Electronic Supporting Information (ESI) for

Unveiling the Potential of Tailored β -Substituted Iron-Porphyrins for Highly Efficient Oxygen Reduction Reactions (ORR)

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EXPERIMENTAL SECTION:

Materials and instrumentation

The required chemicals were purchased from reputable suppliers, including Alfa Aesar, Sigma-Aldrich, HiMedia, and Thomas Baker. The synthesis of H₂TPPBr₄, H₂TPPPh₄, H₂TPPMe₄ followed established procedures outlined in the literature. MALDI-TOF-MS spectra were obtained using a Bruker UltrafleXtreme-TN MALDI-TOF/TOF spectrometer. Distilled dichloromethane is used as the solvent for various analyses, including electronicspectral, cyclic voltametric assessments, and other research investigations. Crystal data of Fe(III)CITPPMe₄ was collected on a Bruker D8 QUEST instrument equipped with a graphite monochromated Mo K α radiation source using θ -2 θ scanning mode. The JEOL ECX 500 MHz instrument is used to record ¹H NMR spectra in CDCl₃ as the solvent at a temperature of 298 K. The Shimadzu UV-2600 spectrophotometer is employed to record electronic absorption spectra in quartz cuvettes of a path length of 1 cm and with a volume of 3.5 mL in distilled dichloromethane (DCM). X-band EPR was recorded on Bruker BIOSPIN EMX micro A200-9.5/12/S/Win toluene at 100 K. The MALDI-TOF mass spectra were recorded on Bruker UltrafleXtreme-TN MALDI-TOF mass spectrometer in a positive ion mode. Cyclic voltammetric studies were performed using CH instruments (CHI 7044E) and involving a 3electrode assembly of carbon as the working electrode, Pt wire as the counter electrode, and an Ag/AgCl as a reference electrode in argon gas atmosphere. The concentration of porphyrins utilized in the electrochemical analyses was kept at around 1 mM, with a scan rate of 0.1 V/s being applied.



Scheme S1: Synthetic strategy for Fe(III)ClTPPMe₄.



Scheme S2: Synthetic strategy for Fe(III)ClTPPPh₄.



Scheme S3: Synthetic strategy for Fe(III)ClTPPBr₄.

Synthesis of Fe(III)CITPPMe₄

100 mg (0.107 mmol) of H₂TPPBr₄ was dissolved in THF and was purged for 5 min in Ar atmosphere. After that 356.23 mg (2.577 mmol) K₂CO₃ was added to it and purged for 5 min. Then 116.08 mg (1.934 mmol) of phenylboronic acid (Me(B(OH)₂) was added and Ar was purged for 5 min. After that distilled toluene was added and was purged for 10 min. To this, 24.28 mg (20 mol%) Pd(PPh₃)₄ was added and again purged for 15 min. The reaction mixture was stirred at 90-100°C for 2 days under an inert atmosphere. After the completion of reaction, the reaction mixture was cooled to room temperature. Solvent was evaporated to dryness, and the crude porphyrin was washed with sodium bicarbonate solution followed by distilled water. The organic layer was separated and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure. The crude solid was purified by column chromatography using chloroform. The title compound was obtained as purple solid. Yield: 55%. After that 60 mg of H₂TPP(Me)₄ was dissolved in 20-25 mL of DMF. To this, 12 equiv. of ferrous chloride was added, and the resulting mixture was refluxed for 5 hrs. As the starting material was consumed (reaction monitored by UV-Vis and TLC) the reaction mixture was cooled to room temperature. Then acidic water workup was done. And solvent was evaporated till dryness under reduced pressure. The resulting crude metalloporphyrin was purified by column chromatography using CHCl₃ as an eluent.

H₂TPPMe₄: UV/vis (CH₂Cl₂): λ_{max} (nm): 421, 520, 589, 643. ¹H NMR (500 MHz, CDCl₃) δ(ppm): 8.46 (s, 4H, β-H), 8.09 (dt, J = 6.6, 1.5 Hz, 8H, *meso-o*-Ph-H), 7.75 – 7.69 (m, 12H, *meso-m*, *p*-Ph-H), 2.41 (s, 12H, Me-H), -2.77 (s, 2H, Inner NH).

Fe(III)CITPPMe₄ : UV/vis (CH₂Cl₂): λ_{max} (nm) ($\epsilon \times 10^{-3}$ L mol⁻¹ cm⁻¹): 416(41), 516(4.8), 558(3.0). MALDI-TOF-MS. Found: m/z 724.20 ([M-Cl]⁺) Calcd: m/z 724.23.

Synthesis of Fe(III)CITPPPh₄

260 mg (0.279 mmol) of H₂TPPBr₄ was dissolved in toluene and was purged for 5 min in Ar atmosphere. After that 927 mg (6.707 mmol) K₂CO₃ was added to it and purged for 5 min. Then 408.22 mg (3.348 mmol) of phenylboronic acid ($Ph(B(OH_{12}))$ was added and Ar was purged for 5 min. To this, 65 mg (20 mol%) Pd(PPh₃)₄ was added and again purged for 15 min. The reaction mixture was stirred at 90-100 °C for 2 days under an inert atmosphere. After the completion of reaction, the reaction mixture was cooled to room temperature. Solvent was evaporated to dryness, and the crude porphyrin was washed with sodium bicarbonate solution followed by distilled water. The organic layer was separated and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure. The crude solid was purified by column chromatography using chloroform. The title compound was obtained as purple solid. Yield: 60%. After that 35 mg of H₂TPP(Ph)₄ was dissolved in 20-25 mL of DMF. To this, 12 equiv. of ferrous chloride was added, and the resulting mixture was refluxed for 5 hrs. As the starting material was consumed (reaction monitored by UV-Vis and TLC) the reaction mixture was cooled to room temperature. Then acidic water workup was done. And solvent was evaporated till dryness under reduced pressure. The resulting crude metalloporphyrin was purified by column chromatography using CHCl₃ as an eluent.

H₂**TPPPh**₄: UV/vis (CH₂Cl₂): λmax (nm): 433, 529, 600, 675. ¹H NMR (500 MHz, CDCl₃) δ(ppm): 8.37 (s, 4H, β-H), 7.84 (dt, J = 6.8, 1.4 Hz, 8H, *meso-o*-Ph-H), 7.31 – 7.26 (m, 4H, *meso-p*-Ph-H), 7.23 – 7.20 (m, 8H, , β-o-Ph-H), 6.94 – 6.91 (m, 8H, *meso-m*-Ph-H), 6.87 – 6.83 (m, 12H, β-m, p-Ph-H), -2.05 (s, 2H, Inner NH).

Fe(III)CITPPPh₄: UV/vis (CH₂Cl₂): λmax (nm) (ε × 10⁻³ L mol⁻¹ cm⁻¹): 430(67), 518(8.5), 595(3.4). MALDI-TOF-MS. Found: m/z 972.12 ([M-Cl]⁺) Calcd: m/z 972.29, m/z 1007.85 ([M]⁺) Calcd: m/z 1007.85.

Synthesis of Fe(III)CITPPBr₄

 $300 \text{ mg} (0.488 \text{ mmol}) \text{ of } \text{H}_2\text{TPPPh}_4$ was dissolved in CHCl₃ and was refluxed for few minutes. After that 521 mg (2.93 mmol) of NBS was added to it. Then the reaction mixture was refluxed for 4 hrs. Then the reaction mixture was cooled down. The solvent was removed under reduced pressure. After that the crude solid was purified by column chromatography using chloroform. The title compound was obtained as purple solid. Yield: 79%. After that 50 mg of H₂TPPBr₄ was dissolved in 20-25 mL of DMF. To this, 12 equiv. of ferrous chloride was added, and the resulting mixture was refluxed for 5 hrs. As the starting material was consumed (reaction monitored by UV-Vis and TLC) the reaction mixture was cooled to room temperature. Then acidic water workup was done. And solvent was evaporated till dryness under reduced pressure. The resulting crude metalloporphyrin was purified by column chromatography using CHCl₃ as an eluent.

H₂TPPBr₄: UV/vis (CH₂Cl₂): λ_{max} (nm): 434, 533, 613, 681. ¹H NMR (500 MHz, CDCl₃) δ(ppm): 8.69 (d, J = 1.4 Hz, 4H, β-H), 8.17 (dt, J = 6.3, 1.6 Hz, 8H, *meso-o*-Ph-H), 7.81 – 7.76 (m, 12H, *meso-m*, *p*-Ph-H), -2.81 (s, 2H, Inner NH).

Porphyrins	λ_{abs} , nm		
	Soret band	Q bands	
H ₂ TPPMe ₄	421	520, 589, 643	
H ₂ TPPPh ₄	433	529, 600,675	
H ₂ TPPBr ₄	434	533, 613,681	
Fe(III)CITPPMe ₄	416(41)	516(4.8), 558(3.0)	
Fe(III)CITPPPh ₄	430(67)	518(8.5), 595(3.4)	
Fe(III)CITPPBr ₄	431(52)	519(6.5), 595(3.6)	

^{*a*}Values in parentheses refer to $\varepsilon \times 10^{-3}$ (M⁻¹ cm⁻¹).



Fig. S1. Displacement of the porphyrin 24-core atoms from the mean plane for $Fe(III)CITPPMe_4$ in angstroms.

Table S2. Crystallographic data of Fe(III)ClTPPMe_{4.}

Identification code	MS_SR_FeMe4_1235_0m
Empirical formula	$C_{48}H_{36}ClFeN_4$
Formula weight	760.11
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	11.5966(3)
<i>b</i> /Å	12.6443(3)
$c/\text{\AA}$	14.8717(4)
$\alpha/^{\circ}$	68.7250(10)
$\beta^{\prime \circ}$	70.7260(10)
γ/°	67.3450(10)
Volume/Å ³	1828.74(8)
Ζ	2
$\rho_{calc}g/cm^3$	1.380
µ/mm ⁻¹	0.527
F(000)	790.0
Crystal size/mm ³	$0.215 \times 0.189 \times 0.125$
Radiation	MoKa ($\lambda = 0.71073$)
2Θ range for data collection/	° 3.014 to 56.412
Index ranges	$-15 \le h \le 15, -16 \le k \le 16, -19 \le l \le 19$
Reflections collected	111181
Independent reflections	8990 [$R_{int} = 0.0468, R_{sigma} = 0.0234$]
Data/restraints/parameters	8990/0/491
Goodness-of-fit on F ²	1.043
Final R indexes $[I > = 2\sigma(I)]$	$R_1 = 0.0356, wR_2 = 0.0976$
Final R indexes [all data]	$R_1 = 0.0405, wR_2 = 0.1016$

Largest diff. peak/hole / e Å⁻³ 0.64/-0.22 CCDC No 2429858

Table S3: Selected bond lengths (Å) and bond angles (°) form the crystal data of $Fe(III)CITPPMe_4$.

	Bond Length (Å)
M-N	2.1065
M-N'	2.0395
N-C _a	1.3847
N-C _a ,	1.3822
C_{α} - C_{β}	1.4545
C_{α} ,- C_{β} ,	1.4375
C_{β} - C_{β}	1.3665
C_{β} ,- C_{β} ,	1.356
C_{α} - C_{m}	1.3987
C_{α} ,- C_m	1.3982
Δ24 (Å)	0.088
	Bond Angles (°)
M-N-C _a	126.4075
M-N'-C _α ,	125.6325
N-M-N	153.84
N'-M-N'	154.44
$N-C_{\alpha}-C_{m}$	124.085
N'- C_{α} '- C_m	126.39
$N-C_{\alpha}-C_{\beta}$	110.1275
N'- C_{α} '- C_{β} '	109.8475
$C_{\beta}-C_{\alpha}-C_{m}$	125.785
C_{β} ,- C_{α} ,- C_{m}	123.69
C_{α} - C_{m} - C_{α}	124.79
C_{α} - C_{β} - C_{β}	106.852
C_{α} ,- C_{β} ,- C_{β} ,	107.185
C_{α} -N- C_{α}	105.885
C_{α} ,-N'- C_{α} ,	105.875



Fig. S2. ¹H NMR spectrum of H₂TPPMe₄ in CDCl₃ at 298 K.



Fig. S3. ¹H NMR spectrum of H₂TPPPh₄ in CDCl₃ at 298 K.



Fig. S4. ¹H NMR spectrum of H₂TPPBr₄ in CDCl₃ at 298 K.



Fig. S5. MALDI-TOF Mass Spectrum of Fe(III)ClTPPMe₄ before and after stability test.



Fig. S6. MALDI-TOF Mass Spectrum of Fe(III)ClTPPh₄ before and after stability test.



Fig. S7. MALDI-TOF Mass Spectrum of Fe(III)ClTPPBr₄ before and after stability test.



Fig. S8. Observed X-Band EPR spectra of Fe(III)ClTPPMe₄ before and after stability test in toluene at 100K.



Fig. S9. Observed X-Band EPR spectra of Fe(III)ClTPPPh₄ before and after stability test in toluene at 100K.



Fig. S10. Observed X-Band EPR spectra of Fe(III)ClTPPBr₄ before and after stability test in toluene at 100K.

Table	S4	The	X-band	EPR	parameters	of	Fe(III)ClTPPMe _{4,}	Fe(III)ClTPPPh _{4,}	and
Fe(III)	CITP	PBr ₄ ,	both befo	ore and	after stability	y tes	ting in toluene at 10	00 K.	

Porphyrins	g⊥	g∥	$A_{\perp}(\times 10^{-3})$ cm ⁻¹	$A_{\parallel}(\times 10^{-3}) \text{cm}^{-1}$
Fe(III)CITPPMe ₄	5.78	2.46	31.20	19.65
before				
Fe(III)CITPPMe ₄	5.78	2.47	31.20	20.23
after				
Fe(III)CITPPPh ₄	6.09	2.48	31.31	20.37
before				
Fe(III)CITPPPh ₄	6.11	2.49	31.33	19.48
after				
Fe(III)CITPPBr ₄	6.04	2.48	31.30	19.80
before				
Fe(III)CITPPBr ₄	5.99	2.48	31.33	19.80
after				



Fig. S11. Cyclic voltammograms and DPV of Fe(III)ClTPPMe₄ were recorded using 0.1 M TBAPF₆ in CH₂Cl₂ as the electrolyte under inert conditions, with a scan rate of 0.1 V/s.



Fig. S12. Cyclic voltammograms and DPV of Fe(III)ClTPPPh₄ were recorded using 0.1 M TBAPF₆ in CH₂Cl₂ as the electrolyte under inert conditions, with a scan rate of 0.1 V/s.



Fig. S13. Cyclic voltammograms and DPV of $Fe(III)CITPPBr_4$ were recorded using 0.1 M TBAPF₆ in CH₂Cl₂ as the electrolyte under inert conditions, with a scan rate of 0.1 V/s.

Table S5. Half-Wave Potential (V vs Ag/AgCl) of Investigated Porphyrins Containing 0.1 M TBAPF₆ in CH₂Cl₂ at 298 K.

Macrocycles	Oxidations (V)		Reductions (V)		
	Ι	Π	Ι	II	III
Fe(III)CITPPMe ₄	0.93	1.36	-0.39	-1.29	-1.47
Fe(III)CITPPPh ₄	1.38	0.96	-0.33	-1.13	-1.31
Fe(III)ClTPPBr ₄	1.1	1.46	-0.27	-0.96	-1.16

Table S6. A Comparative Study on the Influence of β -Substituents on Redox Activity Derived from Cyclic Voltammograms (CV):

S.	Substituent	Туре	Effect on electronic	CV	References
No.			properties	observations	
				Fe ^{III/II}	
				reduction (V)	
1	FeTPP-OTf,	Control		-0.63	Amanullah,
	FeDEsP-OTf,	EWG	Decreases electron	-0.52	S. <i>et. al.</i> ,
			density on iron		Faraday
	FeTEsP-OTf	EWG	Decreases electron	-0.47	Discuss.
			density on iron		2022, 234
					(0), 143–
					158.
2	FeTPP-C1	Control		-0.29	Kadish, K.
	FeTPPBr ₁ -Cl	EWG		-0.26	M., <i>et. al.</i>
	FeTPPBr ₂ -Cl	EWG		-0.18	Inorg. Chem.
	FeTPPBr ₃ -Cl	EWG	Decreases electron	-0.13	1994, 33
	FeTPPBr ₄ -Cl	EWG	density on iron	-0.07	(23), 5169–
	FeTPPBr ₅ -Cl	EWG		-0.02	5170.
	FeTPPBr ₆ -Cl	EWG		-0.04	
	FeTPPBr ₇ -Cl	EWG		0.06	
	FeTPPBr ₈ -Cl	EWG		0.10	
3	Fe(III)ClTPPMe ₄	EDG	Decreases electron	-0.39	This work
			density on iron		
	Fe(III)ClTPPPh ₄	EWG	Slightly decreases	-0.33	
			electron density on		
			iron	-0.27	
	Fe(III)ClTPPBr ₄	EWG	Decreases electron		
			density on iron		

Electrocatalysis study:

Cyclic voltammetry (CV) and linear sweep voltammetry experiments were conducted using a CH Instruments potentiostat (model CHI 7044E). A three-electrode configuration was employed, where a glassy carbon electrode (GCE) served as the working electrode, Ag/AgCl was the reference electrode, and a platinum wire functioned as the counter electrode. For the oxygen reduction reaction (ORR) studies, the same three-electrode system was utilized with a

modulated speed rotator from BAS Inc. (made in Japan) to control the rotation of the electrode. The reference electrode used was a saturated silver electrode (Ag/AgCl), the counter electrode was platinum wire, and the working electrode was either a glassy carbon electrode (GCE) with a surface area of 0.071 cm² or a glassy carbon rotating disc electrode (GCRDE) with a surface area of 0.196 cm². The working electrode was polished on a wet Buehler-felt pad using 0.05 μ and 0.1 μ neutral alumina powder, followed by rinsing with water and a 2 min sonication. To prepare the material slurry, 2 mg of the substance was dissolved in 500 μ L of DCM, followed by 10 min of sonication. A 6 μ L portion of the resulting slurry was applied to the GC electrode, while 14 μ L was used for the GCRDE. The measured potentials were converted to the reversible hydrogen electrode (RHE) scale using the Nernst equation.

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E^{0}_{Ag/AgCl}$$
(S1)

The experimentally measured potential versus the Ag/AgCl reference electrode is represented as $E_{Ag/AgCl}$ while the standard potential of Ag/AgCl at 25 °C is $E_{Ag/AgCl} = 0.199$ V

The oxygen reduction reaction was investigated using CV and LSV in a 0.1 M KOH solution under argon gas and oxygen-saturated conditions. The CV measurements were conducted in a non-stirred system within a potential window of -0.4 to 0.6 V vs. SCE, with a scan rate of 10 mV/s. LSV technique was conducted at a rotation speed of 1600 rpm with scan rate of 10 mV/s. The Koutecky-Levich (K-L) equation was employed to computed the number of electrons transferred per oxygen molecule during the ORR catalytic activity.

$$IJ = 1 J_K + 1 J_L = 1 B\omega 1/2 + 1 j_k$$
 S2

$$B = 0.62 n F C_{O} (D_0)^{2/3} \Upsilon^{-1/6}$$
 S3

Where J represent the current density, J_K denote kinetic limiting current density and J_L signify diffusion limiting current density respectively. The angular velocity of the electrode is denoted by ω , while n represents the number of electrons transferred for each molecule of O₂. The Faraday constant, F, is 96,485 C mol⁻¹. The concentration (Co) of O₂ is given as 1.2×10^{-6} mol cm⁻³. C₀ is the concentration of O₂ (1.2×10^{-6} mol cm⁻³), The diffusion coefficient (D₀) of O₂ is 1.9×10^{-5} cm² s⁻¹, and the kinematic viscosity (Y) of the electrolyte is measured at 0.01 cm² s⁻¹.

To validate the electrochemical setup, we prepared a 1 mM ferro/ferricyanide solution in 0.1 M KCl and used an Ag/AgCl electrode as the reference, a Pt wire as the counter electrode and a glassy carbon electrode as the working electrode. The setup showed oxidation and reduction peaks at ~0.31 V and ~0.18 V, respectively, consistent with reported data. These peaks arise from diffusion-controlled redox reactions. The CV of ferrocyanide provides valuable insights into electrode behaviour, reaction kinetics, and system reliability.



Fig. S14: CV responses of (a) in 1 mM ferro/ferricyanide solution in 0.1 M KCl at a scan rate of 10 mV s⁻¹ to 500 mV s⁻¹ (b) and the corresponding current vs. (scan rate)^{1/2} plot.



Fig. S15: (a) Calculated values of the ORR apparent electron transfer number (n), (b) Amperometric responses of Fe(III)ClTPPMe₄, Fe(III)ClTPPPh₄ and Fe(III)ClTPPBr₄ recorded on ITO electrodes over 11,000 s at an applied potential of 0.5 V vs. RHE and a rotation speed of 1600 rpm. (c) EIS study of Fe(III)ClTPPMe₄, Fe(III)ClTPPPh₄ and Fe(III)ClTPPBr₄.



Fig. S16: Normalized UV-visible absorption spectra (a) $Fe(III)CITPPMe_4$ (b) $Fe(III)CITPPPh_4$ (c) $Fe(III)CITPPBr_4$ electrolytes before and after electrolysis.



R=Br, Ph, Me



 Table S7. Selected bond lengths (Å) and bond angles (°) for the B3LYP/LANL2DZ optimised

 geometries of Fe(III)CITPPBr₄, Fe(III)CITPPPh₄ and Fe(III)CITPPMe₄.

Bond Length						
	Fe(III)CITPPPh ₄	Fe(III)CITPPMe ₄	Fe(III)TPPBr ₄			
M-N	2.0035	1.997	2.014			
M-N'	1.967	1.983	1.9425			
C_{α} - C_{β}	1.4625	1.458	1.458			
C_{α} ,- C_{β} ,	1.4465	1.4505	1.448			
$C_{\beta}-C_{\beta}$	1.388	1.386	1.376			
C_{β} ,- C_{β} ,	1.375	1.373	1.374			
C _a -C _m	1.41	1.406	1.4075			
C_{α} ,- C_m	1.4045	1.406	1.448			
$\Delta C_{\beta} (\text{\AA})$	0.8718	0.8575	0.908			
Δ24 (Å)	0.449	0.420	0.462			

Bond Angles (°)							
	Fe(III)CITPPPh ₄	Fe(III)CITPPMe ₄	Fe(III)TPPBr ₄				
M-N-C _a	126.99	124.80	124.88				
M-N'-C _{α'}	123.9	126.875	127.07				
N-M-N	160.82	171.79	176.90				
N'-M-N'	170.66	159.62	157.00				
N-C _a -C _m	123.202	123.055	122.73				
N'- C_{α} '- C_m	125.07	125.57	126.17				
$N-C_{\alpha}-C_{\beta}$	110.137	110.067	108.88				
N'- C_{α} '- C_{β} '	109.80	109.74	109.47				
$C_{\beta}-C_{\alpha}-C_{m}$	126.367	126.715	128.07				
C_{β} ,- C_{α} ,- C_{m}	125.017	124.53	124.125				
C_{α} - C_{m} - C_{α} ,	121.205	121.68	121.43				
$C_{\alpha}-C_{\beta}-C_{\beta}$	106.60	106.895	107.32				
C_{α} ,- C_{β} ,- C_{β} ,	107.305	107.185	107.36				
C_{α} -N- C_{α}	105.57	105.385	106.79				
C_{α} ,-N- C_{α} ,	105.65	105.85	105.78				



Fig. S17. B3LYP/LANL2DZ–optimized geometries showing top view of (a) $Fe(III)CITPPMe_4$ (b) $Fe(III)CITPPPh_4$ and (c) $Fe(III)CITPPBr_4$ respectively. In the side view (d) $Fe(III)CITPPMe_4$ (e) $Fe(III)CITPPPh_4$ and (f) $Fe(III)CITPPBr_4$, the *meso*–phenyl groups are not shown for clarity.



Fig. S18: Frontier molecular orbital energy profile of β -disubstituted iron porphyrin complexes.

The comparison between DFT-calculated HOMO–LUMO energy gaps and experimentally derived redox behavior from cyclic voltammetry (CV) offers valuable insight into the oxygen reduction reaction (ORR) activity of Fe(III) porphyrins. A smaller HOMO–LUMO gap, as predicted by DFT, indicates increased redox flexibility which is an essential feature for efficient multielectron transfer processes like ORR. This theoretical prediction aligns with CV data for all the three porphyrins, which exhibits favorable redox potentials, confirming their suitability for ORR. The combined DFT and CV analysis thus establishes a clear link between electronic structure and electrochemical performance.

Table S8: Comparative Analysis of DFT and CV Data for Iron Porphyrins:

Reduction Behaviour vs LUMO Energies:

Lower LUMO \rightarrow Easier reduction (more positive potential)

Porphyrin	LUMO (eV)	CV Red I (V)	Alignment
Fe(III)CITPPMe ₄	-2.95	-0.39	Yes
Fe(III)CITPPPh ₄	-3.27	-0.33	Yes
Fe(III)CITPPBr ₄	-3.57	-0.27	Yes

Oxidation Behaviour vs HOMO Energies:

Higher HOMO \rightarrow Easier oxidation (lower potential)

Porphyrin	HOMO (eV)	CV Ox I	Alignment
		(V)	
Fe(III)CITPPMe ₄	-5.29	0.93	Yes
Fe(III)CITPPPh ₄	-5.39	0.96	Yes
Fe(III)CITPPBr ₄	-5.87	1.1	Yes

Table S9. Comparison of the ORR efficiency of β -substituted iron porphyrins (Fe(III)ClTPPMe₄, Fe(III)ClTPPBr₄ and Fe(III)ClTPPPh₄ with other catalysts in terms of E_{onset} and E_{1/2} values.

S. No.	Catalysts	E _{onset} (V	$E_{1/2}$ (V vs.	References
		vs. RHE)	RHE)	
1	PtCuSn	1.09	0.86	Int. J. Hydrogen
				<i>Energy</i> 2023 , 48 (1),
				160–170.
2	Pt/C	0.92	NA	Inorg. Chem. 2022,
				61 (33),
				13085-
				13095.
3	Fe/Co-CMP	0.88	0.78	J. Mater. Chem. A,
				2015 , <i>3</i> (47),
				23799–23808.
4	FeTMPPC1-XC72	NA	0.34 ± 0.02	ACS Catal., 2022,
	FeTMPPC1-MoS ₂		-0.15 ± 0.03	12 (2), 1139–1149.
	FeTMPPC1-g-C ₃ N ₄		-0.23 ± 0.02	
5	MWCNTs-Im-Fe ^{II} F ₂₀ TPP	1.04	0.87	Chem. – A Eur. J.,
	MWCNTs-Thi-FeF ₂₀ TPP	0.93	0.81	2021 , <i>27</i> (38),
	MWCNTs-Ox-FeF ₂₀ TPP	0.92	0.77	9898–9904.
6	NPME-FeTMPPC1	0.936	0.75	Adv. Funct. Mater.,
				2017, 27 (3),
				1604356.
7	iron porphyrin@MOF-5	1.002	0.903	J. Electroanal.
	derived Fe-N-C			Chem., 2023 , 936,

				117381.
8	Fe(III)ClTPPMe ₄	0.77	0.59	This work
	Fe(III)ClTPPPh ₄	0.98	0.78	
	Fe(III)ClTPPBr ₄	0.79	0.63	

NA: Not Available

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