



Light stimulated donor-acceptor forms charge transfer complex in chlorinated solvents

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Abstract. Control over charge transfer, energy or electron transfer process in a donor-acceptor system is rather significant for organic electronics. Although, numerous reports emphasize the balancing between the strength of donor and acceptor direct the specific phenomenon, however, stimuli-responsive D-A system are very few till now. Thereby, we have selected the thianthrene and porphyrin as an electron donor and acceptor for designing the D-A systems and investigated their physico-chemical properties under external stimuli. Herein, free base and metalated thianthrene-porphyrin-based derivatives such as **P-TA** and **P_{Zn}-TA** were designed and synthesized by using Suzuki coupling reaction followed by metalation. Photophysical analysis of two derivatives in chlorinated solvents revealed that charge transfer complex formation whilst application of light as an external stimulus. Cyclic voltammetry studies depict the ease of oxidation suggests that efficient electron transfer from donor to acceptor *via* CT complex. Therefore, these results promote the design of novel thianthrene based D-A systems for organic light-emitting diode applications.

Keywords. Donor-acceptor system; Thianthrene; Porphyrin; Charge transfer complex; Light stimuli.

1. Introduction

Organic donor-acceptor (D-A) systems have attracted much attention in solar cells, light-emitting diodes, field-effect transistor, sensors and biomedical applications owing to their excellent physico-chemical properties, flexibility in optoelectronic properties and thermal stability.^{1–7} In this context, a wide variety of electron donor and acceptors have been developed *via* covalent or non-covalent approach and reported their electron/energy/charge transfer process in detail. For example, electron donors such as thiophene, tetrathiafulvalene, porphyrin, phthalocyanines and electron acceptors are benzothiadiazole, fullerene, arylene diimides and diketopyrrolopyrrole are well-known derivatives towards the construction of D-A systems until now.^{8–10} Our research group also involved to develop the porphyrin-based donor-acceptor systems

and applied them in dye-sensitized solar cells and sensors. Recently, we have reported the self-assembly and electronic properties of few porphyrins based D-A systems consisting of porphyrin as an electron donor and linked with different acceptors such as benzothiadiazole and quinoxaline.^{11–14} Since, the porphyrin possesses highly symmetrical planar structures, 18 π -electron system shows excellent optical and electrochemical properties, large molar absorption coefficient values in the visible region, high thermal and chemical stability. On the other hand, metalloporphyrins also showed significant importance in biology, thus, various metals ions inserted in free-base porphyrin and study their physicochemical properties.^{15,16} Hence, we have selected the two derivatives such as porphyrin and thianthrene for designing D-A systems. In this report, thianthrene as an excellent electron donor and tethered with free base or metalated porphyrin promote the donor-acceptor

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system. On the other hand, thianthrene tends to undergo oxidation in the presence of external stimuli due to the presence of two electron-rich thiophene moieties.^{17–19} Herein, we have designed two porphyrin derivatives **P-TA** and **P_{Zn}-TA** comprised of the thianthrene linked at the meso position of free base and Zn metalated porphyrin (Figure 1). Subsequently, we have investigated to check the charge transfer or electron transfer phenomenon for these two derivatives before and after light illumination. Interestingly, photo-driven molecules showed near-infrared (NIR) absorption bands in chlorinated solvents suggest the formation of charge-transfer complex, confirmed by optical and electrochemical properties. Consequently, such thianthrene based donor-acceptor derivatives pave the way towards the design of novel derivatives for future generated organic electronics.

2. Experimental

2.1 Materials and methods

The reagents and chemicals were purchased from Sigma Aldrich. Analytical reagent grade solvents used

for synthesis and distilled laboratory-grade solvents were utilized for column chromatography. All the reactions carried out under nitrogen/argon atmosphere and the apparatus were protected from ambient light.

2.2 Synthesis of P-TA

A mixture of 1-Thianthrene boronic acid (**1**) (1160 mg, 2.296 mmol) and dibromoporphyrin (500 mg, 0.537 mmol) taken in 5 mL THF and 20 mL toluene, 1M Na₂CO₃ and Bis(triphenylphosphine)palladium(II) dichloride Pd(PPh₃)₂Cl₂ (catalytic amount) added and refluxed for 12 h at 90 °C under N₂ atmosphere in a two necked round bottom flask. The reaction mixture was washed with ethyl acetate/water and organic layer was collected and dried over Na₂SO₄. The crude product was purified by column chromatography (silica gel 100–200 mesh, DCM/hexane) to give purple solid **P-TA** (yield: 60%). ¹H-NMR (CDCl₃, 500 MHz, TMS) δ (ppm) = 8.76 (d, 3H) 8.58 (d, 3H) 8.11 (d, 2H) 8.05 (d, 2H) 7.90 (d, 2H) 7.65 (t, 2H) 7.54 (m, 2H) 7.14 (s, 4H) 6.96 (dd, 2H) 6.87 (d, 6H) 6.58 (d, 2H) 3.82 (m, 8H) 2.15 (m, 6H) 1.38 (d, 15H) 0.86 (dt, 15H) 0.68 (s, 20H) 0.52 (ddd, 15H) -2.45 (s, 1H); **MALDI-TOF-MS** (m/z) = 1402.04 (calculated mass = 1402.65).

2.3 Synthesis of P_{Zn}-TA

P-TA (200 mg, 0.00142 mmol), Zn(OAc)₂ (261 mg, 0.0023 mmol) taken in 1:3 ratio of DCM/ CH₃OH solution and refluxed for 3 h under N₂ atmosphere at 25 °C. The progress of the reaction monitored by TLC and excess solvent removed under reduced pressure. The extraction performed with hexane/DCM. The organic layer was washed with water and dried over Na₂SO₄. The solid residue was subjected to column chromatography (silica gel: 100–200 mesh, DCM/hexane) to give pink coloured solid (yield: 70%) ¹H-NMR (CDCl₃, 500 MHz, TMS) δ (ppm) = 8.76 (d, 4H) 8.58 (m, 3H) 7.65 (t, 2H) 7.51 (s, 3H) 6.88 (t, 3H) 6.96 (dd, 2H) 6.56 (m, 3H) 3.81 (s, 8H) 0.98 (s, 17H) 0.84 (s, 17H) 0.51(m, 34H); **MALDI-TOF-MS** (m/z) = 1464.79 (calculated mass = 1464.56).

2.4 Characterization techniques

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry of **P-TA** and **P_{Zn}-TA** performed on Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron-HiRes,

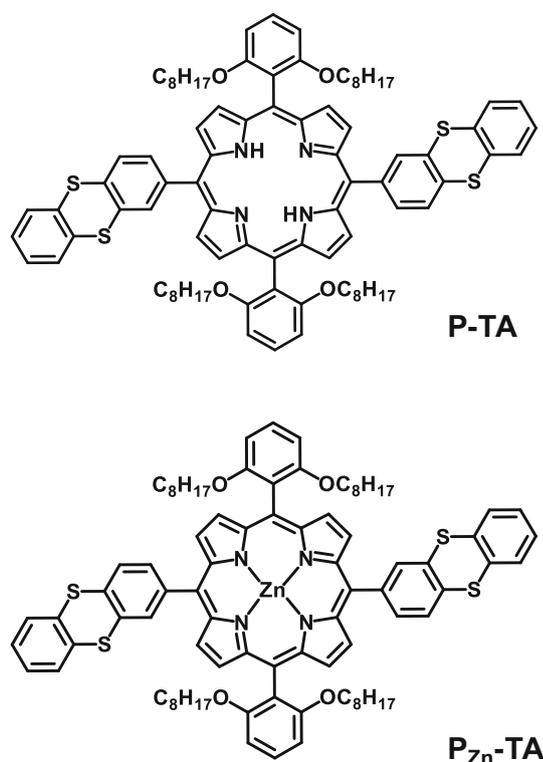


Figure 1. Molecular structures of free base (**P-TA**) and Zn-porphyrin thianthrene (**P_{Zn}-TA**) derivatives.

Power: 85. ^1H Nuclear magnetic resonance (NMR) spectra of samples recorded on a 500 MHz INOVA spectrometer using CDCl_3 as an internal reference.

2.5 UV-visible and fluorescence measurements

UV-vis absorption spectra of **P-TA** and **P_{Zn}-TA** were recorded before and after application of light on Shimadzu (Model UV-3600) spectrophotometer. Steady-state fluorescence spectra of solutions were recorded on a Fluorolog-3 spectrofluorometer (Spex model, JobinYvon) at wavelength of excitation (λ_{exc}) = 420 and 545 nm. Photoluminescence decay profiles measured on a picoseconds time-correlated single photon (TCSPC) setup (Fluoro Log3-Triple Illuminator, IBH Horiba JobinYvon) employing a picoseconds light-emitting diode laser (NanoLED, λ_{exc} = 440 nm). All the analyses were performed in CHCl_3 and measured in 1 cm cuvette at 25 °C.

2.6 Electrochemical studies

Cyclic voltammetry experiments of **P-TA** and **P_{Zn}-TA** were performed on a PC-controlled CH instruments model CHI 620C electrochemical analyzer in CHCl_3 at a scan rate of 200 mV/s using 0.1 M tetrabutylammonium hexafluorophosphate (NBu_4PF_6) before and after exposure to UV light. The working electrode is glassy carbon, saturated calomel electrode (SCE) is reference electrode and platinum wire is an auxiliary electrode.

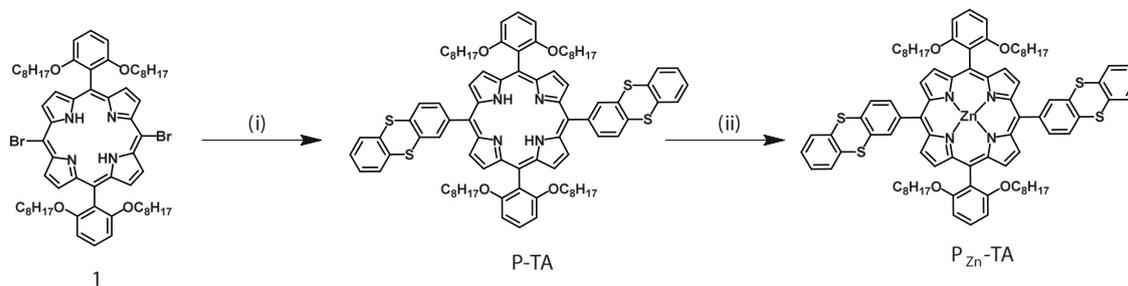
3. Results and Discussions

The two derivatives of **P-TA** and **P_{Zn}-TA** synthesized by using Suzuki coupling reactions followed by metalation with Zn acetate. **P-TA** prepared from the reaction of dibromo porphyrin and 1-thianthrene

boronic acid *via* Suzuki coupling. Subsequently, the metalation of **P-TA** with Zn acetate forms **P_{Zn}-TA** (Scheme 1). These two derivatives were characterized by spectroscopic studies such as ^1H nuclear magnetic resonance, High resolution-mass spectrum (HR-MS), matrix-assisted laser desorption ionization-time of the flight-mass spectrum (MALDI-TOF-MS) (Figures S1-S4, Supplementary Information (SI)), density functional theory (DFT) calculations, Ultraviolet-visible optical absorption, fluorescence and cyclic voltammetry analysis.

Theoretical analysis of **P-TA** and **P_{Zn}-TA** were carried out to estimate the electron density distribution using DFT calculation of Gaussian 09 packages with a functional basis set of the B3LYP/6-31G (d, p) level. Figure 2 represents the optimized structures of the **P-TA** and **P_{Zn}-TA** suggest that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of -4.84 , -4.81 eV and -1.97 , -1.89 eV, respectively (Figure 2a and 2b). Although, **P-TA** and **P_{Zn}-TA** showed marginal electron density distribution at HOMO and LUMO but HOMO - 1, LUMO + 1 and HOMO - 2 and LUMO + 2 depict considerable changes in electron density distribution on porphyrin and thianthrene (Figure 2b). Therefore, the theoretical analysis revealed that **P_{Zn}-TA** might show better donor-acceptor characteristics when compared to freebase derivatives. Moreover, the significant changes in electron distribution on donor and acceptor facilitate to generate the intramolecular charge transfer complex upon application of external stimuli. Inspired by the theoretical analysis, we have performed the detailed photophysical and electrochemical analysis of two derivatives to find the possibilities of occurring charge or electron transfer phenomenon whilst light as external stimuli in chlorinated or non-chlorinated solvents.

In order to investigate the effect of light on the photophysical properties of **P-TA** and **P_{Zn}-TA**, we have chosen the chlorinated/non-chlorinated solvents



Scheme 1. Reagents and Conditions: (i) 1-Thianthrene boronic acid, aq. Na_2CO_3 , THF, Toluene, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 12 h, 90 °C. (ii) $\text{Zn}(\text{OAc})_2$, DCM, CH_3OH , 3 h, 25 °C.

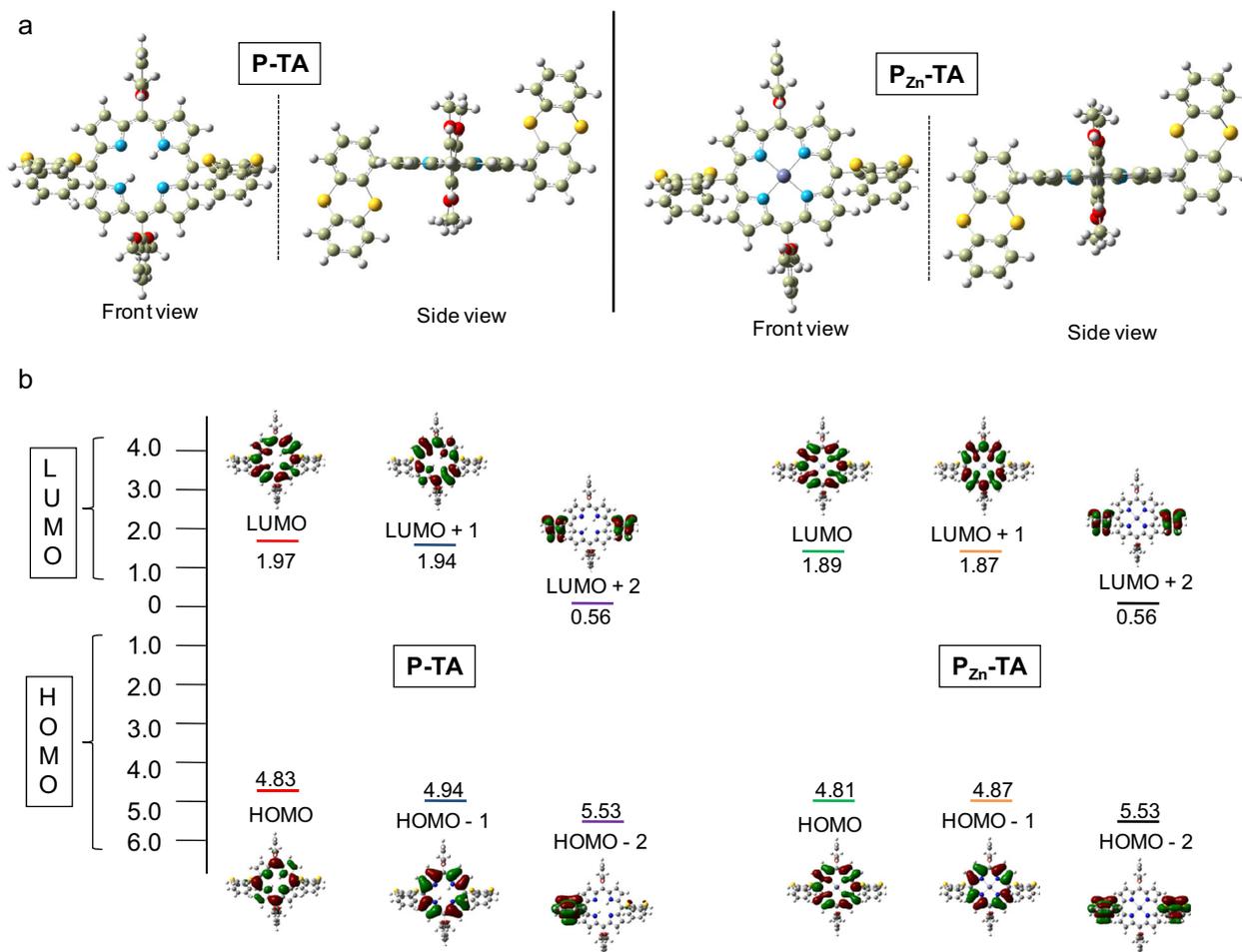


Figure 2. a) Optimized structures **P-TA** and **P_{Zn}-TA** (Front view and back view) and b) their corresponding HOMO-LUMO energy levels.

specifically. Since our previous reported data proved that porphyrin-based D-A system showed significant changes in ground and excited electronic properties in chlorinated solvents upon stimulated with light by the production of hydrochloric acid from chlorinated solvents which induces the protonation on porphyrin derivative.¹³ Thereby, UV-visible absorption spectral analysis of **P-TA** and **P_{Zn}-TA** were recorded in various chlorinated/non-chlorinated solvents: chloroform (CHCl₃), dichloromethane (CH₂Cl₂), tetrahydrofuran (C₄H₈O), toluene (C₇H₈) and acetonitrile (CH₃CN) at a concentration of 1×10^{-5} M (Figure 3a). **P-TA** showed the maximum absorption band at 420 nm corresponding to the Soret band and the other four bands appeared between 500-700 nm represents the Q bands. Whereas **P_{Zn}-TA** exhibits a similar Soret band at 420 nm alike **P-TA** but Q bands changed from four to two bands at 550-650 nm due to the minor tilting in the planarity of the structure as of the presence of Zn metal (Figure 3b). From the initial results, solvent not shown any effect on ground-state electronic properties.

Subsequently, we have illuminated with light and studied their photophysical properties in chlorinated/non-chlorinated solvents. Remarkably, UV-visible absorption spectra of light illuminated two derivatives in chlorinated solvents showed 36 nm bathochromic shift at Soret band along with predominant broadband between 800-1000 nm indicate the charge transfer band in NIR region (Figure 3c). However, the absorption spectra of two derivatives exhibit similar spectral features before and after light in non-chlorinated solvents. In addition, we have observed the visual colour changes in solution from brown to green (**P-TA**) and red to yellow (**P_{Zn}-TA**) represent the photochromism in chlorinated solvents whilst illumination with UV light. Furthermore, we have carried out acid/base analysis in tetrahydrofuran to investigate the importance of chlorinated solvents for the charge transfer phenomenon in **P-TA** and **P_{Zn}-TA**. UV-visible absorption spectra of two derivatives showed the new band at 455-460 nm together with broadband at 800-1000 nm in THF upon addition of dilute HCl,

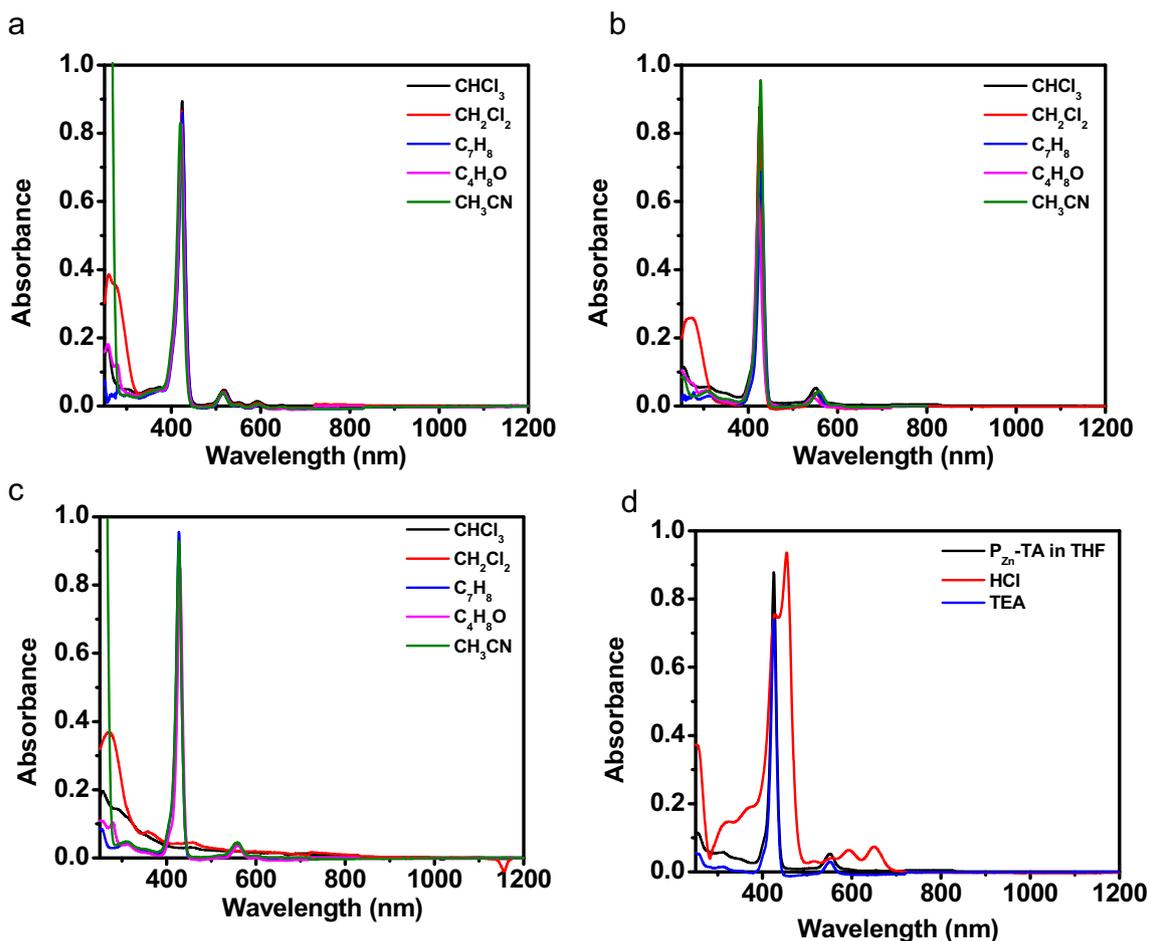


Figure 3. UV-vis optical absorption spectra of (a) **P-TA**, (b) **P_{Zn}-TA**, and (c) light illuminated **P_{Zn}-TA** at a concentration of 1×10^{-5} M in various polar/non polar solvents. (d) UV-Vis optical absorption spectra of **P_{Zn}-TA** in THF whilst addition of HCl and neutralization with TEA.

alike the absorption spectra of light stimulated D-A systems in chlorinated solutions (Figure S5, SI). Subsequently, triethylamine (TEA) as a base added to the solution and the spectrum is a reversal back to the initial state. As a result, light stimulated chloroform to produce the HCl which induces the protonation in porphyrin derivatives results charge transfer complex formation while the absence of HCl generation in non-chlorinated restrict the charge transfer mechanism (Figure 3d).¹¹ Afterwards, we have proved this mechanism by addition of TEA to the light irradiated **P-TA** and **P_{Zn}-TA** in chlorinated solutions and found that UV-visible absorption spectral features exhibits similar to the previous absorption spectra of two derivatives in acid/base analysis (Figure S6, SI). Further, we have investigated the kinetics of **P-TA** and **P_{Zn}-TA** at time lag of 10 seconds to prove the light-induced charge transfer phenomenon in chlorinated solvents (Figure S7, SI). Kinetic analysis revealed that **P-TA** and **P_{Zn}-TA** showed the bathochromic shift in Soret and broad Q bands within 15 min and still remains

stable until 2 h. Therefore, the detailed UV-visible absorption spectral analysis depicts the light stimulated free base or metalated thianthrene-porphyrin showed the charge transfer phenomenon in chlorinated solvents exclusively.

Later, the fluorescence spectral analysis of **P-TA** and **P_{Zn}-TA** were performed in chlorinated/non-chlorinated solvents to check the excited state electronic properties. Thereby, the emission studies of two derivatives recorded at excitation wavelength of 420 nm and 545 nm and revealed the emission maxima at 653 and 719 nm, respectively. Hence, changing the solvent is not playing any role at the ground and excited state electronic properties of two derivatives (Figure 4a). However, absorption studies proved that light illuminated samples showed the charge transfer phenomenon in chlorinated solvents exclusively, thus, emission analysis also performed in CHCl₃ with different intervals of time. Interestingly, emission spectra of two derivatives showed the quenching of the emission upon light

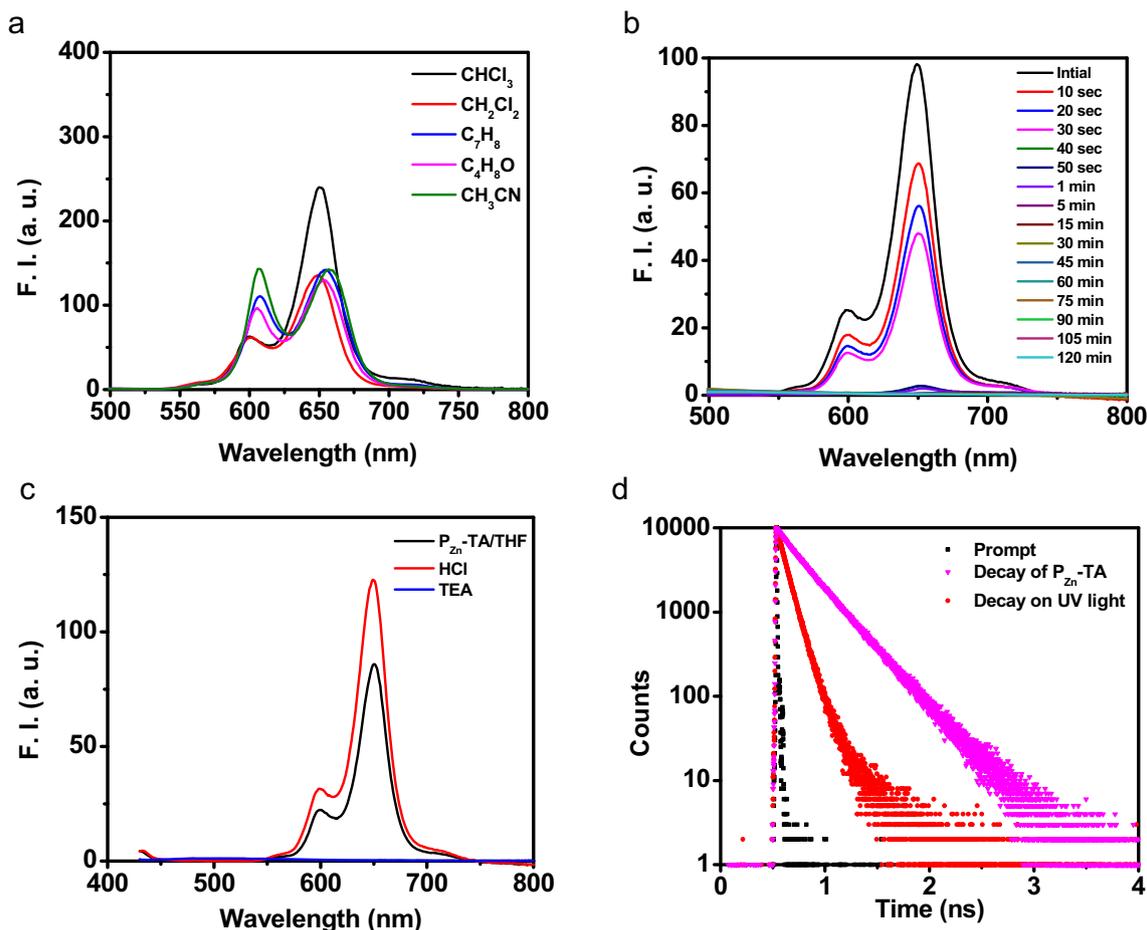


Figure 4. (a) Emission spectra of (a) P_{Zn} -TA in various polar/non polar solvents. (b) Kinetics of P_{Zn} -TA upon UV light irradiation with different intervals of time. (c) Emission spectra of P_{Zn} -TA in THF after addition of HCl and neutralization with triethylamine (TEA). (d) TCSPC studies of P_{Zn} -TA before and after UV light exposure with 440 nm Nano LED.

illumination in $CHCl_3$. The emission spectra of P_{Zn} -TA depict the blue shift in emission maxima at 596 nm and 647 nm followed by quenching of emission after 30 sec and persistent up to 2 h suggest the formation of charged state promote the efficient electron transfer between thianthrene and porphyrin (Figure 4b and S8, SI). Likewise, emission spectra of P -TA and recorded in $CHCl_3$ with different intervals of time and emission maxima observed at 653 nm and 719 nm together with a decrease in intensity of emission maxima (Figure S9, SI). In addition, emission studies performed using the addition of HCl/TEA (acid/base) and proved the quenching of emission while CT state (Figure 4c and Figure S10, SI). Consequently, the fluorescence quantum yields (ϕ) calculated for the light-induced chlorinated solutions of P -TA and P_{Zn} -TA utilizing Zn-tetraporphyrin (ZnTTP) as the internal standard. The resultant quantum yields were 0.10 and 0.09, respectively. Furthermore, the photoluminescence decay profiles were estimated to find the

lifetime values for the initial and light-induced chlorinated solutions of the P -TA and P_{Zn} -TA. The lifetime values calculated by excitation at 440 nm NanoLED source and recorded with an emission maximum at 647 nm. Light stimulated P_{Zn} -TA to exhibit the biexponential decay profile with lifetime values of 1.80 and 5.60 ns lower than initial values of 2.39 and 7.98 ns propose the efficient electron transfer in charged state (Figure 4d). On the other hand, P -TA and displayed the marginal changes in the decay profiles prior and after light exposure (Figure S11 and Table S1, SI). Therefore, photophysical properties of two derivatives suggest that application of light plays a vital role in the formation of charge-transfer complex from D-A systems in chlorinated solvents promote the development of organic light-emitting diodes and field-effect transistors applications.^{20–22}

Having confirmed the charge transfer phenomenon from light stimulated D-A system, we have performed the electrochemical analysis of P -TA and P_{Zn} -TA to

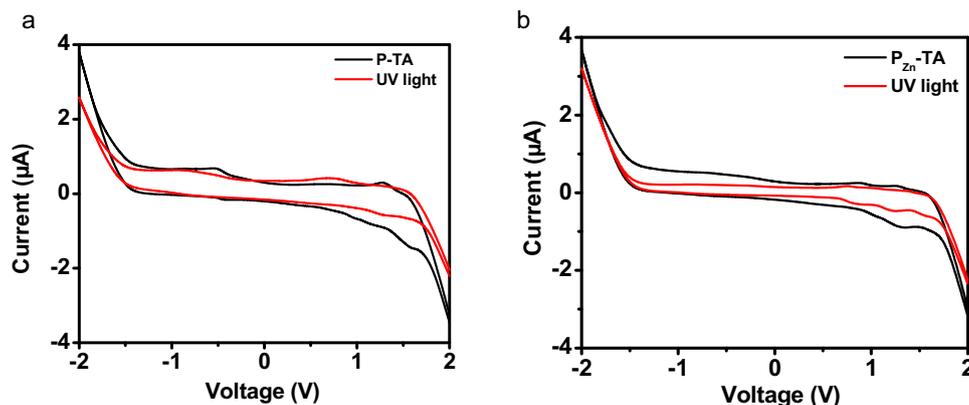


Figure 5. Cyclic voltammetry of (a) **P-TA** and (b) **P_{Zn}-TA** in CHCl_3 before and after UV light exposure at scan rate of 200 mV/s.

understand the redox-active nature of the thianthrene-porphyrin derivatives. Thus, the redox potentials were measured using cyclic voltammetry (CV) for the initial and light illuminated chlorinated solutions of two derivatives using a 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. The saturated calomel electrode, glassy carbon and platinum wire function as a reference, working and counter electrodes with scan rate of 200 mV/s. CV of **P-TA** and showed the oxidation potentials are 1.34 and 1.05 V for initial and light illuminated samples. In case of **P_{Zn}-TA**, the oxidation potentials displayed at 1.28 and 0.96 V for both conditions suggest the ease of oxidation whilst CT state. Hence, the optoelectronic and redox properties correlate well with each other to prove the charge transfer property in thianthrene-porphyrin derivatives upon light stimuli in chlorinated solvents (Figure 5).

4. Conclusions

In summary, we have demonstrated the novel design and synthesis of thianthrene-porphyrin based donor-acceptors system and their photophysical and electrochemical properties proved the charge transfer phenomenon in chlorinated solvents whilst light used as an external stimulus. Detailed UV-visible absorption and fluorescence analysis of light stimulated D-A systems revealed that NIR broad absorption and quenching in emission suggest that charge transfer complex formation leading to an efficient electron transfer process. Electrochemical studies also proved the ease of oxidation from CT state. Consequently, the design of thianthrene based D-A systems showed remarkable optoelectronic properties promote to develop the novel smart

materials for improving the performance of future generated organic electronics.

Supplementary Information (SI)

The ^1H NMR and MALDI-TOF-MS of **P-TA** and **P_{Zn}-TA**. The photophysical studies and electrochemical studies of **P-TA** and **P_{Zn}-TA** shared in Figures S1-S11 and Table S1 are available at www.ias.ac.in/chemsci.

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Declarations

Conflict of interest The authors declare no conflict of interest.

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