Supporting Information for

A three-dimensional porphyrin-based porous organic polymer with excellent biomimetic catalytic performance

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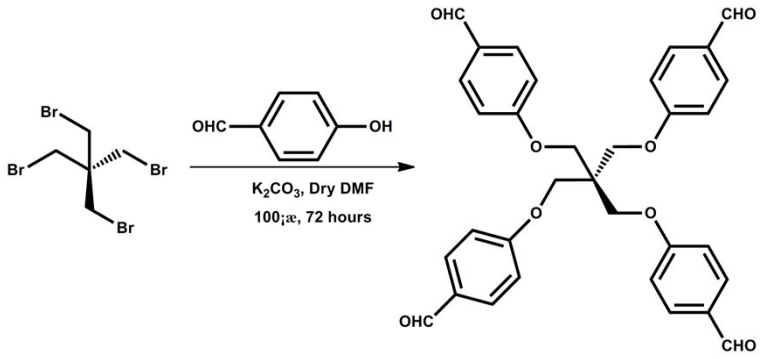
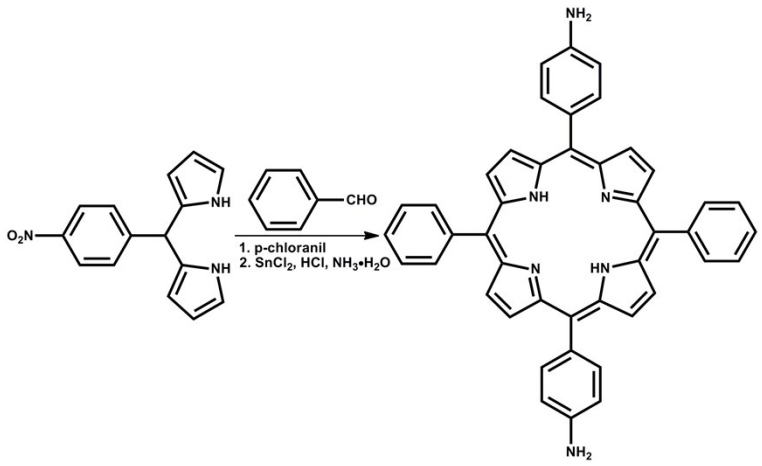
Synthesis

Synthesis of 4-{2,2-bis[(4-formylphenoxy)methyl]-3-(4-formylphenoxy)propoxy}benzaldehyde (BFPB)



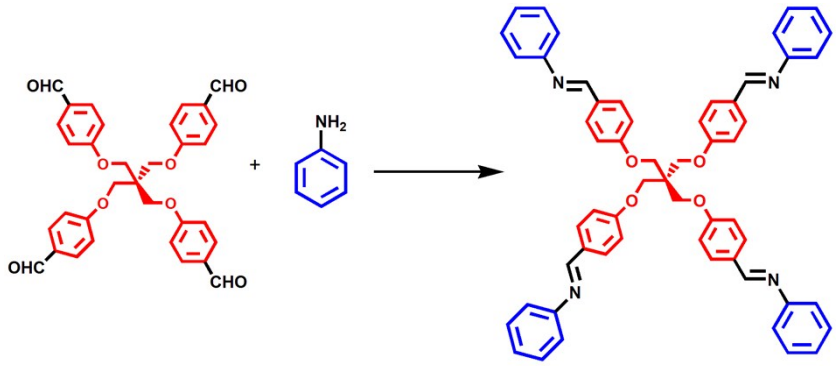
This compound was prepared by the method described in previous literature with slight modifications as follows [1]. To a 100 mL round bottom flask equipped with a stir bar and condenser was added the 4-Hydroxybenzaidehyde (1.259 g, 10.3 mmol) in 15 mL of dry DMF was treated with potassium carbonate (4.275 g, 30.9 mmol) at 70 °C for 1 h under a nitrogen atmosphere. Then a solution of pentaerythritol tetrabromide (1 g, 2.58 mmol) in 5 mL dry DMF was slowly added and the reaction mixture was heated under vigorous stirring at 100 °C for 72 h. After being allowed to cool to room temperature, most of the solvent was removed under reduced pressure. Ice cold water was added and it was extracted with CH_2Cl_2, the organic part was repeatedly washed with ice cold water and it was then dried over anhydrous $MgSO_4$, solvent was removed to afford BFPP 1.4 g, yield 95%. FT-IR (KBr cm^{-1}): 742, 1024, 1162, 1202, 1452, 1481, 1722, and 2863. ^1H NMR ($CDCl_3$): δ 4.43 (s, 8H), 6.98 (d, 8H, J = 8.6 Hz), 7.75 (d, 8H, J = 8.6 Hz), 9.79 (s, 4H).^{13}C NMR ($CDCl_3$): δ 31.2, 66.4, 114.8, 130.5, 131.9, 163.2, 190.6.

Synthesis of 5,15-di(4-aminophenyl)-10,20-diphenylporphyrin (DAPP)



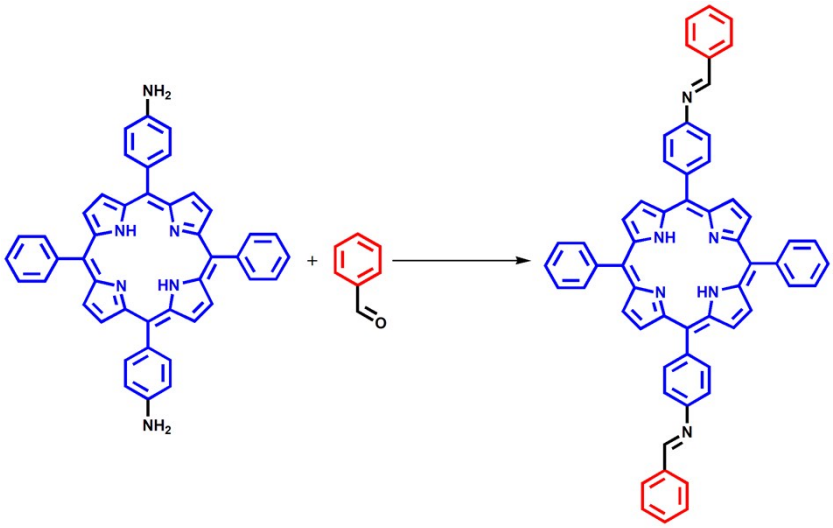
This compound was prepared by the method described in previous literature with slight modifications as follows [2]. To a 100 mL round bottom flask equipped with a stir bar and condenser was added the 5-(4-Nitrophenyl)dipyrromethane (0.5 g, 1.87 mmol) and benzaldehyde (0.212 g, 2 mmol) under a nitrogen atmosphere. The solids were dissolved in 50 mL propanoic acid. The reaction was heated at 120 °C for 3h. The reaction mixture was then cooled and propanoic acid was removed by reduced pressure distillation. The residue was dissolved with 50 mL $CHCl_3$. This purple solution was washed with saturated aqueous solution of potassium chloride, and dried with anhydrous magnesium sulfate. After filtration, the solvent was removed on a rotary evaporator to yield the red residue. The residue was first passed through flash column chromatography on silica gel (eluent: CH_2Cl_2) and reprecipitation with chloroform–methanol afforded a vivid reddish purple solid. $SnCl_2$ (1.5 g, 7.9 mmol) was added to a suspension of the above crude product (142 mg) in concentrated HCl solution (35 mL). This mixture was heated to 65 °C for 1.5 h with stirring. After cooling, the mixture was adjusted to pH 8-9 with concentrated ammonium hydroxide. The aqueous phase was extracted with CH_2Cl_2, and the obtained phase was washed with water and dried over Na_2SO_4. After filtration, the solvent was removed on a rotary evaporator, and the residue was passed through column chromatography on silica gel (eluent: CH_2Cl_2:CH_3OH = 100:1) to afford DAPP. This deep violet powder was dried in a vacuum drying oven at 60 °C for 12 h, 40 mg, yield 6%. ^1H NMR ($CDCl_3$): δ 8.95 (d, 4H), 8.82 (d, 4H), 8.23-8.25(m, 4H), 8.01-8.03(d, 4H), 7.79(d, 4H), 7.10(d, 4H), 4.06(s, 4H), 2.72(s, 2H).

Synthesis of model compound



MC-1

BFPB (0.3 g, 0.54 mmol) and aniline (0.3 mL, 3.26 mmol) were added to ethanol (15 mL) and chloroform (15 mL), and the mixture was refluxed for one night.[3] The solvent was removed under reduced pressure and a crystalline product was collected. The product was dissolved in chloroform and the resulting yellow solution was filtered. X-ray quality crystals of product were grown on the test tubes after 5 days through slow volatilization at room temperature, yield 52%. FT-IR (KBr cm^{-1}): 761, 1162, 1243, 1305, 1510, 1604 and 1626.

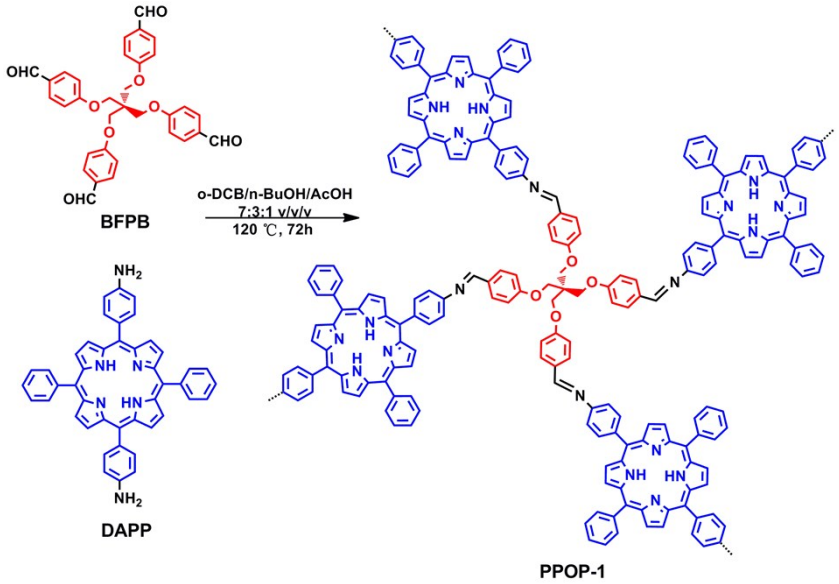


MC-2

MC-2 was synthesized according to our previous work.[4] DAPP (129 mg, 0.2 mmol) and p-Hydroxybenzaldehyde (48.9 mg, 0.4 mmol) were added to MeOH (10 mL) followed by the dropwise addition of trifluoroacetic acid (0.95 uL, 0.012 mmol) under a nitrogen atmosphere. The mixture was

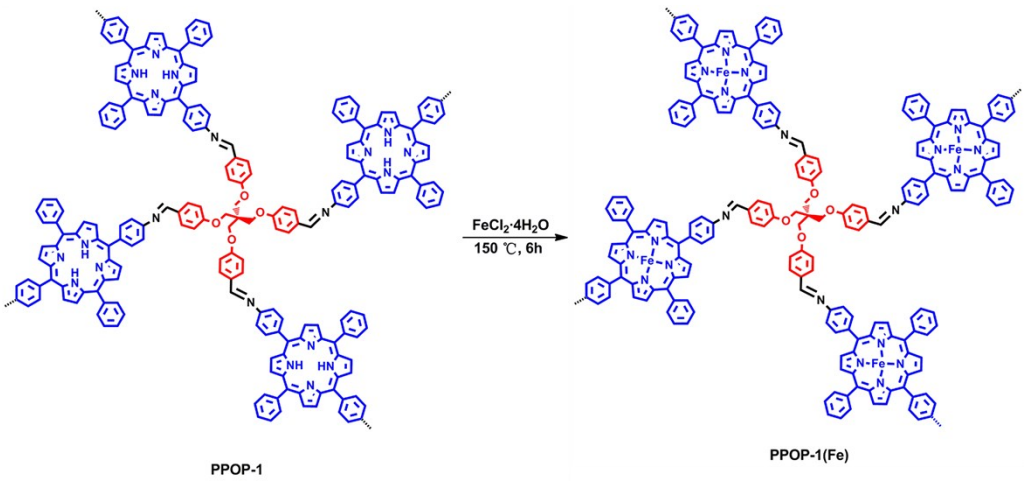
refluxed for one night and a crystalline product was collected by filtering and washed with hot MeOH (3 × 5 mL), yield 65%. FT-IR (KBr cm^{-1}): 690, 795, 964, 1169, 1473 and 1625.

Synthesis of PPOP-1



A Pyrex glass tube was charged with BFPB (2.76 mg, 0.005 mmol), DAPP (6.45 mg, 0.01 mmol), 0.7 mL o-dichlorobenzene, 0.3 mL n-butanol and 0.1 mL of 6 M aqueous acetic acid. This mixture was sonicated for 10 minutes in order to get a homogenous dispersion. After being degassed by freeze-pump-thaw technique for three time and then the tube was sealed under the frame. The tube was placed in an oven at 120 °C for 72 h to afford a purple red precipitate by fitration. The resulting precipitate was filtered, washed with anhydrous tetrahydrofuran and extracted by Soxhlet extractor for 24 h. The solid was dried at 80 °C under vacuum for 12 h to yield PPOP-1, yield 62%. FT-IR (KBr cm^{-1}): 692, 815, 1043, 1193, 1508 and 1618. ^{13}C NMR ($CDCl_3$): δ 33.2, 73.1, 120.1, 129.6, 151.8, 163.1.

Synthesis of PPOP-1(Fe)



In a typical synthesis of PPOP-1(Fe), pre-synthesized PPOP-1 (30 mg) and $FeCl_2 \cdot 4H_2O$ (100 mg) were dispersed in 15 mL of DMF. The mixture was refluxed for 6 h under a nitrogen atmosphere. After cooling down to room temperature, powder was obtained by centrifuging. The resulting precipitate was washed with DMF and anhydrous THF and dried at 80 °C under vacuum for 12 h to yield PPOP-1(Fe), yield 71%.

Characterization

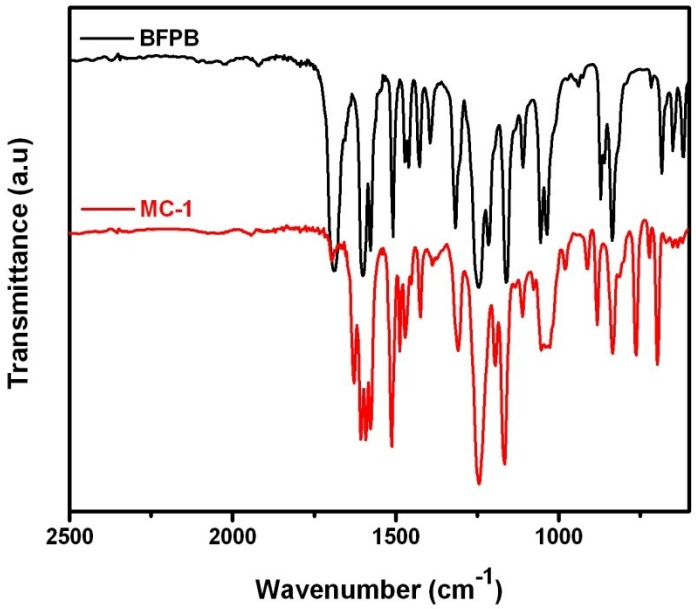


Fig. S1 FT-IR spectra of BFPB and MC-1.

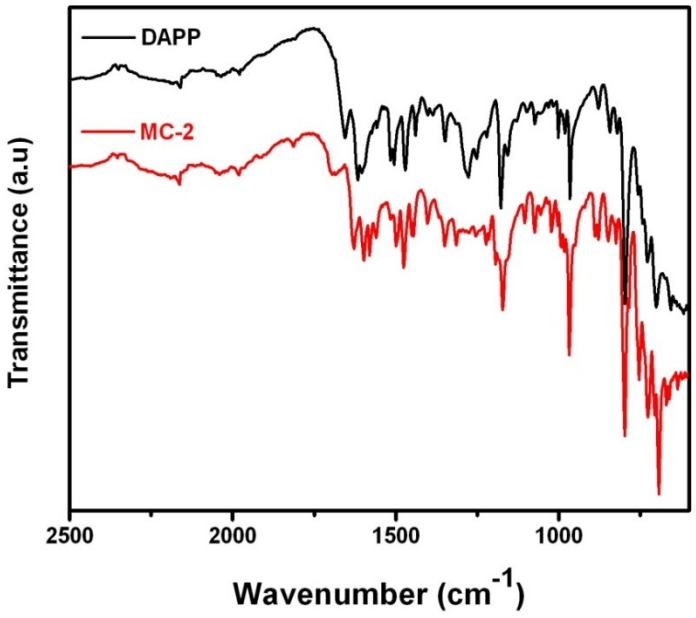


Fig. S2 FT-IR spectra of DAPP and MC-2.

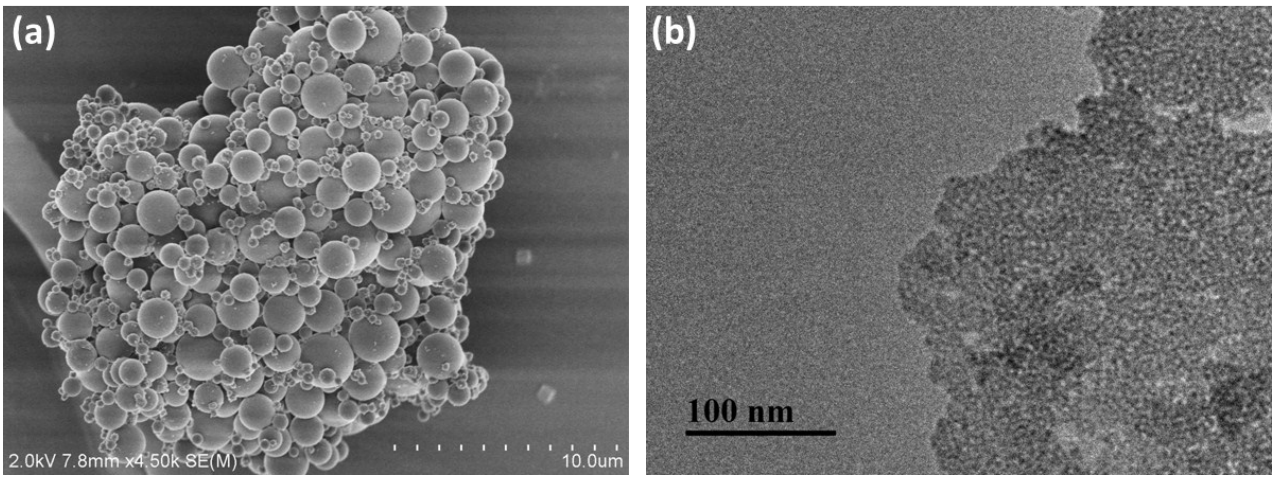


Fig. S3 (a) SEM image of PPOP-1. (b) TEM image of PPOP-1.

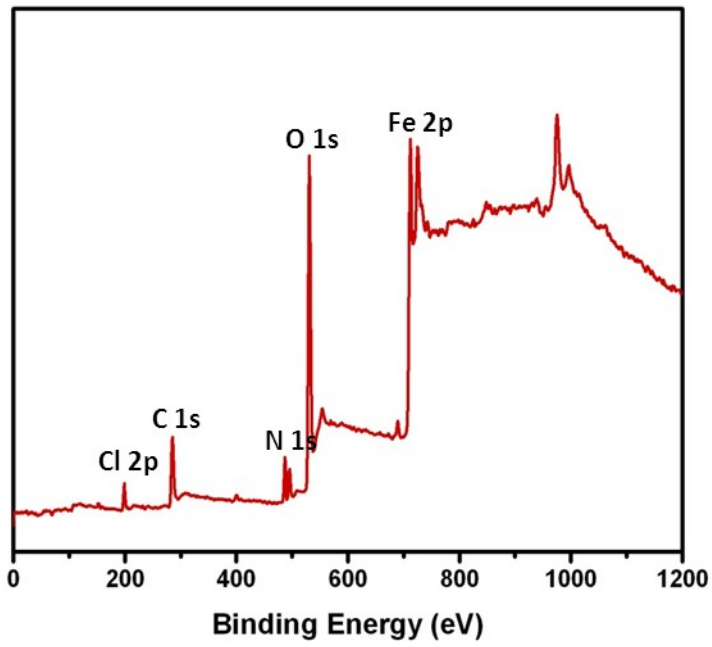
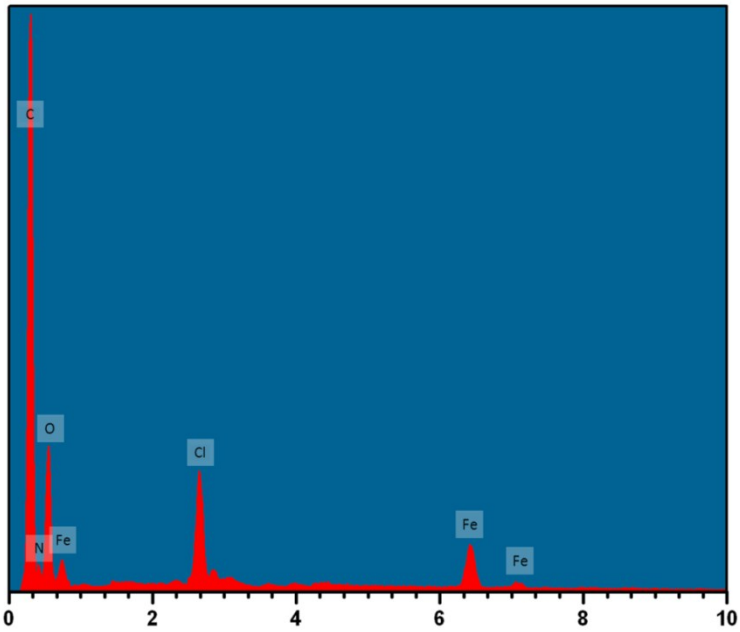


Fig. S4 XPS survey scan of PPOP-1(Fe).



Lsec: 158.60 Cnts 0.000keV Det: Apollo x-SDD Det

Element	Weight %	Atomic %
C K	31.08	55.38
N K	22.21	20.40
O K	19.28	16.19
Cl K	3.08	1.72
Fe K	24.35	6.31
Totals	100.00	

Fig. S5 Energy dispersive X-ray Spectroscopy (EDX) spectrum of PPOP-1(Fe).

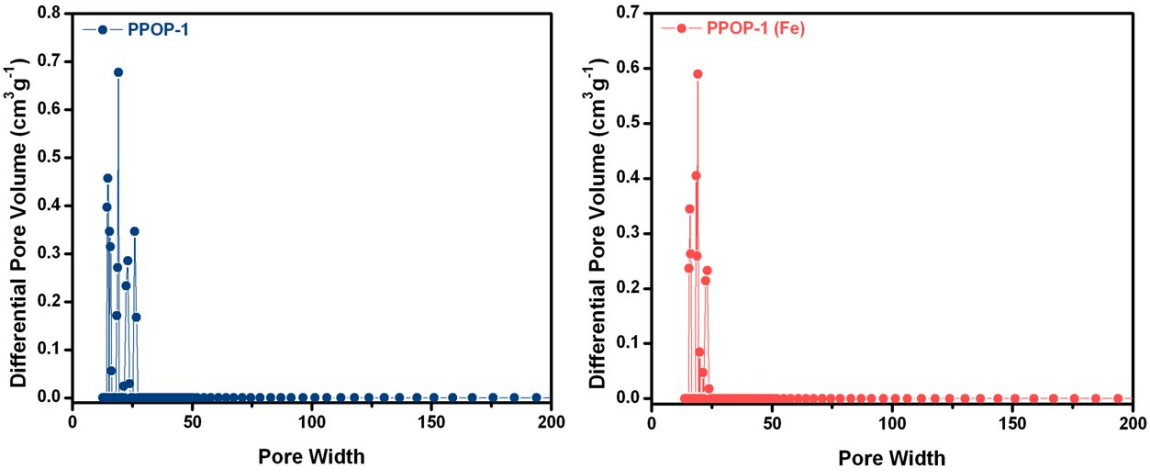


Fig. S6 Pore size distribution for PPOP-1 and PPOP-1(Fe) calculated based on collected N_2 isotherms.

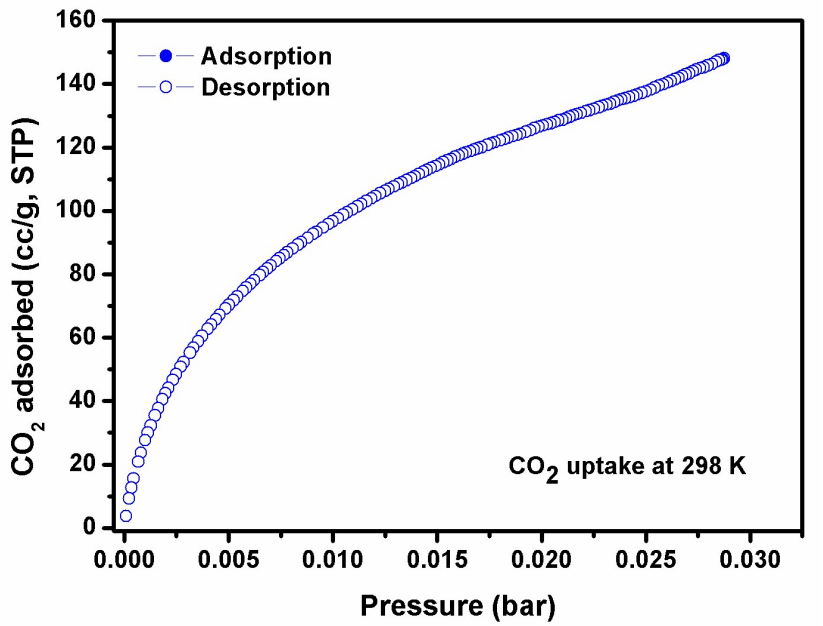


Fig. S7 Volumetric CO_2 uptake isotherms of PPOP-1(Fe) at 298 K.

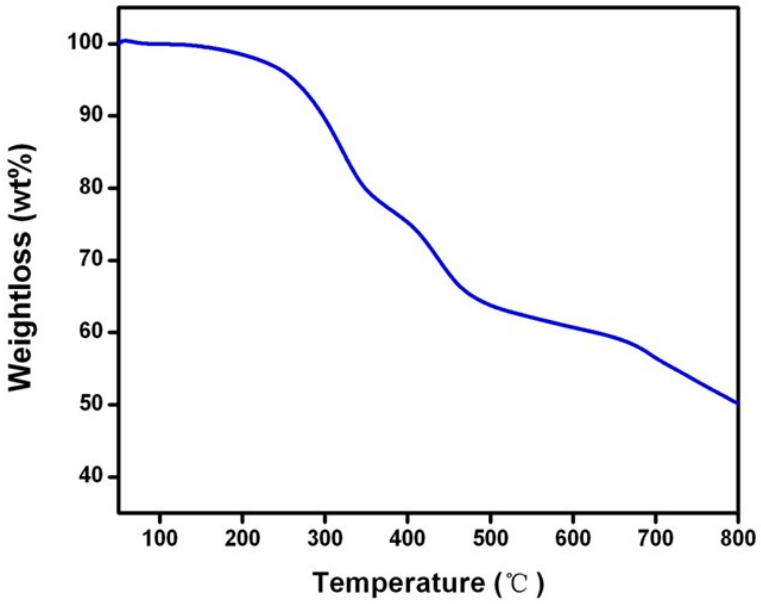


Fig. S8 TGA data of PPOP-1(Fe).

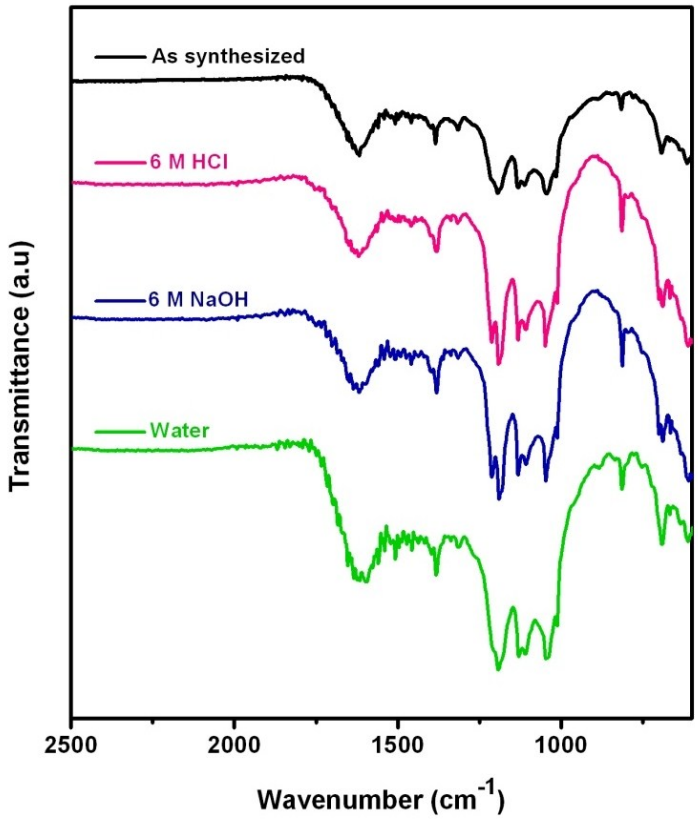


Fig. S9 FT-IR spectra of PPOP-1(Fe) after treatment for 3 days in HCl (6 M) solutions, NaOH (6 M) solutions, and boiling water.

X-ray Crystallography

The crystal structures were determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) at 173 K. Cell parameters were retrieved using SMART software and refined using SAINT[5] on all observed reflections. The highly redundant data sets were reduced using SAINT[5] and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS[6] supplied by Bruker. Structures were solved by direct methods using the program SHELXL-97.[7] All of the non-hydrogen atoms were refined with anisotropic thermal displacement coefficients. Hydrogen atoms of organic ligands were located geometrically and refined in a riding model. For MC-1, two phenylamine groups are disordered. Disorder was modelled using standard crystallographic methods including constraints, restraints and rigid bodies where necessary. Despite rapid handling and long exposure times, the data collected are

less than ideal quality. Nevertheless, the data for MC-1 is of more than sufficient quality to unambiguously establish the connectivity of the structures. The data resolution of crystal is low in spite of the explosure time increased to 200 s per degree. Final crystallographic data and values of R_1 and *wR* for MC-1 are listed in Table S1.

Table S1 Summary of crystallographic data for MC-1.

	MC-1
formula	$C_{456}H_{384}N_{32}O_{32}$
fw	6824.24
T (K)	173(2)
λ (Å)	0.71073
crystal system	Triclinic
space group	*P-1 (2)*
a (Å)	21.1700(16)
b (Å)	22.5739(14)
c (Å)	24.0674(16)
α (^{0})	62.949
β (^{0})	71.882
γ (^{0})	67.422
V (Å^3)	9327.29(112)
D_{calc} (Mg/m^3)	1.215
μ (mm^{-1})	0.077
F(000)	3600
θ (^{0})	2.88-22.00
index ranges	-22<=h<=21 -23<=k<=23 -25<=l<=25
reflections collected	48685
GOF (F^2)	1.077
R_1[a],wR_2[b](I>2σ(I))	0.0809, 0.1805
R_1[a],wR_2[b](all data)	0.1963, 0.2394

$R_1{}^a = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2{}^b = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)]^{1/2}$

Catalytic Activity Test

The mixture of the substrates with specific concentrations and H_2O_2 in 3 mL of buffer solution was catalyzed by PPOP-1(Fe). The products were confirmed by scanning the UV-vis absorbance on spectrophotometer and the concentrations of products were calculated by their molar extinction coefficients at respective wavelengths (for $ABTS^{\bullet+}$, the peroxidized product of ABTS, is 12000 M^{-1} cm^{-1} at 660 nm; for purpurogallin, the peroxidized product of THB, is 2640 M^{-1} cm^{-1} at 420 nm; for phenazine-2,3-diamine, the peroxidized product of OPD, is 16300 M^{-1} cm^{-1} at 450 nm). For comparison, experiments were also carried out for the heme protein myoglobin (Mb) in the homogeneous system under similar conditions (5 uM free Mb were used).

For the oxidation of 2,2'-azinodi(3-ethylbenzothiazoline)-6-sulfonate (ABTS) to $ABTS^{\bullet+}$ (660 nm) involving electron transfer, a series of concentrations of substrate varied from 2 mM to 10 mM along with a fixed amount of PPOP-1(Fe) catalyst (*ca.* 40 ug) and hydrogen peroxide concentration (40 mM) in 3 mL of 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer. Kinetic measurements were carried out in time-course mode by monitoring the absorbance change at 660 nm for $ABTS^{\bullet+}$ on a Jasco V550 UV−vis spectrophotometer with 500 rpm at 25 °C. The Michaelis−Menten constant was calculated using the Michaelis−Menten curve fit. Meanwhile, we recorded the color change for the whole process, which changed from colorless to dark green in just 2 minutes (Fig. S10).

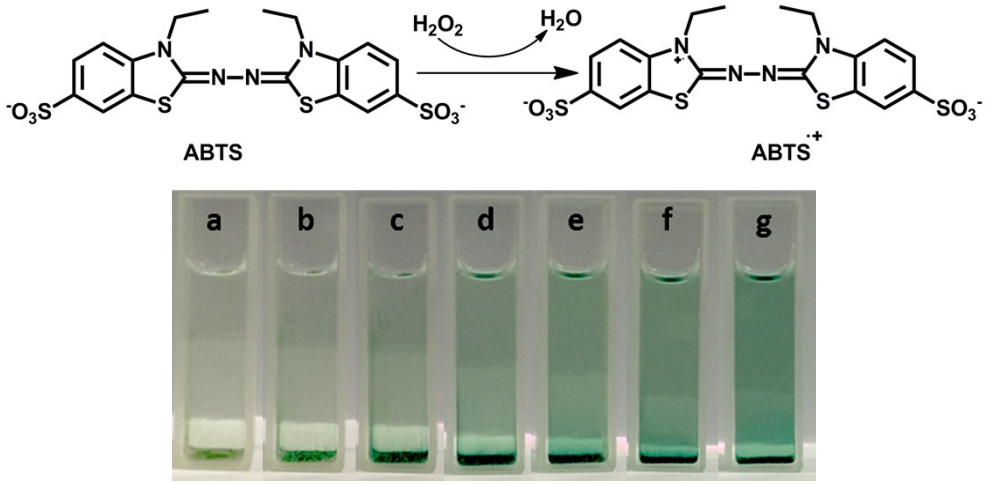


Fig. S10 The colour changes of solution after (a) 10 s, (b) 20 s, (c) 30 s, (d) 50 s, (e) 70 s, (f) 90 s, and (g) 120s.

For the oxidation of pyrogallol (THB) to purpurogallin (420 nm), a series of concentrations of substrate varied from 2 mM to 10 mM along with a fixed amount of PPOP-1(Fe) catalyst (*ca.* 40 ug) and hydrogen peroxide concentration (40 mM) in 3 mL of phosphate buffer. Kinetic measurements were carried out in time-course mode by monitoring the absorbance change at 420 nm for purpurogallin on a Jasco V550 UV−vis spectrophotometer with 500 rpm at 25 °C. The Michaelis−Menten constant was calculated using the Michaelis−Menten curve fit. Meanwhile, we recorded the color change for the whole process, which changed from colorless to yellow in just 5 minutes (Fig. S11).

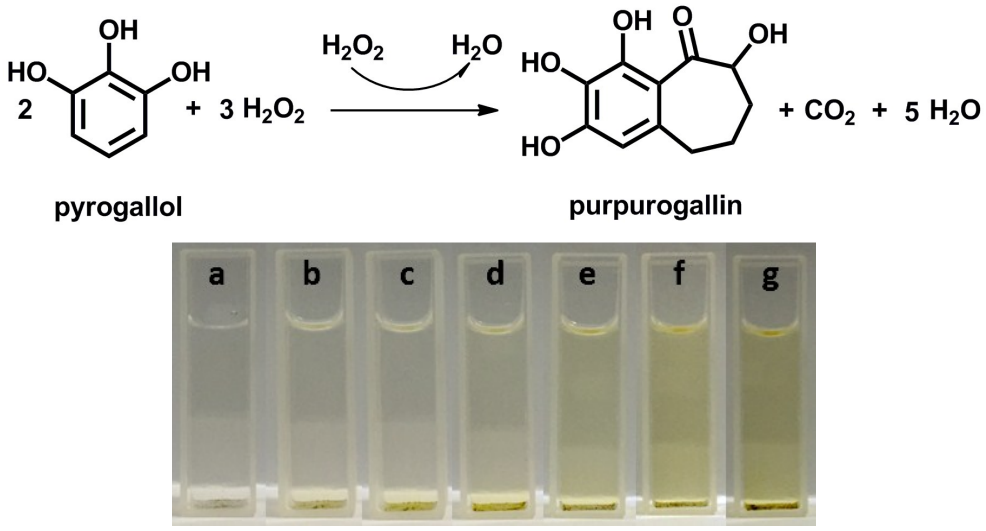


Fig. S11 The colour changes of solution after (a) 10 s, (b) 30 s, (c) 60 s, (d) 90 s, (e) 150 s, (f) 200 s, and (g) 300 s.

For the oxidation of o-phenyldiamine (OPD) to 2-amino-3*H*-phenoxazin-3-one (450 nm), a series of concentrations of substrate varied from 2 mM to 7.5 mM along with a fixed amount of PPOP-1(Fe) catalyst (*ca.* 40 ug) and hydrogen peroxide concentration (40 mM) in 3 mL of phosphate buffer. Kinetic measurements were carried out in time-course mode by monitoring the absorbance change at 450 nm for 2-amino-3*H*-phenoxazin-3-one on a Jasco V550 UV−vis spectrophotometer with 500 rpm at 25 °C. The Michaelis−Menten constant was calculated using the Michaelis−Menten curve fit.

Meanwhile, we recorded the color change for the whole process, which changed from colorless to orange in just 5 minutes (Fig. S12).

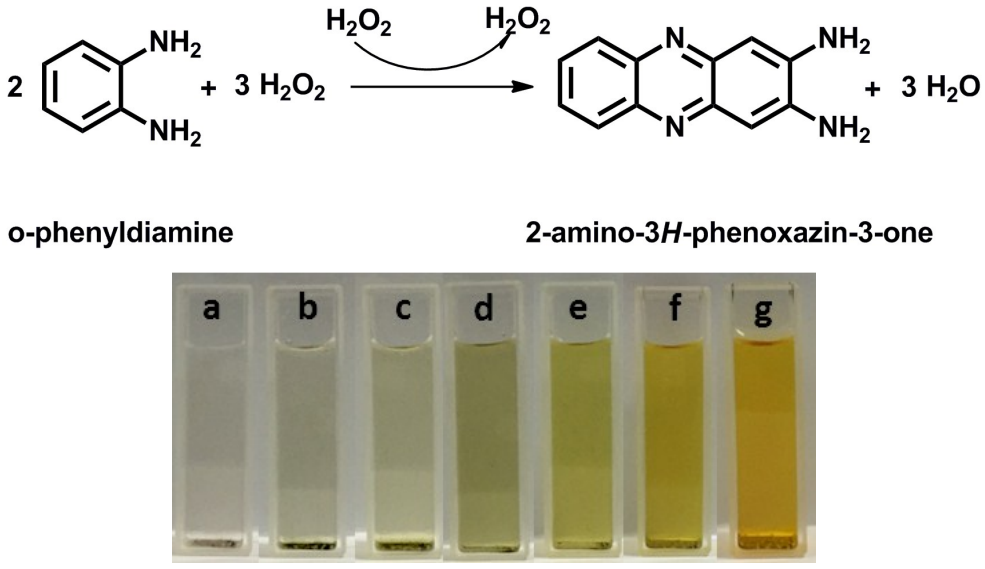


Fig. S12 The colour changes of solution after (a) 10 s, (b) 30 s, (c) 60 s, (d) 90 s, (e) 150 s, (f) 200 s, and (g) 300 s.

Reference

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