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Spontaneous charge transfer between zinc tetramethyl-tetra-2,3-pyridinoporphyrazine and CdTe and ZnS quantum dots

Sharon Moeno, Mopelola Idowu, Tebello Nyokong *

Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

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ABSTRACT

Zinc tetramethyl-tetra-2,3-pyridinoporphyrazine (ZnTmtppa(-2)) gets reduced to the ZnTmtppa(-3) species on interaction with CdTe QDs capped with 2-mercaptoethanol (2-ME) or thioglycolic acid (TGA) and ZnS QDs capped with 2-ME. The interaction occurs without photolysis. The fluorescence of the QDs is quenched by ZnTmtppa resulting in large quenching constants. Binding of ZnTmtppa to QDs occurs with two molecules of the former binding to the latter.

1. Introduction

Quantum dots (QD's) are nanosized semiconductor materials and are referred to as zero-dimensional structures [1–8]. They are constituted of a few thousand atoms which serve to maintain the main structural features of the bulk material, but exhibit different electronic properties from the bulk by virtue of their size [4,8]. A variety of colloidal semiconductor quantum dots have been prepared [6,9–18]. Quantum dots exhibit tunable optical properties. Changes in the size and the composition result in the photoluminescence spectra (PL) spanning the UV to the infrared region [2,15–18]. In addition to the broad absorption spectra, they also show high resistance to photobleaching and excellent resistance to degradation and they have narrow emission spectra [10–23]. Quantum dots have a diverse range of applications and methods of preparation [24–27], and various capping agents may be used to passivate the surface of the QDs. A well passivated surface of the QDs leads to high luminescence. Organic cappings are frequently used to allow functionalisation, thus turning the QDs into chemical reagent species in their own right [1,2,28]. Depending on the capping used, QDs may be soluble in water or in organic media, but water-dispersible QDs are desirable for some applications such as photodynamic therapy (PDT) [28].

PDT is one of the promising applications of quantum dots because of their high fluorescent quantum yields. For PDT purposes, the quantum dots may be conjugated to photosensitizers, e.g., phthalocyanines (Pc). An energy transfer process then takes place when the photosensitizer is excited by the emission from quantum dots (primary energy donor) in a process called fluorescence resonance energy transfer (FRET) [20,24]. However, it has been reported that photolysis of CdSe QDs in the presence of ruthenium-polypyridine complexes resulted in charge transfer rather than FRET [29]. In this work we report on a spontaneous charge transfer between quantum dots of CdTe capped with thioglycolic acid (TGA) or 2-mercaptoethanol (2-ME) and ZnS capped with 2-ME and a zinc tetramethyl-tetra-2,3-pyridinoporphyrazine (ZnTmtppa). This work presents the first report on the transfer of charge rather than energy between QDs and a positively charged MPc photosensitizer.

Tetrapyridinoporphyrazines (Mtppa 1, Fig. 1) are derivatives of phthalocyanines which have pyridine rings instead of outer benzene rings [30,31]. *N*,*N*′,*N*″,*N*‴- Tetramethylated quarternized (MTmtppa, Fig. 1) forms of tetrapyridinoporphyrazines bear a tetrapositive charge and have high solubility in aqueous media. These quarternized complexes do not form aggregates as mentioned in literature reports [32,33]. M-2,3-Tmtppa consists of a mixture of constitutional symmetric and unsymmetrical isomers [31,32], hence these complexes may show splitting of the Q-band.

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* Corresponding author. Tel.: +27 46 6038260; fax: +27 46 6225109.
E-mail address: t.nyokong@ru.ac.za (T. Nyokong).

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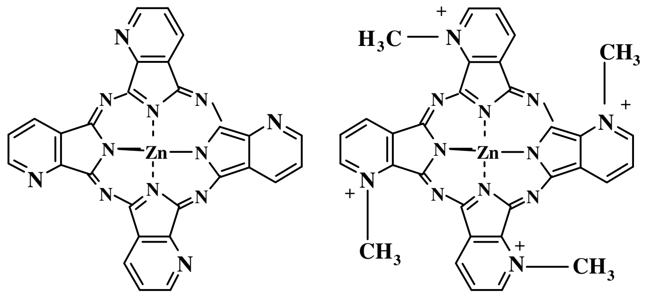

Fig. 1. Molecular structure of zinc tetrapyridinoporphyarzine (Zntppa) and *N*,*N*′,*N*″,*N*‴ zinc tetramethyl-tetra-2,3-pyridinoporphyrazine (ZnTmtppa).

2. Experimental

2.1. Materials

Zinc tetrapyridinoporphyrazine (Zntppa) and zinc tetramethyl-tetra-2,3-pyridinoporphyrazine (ZnTmtppa) were synthesized and characterized according to reported methods [32,33]. Thioglycolic acid (TGA), 2-mercaptoethanol (2-ME), 2,3-pyridine dicarboxylic acid, urea, tellurium powder (200 mesh) and zinc acetate dihydrate were obtained from Sigma–Aldrich. Cadmium chloride monohydrate ($CdCl_2 \cdot H_2O$), sodium borohydride ($NaBH_4$), ammonium chloride, ammonium molybdate, dimethylformamide, and sodium sulfide, were obtained from Saarchem. Dimethyl sulfate was obtained from Merck. Ultra pure water was obtained from a Milli-Q Water System (Millipore Corp, Bedford, MA, USA). Phosphate buffer saline (PBS) solution (0.01 M, pH 7.4) was employed for aqueous solutions.

2.2. Synthesis of quantum dots

CdTe quantum dots were synthesized using wet chemical routes with thioglycolic acid and 2-mercaptoethanol cappings, using reported methods with some modifications [2,34,35]. Briefly, $CdCl_2$ (0.22 g, 1.18 mmol) was dissolved in 65 mL of deionized water, and TGA or 2-ME (0.26 g, 2.86 mmol) was added to the $CdCl_2$ solution. The pH of this precursor solution was adjusted to 11.5 with 1 M NaOH. The solution of NaHTe was prepared by modified literature method [34] as follows: 0.05 M NaOH was reacted with H_2Te gas (the latter generated by reaction of $NaBH_4$ with Te powder in the presence of 0.5 M H_2SO_4 under a flow of nitrogen gas). Then freshly prepared NaHTe (0.091 g, 0.60 mmol) was added to the precursor solution. The solution was then refluxed under air at 100 °C for different times to control the size of the CdTe QDs. Precipitation of the QDs from the aqueous colloidal solution was achieved by using propan-2-ol yielding a yellow-green and orange-maroon colour of CdTe quantum dots powder for 2-ME and TGA cappings, respectively.

ZnS quantum dots were synthesized by the wet chemical method using 2-ME as a capping agent, following literature methods with slight modification as follows [35,36]: $ZnAc_2 \cdot 2H_2O$ (0.44 g, 2 mmol) and 2-ME (0.19 g, 2.39 mmol) were dissolved in 25 mL deionized water under inert atmosphere. Then 10 mL of 0.2 M sodium sulfide solution was added to the reaction mixture. The white suspension formed was left stirring for different times (up to 6 days) while heating at 100 °C to control the size of the QDs. Centrifuging the white suspension afforded the particles which were then washed with distilled water and once with ethanol. The white powder was then left to dry in a vacuum desiccator for about 15 h. The ZnS quantum dots powder was redispersed in a pH 7.4 phosphate buffer solution.

The size of the quantum dots was estimated using the polynomial fitting function (Eq. (1)) derived in the literature [37]. Only one size (the largest possible) of the ZnS QDs was synthesized.

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - (194.84) \quad (1)$$

2.3. Interaction of ZnTmtppa with QD

The interaction of the ZnTmtppa with QDs was studied by spectrofluorometry at room temperature. An aqueous solution of QDs (fixed concentration of 1 mg mL^{-1}) was titrated with varying concentrations ($0–1.71 \times 10^{-6}$ M) of the ZnTmtppa complex. The QDs were excited at 400 nm and fluorescence was recorded between 400 and 800 nm. The steady decrease in the fluorescence intensity of QDs with increase in ZnTmtppa concentration was noted and used in the determination of the binding constants and the number of binding sites on QDs, according to Eq. (2) [38–41].

$$\log\left[\frac{(F_0 - F)}{F - F_\infty}\right] = \log k_b + n \log[\mathrm{ZnTmtppa}] \quad (2)$$

where F_0 and F are the fluorescence intensities of QDs in the absence and presence of ZnTmtppa, respectively; F_∞ is the fluorescence intensity of QDs saturated with ZnTmtppa; k_b, the binding constant; n, the number of binding sites on a QD. Plots of $\log\left[\frac{(F_0-F)}{F_{-}F_\infty}\right]$ against log[ZnTmtppa] provided the values of n (from slope) and k_b (from the intercept). The changes in QD fluorescence intensity were related to ZnTmtppa concentrations by equation [41] (Eq. (3)):

$$\frac{F_0}{F} = 1 + K[\mathrm{ZnTmtppa}] \quad (3)$$

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

Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer. UV–Vis spectra were recorded on a Varian 500 UV–Vis/NIR spectrophotometer.

2.4. Cyclic voltammetry

Cyclic (CV) voltammetry data were obtained with Autolab potentiostat PGSTAT 30 (Eco Chemie, Utretch, The Netherlands) driven by the General Purpose Electrochemical Systems data processing software (GPES, software version 4.9, Eco Chemie), using a three-electrode set-up with platinum electrode (1.6 mm diameter) as a working electrode, platinum wire as counter electrode and Ag|AgCl wire as pseudo-reference electrode. Electrochemical experiments were performed in doubly distilled water containing 0.1 M $NaSO_4 \cdot 10H_2O$ and 0.02 M $Na_2B_4O_7 \cdot 10H_2O$. Prior to scans, the working electrode was polished with alumina paste on a Buehler felt pad, followed by washing with deionized water and rinsing with methanol and doubly distilled water.

3. Results and discussion

3.1. Absorption and emission spectra

The optical absorption spectrum of CdTe quantum dots (capped with TGA) began to appear at 430 nm after 5–10 min of refluxing. The spectrum continued to shift to longer wavelengths with refluxing time since the particles grow during the course of the heating as a result of the quantum confinement effect. Fig. 2a shows the absorption and emission spectra obtained for 2-ME-capped CdTe after heating for 64 h, and Fig. 2b the absorption and emission