Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information for

Protonic Nanoenvironment Engineering for Tuning the Electrocatalytic Efficiency and Product Selectivity of O_2 Reduction

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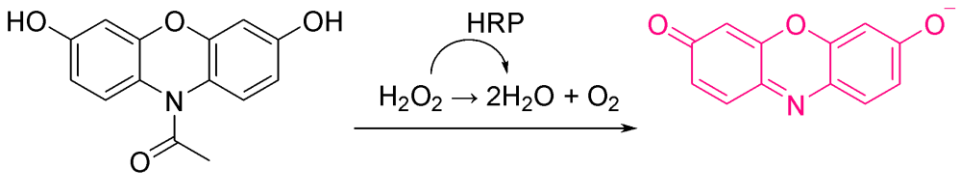
Supplementary Figures S1-S12 and Tables S1.



Amplex Red Resorufin

Figure S1. Reaction between Amplex Red and H_2O_2 in a 1:1 stoichiometry in the presence of horseradish peroxidase (HRP), generating resorufin with a UV-vis absorption band at 571 nm.

Note S1. Equations to calculate the number of electrons transferred per O_2 during ORR in (a) M-TPY SAM, (b) M-TPY HBM, and (c) M-TPY HBM DBA.

Given that the ORR catalyzed by M-TPY SAM undergoes a mixture of $2e^-$ and $4e^-$ processes, while the ORR facilitated by M-TPY HBM and M-TPY HBM DBA respectively involves a mixture of $1e^-$ and $4e^-$,[1]

(a) $\phi(\text{M-TPY SAM}) = 2(X) + 4(1 - X)$

(b) $\phi(\text{M-TPY HBM}) = (X) + 4(1 - X)$

(c) $\phi(\text{M-TPY HBM DBA}) = (X) + 4(1 - X)$, where

$$\boldsymbol{X} = \left(\frac{mole\ of\ O_2\ required\ for\ H_2O_2\ generation}{mole\ of\ O_2\ required\ for\ both\ H_2O\ and\ H_2O_2\ generation}\right)$$

$$\boldsymbol{mole\ of\ O_2\ required\ for\ H_2O_2\ generation}$$
$$= mole\ H_2O_2\ of\ generated\ during\ ORR$$

$$\boldsymbol{mole\ of\ O_2\ required\ for\ H_2O\ generation}$$
$$= \left(\frac{total\ charge\ required\ for\ both\ H_2O\ and\ H_2O_2\ generation - charged\ required\ for\ H_2O_2\ generation}{Faraday\ constant \times number\ of\ electrons\ required\ by\ 1\ mole\ of\ O_2\ for\ H_2O\ generation}\right)$$

Faraday constant = 96500 C/mol

Number of electrons required by 1 mole of O_2 for H_2O generation = 4

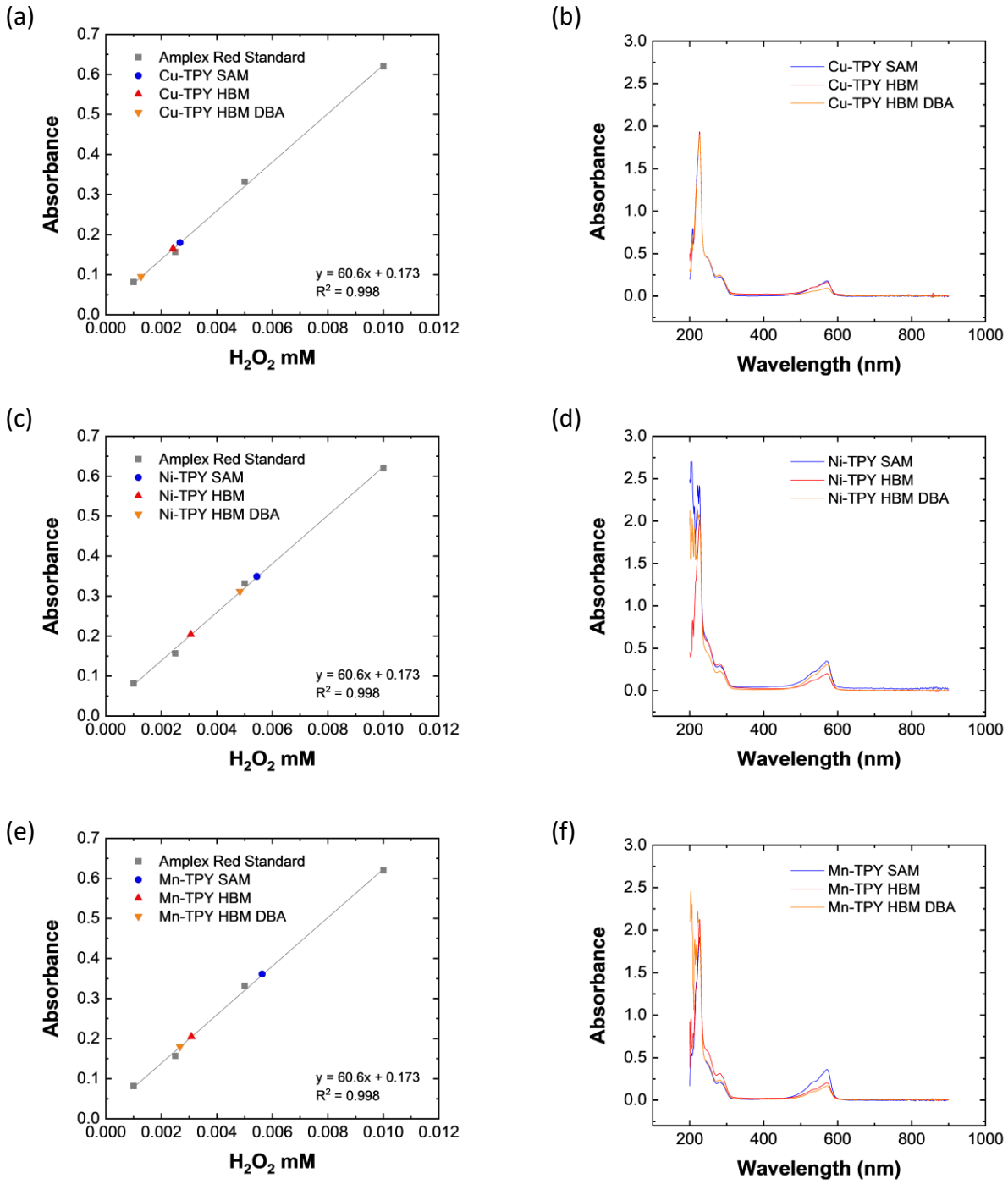


Figure S2. Quantification of H_2O_2 generated during ORR catalyzed by M-TPY SAM, M-TPY HBM, and M-TPY HBM DBA (M = Cu, Ni, Mn). (a, c, d) Standard calibration curve for H_2O_2 in different concentrations including 0.001 mM, 0.0025 mM, 0.005 mM, and 0.010 mM), and (b,c,f) UV-vis characterization of resorufin at 571 nm.

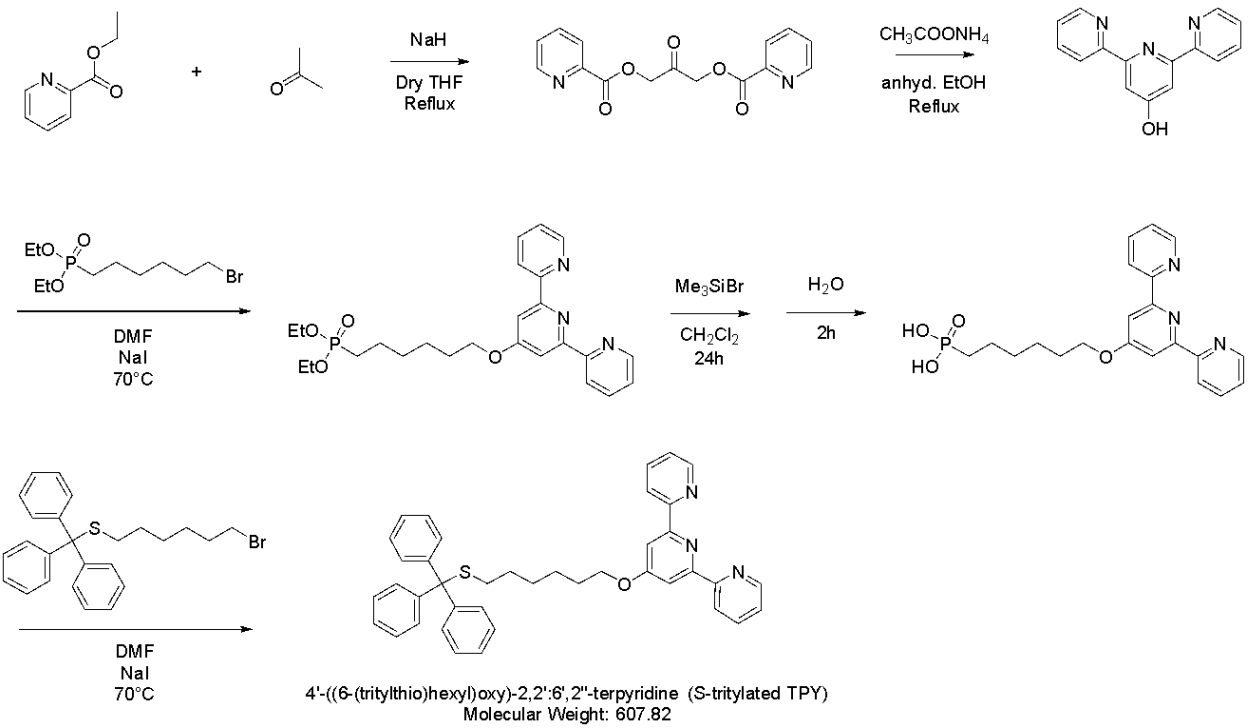


Figure S3. Preparation procedure of S-tritylated TPY.

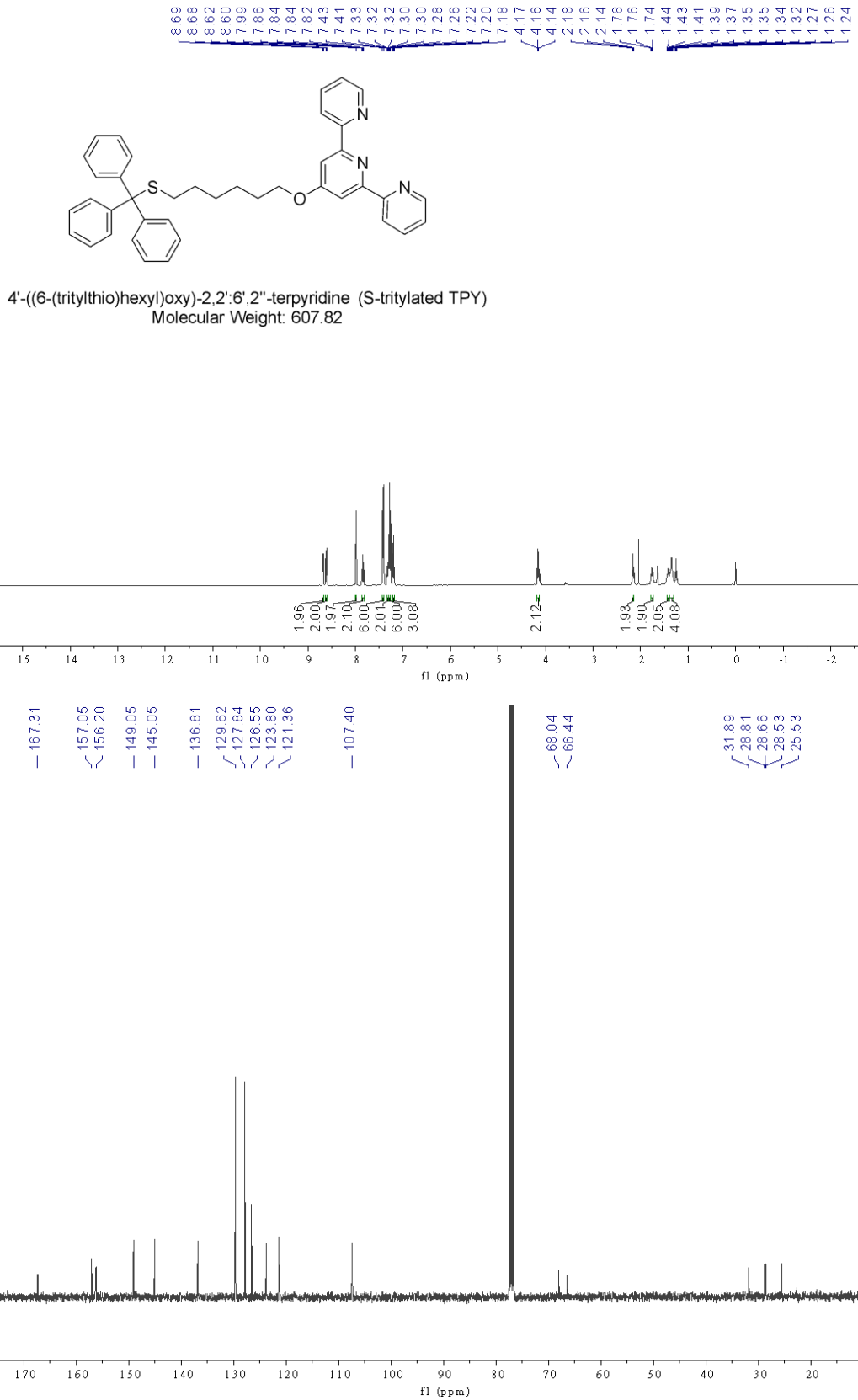


Figure S4. ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of S-tritylated TPY.

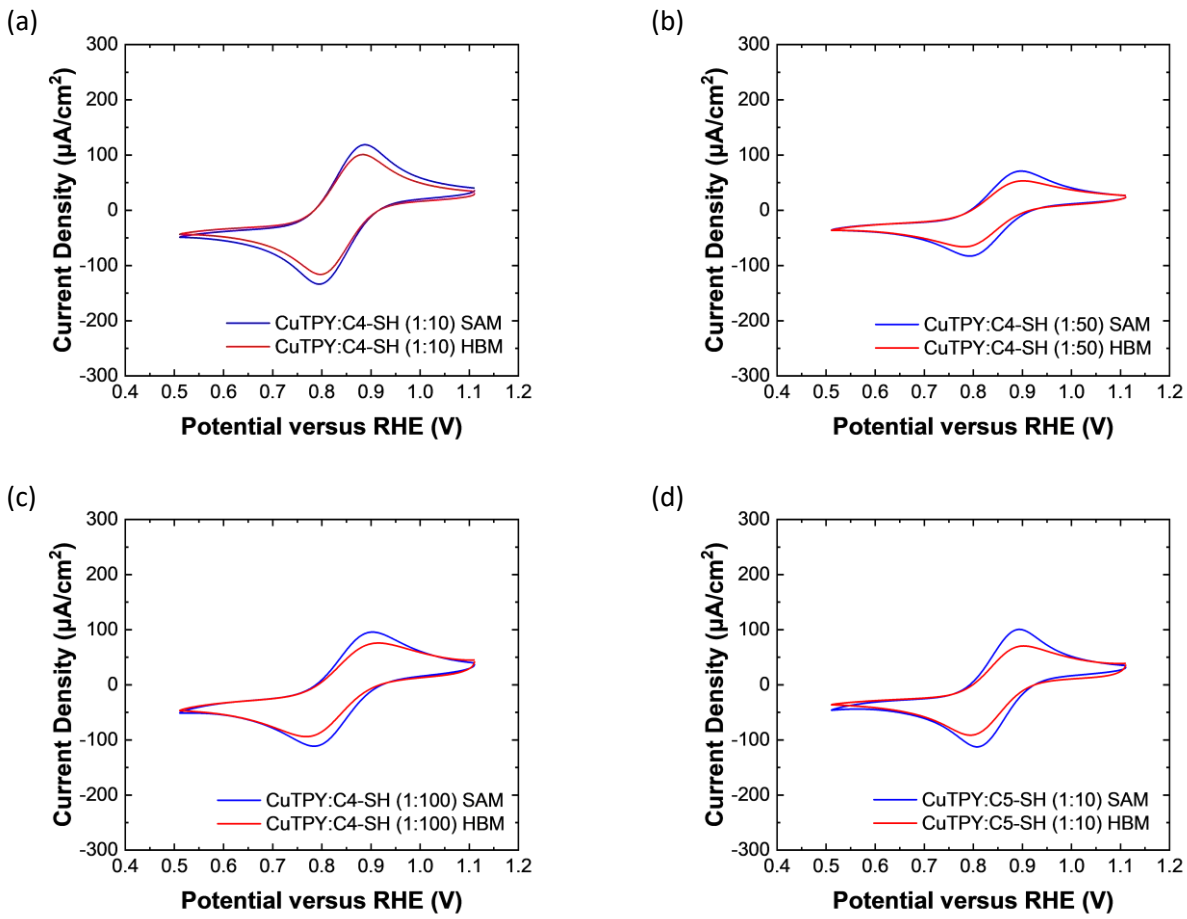


Figure S5. Effect of ligand dilution ratios on structural integrity of Cu-TPY HBM. Cyclic voltammograms of a SAM of Cu-TPY diluted with 1-butanethiol (C4-SH) in a (a) 1:10, (b) 1:50 or (c) 1:100 ratio (blue) or diluted with 1-pentanethiol (C5-SH) in a (d) 1:10 ratio (blue) covered by a monolayer of DMPC lipids (red) in a solution of 1 mM $K_3Fe(CN)_6$ in 100 mM KCl at a scan rate of 50 mV/s.

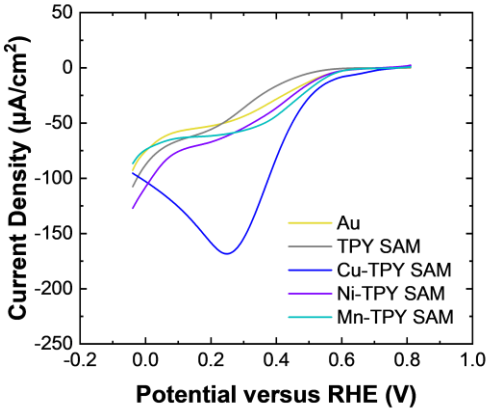


Figure S6. Comparison of oxygen reduction activity on different electrode surfaces. Linear sweep voltammograms of a bare Au electrode (yellow), a SAM of TPY ligands (grey), Cu-TPY SAM (blue), Ni-TPY SAM (purple), and Mn-TPY SAM (cyan) on Au electrode in an O_2-saturated 100 mM pH 7 sodium phosphate buffer solution at a scan rate of 10 mV/s. The changes in ORR current densities measured at 0.400 V versus RHE.

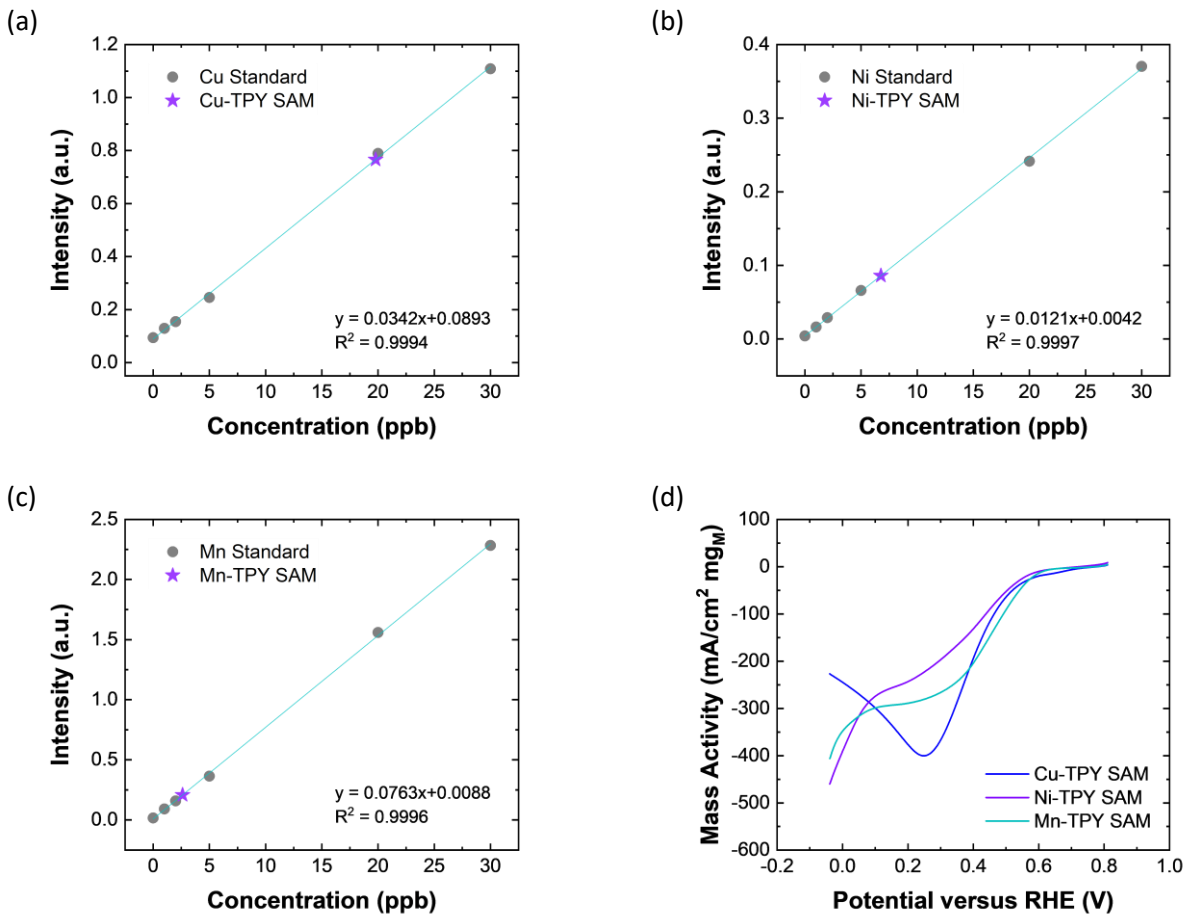


Figure S7. Metal content characterization of M-TPY SAM (M = Cu, Ni, Mn) by (a-c) ICP-MS analysis, and (d) their mass activity of ORR in a pH 7 100 mM sodium phosphate buffer at a scan rate of 10 mV/s.

Table S1. Metal quantification results of M-TPY SAM (M = Cu, Ni, Mn).

Sample	Relative to I_{std} (M:Rh)	Metal Content[(a)] (nmol/cm^2)	Metal Content[(b)] (mol/cm^3)
Cu-TPY SAM	0.77	6.62	0.033
Ni-TPY SAM	0.09	4.70	0.024
Mn-TPY SAM	0.21	3.88	0.019

[(a)] represents the metal content that was measured on the Au electrode, with each having a surface area of 1 x 1 cm^2. [(b)] represents the metal content that was measured within the overall volume of M-TPY SAM, considering its 2-nm thickness. [2]The total volume amounts to 1 x 1 x 2 x 10^{-7} cm^3.

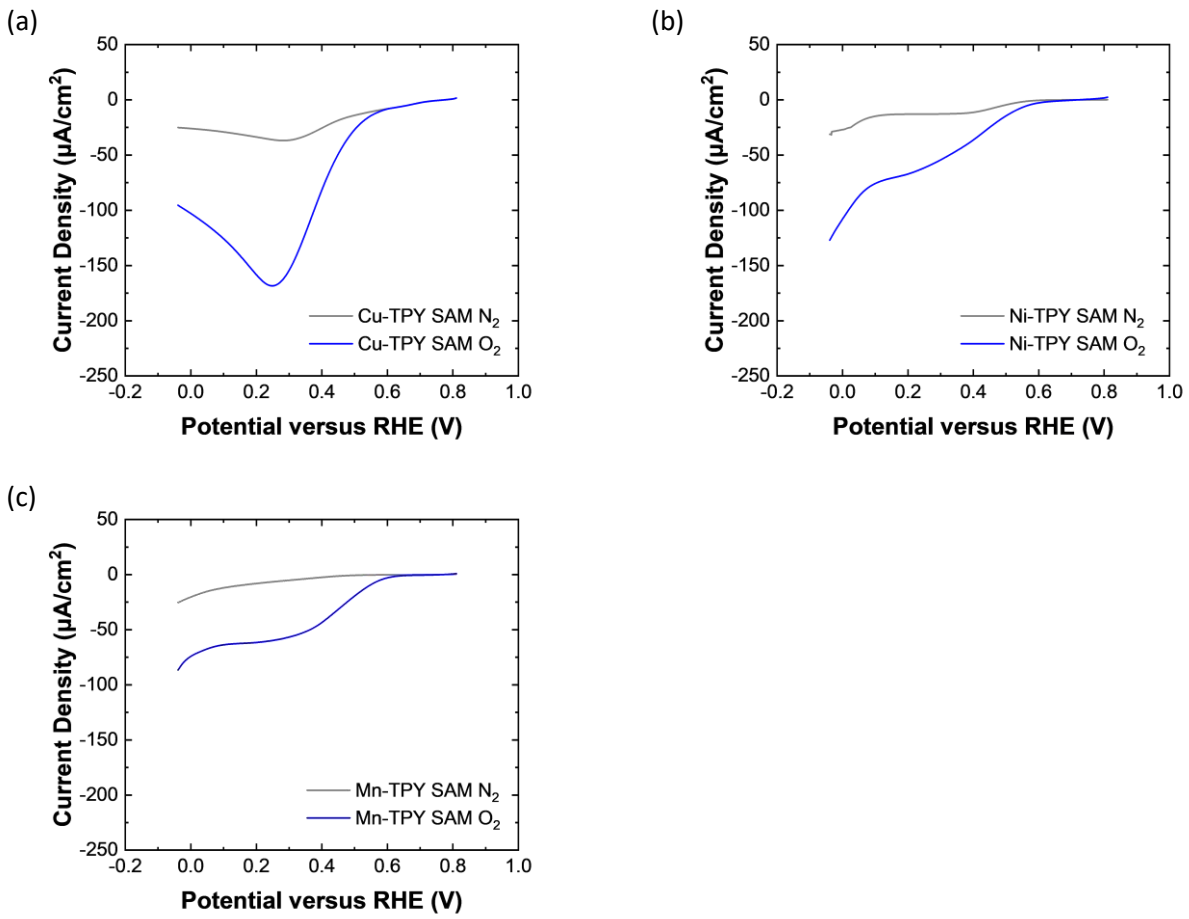


Figure S8. Oxygen reduction activity of M-TPY SAM (M= Cu, Ni, Mn) in absence and presence of O_2. Linear sweep voltammograms of a SAM of M-TPY on Au electrode in a N_2-saturated (grey) or a O_2-saturated (blue) 100 mM pH 7 sodium phosphate buffer solution at a scan rate of 10 mV/s.

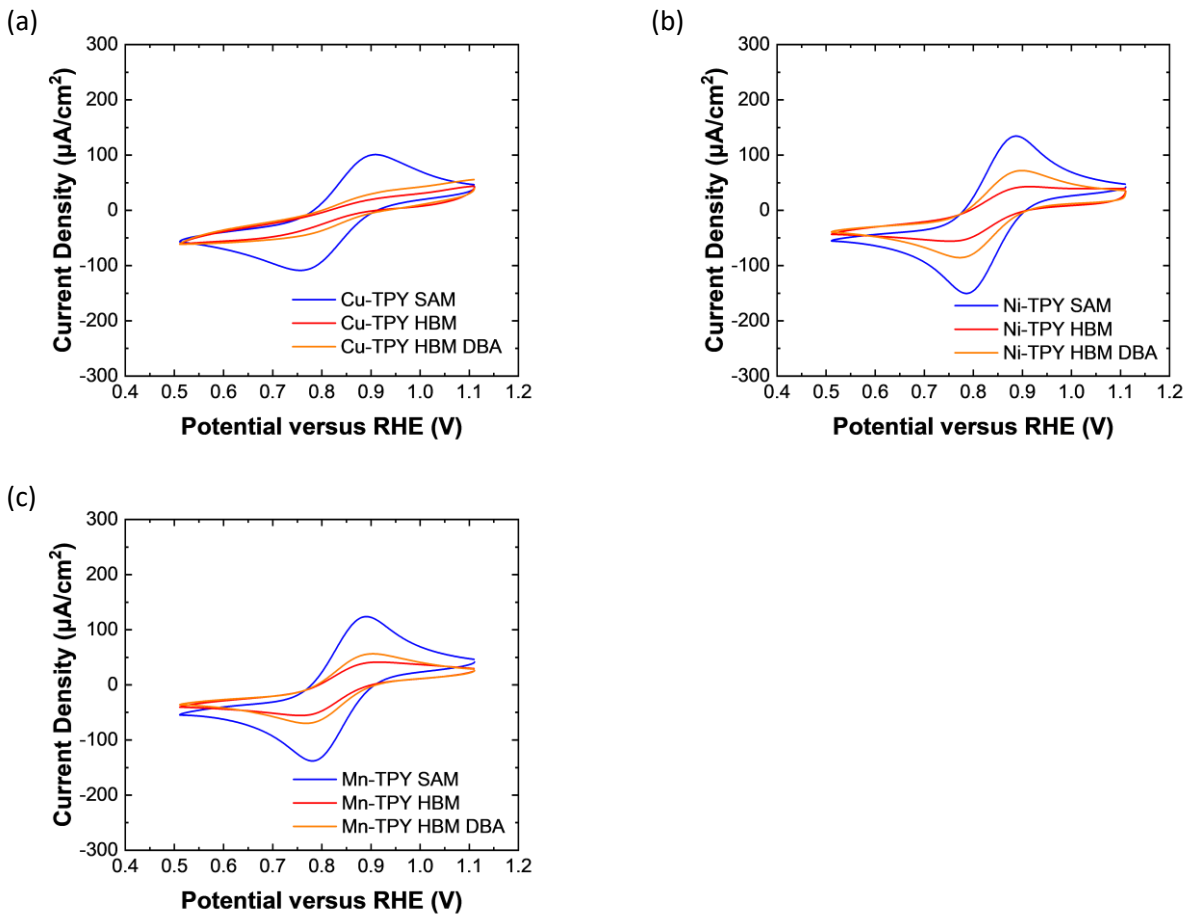


Figure S9. Structural integrity of lipid monolayer in M-TPY HBM (M = Cu, Ni, Mn). Cyclic voltammograms of a SAM of M-TPY (blue) covered by a monolayer of DMPC lipids (red) incorporated with 1 molar equivalent of DBA (orange) in a solution of 1 mM $K_3Fe(CN)_6$ in 100 mM KCl at a scan rate of 50 mV/s.

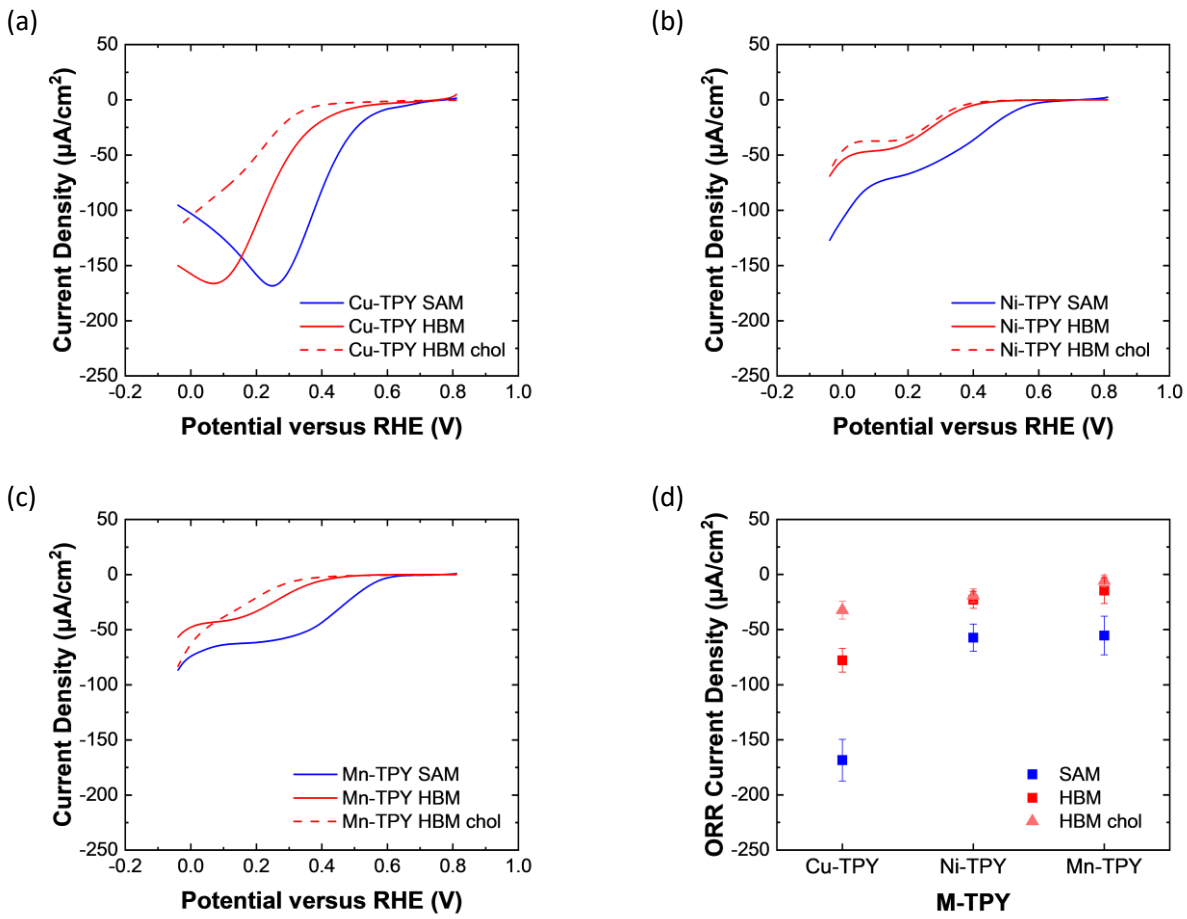


Figure S10. Oxygen reduction activity of M-TPY HBM (M = Cu, Ni, Mn) with or without cholesterol incorporation. Linear sweep voltammograms of a SAM of M-TPY (blue) covered by a monolayer of DMPC lipids (red) or a monolayer of DMPC lipids incorporated with 20% w/w cholesterol (red, dotted) in a O_2-saturated 100 mM pH 7 sodium phosphate buffer solution at a scan rate of 10 mV/s.

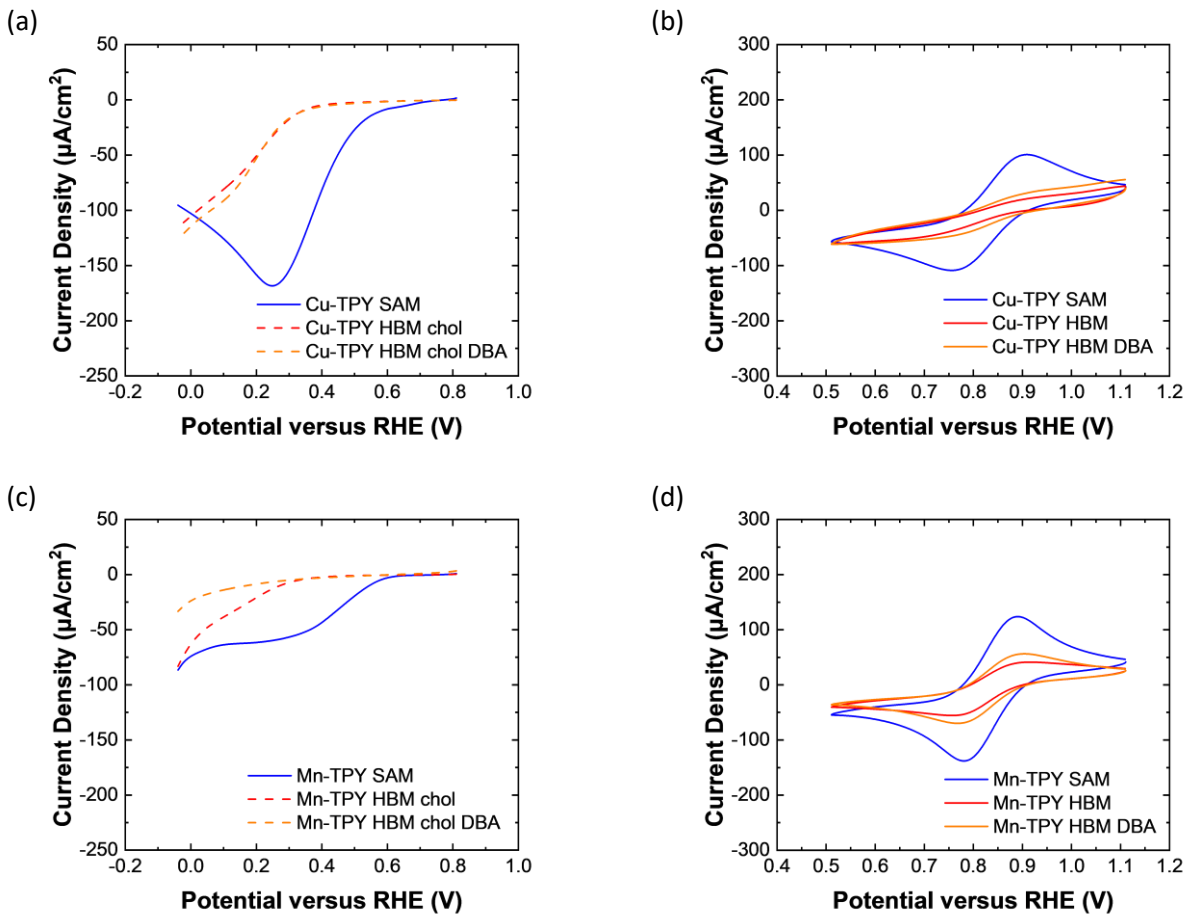


Figure S11. Oxygen reduction activity of M-TPY HBM (M = Cu, Ni, Mn) incorporated with cholesterol and DBA. Linear sweep voltammograms of a SAM of M-TPY (blue) covered by a monolayer of DMPC lipids incorporated with 20% w/w cholesterol (red, dotted) and 1 molar equivalent of DBA (orange, dotted) in a O_2-saturated 100 mM pH 7 sodium phosphate buffer solution at a scan rate of 10 mV/s.

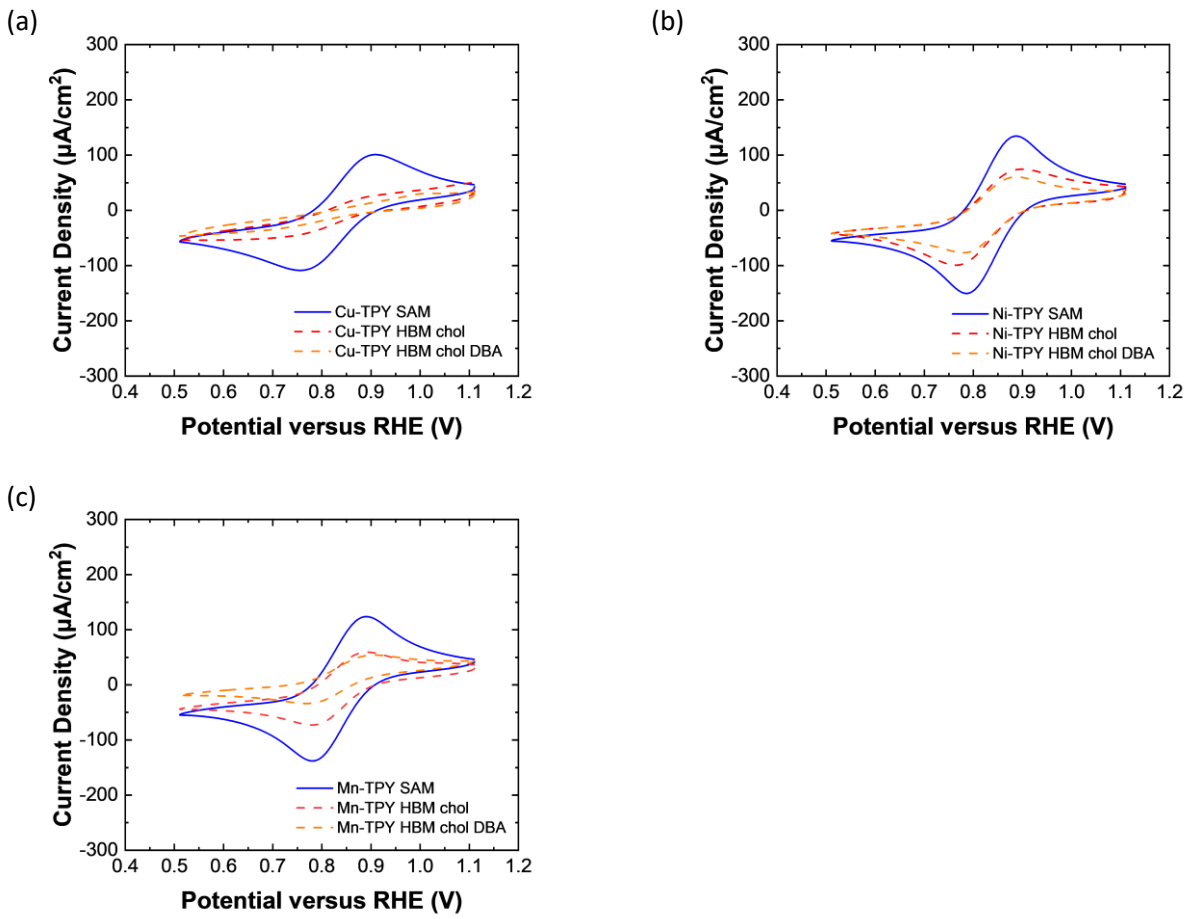


Figure S12. Structural integrity of lipid monolayer in M-TPY HBM (M = Cu, Ni, Mn) incorporated with cholesterol and DBA. Cyclic voltammograms of a SAM of M-TPY (blue) covered by a monolayer of DMPC lipids incorporated with 20% w/w cholesterol (red, dotted) and 1 molar equivalent of DBA (orange, dotted) in a solution of 1 mM $K_3Fe(CN)_6$ in 100 mM KCl at a scan rate of 50 mV/s.

References

1. E. C. M. Tse, C. J. Barile, N. A. Kirchschlager, Y. Li, J. P. Gewargis, S. C. Zimmerman, A. Hosseini and A. A. Gewirth, Proton Transfer Dynamics Control the Mechanism of O_2 Reduction by a Non-precious Metal Electrocatalyst, *Nature Materials*, 2016, **15**, 754-759.
2. T. Zeng, H.-L. Wu, Y. Li, E. C. M. Tse and C. J. Barile, Physical and Electrochemical Characterization of a Cu-based Oxygen Reduction Electrocatalyst inside and outside a Lipid Membrane with Controlled Proton Transfer Kinetics, *Electrochimica Acta*, 2019, **320**, 134611.