Supporting Information

The Detailed Preparation of the Dinucleating Ligand TPPAP. The preparation of TPPAP is summarized in Scheme S1-S3. All reagents 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 CH₂Cl₂ (300 mL) was added a solution (100 mL) of pivaloyl chloride (60.9 g, 555 mmol) in CH₂Cl₂. After stirring until initiation of the exothermic reaction, white precipitate was removed. The CH₂Cl₂ solution was washed with H₂O (x 3), 1 N HCl, 0.5 N NaHCO₃, and brine. After drying with anhydrous MgSO₄, the solution was evaporated. The resultant solid was recrystallized from Et₂O. 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 CCl₄ (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 NaHCO₃ and brine. The solution was dried with anhydrous MgSO₄, 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 H₂O (50 mL), the resulting mixture was extracted with CHCl₃. All organic layers were combined, washed with brine and dried with anhydrous MgSO₄. After
removal of MgSO₄, the solution was evaporated completely. The resulting brown solid was recrystallized from CHCl₃, 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 CHCl₃ (100 mL), the insoluble white solid (phthalhydrazide) was removed. The solution was evaporated completely, and the resulting white solid was recrystallized from CHCl₃/Et₂O. White crystal was obtained (6.49 g, yield 75%). ¹H-NMR (300 MHz, CDCl₃): δ 1.34 (s, 9H, t-Bu), 1.80 (s, 2H, NH₂), 3.88 (s, 2H, CH₂), 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 CCl₄ (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 (1.00 g, 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 H₂O (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 NaHCO₃. After removal of the aqueous layer, the organic layer was washed with brine and dried with anhydrous MgSO₄. The resulting solution was evaporated completely and white crystals were obtained (19.1 g, 54.5 %). ¹H-NMR (300 MHz, CDCl₃): δ 1.35 (s, 9H, t-Bu), 6.51 (s, 1H, Br₂CH), 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 AgNO₃ (27.8 g, 160 mmol) in H₂O (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 CH₂Cl₂ washed successively with H₂O, 0.5 N NaHCO₃, and brine. After drying with anhydrous MgSO₄, the organic layer was evaporated. Yellow oil was obtained (9.95 g, 89%). ¹H-NMR (300 MHz, CDCl₃): 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 PtO₂ in MeOH (100 mL) was stirred under 3 atom of H₂ pressure while the generation of BPA was monitored by TLC and the ninhydrin reaction). After removal of PtO₂, the resulting yellow oil was evaporated and purified by column chromatography (silica gel; CHCl₃). The resulting orange oil was dissolved in acetone (50 mL). Colorless crystals were obtained by slow evaporation of acetone. Yield 7.66 g (41%). ¹H-NMR (300 MHz, CDCl₃): δ 1.33 (s, 18H, t-Bu), 3.86 (s, 18H, CH₂), 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. H₂SO₄ (21.9 mL) in CH₃COOH (100 mL) was stirred for 35 h at 60 °C. To the mixture was added H₂O (300 mL). After neutralization with K₂CO₃, the white precipitate was collected and washed with cold H₂O. After drying with silica gel, the resulting white solid was recrystallized from EtOH, producing white crystals. Yield: 14.3 g (56%). ¹H-NMR (300 MHz, CDCl₃): δ 2.17 (s, 3H, CH₃), 4.97 (s, 2H, CH₂), 5.17 (s, 2H, CH₂), 5.38 (s, 2H, CH₂), 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 CHCl₃. The white crystal was obtained.
Yield 2.01 g, (78%). $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 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$_3$N (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$_2$Cl$_2$. This solution was washed with H$_2$O 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 ($\nu$O-H), 3407 ($\nu$N-H), 1692 ($\nu$C=O), 1517 ($\nu$NO$_2$), 1335 ($\nu$NO$_2$), 1286 ($\nu$NO$_2$), 1208 ($\delta$O-H), 752 ($\delta$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$_2$O. The solid was added to dry CH$_2$Cl$_2$. 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$_2$Cl$_2$ and reprecipitated by slow evaporation of CH$_2$Cl$_2$. 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 ($\nu$O-H), 3433 ($\nu$N-H), 3393 ($\nu$N-H), 1688 ($\nu$C=O), 1211 ($\delta$O-H). Anal. Calcd. for TPPAP•2.5 H$_2$O (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 single 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.
Supplementary Material (ESI) for Chemical Communications
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Fig. S1. ORTEP plots of (a) cation of Fe\textsubscript{2}-TPPAP, [Fe\textsuperscript{II}\textsubscript{2}(TPPAP)(PhCOO)\textsubscript{2}]\textsuperscript{+}, 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 O₂ for Fe₂-TPPAP in acetone under (a) Ar, (b) O₂ at –30 °C, and (c) O₂ with rising up to room temperature, respectively.
Fig. S3. Cyclic voltammograms of Fe₂-TPPAP in CH₂Cl₂ containing 0.1 M TBABF₄. [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.

<table>
<thead>
<tr>
<th>bridging benzoate</th>
<th>p-MeO-benzoate</th>
<th>benzoate</th>
<th>p-NC-benzoate</th>
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</thead>
<tbody>
<tr>
<td>wave 1(^a)</td>
<td>-0.40(^b)</td>
<td>-0.32(^b)</td>
<td>-0.27(^b)</td>
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<tr>
<td>wave II(^a)</td>
<td>-0.48(^b)</td>
<td>-0.38(^b)</td>
<td>-0.35(^b)</td>
</tr>
</tbody>
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\(^a\) Wave I and II are corresponded to Fig.2a. \(^b\) E/V vs. Ag/AgCl