RASĀYAN *J. Chem.*
Vol. 10 | No. 4 |1242-1246 | October - December | 2017
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

SYNTHESIS CHARACTERIZATION AND PHOTOPHYSICAL INVESTIGATION OF AGGREGATED ELECTRON RICH ZINC PHTHALOCYANINE

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ABSTRACT

Zn-Phthalocyanine is well known for its chemical and thermal stability. In the present work, we have synthesized an electron-rich tetra carboxyl substituted Zn-Phthalocyanine derivative possess S atom. The synthesis is carried out by employing phthalimide as starting material. The final ZnPc derivative was synthesized by employing hexamethyl disilazane (HMDS) as the nitrogen source, which involves the cyclization of phthalonitriles co-ordinated by zinc metal ion. The synthesized molecules were characterized by IR, NMR and HR-MS spectroscopy techniques. Absorption, fluorescence and time-correlated single photon counting studies were carried out. Aggregation of ZnPc in DMF was revealed from absorption spectral studies. Singlet and triplet quantum yields were calculated. Further transient absorption studies were also carried out for triplet lifetime.

Keywords: ZnPc, TCTZnPc, aggregation, stacking, phthalonitrile, DMF

INTRODUCTION

In recent years, π-conjugated molecules have found many interesting applications in technological areas.[1] Pcs have been widely used as dyes and pigments because of their intense blue-green color. For many years, Pcs have been a target of the intensive investigations, particularly considering their properties as dyes.[2] Currently, the focus of research on Pcs has been directed to applications in material science.[3] This includes Pcs as liquid crystal[4], Longmuir-Blodgett films[5], in electrophotographic applications[6], optical data storage[7], in fuel cells[8], electrochemical sensors[9], and in nonlinear optics (NLO).[10] Pcs have also attracted a lot of attention in medical applications, in particular, photodynamic therapy (PDT), a cancer treatment[11] that uses photo sensitizers[11] to produce singlet oxygen. Phthalocyanines (Pcs) are the most charismatic functional π-conjugated molecules. Phthalocyanines possess intense absorption in the Q-band (around 700nm), as well as promising electrochemical, photochemical, and thermal properties.[12]

Zn-Phthalocyanines substituted with various functional groups have been reported[1]. The propensity of Pcs to self-aggregate has been attributed to the strong $\pi - \pi$ interactions between the large, π-conjugated aromatic molecules and two-dimensional surface.[13] Different studies have revealed the preferential association of the Pc rings to form dimers and the influence of the central metal ion on the aggregation properties of Pcs.[14] Phthalocyanines (Pcs) aggregation has been shown to be strongly solvent dependent. Pcs exhibit a high propensity to dimerize in nonpolar solvents such as toluene, whereas they remain mainly monomeric in polar solvents.[20]

Aggregation produces a decrease in the absorption coefficient of Pcs and also induces a decrease in fluorescence quantum yield. On the other hand, the formation of well-defined Pc aggregates is useful in material applications where the self-assembly of Pc cores in close proximity is beneficial.[15]π-Conjugated molecules can be self-assembled as one-dimensional stacks by aggregation of their π-systems through $\pi - \pi$ interactions.[16]

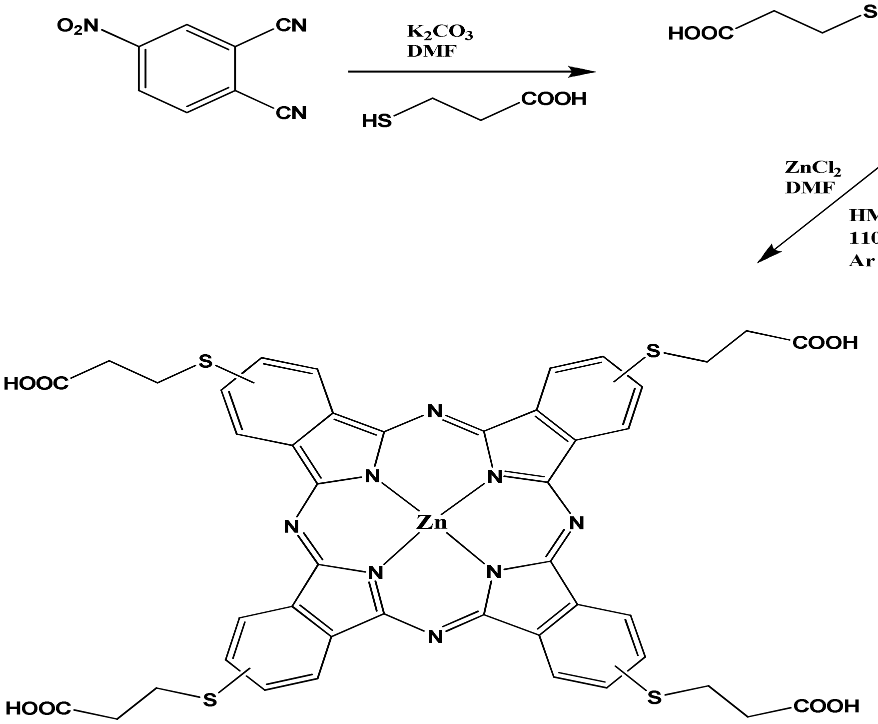
Rasayan J. Chem., 10(4), 1242-1246(2017)
http://dx.doi.org/10.7324/RJC.2017.1041921

It is necessary to synthesize a π-conjugated macromolecule which forms stacking for the supramolecular assembly. In the present work Zn-phthalocyanine with thiol linker was synthesized by treatment of 4-nitrophthalonitrile with 3-mercaptopropionic acid to get thiol-substituted phthalonitrile derivative, which was used for the synthesis of ZnPc. The synthesized molecules were characterized by IR, NMR, and HR-MS spectroscopy techniques. Absorption coefficient, singlet and triplet quantum yields are calculated. The photophysical investigation was carried out to find out the aggregation of ZnPc in DMF and singlet and triplet lifetime.

EXPERIMENTAL

All the solvents were purchased from Fischer Scientific and used as such without further purification, and the materials employed in synthesis were purchased from SRL and Aldrich. For spectroscopic studies, we used HPLC grade solvents.

Synthesis and Characterization



Scheme-1: Synthesis of TCTZnPc

Synthesis of 4-(p-carboxyl)ethylthiophthalonitrile

0.5 g of 4- nitrophthalonitrile and 0.1 g of 3- mercaptopropanoic acid were taken in a 50 mL RB flask. The above mixture was dissolved in 8 mL of DMF. The reaction mixture was stirred under Argon atmosphere at room temperature, to this 0.7 g of potassium carbonate (K_2CO_3) was added in small aliquots. The stirring was continued for 16 hrs and poured into ice water. The product was neutralized with dil. HCl. The precipitate obtained was filtered off and dried. Yield: 0.35 g (70 %).

Synthesis of 2(3),9(10),16(17),23(24)-Tetra(4-carboxyethylthio)phthalocyaninato Zinc(ll) (TCTZnPc)

0.3 g of 4-(p-carboxyl)ethylthiophthalonitrile 0.03 g of $ZnCl_2$, 0.4 ml HMDS, 0.17 mL DMF was taken in a 50 mL RB flask. The reaction mixture was stirred in an oil bath at 100^0C providing water condenser under Argon atmosphere for 10 hrs. The product was washed with water and methanol. The product was purified by Soxhlet extraction using Methanol as a solvent. mp > 300^0C, IR (KBr): 3409.66 (br, -OH), 2921.47 and 2853.81 cm^{-1} (s, aromatic CH)1717.67 (s, CO), 1598.19 (s, C=N), 1308.29 (s, -C=C-), 1024.52 (s, C-O) cm^{-1}. ^{1}H NMR (d_6–DMSO, ppm): 10.91 (s, 4H; OH), 8.65-8.69 (d, 4H; Pc-H), 8.10-8.36 (m, 4H; Pc-H), 7.47-7.80 (m, 4H; Pc-H), 3.05 (s, 2H, CH_2), 2.75 (s, 2H, CH_2). HRMS, molecular formula $C_{44}H_{32}N_8O_8S_4Zn$, calculated molecular mass – 992.0517, found – 992.0535.

Experimental Setup

IR spectra were recorded using a Thermo Scientific NICOLET iS5 model using iD1 Transmission with KBr pellets. 1H NMR spectra were recorded using a Bruker 300 MHz instrument. HR-MS was carried out using a Micromass Q-Tof microanalyzer with a Q-Tof Lockspray dual electrospray source. The absorption spectra of the samples were recorded using an Agilent 8453 UV-vis diode-array spectrophotometer. The fluorescence spectral measurements were carried out using a Fluoromax-4 spectrophotometer (Horiba Jobin Yvon). Time-resolved picosecond fluorescence decays were obtained by the time-correlated single-photon counting (TCSPC) technique with a microchannel plate photomultiplier tube (Hamamatsu, R3809U) as the detector and a 635 nm LED was used as the excitation source. Transient absorption experiments were carried out using nanosecond laser flash photolysis (Applied Photophysics, UK).

Quantum Yield Measurements

Fluorescence and triplet quantum yield measurements were carried out using the following methods as reported earlier[17].

RESULTS AND DISCUSSION

Photophysical Studies

The absorption spectrum (Fig.-1a) of TCTZnPc (TetraCarboxylThiol Zn-Phthalocyanine) in DMF shows a maximum at 352, 640 and 684 nm. The B-band absorption at 352 nm corresponds to the π-π* transition. The Q-band absorption appears at 684 nm corresponds to π-π* transition. A broad absorbance around 640 nm indicates the tendency of the ZnPc to form H-aggregates, whereas the sharp Q band indicates the absence of J aggregation in DMF. In general Pcs exhibit a high propensity to dimerize in nonpolar solvents, whereas they remain mainly monomeric in polar solvents[1]. But in the present investigation H aggregation is observed even in the polar solvent DMF. This indicates TCTZnPc has the ability to form stacking, irrespective of the polarity of the solvents[19].

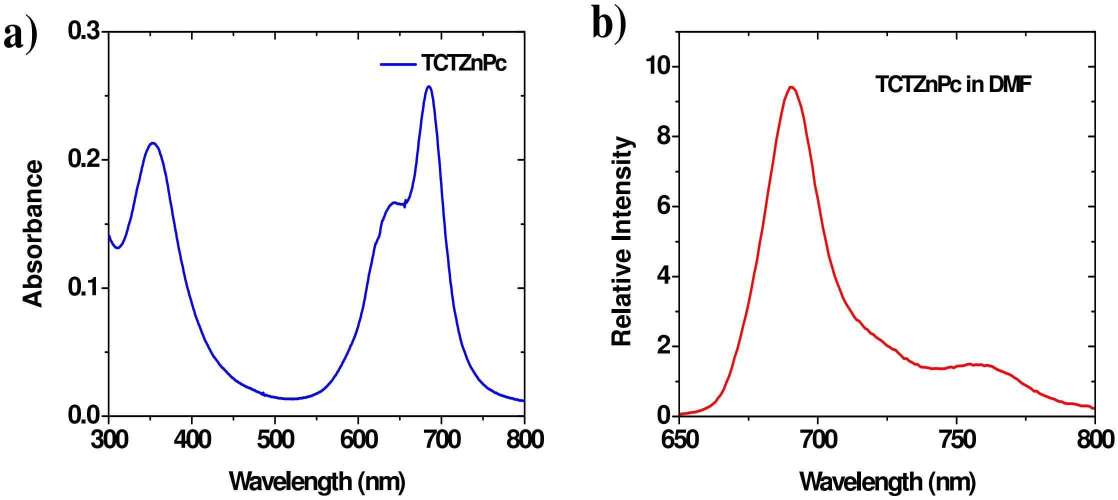


Fig.-1: (a) Absorption and (b) Emission spectrum of TCTZnPc in DMF.

The absorption coefficient of TCTZnPc is 1.2 at 684 nm. When compared to our previously reported carboxyl ZnPc[17], the absorption spectrum of TCTZnPc shows 7 nm redshift. This is due to the presence of electron rich sulfur between ZnPc ring and COOH group, which facilitates the extended conjugation between lone pair of electrons present on the sulfur atom and the ZnPc ring.

The fluorescence spectrum of TCTZnPc in DMF (Fig.-1b) was recorded by exciting at 684 nm, show the emission maximum at 693 nm. Fluorescence quantum yield was found to be 0.14. The fluorescence decay was recorded by exciting the sample at 410 nm and monitoring the decay at 693 nm (Fig.-2). The fluorescence decay of TCTZnPc in DMF was fit in single exponential function with a lifetime of 2.7 ns, corresponds to the conversion from S_1 to S_0 state.

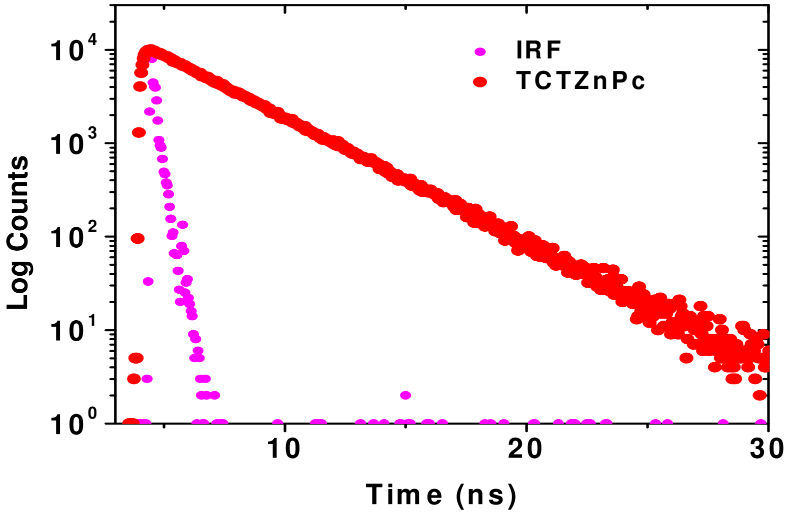


Fig.-2: Time-resolved fluorescence decay of TCTZnPc in DMF after excitation at 410 nm

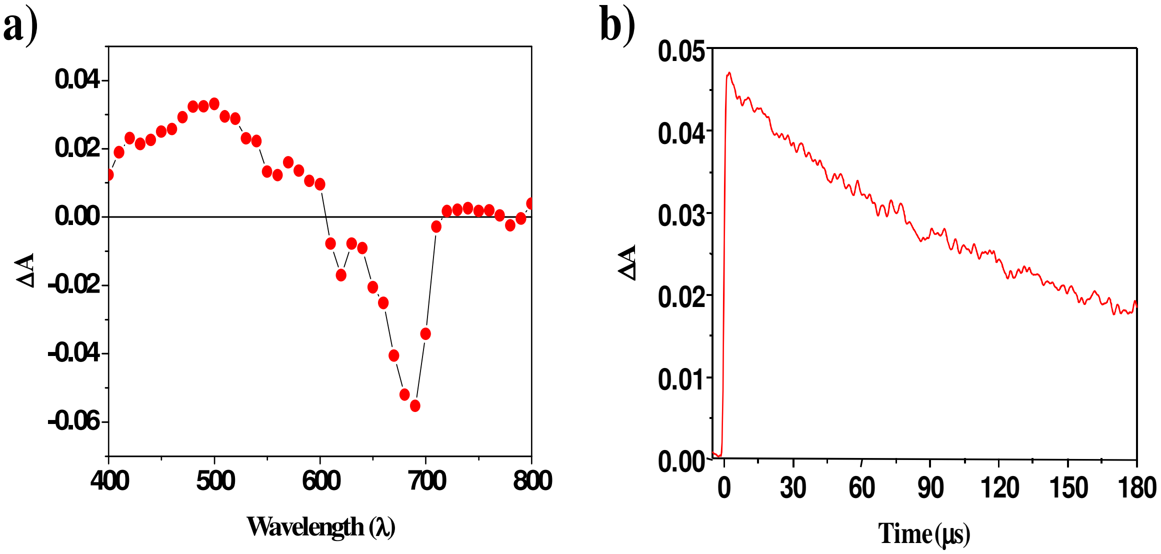


Fig.-3: (a) Time-resolved absorption spectrum of TCTZnPc after excitation at 532 nm for 1 μs, (b) Transient absorption decay of TCTZnPc monitored at 500 nm

Transient absorption studies were carried out by exciting the sample at 355 nm and recorded the spectrum from 400 to 800 nm. The transient absorption spectrum shows broad absorption from 400 to 600 nm, maximum at 500 nm (Fig. 3a), which corresponds to triplet-triplet absorption and bleaching at 690 nm corresponds to the ground state absorption. The triplet lifetimes of the ZnPc is 182 μs, obtained from the kinetic traces (Fig. 3b) at 500 nm, The triplet quantum yield Φ_T is 0.83 calculated by earlier reported method[17,18]. The higher triplet lifetime and triplet quantum yield are attributed to the presence of four carboxyl group and sulfur atom bearing an alone pair of electrons. This may be ascribed to the enhancement of the n–π* character of ZnPc absorption. Since the energy of the n– π* transition is less than the π–π* transition, the presence of a carbonyl group in an aromatic ring generally favor intersystem crossing.

CONCLUSION

In the conclusion, we have synthesized and characterized electron rich ZnPc derivative with thiol linker. Complete photophysical studies were also carried out. From the absorption spectral studies, it is revealed that the ZnPc form H-aggregation in polar solvents, indicates its ability to form stacking irrespective of the polarity of the solvents. This behavior will help for the framing of supramolecular architecture. It exhibits higher triplet lifetime and triplet quantum yield. The 7 nm red shift of absorption spectrum and higher triplet lifetime and triplet quantum yield are due to the presence of electron rich sulfur atom and a carbonyl group. Electron-rich ZnPc with higher triplet lifetime and quantum yield and ability to form stacking will be applicable in various fields of materials application.

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[RJC-1921/2017]