Supporting Information

Calix[*n*]metallocenyl[*m*]phyrins (*n* = 1, 2 and *m* = 2, 4): Aryl *vs* Alkyl

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1. General Information:

NMR spectra were recorded with Bruker 300 MHz or 500 MHz machine with CDCl₃ as solvent. Chemical shifts are expressed in parts per million (ppm) relative to TMS. FAB mass spectra were obtained on a JEOL SX-120/DA6000 spectrometer using argon (6 KV, 10 mA) as the FAB gas. Electronic absorption spectra were recorded with Perkin Elmer – Lambda 25 UV-Visible spectrophotometer. The single crystal X-ray diffraction data of **1b** and **4b** were collected on a Bruker AXS Kappa Apex 2 CCD diffractometer at 293(2) K. The single crystal X-ray diffraction data of **3a**, **6b** and **7** were collected on a Bruker SMART Apex diffractometer equipped with CCD area detector at 100(2) K. All the crystals have been deposited in the Cambridge Crystallographic Data Centre with reference no. CCDC-732747 (for **1b**), CCDC-732748 (for **3a**), CCDC-732749 (for **4b**), CCDC-732750 (for **6b**), and CCDC-732751 (for **7**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

2. Syntheses:

a) Synthesis of 3a:



To a 250 mL flask containing **1a** (200 mg, 0.31 mmol) and 4-nitro benzaldehyde (46 mg, 0.31 mmol), 100 mL of dry CH₂Cl₂ was added and stirred for 15 min at room temperature under nitrogen atmosphere with light protection. *p*-toluenesulphonic acid (*p*-TSA) (12 mg, 0.062 mmol) was added and the mixture was allowed to stir for 2 hrs. To the reaction mixture, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (176 mg, 0.78 mmol) was added, solution was opened to air and stirred for further 2 hrs. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). The first moving red fraction eluted with CH₂Cl₂: petroleum ether (40 : 60) was identified as **3a** in 18% yield. M.p. > 300°C; ¹H NMR (300 MHz, CDCl₃, 298K) : δ = 16.19 (brs, 1NH), 8.36 – 8.33 (d, J = 8.65 Hz, 2H, Ph), 7.86 – 7.83 (d, J = 8.7 Hz, 2H, Ph), 7.39 – 7.35 (m, 10H, Ph), 7.18 – 7.16 (m, 6H, Ph), 6.97 – 6.91 (m, 4H, Ph), 6.5 – 6.48 (d, J = 4 Hz, 2H, Py), 5.9 – 5.87 (d, J = 4 Hz, 2H, Py), 4.58 (s, 2H), 3.97 (s, 2H), 3.87 (s, 2H), 2.93 (s, 2 H); UV-Vis (CH₂Cl₂): λ_{max}/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) = 489 (14000); FAB mass (m/z) = Calcd for C₅₁H₃₇FeN₃O₂ = 779.22; Observed = 778.59 (100%, M⁺).

b) Synthesis of 3b:



To a 250 mL flask containing **1a** (200 mg, 0.31 mmol) and pentafluorobenzaldehyde (0.04 mL, 0.31 mmol), 100 mL of dry CH₂Cl₂ was added and stirred for 15 min at room temperature under nitrogen atmosphere with light protection. *p*-toluenesulphonic acid (*p*-TSA) (12 mg, 0.062 mmol) was added and the mixture was allowed to stir for 2 hrs. To the reaction mixture, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (176 mg, 0.78 mmol) was added, solution was opened to air and stirred for further 2 hrs. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). The first moving red fraction eluted with CH₂Cl₂: petroleum ether (30 : 70) was identified as **3b** in 19% yield. ¹H NMR (300 MHz, CDCl₃, 298 K) : δ = 16.03 (brs, 1NH), 7.4 – 7.37 (m, 11H, Ph), 7.17 – 7.16 (d, J = 3.13 Hz, 5H, Ph), 6.95 – 6.91 (m, 4H, Ph), 6.43 – 6.42 (d, J = 4 Hz, 2H, Py), 5.88 – 5.86 (d, J = 4 Hz, 2H, Py), 4.58 (s, 2H), 3.97 (s, 2H), 3.85 (s, 2H), 2.94 (s, 2H). λ_{max} /nm (ϵ /M⁻¹cm⁻¹) = 480 (49000), FAB mass (m/z) = Calcd for C₅₁H₃₃F₅FeN₂ = 824.19; Observed = 824.86 (100%, M⁺).

c) Synthesis of 4a and 6a:



To a 250 mL flask containing 1b (200 mg, 0.5 mmol) and 4-nitrobenzaldehyde (76 mg, 0.5 mmol), 100 ml of dry CH₂Cl₂ was added and stirred for 15 min at room temperature under N₂ atm with light protection. *p*-toluenesulphonic acid (*p*-TSA) (19 mg, 0.1 mmol) was added and the mixture was allowed to stir for 2 hrs. To the reaction mixture, 2,3-dichloro-5,6dicyano-p-benzoquinone (DDQ) (283 mg, 1.25 mmol) was added, solution was opened to air and stirred for further 2 hrs. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 - 200 mesh). The first red fraction eluted with CH₂Cl₂: petroleum ether (20 : 80) was identified as **4a** in 18% yield. ¹H NMR (300 MHz, $CDCl_3$, 298 K) : $\delta = 15.71$ (brs, 1NH), 8.35 – 8.32 (d, J = 8.68 Hz, 2H, Ph), 7.81 – 7.78 (d, J = 8.67 Hz, 2H, Ph), 6.54 – 6.53 (d, J = 4 Hz, 2H, Py), 6.34 – 6.33 (d, J = 4 Hz, 2H, Py), 4.29 (s, 8H), 1.55 (s, 12H). λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$) = 483.5 (16800), FAB mass (m/z) = Calcd for $C_{31}H_{29}FeN_{3}O_{2} = 531.16$; Observed = 532.37 (100%, M + 1⁺). The second red fraction eluted with CH₂Cl₂: petroleum ether (40 : 60) was identified as **6a** in 4% yield. ¹H NMR (300 MHz, CDCl₃ 298 K) : $\delta = 12.74$ (brs, 2NH), 8.25 - 8.23 (d, J = 8.63 Hz, 4H, Ph), 7.59 - 7.54 (m, 4H, Ph), 6.28 (s, 8H, Py), 4.18 (s, 10H), 3.98 (s, 6H), 1.75 (s, 12H), 1.57 (s, 12H). λ_{max}/nm $(\epsilon/M^{-1}cm^{-1}) = 450 (39900)$, FAB mass (m/z) = Calcd for $C_{62}H_{58}Fe_2N_6O_4 = 1062.32$; Observed $= 1062.80(80\%, M^{+}).$

d) Synthesis of 4b and 6b:



To a 250 mL flask containing **1b** (200 mg, 0.5 mmol) and pentafluorobenzaldehyde (0.06 mL, 0. 5 mmol), 100 mL of dry CH₂Cl₂ was added and stirred for 15 min at room temperature under N_2 atm with light protection. *p*-toluenesulphonic acid (*p*-TSA) (19 mg, 0.1 mmol) was added and the mixture was allowed to stir for 2 hrs. To the reaction mixture, 2,3dichloro-5,6-dicyano-p-benzoquinone (DDQ) (283 mg, 1.25 mmol) was added, solution was opened to air and stirred for further 2 hrs. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 - 200 mesh). The first moving red fraction was eluted with CH_2Cl_2 : petroleum ether (20 : 80) was identified as **4b** in 16% yield. M.p. > 300°C; ¹H NMR (500 MHz, CDCl₃, 298K): $\delta = 15.65$ (brs, 1NH), 6.46 - 6.45 (d, J = 4 Hz, 2H, Py), 6.3 – 6.29 (m, 2H, Py), 4.28 (s, 8H), 1.55 (s, 12H, methyl); UV-Vis (CH₂Cl₂): $\lambda_{max}/nm (\epsilon/M^{-1}cm^{-1}) = 473 (22000);$ FAB mass (m/z) = Calcd for $C_{31}H_{25}F_5FeN_2 = 576.13;$ Observed = 576.49 (100%, M^+). The second red fraction eluted with CH₂Cl₂: Petroleum ether (40 : 60) was identified as **6b** in 5% yield. m.p. $> 300^{\circ}$ C; ¹H NMR (500 MHz, CDCl₃, 298K): $\delta = 12.33$ (brs, 2NH), 6.2 (s, 8H, Py), 4.07 (t, 8H), 3.9 (t, 8H), 1.64 (s, 24H); UV-Vis (CH_2Cl_2) : $\lambda_{max}/nm (\epsilon/M^{-1}cm^{-1}) = 441 (21000)$; FAB mass (m/z) = Calcd for $C_{62}H_{50}F_{10}Fe_2N_4 =$ 1152.26; Observed = $1151.57 (80\%, M^+)$.

e) Synthesis of 5 and 7:



To a 250 mL flask containing **2** (200 mg, 0.45 mmol) and pentafluorobenzaldehyde (0.05 mL, 0.45 mmol), 100 mL of dry CH₂Cl₂ was added and stirred for 15 min at room temperature under N₂ atm with light protection. *p*-toluenesulphonic acid (*p*-TSA) (17 mg, 0.09 mmol) was added and the mixture was allowed to stir for 2 hrs. To the reaction mixture, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (255 mg, 1.12 mmol) was added, solution was opened to air and stirred for further 2 hrs. After removal of the solvent, the crude product was purified by silica gel column chromatography (100 – 200 mesh). The first red fraction eluted with CH₂Cl₂: petroleum ether (20 : 80) was identified as **5** in 16.4% yield. ¹H NMR (300 MHz, CDCl₃, 298 K) : $\delta = 15.62$ (brs, 1NH), 6.4 - 6.38 (d, J = 4 Hz, 2H, Py), 6.26 - 6.24 (d, J = 4 Hz, 2H, Py), 4.27 (s, 8H), 1.65 (s, 12H). λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$) = 473 (28000), FAB mass (m/z) = Calcd for C₃₁H₂₅F₅RuN₂ = 622.09; Observed = 622.44 (100%, M⁺). The second red fraction eluted with CH₂Cl₂: petroleum ether (40 : 60) was identified as **7** in 4% yield. ¹H NMR (300 MHz, CDCl₃, 298 K) : $\delta = 12.34$ (brs, 2NH), 6.29 - 6.27 (t, 8H, Py), 4.6 (t, 8H), 4.35 - 4.34 (t, 8H), 1.62 (s, 24H). λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$) = 447 (25000), FAB mass (m/z) = Calcd for C₆₂H₅₀F₁₀Ru₂N₄ = 1244.19; Observed = 1244.48 (80%, M⁺).

3. Spectral Analyses of 3a:



Fig. S2 ¹H NMR Spectrum of 3a in CDCI₃

4. Spectral Analyses of 3b:





5. Spectral Analyses of 4a:



Fig. S6 ¹H NMR Spectrum of 4a in CDCI₃

6. Spectral analyses of 4b:





7. Spectral Analyses of 5:





8. Spectral Analyses of 6a:





9. Spectral Analyses of 6b:



Fig. S14 ¹H NMR Spectrum of 6b in CDCl₃

10. Spectral Analyses of 7:



Fig. S16 ¹H NMR Spectrum of 7 in CDCl₃





Fig. S17 FAB MS Spectrum of Calix[3]ferrocenyl[6]phyrin (8)



Fig. S18 ¹H NMR Spectrum of Calix[3]ferrocenyl[6]phyrin (8)



Fig. S19 FAB MS Spectrum of Calix[3]ruthenocenyl[6]phyrin (9)

12. Spectrophotometric analysis:



Fig. S20 Electronic absorption spectrum of 3a in CHCl₃



Fig. S21 Electronic absorption spectrum of 3b in CHCl₃



Fig. S22 Normalized electronic absorption spectrum of 4a and 6a in CHCl₃



Fig. S23 Normalized electronic absorption spectrum of 4b, 6b and 8 in CHCl₃



Fig. S24 Normalized electronic absorption spectrum of 5, 7 and 9 in $CHCl_3$

13. Electrochemical analyses:



Fig. S25 Cyclic voltammogram of 4b, 6b and 8 in CHCl₃



Fig. S26 Cyclic voltammogram of 5, 7 and 9 in CHCl₃

14. Single crystal X- ray structures and analyses of 1a, 1b, 3a, 4b, 6a and 7:



Fig. S27 Single crystal X-ray structure of **1a**. a) top view, b) side view and c) 1-D array. The *meso*diaryl groups in (b) and the groups which are not involved in the hydrogen bonding interaction in (c) are omitted for clarity. The distances and angles in (c) are; C42-H42...N2(π): 2.69 Å, 154°; C15-H15...N1(π): 2.79Å, 135° and C16A-H16A...N1(π): 2.82 Å, 147°. The intermolecular distance between the two closest pyrrolic π -clouds is 8.76 Å.



Fig. S28 Single crystal X-ray structure of **1b**. a) top view and b) side view. The *meso*-dialkyl groups in (b) are omitted for clarity.





Fig. S29 Single crystal X-ray analyses of **1b**. a) and b) Two different 1-D array. The groups which are not involved in the hydrogen bonding interactions are omitted for clarity. The distances and angles in (a) and (b) are; C19-H19C...N1(π): 2.86 Å, 172°; C1-H1...N1(π): 2.74 Å, 155° and N1-H1A ...N2(π): 2.93 Å, 174°. The intermolecular distance between the two closest pyrrolic π -clouds in (a) and (b) are 5.07 and 4.93 Å.





Fig. S30 Single crystal X-ray structure and analyses of **3a**. a) top view, b) side view, c) Self-assembled dimer and d) 1-D array. The *meso*-diaryl groups in (b) and the groups which are not involved in the hydrogen bonding interactions in (c) and (d) are omitted for clarity. The distances and angles in (a), (c) and (d) are; N1-H1A...N2: 1.81 Å, 144°, C26-H26...O1: 2.78 Å, 151°, C26-H26...O2: 2.78 Å, 163° and C20-H20 ...Ph(π): 2.88 Å, 145°.



Fig. S31 2-D array of **3a**. The distances and angles are; C26-H26...O1: 2.78 Å, 151°, C26-H26...O2: 2.78 Å, 163° and C20-H20 ...Ph(π): 2.88 Å, 145°.



Fig. S32 Single crystal X-ray structure and analyses of **4b**. a) top view, b) side view and c) Self-assembled dimer. The *meso*-dialkyl groups in (b) and the groups which are not involved in the hydrogen bonding interactions in (c) are omitted for clarity. The distances and angles in (a) and (c) are; N2-H2A...N1: 1.93 Å, 136°, C10-H10...F1: 2.82 Å, 156° and C12-H12A...F1: 2.68Å, 137°.



Fig. S33 Single crystal X-ray analyses of **4b**. a) 1-D array and b) 2-D array. The groups which are not involved in the hydrogen bonding interactions are omitted for clarity. The distances and angles are; C2-H2...F3: 2.83 Å, 149°, C30-H30C...F2: 2.77 Å, 155° and C31-H31B...F2: 2.88 Å, 151°.



Fig. S34 Single crystal X-ray structure of **6b**. a) top view and b) side view. The *meso*-dialkyl groups in (b) are omitted for clarity. The distance and angle in (a) is; N1-H1C...N2: 2.05 Å, 132°.





Fig. S35 Single crystal X-ray analyses of **6b**. a) and b) 1-D arrays. The groups which are not involved in the hydrogen bonding interactions are omitted for clarity. The distances and angles are; C8-H8...F2: 2.71 Å, 157° and C28-H28A...N2(π): 2.73 Å, 153°.



Fig. S36 2D array of 6b. The distances and angles are; C8-H8...F2: 2.71 Å, 157° and C28-H28A...N2(π): 2.73 Å, 153°.



Fig. S37 Single crystal X-ray structure of **7**. a) top view and b) side view. The *meso*-dialkyl groups in (b) are omitted for clarity. The distance and angle in (a) is; N1-H1C...N2: 2.00 Å, 141°.



Fig. S38 Single crystal X-ray analyses of **7**. a) and b) 1-D arrays. The groups which are not involved in the hydrogen bonding interactions are omitted for clarity. The distances and angles are; C3-H3...F4: 2.83 Å, 147° and C30-H30A...N2(π): 2.82 Å, 146°.



Fig. S39 2D array of 7. The distances and angles are; C3-H3...F4: 2.83 Å, 147° and C30-H30A...N2(π): 2.82 Å, 146°.

15. Crystallographic data of 1b, 3a, 4b, 6b and 7:

- a) Crystallographic data of 1b (CHCl₃/n-heptane): C₂₄H₂₈FeN₂, Mw = 400.33, Triclinic, space group *P*-1, a = 7.3633 (3)Å, b = 12.0119 (5) Å, c = 12.4506 (6) Å, α = 105.413 (2)°, β = 95.925 (2)°, γ = 106.768 (2)°, V = 996.98 (8) Å³, Z = 2, D_{calc} = 1.334 mg/m³, T = 293 (2) K, 27755 reflections collected, 7805 unique, R_(int) = 0.0214, R indices (all data): R₁ = 0.0619, wR2 = 0.1221, Final R indices: R1 = 0.0391 {*I* > 2σ(*I*)}, wR2 = 0.1006, GOF = 1.099.
- b) Crystallographic data of **3a** (CHCl₃/n-heptane): C₅₉H₅₄Cl₃FeN₃O₂, Mw = 999.25, Monoclinic, space group P21/n, a = 10.8374 (12)Å, b = 25.707 (3) Å, c = 18.728 (2) Å, $\alpha = 90.00^{\circ}$, $\beta = 105.443$ (3)°, $\gamma = 90.00^{\circ}$, V = 5029.2 (9) Å3, Z = 4, Dcalc = 1.320 mg/m3,T = 100 (2) K, 46883 reflections collected, 8837 unique, R(int) = 0.0327, R indices (all data): R1 = 0.1037, wR2 = 0.2615, Final R indices: R1 = 0.0858 {I > $2\sigma(I)$ }, wR2 = 0.2433, GOF = 1.032.
- c) Crystallographic data of **4b** (CHCl₃/*n*-heptane): C₃₁H₂₅F₅FeN₂, Mw = 576.38, Monoclinic, space group *P*21/c, a = 11.1820 (2) Å, b = 10.4371 (2) Å, c = 21.7536 (4) Å, $\alpha = 90.00^{\circ}$, $\beta = 90.4690 (10)^{\circ}$, $\gamma = 90.00^{\circ}$, V = 2538.73 (8) Å³, Z = 4, $D_{calc} = 1.508$ mg/m³, T = 293 (2) K, 32605 reflections collected, 7550 unique, $R_{(int)} = 0.0328$, R indices (all data): R₁ = 0.0625, wR2 = 0.1212, Final R indices: R1 = 0.0391 { $I > 2\sigma(I)$ }, wR2 = 0.1035, GOF = 1.053.
- d) Crystallographic data of **6b** (CHCl₃/*n*-heptane): $C_{62}H_{50}F_{10}Fe_2N_4$, Mw = 1152.76, Triclinic, space group *P*-1, a = 11.0784 (17) Å, b = 11.4123 (17) Å, c = 12.3519 (19) Å, $\alpha = 117.468 (2)^{\circ}$, $\beta = 99.411 (2)^{\circ}$, $\gamma = 106.469 (2)^{\circ}$, $V = 1246.8 (3) Å^3$, Z = 1, $D_{calc} = 1.535 \text{ mg/m}^3$, T = 100 (2) K, 10763 reflections collected, 5645 unique, $R_{(int)} = 0.0264$, *R* indices (all data): R₁ = 0.0625, wR2 = 0.1210, Final *R* indices: *R*1 = 0.0524 { $I > 2\sigma(I)$ }, wR2 = 0.1162, GOF = 1.085.
- e) Crystallographic data of **7** (CHCl₃/*n*-heptane): C₆₂H₃₈F₁₀Ru₂N₄, Mw = 1231.10, Triclinic, space group *P*-1, a = 11.2539 (10) Å, b = 11.5076 (10) Å, c = 12.2368 (11) Å, $\alpha = 117.3260 (10)^{\circ}$, $\beta = 99.1430 (10)^{\circ}$, $\gamma = 107.6930 (10)^{\circ}$, V = 1255.16 (19) Å3, *Z* = 1, *D*calc = 1.629 mg/m3, *T* = 100 (2) K, 8079 reflections collected, 3893 unique, *R*(int) = 0.0166, *R* indices (all data): R1 = 0.1162, wR2 = 0.2328, Final *R* indices: *R*1 = 0.1092 {*I* > 2 σ (*I*)}, wR2 = 0.2284, GOF = 1.180.