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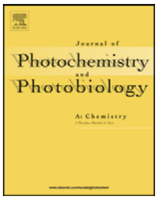

Opposing responses elicited by positively charged phthalocyanines in the presence of CdTe quantum dots

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ABSTRACT

Tetrapositively charged phthalocyanines and CdTe quantum dots (QDs) capped with thioglycolic acid (TGA) and mercaptopropionic acid (MPA) were synthesized. The response of the tetrapositively charged zinc phthalocyanines in the presence of quantum dots was studied. Aggregation and charge transfer were observed for [tetramethyl-2,(3)-[tetra-(2-mercaptopyridinephthalocyaninato)]zinc(II)]$^{4+}$ (TmTMPyZnPc), however aggregation proved to be the more prominent process of the two. Fluorescence resonance energy transfer (FRET) was observed with [tetramethyl-2,(3)-[tetra-(2-pyridyloxyphthalocyaninato)]zinc(II)]$^{4+}$ (TmTPyZnPc). In the FRET study the efficiency of FRET with TmTPyZnPc was determined to be 21% for both MPA and TGA capped CdTe QDs. For the charge transfer study the fluorescence of the quantum dots was quenched by the TmTMPyZnPc used, and from these quenching studies the quenching constants, binding constants and number of binding sites on the quantum dots were determined.

1. Introduction

In recent years quantum dots (QDs), which are nanometer sized semiconductor particles, have become a major field of interest in various branches of science [1–10]. They exhibit size-dependent physico-chemical properties such as tunable narrow emission spectrum, excellent photostability and broad excitation spectra [1–15]. All these properties allow for the exploitation of QDs in a variety of fields. Some fields of application of QDs include biological labeling, use in optoelectronic devices and they also have a potential for use in photodynamic therapy (PDT) [16–26].

QDs are highly photoluminescent with moderate fluorescence quantum yield values [1–3,6,11,27]. The organic molecules used for passivation are diverse and have varied functional groups which further aid in functionalizing the QD. The capping groups thus allow the nanoparticles to interact with the surrounding environment via either electrostatic, covalent, hydrophobic interactions or hydrogen bonding [5].

In this work, water soluble CdTe QDs which were capped with thioglycolic acid (TGA) and mercaptopropionic acid (MPA) were prepared and the responses to the addition of tetrapositively charged zinc metallophthalocyanines (ZnPcs) were studied. The tetrapositively charged metallophthalocyanines (ZnPcs) are [tetramethyl-2,(3)-[tetra-(2-mercaptopyridinephthalocyaninato)]zinc(II)]$^{4+}$ (TmTMPyZnPc, **4**) and [tetramethyl-2,(3)-[tetra-(2-pyridyloxyphthalocyaninato)]zinc(II)]$^{4+}$ (TmTPyZnPc, **6**) (Scheme 1). These complexes are tetra substituted and consist of a mixture of isomers which are not easy to separate [28].

A number of studies has shown that QDs can serve as near infrared (IR) energy donors to photosensitizers, e.g. metallophthalocyanines (MPcs). The photosensitizer can then accept this energy in a process known as fluorescence resonance energy transfer (FRET). FRET is a non-radiative energy transfer between the fluorescent donor and a suitable energy acceptor fluorophore [29–35]. On the other hand, QDs are also known to engage in charge transfer processes, some of which are spontaneous [36–38]. We have recently shown a spontaneous charge transfer from QDs to a positively charged porphyrazine where the benzene ring was substituted with a pyridine ring [38]. In this work ZnPcs were substituted with thiopyridine or oxopyridine groups.

2. Experimental

2.1. Materials

Thioglycolic acid 99%, tellurium powder (200 mesh, 99.8%), phthalimide, quinoline, 2-mercaptopyridine, 2-hydroxypyridine, chlorophyll a, 1,3-diphenylisobenzofuran (DPBF) and zinc acetate dihydrate were obtained from Sigma–Aldrich, sodium borohydride ($NaBH_4$), sodium hydroxide (NaOH), sulphuric acid (H_2SO_4), potassium carbonate (K_2CO_3), ferric chloride ($FeCl_3$), nitric acid (HNO_3), ethanol, tetrahydrofuran (THF), chloroform ($CHCl_3$),

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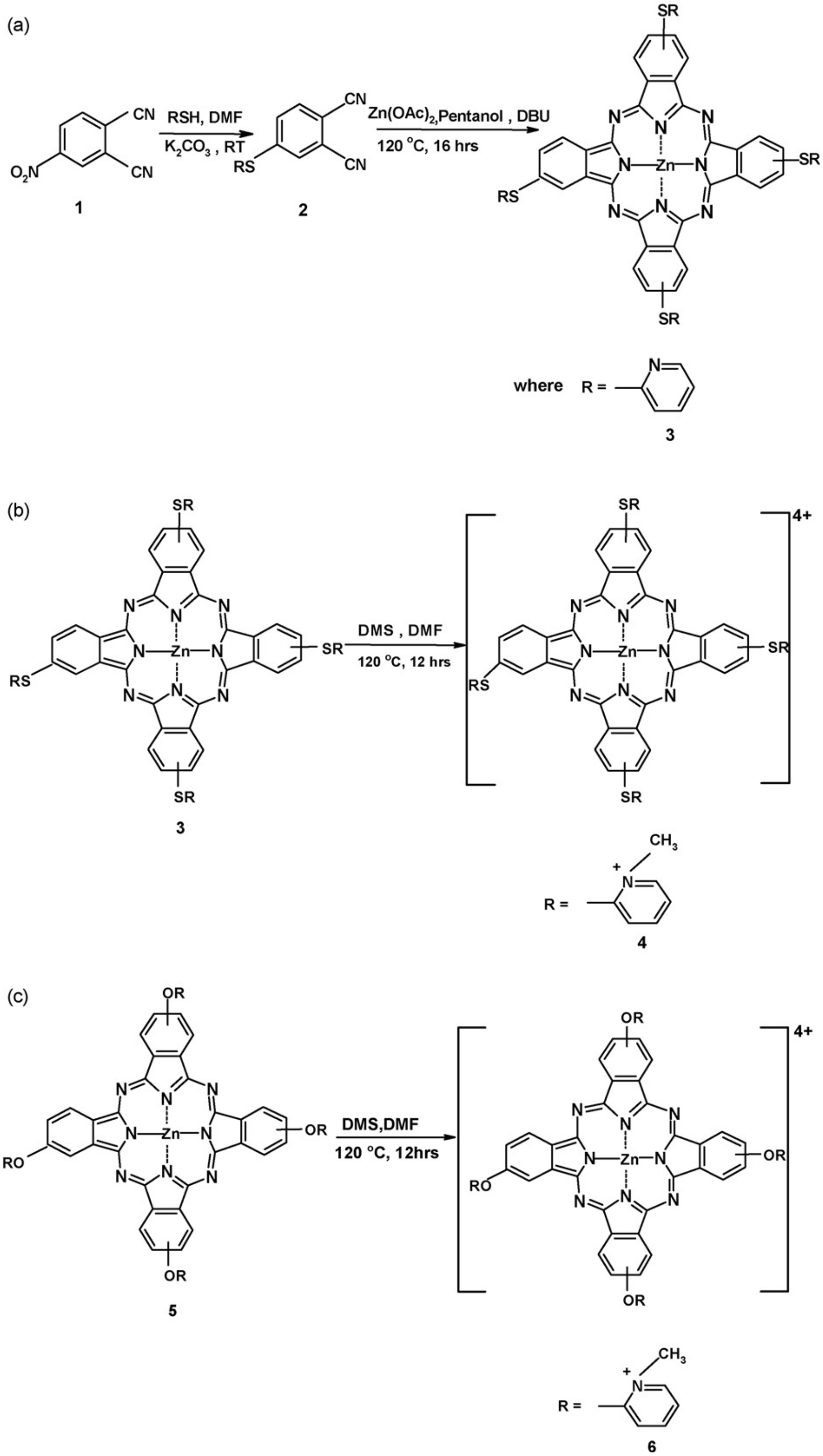

Scheme 1. Synthetic route of (a) 2-mercaptopyridine tetra substituted zinc(II) phthalocyanine (TmTMPyZnPc) complex, (b) quaternized 2-mercaptopyridine tetra substituted zinc(II) phthalocyanine (TmTMPyZnPc) complex and (c) quaternized 2-pyridyloxy tetra substituted zinc(II) phthalocyanine (TmTPyZnPc) complex.

hexane, diethyl ether, acetone, and dimethylformamide (DMF) were obtained from Saarchem. Pyridine, dimethyl sulphoxide and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) were obtained from Fluka and cadmium chloride monohydrate ($CdCl_2 \cdot H_2O$) and dimethyl sulphate (DMS) were obtained from Merck. Ultra pure water was obtained from a Milli-Q Water System (Millipore Corp., Bedford, MA, USA). A 50/50 pyridine:H_2O solution was employed for photophysical studies. This solvent mixture allows