Supplementary Information

Hollow Zinc Phthalocyanine Nanoshells: Quick Low Temperature Synthesis, Enhanced Near-IR Absorption and Water-dispersibility for Photocatalysis and Phototherapy

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S1. Experimental details (materials and methods)

S1.1 Materials

Zinc Phthalocyanine (ZnPc), 96% and thioglycolic acid (TGA), 98% were purchased from ThermoFisher Scientific and Spectrochem Pvt. Ltd., respectively. Dimethylsulfoxide (DMSO), 99% and methyl orange(MO), was procured from Sigma-Aldrich. All the aforementioned chemicals have been used without further purification.

S1.2 Synthesis of TGA-capped hollow ZnPc nanoshells (HZPNS) in colloidal state

All the steps involved in the synthesis of TGA-capped hollow ZnPc nanoshells are discussed. A solution of ZnPc (10 ml, 10 mM) is prepared in DMSO, named as solution A. Another solution of thioglycolic acid (20 ml, 1.4 mM) is prepared in deionized water which is named as solution B. Both the solutions A and B are kept in ice-bath at 10 °C for 15 minutes. The solution B is then transferred to the ultrasonic bath (Labman, LMU). Immediately, 100 µl of solution A is added to the solution B and the ultrasonication is continued for two minutes at 10 °C. In this soft chemical synthesis, TGA-capped hollow ZnPc nanoshells (HZPNS) are obtained in quick time of two minutes.

The as-prepared HZPNS solution were directly used for photocatalytic degradation of methyl orange dye.

S1.3 Transformation of HZPNS from colloidal state to nanopowders

The process of converting the colloidal solution of TGA-capped HZPNS into solid nanopowders is described here. The final solution obtained in S1.1 is spread in a petridish of 150 mm diameter and mildly heated at 60 ^{o}C in the hot air oven for 8 hours. A thin layer of TGA-capped HZPNS is obtained which is dissolved in 1 ml of deionized water and centrifuged at 5000 rpm for 10 minutes. The precipitate is then washed with methanol and acetone, alternately, twice. The precipitate is dried in vacuum desiccator for eight hours. Thus, nanopowders of TGA-capped HZPNS is obtained which can be redispersed in water easily.

S1.4 Characterization of nanoparticles

Absorption spectra of all the samples were recorded on UV-Vis-NIR absorption spectrophotometer. Raman spectroscopy was conducted on RI-Nanotech Raman spectrometer using a 532 nm CW laser. HR-TEM imaging was performed on JEOL-2010 electron microscope at an accelerating voltage of 200 kV. FTIR spectra were recorded on Jasco FTIR-4600 spectrometer with ATR accessory having ZnSe window. X-ray diffraction (XRD) was carried out using Bruker D8 Advance diffractometer with the copper target (λ = 1.54 Å). Average crystallite size was determined by Debye-Scherrer equation, $D = 0.94\ \lambda/\beta\cos\ \theta$, where D is crystallite size, λ is X-ray wavelength, β is full width at half maximum (FWHM) and θ is Bragg's angle.

S1.5 Photocatalytic degradation of methyl orange by as-prepared hollow ZnPc nanoshells

Photocatalytic degradation of Methyl Orange (MO) dye under in-house lighting condition with four white LED bulbs of 9W each. To start with, 50 ml stock solution of MO dye (10 ppm) was prepared. One set of 25 ml is used as control. To the control set 5 ml deionized water is added and it is kept in dark. To the another set of 25 ml MO dye, 5 ml of *as-pepared TGA-capped hollow ZnPc nanoshells* was added. The subsequent reactions were monitored by UV-Vis-NIR absorption spectrophotometer (Jasco V 770) at regular time intervals. The decrease in MO absorption was followed at 497 nm. The absorption spectra were taken at different time intervals, 0 min, 1 hour, 3 hours , 7 hours and 11 hours. For the uncapped ZnPc nanoparticles the experiment was conducted in similar manner with an extended irradiation time upto 24 hours.

S1.6. Investigation of photothermal effect under NIR LED irradiation

An aqueous solution of TGA-capped HZPNS (10 ml, 0.1mg/ml) was taken in a glass vial and side walls were covered with Styrofoam. The top side was left open for light irradiation. The vial was placed under a panel (make: Hottoerak; model: LLD-P40-LED) comprising of with 20 pcs LEDs (660 nm, 36 W, 40mW/cm^2). The LED panel was switched on and NIR irradiation was done for 90 minutes. At regular time intervals, the temperature of the solution was monitored using a digital thermometer.

S2. Deconvolutions of the Q-band into component peaks

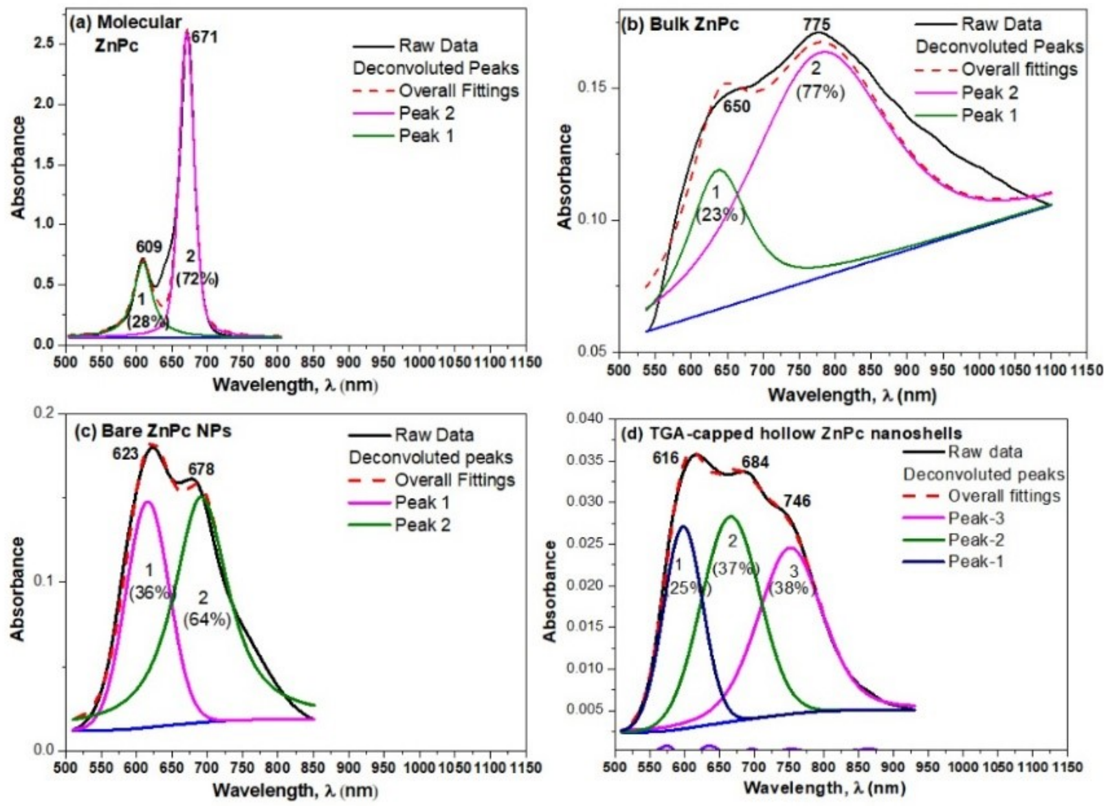

Fig. S1. Deconvolutions of the Q-band showing all the component peaks and their relative contributions in different forms of ZnPc: (a) Molecular state, (b) Bulk state, (c) Bare (uncapped) NPs, and (d) TGA-capped hollow nanoshells. The x-axis has been kept same in all the four graphs for ease of visualization of the widening of the band and its red-shift

S3. TEM images and size distribution histogram of bare ZnPc nanoparticles

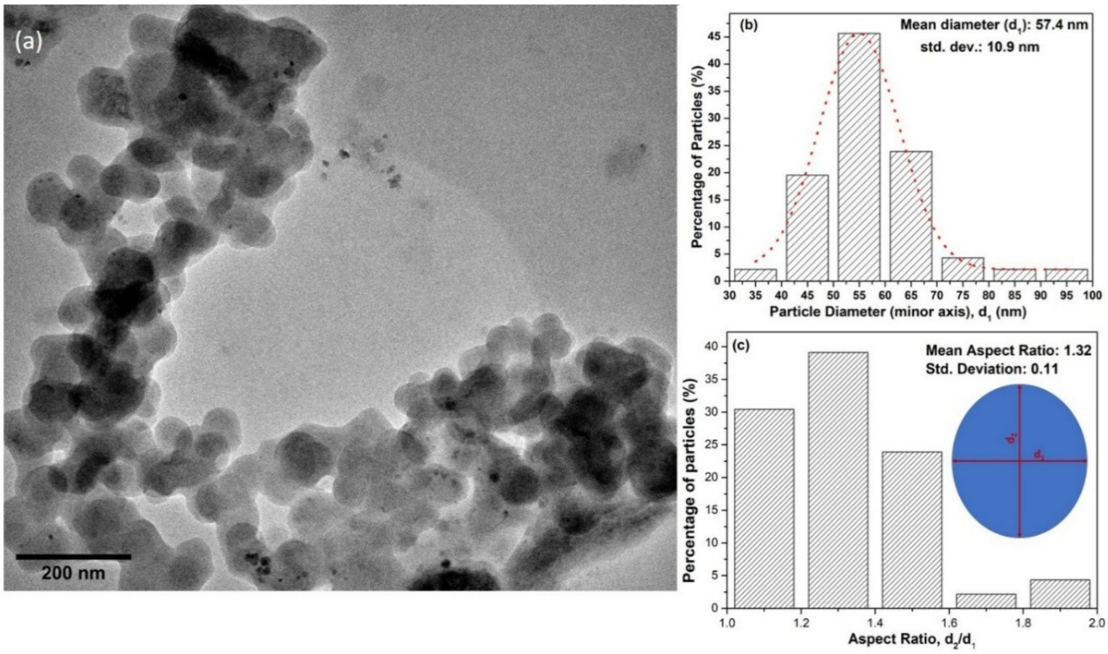

Figure S2. (a) TEM image of bare (or uncapped) ZnPc NPs, (b) Histogram showing distribution of diameter (d_1) along minor axis in bare ZnPc NPs (c) Histogram showing distribution of aspect ratio(d_2/d_1) along minor axis in bare ZnPc NPs.

S4. Photoluminescence Spectra of ZnPc in various forms

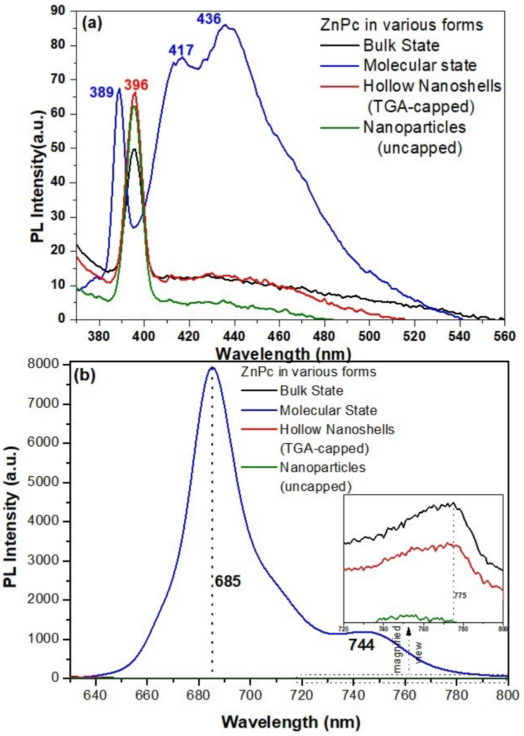

Fig. S3. Photoluminescence (PL) spectra of ZnPc in various forms with different excitation wavelengths: (a) λ_{ex} =350 nm and (b) λ_{ex} =600 nm. Concentration ZnPc monomer units in all the samples was kept constant at 50 μM. For the molecular state of ZnPc, the solvent used was DMSO and for all other samples, deionized water was used as dispersing medium for PL measurements.

S4. FTIR Spectra of ZnPc nanoparticles (2600-3800 cm^{-1})

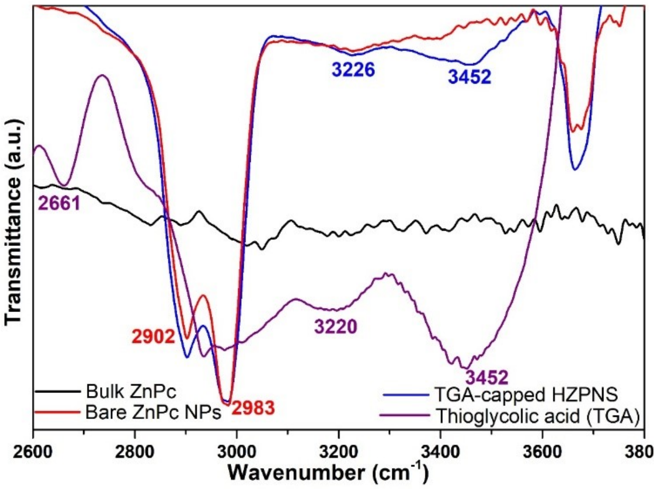

Fig. S4. FTIR spectra in high frequency region, 2600-3800 cm^{-1} for bulk ZnPc, bare ZnPc NPs, thioglycolic acid (TGA) and TGA capped HZPNS.

S5. Zeta potential of the nanoparticles

Due to the binding of TGA molecules to the particle surface, a strong negative potential develops for the hollow nanoshells (Table S1 and Fig. S2.). The thiol end binds to the particle surface while the carboxyl end remains free, which further ionies to impart negative charge to the particles.

Table S1. Zeta potentials of the ZnPc Nanoparticles in aqueous solution

S.No.	Sample	Zeta-Potential (mV)
1.	Bare ZnPc NPs	-3.6
2.	TGA-capped hollow ZnPc Nanoshells	-28.5

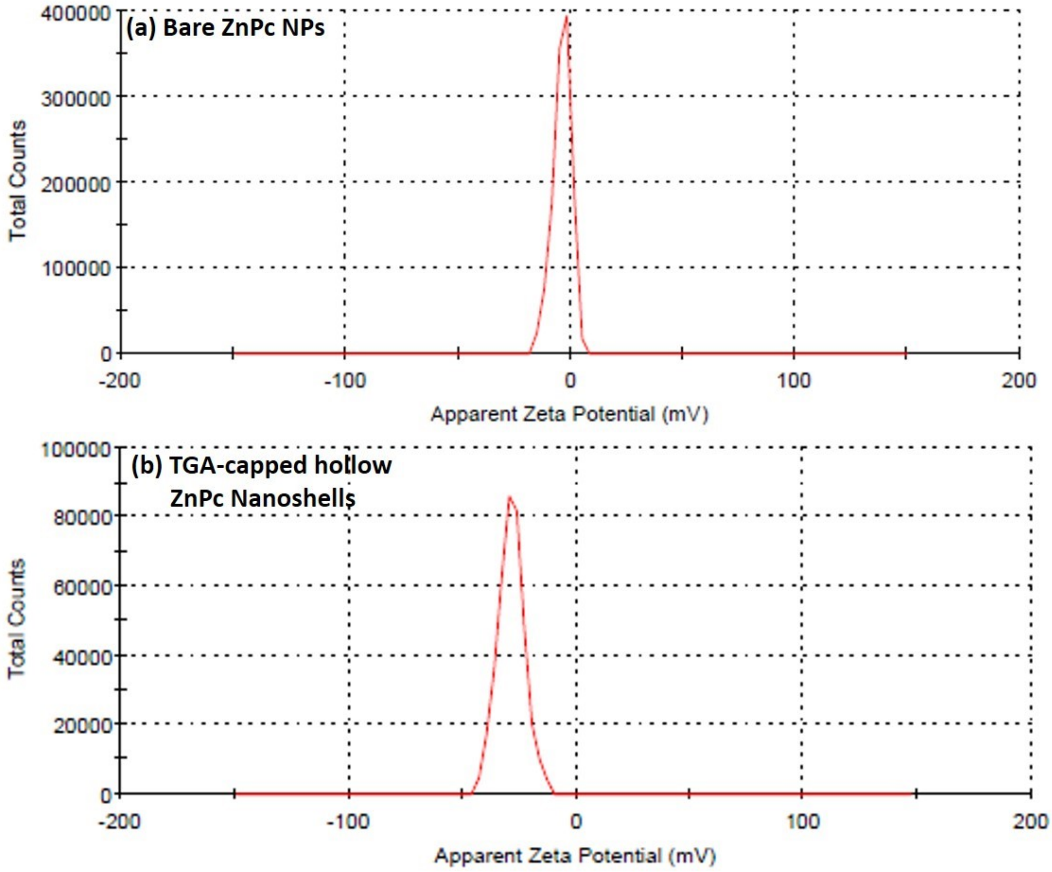

Figure S5. Zeta potential distribution of (a) bare ZnPc NPs and (b) TGA-capped hollow ZnPc Nanoshells.