cl

halogens with primary amines (Scheme 2). This class of compounds are well-known for showing different fluorescence properties depending on the chemical groups used to functionalize the NBD skeleton.^{30,31} The successful inclusion of the as-synthesized NBD(1) derivative in the CD cavity has been demonstrated through PL measurements in the solid state and quantum-chemical calculations. As shown in Table 1, the fluorescence peak position of NBD(1) blue-shifts of about 60 nm and the PL QY increases from 0.7% to 26% when the molecule is included in the CD cavity (see also Fig.S1). The low emission of NBD in the solid state is consistent with its environment sensitivity and with aggregation quenching phenomena that reduce the fluorescence properties of most organic dyes in the solid state.³² The emissive properties of the dyes can be recovered, in the solid state, by their insertion in a proper host. The organic host provides a protective environment and suppresses intermolecular interactions among the guests, so that their molecular fluorescence (typically the emission properties in diluted solutions) is restored.³³ The PL properties of CD/NBD(1) films are comparable with those of NBD(1) solutions (Table S1).

Table 1 PL QY and emission peak wavelength of cast films

	QY [%]	$\lambda_{\text{emission}}$ [nm] ^a
NBD(1)	0.7	615
CD/NBD(1)	26	546
CD(3)/NBD(1)	14	560
QD	35	625
QD/CD(3)	<1	N.A.
QD/CD(3)/NBD(1)	10	557, 622

^a Excitation 450 nm

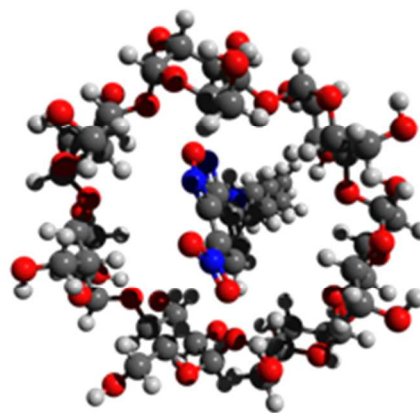


Figure 1 β -cyclodextrin/NBD(1) structure. O (red), N (blue), C (dark gray), H (light gray)

The host-guest structure obtained with the inclusion of the organic dye into β -cyclodextrin is analysed by quantum-chemical calculations. A previous quantum mechanical study on the solvatochromic behavior of NBD(1) has shown that specific intermolecular interactions can affect the optical behavior of NBD(1).³⁴ In particular, it was shown that the formation of H-bonds between NBD(1) and solvent molecules, leads to a decrease of the energy of the first dipole allowed excited state. TD-CAM-B3LYP/6-31G** calculations on the complex CD/NBD(1) indicate that the formation of a hydrogen bond

between the head of the dye and one of the OH group of the β -CD leads to a decrease of the excitation energy. In particular, in the case of a complex in which the NO_2 group of the dye forms a hydrogen bond with the OH of the β -CD (see Figure 1), it is found that the excitation energy decreases by about 0.2 eV (S_0 - S_1 transition 3.58 eV for the isolated molecule and 3.39 eV for the inclusion complex). This value correlates well with the observed decrease in the absorption maximum of the NBD(1) dye in solution with ethyl acetate (2.70 eV) with respect to the NBD(1) dye included in β -CD (2.56 eV). This complex configuration has been chosen because it is the most stable among those considered within this work. A complete mapping of the configuration space should have been undertaken, but, a complete study on the configurational space of the CD/NBD(1) inclusion complex is highly computationally demanding and it is out of the scope of the present investigation. The present calculations, however, indicate that the experimental optical spectra are consistent with the formation of the CD/NBD(1) inclusion complex.

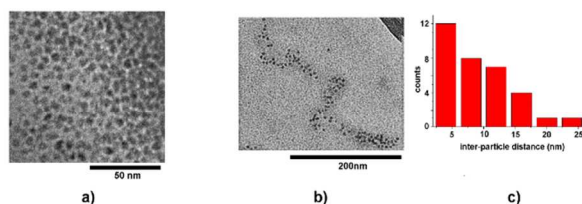


Figure 2 HRTEM details of a) QD and b) QD/CD(3) particles. c) histogram of interparticle distances from b)

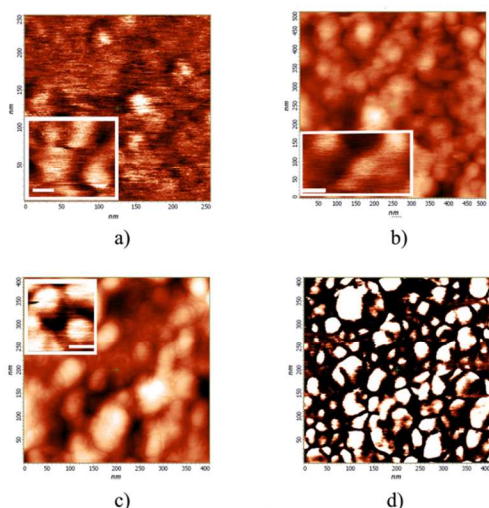


Figure 3 AFM morphology of a) QD, b) QD/CD(3), c-d) QD/CD(3)/NBD(1) cast from solution. In a-c) inset, a magnification is reported where the line-bar corresponds to 15 nm.

In order to link the CD host to the QD surface, perthiolated β -cyclodextrin CD(3), where the primary hydroxyl groups of cyclodextrin have been substituted with thiols (see Scheme 3), has been prepared. The use of thiol groups to immobilize host molecules on the surface of different nanoparticles is a common strategy since thiols are known to have a great affinity for various nanoparticles surfaces.^{35,36} Thiols act as anchoring groups to replace the oleylamine ligands of CdSe/CdS core/shell QDs. The presence of the CD(3) host molecules on the QDs surface is

confirmed by the drastic decrease of the PL QY of the QD/CD(3) nanocrystals (Table 1), while its absorption properties do not show relevant changes (Fig.S2). In fact functionalization of the QD surface with thiols has been proven to quench the nanocrystals fluorescence through CT processes.¹²⁻¹⁴

TEM analysis of QDs (Fig.2a) and cyclodextrin capped QDs (Fig.2b) shows that particle dimensions fall between 8-10 nm. The dark-grey cloud where CdSe/CdS particles are embedded in Fig.1b could be associated to cyclodextrine. In c) the histogram displaying the inter-particle distance distribution within the dark grey cloud shows that about one third of the particles are separated by distances higher than 10 nm, i.e., roughly the dimension of a CD capped particle. This suggests that about 30% of cyclodextrine surrounding the nanoparticles is not directly bonded to the QD. This excess of CD interacts with the neighbour shells thus forming a continuous cloud.

The final hybrid system is then prepared by adding NBD(1) to the CD-capped QDs (Scheme 1). The molecule is included into the hydrophobic cavities of perthiolated β -cyclodextrines, both anchored to the QDs surface and free. The introduction of the neutral dye inside the hydrophobic walls of the cyclodextrin bound to the QD surface is able to switch the QD emission on (see Table 1). As shown later, an efficient RET process, competitive with the CT process, is introduced between the dye and the QD thus switching the emission on.

AFM morphology (Fig.3) shows that particles deposited from solution in all the three cases (QD, QD/CD(3) and QD/CD(3)/NBD(1)) are mostly aggregated. However magnifications (see inlets in panel a),b) and c) of the different cases reveal a difference in shape: when covered by the CD shell or by the host-guest units, the particles become more spherical compared to the pristine case where particles appear more faceted. AFM images taken at different positions for each sample confirm the previous results.

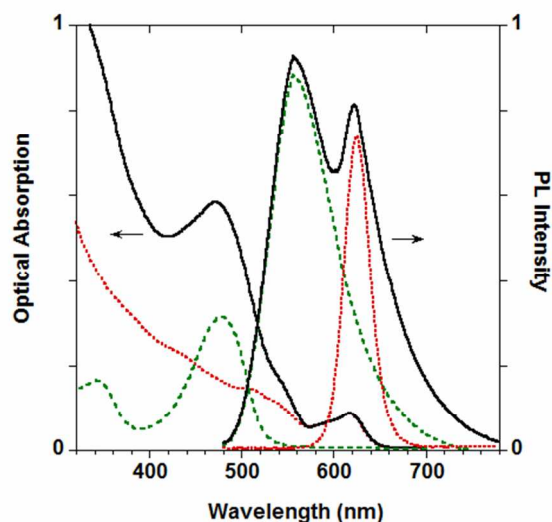


Figure 4 Absorption and PL spectra of cast films of QD/CD(3)/NBD(1) complex (black solid lines), CD(3)/NBD(1) host-guest (green dashed lines), CdSe/CdS QD (red dotted lines). PL are excited at 450 nm.

The optical properties of the hybrid host-guest system and its

components are reported in Fig.4. The absorption spectrum of the dye included in cyclodextrin is negligible at wavelengths longer than 530 nm, where the absorption spectrum of the hybrid system coincides with that of the QDs. On the other hand, below 530 nm, the spectrum of the complex shows the 470 nm band characteristic for the CD(3)/NBD(1) system. The green emission of the CD(3)/NBD(1) host-guest complex well overlaps with the broad absorption of the QDs, as requested in order to have efficient RET processes^{11,37} from the dye to the QDs. By exciting at 450 nm the hybrid composite, both the PL emissions characteristic of the dye included in CD(3) (560 nm) and of the QDs (620 nm) are observed. The presence of the host-guest emission band at 560 nm, in the hybrid film, is consistent with the presence of an excess of CD(3)/NBD(1) host-guest units. From the absorption spectrum of the hybrid film and the molar extinction coefficients of NBD(1) and QD, an experimental molar ratio of about 140 is obtained between NBD(1) and QDs while the molar ratio expected by assuming a complete coverage of the QD surface with host-guest units is about 50 (see ESI). This observation is consistent with the HRTEM analysis (see Fig.2b) showing that about 30% of free cyclodextrines forms a cloud embedding the nanoparticles. The distance among the host-guest units formed by these free CD(3) and the nanohybrids is larger than the Foerster radius³⁷ (6.7 nm) and is obtained from the spectroscopic properties of the host-guest and QDs, see ESI) and does not participate to the RET process. As a consequence an excess of host-guest units, whose distance is larger than the Foerster radius, are responsible of the 560 nm emission in the hybrid film.

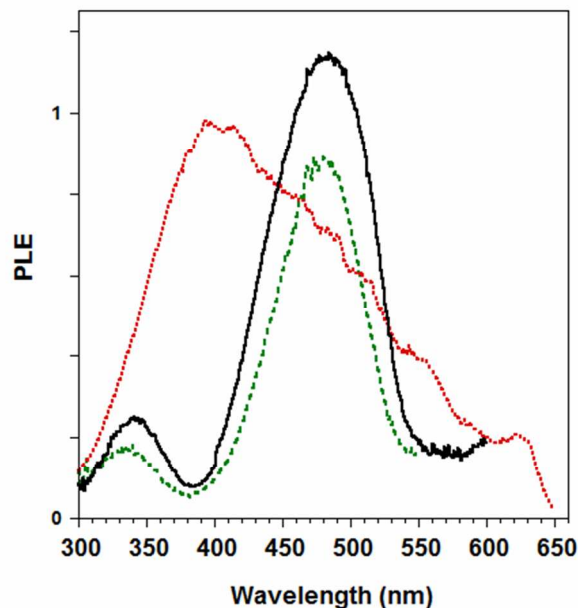


Figure 5 PLE of the QD emission (measured at 655nm) of QD/CD(3)/NBD(1) complex (black solid line) and QD (red dotted line). PLE spectrum of CD(3)/NBD(1) (green dashed line), measured at 560 nm for PVA blend films.

Upon dispersion of the hybrids into the water soluble polymer polyvinylalcohol (PVA), flat polymeric films are easily prepared embedding the nano-hybrids (see ESI). The optical properties of the films are unaltered with respect to those of the hybrid

powders,[‡] thus opening to a variety of photonic and optoelectronic applications.

In order to evidence the harvesting properties of the organic host-guest on the QD emission, we have performed PL excitation profiles (PLE) of the hybrid complex measured at 655 nm, where only the contribution of the QD emission is present. In Fig.5 we report the PLE spectra of the nano-hybrid dispersed in PVA films compared to the PLE of its two components CD(3)/NBD(1) and QD. The strict correspondence of the PLE spectrum of the QD emission in the complex with that of the CD(3)/NBD(1) host-guest demonstrates the presence of an efficient RET process from the dye to the QD in the complex. Interestingly, besides the widening of the emission spectrum (see Fig.4) induced by the simultaneous emission of the host-guest units, the overall red-shift of the PLE profile of the hybrid film, with respect to the single QDs (see Fig.5), allows to shift the excitation from 400 nm to 480 nm, better matching solar spectral properties for photovoltaic applications and reducing the use of harmful UV irradiation to produce the QD emission.³⁸

4. Conclusions

We have reported a hybrid host-guest system based on a nitrobenzoxadiazole derivative dye and CdSe/CdS QDs covered with perthiolated β -cyclodextrin. CdSe/CdS QDs function as nanoscaffolds for the immobilization of cyclodextrin, in turn used as the host compound for the inclusion of a donor chromophore. In this hybrid system resonant energy transfer from the organic dye hosted in the cyclodextrin to the QD has been demonstrated, showing, for the first time, that CdSe/CdS QDs can be used as energy acceptors in a nanohybrid system. Further work on cyclodextrines derivatized with different functional groups is under investigation in order to enhance PL efficiency.

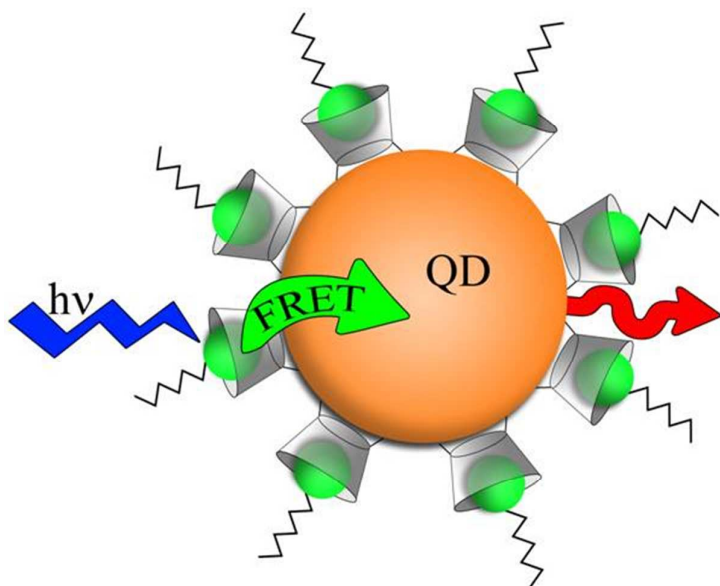
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- ^a Istituto per lo Studio delle Macromolecole, CNR, Via Bassini 15, 20133 Milano, Italy, Fax: +39.02.70636400; Tel: +39.02.23699734; E-mail: chiara.botta@ismac.cnr.it
- ^b University of Milano, Dipartimento di Chimica, Via Golgi 19, 20133, Milano, Italy.
- ^c Politecnico di Milano Dipartimento di Chimica, Materiali e Ing. Chimica CMIC "G. Natta", p.za Leonardo da Vinci 32, 20133, Milano, Italy.
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Nano-hybrids based on red emitting CdSe/CdS QDs covered by β -cyclodextrin hosting a green emitting nitrobenzoxadiazole derivative show emission harvested by the host-guest organic system through resonant energy transfer from the organic host-guest to the QD