

Mono- and di-(2,3,5,6-tetrafluoro-4-*N*,*N*-dimethylaminophenyl) *meso*-tetraarylporphyrins: Synthesis, spectral, structural and electrochemical studies

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Received 24 October 2017 Accepted 28 December 2017

ABSTRACT: A new series of mono-/di-aminated *meso*-tetraarylporphyrins has been synthesized and characterized by conventional spectroscopic methods. Crystal structure analysis shows that interactions involving halogens are the major contributors, and the relative contributions are 56% and 53% respectively for **MB2c** and **MB3c**. All the compounds were electrochemically analyzed under different reaction conditions and showed a positive shift in the reduction and oxidation potentials. The HOMO–LUMO energy gap was altered with respect to the nature of the supporting electrolyte and reference electrodes used. The linear behavior of Randles-Sevcik plots indicate that the redox processes are diffusion controlled; the first reduction/oxidation is a reversible one-electron step whereas the second reduction/oxidation is a quasi-reversible one-electron process. Results also reveal that the mono-aminated porphyrins are more electron deficient than non-aminated and di-aminated porphyrins.

KEYWORDS: fluorinated/aminated porphyrins, synthesis, structure, spectral, electrochemistry.

INTRODUCTION

Porphyrins, the pigments of life, and their related compounds play a crucial role in photosynthetic processes as carriers of small diatomic molecules and also as catalysts in several enzymatic reactions [1]. Synthetic porphyrin analogues have been widely employed as biomimetic models [2] due to their ease of structural functionalization and in medicinal chemistry as photosensitizers in photodynamic therapy to kill cancer cells [3, 4]. Owing to their interesting photophysical properties, synthetic versatility and high photo/thermal stability porphyrins are considered as interesting materials in non-linear optics, photovoltaics, chemical sensors and energy conversion [5]. Their photophysical properties can be altered by introducing various metal ions into the free-base porphyrin. These metalloporphyrins have been widely used as catalysts for oxidation of hydrocarbons and metal mediated redox reactions [6, 7]. Due to their unusual electronic properties, fluorinated metalloporphyrins possess high catalytic activity and are highly stable towards the oxidants [8]. Moreover, the presence of fluorine at the periphery of the porphyrin molecule stabilizes its highest occupied π -orbital and alters the electrochemical properties [9, 10].

In recent years, dipyrromethanes have received much attention owing to their application as building blocks in synthesis of *trans*-substituted porphyrins by two-step one-flask porphyrin synthesis. The trans-porphyrins are well-suited for their application in the preparation of linear porphyrin arrays [11]. It is well known that the photophysical and redox properties of porphyrins can be significantly influenced by the molecular environment around the porphyrin macrocycle. Furthermore, the electrochemical properties of the porphyrins are well studied in the literature, and these electrochemically active tetrapyrrolic π -conjugated compounds are involved in multiple electron transfer processes. The potential difference between the first oxidation and reduction is represented as the HOMO-LUMO gap of the molecule at particular conditions. Depending upon the nature

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of the solvents, planarity of macrocycle, substituents at meso-/beta-positions, the central metal ion, axial ligands, electrolytes, electrodes and redox potentials may vary. Electrochemical properties of porphyrins containing manganese, iron, cobalt, nickel and zinc as metal centers are well studied [12], and recently Fang et al. have reported the electrochemistry of Cu(II/III) [13]. These metal complexes have various applications, such as catalytic epoxidation [14, 15], CO₂ reduction [16, 17], nitrite detection [18] and NO detection in cancer cells [19]. More studies are required for clear understanding of the electrode reactions of porphyrins and other influencing factors. In this context, the present work explains the synthesis spectral, structural and electrochemical properties of aminated (mono- and di-) porphyrins and their metal complexes [Cu(II) and Zn(II)] (Fig. 1). The electrochemistry of the molecules has been investigated using different electrolytes (TBAP/ TBAHFP) as well as different reference electrodes (Ag/ AgCl and Calomel), and the results are discussed.

EXPERIMENTAL

Materials and instrumentation

Commercially-available analytical grade reagents were purchased and used without further purification. Solvents were purified using the standard procedures [20] prior to use. Optical spectra were recorded at room temperature in CH₂Cl₂ using a Shimadzu double beam spectrometer 4600 with 1 cm matched quartz cuvettes at room temperature and ¹H NMR spectra were measured using a Bruker Avance III 400 MHz spectrometer. Mass spectra were recorded under ESI/HR-MS at 61,800 resolution using a Thermo Scientific Exactive mass spectrometer (Thermo Fischer Scientific, Bremen, Germany) or a Waters Xevo G2 Quadrapole-Time-of-Flight (Q-TOF) mass spectrometer. Fluorescence spectra and quantum yield measurements were performed using a Perkin Elmer LS 55 luminescence spectrophotometer. Electrochemical analysis of the porphyrin samples was performed on a CH-instruments Inc, USA (Model: CHI660E) electrochemical analyzer equipped with a potentiostat/galvanostat with a Fourier Transform AC Voltammeter. The electrochemical cell consists of a threeelectrode assembly containing a glassy carbon working electrode, a standard Calomel electrode (SCE)/Ag-AgCl as the reference electrode and a platinum wire as the auxiliary electrode. The concentrations of the porphyrin samples were employed as ~1 mM. All the measurements were performed at 25 °C in DCM under N₂ atmosphere using 0.1 M tetrabutylammonium hexafluorophosphate (TBAHFP)/tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte.

X-ray crystallography

Single crystal X-ray diffraction data of MB2c and MB3c were collected on a Bruker Kappa Apex II single crystal diffractometer. Single crystals of compounds suitable for X-ray diffraction study were obtained by the vapor diffusion method using tetrahydrofuran and methanol at room temperature. Crystal data were collected using graphite monochromated Mo-K_a radiation $(\lambda = 0.71073 \text{ Å})$. The structures were solved by direct methods using the SIR92 [21] (WINGX32) program. Structure refinement was done using the SHELXL97/ SHELXL-2014/7 [22] software via successive Fourier synthesis on $|F|^2$ using the full-matrix least squares refinement. All the non-hydrogen atoms were refined anisotropically. Crystal data are summarized and further details of structure determination and refinement are given in Table 1.

Hirshfeld surface analysis

To quantify and understand the non-covalent interactions, Hirshfeld surface analysis and generation of 2D fingerprint plots were attained using *Crystal Explorer 3.1* [23].

Synthesis of trans-MB(TF5)D(4-/3,5-BrP)P and their metal derivatives (MB1a–MB3a and DB1a–DB3a). The precursor, 5-(pentafluorophenyl)dipyrromethane was prepared using the available literature method [24]. 5-(Pentafluorophenyl)dipyrromethane ($1.5 \text{ g}, 4.8 \times 10^{-3} \text{ mol}$) and 4-bromo benzaldehyde ($0.89 \text{ g}, 4.8 \times 10^{-3} \text{ mol}$) were added to a dry double-necked round-bottomed flask



Fig. 1. Chemical structure of porphyrins under study

	MB2c	MB3c
Empirical formula	$C_{48}H_{28}Br_2F_8N_6Cu$	$C_{156}H_{110}Br_6F_{24}N_{18}O_4Zn$
fw	1064.12	3432.18
CCDC no.	974217	1058022
Solvent systems	CHCl ₃ /MeOH	THF/MeOH
crystal system	Monoclinic	Triclinic
space group	P2/c	P-1
<i>a</i> , Å	14.698	14.0583 (10)
b, Å	6.812	16.0409 (10)
<i>c</i> , Å	22.053	19.3733 (13)
α, (deg)	90	67.515 (2)
β , (deg)	91.63	72.516 (2)
γ, (deg)	90	73.699 (2)
T (K)	293 (2)	293 (2)
λ, Å	0.71073	0.71073
volume (Å ³)	2207.1	3781.5 (4)
Ζ	2	1
D_{calcd} (mg/m ³)	1.601	1.507
no. of unique reflections	2701	11707
no. of parameters refined	171	627
GOF on F^2	1.021	1.055
R_1^{a}	0.0383	0.0562
wR_2^{b}	0.0809	0.1535

Table 1. Crystal structure data of porphyrins under study, MB2c and MB3c.

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |Fc|| / \Sigma |F_{o}|; I_{o} > 2\sigma (I_{o}). {}^{b}wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}.$

containing 700 mL of CH₂Cl₂ and N₂ gas was purged for 10 min. Then, $BF_3 \cdot OEt_2$ (0.75 mL, 2.5 M) was added, then the solution was stirred under N₂ at room temperature for 1 h, followed by the addition of 0.9 g of 2,3-dichloro-5,6dicyano-1,4-benzoquinone (DDQ). The reaction mixture was further stirred at room temperature for an additional 1 h, and then the solvent was removed. The compound was purified by silica column chromatography with a chloroform and hexane mixture (30:70). The compound was collected under vacuum, providing 0.8 g of MB1a as a purple solid (Yield: 35%). The copper(II) (MB2a) and zinc(II) (MB3a) complexes were synthesized in a chloroform/methanol mixture using the corresponding metal acetate, and the yields were found to be quantitative (93–95%). Similar procedures were adapted to synthesize other porphyrins, **DB1a-DB3a**. UV-vis data of porphyrins in CH₂Cl₂ at 298 K, λ_{max} (log ϵ/M^{-1} cm⁻¹): MB1a, 416 (5.65), 510 (4.42), 543 (3.81); 588 (3.96), 641 (3.51);MB2a, 412 (5.72), 537 (4.39), 572 (3.85); MB3a, 417 (5.63), 546 (4.28), 578 (3.52); **DB1a**, 416 (5.57), 509 (4.41), 548 (3.76), 584 (3.94), 639 (3.43); **DB2a**, 412 (5.69), 536 (4.43), 570 (3.92) and DB3a, 417 (5.68), 545 (4.46), 575 (3.91). ¹H NMR data: 400 MHz, CDCl₃, δ (ppm): **MB1a**, 8.95–8.83 (m, 8H), 8.09 (d, J = 8.00 Hz, 4H), 7.94 (d, J = 8.00 Hz, 4H), -2.88 (s, 2H); MB3a, 9.03–8.88 (m, 8H), 8.08 (d, J = 8.00 Hz, 4H), 7.92 (d, J = 8.00 Hz, 4H; **DB1a**, 8.88–8.79 (m, 8H) 8.24 (s, 4H), 8.09 (s, 2H), -3.01 (d, 2H); **DB3a**, (500 MHz), 8.96–8.85 (m, 8H), 8.34-8.32 (m, 4H), 8.15-8.13 (m, 2H). ESI mass data of MB1a (C₄₄H₁₈N₄F₁₀Br₂): 952.43 (Calcd.), 953.00 (Found); **MB2a** ($C_{44}H_{16}N_4F_{10}Br_2Cu$): 1013.96 (Calcd.), 1013.9139 (Found); **MB3a** (C₄₄H₁₆N₄F₁₀Br₂Zn): 1015.81 (Calcd.), 1015.9087 (Found); **DB1a** (C₄₄H₁₆- $N_4F_{10}Br_4$): 1110.22 (Calcd.), 1110.00 (Found); **DB2a** $(C_{44}H_{14}N_4F_{10}Br_4Cu)$: 1171.75 (Calcd.), 1172.7312 (Found); **DB3a** (C₄₄H₁₄N₄F₁₀Br₄Zn): 1173.60 (Calcd.), 1173.7312 (Found). Fluorescence spectral data of porphyrins in CHCl₃ at 298 K (λ_{ex} at Soret band of respective compound, MB1a-MB3a and DB1a-DB3a), λ_{em} for **MB1a**: 646 (s), 710 (s); **MB2a**: **MB2c**: 649 (w), 713 (w); MB3a: 590 (w), 640 (s); DB1a: 644 (w), 708 (s); **DB2a**: 656 (w), 712 (w); **DB3a**: 587 (w), 639 (s).

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Synthesis of M(TF5)(TF4DMA)D(4-/3,5-BrP)P (MB1b-MB3b and DB1b-DB3b), trans-MB(TF4DMA)D(4-/3,5-BrP)P(MB1c-MB3c and DB1c-DB3c) and their metal derivatives. Nucleophilic substitution reaction of 5,15-bis(pentafluorophenyl)-10,20-bis(4'-bromophenyl)porphyrin (MB1a) with N,Ndimethylamine hydrochloride yielded two fractions, namely mono- (MB1b) and di- (MB1c) aminated porphyrins, which were unable to separate in silica column using a CHCl₃/hexane mixture. Instead, the zinc derivative. 5,15-bis(pentafluorophenyl)-10,20-bis(4'bromophenyl)porphyrinato zinc(II) (MB3a) was used, and the obtained two products, mono- (MB3b) and di-(MB3c) aminated porphyrins were separated in silica using 5% CHCl₃ in hexane as eluent. After successful separation of the mono- and di-aminated zinc(II) derivatives, which were subjected for demetallation reactions in CHCl₃ with 5% HCl/H₂SO₄ under vigorous stirring for 30 min in ice cold conditions. Then, the reaction mixture was washed with water, extracted and purified by column chromatography using CHCl₃. The yields of MB1b and MB1c were found to be 72 and 73% respectively. The free-base derivatives (MB1b and **MB1c**) were dissolved further in CHCl₃ and subjected to react with excess copper acetate in methanol, refluxed for 2 h. The solvent was evaporated and the reaction mixture was redissolved in CHCl₃, purified by silica column chromatography using a 5% chloroform/hexane mixture, and quantitative yields of MB2b (93%) and MB2c (95%) were obtained. A similar reaction procedure was adopted for **DB1b–3c** derivatives, and the detailed procedure is given below.

5,15-bis(pentafluorophenyl)-10,20-bis(4'-bromophenyl)porphyrinato zinc(II), **MB3a** (0.5 g, 4.9×10^{-4} mol) and N,N-dimethylamine hydrochloride (2.12 g, 2.6×10^{-2} mol) were added to a dry round bottomed flask containing 50 mL of dimethylformamide. The resultant solution was stirred and refluxed under N₂ at 180°C for 12 h. After that, the reaction mixture was cooled and extracted with ethyl acetate. Two fractions were identified, as per TLC, and they were purified by silica column chromatography using a CHCl₃/Hexane (30:70) mixture. The products MB3b and MB3c were obtained in 14% and 67% yields respectively. The compounds, **MB3b** and **MB3c** were demetallated using HCl/H₂SO₄ (5%), purified by column chromatography, giving **MB1b** and MB1c in 70-73% yields. Further, metallation of **MB1b** and **MB1c** with Cu(OAc)₂ in CHCl₃/MeOH resulted in compounds, MB2b and MB2c quantitatively. A similar procedure was adopted to make the compounds DB1b-1c, DB2b-2c and DB3b-DB3c, which were synthesized from DB3a. UV-vis data of the porphyrins in CH₂Cl₂ at 298 K, λ_{max} (log ϵ/M^{-1} cm⁻¹): MB1b, 417 (5.67), 512 (4.43), 546 (3.97), 588 (3.94), 643 (3.60); **MB1c**, 418 (5.66), 512 (4.45), 546 (4.09), 588 (3.97), 643 (3.70); MB2b, 415 (5.52), 538 (4.30); MB2c, 413 (5.60), 537 (4.32); MB3b, 419 (5.65), 546 (4.32); MB3c, 420 (5.58), 547 (4.27); DB1b, 416 (5.69), 511 (4.48) 587 (4.08); **DB1c**, 418 (5.65), 511 (4.48), 587 (4.08); **DB2b**, 413 (5.60), 536 (4.36); **DB2c**, 413 (5.55), 537 (4.32); **DB3b**, 419 (5.61), 546 (4.34); **DB3c**, 420 (5.61), 547 (4.32). ¹H NMR data: 400 MHz, CDCl₃, δ (ppm): **MB1b**, 8.84-8.72 (m, 8H), 8.01 (d, J = 8.00 Hz, 4H), 7.84 (d, J = 8.00 Hz, 4H, 3.21(s, 6H), -2.94(s, 2H); **MB1c**, 8.86-8.75 (m, 8H), 8.01 (d, J = 8.00 Hz, 4H), 7.84 (d, J = 8.00 Hz, 4H), 3.21 (s, 12H), -2.90 (d, 2H); MB3b, 9.02-8.89 (m, 8H), 8.09 (d, J = 8.00 Hz, 4H), 7.91 (d, J = 8.00 Hz, 4H), 3.29 (s, 6H); **MB3c**, 9.01–8.98 (s, 8H), 8.09 (d, J = 8.00 Hz, 4H), 7.91 (d, J = 8.00 Hz, 4H), 3.28 (s, 12H); DB1c, 9.02-8.92 (m, 8H), 8.33 (s, 4H), 8.13 (s, 2H), 3.29 (s, 12H), -2.88 (s, 2H); **DB3b**, 8.79–8.76 (m, 8H), 8.13 (s, 4H), 8.07 (s, 2H), 3.24 (s, 12H); **DB3c** (300MHz), 8.99-8.89 (m, 8H), 8.31 (s, 4H), 8.15 (s, 2H), 2.86 (d, 12H). ESI mass data of **MB1b** ($C_{46}H_{24}Br_2F_9N_5$): 977.51 (Calcd.), 978.1474 (Found); **MB1c** ($C_{48}H_{30}Br_2F_8N_6$): 1002.59 (Calcd.), 1003.1614 (Found); MB2b (C₄₆H₂₂Br₂-CuF₉N₅): 1039.04 (Calcd.), 1039.00 (Found); MB2c (C₄₈H₂₈Br₂CuF₈N₆): 1064.12 (Calcd.), 1065.00 (Found); **MB3b** (C₄₆H₂₂Br₂F₉N₅Zn): 1040.88 (Calcd.), 1041.0204 (Found); MB3c (C₄₈H₂₈Br₂F₈N₆Zn): 1065.96 (Calcd.), 1066.0721 (Found); **DB1b** ($C_{46}H_{22}Br_4F_0N_5$): 1135.3 (Calcd.), 1135.9261 (Found); **DB1c** ($C_{48}H_{28}Br_4F_8N_6$): 1160.38 (Calcd.), 1160.9930 (Found); DB2b (C₄₆H₂₀Br₄-F₉N₅Cu): 1196.83 (Calcd.), 1197.8522 (Found); DB2c 1221.91 (Calcd.), $(C_{48}H_{26}Br_{4}F_{8}N_{6}Cu)$: 1220.9563 (Found); **DB3b** (C₄₆H₂₀Br₄F₉N₅Zn): 1198.68 (Calcd.), 1198.8512 (Found); **DB3c** (C₄₈H₂₆Br₄F₈N₆Zn): 1223.75 (Calcd.), 1223.9547 (Found). Fluorescence spectral data of porphyrins in CHCl₃ at 298 K (λ_{ex} at Soret band of respective compound, **MB1b–MB3c** and **DB1b–DB3c**), λ_{em} for **MB1b**: 646 (s), 710 (s); **MB1c**: 648 (s), 712 (s); **MB2b**: 653(w), 711(w); **MB2c**: 649(w), 712(w); **MB3b**: 597 (s), 643 (s); **MB3c**: 598 (s), 644 (s); **DB1b**: 645 (s), 707 (s); **DB1c**: 648 (s), 711 (s); **DB2b**: 650(w), 706(w); **DB2c**: 650(w), 711(w); **DB3b**: 592 (w), 641 (s); **DB3c**: 596 (w), 644 (s).

The ¹⁹F NMR spectra of zinc(II) derivatives of parent trans-porphyrins (MB3a and DB3a), mono-aminated porphyrins (MB3b and DB3b) and di-aminated porphyrins (MB3c and DB3c) showed three, five and two signals respectively. ¹⁹F NMR data: 470 MHz, CDCl₃, δ (ppm): **MB3a**, -136.97 – -137.11 (br, d, 4F, F'), -152.24 – -152.56 (br, d, 2F, F'''), -161.89 - -162.05 (br, d, 4F, F''); MB3b, -137.04 - -137.11 (m, 2F, F'), -140.52 - -140.58 $(m, 2F, F'_{sub}), -152.22 - -152.28 (m, 2F, F''_{sub}), -152.79 (t, -152.79)$ J = 21 Hz, 1F, F^{'''}), -162.14 – -162.24 (m, 2F, F^{''}); MB3c, -140.52 (d, J = 24 Hz, 4F, F'_{sub}), -152.31 (d, J = 19 Hz, 4F, F"_{sub}). **DB3a**, -136.95 – -137.12 (m, 4F, F'), -152.18 (t, J = 21 Hz, 2F, F'''), -161.79 - -161.90 (m, 4F, F'');**DB3b**, -136.90 – -137.10 (m, 2F, F'), -140.44 – -140.60 $(m, 2F, F'_{sub}), -152.13 - -152.19 (m, 2F, F''_{sub}), -152.45 (t, -152.45)$ J = 19 Hz, 1F, F^{'''}), -161.94 - -162.05 (m, 2F, F^{''}); **DB3c**, -140.52 (d, J = 14 Hz, 4F, F'_{sub}), -152.23 (s, 4F, F''_{sub}).

RESULTS AND DISCUSSION

Using **MB3a/DB3a** with dimethylamine hydrochloride, the mono-aminated *meso*-tetraarylporphyrins, $M(TF_5)(TF_4DMA)D(4-/3,5-BrP)P$ (**MB1b–3b** and **DB1b–3b**)/di-aminated *meso*-tetraaryl *trans*-porphyrins, MB(TF_4DMA)D(4-/3,5-BrP)P (**MB1c–3c** and **DB1c–3c**) were synthesized [M = 2H, Cu(II) and Zn(II)]. All the synthesized porphyrins (Scheme 1) were isolated, purified by column chromatography and characterized by UV-vis, fluorescence, ¹H NMR spectroscopic methods and mass spectrometry. Several attempts were made to synthesize the cationic porphyrin derivatives (N-trimethylated porphyrins), however the results were unsuccessful.

The electronic absorption data of the synthesized porphyrins are dominated by an intense Soret (B) band which can be attributed to spin allowed π - π transition in the range of 412-420 nm and a medium intensity two or four visible (Q) bands in the range of 509–643 nm [25]. The overlaid UV-vis spectra of MB1a-1c are shown in Fig. 2a. It has been noted that the introduction of mono-/ di-aminated groups at the porphyrin periphery does not influence the electronic properties of the resultant compounds and shows a marginal red shifted Soret band of only 1-3 nm compared to that of the free ligand. The fluorescent spectral pattern of free ligands DB1a-1c is similar to its tetraphenylporphyrin analogue (H₂TPP). On excitation at the Soret band, all the porphyrins exhibit two emission bands (weak or strong) in the range of 590–656 nm and 639–712 nm corresponding to $S_1 \rightarrow S_0$ transitions (Fig. 2b).



Scheme 1. Synthetic route for *trans*-porphyrins



Fig. 2. Overlaid (a) UV-vis spectra of MB1a-1c and (b) fluorescence spectra of DB1a-1c in CH₂Cl₂ at 298 K

The *trans*-porphyrins **MB1a** and **MB1c** are expected to be more symmetric in structure compared to **MB1b**. Hence, the imino (–NH) proton signals of former (**MB1a** and **MB1c**) are expected to show a single peak in the negative region of the ¹H NMR spectrum. However, the imino protons of **MB1a** and **MB1b** appear as only one signal at -2.88 and -2.84 ppm respectively whereas in the case of **MB1c**, it appears as two signals (-2.88 and -2.93 ppm) (Fig. 3). The mass spectral data of selected porphyrins reveal that there is good agreement with the observed and calculated values.

Single crystal X-ray diffraction studies

The successful single crystal XRD characterization of porphyrins, **MB2c** and **MB3c** is performed by the suitable selection of single crystals which were grown at room temperature using appropriate solvents. Compound **MB2c** was crystallized in monoclinic with the space group P2/c whereas **MB3c** was crystallized in triclinic with the space group of P-1. The copper(II) center in **MB2c** is tetra-coordinated with the inner core nitrogens of the porphyrin ring. ORTEP and packing diagrams of **MB2c** are shown in Figs 4a and 4c. Their crystal packing consists of a number of intermolecular interactions involving carbon, fluorine, bromine, hydrogen, oxygen, nitrogen and copper as listed in Table 2. Interestingly, a metal-H (Cu···H) interaction has been identified in **MB2c** and the distance is found to be 2.553 Å, which is further supported by the Hirshfeld surface analysis discussed later.

Two THF molecules are present in **MB3c**, one coordinated to the zinc(II) center at the apex position and the other one appearing in the crystal lattice. The



Fig. 3. Overlaid ¹H NMR spectra (negative region for imino protons) of MB1a-1c

Table 2. Distances (in Å) for the different types of interactions in the crystal packing of porphyrins, MB2c and MB3c.

Interactions ⁱ	MB2c ⁱⁱ	MB3c ⁱⁱ			
(pyrrole)C-H···F(ph)	2.595 (4)				
(ph)C-H···Br(ph)	3.045 (2)				
$_{(ph)}C-Br\cdots C_{(pyrrole)}$	3.341 (2)	3.449-3.453 (2)			
_(ph) C–H…Cu	2.553 (4)				
(pyrrole) C-H···C(pyrrole)	—	2.899 (1)			
(pyrrole) C-H····H (pyrrole)	_	2.327 (1)			
$_{(ph)}C-H\cdots F_{(ph)}$	_	2.617 (1)			
(ph)C-F···C(pyrrole)	_	3.077 (1)			
(ph)C-H···C(pyrrole)	_	2.713-2.781 (2)			
$_{(me)}C-H\cdots F_{(ph)}$	_	2.265-2.638 (3)			
$_{(me)}C\cdots F_{(ph)}$	_	3.164 (1)			
$_{(ph)}C\cdots F_{(ph)}$	_	3.003-3.125 (2)			
(ph)C-H····N(pyrrole)	_	2.742 (1)			
(me)C-H···Br(ph)	_	2.941 (1)			
(me)C-H···O(THF)	_	2.702 (1)			
(me)C-N····O _(THF)		3.022 (1)			

ⁱDifferent types. ⁱⁱValue in parenthesis gives the number of interactions of each types per molecule.

bound or unbound THF solvate molecules in **MB3c** show a well-known envelope conformation as observed in the literature [26]. ORTEP and packing diagrams of **MB3c** are shown in Figs 4b and 4d. The Zn-N and Zn-O distances in **MB3c** are found to be 2.056 (5) Å and 2.183 (7) Å.

For quantifying and understanding the weak intermolecular interactions, the crystal structures of porphyrins **MB2c** and **MB3c** were analyzed through Hirshfeld Surface (HS) analysis using Crystal Explorer 3.1. The close contacts can be visualized by color-coding short (red) or long (blue) contacts, with the color intensity representing the relative strength of the interactions.

The front and back view of the HSs for **MB2c** are quite similar, indicating that the two sides of the molecules involved in quite similar crystal packing, whereas in **MB3c** it is different due to the solvent THF molecule which is coordinated axially to the zinc center. The HSs mapped with d_{norm} for **MB2c** highlights medium intense red spots for H···H close contacts and faint red spots for N···H contacts, whereas **MB3c** shows big intense red spots only for O···H close contacts. Figures 5b and 5d illustrate the breakdown of fingerprint plots (FPs) of the HSs for porphyrins, which demonstrates the influence of halogen atoms on the intermolecular interactions, which in turn stabilizes the crystal packing motif. The prominent spikes in the plots are associated with close contacts



Fig. 4. (a, b) ORTEP diagram of **MB2c** and **MB3c**; (c) molecular crystal packing of **MB2c** forming two dimensional array of molecules through C-H…Br and C…Br interactions viewed down 'a' axis; (d) molecular crystal packing of **MB3c** viewed down 'c' axis (lattice THF molecule is not shown for clarity)

involving halogen atoms (F/Br) and can be attributed to F···H/F/C, Br···H/F interactions. It is clear from the analysis that the interactions involving halogens are the major contributors to the total Hirshfeld surface area and the relative contributions are 56 and 53%, respectively, for **MB2c** and **MB3c**.

Electrochemical studies

The electrochemical studies of three series of porphyrins, including non-aminated [*trans*-MB(TF₅)D(4-/ 3,5-BrP)P, **MB1a–3a** and **DB1a–3a**]; mono-aminated, [M(TF₅)(TF₄DMA)D(4-/3,5-BrP)P, **MB1b–3b** and **DB1b–3b**] and di-aminated [*trans*-MB(TF₄DMA)D(4-/3,5-BrP)P, **MB1c–3c** and **DB1c–3c**], were examined by cyclic voltammetric/differential pulse voltammetric techniques in CH_2Cl_2 with 0.1 M TBAHFP as supporting electrolyte and Calomel as reference electrode.

As expected [12], the zinc(II) [**MB3a** and **DB3a**] and copper(II) [**MB2a** and **DB2a**] derivatives show two reversible reductions and oxidations, whereas the ligands **MB1a** and **DB1a** show two reversible reductions and one irreversible oxidation. The redox potentials of all the compounds were tabulated and are presented in Table 3. The representative cyclic voltammograms of **MB1a**, **MB1b** and **MB1c** are shown in Fig. 6. There



Fig. 5. Hirshfeld surfaces of porphyrins **MB2c** and **MB3c** with d_{norm} mapped ranging from -0.34 Å (blue) to 2.22 Å (red) [a, c]; 2D fingerprint plots [b, d]; (e) Percentage contribution of non-covalent interactions in porphyrins, **MB2c** and **MB3c** on the basis of HSs



Fig. 6. Overlaid voltammograms of porphyrins, **MB1a–MB1c** in CH₂Cl₂ containing 0.1 M TBAHFP and Calomel as reference electrode

is no appreciable change in the reduction potentials of the compounds irrespective of the aryl group (4-bromophenyl/3,5-dibromophenyl) present at the *meso*-position. However, the oxidation potentials of the mono-aminated porphyrins (**MB1b** and **DB1b**) were shifted more positively about ~300 mV (4-bromophenyl)/ ~140 mV (3,5-dibromophenyl) compared to nonaminated porphyrins (**MB1a** and **DB1a**); revealing that the mono-aminated porphyrins are more electron-deficient than non-aminated and di-aminated porphyrins. Moreover, the oxidation potentials of the di-aminated porphyrins (**MB1c** and **DB1c**) are comparable with non-aminated porphyrins. For comparison, the other ligands H_2TPP , $H_2T(4-BrP)P$ and $H_2T(PFP)P$ were also taken along with $H_2B(PFP)D(4-BrP)P$ (**MB1a**), $H_2B(PFP)-D(3,5-BrP)P$ (**DB1a**), $H_2(TF_5)(TF_4DMA)D(4-BrP)P$ (**MB1b**), $H_2(TF_5)(TF_4DMA)D(3,5-BrP)P$ (**DB1b**), $trans-H_2B(TF_4DMA)D(4-BrP)P$ (**MB1c**) and $trans-H_2B(TF_4DMA)D(3,5-BrP)P$ (**DB1c**) and the data collected under the similar conditions (Table 4).

It is well documented in the literature that halogenation of the porphyrin causes a positive shift in the reduction and oxidation potentials [27] compared to that of H_2 TPP, which is explicitly seen in all the halogenated porphyrins presented in Table 4. Interestingly, the positive shifts in the first oxidation and first reduction potentials of the newly-synthesized compound, **MB1a** are in between the reference

compounds listed in Table 4 [the least electron deficient being tetrakis(4-bromophenyl)porphyrin, $H_2T(4-BrP)P$ (Entry 2) and the most electron deficient being tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrin, $H_2T(PFP)P$ (Entry 3)]. This clearly indicates that the *trans*-porphyrin containing 4-bromophenyl and pentafluorophenyl rings, **MB1a** possess moderate electron deficiency compared to the tetra-substituted $H_2T(4-BrP)P$

Compound	Oxid	Oxidation		Reduction		evel (eV)	Band gap (eV)	
	Ι	Π	Ι	II	HOMO ^a	LUMO ^a		
MB1a	1.31		-0.99	-1.35	-5.71	-3.41	2.30	
MB2a	1.26	1.54	-1.14	-1.56	-5.66	-3.26	2.40	
MB3a	1.08	1.34	-1.18		-5.48	-3.22	2.26	
MB1b	1.61	_	-1.02	-1.40	-6.01	-3.38	2.63	
MB2b	1.21	1.54	-1.15	-1.59	-5.61	-3.25	2.36	
MB3b	1.02	1.29	-1.19	-1.62	-5.42	-3.21	2.21	
MB1c	1.18	1.41	-1.04	-1.40	-5.58	-3.36	2.22	
MB2c	1.17	_	-1.17	-1.62	-5.57	-3.23	2.34	
MB3c	1.01	1.27	-1.21	-1.63	-5.41	-3.19	2.22	
DB1a	1.39	1.62	-0.94	-1.32	-5.79	-3.46	2.33	
DB2a	1.32	1.39	-1.08	-1.48	-5.72	-3.32	2.40	
DB3a	1.11	_	-1.12	-1.51	-5.51	-3.28	2.23	
DB1b	1.53	_	-0.97	-1.34	-5.93	-3.43	2.50	
DB2b	1.30	1.64	-1.08	-1.52	-5.70	-3.32	2.38	
DB3b	1.06	1.32	-1.04	-1.40	-5.46	-3.36	2.10	
DB1c	1.44	_	-0.94	-1.34	-5.84	-3.46	2.38	
DB2c	1.29	_	-1.11	-1.54	-5.69	-3.29	2.40	
DB3c	1.16	1.40	-1.14	-1.53	-5.56	-3.26	2.30	

Table 3. Redox potentials (in V, vs. Calomel) of porphyrins in CH₂Cl₂ containing 0.1 M TBAHFP at 25 °C and calculated HOMO and LUMO energy levels

 ${}^{a}E_{HOMO} = -(E_{Oxdn} + 4.4) \text{ eV}$ and $E_{LUMO} = -(E_{Redn} + 4.4) \text{ eV}$ taken from *Chem. Commun.*, 2012, 48, 8377.

Table 4. Comparison of redox potentials (in V) of free-base porphyrins

Entry	Compound	Potential		
		I Oxdn	I Redn	
1	H ₂ TPP	0.97	-1.27	
2	$H_2T(4-BrP)P$	1.09	-1.19	
3	$H_2T(PFP)P$	1.37	-0.93	
4	H ₂ B(PFP)D(4-BrP)P, MB1a	1.31	-0.99	
5	$H_2(TF_5)(TF_4DMA)D(4-BrP)P, MB1b$	1.61	-1.02	
6	H ₂ B(TF ₄ DMA)D(4-BrP)P, MB1c	1.18	-1.04	
7	H ₂ B(PFP)D(3,5-BrP)P, DB1a	1.39	-0.95	
8	$H_2(TF_5)(TF_4DMA)D(3,5-BrP)P, DB1b$	1.53	-0.97	
9	H ₂ B(TF ₄ DMA)D(3,5-BrP)P, DB1c	1.44	-0.94	

and $H_2T(PFP)P$. Whereas the *trans*-porphyrin bearing 3,5-dibromophenyl and pentafluorophenyl rings, **DB1a** exhibits positive shifts similar to that of $H_2T(PFP)P$ indicating more electron deficiency than **MB1a**. For aminated porphyrins (**MB1b–1c** and **DB1b–1c**), the oxidation potentials are shifted positively ~140–300 mV, except for **MB1c**, whereas the reduction potentials are similar to that of the parent porphyrins (**MB1a** and **DB1a**).

In order to find the effect of the supporting electrolytes as well as the reference electrodes on the redox potentials of porphyrins, we have chosen four different reaction conditions for the measurements, namely (A) TBAHFP with Calomel; (B) TBAHFP with Ag-AgCl; (C) TBAP with Calomel and (D) TBAP with Ag-AgCl (Table 5). The extent of positive shifts in the first oxidation and first reduction potentials of MB1a and DB1a are more pronounced in the reaction conditions of C and D rather than in A and B, indicating the role of supporting electrolyte, TBAP/ TBAHFP. A similar trend was also obtained in the case of metal [Cu(II) and Zn(II)] complexes (Table 6). The overlaid cyclic voltammograms of a representative example of DB2a are shown in Fig. 7 under various reaction conditions.

Furthermore, cyclic voltammograms of compounds (**MB1a–3a** and **DB1a–3a**) were recorded at various scan rates under four different reaction conditions. The representative example of **MB3a** is shown in Fig. 8 in CH_2Cl_2 containing TBAHFP with Ag-AgCl as reference electrode, which shows two well-defined reduction and oxidation peaks. The Randles-Sevcik plot (Figs 8b, 8c, 8e and 8f) validates the linearity between

Reaction conditions	H ₂ TPP		$H_2T(4-BrP)P$		H ₂ T(PFP)P		H ₂ B(PFP)D(4-BrP)P, MB1a		H ₂ B(PFP)D(3,5-BrP)P, DB1a	
	I Oxdn	I Redn	I Oxdn	I Redn	I Oxdn	I Redn	I Oxdn	I Redn	I Oxdn	I Redn
(A) TBAHFP with Calomel	0.97	-1.27	1.09	-1.19	1.37	-0.93	1.31	-0.99	1.39	-0.95
(B) TBAHFP with Ag-AgCl	1.10	-1.17	1.11	-1.18	1.01	-1.32	1.35	-0.94	1.43	-0.89
(C) TBAP with Calomel	1.04	-1.23	1.13*	-1.17	1.55*	-0.78	1.43	-0.93		-0.93
(D) TBAP with Ag-AgCl	1.11	-1.09	1.23*	-1.06		-0.70	1.46	-0.90	—	-0.86

Table 5. Comparison of redox potentials (in V) of free-base porphyrins under different reaction conditions

Table 6. Comparison of redox potentials (in V) of metal derivatives [Cu(II), Zn(II)] of *trans*-MB(PFP)D(4-BrP)P and *trans*-MB(PFP)D(3,5-BrP)P

Reaction conditions	Cu(II), MB2a		Zn(II), MB3a		Cu(II), DB2a		Zn(II), DB3a	
	I Oxdn	I Redn						
(A) TBAHFP with Calomel	1.26	-1.14	1.08	-1.18	1.32	-1.08	1.11	-1.13
(B) TBAHFP with Ag-AgCl	1.31	-1.08	1.12	-1.11	1.38	-1.03	1.18	-1.08
(C) TBAP with Calomel	1.29	-1.10	1.05	-1.11	1.33	-1.04	1.10	-1.08
(D) TBAP with Ag-AgCl	1.34	-1.10	1.07	-1.09	1.37	-1.02	1.15	-1.03



Fig. 7. Cyclic voltammograms of compound **DB2a**, (a) oxidation and (b) reduction potentials using Ag-AgCl/Calomel electrodes and TBAHFP/TBAP as supporting electrolytes at a scan rate of $100 \text{ mV} \cdot \text{s}^{-1}$ in CH₂Cl₂

the peak current and the square root of the scan rate, indicating reversible electron transfer that is consistent with a diffusion controlled process [28].

The HOMO-LUMO energy gap is identified as the potential difference between the first porphyrin ringcentered oxidation and reduction which is calculated in eV for all the compounds, and these values are also tabulated in Table 3. The energy gap for free-base porphyrins (**MB1a–1c** and **DB1a–1c**) varies with respect to the electrolyte and reference electrode. Selective electrochemical data of porphyrins (TBAHFP and Calomel) are given in Fig. 9. Interestingly, the band gap



Fig. 8. (a, d) Cyclic voltammograms of compound **MB3a** at various scan rate in CH₂Cl₂ containing 0.1 M TBAHFP with Ag-AgCl; (b, c) and (e, f) are the Randles-Sevcik plots of $i_p^{\text{oxdn}} vs. v^{1/2}$ and $i_p^{\text{redn}} vs. v^{1/2}$ respectively



Fig. 9. HOMO–LUMO energy gap (in eV) for free-base porphyrins in CH_2Cl_2 containing 0.1 M TBAHFP and Calomel as reference electrode at 25 °C

observed for **MB1b** and **DB1b** is higher (2.50–2.63 eV) than the other two series (2.22–2.38 eV).

CONCLUSIONS

Synthesis of three series of porphyrins, non-aminated [*trans*-MB(TF₅)D(4-/3,5-BrP)P, **MB1a–3a** and **DB1a–**3a]; mono-aminated, [M(TF₅)(TF₄DMA)D(4-/3,5-BrP)P, **MB1b–3b** and **DB1b–3b**] and di-aminated [*trans*-MB(TF₄DMA)D(4-/3,5-BrP)P, **MB1c–3c** and **DB1c–3c**]

meso-tetraarylporphyrins has been achieved, and their metal derivatives [M = Cu(II) and Zn(II)] were prepared and characterized using UV-vis and ¹HNMR spectroscopic methods and mass spectrometry. Optical absorption data of porphyrins showed an intense Soret (B) band owing to spin allowed π - π transition in the range of 412–420 nm and medium intensity two or four visible (Q) bands in the range of 509-643 nm. Upon excitation at the Soret band, all the porphyrins show two (weak or strong) emission bands corresponding to $S_1 \rightarrow S_0$ transitions. Hirshfeld surface analysis shows that interactions involving halogens are the major contributors and the relative contributions are 56% and 53% respectively for MB2c and MB3c. The compounds were also electrochemically analyzed under different reaction conditions, and showed a positive shift in the reduction and oxidation potentials compared to that of H₂TPP, indicating the influence of halogens. The HOMO-LUMO band gap is varied with respect to the nature of supporting electrolyte (TBAHFP/ TBAP) and reference electrodes (Calomel/Ag-AgCl) used under this study. Cyclic voltammograms were recorded at various scan rates, and the linear behavior of Randles-Sevcik plots indicates that the redox processes are diffusion controlled. The oxidation potentials of the mono-aminated porphyrins were shifted more positively about ~300 mV (4-bromophenyl)/~140 mV (3,5-dibromophenyl) and the di-aminated porphyrins are comparable with non-aminated porphyrins. The electrochemical studies also reveal that the monoaminated porphyrins are more electron deficient than non-aminated and di-aminated porphyrins, and hence the former may act as better catalysts.

Acknowledgments

DST, New Delhi is gratefully acknowledged for the financial support through EMR/2016/002396. We would like to thank Dr. Babu Varghese, SAIF, IIT Madras, Chennai, Tamilnadu for the data collection, structure solution and refinement.

Supplementary information

Crystallographic data of the porphyrins, **MB2c** and **MB3c** have been deposited with the Cambridge Crystallographic Data Centre with the CCDC numbers 974217 and 1058022. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving. html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: + 44 123 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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