Sterically hindered 5,15-tetraphenylbenzene-porphyrins: syntheses, structures, atropisomerism and photophysical properties

R V RAMANA REDDY, BIJU BASUMATARY, MUTHUCHAMY MURUGAVEL, KARUNESH KESHAV, ADIKI RAJA SEKHAR and JEYARAMAN SANKAR*

Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal Bypass Road, Bhauri, Bhopal 462 066, Madhya Pradesh, India

E-mail: sankar@iiserb.ac.in

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Abstract. *meso*-Tetraphenylbenzene (TPB) substituted porphyrin hybrids have been designed and synthesized. The *meso*-TPB-porphyrin hybrids exhibit two discrete atropisomers due to restricted rotation around $C_{meso}-C_{TPB}$ bond. Both the atropisomers could be structurally characterized. The photophysical and electrochemical properties of the synthesized hybrids have been investigated with respect to tetraphenylporphyrin (TPP) and tetraphenylporphyrinatozinc(II) (ZnTPP). These hybrids exhibit reminiscent absorption and emission properties. Moreover, the redox potentials of the TPB conjugates are found to be sensitive to the *meso*-substituents as in the case of *meso*-aryl substituents.

Keywords. Porphyrin; atropisomer; tetraphenylbenzene.

1. Introduction

In the myriad of organic π -conjugated materials, π -extended porphyrins play a vital role because of their potential applications in the fields of photovoltaics,¹ organic semiconductors,² photodynamic therapy,³ and non-linear optics.⁴ Recently, interest has been increased towards designing porphyrins decorated with polycyclic aromatic hydrocarbons (PAHs) which results in promising candidates for organic electronic applications.⁵ The intense absorption of porphyrins is often confined to visible region. Porphyrins can be exploited to the fullest extent for various applications if their absorption can be bathochromically shifted towards NIR range. Typically, π -extension is associated with a bathochromic shift of the electronic absorption spectra of these compounds in comparison to the parent tetraphenylporphyrin (TPP).

Fusion of porphyrins with PAH substituents through the formation of an additional bond between the substituent and the β -pyrrolic position of the porphyrin core could be another advanced strategy.⁶ A wide

variety of π -extended porphyrins fused at *meso*- and β -positions of porphyrins with azulene, benzene, naphthalene, and pyrene have been reported.⁷ Anderson and co-workers reported anthracene and *bis*-anthracene fused porphyrin monomer and dimer with near-infrared (NIR) absorption at 973 nm and 1495 nm, respectively.⁸ However, in these systems, the optical properties of the molecular superstructure depends solely on the porphyrin moiety. Reports on carbon-rich porphyrins with structural features that are dominated by PAHs are limited. While the phenyl moieties mainly impart solubility, large PAHs are believed to have noticeable impact on the molecular properties of TPP and it paves the way towards novel materials for nanoelectronics. The combination of graphene model systems and porphyrins has been recently achieved with the close-contact chromophores; for example, hexa-perihexabenzocoronene(HBC)-“superbenzene”-porphyrin conjugates by Jux and co-workers.⁹ With the aim of developing such closest contact chromophores, we have designed and synthesized a series of *meso*-tetraphenylbenzene substituted porphyrins (Figure 1).

*For correspondence

Figure 1. Chemical structures of polyphenyl substituted porphyrins.

2. Experimental section

2.1 General methods

All manipulations of the complexes were carried out using standard Schlenk techniques under nitrogen atmosphere. All the solvents were freshly distilled using standard procedures. Tetraphenylcyclopentadienone, ethyl propiolate, mesitaldehyde, DDQ, triethylamine, zinc acetate were procured from Aldrich and were used as such. Pyrrole was distilled before use. Fluorescence quantum yields were measured by using the reference compounds TPP and ZnTPP in toluene.

2.2 Instrumentation

All 1D and 2D NMR spectra (COSY and NOESY) were recorded on Bruker 400 and 500 MHz instruments. HRMS-Electro Spray Ionization (ESI) mass spectra were recorded on Bruker micro TOF-Q II. Matrix Assisted Laser Desorption/Ionization (MALDI) was recorded on a Bruker ultraflex TOF/TOF mass Spectrometer. UV-Visible absorption studies were performed on an Agilent Cary-100 and fluorescence emission spectra were recorded on a Horiba Fluorolog spectrophotometer with 1 cm, same pair of cuvettes. Lifetime measurements were obtained using a time-correlated single photon counting (TCSPC) spectrometer (Delta Flex-01-DD/HORIBA), using a pulsed diode laser (NanoLED, N-375) source at 408 nm. Picosecond photon detection module

with photomultiplier tube was used as detector. Instrument response function was recorded by using aqueous solution of Ludox. All TCSPC measurements gave 10000 counts in the peak channel, and IBH DAS6 (version) software was used for fitting the decays. All spectra were taken at 298 K. Cyclic and Differential Pulse voltammograms were carried out using a three-electrode system consisting of a Pt disk working electrode, Ag/Ag⁺ reference electrode and Pt-wire counter electrode. Tetrabutyl ammonium hexafluorophosphate (TBAPF₆) was the supporting electrolyte (0.1 M).

2.3 X-ray crystallography

Single-crystal X-ray diffraction data was collected on a Bruker APEX II diffractometer equipped with a graphite monochromator and Mo-K α ($\lambda = 0.71073$ Å) radiation. Data collection was performed using ϕ and ω scans. All crystal structures were solved by direct methods. The structures were solved using direct methods followed by full matrix least square refinements against F₂ (all data HKLF 4 format) using SHELXTL. All calculations were carried out using SHELXL-2014, PLATON 99, and WinGXsystemVer-1.6414 software. Disordered solvent molecules were taken out using the SQUEEZE command in PLATON. All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters.

2.4 Computational details

Computational calculations were performed with the Gaussian O9 program on KANAD– HPC (IISER-B). The calculations were performed by density functional theory (DFT) method with restricted B3LYP (Becke's three-parameter hybrid exchange functional and Lee–Yang–Parr correlation function) level, employing basis sets 6-31G (d) for H, C, N and LANL2DZ for Zn in gas phase. To simulate the ground-state absorption spectra, the time-dependent DFT (TD-DFT) calculations were further carried out at the same level of theory to determine first 20 vertical excitations to the excited state of the molecule. All the optimized structures and molecular orbitals (see in Supporting Information) were visualized by the software Jmol viewer.

2.5 Synthesis and characterization of compounds

2.5a Ethyl-5',6'-diphenyl-[1,1':2'',1''-terphenyl]-3'-carboxylate (1b**):** A mixture of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (**1a**, 0.5 g, 1.30 mmol) and ethyl propiolate (0.191 g, 1.95 mmol) was refluxed in toluene (2 mL) for 3 h. After cooling to room temperature, the crude reaction mixture was filtered through a plug of silica, washed with CH₂Cl₂, followed by removal of the solvent *in vacuo* and purified by column chromatography (3% ethyl acetate/hexane) gave **1b** (0.54 g, 87%). ¹H NMR (400 MHz, CDCl₃) δ 7.88 (s, 1H), 7.22–7.07 (m, 8H), 7.04 (m, 2H), 6.98–6.83 (m, 6H), 6.77 (m, 4H), 4.03 (q, *J* = 7.1 Hz, 2H), 0.93 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 168.82, 142.96, 142.24, 140.98, 140.95, 140.08, 139.97, 139.32, 139.23, 132.06, 131.27, 131.12, 129.85, 127.66, 127.14, 126.99, 126.72, 126.55, 126.33, 125.95, 125.66, 61.00, 13.66. HR-MS (ESI): *m/z* = 477.1835 (found, [M+Na]⁺); 477.1830 (calcd. for C₃₃H₂₆O₂Na).

2.5b (3',6'-diphenyl-[1,1',2'',1''-terphenyl]-4'-yl)methanol (1c**):** To a solution of **1b** (0.642 g, 1.41 mmol) in THF (40 mL) was added LiAlH₄ (0.234 g, 6.18 mmol) and the resulting mixture was stirred at room temperature for 15 h. The reaction was quenched with H₂O (100 mL) and extracted with CH₂Cl₂ (2 × 100 mL). The combined organic layers were dried (Na₂SO₄), filtered and evaporated to give **1c** as a white solid (0.57 g, 98%). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 1H), 7.22–7.05 (m, 10H), 6.95–6.71 (m, 10H), 4.56 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 206.89, 141.75, 141.10, 139.89, 139.81, 139.69, 139.54, 139.09, 137.91, 131.46, 131.19, 130.13, 129.90, 128.91, 127.68, 127.59, 126.90, 126.61, 126.56, 126.26, 125.61, 125.39, 63.75, 30.93, 21.04. HR-MS (ESI): *m/z* = 435.1757 (found, [M+Na]⁺); 435.1719 (calcd. for C₃₁H₂₄ONa).

2.5c Tetraphenylbenzaldehyde (1d**):** To a solution of **1c** (0.412 g, 1 mmol) in CH₂Cl₂ (15 mL) containing 4 Å molecular sieves was added *N*-methylmorpholine-*N*-oxide (NMO, 0.203 g, 1.74 mmol) followed by tetrapropylammonium perruthenate (TPAP, 0.018 g, 0.05 mmol). The

reaction mixture darkened quickly and was stirred for 1 h at room temperature before washing with sodium sulphite solution (10 mL), brine (10 mL) and saturated CuSO₄ solution (10 mL). The solution was dried (Na₂SO₄), filtered, evaporated and redissolved with the minimum volume of CH₂Cl₂. A dark solid precipitate was separated and filtrate was evaporated to give **1d** as a white solid (0.38 g, 93%). ¹H NMR (400 MHz, CDCl₃) δ 9.82 (s, 1H), 8.14 (s, 1H), 7.22–7.16 (m, 6H), 7.15–7.09 (m, 4H), 6.93 (m, 3H), 6.91–6.86 (m, 3H), 6.81 (m, 2H), 6.77 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 192.58, 145.62, 144.29, 142.56, 141.63, 140.74, 139.14, 138.67, 136.39, 133.46, 131.18, 131.07, 130.94, 129.81, 127.92, 127.74, 127.55, 127.23, 127.10, 126.91, 126.69, 126.21, 125.89. HR-MS (ESI): *m/z* = 411.1765 (found, [M+H]⁺); 411.1749 (calcd. for C₃₁H₂₃O).

2.5d 5,15-bis(tetraphenylbenzene)-10,20-bis(2,4,6-trimethylphenyl)-21,23H-porphine (trans-2a** and cis-**2a**):** Tetraphenylbenzaldehyde (**1d**, 0.052 g, 0.128 mmol) and mesityl dipyrromethane (0.034 g, 0.128 mmol) were placed in a dry flask under N₂ and dissolved in CH₂Cl₂ (30 mL). The solution was degassed for 20 min by repeated evacuation and purging with nitrogen. Trifluoroacetic acid (0.984 μL, 0.013 mmol) was added and the reaction mixture was stirred for 8 h in dark at room temperature. DDQ (0.038 g, 0.167 mmol) was then added and stirring continued for 15 min. After quenching the reaction mixture by the addition of triethylamine (2 mL), the mixture was passed over a short plug of silica (CH₂Cl₂). After evaporation, the residue was purified by column chromatography over silica to give a purple solid (0.01 g, 3%) (*trans*-**2a**) and (0.018 g, 5%) (*cis*-**2a**). Compound *trans*-**2a**: ¹H NMR (400 MHz, CDCl₃) δ 8.95 (d, *J* = 4.6 Hz, 2H), 8.52 (d, *J* = 4.5 Hz, 2H), 8.29 (s, 1H), 7.28 (d, *J* = 6.7 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 6H), 7.09–6.97 (m, 6H), 6.88 (m, 4H), 6.73 (d, *J* = 7.4 Hz, 2H), 5.97 (m, 3H), 2.62 (s, 3H), 1.74 (s, 6H), -2.88 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 150.33, 143.92, 141.73, 140.74, 140.41, 140.23, 139.91, 139.44, 138.47, 137.57, 135.66, 131.90, 131.83, 131.76, 130.95, 130.27, 127.67, 127.08, 126.67, 126.23, 125.84, 125.39, 124.57, 118.29, 117.78, 29.72, 21.51, 1.03. HR-MS (ESI): *m/z* = 1307.6057 (found, [M+H]⁺); 1307.5986 (calcd. for C₉₈H₇₅N₄). UV-Vis (dichloromethane) λ_{max}, nm (ε): 424 nm (9.62 × 10⁵ M⁻¹ cm⁻¹), 520 nm (0.53 × 10⁵ M⁻¹ cm⁻¹). Compound *cis*-**2a**: ¹H NMR (400 MHz, CDCl₃) δ 8.96 (d, *J* = 4.6 Hz, 2H), 8.53 (d, *J* = 4.6 Hz, 2H), 8.10 (s, 1H), 7.26 (s, 2H), 7.07 (m, 12H), 6.98 – 6.84 (m, 6H), 6.22 (t, *J* = 7.4 Hz, 2H), 6.14 (t, *J* = 7.2 Hz, 1H), 2.62 (s, 3H), 1.84 (s, 3H), 1.67 (s, 3H), -2.82 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 143.32, 141.68, 140.92, 140.47, 140.27, 140.16, 140.00, 139.66, 139.30, 138.54, 138.39, 137.54, 136.24, 131.88, 131.78, 131.18, 130.26, 127.69, 127.60, 127.07, 126.68, 126.17, 125.77, 125.36, 124.88, 118.27, 118.23, 117.75, 29.72, 21.74, 21.67, 21.62, 21.49, 1.04. HR-MS (ESI): *m/z* = 1307.6057 (found, [M+H]⁺); 1307.5986 (calcd. for C₉₈H₇₅N₄). UV-Vis (dichloromethane) λ_{max}, nm (ε): 424 nm (10.16 × 10⁵ M⁻¹ cm⁻¹), 520 nm (0.41 × 10⁵ M⁻¹ cm⁻¹).

2.5e 5,15-bis(tetraphenylbenzene)-10,20-bis(2,4,6-trimethylphenyl)porphyrinato Zn(II) (trans-2b): To a chloroform (5 mL) solution of compound *trans-2a* (0.05 g, 0.04 mmol) was added zinc acetate dihydrate (0.252 g, 1.15 mmol) in methanol (5 mL). The reaction mixture was stirred for 1 h at room temperature and concentrated by rotary evaporation. The crude mixture was passed through a short pad of silica gel, eluting with dichloromethane/petroleum ether (1:9). All fractions containing *trans-2b* were rotary-evaporated to give a bright red solid (0.047 g, 90%). ^1H NMR (700 MHz, CDCl_3) δ 9.04 (d, $J = 4.4$ Hz, 2H), 8.61 (d, $J = 4.3$ Hz, 2H), 8.39 (s, 1H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.09 (m, 11H), 6.88 (d, $J = 7.6$ Hz, 4H), 6.66 (d, $J = 7.9$ Hz, 2H), 5.90 (t, $J = 7.5$ Hz, 2H), 5.84 (s, 1H), 2.63 (s, 3H), 1.74 (s, 6H). ^{13}C NMR (176 MHz, CDCl_3) δ 150.29, 150.23, 150.19, 149.42, 144.04, 141.88, 141.21, 140.47, 140.44, 140.31, 140.16, 139.79, 139.26, 139.14, 138.30, 137.28, 135.01, 132.42, 131.95, 131.75, 130.77, 130.33, 130.14, 127.65, 127.57, 127.08, 126.64, 126.20, 125.75, 125.43, 125.34, 124.31, 119.00, 118.62, 41.36, 36.10, 36.09, 34.68, 34.54, 31.61, 29.07, 22.67, 22.64, 21.50, 21.45, 18.78, 14.34, 14.14, 11.45. MS (MALDI-TOF, without matrix) m/z calcd. for $\text{C}_{98}\text{H}_{72}\text{N}_4\text{Zn}$: 1368.5048, found: 1368.547. UV-Vis (dichloromethane) λ_{max} , nm (ϵ): 425 nm ($6.04 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), 554 nm ($0.29 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$).

2.5f 5,15-bis(tetraphenylbenzene)-10,20-bis(2,4,6-trimethylphenyl)porphyrinato Zinc(II) (cis-2b): To a chloroform (5 mL) solution of compound *cis-2a* (0.05 g, 0.04 mmol) was added zinc acetate dihydrate (0.252 g, 1.15 mmol) in methanol (5 mL). The reaction mixture was stirred for 1 h at room temperature and concentrated by rotary evaporation. The crude mixture was passed through a short pad of silica gel and eluted with dichloromethane/petroleum ether (1:9). All fractions containing *cis-2b* were rotary-evaporated to give a bright red solid (0.049 g, 94%). ^1H NMR (700 MHz, CDCl_3) δ 8.97 (d, $J = 4.4$ Hz, 2H), 8.54 (d, $J = 4.4$ Hz, 2H), 8.23 (s, 1H), 7.23 (s, 1H), 7.18 (d, $J = 5.1$ Hz, 3H), 7.08 (d, $J = 7.3$ Hz, 2H), 7.05 (t, $J = 7.5$ Hz, 2H), 6.98 (m, 6H), 6.84–6.76 (m, 5H), 6.03 (s, 2H), 5.95 (s, 1H), 2.56 (s, 3H), 1.72 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (176 MHz, CDCl_3) δ 171.19, 150.18, 149.41, 143.54, 141.83, 141.12, 140.59, 140.50, 140.32, 139.72, 139.43, 139.21, 139.16, 138.26, 137.25, 135.57, 132.37, 131.94, 131.76, 131.06, 130.34, 130.15, 127.59, 127.53, 127.07, 126.64, 126.18, 125.74, 125.71, 125.32, 124.48, 118.92, 118.62, 60.42, 35.08, 34.69, 31.62, 29.08, 25.30, 22.68, 21.67, 21.55, 21.51, 21.06, 20.73, 18.79, 14.21, 14.15, 11.46. MS (MALDI-TOF, without matrix) m/z calcd. for $\text{C}_{98}\text{H}_{72}\text{N}_4\text{Zn}$: 1368.5048, found: 1368.547. UV-Vis (dichloromethane) λ_{max} , nm (ϵ): 425 nm ($4.87 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), 554 nm ($0.122 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$).

2.5g 10,20-bis(tetraphenylbenzene)-21,23H-porphine (cis-3a): Compound **1d** (0.2 g, 0.49 mmol) and meso free dipyrromethane (0.071 g, 0.49 mmol) were placed in a dry round bottomed flask under N_2 and dissolved in CH_2Cl_2 (80 mL). The solution was degassed for 20 min, by repeated

evacuation and purging with nitrogen. Trifluoroacetic acid (3.7 μL , 0.049 mmol) was added and the reaction mixture was stirred for 8 h in dark at room temperature. DDQ (0.144 g, 0.633 mmol) was added and stirring continued for 15 min. After quenching the reaction mixture by the addition of triethylamine (3 mL), the mixture was passed over a short plug of silica (CH_2Cl_2). After evaporation, the residue was purified by column chromatography over silica to give a desired compound *cis-3a* (0.135 g, 13%). ^1H NMR (400 MHz, CDCl_3) δ 10.09 (s, 1H), 9.24 (s, 4H), 8.18 (s, 1H), 7.28 (d, $J = 6.8$ Hz, 2H), 7.18–7.02 (m, 10H), 6.98–6.86 (m, 5H), 6.16 (t, $J = 7.6$ Hz, 2H), 6.10–6.02 (m, 1H), -3.35 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.35, 141.64, 141.02, 140.45, 140.24, 140.17, 140.08, 140.02, 139.73, 138.61, 136.37, 131.88, 131.80, 131.22, 131.15, 130.26, 127.63, 127.13, 126.73, 126.26, 126.16, 125.82, 125.78, 125.43, 124.89. HR-MS (ESI): m/z = 1071.4448 (found, $[\text{M}+\text{H}]^+$); 1071.4421 (calcd. for $\text{C}_{80}\text{H}_{55}\text{N}_4$). UV-Vis (dichloromethane) λ_{max} , nm (ϵ): 412 nm ($10.46 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), 507 nm ($0.84 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$).

2.5h 10,20-bis(tetraphenylbenzene)porphyrinato Zn(II) (cis-3b): Compound *cis-3a* (0.1 g, 0.0933 mmol) was dissolved in 8 mL chloroform. To this solution 8 mL methanolic solution of zinc acetate dihydrate (0.615 g, 2.80 mmol) was added. The reaction mixture was stirred for 1 h at room temperature. After concentrating the reaction mixture by rotary evaporation, the crude mixture was eluted with petroleum ether/dichloromethane through a short pad of silica gel. All fractions containing compound *cis-3b* were rotary-evaporated to give a bright red solid (0.093 g, 88%). ^1H NMR (700 MHz, CDCl_3) δ 10.04 (s, 1H), 9.26 (d, $J = 9.2$ Hz, 4H), 8.29 (s, 1H), 7.23–6.93 (m, 11H), 6.78 (m, 6H), 6.00–5.71 (m, 3H). ^{13}C NMR (176 MHz, CDCl_3) δ 150.31, 149.16, 143.54, 141.80, 141.03, 140.64, 140.50, 140.34, 139.88, 138.42, 135.68, 132.71, 132.62, 131.96, 131.81, 131.39, 131.01, 130.82, 130.35, 127.68, 127.64, 127.15, 126.71, 126.24, 125.81, 125.73, 125.63, 125.39, 124.46, 118.69, 105.87, 31.62, 29.73, 22.69, 14.16. MS (MALDI-TOF, without matrix) m/z calcd. for $\text{C}_{80}\text{H}_{52}\text{N}_4\text{Zn}$: 1132.3483, found: 1132.442. UV-Vis (dichloromethane) λ_{max} , nm (ϵ): 414 nm ($4.89 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), 541 nm ($0.154 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$).

3. Results and Discussion

3.1 Synthesis and characterization

The PAH-appended porphyrins reported earlier have been mostly synthesized by Suzuki-Miyaura cross coupling reaction of *meso*-brominated porphyrin with boronic acid of PAH which requires post-functionalization of the porphyrin moiety.¹⁰ In the present work, our synthetic strategy involves MacDonald [2+2] cross condensation reaction of dipyrromethane with a carboxaldehyde.¹¹ This approach provides the

Scheme 1. Synthesis of **1b**, **1c** and **1d**. (a) ethyl propionate, toluene, reflux, 3 h, 87%; (b) LiAlH_4 , THF, 15 h, rt, 98%; (c) NMO, TPAP, CH_2Cl_2 , 1 h, rt, 93%.

Scheme 2. Synthesis of *trans*-**2a/2b**, and *cis*-**2a/2b**. (a) CF_3COOH , 8 h, DDQ, 3% (*trans*-**2a**) and 5% (*cis*-**2a**); (b) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{MeOH}/\text{CHCl}_3$ (1:1), 90% (*trans*-**2b**) and 94% (*cis*-**2b**).

scope for realizing more examples for introducing highly conjugated porphyrins with a variety of polyphenyl or polyaromatic substituents by one-pot synthesis. For the synthesis of precursor **1d**, tetraphenylcyclopentadienone (**1a**) was refluxed with an excess of ethyl propionate in toluene to give compound **1b** in quantitative yield. Reduction of the tetraphenylbenzene ester (**1c**) by LiAlH_4 and subsequent oxidation in presence of stoichiometric *N*-methylmorpholine-*N*-oxide (NMO)/catalytic tetrapropylammonium per-ruthenate (TPAP) gave **1d** in 93% of yield¹² (Scheme 1).

An acid-catalyzed condensation of an equimolar mixture of 5-(2,4,6-trimethylphenyl)dipyrromethane with tetraphenylbenzenecarboxaldehyde (**1d**) in the presence of trifluoroacetic acid gave compound 5,15-bis(tetraphenylbenzene)-10,20-bis(2,4,6-trimethylphenyl)-21,23H-porphine *trans*-**2a** and *cis*-**2a** in 3% and 5% yield, respectively (Scheme 2). Thin layer chromatography (TLC) of the reaction mixture showed two spots which were separated by column chromatography. Both the compounds exhibited identical isotopic pattern in high resolution-electron spray ionization-mass spectrometry (HR-ESI-MS) with molecular ion peak at $m/z =$

Figure 2. 400 MHz ^1H NMR spectra of *trans*-**2a** (bottom) and *cis*-**2a** (top) in CDCl_3 at 25 °C. The asterisks (*) denote residual solvent peaks.

Scheme 3. Synthesis of *cis*-**3a** and *cis*-**3b**. (a) CH_3COOH , 8 h, DDQ, 13%; (b) $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{MeOH}/\text{CHCl}_3$ (1:1), 88%.

1307.5986 (calcd. for $\text{C}_{98}\text{H}_{74}\text{N}_4 [\text{M}]^+ = 1307.6057$) (see in Supporting Information).

Both the compounds had identical UV-Visible absorption spectrum and only a subtle difference was observed in ^1H NMR spectrum (Figure 2, Figures S10–S13 in Supporting Information). Single crystal X-ray diffraction studies confirmed the molecules to be atropisomers (*vide infra*). The eight β -pyrrolic protons of *trans*-**2a** resonate as two doublets at δ 8.52 and δ 8.29 ppm with a typical coupling constant of $^3J_{\text{H-H}} \sim 4.5$ Hz. The unsubstituted *meso*-phenylic protons resonate as a singlet at δ 8.29 ppm. The remaining phenylic protons resonate in a range of δ 5.97 to 7.28 ppm. The ^1H NMR spectra of *cis*-**2a** was similar to that of *trans*-**2a**, except slight upfield shift for unsubstituted *meso*-phenylic proton (Figure 2). Zinc metallation for *trans*-**2a** and

cis-**2a** have been carried out with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in chloroform/methanol (1:2, *v/v*) (Scheme 2). Matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry showed molecular ion peak at $m/z = 1368.547$ (calcd. for $\text{C}_{98}\text{H}_{72}\text{N}_4\text{Zn} [\text{M}]^+ = 1368.5048$) (see in Supporting Information) for both the compounds.

Intriguingly, condensation of 1:1 molar ratio of **1d** with *meso*-free dipyrromethane in the presence of TFA followed by oxidation with DDQ gave exclusively only one product *cis*-**3a** (Scheme 3). Zinc metallated compound *cis*-**3b** was achieved by treating *cis*-**3a** with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ in chloroform/methanol (1:2, *v/v*) (Scheme 2). The compound *cis*-**3a** was confirmed by HRMS with a molecular ion peak at $m/z = 1071.4448$ (calcd. for $\text{C}_{80}\text{H}_{55}\text{N}_4 [\text{M}]^+ = 1071.4421$).

Figure 3. ^1H NMR variable temperature of *trans*-2a (a) and *cis*-3a (b). The asterisks (*) denote residual solvent peaks.

The *meso*-protons of *cis*-3a resonate as a singlet at δ 10.09 ppm and eight β -pyrrolic protons resonate as a doublet at δ 9.24 ppm, and unsubstituted *meso*-phenylic protons resonate at δ 8.18 ppm. The remaining phenylic protons resonate in the range of δ 6.2 to 7.28 ppm. The ^1H NMR for all compounds was assigned and correlated by ^1H - ^1H COSY and ^1H - ^1H ROESY (see Supporting Information).

Indeed, we were surprised to observe the formation of atropisomers in the case of *meso*-mesityl-substituted porphyrins and the appearance of exclusively only one product in the case of *meso*-free porphyrin. To understand this counter-intuitive observation, variable temperature ^1H NMR investigations for *trans*-2a and

cis-3a were conducted. Variable temperature NMR studies indicated restriction of rotation around $\text{C}_{\text{meso}}\text{-C}_{\text{TPB}}$ bond (C_{meso} = *meso*-carbon of porphyrin, C_{TPB} = carbon of TPB) (Figure 3). Probably, the splitting of ^1H resonance at lower temperature in *trans*-2a and *cis*-3a is due to the unsymmetrical conformation, which can be attributed to restricting of conformational dynamics with decreasing temperature.

3.2 Single crystal X-ray diffraction studies

X-ray quality single crystals for solid state structure determination were obtained from slow evaporation

Figure 4. X-Ray crystal structures of *trans*-**2a** (a and c), *cis*-**2a** (b and d), and *cis*-**3a** (c and e). Thermal ellipsoids are drawn at the 50% (*trans*-**2a**) and 15% (*cis*-**2a** and *cis*-**3a**) probability levels. All hydrogen atoms are omitted for clarity.

of MeOH/CHCl₃ solutions. The structures for *trans*-**2a**, *cis*-**2a** and *cis*-**3a** are presented in Figure 4. The porphyrin macrocycles are found to be almost planar despite two sterically hindered tetraphenylbenzene moieties in proximity to porphyrin macrocycle.

The unambiguous evidence of atropisomers *trans*-**2a** and *cis*-**2a** had emerged from single crystal X-ray analysis (Figures 4a and 4b). These conformational isomers probably exist because of restricted rotation around C_{meso}–C_{TPB} bond between porphyrin and tetraphenylbenzene. The C_{meso}–C_{TPB} bond length in *cis*-**2a** is 1.514 Å and 1.510 Å, and dihedral angles (Φ) between planes containing porphyrin and TPB are 77.18° and 81.70°. In sharp contrast, the C_{meso}–C_{TPB} bond length on both sides of *trans*-**2a** is 1.499 Å and dihedral angles (Φ) between planes containing porphyrin and TPB are 73.59° and 73.59°. The summary of crystal parameters is presented in Table S1 (in Supplementary Information).

3.3 Photophysical properties

The photophysical properties of free-base porphyrins and their metal complexes have been investigated in dichloromethane. As anticipated, the *trans*-porphyrin and *cis*-porphyrin exhibited identical UV-Visible absorption and emission spectra (Figure 5). In comparison to tetraphenylporphyrin (TPP),¹³ the absorption λ_{max} for *meso*-mesityl substituted A₂B₂ porphyrins (*trans*-**2a/2b** and *cis*-**2a/2b**) are red-shifted, while the *meso* free porphyrin (*cis*-**3a** and *cis*-**3b**) showed blue-shifted absorption.

The fluorescence lifetime of *cis*-**2a** is longer than that of *trans*-**2a** and *cis*-**3a** (Table 1). It is noteworthy here to mention that the lifetimes of free base porphyrins are shorter than that of tetraphenyl porphyrin (TPP). This may be due to non-radiative losses *via* phenyl ring rotation. On the other hand, Zn(II)-metallated porphyrins

Figure 5. UV-vis (solid lines), emission spectra (dotted lines) for *trans*-2a, *cis*-2a, *cis*-3a (a) and *trans*-2b, *cis*-2b, *cis*-3b (b) recorded in CH_2Cl_2 .

have longer lifetimes than Zn(TPP). The metallated complexes *trans*-2b, *cis*-2b and *cis*-3b exhibits similar trends as that of free bases in UV-visible and emission studies. In sharp contrast, the fluorescence lifetime of *cis*-3b is lesser than that of *cis*-2b and *trans*-2b. The summary of photophysical data is represented in Table 1.

3.4 Electrochemical studies

Cyclic and differential pulse voltammetric studies have been carried out in CH_2Cl_2 containing 0.1 M TBAPF₆

against Ag/Ag⁺ electrode and the redox potentials are summarized in Table 2. The *trans*-2a and *cis*-2a isomers both exhibit two oxidation and one reduction waves at 1.32 V, 0.9 V and −1.43 V, respectively. These results suggest that the conformational difference does not lead to any noticeable electronic perturbation.

The zinc(II) metallated (*trans*-2b and *cis*-2b) TPB-porphyrins have shown similar redox peaks as that of free-base porphyrin. However, the oxidation and reduction potentials were found to be modified compared to that of free-base porphyrin. The presence of electron donating mesityl group on *cis*- and *trans*-TPB porphyrins resulted cathodically shifted oxidation and reduction waves with respect to *meso*-free-porphyrin *cis*-3a and *cis*-3b (Figures S36–S37 in Supporting Information). The electrochemical HOMO-LUMO gaps are fairly consistent with the computed energy gaps (Table 2).

3.5 Computational studies

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were conducted for all the compounds by using B3LYP/6-31G(d) (C, H, N) + LANL2DZ (Zn) level of theory. The Kohn-Sham frontier molecular orbital diagrams for all the compounds are presented in Figure 6. The distribution of electron density in degenerate pairs of HOMO and LUMO of free-base porphyrin and metallated porphyrin are delocalized only onto the π -system of the porphyrin as predicted by the Gouterman four orbitals model. Perpendicular arrangement of TPB with respect to mean plane of porphyrin macrocycle prevents π -extension to the *meso*-aryl substituents (Figure S39 in Supporting Information).

The excitation energies, oscillator strengths, and electronic configuration for all the compounds are listed in Tables S2–S7 (in Supporting Information). The simulated absorption spectra are in close agreement with

Table 1. Summary of absorption and emission data for free base and metallated TBP-porphyrin derivatives in CH_2Cl_2 .

Compd.	Soret-band, λ_{max} , nm ($\epsilon/10^5, \text{M}^{-1}\text{cm}^{-1}$)	Q-bands, λ_{max} , nm ($\epsilon/10^5, \text{M}^{-1}\text{cm}^{-1}$)	λ_{em} , nm (Φ_{fl})	τ_{fl} , ns
<i>trans</i> -2a	424 (9.62)	520 (0.53), 552 (0.28), 595 (0.27), 652 (0.133)	657, 724 (0.20)	9.42
<i>cis</i> -2a	424 (10.16)	520 (0.41), 552 (0.14), 595 (0.11), 652 (0.08)	657, 724 (0.20)	9.52
<i>cis</i> -3a	412 (10.46)	507 (0.84), 539 (0.41), 579 (0.38), 634 (0.22)	635, 702 (0.13)	9.44
<i>trans</i> -2b	425 (6.04)	554 (0.29)	600, 655 (0.16)	6.37
<i>cis</i> -2b	425 (4.87)	554 (0.12)	600, 655 (0.15)	6.12
<i>cis</i> -3b	414 (4.89)	541 (0.13)	580, 635 (0.12)	2.04
TPP ^{13a}	417	513, 548, 589, 646	650, 714 (0.12)	9.62
ZnTPP ^{13b}	421	556, 603	603, 650 (0.033)	1.98

Table 2. Summary of electrochemical potentials for free-base and metallated TBP-porphyrin derivatives vs Ag/Ag⁺.

Compd.	E ^{ox2} (V)	E ^{ox1} (V)	E ^{red} (V)	HOMO-LUMO gap (eV)	
				CV	DFT
<i>trans</i> -2a	1.32	0.90	−1.43	2.33	2.71
<i>cis</i> -2a	1.32	0.90	−1.43	2.33	2.71
<i>cis</i> -3a	1.36	0.98	−1.32	2.30	2.77
<i>trans</i> -2b	1.03	0.72	−1.28	2.00	2.80
<i>cis</i> -2b	1.03	0.72	−1.28	2.00	2.80
<i>cis</i> -3b	1.09	0.78	−1.21	1.99	2.87
TPP ^{14a}		1.02	−1.20	2.22	–
ZnTPP ^{14b}		0.78	−1.39	2.17	–

Figure 6. DFT-predicted orbital energies for free-base and metallated TBP-porphyrin derivatives calculated based on B3LYP/6-31G(d) (C,H,N) + LANL2DZ (Zn) level.

the experimental trend (Figures S40–S45 in Supporting Information). Time-dependent density functional theory calculations revealed significant contributions in vertical electronic transition from HOMO to LUMO, HOMO-1 to LUMO+1; HOMO-1 to LUMO, HOMO to L+1 as shown in Tables S1–S6 (in Supporting Information).

4. Conclusions

In summary, closest-contact *meso*-Tetraphenylbenzene (TPB) substituted porphyrins have been designed and synthesized. Unlike pentaphenylbenzene substitution, these aryl groups present an unsymmetrical environment around the *meso*-positions. Due to this unsymmetrical substitution, the *meso*-mesityl TPB-porphyrins exhibit

two discrete atropisomers *trans*-2a and *cis*-2a due to restricted rotation around C_{meso}–C_{TPB} bond. The photophysical and electrochemical properties of the synthesized hybrids have been investigated with respect to tetraphenylporphyrin (TPP) and tetraphenylporphyrinato zinc(II) (ZnTPP). Moreover, the redox potentials of the TPB conjugates are found to be sensitive to the *meso*-substituents. Therefore, this work opens up the possibility to investigate the applications of these novel atropisomers towards opto-electronic applications to understand the effect of structural isomerism. Achieving highly conjugated *meso*–*meso* directly linked and *meso*–*meso* triply fused dimers *via* oxidative coupling strategy is the main objective of our future work.

Supplementary Information (SI)

Details of synthesis, characterization, computational, photophysical and electrochemical studies are available in SI at www.ias.ac.in/chemsci.

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