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Unsymmetrical β-functionalized 'push–pull' porphyrins: synthesis and photophysical, electrochemical and nonlinear optical properties†

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Two new series of β -triphenylamine-appended porphyrins (MTPP(TPA)₂X, (where M = 2H, Co(II), Ni(II), Cu(III), Zn(III) and X = NO₂/CHO) have been synthesized and characterized by various spectroscopic techniques, namely, UV-vis, fluorescence, NMR spectroscopy, mass spectrometry, cyclic voltammetry, density functional theory and ultrafast nonlinear optical (NLO) studies. They exhibited 16–22 nm and 39–58 nm red-shifts in the Soret and Q_x(0,0) bands, respectively, as compared to MTPPs due to the resonance and inductive effects of β -substituents on the porphyrin π -system. The first reduction potential of **CuTPP** (**TPA**)₂**NO**₂ and **CuTPP(TPA**)₂**CHO** exhibited an anodic shift by 0.44 and 0.36 V, respectively, as referenced to CuTPP, due to the electronic nature of β -substituents (NO₂ and CHO), which led to their easier reduction compared with CuTPP. **H**₂**TPP(TPA**)₂**NO**₂ and **H**₂**TPP(TPA**)₂**CHO** exhibited the largest resultant dipole moments (7.66 D and 4.55 D, respectively) as compared to H₂TPP (0.052 D) due to the cross-polarized push-pull effect of β -substituents (NO₂/CHO and triphenylamino groups) and the nonplanarity of the macrocyclic core. Third-order nonlinear optical properties of **MTPP(TPA)**₂**NO**₂ and **MTPP** (**TPA)**₂**CHO** (M = 2H and Zn(III)) were investigated in a broad spectral range (680–850 nm) using the *Z*-scan technique with femtosecond 80 MHz pulses. These materials demonstrate strong nonlinear optical coefficients, endowing them with potential for prominent photonic applications.

Introduction

The widespread use of optical radiation created from natural or artificial sources in important fields of application, such as communication, machining, surgery, imaging and energy conversion, requires the development of adequate tools to control the radiation features to achieve the desired functions driven by the light in the fastest, most durable, and efficient way. Significant attention has been focused on third-order nonlinear optical (NLO) materials for their potential in optical communication, ultrahigh-speed signal processing and aberration-corrected imaging.^{1–3} NLO is described by a set of nonlinear response properties such as polarization, frequency, phase and the path of incident light exhibited by materials, which can be further used for photonic applications.⁴ NLO

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materials have attracted the interest of physicists, chemists and materials chemists since past three decades due to their great potential in various applications such as optical limiting, optical communication, data storage devices, multiphoto imaging, fluorescence and surface-enhanced Raman scattering.^{5,6} Nonlinear optical activity was first investigated in inorganic crystals (LiNbO₃) and was further extended to a variety of compounds.7 Organic, inorganic and organometallic compounds with highly conjugated π -systems and fascinating photophysical and electrochemical properties are able to display nonlinear optical properties.8 Exceptional organic molecules like porphyrins exhibit significant nonlinear optical properties, making them useful for various applicationoriented aspects, e.g. nanophotonics and biomedical imaging. Porphyrins are aromatic macromolecules that have extensive π -conjugation; they have a central metal ion in their ring structure, which allows them to display tuneable NLO properties.9 Due to these structural characteristics, they are easily used in the harvesting of suitable NLO coefficients for specific application purposes. Some materials with saturable absorption (SA) are used for mode-locking in lasers, and others that display high two/three-photon nonlinear absorption are used

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in optical limiting. Porphyrins can be restructured by replacing their central or peripheral network elements to vary their nonlinear optical fundamentals by playing with the broad-band range of wavelength. The nonlinear response of porphyrin molecules can be enhanced by peripheral substitution, which tunes the photophysical and electrochemical redox properties of porphyrin. Several porphyrins and corroles have been investigated for NLO studies.^{10,11} A number of unsymmetrically substituted porphyrins have been reported for use in nonlinear optics. In 1998, Albert et al. reported the NLO response on push-pull porphyrins and suggested that the NLO response was obtained by (1) reducing the dihedral twist of the phenyl substituents with respect to the plane of the porphyrin macrocycle, (2) $\beta/meso$ functionalization of the macrocycle *via* electron donor and acceptor substituents.¹² Molecules possessing large, conjugated π -systems with acceptor and donor groups at antipodal positions are potentially strong NLO materials. The NLO properties can be tuned by the β -functionalization of porphyrin molecules with both electron-withdrawing and electron-donating groups due to altered optoelectronic and redox properties. Triphenylamine, an electron-donating group, is a famous building block in material chemistry and is mainly utilized in photovoltaic devices.¹³ Triphenylamino (TPA) groups are used in optoelectronic materials due to their good electron-donating ability and hole transport mobility.¹⁴ It was also found that many nitro group-containing porphyrinoids are used in NLO applications where the nitro group acts as an acceptor and generates the asymmetry in the porphyrin molecule.^{10a,15} Porphyrins and their metal complexes have been utilized in various fields such as materials, dye-sensitized solar cells (DSSCs), medicine and catalysis.¹⁶⁻¹⁹ The studies on the nonplanarity of porphyrins are of special interest due to their biological significance. Herein, we report two series of β-trisubstituted 'push-pull' porphyrins having the formyl/ nitro group as an acceptor group and triphenylamine as the donor group (Chart 1). Likewise, in the present work, we present the variations in two-photon absorption, NLO coefficients and the third-order NLO susceptibility of MTPP $(TPA)_2NO_2$ and $MTPP(TPA)_2CHO$ (M = 2H and Zn(II)) for different wavelengths by the Z-scan experiment.²⁰ In open aperture Z-scan experiments, we obtained two-photon absorption coefficients (β) along with the third-order NLO susceptibility $[\chi^{(3)}]$ by fitting the experimental data, whereas closed aperture Z-scan data revealed the magnitude as well as the sign of the nonlinear optical refractive index (n_2) .

In the *Z*-scan technique, we performed the experiment with a single beam, which provided almost the exact information regarding the sign as well as the magnitude of third-order NLO susceptibility $[\chi^{(3)}]$. The transmitted light is a linear function of α (linear absorption coefficient) and *I* (the intensity of light), *i.e.* $\alpha(I) = \alpha + \beta(I)$ and $dI/dZ = \alpha(I)I$, where β is the nonlinear (two-photon) absorption coefficient. The intensity-dependent refractive index varies as $n = n_0 + n_2I$, with n_0 and n_2 being the linear refractive index and nonlinear refractive index, respectively. Considering a Gaussian profile for the input laser pulses, the normalized transmittance can be achieved for the open



Chart 1 Molecular structure of synthesized β -trisubstituted "push-pull" porphyrins.

aperture mode multiphoton absorption theory and for closed aperture configuration as follows:

$$Transmittance, T_{OA(2PA)} = \frac{1}{1 + \beta L_{eff} \left(\frac{I_{00}}{1 + \left(\frac{z}{z_0} \right)^2} \right)}$$
(1)
$$Transmittance, T_{CA(2PA)} = \left(1 \pm \left(\frac{4 \left(\frac{z}{z_0} \right) \Delta \Phi}{\left[9 + \left(\frac{z}{z_0} \right)^2 \right] \left[1 + \left(\frac{z}{z_0} \right)^2 \right]} \right) \right)$$
(2)

where the effective length of the sample is determined by $L_{\rm eff}({\rm cm}^{-1}) \frac{1-e^{-\alpha L}}{\alpha}(2{\rm PA})$ the Rayleigh Range, $Z_0({\rm mm}) = \frac{\pi \omega_0^2}{\lambda}$ the beam waist at focal point (z = 0); $2\omega_0({\rm mm}) = \frac{4f.\lambda}{\pi.d}$, λ is the wavelength and 'd' is the incident beam diameter. The nonlinear refractive index (n_2) was evaluated from the following relation: $n_2({\rm cm}^2{\rm W}^{-1}) = \frac{\Delta\Phi}{I_0 \cdot L_{\rm eff} \cdot k} = \frac{\Delta\Phi \cdot \lambda}{I_0 \cdot L_{\rm eff} \cdot 2\pi}$ We estimated both the real and imaginary parts of $\chi^{(3)}$ from the following equations: ${\rm Im}|\chi^{(3)}|({\rm m}^2{\rm V}^{-2}) = \frac{c\epsilon_0\lambda n_0^2\alpha_2({\rm mW}^{-1})}{2\pi}$, ${\rm Re}|\chi^{(3)}|({\rm m}^2{\rm V}^{-2}) = 2c\epsilon_0n_0^2n_2({\rm m}^2{\rm W}^{-1})$, from which total $\chi^{(3)}$ can be obtained. We used the relation $|\chi^{(3)}|({\rm e.s.u}) = \frac{(3 \times 10^4)^2|\chi^{(3)}|({\rm m}^2{\rm V}^{-2})}{4\pi}$ for the unit conversion of $\chi^{(3)}$.

Synthesis and characterization

Two new families of free base unsymmetrical β -trisubstituted porphyrins (MTPP(TPA)₂X, M = 2H, Zn(II), Co(II), NI(II) and CU



Scheme 1 Synthesis of mixed β -trisubstituted 'push-pull' porphyrins.

(II); $X = CHO/NO_2$) were synthesized using the Suzuki crosscoupling reaction of H_2 TPPBr₂X (X = CHO/NO₂) with 4-(N,Ndiphenylamino)phenyl-boronic acid, where bromo-groups were substituted by triphenylamine (TPA) groups (Scheme 1). As per our knowledge, this is the first time that β -triphenylamine-substituted push-pull porphyrins have been reported. All the synthesized porphyrins were characterized by various spectroscopic techniques such as UV-Vis, fluorescence, ¹H NMR spectroscopic techniques, MALDI-TOF mass spectrometry and elemental analysis. NMR spectra of MTPP(TPA)₂X (where X = NO_2/CHO and M = 2H, Ni, Zn) exhibited resonance arising from β-triphenylamine, meso-phenyl, β-pyrrole, -CHO proton and inner -NH protons. NMR spectra are shown in Fig. S1-S12 in the ESI[†]. The integrated intensity and the positions of protons were found to be in close agreement with the proposed structure. MALDI-TOF-mass spectra of the synthesized porphyrins are shown in Fig. S13-S22,[†] and the IR spectra of $MTPP(TPA)_2X$ (X = CHO/NO₂ and M = 2H, Zn(II)) are presented in Fig. S23 and S24, in the ESI.†

Electronic spectral studies

The electronic properties of porphyrins are influenced by the electronic nature of the β -substituents (electron donor/electron acceptor), core metal ions and the nonplanarity of the macrocyclic core.²¹ The optical absorption and emission spectra of the synthesized free base porphyrins are shown in Fig. 1. Table S1 in the ESI† lists the absorption and emission data of all synthesized porphyrins. The Soret band of these porphyrins was found in the range of $\lambda_{max} = 432-438$ nm and the last Q band was in the range of 593-690 nm. MTPP(TPA)₂X (X = NO₂/ CHO, M = 2H, Co(II), NI(II) and Cu(II), Zn(II)), exhibited 16–22 nm redshifts in the Soret band and 39–58 nm red-shifts



Fig. 1 (a) UV-visible absorption and (b) fluorescence spectra of H_2TPP (TPA)₂NO₂ and H_2TPP (TPA)₂CHO in CH₂Cl₂ at 298 K.

in the last Q band as compared to MTPPs (M = 2H, Co(II), Ni(II) and Cu(II), Zn(II)) due to the resonance and inductive effects of β -substituents on the π -systems of the porphyrins and it is well known that the nonplanar conformation of porphyrins also induces the unusual red-shift in their spectral properties.^{21g,22} The full widths at half maximum (FWHM) of MTPP(TPA)₂X (X = NO₂/CHO; M = 2H, Zn) were greater as compared to MTPPs (M = 2H, Zn), which reflected the greater extent of charge transfer from the HOMO of triphenylamine moieties (electron donor) to the π^* orbitals of the -NO₂/CHO group (electron acceptor) and revealed the intramolecular charge-transfer from the donor to the acceptor group.²³ The synthesized porphyrins (MTPP(TPA)₂X) exhibited 3–26 nm red-shifted absorption spectral features as compared to the β -dimethyl appended porphyrins (MTPP(CH₃)₂X).^{23a}

The emission spectra of MTPP(TPA)₂X (X = NO₂/CHO, M = 2H and Zn(II)) were recorded in CH₂Cl₂ at 298 K. The free base and Zn(II) derivatives of synthesized porphyrins exhibited broad and red-shifted emission spectra due to the unsymmetrical arrangement of β -substituents as compared to H₂TPP and ZnTPP. H₂TPP(TPA)₂NO₂ and H₂TPP(TPA)₂CHO exhibited emission spectra at 754 and 701 nm, respectively, which were found to be red-shifted by 15–25 nm as compared to H₂TPP (CH₃)₂NO₂ and H₂TPP(CH₃)₂CHO, and red-shifted by 47–100 nm as compared to H₂TPP.^{23a} These porphyrins exhibited reduced quantum yields and shorter lifetimes, possibly due to the nonplanar conformation of the porphyrin macrocycle and intramolecular charge-transfer (ICT).²⁴

Electrochemical redox properties

Triphenylamine is a highly conjugated tertiary amine group that acts as a very good electron-donating group in its initial state. Triphenylamine also stabilizes the charge transfer in the excited state.²⁵ Hence, to probe the effect of β -triphenylamine on MTPP(TPA)₂X (X = NO₂/CHO; M = 2H, Co(II), Ni(II) and Cu (II), Zn(II)), the electrochemical redox behaviour was studied in CH₂Cl₂ at 298 K, as shown in Fig. 2 and S25 in the ESI,† and the results were compared with MTPP, MTPPBr₂NO₂ and



Fig. 2 Cyclic voltammograms of (a) CuTPP, CuTPPBr₂NO₂ and **CuTPP** (**TPA**)₂**NO**₂, and (b) NiTPP, NiTPPBr₂CHO and **NiTPP(TPA**)₂**CHO** in CH₂Cl₂ with a scan rate of 0.1 V s⁻¹ at 298 K.

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MTPPBr₂CHO derivatives under similar experimental conditions. The electrochemical redox data of porphyrins are listed in Table S2 in the ESI.† The presence of two bromogroups and one -CHO or -NO2 group in MTPPBr2NO2 and MTPPBr₂CHO results in the anodic shift in their redox potentials to their corresponding MTPPs as the electron-withdrawing nature of the β -substituents leads to the anodic shift in the redox potentials. When two of the bromo-groups were replaced with triphenylamino substituents in MTPP(TPA)₂X (X = CHO/ NO₂), the TPA groups exhibited considerable cathodic shifts in their redox potentials. Comparative representations of the CVs of CuTPP, CuTPPBr₂NO₂ and CuTPP(TPA)₂NO₂, and NiTPP, NiTPPBr₂CHO and NiTPP(TPA)₂CHO are shown in Fig. 2a and b, respectively. CuTPP exhibited two reversible reduction potentials at -1.33 and -1.72 V and two oxidation potentials were found at 0.97 and 1.35 V. CuTPPBr₂NO₂ exhibited anodic shifts by 0.10 V and 0.48 V in the first oxidation and reduction potentials, respectively, from CuTPP. Further, CuTPP (TPA)₂NO₂ showed two reversible oxidation potentials at 1.0 and 1.50 V and three reversible reduction potentials at -0.89, -1.14 and -1.34 V. CuTPP(TPA)₂NO₂ exhibited cathodic shifts in the first oxidation and first reduction potentials by 0.07 and 0.04 V, respectively, as compared to CuTPPBr₂NO₂, due to the electron-donating nature of the TPA group, whereas the first reduction potentials of CuTPP(TPA)2NO2 were anodically shifted as compared to CuTPP due to the effect of the nitro group. Similarly, the first reduction potential of NiTPP (TPA)₂CHO was cathodically shifted as compared to NiTPPBr₂CHO, and anodically shifted as compared to NiTPP and NiTPP(CH₃)₂CHO.^{23a} Other MTPP(TPA)₂X porphyrins followed the same trend. The order of the first reduction potential is as follows: $MTPPBr_2X > MTPP(TPA)_2X > MTPP$. The order of the first oxidation potential is as follows: MTPP < $MTPP(TPA)_2X < MTPPBr_2X$, where $X = CHO/NO_2$ and M = 2H, $Co(\pi)$, Ni(π) and Cu(π), Zn(π), indicating the cathodic shift in their redox potential of MTPP(TPA)2X as compared to MTPPBr₂X due to the electron-donating effect of the TPA substituent. Overall, in the case of MTPP(TPA)₂X, the attachment of the TPA group on the porphyrin core in the place of the bromo-substituents leads to a cathodic shift in the redox potential as compared to MTPPBr₂X, due to the electrondonating nature and inductive effect of the TPA group. The presence of the electron-withdrawing -CHO/NO₂ group in these porphyrins still favours more difficult oxidation and easier reduction as compared to the corresponding MTPPs and the tunable redox behaviour of MTPP(TPA)NO2/CHO revealed a "push-pull" effect of the β -substituents (TPA, NO₂/ CHO) at the periphery of the porphyrin system. Notably, the first reduction potential of MTPP(TPA)NO2/CHO was anodically shifted as compared to MTPP(CH₃)₂NO₂/CHO, possibly due to the push-pull effect of the β-substituents and the extended π -conjugation of the TPA groups.^{23a} By appending the electron-releasing TPA groups and electron-accepting nitro or formyl groups at the β -position of the macrocycle, the HOMO-LUMO gap was reduced as compared to MTPPs and MTPP(CH_3)₂X, where X = NO₂ and CHO. Notably, the HOMO-



Fig. 3 Comparative HOMO–LUMO variation of CuTPP, CuTPPNO₂, CuTPPBr₂NO₂, CuTPPCHO, CuTPPBr₂CHO and CuTPP(TPA)₂CHO.

LUMO energy variations in the synthesized β -trisubstituted porphyrins were compared with MTPP (M = 2H, Co(II), Ni(II) and Cu(II), Zn(II)), mono and tri- β -substituted porphyrins as shown in Fig. 3; the values have been taken from the literature.²⁶ The highest HOMO–LUMO gap was found for MTPPs and linearly decreased on moving from MTPPX to MTPPBr₂X and MTPP(TPA)₂X, where X = CHO/NO₂. The HOMO–LUMO decrement can be ascribed to the presence of electron-withdrawing/donating substituents and structural effects as steric crowding increases around the porphyrin macrocycle. The presence of formyl, nitro or bromo-substituents (electron pulling group) at the porphyrin leads to stabilization of the LUMO level, which decreases the HOMO–LUMO energy gap. Conversely, the triphenylamino group destabilizes the HOMO level.

The HOMO–LUMO gap of **MTPP(TPA)**₂**NO**₂ is lower than that of MTPPBr₂NO₂. However, the HOMO–LUMO gaps of **MTPP(TPA)**₂CHO and MTPPBr₂CHO are comparable. The order of the HOMO–LUMO was observed as follows: MTPPS > MTPPX > MTPPBr₂X and MTPP(TPA)₂X. The trend is more consistent in the case of the nitro-substituted porphyrin as compared with the formyl-substituted porphyrins due to the strong electron-withdrawing nature of the nitro substituent.

DFT studies

The porphyrin core structures of MTPP(TPA)₂X (X = CHO/NO₂ and M = 2H, Co(π), Ni(π) and Cu(π), Zn(π)) are expected to be nonplanar as compared to their corresponding MTPPBr₂X porphyrins since two bromo-substituents were replaced with bulky triphenylamino groups at the β -pyrrole positions. To further investigate the conformational changes in these porphyrins, the optimized geometries of MTPP(TPA)₂X, X = CHO/ NO₂ and M = 2H, Zn(π) were carried out using the B3LYP func-

tional and LANL2DZ basis set, and the results were compared with H_2 TPPBr₂X, X = CHO/NO₂ reported in literature.^{26,27} The optimized geometries of MTPP(TPA)₂X (X = CHO/NO₂ and M = 2H, Zn(II)) are shown in Fig. 4 and S26 in the ESI[†] and the frontier molecular orbitals (FMOs) are shown in Fig. 5. The selected average bond lengths and bond angles of MTPP $(TPA)_2X$ (M = 2H and Zn(II), X = CHO or NO₂) and H₂TPPBr₂X $(X = CHO \text{ or } NO_2)$ are listed in Table S3 in the ESI.[†] The synthesized porphyrins exhibited a saddle-shaped nonplanar conformation of the porphyrin macrocycle due to two triphenylamino groups and one CHO/NO₂. H₂TPP(TPA)₂CHO had ΔC_{β} = ± 0.636 Å and the 24 core atoms $\Delta 24 = \pm 0.312$ Å, which are higher as compared to H2TPPBr2CHO. H2TPPBr2NO2 showed $\Delta C_{\beta} = \pm 0.642$ Å and $\Delta 24 = \pm 0.317$ Å which are similar to H₂TPPBr₂NO₂. These porphyrins showed increments in the $C_{\beta}-C_{\beta}$ bond length along with increments in $C_{\beta}-C_{\alpha}-C_{m}$



Fig. 4 Optimized gas-phase geometries of $H_2 TPP(TPA)_2 NO_2$ and $H_2 TPP(TPA)_2 CHO.$



Fig. 5 FMOs of MTPP(TPA)₂NO₂/CHO, M = 2H, Zn(II).



Fig. 6 Theoretically calculated dipole moment direction of H_2TPP (TPA)₂NO₂ and H_2TPP (TPA)₂CHO.

(Table S3, in the ESI†), which clearly indicate that the pyrrole ring tilted from the mean plane of the porphyrin core to adjust the two new bulky groups at the β -positions, resulting in the nonplanar saddle-shaped conformation. Zn(II) derivatives of synthesized porphyrins exhibited the nonplanar conformation of the macrocycle with the displacement of the β -pyrrole carbon ($\Delta C_{\beta} = \pm 0.580-0.593$ Å). This was further supported by the increment in the $C_{\beta}-C_{\alpha}-C_{m}$ (126.41–126.45 Å) angle with decrements in the N– C_{α} -C_m (124.57–124.71 Å) and M–N– C_{α} (125.18–125.27 Å) angles along with large $C_{\beta}-C_{\beta}$ and $C_{\beta}-C_{\beta'}$ bond lengths (1.372–1.390 Å) as shown in Table S3.†

The Zn(Π) ion was found (0.011–0.033 Å) above the mean plane of the porphyrin core. The N–M–N and N'–M–N' angles (177.23–179.75 Å) deviated from 180°, showing the nonplanar conformation of the M–(N)₄ core. Hence, the synthesized freebase porphyrins were found to be more nonplanar as compared to Zn(Π) porphyrins.

From Fig. 5, it can be seen that the electron density of the HOMO level was spread only at the triphenylamino unit and the electron density of the LUMO level was spread only at the porphyrin core and β-CHO or NO₂ groups. Thus, the triphenylamine moiety acts as the donor group and the formyl or nitro groups act as acceptor groups, which facilitate the 'push-pull' nature of the porphyrin. This electron density distribution also suggests the possibility of intramolecular charge transfer from triphenylamino donors to acceptor porphyrin units. The pictorial representations of the resultant dipole moments of $MTPP(TPA)_2X$ (X = CHO/NO₂ and M = 2H, Zn(II)) triβ-substituted porphyrins are shown in Fig. 6 and S27 in the ESI.[†] H₂TPP(TPA)₂NO₂ and ZnTPP(TPA)₂NO₂ have higher dipole moments (μ = 7.66 and 7.04 D, respectively) as compared to $H_2TPP(TPA)_2CHO$ and $ZnTPP(TPA)_2CHO$ ($\mu = 4.55$ and 4.11 D, respectively) due to the stronger electron-withdrawing nature of the nitro substituent.

These porphyrins exhibited higher dipole moments as compared to H_2 TPP ($\mu = 0.052$ D) due to the nonplanarity of the porphyrin macrocycle and the electronic nature of the β -substituents.

NLO studies using femtosecond pulses

We have obtained prominent Z-scan experimental results for different wavelengths and were able to extract various para-

Table 1	Summary of the NLO co	oefficients of H2TPP(TPA)2NO2,	H ₂ TPP(TPA) ₂ CHO,	ZnTPP(TPA)2NO2 and Zi	nTPP(TPA) ₂ CHO obtain	ned from Z-scan studies
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λ (nm)	$eta imes 10^{-8} \ ({ m cm}~{ m W}^{-1})$	$\sigma_{ m 2PA} \over m (GM) imes 10^5$	Im $(\chi^{(3)}) \times 10^{-11}$ (e.s.u.)	$n_2 imes 10^{-13}$ (cm ² W ⁻¹)	Re $\chi^{(3)} \times 10^{-11}$ (e.s.u.)	Total $\chi^{(3)} \times 10^{-11}$ (e.s.u.)
H ₂ TPP(TPA	$)_2 NO_2$					
680	5.5	2.65	2.538	_	_	_
700	8	3.75	3.8	_	_	_
750	0.16	0.07	0.081	6.8	5.797	5.798
800	0.73	0.29	0.39	0.22	0.187	0.433
850	0.2	0.0773	0.115	_	_	_
H ₂ TPP(TPA) ₂ CHO					
680	1.9	0.918	0.88	7.9	6.73	6.787
700	0.77	0.362	0.37	9.7	8.27	8.28
750	0.39	0.171	0.19	2.97	2.53	2.54
800	0.41	0.168	0.22	3.27	2.79	2.798
850	0.3	0.116	0.173	1.66	1.415	1.426
ZnTPP(TPA	$(2)_2 NO_2$					
680	0.68	1.65	0.899	10.3	8.01	8.06
700	1.32	3.11	1.797	8.8	6.85	7.08
750	1.1	2.42	1.6	7.84	6.10	6.31
800	0.49	1.01	0.76	6.08	4.73	4.79
850	0.53	1.03	0.88	5.73	4.458	4.54
ZnTPP(TPA) ₂ CHO					
680	3.8	9.23	5.03	5.45	4.24	6.58
700	2.25	5.3	3.06	5.33	4.15	5.16
750	0.7	1.54	1.02	5.63	4.38	4.497
800	0.38	0.78	0.591	5.58	4.34	4.38
850	0.43	0.84	0.71	4.69	3.65	3.72

meters like the two-photon absorption coefficient (β) (cm W⁻¹), two-photon absorption cross-section σ_{2PA} (GM), nonlinear refractive index n_2 (cm² W⁻¹) and NLO susceptibility $[\chi^{(3)}]$.²⁸ For all the samples investigated (for **MTPP(TPA)_2NO_2** and **MTPP(TPA)_2CHO** where M = 2H and Zn) in this study, we noticed RSA behaviour in open aperture experimental data, whereas in the closed aperture case, the data displayed a peak-valley nature revealing the defocusing nature (suggesting negative refractive index). The summary of all the NLO data obtained in the presented study is presented in Table 1.

Fig. 7a-e illustrate the open aperture Z-scan data obtained for the H₂TPP(TPA)₂NO₂ for different wavelengths. Fig. 7a displays the open aperture (OA) data for the mentioned sample with a peak intensity of 4.54×10^8 W cm⁻² and the calculated 2PA coefficient (β) was 5.5 × 10⁻⁸ cm W⁻¹ at 680 nm. Fig. 7b exhibits the open aperture data obtained with a peak intensity of 4.02×10^8 W cm⁻² and the calculated β was 8×10^{-8} cm W^{-1} at 700 nm. Fig. 7c presents the OA data (peak intensity of 3.73×10^8 W cm⁻²) and the estimated β was 0.16×10^{-8} cm W^{-1} at 750 nm. Similarly, in Fig. 7d we found the OA data (peak intensity 3.22×10^8 W cm⁻²) were fit to give a β value of 0.73×10^{-8} cm W⁻¹ at 800 nm and Fig. 7e illustrates the OA data for a peak intensity of $2.92 \times 10^8 \text{ W cm}^{-2}$ resulting in the calculated β as 0.2×10^{-8} cm W⁻¹ at 850 nm. In the case of CA we have extracted the value of NLO refractive index (n_2) for 750 nm (Fig. 7f) to be 6.80×10^{-13} cm² W⁻¹ and for 800 nm (Fig. 7g) to be $0.22 \times 10^{-13} \text{ cm}^2 \text{ W}^{-1}$.

For H_2 TPP(TPA)₂CHO, we performed the same *Z*-scan studies in both OA and CA modes; the obtained nonlinear absorption and refractive index coefficients were evaluated (*Z*-scan data and the fits are illustrated in Fig. 8). We achieved



Fig. 7 Experimental and theoretically fitted Z-scan data for sample $H_2TPP(TPA)_2NO_2$ in OA mode at (a) 680 nm, (b) 700 nm, (c) 750 nm, (d) 800 nm, (e) 850 nm. CA data at (f) 750 nm (g) 800 nm. Open circles represent the experimental data points while the solid lines are the theoretical fits.

the coefficients as follows: at wavelengths of 680 nm, 700 nm, 750 nm, 800 nm and 850 nm, we obtained β with magnitudes of 1.9×10^{-8} cm W⁻¹, 0.77×10^{-8} cm W⁻¹, 0.39×10^{-8} cm W⁻¹, 0.41×10^{-8} cm W⁻¹, 0.3×10^{-8} cm W⁻¹, respectively, while the n_2 values were 7.9×10^{-13} cm² W⁻¹, 9.7×10^{-13} cm² W⁻¹, 2.97×10^{-13} cm² W⁻¹, 3.27×10^{-13} cm² W⁻¹ and 1.66×10^{-13} cm² W⁻¹, respectively. Fig. S28 and S29† depict the open and closed aperture data for sample Zn(TPA)₂NO₂ and Zn(TPA)₂CHO, respectively in the same wavelength range. The β values were in the range of $0.38-3.8 \times 10^{-8}$ cm W⁻¹, while the magnitudes of n_2



Fig. 8 Experimental and theoretically fitted Z scan data for sample $H_2TPP(TPA)_2CHO$ in OA mode at (a) 680 nm, (b) 700 nm, (c) 750 nm, (d) 800 nm, (e) 850 nm and CA mode at (f) 680 nm, (g) 700 nm, (h) 750 nm, (i) 800 nm, (j) 850 nm. Open circles represent the experimental data points while the solid lines are the theoretical fits.

were in the 4.69–5.63 \times 10⁻¹³ cm² W⁻¹ range. Table 1 summarizes the NLO coefficients obtained in the present study.

Except at 750 nm and 850 nm, the NLO coefficients (and cross-sections) of H₂TPP(TPA)₂NO₂ were found to be higher as compared to H₂TPP(TPA)₂CHO, which clearly suggests the role of the nitro group (electron-withdrawing) in the case of the former and the 'push-pull' effect of the β-substituents. Similarly, the n_2 values of **ZnTPP(TPA)**₂**NO**₂ were found to be higher than those of ZnTPP(TPA)₂CHO at all the wavelengths. To put this in perspective, the NLO coefficients obtained for these molecules were compared with some of the recently reported moieties. Several novel trans-A2B corroles were investigated by Yadav et al.¹¹ under similar experimental conditions and the magnitudes of β were 10^{-8} cm W⁻¹, which are on par with the values obtained in the present case. The n_2 magnitudes were $\sim 10^{-11}$ cm² W⁻¹, whereas in the present case we achieved ~10⁻¹²-10⁻¹³ cm² W⁻¹. Bharati et al.⁹ investigated zinc porphyrin and a zinc phthalocyanine using similar experimental conditions and obtained $\sim 10^{-11}$ cm² W⁻¹ and $\sim 10^{-7}$ cm W^{-1} for n_2 and β , which are slightly superior as compared to the coefficients obtained here. Yadav et al.11 and Bharati et al.9 performed detailed comparative studies on the NLO coefficients of various porphyrinoids/composites obtained with fs MHz pulses. It is evident from the comparison with their data that the NLO coefficients obtained for the molecules investigated in this study are either on par or superior to a few of them. It is well-established that the NLO coefficients presented here will have contributions from thermal lensing/nonlinearities since the repetition rate is high. All the investigated molecules have small linear absorption at wavelengths <800 nm. The absorption increases towards 600 nm. With sufficient peak intensities (which is the case with the femtosecond pulses used here) there will be absorption to higher excited states from the first excited state (S_1) resulting in nonlinear absorption (in this case there are S_n states absorbing two photons). In the case of >800 nm excitation there is no linear absorption; the nonlinear absorption will result from

virtual states (again sufficient peak intensities should be available). The 2PA coefficients in the non-resonant case are usually weaker as compared to the resonant case, which is what we observed in this case. Further, we calculated the ΔZ_{P-V} values, which were higher than the theoretical $1.7 \times Z_R$ values, indicating the contribution from a component other than pure electronic nonlinearity, which is thermal in origin in this case. We are planning to repeat the NLO measurements with fs kHz pulses (from a femtosecond amplifier), wherein we can expect true electronic nonlinearities. Further, we plan to perform the transient absorption measurements to understand the dynamics in such molecules.

Biswas et al.32 reported in their work that the nonlinear absorption coefficient (β_{2PA}) and third-order nonlinear susceptibility (χ^3) of 2D h-BN nanosheets (BNNS)-GO were significantly enhanced by 13.4% and 21.7%, respectively, when compared to those of bare BNNS. The 2PA coefficients were found to be in the 10–17 cm GW^{-1} range, while the magnitude of n_2 was $\sim 10^{-13}$ cm² W⁻¹. Further, Kumbhakar *et al.*³³ showed the NLO properties of 2D h-BN nanosheets (BNNS), for the first time, using 1064 nm NIR laser radiation with a pulse duration of 10 ns using the Z-scan technique. They discussed the reverse saturable absorption occurring for aqueous colloidal solutions of BNNS with a very large two-photon absorption cross-section (σ_{2PA}) of 57 \times 10⁴ GM. The 2PA coefficients obtained were ~75 cm GW⁻¹. Such large cross-sections can be attributed to the nanosecond excitation and the nano entities used in their work.

Experimental section

Chemicals and instruments

Benzaldehyde and pyrrole were purchased from HiMedia and Alfa Aesar, respectively, and were used as received. All metal salts, CaH₂, *N*-bromosuccinimide and P₂O₅ were purchased from HiMedia. 4-(*N*,*N*-Diphenylamino)phenylboronic acid was prepared according to reported literature.²⁹ Pd(PPh₃)₄ was purchased from Sigma-Aldrich (India) and used as received. Toluene was of analytical grade; it was dried and distilled over P₂O₅ for use. TBAPF₆ was purchased from HiMedia, India, and recrystallized before use. Silica gel employed in this work was purchased from Thomas Baker. H₂TPP, H₂TPPNO₂, H₂TPPBr₂CHO and H₂TPPBr₂NO₂ were synthesized according to the reported literature.^{21g,26,30}

UV-Visible and emission spectra were recorded using a Shimadzu spectrophotometer (UV-2600) and Hitachi F-4600 fluorescence spectrophotometer, respectively, using a quartz cell with a path length of 1 cm. All MALDI-TOF mass spectra were recorded with a Bruker Ultra-fleXtreme TN MALDITOF/ TOF spectrometer and HABA (2-(4-hydroxyphenylazo)benzoic acid) was used as the matrix.¹H and ¹³C NMR spectra were recorded with a Bruker AVANCE 400 MHz NMR spectrometer in CDCl₃ at 298 K. DFT studies were carried out using the B3LYP functional and the LANL2DZ basis set. Electrochemical measurements were carried out using a (CH 620E) CH instru-

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ment. Cyclic voltammetry studies were performed in distilled CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) and three-electrode assemblies were used containing Ag/AgCl as the reference electrode, a platinum wire counter electrode and a platinum working electrode.

We utilized a Ti-sapphire laser oscillator (Chameleon, M s⁻¹ Coherent; 150 fs, 80 MHz, 2-2.5 mm input beam diameter) for Z-scan experiments in the 680-850 nm spectral range. We engaged a 10 cm lens for focusing the beam onto the sample. We performed the experiments in the 680-850 nm range with corresponding Rayleigh range of 2.0-2.5 mm. The fine powderlike samples were dissolved in toluene (10 mM concentration) and they resulted in a linear transmittance of 70-80% in the 680-850 nm wavelength range. We used a 1 mm thick glass cuvette for holding the sample solution while scanning with a linear translation stage and we fed the transmittance data to a photo-diode connected to a power meter. For the closed aperture mode, a varying aperture was kept in front of the photodiode and the experiments were repeated several times to obtain the averaged best data for extracting the NLO coefficients.³¹ The major sources of error in these measurements arise from the estimation of the beam waist (at focus) and the corresponding input peak intensities. The errors in the NLO coefficients were estimated to be $\pm 10\%$.

Synthesis of H₂TPP(TPA)₂NO₂ and H₂TPP(TPA)₂CHO

Free base, 2-nitro-12,13-dibromo-5,10,15,20-tetraphenylporphyrin (0.16 g, 0.196 mmol), was taken in a two-necked round bottom (RB) flask. To this, a solution of 4-(N,N-diphenylamino)phenylboronic acid (0.676 g, 2.35 mmol) in toluene (80 mL) and K₂CO₃ (0.648 g, 4.68 mmol) were added and argon was purged for 15 min. Further, Pd(PPh₃)₄ (0.045 g, 0.039 mmol) was added under an inert atmosphere and the reaction mixture was heated to 95 °C for 20 h. After completion of the reaction, the mixture was cooled to room temperature and concentrated by rotary evaporation. The residue was dissolved in chloroform and washed with aqueous sodium bicarbonate followed by brine solution. The organic layer was separated, dried over anhydrous Na2SO4 and concentrated to a small volume. The crude product was purified by silica gel column chromatography using a $CHCl_3$ /hexane mixture (3:1 v/v) and the polarity was enhanced up to 100% CHCl₃. The product was obtained with a 75% yield (121 mg, 0.104 mmol).

 H_2 TPP(TPA)₂CHO was also synthesized using a similar procedure and the yield was found to be 45% (72 mg, 0.065 mmol).

H₂**TPP(TPA)**₂**NO**₂: UV-Vis. λ_{max} (nm), (log ε): 308 (4.65), 438 (5.13), 539 (4.12), 660 (3.83).¹H NMR in CDCl₃, 400 MHz: δ (ppm): 8.98 (s, 1H, β-H), 8.79–8.83 (m, 2H, β-H), 8.62 (t, J = 4 Hz, 2H, β-H), 8.29 (dd, J = 4 Hz, 8 Hz, 4H, meso-o-Ph–H), 7.93–7.99 (m, 8H, meso-o-Ph–H), 7.73–7.80 (m, 6H, meso-m-Ph–H), 7.51 (m, 2H, meso-m-Ph–H), 7.42–7.45 (m, 4H, meso-p-Ph–H), 7.28 (s, 2H, TPA–H), 7.24 (s, 2H, TPA–H), 6.98–7.03(m, 12H, TPA–H), 6.78–6.81(m, 4H, TPA–H), 6.65 (d, J = 8 Hz, 4H, TPA) –2.29 (s, 2H, -NH).¹³C NMR in CDCl₃ (100 MHz) δ: 147.96, 145.13, 141.26, 141.02, 140.87, 140.38, 136.15, 135.73,

135.23, 132.33, 129.70, 129.14, 128.64, 127.39, 127.24, 126.46, 123.76, 123.13, 122.95, 122.38, 121.95, 29.79. MALDI-TOF-MS (*m*/*z*): found $[M + H]^+$ 1146.86, calcd 1146.44. Elemental analysis calcd for $C_{80}H_{55}N_7O_2$: C, 83.82; H, 4.84; N, 8.55% and found: C, 84.67; H, 5.10; N, 8.73%.

H₂**TPP(TPA)**₂**CHO**: UV-Vis. λ_{max} (nm), (log ε): 308 (4.59), 438 (5.24), 535 (4.06), 576 (3.88), 612(3.72), 678(3.61).¹H NMR in CDCl₃, 400 MHz: δ (ppm): 9.34 (s, 1H, CHO), 9.24(s, 1H, β -H), 8.76 (d, *J* = 4 Hz, 2H, β -H), 8.58 (t, *J* = 8 Hz, 2H, β -H), 8.25 (dd, *J* = 8 Hz, 4 Hz 4H, *meso-o*-Ph-H), 7.81–7.95 (t, *J* = 4 Hz, 4H, *meso-o*-Ph-H), 7.74–7.80 (m, 8H, *meso-m*-Ph-H), 7.50–7.54 (t, *J* = 4 Hz, 2H, *meso-p*-Ph-H), 7.33–7.39 (m, 2H, *meso-p*-Ph-H), 7.31 (m, 4H, TPA-H), 6.98–7.13 (s, 16H, TPA-H), 6.81–6.86(m, 4H, TPA-H), 6.66(d, *J* = 4 Hz, 4H, TPA-H), -2.26 (s, 2H, -NH).¹³C NMR in CDCl₃ (100 MHz) δ : 222.91, 147.96, 135.92, 135.67, 135.34, 132.48, 129.15, 127.04, 126.15, 123.78, 123.08, 122.38. MALDI-TOF-MS (*m*/*z*): found [M + H]⁺ 1129.53, calcd 1129.45. Elemental analysis calcd for C₈₁H₅₆N₆O: C, 85.90; H, 5.06; N, 7.03% and found: C, 85.98; H, 5.21; N, 7.27%.

Synthesis of MTPP(TPA)₂NO₂ and MTPP(TPA)₂CHO, where $M = Co(\pi)$, Ni(π), Cu(π), Zn(π)

In a 100 mL RB, H₂TPP(TPA)₂NO₂/H₂TPP(TPA)₂CHO (0.052 mmol) was dissolved in 12 mL of chloroform. To this, 10 equiv. of $M(OAc)_2 \cdot nH_2O$ (where M = Co, Cu and Zn) dissolved in CH₃OH was added, then the reaction mixture was allowed to reflux for half an hour. The reaction mixture was washed with water to remove excess metal acetate. The organic layer was separated, dried over anhydrous Na₂SO₄ and the solvent was removed by rotatory evaporation. The product was subjected to silica column chromatography for purification using CHCl₃ as an eluent. Further, the NiTPP(TPA)₂NO₂ or NiTPP(TPA)₂CHO complex was prepared by refluxing H₂TPP $(TPA)_2NO_2$ or $H_2TPP(TPA)_2CHO$ and $Ni(OAc)_2 \cdot 2H_2O$ in the DMF for 3 h, then it was cooled to room temperature and water was added to obtain the precipitate, which was filtered using a G-4 crucible. The crude product was further purified via silica gel column chromatography using CHCl₃ as the eluent. The yield was found to be 80-90%.

CoTPP(TPA)₂**NO**₂: UV-Vis. λ_{max} (nm), (log ε): 308 (4.76), 432 (5.01), 551 (4.11), 597 (4.10). MALDI-TOF-MS (*m*/*z*): found [M + H]⁺ 1203.26, calcd 1203.36. Elemental analysis calcd for C₈₀H₅₃CoN₇O₂: C, 79.85; H, 4.44; N, 8.15% and found: C, 79.67; H, 4.62; N, 8.38%.

NiTPP(TPA)₂NO₂: UV-Vis. λ_{max} (nm), (log ε): 309 (4.77), 438 (5.11), 553 (4.17), 602 (4.14). 1H NMR in CDCl₃, 400 MHz: δ (ppm): 8.91 (s, 1H, β-H), 8.56 (d, J = 4 Hz, 1H, β-H), 8.45 (d, J = 4 Hz, 1H, β-H), 8.32 (d, J = 4 Hz, 1H, β-H), 8.26 (d, J = 4 Hz, 1H, β-H), 7.96–7.99 (m, 4H, *meso-o*-Ph-H), 7.56–7.70 (m, 12H, *meso-o*. *m* and *p*-Ph–H), 7.41–7.45 (m, 3H, *meso-p*-Ph–H), 7.28–7.30 (m, 4H, TPA), 7.23–7.25 (m, 4H, TPA–H), 6.98–7.05 (m, 12H, TPA–H), 6.60–6.75(m, 8H, TPA–H).¹³C NMR in CDCl₃ (100 MHz) δ : 147.96, 145.13, 141.26, 141.02, 140.87, 140.38, 136.15, 135.73, 135.23, 132.33, 129.70, 129.14, 128.64, 127.39, 127.24, 126.46, 123.76, 123.76, 123.13, 122.95, 122.38, 121.95, 29.79. MALDI-TOF-MS (*m/z*): found [M]⁺ 1201.66, calcd

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1201.36. Elemental analysis calcd for C₈₀H₅₃N₇NiO₂: C, 79.87; H, 4.44; N, 8.15% and found: C, 79.71; H, 4.72; N, 8.38%.

CuTPP(TPA)₂**NO**₂: UV-Vis. λ_{max} (nm), (log ε): 309 (4.73), 432 (5.17), 559 (4.16), 606 (4.10). MALDI-TOF-MS (*m*/*z*): found [M + H]⁺ 1207.819, calcd 1207.37. Elemental analysis calcd for C₈₀H₅₃CuN₇O₂: C, 79.55; H, 4.42; N, 8.12% and found: C, 79.72; H, 4.69; N, 8.38%.

ZnTPP(TPA)₂NO₂: UV-Vis. λ_{max} (nm), (log ε): 309 (4.85), 434 (5.50), 560 (4.47), 609 (4.36).¹H NMR in CDCl₃, 400 MHz: δ (ppm): 9.16 (s, 1H, β-H), 8.86 (d, *J* = 8 Hz, 1H, β-H), 8.83 (d, *J* = 4 Hz, 1H, β-H), 8.59–8.61 (m, 2H, β-H), 8.17–8.21 (m, 4H, *meso-o*-Ph–H), 7.84–7.88 (m, 4H, *meso-o*-Ph–H), 7.66–7.79 (m, 6H, *meso-m*-Ph–H), 7.49–7.52 (m, 2H, *meso-m*-Ph–H), 7.32–7.36 (m, 4H, *meso-p*-Ph–H), 7.27–7.29 (m, 6H, TPA–H), 7.25 (s, 2H, TPA–H), 6.98–7.07 (m, 12H, TPA–H) 6.86 (d, *J* = 8 Hz, 4H, TPA–H), 6.69 (d, *J* = 8 Hz, 4H, TPA–H).¹³C NMR in CDCl₃ (100 MHz) δ: 147.96, 145.13, 141.26, 141.02, 140.87, 140.38, 136.15, 135.73, 135.23, 132.33, 129.70, 129.14, 128.64, 127.39, 127.24, 126.46, 123.76, 123.13, 122.95, 122.38, 121.95, 29.79. MALDI-TOF-MS (*m*/*z*): found [M + H]⁺ 1208.750, calcd 1208.36. Elemental analysis calcd for C₈₀H₅₃N₇NiO₂: C, 79.43; H, 4.42; N, 8.10% and found: C, 79.58; H, 4.66; N, 8.33%.

CoTPP(TPA)₂**CHO**: UV-Vis. λ_{max} (nm), (log ε): 308 (4.70), 434 (5.11), 555 (4.16), 593 (4.09). MALDI-TOF-MS (*m*/*z*): found [M + H]⁺ 1186.82, calcd 1186.37. Elemental analysis calcd for C₈₁H₅₄CoN₆O: C, 80.18; H, 4.49; N, 6.56% and found: C, 79.97; H, 4.62; N, 6.69%.

NiTPP(TPA)₂CHO: UV-Vis. λ_{max} (nm), (log ε): 309 (4.76), 437 (5.34), 554 (4.11), 598 (4.08).¹H NMR in CDCl₃, 400 MHz: δ (ppm): 9.24 (s, 1H, CHO), 9.18(s, 1H, β -H), 8.56–8.59(m, 2H, β -H), 8.31–8.35 (m, 2H, β -H), 7.98 (dd, J = 4 Hz, 4 Hz 2H, mesoo-Ph–H), 7.95 (dd, J = 4 Hz, 4 Hz 2H, meso-o-Ph–H), 7.65–7.72 (m, 10 H, meso-o- and m-Ph–H), 7.57 (d, J = 8 Hz, 4H, meso-m and p-Ph–H), 7.40–7.44 (m, 2H, meso-p-Ph–H), 7.23 (s, 4H, TPA–H), 6.98–7.07 (m, 16H, TPA–H), 6.72 (d, J = 4 Hz, 4H, TPA–H), 6.62 (d, J = 4 Hz, 4H, TPA–H).¹³C NMR in CDCl₃ (100 MHz) δ : 196.23, 147.84, 134.84, 133.76, 132.51, 129.17, 127.38, 126.12, 123.99, 122.89, 122.49, 29.77. MALDI-TOF-MS (m/z): found [M + H]⁺ 1185.70, calcd 1185.37. Elemental analysis calcd for C₈₀H₅₃N₇NiO₂: C, 80.20; H, 4.49; N, 6.56% and found: C, 80.45; H, 4.61; N, 6.48%.

CuTPP(TPA)₂**CHO**: UV-Vis. λ_{max} (nm), (log ε): 309 (4.81), 434 (5.46), 559 (4.25), 600 (4.20). MALDI-TOF-MS (*m*/*z*): found [M + H]⁺ 1190.49, calcd 1190.38. Elemental analysis calcd for C₈₁H₅₄CuN₆O: C, 79.75; H, 4.46; N, 6.53% and found: C, 79.93; H, 4.62; N, 6.65%.

ZnTPP(TPA)₂**CHO**: UV-Vis. λ_{max} (nm), (log ε): 311 (4.42), 434 (5.16), 562 (3.91), 603 (3.83).¹H NMR in CDCl₃, 400 MHz: δ (ppm): 9.51(s, 1H, CHO), 9.29 (s, 1H, β -H), 8.84 (d, J = 4 Hz, 2H, β -H), 8.61–8.64 (m, 2H, β -H), 8.24 (d, J = 8 Hz, 2H, *meso-o*-Ph-H), 8.17 (d, J = 8 Hz, 2H, *meso-o*-Ph-H), 7.85–7.88 (m, 4H, *meso-m*-Ph-H), 7.69–7.81 (m, 10H, *meso-m* and *p*-Ph-H), 7.47–7.52 (m, 2H, *meso-p*-Ph-H), 7.24–7.35 (m, 4H, TPA-H), 7.06 (d, J = 8 Hz, 2H, TPA-H), 6.99 (t, J = 8 Hz, 4H, TPA-H). ^{6.89} (d, J = 4 Hz, 4H, TPA-H), ^{6.69} (d, J = 8 Hz, 4H, TPA-H). ¹³C NMR in CDCl₃ (100 MHz) δ : 198.17, 148.01, 129.15, 124.16,

123.76, 123.12, 122.65, 122.33, 33.91, 32.01, 29.78, 29.45, 22.78, 14.21. MALDI-TOF-MS (m/z): found [M + H]⁺ 1191.94, calcd 1191.37. Elemental analysis calcd for C₈₀H₅₃N₇NiO₂: C, 79.58; H, 4.45; N, 6.51% and found: C, 79.68; H, 4.49; N, 6.68%.

Conclusions

We have successfully synthesized two new families of β-triphenylamine-appended push-pull porphyrins, MTPP $(TPA)_2X$ where $X = NO_2/CHO$ and M = 2H, $Co(\pi)$, $Ni(\pi)$, $Cu(\pi)$ and Zn(II), for the first time, using a Pd-catalysed Suzuki-Miyaura cross-coupling reaction. The synthesized porphyrins were characterized by various spectroscopic techniques, mass spectrometry, DFT and electrochemical studies and finally, we explored the ultrafast NLO behaviour of free base porphyrins. MTPP(TPA)2NO2/CHO exhibited 16-22 nm and 39-58 nm red-shifts in the Soret and $Q_{x(0,0)}$ bands, respectively, as compared to MTPPs, due to the resonance and inductive effects of β-substituents on the porphyrin π -system. The quantum yields, as well as the fluorescence lifetimes of nitro-substituted porphyrins, have been found to be very low as compared to those of formyl-substituted porphyrins, which clearly suggests the greater extent of chargetransfer from the donor moiety (TPA) to the nitro group via the porphyrin spacer due to the better electron-accepting ability of the nitro group. $H_2TPP(TPA)_2NO_2$ and H_2TPP (TPA)₂CHO revealed large resultant dipole moments (7.66 D and 4.55 D, respectively) as compared to H₂TPP (0.052 D) due to the nonplanarity of the macrocycle core and the cross-polarized 'push-pull' effect of β-substituents. MTPP $(TPA)_2X$, X = CHO/NO₂ and M = 2H, Zn(II), exhibited a nonplanar saddle shape conformation of the macrocyclic core as was confirmed by DFT calculations. The first reduction potential of CuTPP(TPA)2NO2 and CuTPP(TPA)2CHO was found to be anodically shifted by 0.44 and 0.36 V, respectively, as referenced to CuTPP, due to the electronic nature of the β -substituents (NO₂ and CHO), which made them easier to reduce as compared to CuTPP. Redox potentials were found to be less altered in the case of formyl-substituted porphyrins as compared to those of the nitro-substituted porphyrins. The HOMO-LUMO energy levels were also found to be modulated due to peripheral substitutions of the macrocycle. Ultrafast NLO properties of the investigated porphyrins in the visible range were estimated using the femtosecond Z-scan technique. Broadband Z-scan studies with fs MHz pulses revealed strong NLO coefficients and cross-sections for the investigated porphyrins. Due to the high repetition rate of the input pulses, the obtained nonlinearities predominantly have thermal contributions, which can be overcome by performing the measurements with kHz fs pulses. The detailed photophysical, electrochemical, DFT, and NLO studies suggest that these porphyrins have good potential for use in photonic/bio-imaging applications.

Conflicts of interest

There are no conflicts to declare.

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