

Synthesis and characterization of free base and metal porphyrins and their interaction with CdTe QDs



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ABSTRACT

Free base porphyrins and metalloporphyrins with different number of methoxy groups were synthesized to investigate the consequence of methoxy groups in the porphyrins on interaction with quantum dots through steady state, time resolved and transient absorption measurements. Spectral changes in the absorption and photoluminescence of quantum dots in the presence of porphyrins elucidate the binding affinity between them. From the photoluminescence quenching analysis, higher number of methoxy substituted zinc porphyrin was found to possess better binding affinity with quantum dots than the other porphyrins which divulges the role of methoxy substituents. The calculated reduction potential of the synthesized porphyrins was feasible for accepting electrons from the photoexcited quantum dots. Electron transfer mechanism is suggested based on energy level diagram, Rehm–Weller equation and transient absorption measurements.

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1. Introduction

Quantum dots (QDs) have received great attention in various fields such as photovoltaic and biological applications [1–6]. Among these potential applications, quantum dot sensitized solar cells (QDSSC) is currently of great interest due to their unique properties such as quantum confinement effect [7], larger extinction coefficient [8], multiple excitation generation [9], narrow emission bands with broad absorption wavelength, photostability, etc. However, the photocurrent efficiency of QDSSC is very low due to difficulty of assembling a sufficiently large number of QDs on a mesoporous TiO₂ matrix in order to obtain a well-covered monolayer without cluster formation [7] and also the presence of surface states possessing both electron and hole traps in the QDs, which results in lower short circuit current and open-circuit photovoltage [10,11]. The retardation of blocking of the surface states was achieved through the surface passivation of QDs by using ZnS [12], amorphous TiO₂ layer [13], dyes [14], etc. Surface passivation of QDs and organic dye molecules results in a class of new materials which will be important for photovoltaics [15]. The electron accepting properties of organic compounds have been utilized for photocurrent generation, and thus to improve the capture of photogenerated electrons from QDs [16].

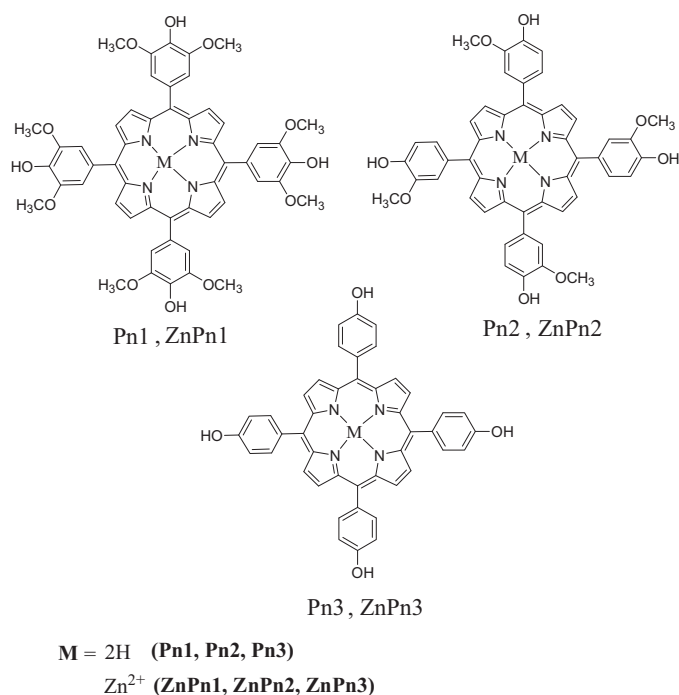
Porphyrin is a macrocyclic molecule with unique photophysical and electrochemical properties. The optoelectronic properties of the porphyrins were tuned by varying the meso-functional ligands and metal insertion sites [13]. For electron transfer to occur the potential values of the QDs and Porphyrins should be favorable and they should possess efficient binding between them. The electron transfer from QDs to organic photosensitizers was evidenced by transient absorption measurements in literature [17,18]. Recently, Patra et al. utilized the QDs–porphyrin systems as optical-based sensor for bio applications [18]. Borczykowski et al. have widely analyzed the photophysical properties of QDs with porphyrin systems [19]. Based on this, the effect of methoxy substituted free base (Pn1, Pn2 and Pn3) and metal porphyrins (ZnPn1, ZnPn2 and ZnPn3) (Scheme 1) on interaction with thioglycolic acid stabilized CdTe QDs were probed by using steady state, time resolved and transient absorption measurements.

2. Experimental

2.1. Materials

Thioglycolic acid (TA), CdCl₂·2.5H₂O (99.99%), tellurium powder (99.997%), sodium borohydride (95%), syringaldehyde (>98%), pyrrole (98%) and tetra butyl ammonium hexafluoro phosphate were purchased from Sigma–Aldrich. 4-Hydroxy benzaldehyde and solvents were of analytical grade purchased from LOBA Chemicals (India). Vanillin, propionic acid and Zn(OAc)₂·2H₂O were

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Scheme 1. Structures of porphyrins and metalloporphyrins.

obtained from Merck chemicals. Double distilled water was used for preparing solutions. All measurements were performed at ambient temperature. CdTe quantum dots were synthesized by using the following method as reported earlier [20]. The quantum yield of prepared QDs was 15%, calculated using rhodamine B as the reference.

2.2. Instrumentation

Absorption measurements were recorded using JASCO V630 UV–visible spectrophotometer. Photoluminescence (PL) measurements were carried out using Perkin Elmer LS 55 spectrofluorimeter. The excitation and emission wavelength of TA-CdTe QDs were 500 and 595 nm, respectively. Silt width (10 nm) and scan rate (200 nm/min) were kept constant for all measurements. Quartz cells ($4 \times 1 \times 1$ cm) with high vacuum Teflon stopcocks were used for measurements. Samples for absorption and photoluminescence measurements were prepared by adding various concentration [0 – 5×10^{-5} M] of porphyrins to the test tubes containing QDs [1×10^{-6} M] and then kept as such for 1 h and used for further experiments. Cyclic voltammogram was acquired with Princeton EG and G-PARC model potentiostat using Glassy carbon working electrode, Ag/AgCl reference electrode and platinum wire counter electrode. Tetrabutyl ammonium hexafluoro phosphate (0.1 M) was used as supporting electrolyte for porphyrins/metalloporphyrins in DMF solvent. All samples were deaerated by bubbling with nitrogen gas for ca.5 min at room temperature. 1H NMR and ^{13}C NMR spectrum were obtained using a Bruker spectrometer (400 MHz). FT-IR spectra were obtained by using Perkin–Elmer Spectrum RXI FT-IR Spectrometer at room temperature in the range of 4000 – 400 cm^{-1} .

PL lifetime measurements were carried out in a picosecond time correlated single photon counting (TCSPC) spectrometer. The excitation source was the tunable Ti-sapphire laser (TSUNAMI, Spectra Physics, USA). The data analysis was carried out by the software provided by IBH (DAS-6). For Laser Flash Photolysis measurements, the Nd–YAG laser source produces nanosecond pulses (8 ns) of 532 nm light and energy of the laser pulse was around 150 mJ. Dichroic

mirrors were used to separate the third harmonic from the second harmonic and the fundamental output of the Nd–YAG laser. The monitoring source was a 150 W pulsed xenon lamp which was focused on the sample at 90° to the incident laser beam. The beam emerging through the sample was focused onto a Czerny–Turner monochromator using a pair of lenses. The detection was carried out using a Hamamatsu R-928 photomultiplier tube. The transient signals were captured with an Agilent infiniiium digital storage oscilloscope interfaced to a computer.

2.3. General synthesis of free base porphyrins and metalloporphyrins

Corresponding aldehyde precursors (5.4 mmol) was dissolved in propionic acid (54.65) and the solution was heated to $140^\circ C$. A freshly distilled pyrrole (5.4 mmol) was slowly added and refluxed for 1 h. Under hot condition 55 ml of anhydrous alcohol was added and the solution was transferred into beaker cooled to room temperature and kept 1 h at $-5^\circ C$. Filtered the solution to obtain blue powder and dried. A solution of $Zn(OAc)_2 \cdot 2H_2O$ (2 mol) in ethanol (1 ml) was added to the solution of free base porphyrins (1 mol) in $CHCl_3$ and stirred overnight at room temperature under N_2 in the dark. This was monitored by TLC and the mixture was washed with water and evaporated to dryness to get desired compound.

2.3.1. Meso-tetrakis (4-hydroxy-3,5-dimethoxy phenyl) porphyrin (Pn1)

Yield – 4.23%, color: glittering purple color, 1H NMR (400 MHz, DMSO): δ (ppm), 8.92 (s, 8H, β pyrrole), 7.45 (s, 8H, 2,6-phenyl), 3.88 (s, 24H, –OCH₃), –2.47 (s, 2H, NH-pyrrole), 8.86 (s, 4H, –OH). ^{13}C NMR (400 MHz, DMSO): 146.35, 135.61, 131.37, 120.86, 112.86, 56.27. IR (KBr, cm^{-1}): 3464, 2929, 1603, 1509, 1453, 1411, 1341, 921, 800, 730 cm^{-1} . MS (MALDI) m/z calculated for $C_{52}H_{46}N_4O_{12}$ (M+H): 918.31, Found: 919.23.

2.3.2. Meso-tetrakis (4-hydroxy-3-methoxy phenyl) porphyrin (Pn2)

Yield – 8.1%, color: purple powder, 1H NMR (400 MHz, DMSO): δ (ppm), 9.51 (s, 4H, –OH), 8.9 (s, 8H, β pyrrole), 7.76 (s, 4H, 2-phenyl), 7.58–7.57 (d, 4H, 6-phenyl), 7.1–7.2 (d, 4H, 5-phenyl), 3.89 (s, 12H, –OCH₃) –2.88 (s, 2H, NH-pyrrole). ^{13}C NMR (400 MHz, DMSO): 146.63, 146.01, 132.34, 127.48, 120.03, 118.89, 114.03, 55.85. FT-IR (KBr, cm^{-1}): 3492, 3427, 2929, 1603, 1509, 1463, 1416, 1341, 1229, 1262, 1117, 1033, 916, 865, 730 cm^{-1} . MS (MALDI) m/z calculated for $C_{48}H_{38}N_4O_8$ (M+H): 798.27, Found: 799.02.

2.3.3. Meso-tetrakis (4-hydroxy phenyl) porphyrin (Pn3)

Yield – 3.1%, color: glittering green color, 1H NMR (400 MHz, DMSO): δ (ppm), 9.96 (s, 4H, –OH), 8.86 (s, 8H, β pyrrole), 7.9–8 (d, 8H, 2,6-phenyl), 7.1–7.2 (d, 8H, 3,5-phenyl), –2.89 (s, 2H, NH-pyrrole). ^{13}C NMR (400 MHz, DMSO): 157.37, 135.49, 131.90, 119.97, 113.90. IR (KBr, cm^{-1}): 3412, 3220, 1509, 1603, 1478, 1379, 1279, 1171, 1112, 846 cm^{-1} . MS (MALDI) m/z calculated for $C_{44}H_{30}N_4O_4$ (M+H): 678.23, Found: 679.016.

2.3.4. Zn(II)-[meso-tetrakis (4-hydroxy-3,5-dimethoxy phenyl) porphyrin] (ZnPn1)

Yield – 68%, color: blue solid, 1H NMR (400 MHz, DMSO): δ (ppm), 8.92 (s, 8H, β pyrrole), 7.45 (s, 8H, 2,6-phenyl), 3.88 (s, 24H, –OCH₃), 8.86 (s, 4H, –OH). ^{13}C NMR (400 MHz, DMSO): 149.53, 146.07, 135.22, 132.95, 131.49, 120.39, 112.82, 56.25. IR (KBr, cm^{-1}): 3464, 2929, 2845, 1607, 1509, 1453, 1411, 1341, 1206, 1114, 940, 795 cm^{-1} . MS (MALDI) m/z calculated for $C_{52}H_{44}N_4O_{12}Zn$ (M⁺): 980.22, Found: 979.85.

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