

Fluorescence studies of quantum dots and zinc tetraamino phthalocyanine conjugates

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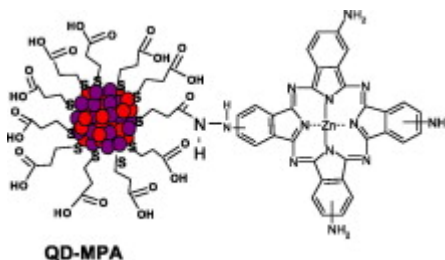
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Abstract

CdTe Qds capped with mercapto propionic acid (MPA) were covalently linked to zinc tetraamino phthalocyanine (ZnTAPc) using *N*-ethyl-*N*(3-dimethylaminopropyl) carbodiimide (EDC) and *N*-hydroxy succinimide (NHS) as the coupling agents. The results presented give evidence in favour of the formation of an amide bond between ZnTAPc and CdTe QDs. Both the linked ZnTAPc–QD complexes and a mixture of QDs and ZnTAPc (i.e. without chemical linking) showed Förster resonance energy transfer (FRET). ZnTAPc quenched the QDs emission, giving quenching constants in the order of 10^3 M^{-1} .

Graphical abstract

Chemical linking of CdTe Qds capped with mercapto propionic acid (MPA) to zinc tetraamino phthalocyanine (ZnTAPc) showed Förster resonance energy transfer (FRET).

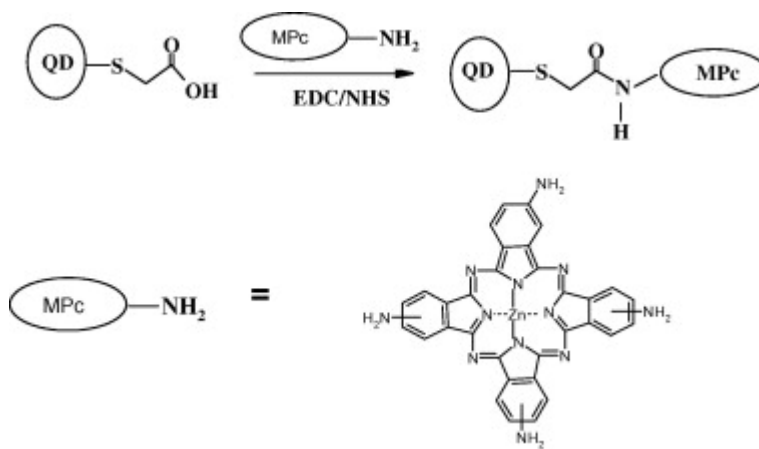


Quantum dots (QDs) are nano-sized semiconductor crystals which exhibit size-dependent physico-chemical properties such as a tunable, narrow emission spectrum, excellent photostability and a broad excitation spectrum [1], [2], [3], [4], [5], [6] and [7]. All these properties allow the exploitation of QDs in a variety of fields. Some applications include biological labeling, use in photodynamic therapy (PDT) [8] and in non-linear optics [9].

Metallo phthalocyanines (MPcs) are a family of promising photosensitizers for a variety of applications such as in PDT [10] and non-linear optics (NLO) [11] and [12]. Their distinctive properties such as intense absorption in the red region of the visible spectrum, effective singlet oxygen generation, coupled with their non-toxicity (in the absence of light) [13], [14] and [15] have made them a focus of extensive research.

Energy transfer from QDs to different phthalocyanine photosensitizers has been demonstrated in a number of studies [16], [17], [18] and [19]. The photosensitizer accepts this energy from the QDs in a process known as Förster resonance energy transfer (FRET). FRET is a non-radiative energy transfer between the fluorescent donor and a suitable acceptor [8]. Apart from a report on the conjugates of SiPc with CdSe QDs through axial ligation [20], the chemical coordination of QDs to the Pc ring has not received much attention. In most reported studies, quantum dots were not chemically bound to phthalocyanines. In this work, CdTe QDs are chemically linked to the periphery of zinc tetraamino phthalocyanines (ZnTAPc, [Scheme 1](#)) using linking agents. *N*-ethyl-*N*(3-dimethylaminopropyl) carbodiimide (EDC) and *N*-hydroxy succinimide (NHS) were employed as linking agents, catalyzing the formation of the amide bond between the carboxylic acid of QDs and the amine groups of the ZnTAPc. Jiang et al. [21] have estimated that when using a mixture of EDC and NHS, about 60% of carboxylic acid groups are NHS-activated and 30% EDC-activated leaving only 10% not activated. The QDs–ZnTAPc

complex was purified of unlinked QDs by precipitating it out with THF and then ethanol, which was afterwards evaporated off, thus ensuring that the effects of mixed QDs:ZnTAPc (not chemically linked) are eliminated. Ethanol was employed since neither QDs nor ZnTAPc dissolve in this solvent. It is possible for more than one amino group of the ZnTAPc to be linked to the QDs.



Scheme 1. Linking of QD to ZnTAPc using EDC/NHS as coupling agents. MPC-ZnTAPc and QD represents CdTe QDs.

Fig. 1 shows the UV-Vis spectrum of ZnTAPc, typical of amino phthalocyanine complexes, with a Q band at 710 nm in DMF/water (3:2). This solvent mixture was used in order to enable both ZnTAPc and the QDs to dissolve. The UV/visible spectra showed that there is only a 2 nm shift of the Q band from 710 nm (for ZnTAPc alone in DMF:water) to 708 nm for linked QD-ZnTAPc and mixed QD-ZnTAPc.

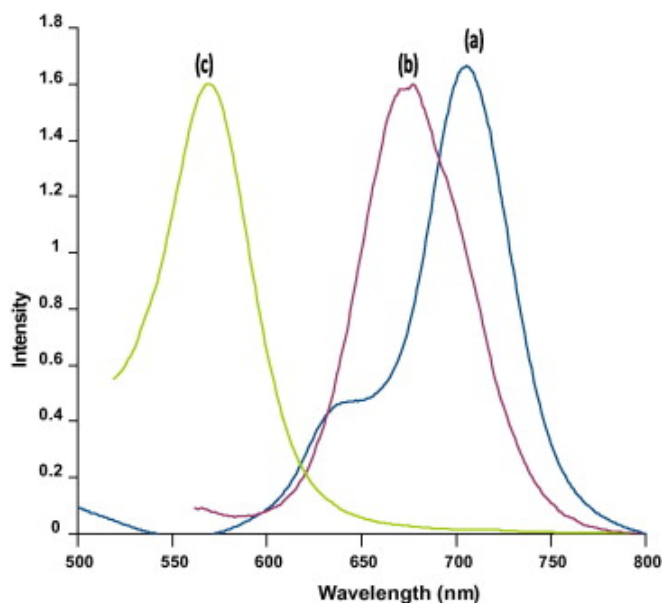


Fig. 1. Normalized absorption spectrum of (a) ZnTAPc in DMF:water (3:2), (b) emission spectra of 3.6 nm size CdTe QD and (c) 3 nm size CdTe QD DMF:water (3:2) solutions, showing overlap of the emission spectra of the CdTe QDs with the absorption spectrum of ZnTAPc. Excitation = 510 nm.

QDs grow through the Ostwald ripening process during the course of heating. As they grow, both the absorbance and the emission spectra shift to longer wavelengths. The mercaptopropionic acid (MPA) capped CdTe QDs displayed their first emission peak at 512 nm after 30 min of refluxing and were grown until their emission peak reached a maximum of 746 nm indicating different sizes. CdTe QDs were mixed with ZnTAPc in the absence of EDC/NHS (represented as mixed QD:ZnTAPc). For the mixed QD:ZnTAPc, the mode of interaction is most likely adsorption. Studies where QDs were coupled with ZnTAPc using EDC/NHS, (complex represented as linked QD–ZnTAPc) were also carried out.

In order to establish our assumption of the formation of a link (amide bond), between the QDs and ZnTAPc, IR spectroscopy was carried out, [Fig. 2](#). In the linked QD–ZnTAPc, there was an indication of amide bond formation by the presence of a band at 3400 cm^{-1} (ν_{NH} (CONH)). In addition, a band characteristic of the amides was observed at about 1654 cm^{-1} in the linked complex, while it was not observed in ZnTAPc alone or in the mixture of QDs with ZnTAPc. Raman spectra were additionally employed to characterize the new complex, [Fig. 3](#). What was observed as predominantly different between the mixed QD:ZnTAPc and the linked QD:ZnTAPc was the absence of the peaks between 3000 and 3300 cm^{-1} , attributed to the QD structure, and absence/reduction of the peaks around 1500 cm^{-1} , attributed to the ZnTAPc structure, in the linked QD:ZnTAPc Raman spectrum, whereas these peaks were present in the mixed QD:ZnTAPc Raman spectrum.

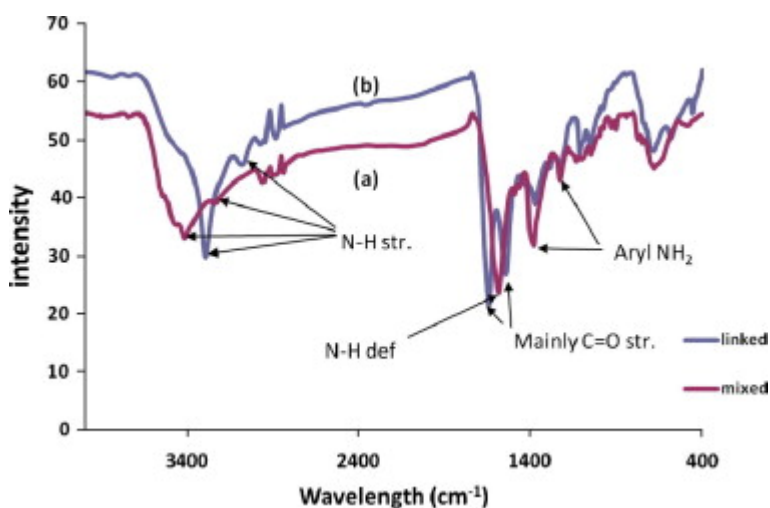


Fig. 2. IR spectra of ZnTAPc + CdTe-MPA mixed (a) and ZnTAPc – CdTe-MPA linked (b).

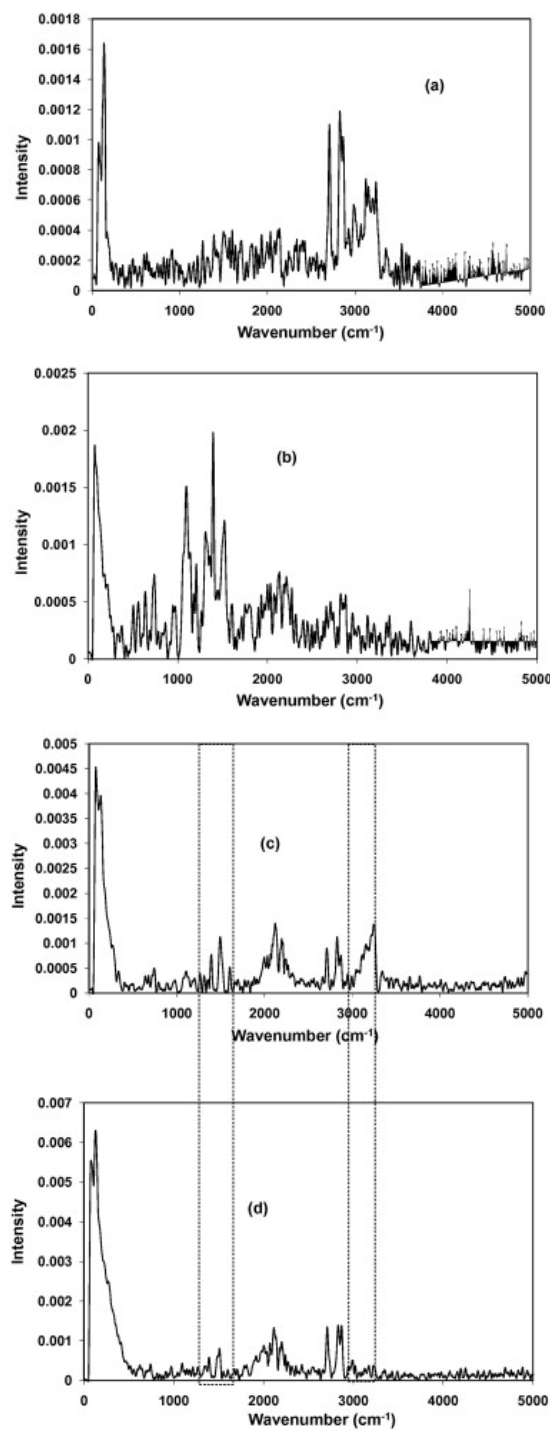


Fig. 3. Raman spectra of (a) QDs alone, (b) ZnTAPc alone, (c) mixed ZnTAPc-QDs and (d) linked ZnTAPc-QDs.

Fig. 1 shows that an overlap exists between the emission spectra of the CdTe QDs (donor, 3.6 nm) and the ZnTAPc (acceptor) absorption spectrum. This is a good indication that energy transfer is possible from the CdTe QDs to the ZnTAPc. There is less overlap between ZnTAPc and the slightly smaller 3 nm QDs, Fig. 1. However, both QDs were studied for FRET.

In order to observe FRET, excitation was carried out at 550 nm where QDs absorb (Fig. 4A, inset) but ZnTAPc (in 3:2 DMF:water) does not (Fig. 1). No fluorescence was observed for the ZnTAPc upon excitation at 550 nm, Fig. 4A (curve b). Fig. 4 (curves c and d) shows a clear, but weak, emission peak at 750 nm for the QDs:ZnTAPc (linked or mixed, QDs size 3.6 nm) on excitation at this same wavelength (550 nm). This observation of ZnTAPc emission in the presence of QDs, confirms energy transfer from QDs to ZnTAPc. When excited at 650 nm where only ZnTAPc absorbs, emission peak of ZnTAPc was observed at 750 nm, showing a very high stokes shift for an MPc complex. The stimulated emission observed for the linked (QD–ZnTAPc), Fig. 4, is, however, weaker than that for the mixture (QD:ZnTAPc), though the relative amounts of ZnTAPc and QDs will be different in the mixed and linked QD–ZnTAPc, making comparison difficult. The FRET from 3.6 nm QDs will be affected by interference from QDs emission which extends to the wavelength of ZnTAPc emission, resulting in less resolved peaks. When smaller QDs (3 nm, which did not show much overlap with ZnTAPc absorption) were employed, FRET was still observed, and with more resolved peaks, Fig. 4B.

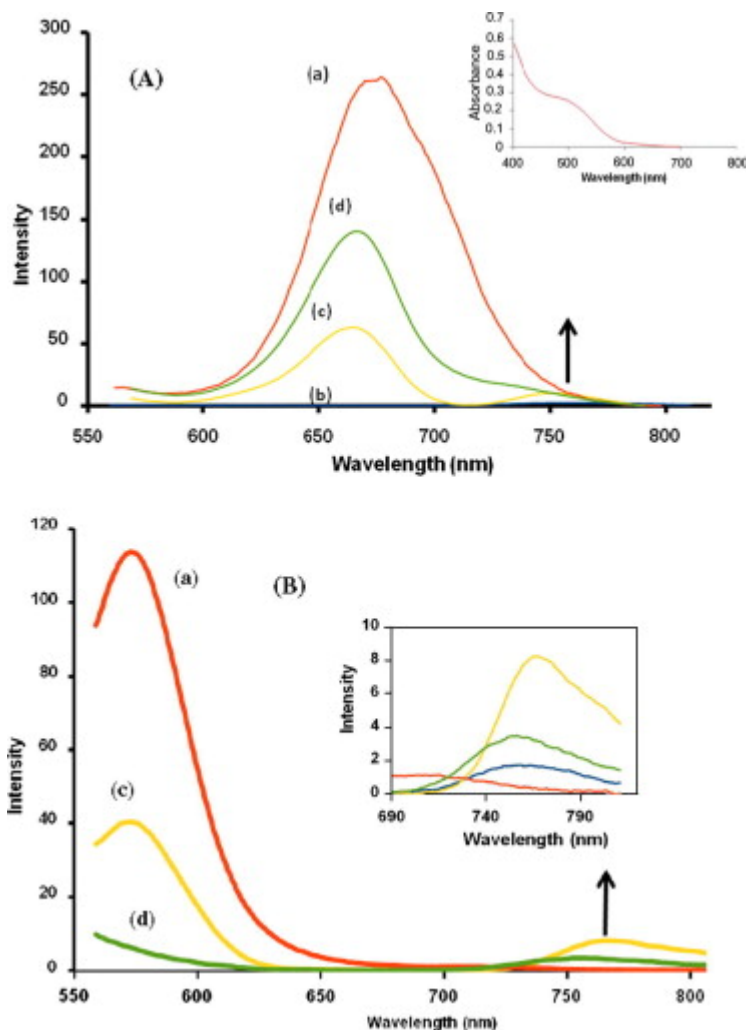


Fig. 4. Emission of (a) QDs alone, (b) ZnTAPc alone, (c) mixed QD:ZnTAPc, (d) linked QD:ZnTAPc in DMF:water (3:2). (A) is 3.6 nm CdTe-MPA; (B) is 3 nm CdTe-MPA. Excitation wavelength = 550 nm. Inset in A: Absorption spectra of QDs. Inset in B: expanded area for stimulated emission of ZnTAPc.

The changes in the fluorescence emission spectra of the 3 nm CdTe QDs (3.7 mg/mL) in the presence of a range of concentrations ($0-7.78 \times 10^{-5}$ M) of the ZnTAPc (hence mixed QD–ZnTAPc) are shown in Fig. 5. The changes observed in Fig. 3, are due to the quenching of the fluorescence of the CdTe QDs by the ZnTAPc, due to energy transfer as discussed above. The QDs fluorescence was found to decrease progressively with increasing concentration of ZnTAPc.

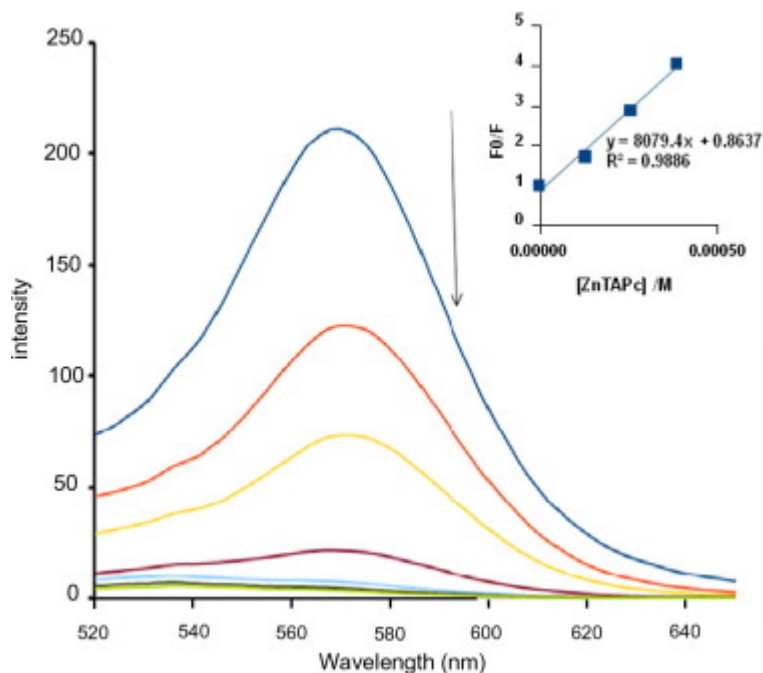


Fig. 5. Emission spectra of CdTe-MPA QDs in DMF:water (3:2) in the presence of increasing concentrations of ZnTAPc.

Using Eq. (1), a plot of $\frac{F_0}{F}$ against $[ZnTAPc]$, Fig. 5 (inset), allowed us to obtain quenching constant (K) values for the fluorescence quenching of the QDs in the presence of ZnTAPc.

$$(1) \quad \frac{F_0}{F} = 1 + K[ZnTAPc]$$

where K represents the quenching constant, F_0 and F are the fluorescence intensities of the QDs in the absence and presence of ZnTAPc, respectively.

The linear plot obtained in Fig. 5 (inset) confirms that the quenching equation (Eq. (1)) is obeyed, with a value of K of 8079 M^{-1} .

A value of unity for the number of MPC complexes attached to the CdTe QDs has been reported before [17], hence it is assumed that similar bonding occurs in this work for the mixed QD:ZnTAPc.

In conclusion, the results presented give evidence in favour of the formation of an amide bond between ZnTAPc and CdTe QDs. This was confirmed by IR and Raman spectral data indicating amide bond formation. Both the linked and mixed QDs–ZnTAPc complexes showed Förster resonance energy transfer (FRET). ZnTAPc quenched the QDs emission with a quenching constant of the order of 10^3 M^{-1} .

Acknowledgements

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