



Photophysical behavior of zinc monoaminophthalocyanines linked to mercaptopropionic acid-capped CdTe quantum dots

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ABSTRACT

Photosensitizing properties of zinc monoaminophthalocyanine (**2**) {in the absence or presence of mercaptopropionic acid (MPA) capped CdTe quantum dots (QDs)} were compared with those of monoaminophenoxy zinc phthalocyanine (**3**), zinc tetrasulfonated phthalocyanine and zinc phthalocyanine. Complexes **2** and **3** were also linked to the MPA capped CdTe quantum dots through the formation of an amide bond. High triplet state quantum yields were obtained for the linked QD–phthalocyanine derivatives (complexes **2** and **3**) compared to when complexes **2** and **3** were mixed with MPA QDs without a chemical bond.

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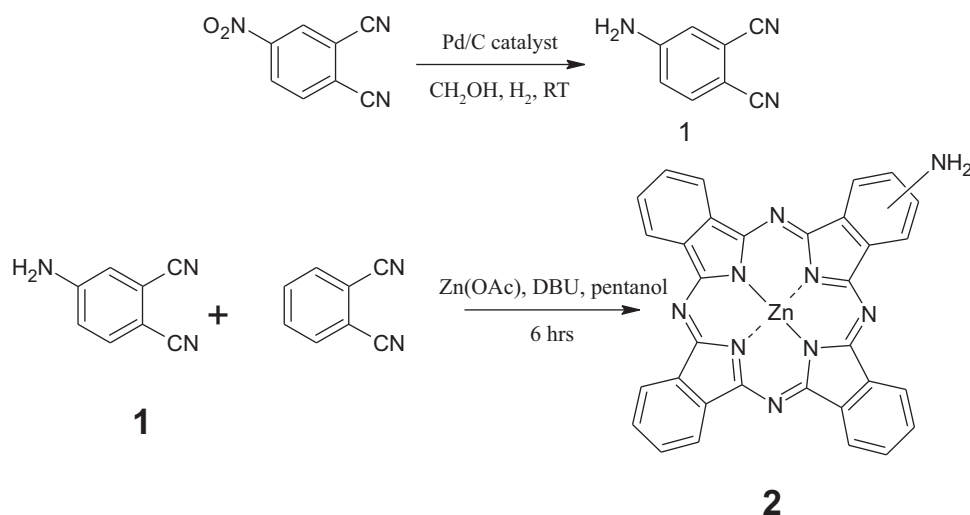
1. Introduction

Metallophthalocyanines (MPcs) have shown great potential as photosensitizers for many applications including photodynamic therapy (PDT) [1–5], due to their intense absorption in the red region of visible light, non-toxicity in the absence of light, selective localization in tumors and efficient generation of singlet oxygen [1]. For applications of MPc complexes as photosensitizers, the use of biocompatible and diamagnetic metals is required and therefore zinc is used as the central metal for this work. Until recently, the development of symmetrical tetra and octa-substituted phthalocyanines has been the main focus of research [6–8], however monofunctionalized phthalocyanines containing carboxy or amino groups are capable of covalently binding to biological targeting agents, such as monoclonal antibodies or lipoproteins, which direct the sensitizer to the tumor, without affecting the normal tissue. This provides an additional level of selectivity allowing for defined coordination.

In this work a monoamino functionalized ZnPc complex is attached to carboxylic acid functionalized quantum dots (QDs). To our knowledge, the synthesis of the monoamino functionalised ZnPc derivatives is reported for the first time. QDs are semi-conducting nanoparticles which range in size between 2 and 10 nm [9,10]. Their unique photophysical properties such as narrow emission spectra, broad absorption band, relatively high fluorescence

intensity and good photochemical stability make them ideal fluorophores with potential applications in fields such as biological labeling [11] and PDT [12]. The physical properties of QDs can be tuned to have a spectral overlap with a particular acceptor, such as phthalocyanines in our case, thereby donating energy to such acceptors. The interactions between QDs and phthalocyanines have been reported [13]. These interactions, which may lead to energy transfer between QDs and MPcs, may be electrostatic [14], by adsorption [15] or by interdigitization [16]. In this work, we study the photophysical behaviour of zinc monoaminophthalocyanine (complex **2**, Scheme 1), either physically mixed or chemically linked to CdTe QDs capped with mercaptopropionic acid (MPA QDs). It is expected that the amino group on the phthalocyanine and the carboxylic group of the MPA QD will form an amide bond on linking; resulting in a covalent attachment between the monoamino zinc phthalocyanine and MPA QD. The effects of QDs on the triplet quantum yields and triplet lifetimes of complex **2** will be studied. The effects of complex **2** on the fluorescence behaviour of QDs will also be investigated. The results are compared to those of the previously synthesized mono-aminophenoxy zinc phthalocyanine (complex **3**, Fig. 1) [17], and with ZnPc and Zn tetrasulfophthalocyanine (ZnTSPc, Fig. 1) on interaction with MPA-QDs. The studies for **2** and **3** will be done in two solvent systems: DMSO:water and DMF:water (9:1) solvent mixtures which are used to allow both QDs and ZnPc derivatives to dissolve. The studies for ZnTSPc and ZnPc will be conducted in DMSO:water. ZnTSPc is water soluble but studies are done in the presence of DMSO or DMF to prevent aggregation. The interaction of QDs with AITSPc has been reported before [15], but the interaction of these

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Scheme 1. (a) Synthesis of compound 1. (b) Synthesis of ZnAPPc derivative (2).

nanoparticles with ZnTSPc and ZnPc is reported here for the first time.

2. Experimental

2.1. Materials

Tellurium powder (200 mesh), 3-mercaptopropionic acid (MPA), dimethylsulfoxide (DMSO), dichloromethane (DCM), tetrahydrofuran (THF) and dimethylformamide (DMF) were obtained from SAARCHEM. Ultra pure water was obtained from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), N-ethyl-N(3-dimethylaminopropyl) carbodiimide (EDC), N-hydroxy succinimide (NHS) and 4-nitrophthalonitrile were purchased from Fluka. Zinc acetate dihydrate was obtained from British Drug House (BDH) Chemicals. DMSO-*d*₆, H₂O-*d*₆, Pd/C and phthalonitrile were obtained from Aldrich. Zinc phthalocyanine (ZnTSPc) was synthesized according to literature [18]. C₁₈ Phenomenex reverse phase column and Sephadex G25 column were employed for chromatographic separations. The rest of the reagents were obtained from commercial suppliers and used as received.

2.2. Equipment

Ultraviolet-visible (UV-vis) spectra were recorded on a Cary 500 UV/Vis/NIR spectrophotometer and fluorescence emission and

excitation spectra on Varian Eclipse spectrofluorimeter using a 360–1100 nm filter. Mass spectra data were collected with a Bruker AutoFLEX III Smartbeam TOF/TOF mass spectrometer. The instrument was operated in positive ion mode using a *m/z* range of 400–3000. The voltage of the ion sources was set at 19 and 16.7 kV for ion sources 1 and 2, respectively, while the lens was set at 8.50 kV. The reflector 1 and 2 voltages were set at 21 and 9.7 kV, respectively. The spectra were acquired using dithranol as the MALDI matrix and using a 355 nm nitrogen laser.

¹H NMR spectra were obtained using a Bruker AMX 400 MHz or a Bruker Advance II+ 600 MHz NMR spectrometer. Elemental analysis was carried out using a VARIO ELEMENTAR EL III CHNS instrument. FT-IR spectra were recorded on a Perkin-Elmer Universal ATR Sampling accessory spectrum 100 FT-IR spectrometer.

Laser flash photolysis experiments were performed to determine the triplet decay kinetics and transient absorption spectra. Light pulses were produced by a Quanta-Ray Nd:YAG laser providing 100 mJ, 9 ns pulses of laser light at 10 Hz, pumping a Lambda Physik FL 3002 dye (Pyridin 1 dye in methanol). Single pulse energy ranged from 1 to 3 mJ. The analyzing beam source was from a Thermo Oriel 66902 xenon arc lamp, and a photomultiplier tube (Hamamatsu) mounted to a monochromator was used as a detector. Signals were recorded with a two-channel 300 MHz digital real-time oscilloscope (Tektronix TDS 3032C); the kinetic curves were averaged over 256 laser pulses. OriginPro 7.5 was used to fit the kinetic curves in order to determine the triplet lifetimes. The transient absorption spectrum was measured in 5 nm steps between 400 and 800 nm.

Fluorescence lifetimes were measured using a time correlated single photon counting (TCSPC) setup (FluoTime 200, Picoquant GmbH). For study of the fluorescence lifetimes of the ZnPc derivatives, a diode laser (LDH-P-670 driven by PDL 800-B, 670 nm, 20 MHz repetition rate, Picoquant GmbH) was employed. For QDs, a diode laser (LDH-P-C-485 driven by PDL 800-B, 480 nm, 10 MHz repetition rate, Picoquant GmbH) was employed. Fluorescence was detected under the magic angle with a Peltier cooled photomultiplier tube (PMT) (PMA-C 192-N-M, Picoquant GmbH) and integrated electronics (PicoHarp 300E, Picoquant GmbH). A monochromator with a spectral width of about 4 nm was used to select the required emission wavelength band. The response function of the system, which was measured with a scattering Ludox solution (DuPont), had a full width at half maximum (FWHM) of about 300 ps. The ratio of stop to start pulses was kept low (below 0.05) to ensure good statistics. All luminescence decay curves were

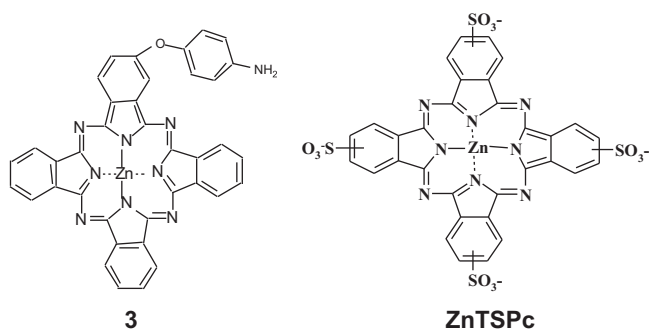


Fig. 1. Molecular structures of 4-mono-aminophenoxy zinc phthalocyanine (3) and Zn tetrasulphophthalocyanine (ZnTSPc).

measured at the maximum of the emission peak. The data were analyzed with the program FluoFit (Picoquant GmbH). The support plane approach was used to estimate the errors of the decay times.

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8, Discover equipped with a proportional counter, using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$, nickel filter). Data were collected in the range from $2\theta = 5^\circ$ to 60° , scanning at 1° min^{-1} with a filter time-constant of 2.5 s per step and a slit width of 6.0 mm. Samples were placed on a silicon wafer slide. The X-ray diffraction data were treated using the freely available Eva (evaluation curve fitting) software. Baseline correction was performed on each diffraction pattern by subtracting a spline fitted to the curved background and the full-width at half-maximum values used in this study were obtained from the fitted curves.

2.3. Photophysical parameters

2.3.1. Fluorescence quantum yields

Fluorescence quantum yields (Φ_F) of the QDs or complex **2** were determined by the comparative method [19] Eq. (1):

$$\Phi_F = \Phi_{F(\text{Std})} \frac{F \cdot A_{\text{Std}} \cdot n^2}{F_{\text{Std}} \cdot A \cdot n_{\text{Std}}^2} \quad (1)$$

where F and F_{Std} are the areas under the fluorescence curves of the QDs (or complex **2**) and the reference, respectively. A and A_{Std} are the absorbances of the sample and reference at the excitation wavelength, respectively, and n and n_{Std} are the refractive indices of solvents used for the sample and reference, respectively. ZnPc in DMSO was employed as a standard, $\Phi_F = 0.2$ [20] for complex **2**, while Rhodamine 6G in ethanol with $\Phi_F = 0.94$ was employed as the standard for the quantum dots [21,22]. Both the sample and reference were excited at the relevant wavelength (603 nm for complex **2** and 500 nm for QDs). The absorbance ranged between 0.04 and 0.05 at the excitation wavelength for all complexes. The determined fluorescence quantum yield values of the QDs were employed in determining their fluorescence quantum yields in the mixture with complex **2**, ZnPc or ZnTSPc ($\Phi_{F(\text{QD})}^{\text{Mix}}$, Eq. (2a)). For complex **2** the QDs were also chemically linked and the fluorescence quantum yield is represented as $\Phi_{F(\text{QD})}^{\text{linked}}$ Eq. (2b):

$$\Phi_{F(\text{QD})}^{\text{Mix}} = \Phi_{F(\text{QD})} \frac{F_{\text{QD}}^{\text{Mix}}}{F_{\text{QD}}} \quad (2a)$$

$$\Phi_{F(\text{QD})}^{\text{linked}} = \Phi_{F(\text{QD})} \frac{F_{\text{QD}}^{\text{linked}}}{F_{\text{QD}}} \quad (2b)$$

where $\Phi_{F(\text{QD})}$ is the fluorescence quantum yield of the QDs alone and was used as standard, $F_{\text{QD}}^{\text{Mix}}$ (or $F_{\text{QD}}^{\text{linked}}$) is the fluorescence intensity of QDs, in the mixture (or linked, for complex **2** only) with complex **2**, ZnPc or ZnTSPc, when excited at the excitation wavelength of the QDs (500 nm) and F_{QD} is the fluorescence intensity of the QD alone at the same excitation wavelength.

2.3.2. Triplet quantum yields and lifetimes

Triplet quantum yields were determined using a comparative method based on triplet decay [23] using ZnPc as the standard, Eq. (3):

$$\Phi_T^{\text{Sample}} = \frac{\Phi_T^{\text{Std}} (\Delta A_T^{\text{Sample}} \varepsilon_T^{\text{Std}})}{\Delta A_T^{\text{Std}} \varepsilon_T^{\text{Sample}}} \quad (3)$$

where $\Delta A_T^{\text{Sample}}$ and ΔA_T^{Std} are the changes in the triplet absorbance of the ZnPc derivatives and the standard, respectively. $\varepsilon_T^{\text{Sample}}$ and $\varepsilon_T^{\text{Std}}$ are the triplet state extinction coefficients for the ZnPc derivative and standard, respectively. Φ_T^{Std} is the triplet state quantum yield for zinc phthalocyanine (ZnPc) used as the standard

in DMSO, $\Phi_T^{\text{Std}} = 0.65$ [23] and $\Phi_T^{\text{Std}} = 0.58$ in DMF [24]. Φ_T was also determined for ZnPc derivatives in the presence of QDs. The Φ_T values reported in this work are an estimation since the solvents used, DMF and DMSO contain some water while the standards do not, hence the Φ_T values will be used for comparative purposes only to establish trends among the complexes discussed in this work.

2.3.3. Förster resonance energy transfer (FRET) efficiency

Förster resonance energy transfer (FRET) is a non-radiative energy transfer from a photoexcited donor fluorophore, to an acceptor fluorophore of a different species which is in close proximity. FRET efficiency (Eff) was calculated from the lifetimes of the donor (QDs), in the absence (τ_D) and presence (τ_{DA}) of the acceptor (Pc) using Eq. (4) [22,25]:

$$Eff = 1 - \frac{\tau_{DA}}{\tau_D} \quad (4)$$

This equation however, makes the assumption that the decay of the donor is a single exponential in the absence (τ_D) and presence (τ_{DA}) of acceptor and is therefore only valid for a homogeneous system (i.e. identical donor-acceptor complexes) [22]. These single-exponential decays are rare in biomolecules; so for donor-acceptor systems decaying with multiexponential lifetimes the energy transfer efficiency must be determined from the amplitude weighted lifetimes Eq. (5):

$$\tau = \sum_i \alpha_i \tau_i \quad (5)$$

where α_i is the relative amplitude contribution to the lifetime τ . As such we used the amplitude weighted time constants for τ_D and τ_{DA} to determine the transfer efficiency, for the mixed and linked species, using Eq. (4).

2.4. Syntheses

2.4.1. CdTe quantum dots

The preparation of thiol capped QDs was via a modified method adopted from literature [15,26]. Briefly, 2.35 mmol of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ was dissolved in 125 mL of water and 5.7 mmol of 3-mercaptopropionic acid (MPA) was added under stirring. The solution was adjusted to a pH between 11 and 12 with 1 M NaOH. Nitrogen gas was bubbled through the solution for about 1 h. The aqueous solution was reacted with H_2Te gas, which was generated by the reaction of NaBH_4 with Te powder in the presence of 0.5 M H_2SO_4 under a flow of nitrogen gas. A change of color of the solution containing CdCl_2 and the thiol was observed on addition of H_2Te gas. The solution was then refluxed under air at 100°C until the desired size of the CdTe QDs was obtained. On cooling, the QDs were precipitated out from solution using excess ethanol, the solutions were then centrifuged to harvest the QDs.

Sizes (D) of the synthesized QDs were estimated using the polynomial fitting function [27] Eq. (6):

$$D = 9.8127 \times 10^{-7} \lambda^3 - 1.7147 \times 10^{-3} \lambda^2 + 1.0064 \lambda - 194.84 \quad (6)$$

where λ is the absorption maxima of the QDs. The fitting function is not valid for sizes of quantum dots outside the size range 1–9 nm [27]. The QDs size was also determined using XRD. The particle diameter, d , for XRD data was determined using the Scherrer equation, Eq. (7):

$$d \text{ (\AA)} = \frac{k\lambda}{\beta \cos \theta} \quad (7)$$

where k is an empirical constant equal to 0.9, λ is the wavelength of the X-ray source (1.5405 Å), β is the full width at half maximum of the diffraction peak, and θ is the angular position of the peak. The size of the CdTe-MPA capped QD used in this work is 3.85 nm

(determined by XRD). The size is 3.45 when estimated by the polynomial, Eq. (6). Since the polynomial is just an estimate the size determined by the XRD is the one used in this work.

2.4.2. Synthesis of zinc monoaminophthalocyanine (**2**, Scheme 1)

2.4.2.1. Monoaminophthalonitrile (1) (Scheme 1a). The preparation of 4-aminophthalonitrile was via a modified method adapted from literature [28]. 4-Nitrophthalonitrile 1.0 g (0.058 mol) was placed in a round bottom flask and 250 mL of ethanol added to obtain a suspension. The catalyst Pd/C (150 mg) was added to the flask, the apparatus evacuated and then filled with hydrogen and the mixture vigorously stirred at room temperature until the absorption of hydrogen had completely stopped. The reaction mixture was subsequently filtered over celite and the solution evaporated in vacuo. Yield: 0.87 g (87%). IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3495, 3391, 3375 (NH₂), 2214 (CN). ¹H NMR (DMSO-*d*₆): δ , ppm 7.60–7.65 (1H, d, Ar-H), 7.27–7.29 (1H, d, Ar-H), 6.84–6.89 (1H, m, Ar-H).

2.4.2.2. Zinc monoaminophthalocyanine (2) (Scheme 1b). To a suspension of 1,2-dicyanobenzene (1 g, 7.8 mmol), 4-aminophthalonitrile (1, 0.38 g, 2.6 mmol) and zinc acetate (0.68 g, 3.1 mmol) in 25 mL of pentanol, DBU (10 drops) was added. The mixture was left to reflux under argon overnight with stirring. After cooling, the solution was dropped in methanol. The green solid product was precipitated and collected by filtration and washed with methanol. The product was purified by passing through a silica gel column, using 1:1 THF:DCM mixture as the eluting solvent. Yield: 0.166 g (10.3%). UV-vis (DMSO), λ_{\max} (nm) ($\log \epsilon$): 670 (5.2), 605 (4.4), 350 (4.7). IR [(KBr) $\nu_{\max}/\text{cm}^{-1}$]: 3272 (NH₂), 1602 (NH bend), 1124–1080 (CN), 718 (Zn-N). ¹H NMR (DMSO-*d*₆): δ , ppm 8.29–8.31 (7H, dd, Pc-H), 7.66–7.73 (7H, dd, Pc-H), 7.24–7.27 (1H, m, Pc-H). Anal. calcd. for C₃₂H₁₇N₉Zn: C, 64.82; H, 2.89. Found: C, 64.03; H, 2.75%. MALDI-TOF-MS (*m/z*) calcd.: 592.94. Found [*M*]⁺: 591.10.

2.4.3. Synthesis of linked QD-2 complex, Scheme 2

For the formation of the amide linked QD-2, a mixture containing 2 mM NHS, 5 mM EDC, CdTe QDs (0.001 g/mL) and complex **2** (1×10^{-4} M) in DMSO was allowed to react for 1 h. NHS and EDC were used for the activation of the carboxylic acid group of the QDs, and the resulting complex is represented as linked QD-2. Experiments where complex **2** was mixed with QDs, without chemical linking, were also performed. The same ratio of QDs to complex **2** which was used for the mixed complex was used for the formation of the linked complex. The linked QDs-2 complex was purified by first washing with water to remove excess NHS, EDC and unlinked QDs (as the linked complexes are not soluble in water only). The sample was then run through a Sephadex column to separate any residual impurities such as the unlinked complex **2** from the linked which elutes first while the remaining bands are discarded.

3. Results and discussion

3.1. Synthesis and characterization

3.1.1. MPA-QDs

The CdTe MPA QDs were hydrothermally grown to the size of 3.85 nm. The absorption and emission spectra of CdTe MPA QDs are shown in Fig. 2A, which exhibits the broad absorption and the narrow emission spectra, typical of QDs. CdTe QDs capped with thiols are known to aggregate when pH is lower than 7 due to detachment of surface ligands [29,30]. Aggregation of QDs results in red shifting in the emission spectra accompanied by broadening. Some aggregation of nanocrystals capped in organic media has also been reported [31], hence there is an importance in studying the

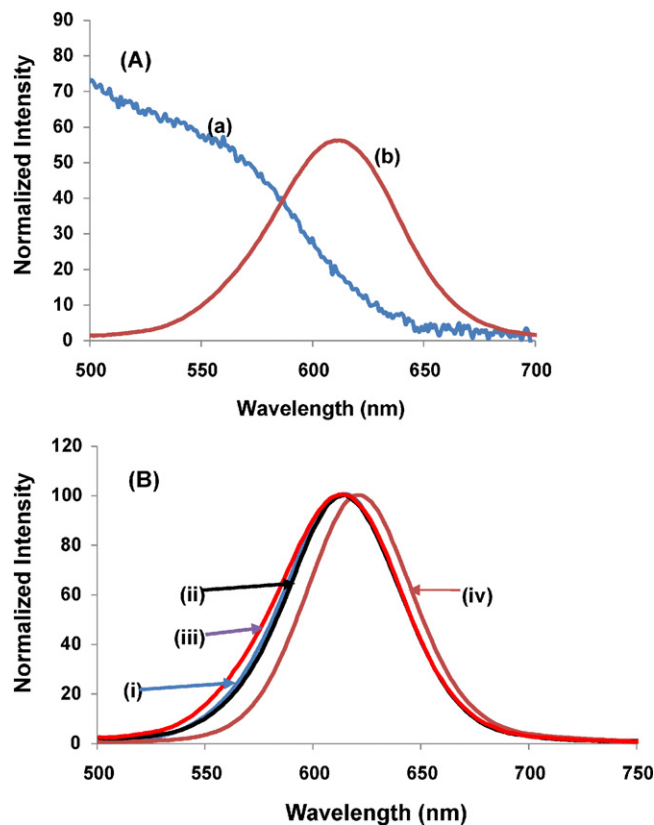


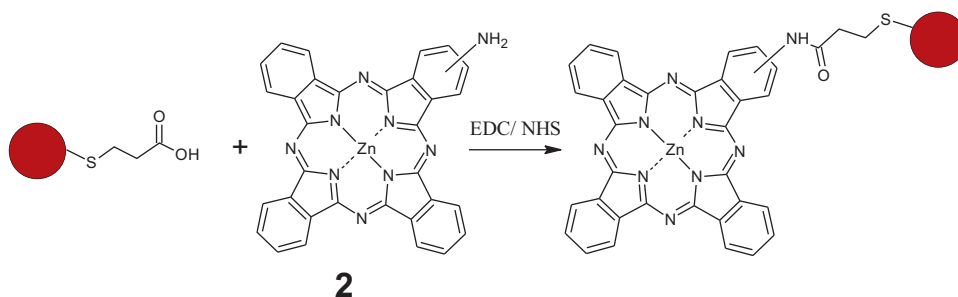
Fig. 2. (A) (a) Absorption and (b) emission spectra of QDs in DMSO:water and (B) comparison of emission spectra of QDs in (i) 0.1 M NaOH, (ii) DMF:water (9:1), (iii) DMSO:water (9:1) solvent mixtures and (iv) water. $\lambda_{\text{Exc}} = 500$ nm.

aggregation behaviour of QDs in different solvents employed in this work.

The 3.85 nm CdTe MPA QDs gave an emission wavelength of about 610 nm in 0.1 M NaOH, DMSO:water (9:1) and DMF:water (9:1) (Fig. 2B(i–iii)). The MPA QDs showed a red shift in unbuffered water alone (and without NaOH) with an emission wavelength of 621 nm, Fig. 2B(iv). The red shift suggests aggregation in water, which has a pH of slightly less than 7 (pH = 6.8). This shows that the use of a solvent mixture (or basic media) results in the blue shifting of the respective emission wavelengths. These solvent mixtures (DMF:water and DMSO:water) were employed in order to reduce the aggregated nature of the zinc phthalocyanine derivatives and to enable both ZnPc derivatives and the QDs to dissolve.

3.1.2. Complex 2

The synthesis of the dinitrile precursor (**1**), Scheme 1a, was adapted from literature [28] for similar compounds with moderate yields. The synthetic procedure outlined in Scheme 1b shows the statistical condensation approach used for the synthesis of complex **2**. This method is based on the reaction of two differently substituted phthalonitriles in a ratio of 3:1. Following extensive purification, the target compound was obtained in low yields (10%) with the Q band at 670 nm in DMSO (Fig. 3). The Beer-Lambert law was obeyed for complex **2** for concentrations less than 2.53×10^{-5} M (Fig. 3 insert). The inset in Fig. 3 does go through zero as expected for Beer's law, the plot shows the higher concentrations which are associated with aggregation. The complex is unsymmetrically substituted and it would be expected that there is some Q band splitting due to loss of symmetry, however, this is not clear from the absorption spectra in Fig. 3. Fig. 4 shows broadening (and splitting) of the excitation spectrum when compared to the absorption spectrum, suggesting loss of symmetry on



Scheme 2. Representation of the link formation of QDs to complex **2**.

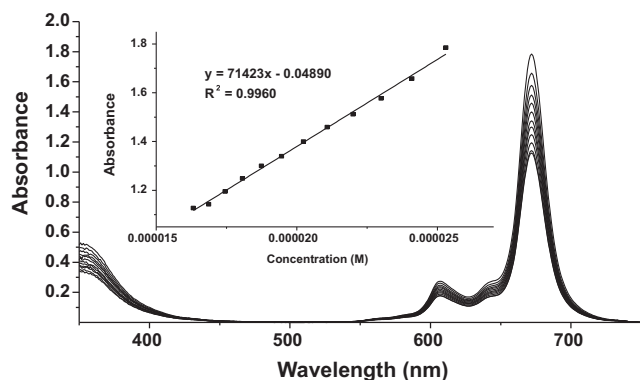


Fig. 3. Absorption spectra of **2** in DMSO at different concentrations. Inset a plot of absorbance versus concentration (1.63×10^{-5} to 2.53×10^{-5} M).

excitation due to unsymmetric nature of the molecule. The emission spectrum is also broad and split but to a lesser extent compared to the excitation spectrum. The loss of symmetry would result in the splitting of the e_g orbital (the lowest unoccupied molecular orbital) of the phthalocyanines resulting in two transitions from the highest occupied molecular orbital instead of one as is typical of low symmetry Pcs such metal free complexes [32]. A Stokes shift of 9 nm was observed and is typical of MPc complexes [20].

Absorption spectra were used for further characterization of the mixed and linked species in the DMSO:water solvent mixture (Fig. 5). Please note the shift in wavelength for complex **2** in Fig. 5 (recorded in DMSO:water) compared to Fig. 2 which was DMSO.

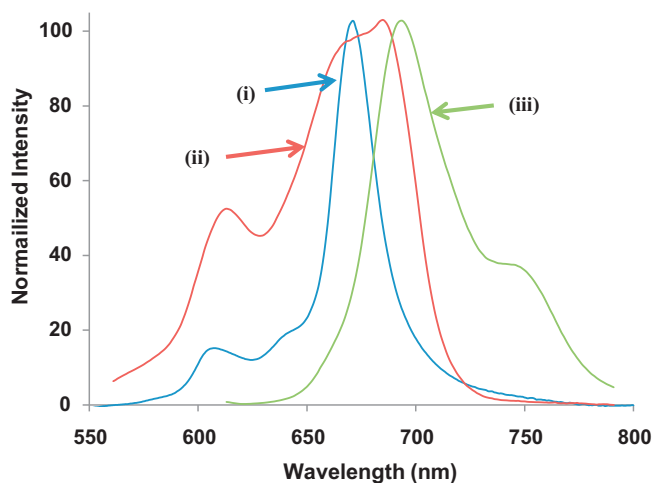


Fig. 4. Absorbance (i), excitation (emission wavelength set at 690 nm) (ii) and emission (excitation wavelength = 603 nm) (iii) spectra of complex **2** in DMSO. Concentration = 2.53×10^{-5} M for absorption spectrum and 3.15×10^{-7} for fluorescence studies. Absorbance at the excitation wavelength = 0.05.

There was only a slight shift in the Q band from 676 nm (of **2** alone) to 674 nm upon formation of the linked complex between **2** and QDs, showing changes in the environment. However, the value for **2** mixed with QDs was similar to the linked at 674 nm in DMSO:water. Small shifts in phthalocyanine spectra may be attributed to changes in the environment. There was an increase in absorption in the 500 nm region for **2** linked to QDs and **2** mixed with QDs due to the presence of QDs.

3.2. Fluorescence parameters of MPA CdTe QDs in the absence and presence of ZnPc derivatives

3.2.1. Fluorescence quantum yields

The fluorescence quantum yields for ZnPc were $\Phi_F = 0.17$ in DMSO:water, and $\Phi_F = 0.15$ in DMF:water, for ZnTSPc the values were $\Phi_F = 0.25$ and $\Phi_F = 0.19$ in DMSO:water and DMF:water, respectively, Table 1. The Φ_F value for complex **2** was determined to be 0.16 in DMSO:water and 0.14 in DMF:water, and for **3** these values are 0.16 and 0.13, respectively. These values are typical of MPc complexes containing Zn [20]. For the corresponding $\text{ZnPc}^\alpha(\text{NH}_2)_4$ which is substituted at non-peripheral positions with amino groups and the corresponding $\text{ZnPc}^\beta(\text{NH}_2)_4$ which is peripherally substituted, very low Φ_F values (0.0011 and 0.0043, respectively) were obtained in DMF [33], due to the quenching effects of the amino group. For the corresponding monosubstituted derivative discussed in this work (complex **2**) in DMF:water mixture, the value of Φ_F of 0.14 is quite high due to the presence of a fewer number of amino groups. The low value of $\Phi_F = 0.0020$ was also obtained for $\text{ZnPc}^\alpha(\text{PhNH}_2)_4$ (Ph = phenyl) [34], while the corresponding mono substituted derivative (complex **3**), gave a high value of $\Phi_F = 0.13$ in DMF:water, Table 1, showing the effects of the number of substituents. The presence of water in the solvent mixtures employed in this work is not expected to increase Φ_F values.

Fluorescence quantum yields ($\Phi_{F(\text{QD})}$) of CdTe MPA QDs were calculated using Eq. (1). The ($\Phi_{F(\text{QD})}$) of CdTe MPA QDs is 0.57 in DMSO:water. On mixing the QDs with complex **2** in DMSO:water,

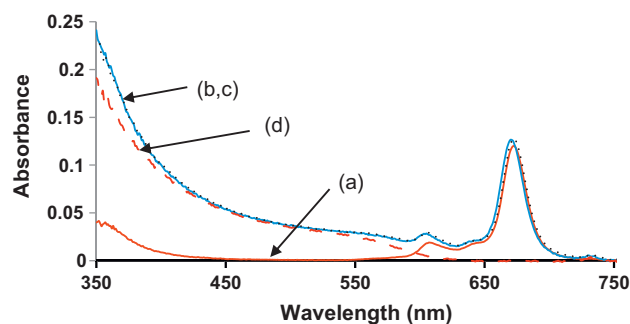


Fig. 5. Ground state electronic absorption spectra (a) **2** alone (676 nm), (b) **2**:QD mixed (674 nm) and (c) **2**-QD linked (674 nm) and (d) CdTe-MPA QDs alone in 9:1 (v/v) DMSO:water solution.

Table 1
Fluorescence quantum yield parameters for complex **2**: CdTe (size = 3.85 nm) core QD interaction in DMSO:water (9:1) or DMF:water (9:1) mixture for both the linked (complexes **2** and **3** only) and mixed (complexes **2**, **3**, ZnPc and ZnTSPc) complexes.

ZnPc derivative	Solvent	$\Phi_{F(\text{ZnPc})}$	$\Phi_{F(\text{QD})}^{\text{Mix}} (\lambda_{\text{Exc}} = 500 \text{ nm})^{\text{a}}$	$\Phi_{F(\text{QD})}^{\text{linked}} (\lambda_{\text{Exc}} = 500 \text{ nm})$	Reference ^b
2	DMSO:water	0.16 ($\lambda_{\text{Exc}} = 615 \text{ nm}$)	0.06	0.06	TW
2	DMF: water	0.14 ($\lambda_{\text{Exc}} = 615 \text{ nm}$)	0.03	0.01	TW
3	DMSO: water	0.16 ($\lambda_{\text{Exc}} = 611 \text{ nm}$)	0.21	0.04	17
3	DMF: water	0.13 ($\lambda_{\text{Exc}} = 611 \text{ nm}$)	0.18	0.09	TW
ZnPc	DMSO: water	0.17 ($\lambda_{\text{Exc}} = 613 \text{ nm}$)	0.13	–	TW
ZnPc	DMF: water	0.15 ($\lambda_{\text{Exc}} = 613 \text{ nm}$)	0.08	–	TW
ZnTSPc	DMSO:water	0.25 ($\lambda_{\text{Exc}} = 627 \text{ nm}$)	0.11	–	TW
ZnTSPc	DMF: water	0.19 ($\lambda_{\text{Exc}} = 620 \text{ nm}$)	0.31	–	TW

^a $\Phi_{F(\text{QDs})}$ alone ($\lambda_{\text{Exc}} = 500 \text{ nm}$) in DMF:water = 0.58 and in DMSO:water = 0.57.

^b TW = this work.

the ($\Phi_{F(\text{QD})}$) of CdTe MPA QDs decreases to 0.06 with the linked species giving the same value. This decrease was also reported for complex **3**, Table 1 [17], and is also observed on mixing with ZnPc and ZnTSPc, Table 1 for DMSO:water solutions. The Φ_F value of QDs alone in DMF:water is 0.58, and shows a decrease on mixing or linking for complexes **2** and **3**, Table 1. The decrease in ($\Phi_{F(\text{QD})}$) of CdTe MPA QDs in the presence of ZnPc derivatives has been observed before [15,35,36] and was attributed to the transfer of energy from the donor QDs to the phthalocyanine acceptor molecules. Non-radiative (NR) decay processes may also be used to account for the decline in Φ_F values. There is only one linking point for the QD onto complex **2**, but it is possible that more than one Pc molecules are linked to QDs. We have earlier reported that one or two MPc molecules is associated to one QD depending on the size of the QD [15,37], for the mixed MPc:QDs conjugates. This is also possible for the linked QDs–complex **2** conjugates.

3.2.2. Fluorescence lifetimes

Fluorescence lifetimes (τ_F) were determined in a DMSO:water or DMF:water 9:1 (v/v) mixture, the data obtained is shown in Tables 2 and 3, respectively. Photoluminescence decay curves of CdTe MPA QDs (alone or linked to complex **2**) in DMSO:water (9:1) solvent mixture on excitation at 480 nm are shown in Fig. 6. The quality of the fit was judged on the basis of χ^2 values which were close to unity, Tables 2 and 3.

Tables 2 and 3 show that changing the solvent has an effect on the fluorescence lifetimes for all samples. For complexes **2** and **3**, two lifetimes are observed, however the second lifetimes are insignificant with an amplitude of less than or close to 0.1. The lifetimes are in the reported range for ZnPc derivatives [38]. The second lifetimes (corresponding to a species that are present in insignificant amounts) could be due to traces of ZnPc(NH₂)₄. Although biexponential decay kinetics have been shown to occur for QDs [36], this report presents the presence of triple decay kinetics, Fig. 6a and b, which have also been observed by other researchers [39]. The longer lifetime component τ_{F1} may be due to the involvement of surface states in the carrier recombination process [40], where the increase in radiative lifetime as a result of trapping of carrier states, by surface states, is a well-established feature [40]. This is clearly observed by the large decrease in τ_{F1} (for QDs at 18.8 ns in DMF:water) compared to τ_{F2} and τ_{F3} , due to attachment or mixing of Pcs which affects the surface, resulting in the shorter fluorescence lifetime. The second fluorescence lifetime component (τ_{F2}) is a result of radiative electron–hole recombination processes due to surface defects [41]. According to some researchers [25,39,41] the shortest component, τ_{F3} is caused by the band-edge recombination at the surface; but this is contradicted by others who attribute this short lifetime to intrinsic recombination of initially populated core states [40,42–44]. As expected, the mixed conjugates show longer lifetimes than the linked, though the changes are insignificant in DMF:water, for complex **2** (for all lifetimes) and complex **3**, the

third lifetime. The reasons for the differences in the fluorescence lifetime behaviour of QDs linked or mixed with complexes **2** and **3** are not clear, but they could be related to the presence of a phenyl linker between the Pc ring and the amino group in **3**, and the direct coordination of the amino group in **2**. Judging by a larger decrease in the long lifetime (τ_{F1}) in the presence of complex **3** compared to **2**, the former attaches to the QDs surface more efficiently in both DMF:water and DMSO:water, Tables 2 and 3. It is however not clear why τ_{F1} for complex **2** mixed with QDs or linked to them remain the same in DMF:water. We can only postulate that since the NH₂ group is directly on the ring for complex **2**, the distances between the QDs and Pc in the linked and mixed are not too different and hence affect the fluorescence lifetimes the same way. However, this is solvent dependent since in DMSO:water, there is a difference in τ_{F1} for linked and mixed complexes. The covalent bond in the linked conjugates allows a closer proximity between the QD and Pc deriva-

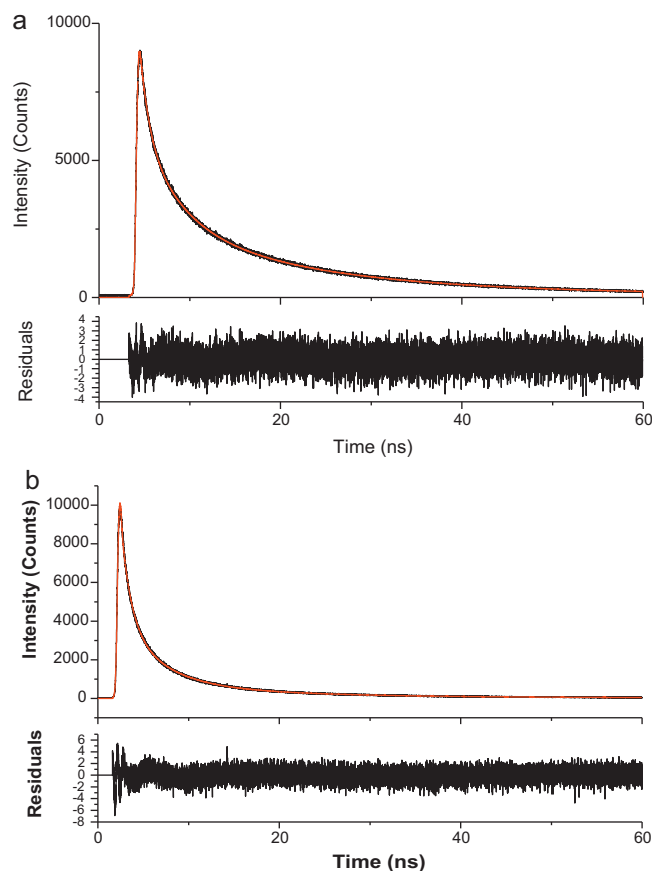


Fig. 6. Photoluminescence decay curves of (a) CdTe QDs and (b) CdTe QDs in the presence of **2** in DMSO:water (9:1) solvent mixture.

Table 2Fluorescence lifetimes of QDs in the presence of complexes **2** and **3** in DMSO:water (9:1). $\lambda_{\text{Exc}} = 480$ nm unless otherwise stated.

Compound	τ_{F1} (ns) (± 2.7)	Rel. A_1	τ_{F2} (ns) (± 1.2)	Rel. A_2	τ_{F3} (ns) (± 0.2)	Rel. A_3	χ^2	Eff_{tr}
Complex 2 alone ^a	3.0	0.90	4.1	0.10	–	–	1.06	–
Complex 3 alone ^a	3.0	0.92	4.3	0.08	–	–	1.11	–
MPA QDs alone	19.0	0.23	4.8	0.33	0.9	0.45	1.04	–
QDs mixed with 2	16.7	0.21	4.2	0.33	0.8	0.45	1.03	0.17
QDs linked to 2	9.0	0.15	2.6	0.30	0.5	0.55	1.07	0.62
QDs mixed with 3	14.1	0.25	3.8	0.37	0.8	0.38	1.29	0.18
QDs linked to 3	8.5	0.16	3.1	0.34	0.6	0.50	1.37	0.57

^a $\lambda_{\text{Exc}} = 670$ nm.**Table 3**Fluorescence lifetimes of QDs in the presence of ZnPc derivatives in DMF:water (9:1). $\lambda_{\text{Exc}} = 480$ nm unless otherwise stated.

Compound	τ_{F1} (ns) (± 1.5)	Rel. A_1	τ_{F2} (ns) (± 0.6)	Rel. A_2	τ_{F3} (ns) (± 0.2)	Rel. A_3	χ^2	Eff_{tr}
Complex 2 alone ^a	3.0	0.94	1.2	0.06	–	–	1.02	–
Complex 3 alone ^a	3.0	0.93	1.0	0.07	–	–	1.13	–
MPA QDs alone	18.8	0.20	5.6	0.4	1.4	0.40	1.07	–
QDs mixed with 2	12.2	0.12	3.4	0.35	0.8	0.53	1.10	0.53
QDs linked to 2	12.1	0.12	3.4	0.35	0.8	0.53	1.27	0.53
QDs mixed with 3	11.1	0.06	3.1	0.27	0.7	0.68	1.32	0.70
QDs linked to 3	9.8	0.1	2.8	0.34	0.7	0.56	1.30	0.65

^a $\lambda_{\text{Exc}} = 670$ nm.

tive, further encouraging the possibility of FRET or the radiationless loss of energy through the bonds.

3.3. Triplet quantum yields (Φ_T) and lifetimes (τ_T) of ZnPc derivatives in the presence of MPA CdTe QDs

The transient absorption spectra were recorded in argon-degassed solutions by exciting the photosensitizer (in DMSO) in the Q band region and recording the spectra point by point from 400 to 800 nm (see Fig. 7). A representative decay profile is shown in Fig. 8. The data in Fig. 7 are obtained using absorbances from a series of traces similar to the one shown in Fig. 8 at different wavelengths. Fig. 7 shows singlet depletion and a very weak triplet-triplet absorption at 500 nm (Fig. 7 inset) in DMSO.

Triplet quantum yields (Φ_T) are a measure of the fraction of absorbing molecules that undergo intersystem crossing (ISC) to populate the triplet state. The triplet quantum yields studies of the monofunctionalized Pcs in the presence of QDs (mixed or linked), were carried out in a DMSO:water or DMF:water 9:1 (v/v) mixtures and are shown in Table 4. Values of $\Phi_T = 0.48$ and 0.39 in DMSO:water and DMF:water, respectively, are observed for **2**. For the corresponding ZnPc $^{\alpha}(\text{NH}_2)_4$ or ZnPc $^{\alpha}(\text{PhNH}_2)_4$ which are substituted at non-peripheral positions with amino or phenylamino groups, respectively, triplet-triplet absorption did not occur [33,34], due to the quenching of the first excited singlet state by

the presence of amino group, inhibiting the formation of its triplet state by intersystem crossing. Even though DMF was employed for ZnPc $^{\alpha}(\text{NH}_2)_4$ and ZnPc $^{\alpha}(\text{PhNH}_2)_4$ and this work DMSO:water is employed, the quenching effect of the amino group is not expected to be affected much by the differences in solvents. However, in case of complexes **2** and **3** triplet state parameters were observed due to the presence of only one amino (or phenyl amino) group resulting in less quenching.

It is expected that the Φ_T of MPA complexes will increase in the presence of QDs due to the heavy atom effect of the atoms making up the QDs. However, for complex **2**, there is an increase only on linking but a decrease on mixing in DMSO:water. For complex **3**, there is no change on mixing, but an increase on linking with QDs in DMSO:water. In DMF:water there is a decrease for both linked and mixed complexes **2** and **3**. The lifetimes for complexes in DMF:water are very short. Triplet lifetime values decreased where there is an increase in triplet yields as expected by the heavy atom effect.

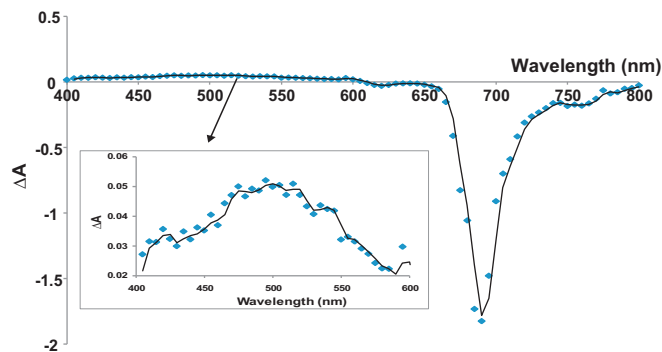


Fig. 7. Transient differential spectrum of complex (**2**) in DMSO. Excitation wavelength = 672 nm. Inset: expansion of the transient absorption between 400 and 600 nm. Absorbance at the excitation wavelength = 1.5.

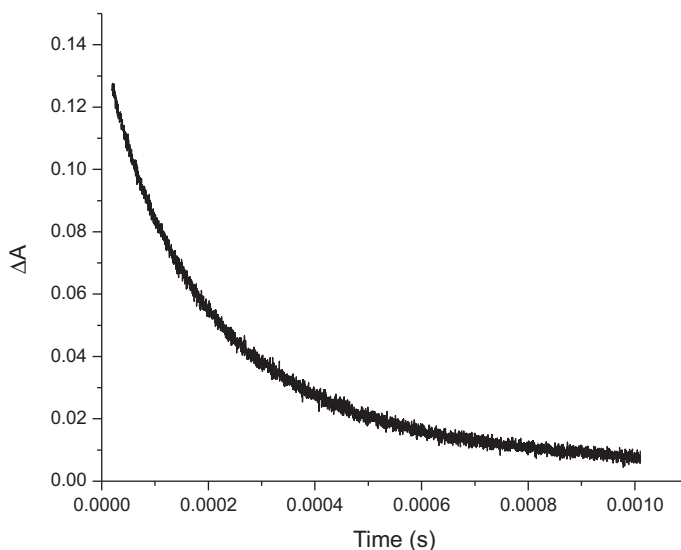


Fig. 8. Triplet decay curve of complex (**2**) in DMSO at 490 nm. Excitation wavelength = 672 nm. Delay time ~ 20 μs .

Table 4
Photophysical parameters of ZnPc in the presence of QDs in DMSO:water or DMF:water (9:1).

Compound	DMSO:water (9:1)		DMF:water (9:1)	
	Φ_T	τ_T (μ s)	Φ_T	τ_T (μ s)
Complex 2 alone	0.48	208	0.39	3.1
Complex 2 mixed with QDs	0.32	221	0.34	5.2
Complex 2 linked to QDs	0.60	186	0.31	4.0
Complex 3 alone	0.65	216	0.37	3.6
Complex 3 mixed with QDs	0.64	206	0.25	2.7
Complex 3 linked to QDs	0.69	205	0.21	5.3

3.4. Determination of FRET parameters

The FRET efficiencies were calculated using Eqs. (4) and (5) and are shown in Tables 2 and 3 for DMSO:water and DMF:water solvent systems. Only a very weak stimulated emission was observed as shown in Fig. 8 for complex **3**, on excitation. It is important to note that FRET can be detected by appearance of the fluorescence of the acceptor or by quenching of the donor fluorescence. The efficiency of FRET is dependent upon donor acceptor proximity whether the acceptor is fluorescent or not [45]. Apart from the fact that the amino substituted MPc complexes show low fluorescence due to the quenching discussed above, clear observation of stimulated emission of the acceptor depends on the solvents employed since the energy can be lost through equilibration with the solvent. In this work solvent mixtures containing a low water content (DMSO:water or DMF:water (9:1)) were employed. The stimulated emission is best observed in aqueous media using QDs and water soluble and non-aggregated MPc derivatives [15]. As stated above, solvents do affect the surface states of QDs hence affect their fluorescence behaviour. Aggregation state of MPc complexes also does affect the observation of stimulated emission [35,36]. Several solvent mixtures were tested for the current studies and the best mixture for dissolving both QDs and MPc derivatives while preventing aggregation of the latter were 9:1 DMSO:water or DMF:water. Increasing the water content does assist in the observation of stimulated emission [27], however in the current work increasing the water content did result in the aggregation of the MPc derivatives (Fig. 9).

The values obtained in Table 2 show that the E_{ff} for the mixed QD–Pc are very low <20%; whereas the linked species show an E_{ff} > 50% for both complexes **2** and **3**. The larger FRET efficiency is expected for the linked complexes due to the presence of a bond. It is feasible that the FRET efficiency observed for the linked species also comprises non-radiative processes, due to the strong involvement of surface states that may deactivate the QD fluorophores. Thus the data obtained may not be a true reflection of FRET alone, hence the weak stimulated emission in Fig. 8.

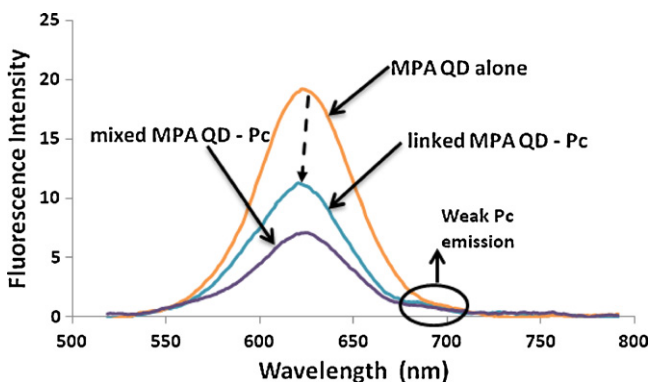


Fig. 9. Emission of QDs alone, MPA QDs in the mixture with complex **3** or complex linked to QDs ($\lambda_{exc} = 500$ nm, in (9:1) DMSO:water solvent mixture).

4. Conclusions

The low-symmetry derivative monoamino zinc phthalocyanine has been successfully synthesized using the statistical condensation method. Triplet quantum yields have been determined for complex **2** in DMSO:water and DMF:water mixtures. The solvent mixture plays a major role, with the species in the DMSO:water mixture generally giving higher triplet quantum yields and longer triplet lifetimes when compared to their respective species in the DMF:water solvent system. The newly synthesized low-symmetry derivative **2** shows good photosensitizing properties which may make them useful as a photosensitizer.

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