Supporting Information

The Detailed Preparation of the Dinucleating Ligand TPPAP. The preparation of TPPAP is summarized in Scheme S1-S3. All regents and dry solvents were purchased and used without further purification.

Preparation of 2-Methyl-6-pivalamidopyridine (MPP). To a stirred solution of 2-amino-6-methylpicoline (AMP, 60.0 g, 550 mmol) and triethylamine (56.1 g, 555 mmol) in CH_2Cl_2 (300 mL) was added a solution (100 mL) of pivaloyl chloride (60.9 g, 555 mmol) in CH_2Cl_2. After stirring until initiation of the exothermic reaction, white precipitate was removed. The CH_2Cl_2 solution was washed with H_2O (x 3), 1 N HCl, 0.5 N $NaHCO_3$, and brine. After drying with anhydrous $MgSO_4$, the solution was evaporated. The resultant solid was recrystallized from Et_2O. Yield 88.2 g (84 %).

Preparation of 2-Bromomethyl-6-pivalamidopyridine (BPP). *N*-bromosuccinimide (NBS, 9.49 g, 53 mmol) and 2,2'-azobis(isobutyronitrile) (AIBN, 0.25 g, 3 mmol) were added to a solution of MPP (30.0 g, 160 mmol) in CCl_4 (300 mL). The resultant mixture was refluxed at 80 °C. After 2 h, NBS (9.49 g, 53 mmol) and AIBN (0.25 g, 3.0 mmol) were added to the mixture. NBS (4.75g, 27 mmol) and AIBN (0.17g, 2.0 mmol) were then added to the mixture twice each hour. After refluxing for an additional hour, the resultant mixture was cooled to room temperature and filtered. The filtrate was washed with 0.5 N $NaHCO_3$ and brine. The solution was dried with anhydrous $MgSO_4$, evaporated and purified with column chromatography (silica gel; hexane/ethyl acetate (AcOEt) = 10/1). The product was obtained as a brown oil. Yield 20.34 g (47 %).

Preparation of 2-Phthalimidomethyl-6-pivalamidopyridine (PPP). To a stirred solution of BPP (20.34 g, 75 mmol) in DMF (50 mL) was added potassium phtalimide (13.89 g, 75 mmol) with stirring. The solution was refluxed for 2 h while the generation of PPP was monitored by TLC). After the addition of H_2O (50 mL), the resulting mixture was extracted with $CHCl_3$. All organic layers were combined, washed with brine and dried with anhydrous $MgSO_4$. After

removal of $MgSO_4$, the solution was evaporated completely. The resulting brown solid was recrystallized from $CHCl_3$, producing brown crystals. Yield 25.31 g (100 %).

Preparation of 2-Aminomethyl-6-pivalamidopyridine (APP). To a stirred solution of PPP (14.1 g, 42 mmol) in EtOH (200 mL) was added hydrazine hydrate (4.20 g, 84 mmol) with stirring. The resulting solution was refluxed for 2 h while the generation of APP was monitored by TLC and the ninhydrin reaction. The solution was filtered, and the filtrate was evaporated. After the addition of $CHCl_3$ (100 mL), the insoluble white solid (phthalhydrazide) was removed. The solution was evaporated completely, and the resulting white solid was recrystallized from $CHCl_3/Et_2O$. White crystal was obtained (6.49 g, yield 75%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.34 (s, 9H, *t*-Bu), 1.80 (s, 2H, NH_2), 3.88 (s, 2H, CH_2), 6.98 (d, 1H, py), 7.63 (t, 1H, py), 8.04 (br, 1H, NH), 8.10 (d, 1H, py).

Preparation of 2-Dibromomethyl-6-pivalamidopyridine (DBPP). NBS (5.36 g, 30 mmol) and AIBN (1.00 g, 6.0 mmol) were added to a solution of MPP (19.2 g, 100 mmol) in CCl_4 (250 mL). The mixture was refluxed at 80 °C. After 2 h, NBS (5.36 g, 30 mmol) and AIBN (1.00 g, 6.0 mmol) were added to the mixture. Additional quantities of NBS (5.35 g, 30 mmol) and AIBN (1.00g, 6.0 mmol) were added to the mixture six times during each hour. After refluxing for an additional 8 h, the solution was cooled to room temperature and filtered. The filtrate was evaporated completely. The resultant reddish brown solid was dissolved in MeOH (120 mL). After addition of a solution of KOH (240 mmol) in H_2O (50 mL), the mixture was stirred for 4 h. The solution was then evaporated and hexane (100mL) was added. The solution was then washed with 6 N HCl and then made alkaline with $NaHCO_3$. After removal of the aqueous layer, the organic layer was washed with brine and dried with anhydrous $MgSO_4$. The resulting solution was evaporated completely and white crystals were obtained (19.1 g, 54.5 %). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.35 (s, 9H, *t*-Bu), 6.51 (s, 1H, Br_2CH), 7.45 (d, 1H, py), 7.78 (t, 1H, py), 8.02 (br, 1H, NH), 8.22 (d, 1H, py).

Preparation of 2-Carbaldehyde-6-pivalamidopyridine (CAPP). To a solution of DBPP

(19.1 g, 55 mmol) in acetone (150 mL) was added a solution of $AgNO_3$ (27.8 g, 160 mmol) in H_2O (40 mL). The mixture was stirred for 12 h at room temperature under light shielding conditions. After filtration of insoluble matter, the filtrate was evaporated completely. The resulting yellow oil was dissolved in CH_2Cl_2 washed successively with H_2O, 0.5 N $NaHCO_3$, and brine. After drying with anhydrous $MgSO_4$, the organic layer was evaporated. Yellow oil was obtained (9.95 g, 89%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.37 (s, 9H, *t*-Bu), 7.69 (d, 1H, py), 7.91 (t, 1H, py), 8.17 (br, 1H, NH), 8.53 (d, 1H, py), 9.94 (s, 1H, CHO).

Preparation of Bis(6-pivalamide-2-pyridylmethyl)amine (BPA). A solution of CAPP (9.95 g, 48 mmol), APP (9.99 g, 48 mmol), and a catalytic amount of PtO_2 in MeOH (100 mL) was stirred under 3 atom of H_2 pressure while the generation of BPA was monitored by TLC and the ninhydrin reaction). After removal of PtO_2, the resulting yellow oil was evaporated and purified by column chromatography (silica gel; $CHCl_3$). The resulting orange oil was dissolved in acetone (50 mL). Colorless crystals were obtained by slow evaporation of acetone. Yield 7.66 g (41%). ^{1}H-NMR (300 MHz ,$CDCl_3$): δ 1.33 (s, 18H, *t*-Bu), 3.86 (s, 18H, CH_2), 7.04 (d, 2H, py), 7.66 (t, 2H, py), 8.00 (br, 2H, NH), 8.13 (d, 2H, py).

Preparation of 8-Acetoxymethyl-6-nitro-1,3-benzodioxene. A solution of paraformaldehyde (12.0 g, 400 mmol), *p*-nitrophenol (13.9 g, 10 mmol), and conc. H_2SO_4 (21.9 mL) in CH_3COOH (100 mL) was stirred for 35 h at 60 ºC. To the mixture was added H_2O (300 mL). After neutralization with K_2CO_3, the white precipitate was collected and washed with cold H_2O. After drying with silica gel, the resulting white solid was recrystallized from EtOH, producing white crystals. Yield: 14.3 g (56%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.17 (s, 3H, CH_3), 4.97 (s, 2H, CH_2), 5.17 (s, 2H, CH_2), 5.38 (s, 2H, CH_2), 7.90 (d, 1H, Ar), 8.15 (d, 1H, Ar).

Preparation of 2,6-Bis(bromomethyl)-4-nitrophenol. 8-Acetoxymethyl-6-nitro-1,3-benzodioxene (2.00 g, 7.9 mmol) was dissolved to 48 % HBr (60 mL) and refluxed for 6 h at 130 °C. The resultant white precipitate was collected and washed with cold water. After drying with silica gel, the precipitate was recrystallized from $CHCl_3$. The white crystal was obtained.

Yield 2.01 g, (78%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.57 (s, 4H, CH_2), 8.23 (s, 2H, Ar).

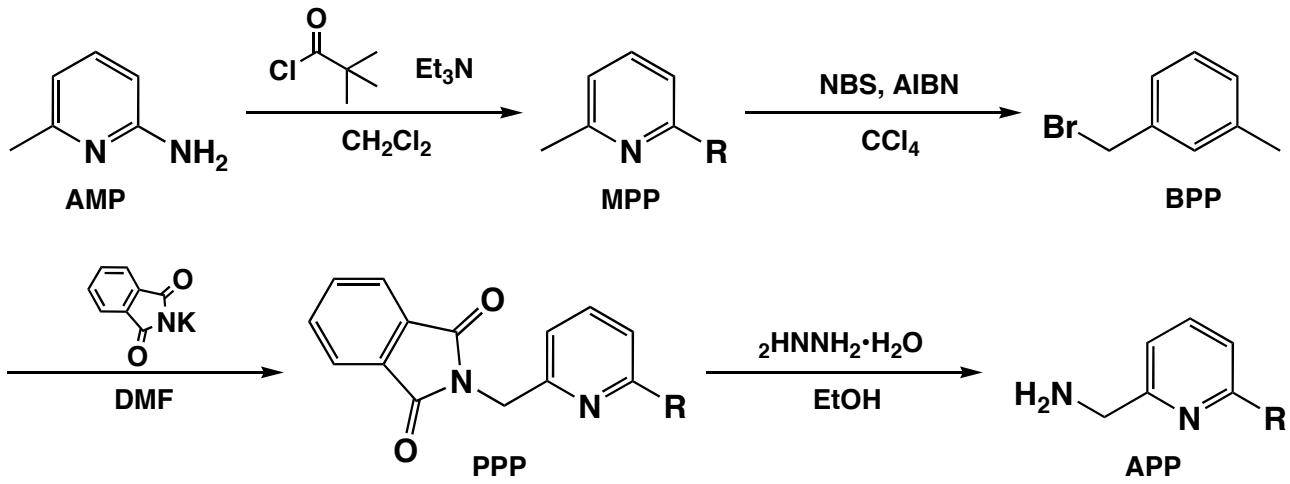
Preparation of 2,6-Bis[bis(6-pivalamide-2-pyridylmethyl)aminomethyl]-4-nitrophenol (TPPNP). To a solution of 2,6-bis(bromomethyl)-4-nitrophenol (1.67 g, 5.19 mmol) in THF (20 mL) in an ice bath was added a solution of BPA (4.45 g, 10.9 mmol) and Et_3N (1.10 g, 10.9 mmol) in THF (30 mL) dropwise under N_2. The mixture was stirred at room temperature for 3 days while the reaction was monitored by TLC. After the removal of precipitate, the solution was evaporated completely. The resulting yellow foam was dissolved in CH_2Cl_2. This solution was washed with H_2O and brine and dried with anhydrous $MgSO_4$. After evaporation of the solution, the resulting yellow oil was purified by column chromatography (silica gel; hexane/AcOEt = 1/1). A whitish yellow foam was obtained. Yield 4.62 g (92.9%). ^{1}H NMR (300 MHz, $CDCl_3$): 1.33 (s, 36H, CH_3), 3.79 (s, 8H, CH_2), 3.82 (s, 4H, CH_2), 7.09 (d, 4H, py, J=7.5 Hz), 7.61 (t, 4H, py, J=8.1 Hz), 8.11 (d, 4H, py, J=8.4 Hz), 8.17 (s, 4H, NH), 8.49 (s, 2H, Ar). IR (KBr, cm^{-1}): 3435 (ν_{O-H}), 3407 (ν_{N-H}), 1692 ($\nu_{C=O}$), 1517 (ν_{NO2}), 1335 (ν_{NO2}), 1286 (ν_{NO2}), 1208 (δ_{O-H}), 752 (δ_{C-NO}).

Preparation of 2,6-Bis[bis(6-pivalamido-2-pyridylmethyl)aminomethyl]-4-aminophenol (TPPAP). TPPNP (3.30 g, 3.44 mmol) and a catalytic amount of 10% Pd-C were added to dry MeOH (30 mL). The mixture was stirred at 45 °C under 1 atom of H_2 pressure until the yellow solution became colorless. After evaporation, the resulting white solid and Pd-C were collected and washed with dry MeOH and dry Et_2O. The solid was added to dry CH_2Cl_2. After removal of Pd-C with a membrane filter (PTFF; pore size 0.5 μm), the solution was evaporated completely. The resulting solid was dissolved in CH_2Cl_2 and reprecipitated by slow evaporation of CH_2Cl_2. Yield 1.89 g (58.7%). ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.32 (s, 36H, CH_3), 3.35 (br, 2H, -NH_2), 3.72 (s, 4H, CH_2), 3.76 (s, 8H, CH_2), 6.67 (s, 2H, Ar), 7.15 (d, 4H, py), 7.59 (t, 4H, py), 8.07 (d, 4H, py), 8.13 (s, 4H, NH), 10.63 (br, 1H, OH). IR (KBr, cm^1): 3439 (ν_{O-H}), 3433 (ν_{N-H}), 3393 (ν_{N-H}), 1688 ($\nu_{C=O}$), 1211 (δ_{O-H}). Anal. Calcd. for TPPAP•2.5 H_2O ($C_{52}H_{72}N_{11}O_{7.5}$): C, 64.17; H, 7.66; N, 15.83. Found: C, 64.04; H, 7.52; N, 15.74.

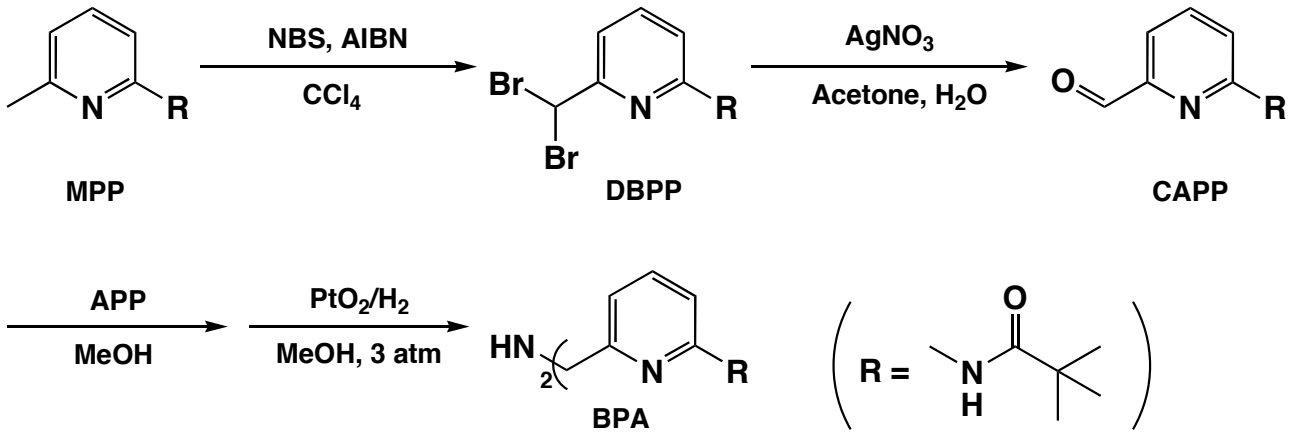
X-ray crystallography of 2. A single crystal of **2** suitable for X-ray diffraction analysis was recrystallized from MeOH under Ar atmosphere. This sigle crystal was mounted on a glass fiber,

and diffraction data were collected on a Rigaku/MSC Mercury CCD using graphite monochromated Mo Kα radiation at –100 °C.

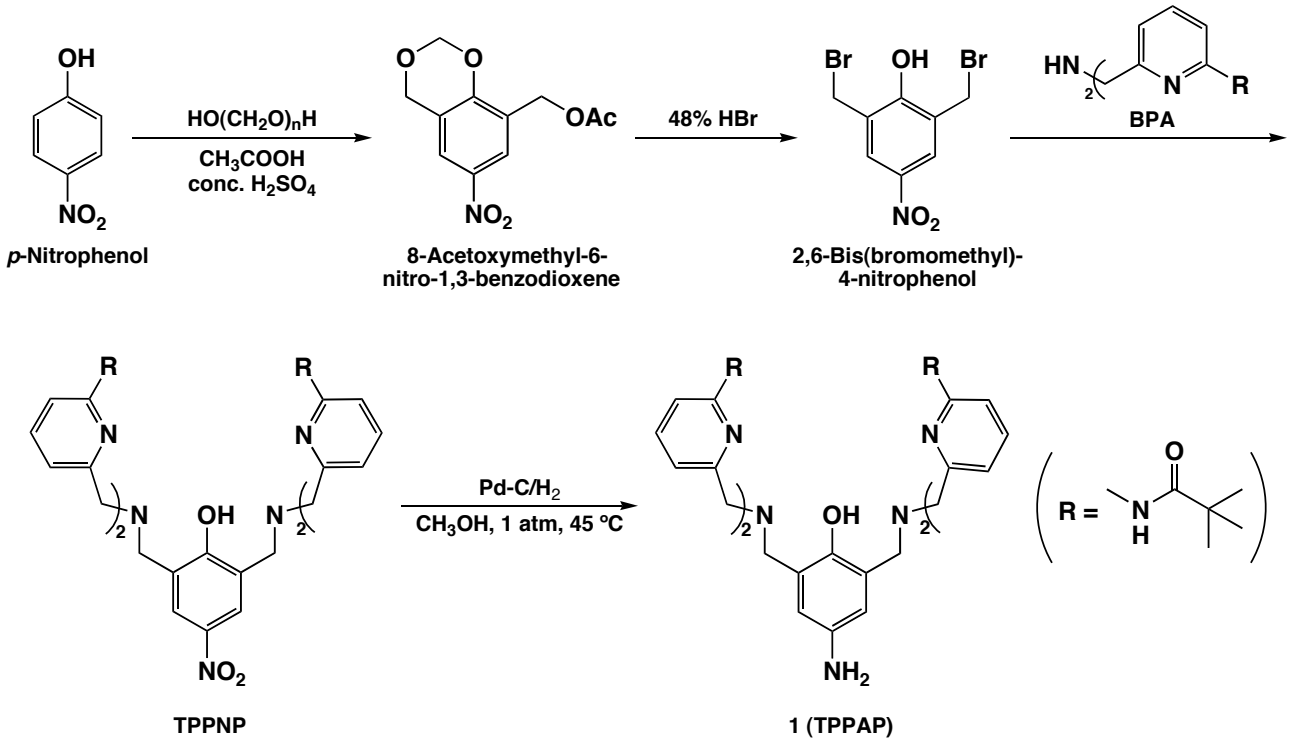
The crystal structure of **2** was solved by a combination of direct methods (SIR 92 and SHELEXS 97) and Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. A Sheldrick weighting scheme was employed. All calculations were performed using the crystallographic software package, Crystal Structure (*Crystal Structure Analysis Package*; Rigaku and Rigaku/MSC (2000-2005): The Woodlands, TX)



Scheme S1. Preparation of APP.



Scheme S2. Preparation of BPA.



Scheme S3. Preparation of **TPPAP**.

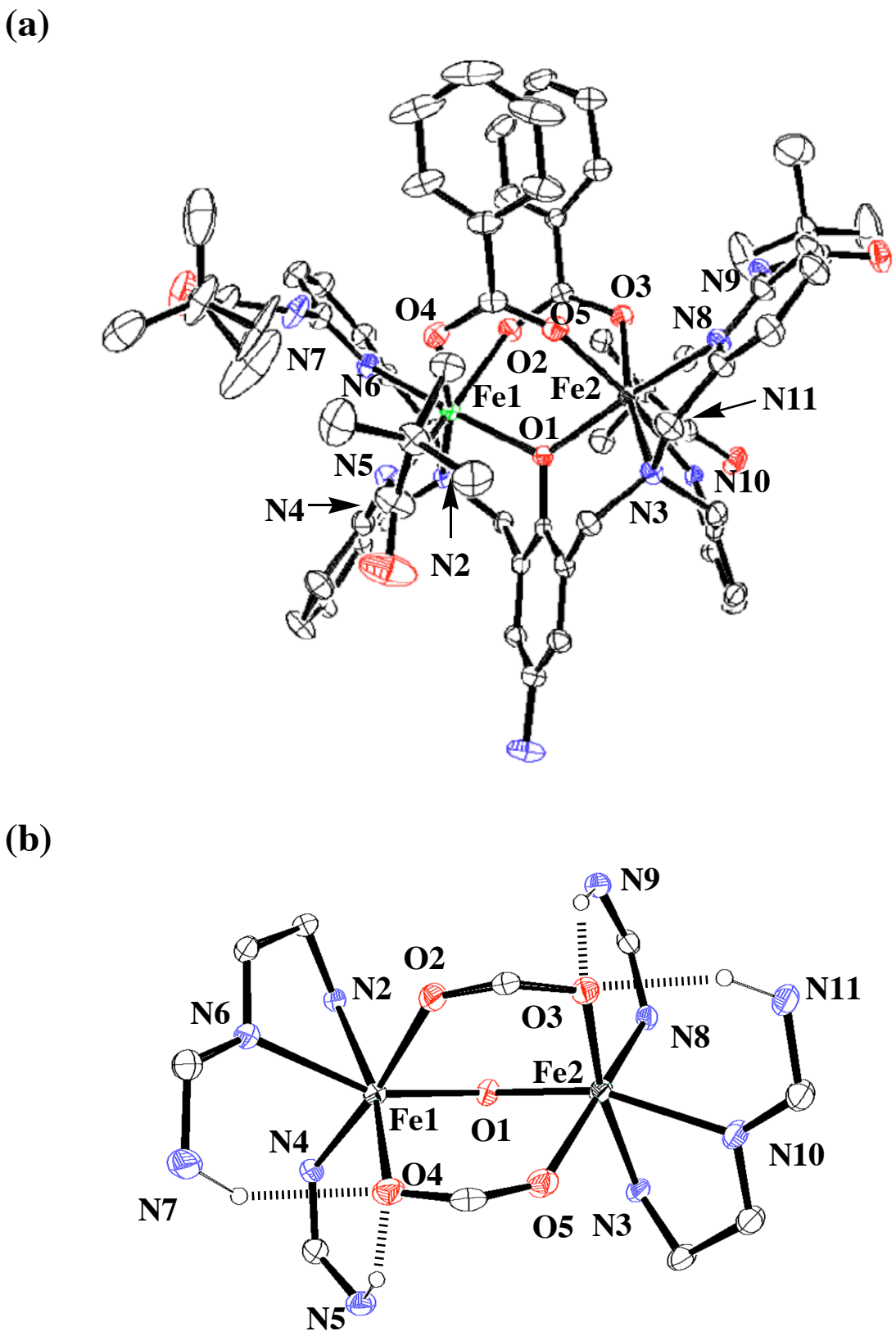


Fig. S1. ORTEP plots of (a) cation of **Fe_2-TPPAP**, $[Fe^{II}_2$(**TPPAP**)$(PhCOO)_2]^+$, and (b) schematic geometries around diiron core, showing 30%, probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity except amide protons. One methyl group is disordered.

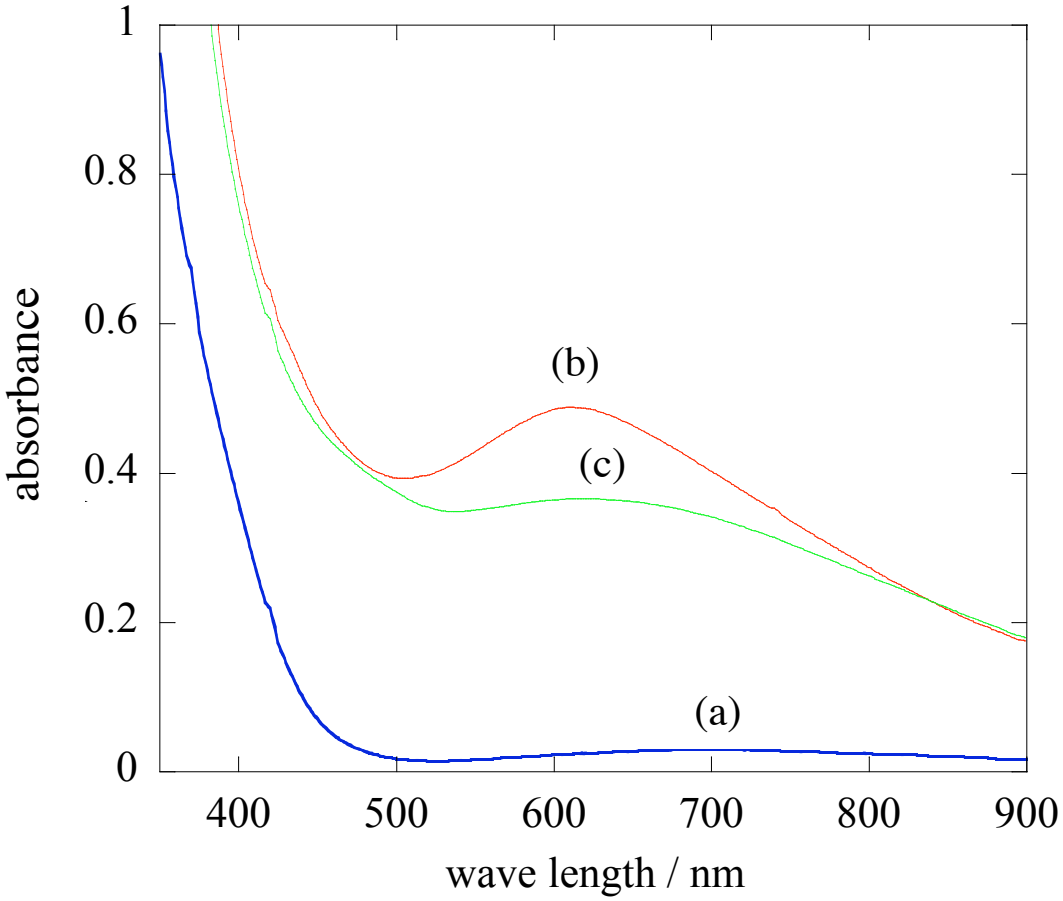


Fig. S2. Electronic absorption spectral change showing the binding of O_2 for **Fe_2-TPPAP** in acetone under (a) Ar, (b) O_2 at –30 ºC, and (c) O_2 with rising up to room temperature, respectively.

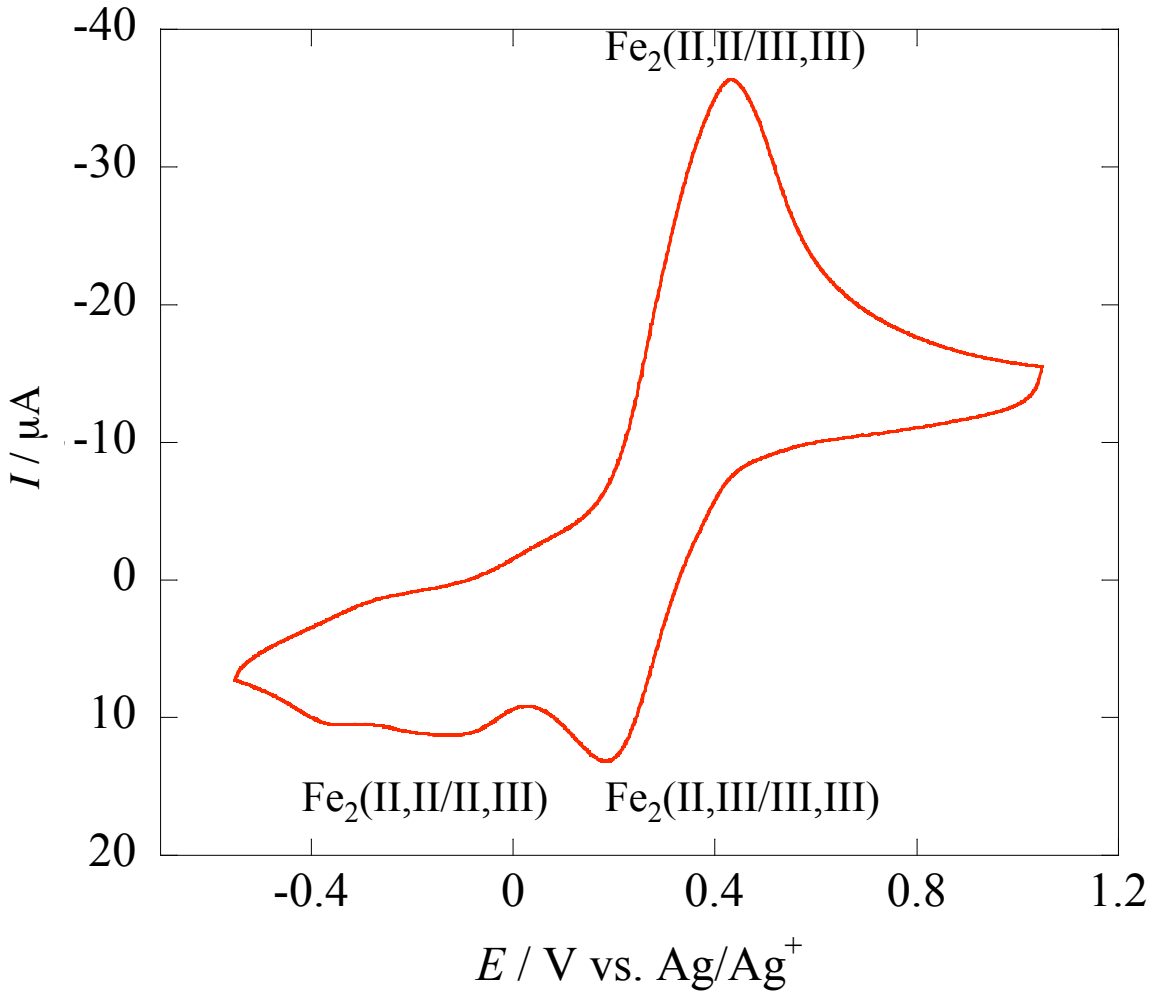


Fig. S3. Cyclic voltammograms of **Fe_2-TPPAP** in CH_2Cl_2 containing 0.1 M $TBABF_4$. [complex] = 1 mM. W.E. GC, C.E. Pt wire, and R.E. Ag/Ag^+, respectively. Scan rate 50 mV s^{-1}.

Table S1. The redox potentials of **2**/Au for various bridging benzoate.

	bridging benzoate		
	p-MeO-benzoate	benzoate	*p*-NC-benzoate
wave I[a]	-0.40[b]	-0.32[b]	-0.27[b]
wave II[a]	-0.48[b]	-0.38[b]	-0.35[b]

[a] Wave I and II are corresponded to Fig.2a. [b] *E*/V vs. Ag/AgCl