The Supporting Information for

Solvent-Dependent fac/mer-Isomerization and Self-Assembly of Triply Helical Complexes Bearing a Pivot Part

Takuma Morozumi, Ryota Matsuoka, Takashi Nakamura, Tatsuya Nabeshima*

Faculty of Pure and Applied Sciences
and Tsukuba Research Center for Energy Materials Science (TREMS),
University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan

*Corresponding Author. E-mail: nabesima@chem.tsukuba.ac.jp
Contents

Materials and methods ........................................................................................................... 3

Synthesis and characterization of the compounds ................................................................. 4

Solvent dependence in the fac/mer-isomerization of [2bFe](TFPB)₂ ........................................ 53

van’t Hoff study of the fac/mer-isomerization in various solvents ......................................... 55

DOSY-NMR spectra of [2bFe](TFPB)₂ in CD₃CN or CDCl₃ ....................................................... 58

Comparison of solvent dependence between [2bFe](TFPB)₂ and the others ............................ 60

Regression analyses with various solvent parameters .......................................................... 63

X-ray diffraction analysis ....................................................................................................... 64

Cycle characteristics of exchanging solvent .......................................................................... 65

Synthesis of imine-linked dimer and tetramer .......................................................................... 66

References for the Supplementary Information ..................................................................... 74
Materials and methods

Unless otherwise noted, the solvents and reagents were purchased from TCI Co., Ltd., FUJIFILM Wako Pure Chemical Industries, Ltd., Kanto Chemical Co., Inc., Nacalai Tesque, Inc., Cambridge Isotope Laboratories, Inc., or Sigma-Aldrich Co., and used without further purification. Dry THF and DMF were purified by Glass Contour Ultimate Solvent System 3S-TCN 1. Silica gel and amine-functionalized silica gel for column chromatography were purchased from Kanto Chemical Co. Inc. (Silica Gel 60 N (spherical, 63–210 μm) and Silica Gel 60 N (spherical, 40–50 μm) NH₂, respectively). GPC purification was performed by a JAI LC-9210 II NEXT system with JAIGEL-1HH/2HH columns using CHCl₃ as the eluent.

Measurements were performed at 298 K unless otherwise noted. ¹H, ¹³C, ¹¹B, ¹⁹F, ³¹P NMR, and other 2D NMR spectra were recorded by a Bruker AVANCE III-600 (600 MHz) spectrometer or a Bruker AVANCE III-400 (400 MHz) spectrometer. Negative values were depicted in red in the spectra. Tetramethylsilane was used as the internal standard (δ 0.00 ppm) for the ¹H and ¹³C NMR measurements when CDCl₃ or a mixed solvent of CDCl₃/CD₂CN = 1/1 was used as the solvent. In the other deuterium solvents, the residual solvent signal was used as the internal standard for the ¹H NMR and ¹³C NMR measurements. BF₃·Et₂O in CDCl₃ (1 wt%) was used as the external standard (δ 0.00 ppm) for the ¹¹B NMR measurements. Hexafluorobenzene in CDCl₃ (1 wt%) was used as the external standard (δ –163.0 ppm) for the ¹⁹F NMR measurements. Triphenylphosphine oxide in CDCl₃ (1 wt%) was used as an external standard (δ 30.0 ppm) for the ³¹P NMR measurements. The assignments of the ¹H and ¹³C signals were based on ¹H-¹H COSY, ¹H-¹H ROESY, ¹H-¹³C HSQC, and ¹H-¹³C HMBC measurements.

The ESI-TOF mass data were recorded by an AB SCIEX TripleTOF 4600 system. The HRMS values of iron complexes were calculated for the strongest peak using PeakView 1.2.0.3 software (AB SCIEX, 2012)).

The single-crystal X-ray crystallographic measurements were performed using a Bruker APEX II ULTRA with MoKα radiation (graphite-monochromated, λ = 0.71073 Å) at 120 K. The collected diffraction images were processed by a Bruker APEX2. The initial structure was solved using SHELXT-2018[81] and refined using SHELXL-2018[82], which were running on Yadokari-XG crystallographic software[83]. CCDC 2067281 contain the data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

The calculation of the structure of mer-[1aFe]²⁺ was performed on a Spartan’18 software (Wavefunction Inc.). The initial structure was obtained by an equilibrium conformer search based on a molecular mechanics calculation (Forcefield: MMFF). The obtained initial structure was optimized by a DFT calculation (B3LYP/6-31G*, vacuum).

The elemental analysis was performed by a Yanaco MT-6 analyzer with tin boats purchased from Elementar. We appreciate Mr. Masao Sasaki of the University of Tsukuba for the elemental analyses.
Synthesis and characterization of the compounds

Synthesis of bpy-OH

\[
\text{bpy-Br} \xrightarrow{\text{NaH, THF, reflux, 17 h}} \text{bpy-OH}
\]

To a suspension of NaH (60 wt% dispersion in mineral oil, 3.60 g, 90.0 mmol) in dry THF (150 mL) was added dry ethylene glycol (15.0 mL, 270 mmol), and the mixture was refluxed under an argon atmosphere. After 1 h, a suspension of bpy-Br\textsuperscript{[S4]} (9.84 g, 30.0 mmol) in dry THF (150 mL) was added to the suspension dropwise over 3 h. Then the reaction mixture was further refluxed for 17 h. After cooling to room temperature, the mixture was concentrated in vacuo. The residue was suspended in satd. NH\textsubscript{4}Cl aq. (500 mL) and extracted with EtOAc (150 mL × 3). The combined organic layer was dried over MgSO\textsubscript{4}, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on amine-functionalized silica gel (EtOAc/hexane = 2/1) to give bpy-OH as a colorless solid (7.98 g, 25.8 mmol, 86%).

bpy-OH: colorless solid; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) δ 8.72 (d, J = 2.4 Hz, 1H), 8.63 (d, J = 2.4 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H), 7.94 (dd, J = 8.4, 2.4 Hz, 1H), 7.82 (dd, J = 8.4, 2.4 Hz, 1H), 4.64 (s, 2H), 3.82–3.79 (m, 2H), 3.66 (t, J = 4.5 Hz, 2H), 3.05 (s, 3H); \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) δ 154.8, 154.4, 150.2, 148.6, 139.5, 136.5, 133.8, 122.3, 121.2, 120.8, 71.8, 70.6, 61.9; Anal. Calcd for C\textsubscript{13}H\textsubscript{13}BrN\textsubscript{2}O\textsubscript{2}: C, 50.51; H, 4.24; N, 9.06. Found: C, 50.26; H, 4.04; N, 8.91.

Synthesis of bpy-OMS

\[
\text{bpy-OH} \xrightarrow{\text{H\textsubscript{3}C-S-Cl, Et\textsubscript{3}N, CH\textsubscript{2}Cl\textsubscript{2}, 0 °C, 2 h}} \text{bpy-OMS}
\]

To a solution of bpy-OH (6.95 g, 22.5 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (150 mL) was added Et\textsubscript{3}N (3.6 mL, 25.9 mmol) and methanesulfonyl chloride (2.0 mL, 25.9 mmol) at 0 °C under an argon atmosphere. The mixture was stirred at 0 °C for 2 h. 0.1 M HCl aq. (50 mL) was added to the reaction mixture, and the organic layer was separated, washed with satd NaHCO\textsubscript{3} aq. (50 mL), dried over MgSO\textsubscript{4}, filtered, and concentrated in vacuo. The residue was washed with diethyl ether to give bpy-OMS as a pale yellow solid (7.48 g, 19.3 mmol, 86%).

bpy-OMS: pale yellow solid; \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) δ 8.72 (d, J = 1.8 Hz, 1H), 8.63 (d, J = 1.8 Hz, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H), 7.94 (dd, J = 8.4, 1.8 Hz, 1H), 7.82 (dd, J = 8.4, 1.8 Hz, 1H), 4.66 (s, 2H), 4.43–4.42 (m, 2H), 3.82–3.80 (m, 2H), 3.05 (s, 3H); \textsuperscript{13}C NMR (151 Hz, CDCl\textsubscript{3}) δ 155.0, 154.3, 150.2, 148.6, 139.5, 136.5, 133.3, 122.4, 121.2, 120.8, 70.7, 68.7, 68.3, 37.7; HRMS (ESI): m/z calcd for C\textsubscript{14}H\textsubscript{16}BrN\textsubscript{2}O\textsubscript{4}S\textsuperscript{+} ([bpy-OMS·H\textsuperscript{+}]): 387.0010; found: 387.0005.
Synthesis of 4-H

A suspension of 4-OH\[^{[55]}\](3.50 g, 10.0 mmol) and Zn powder (11.3 g, 173 mmol) in acetic acid (50 mL) was stirred at 90 °C for 24 h under a hydrogen atmosphere. The reaction mixture was filtered, and H\(_2\)O (100 mL) was added to the filtrate. The suspension was extracted with CHCl\(_3\) (50 mL \(\times 3\)). The organic layer was washed with satd NaHCO\(_3\) aq. (100 mL \(\times 2\)), dried over MgSO\(_4\), filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (CH\(_2\)Cl\(_2\)/hexane = 2/1) to give 4-H as a colorless solid (1.46 g, 4.36 mmol, 44%).

4-H: colorless solid; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.19 (dd, \(J = 7.8, 7.8\) Hz, 3H), 6.75 (dd, \(J = 7.8, 2.4\) Hz, 3H), 6.72 (d, \(J = 7.8\) Hz, 3H), 6.67 (dd, \(J = 2.4, 2.4\) Hz, 3H), 5.44 (s, 1H), 3.73 (s, 9H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 159.7, 145.3, 129.3, 122.1, 115.7, 111.5, 57.0, 55.2; Anal. Calcd for C\(_{22}\)H\(_{22}\)O\(_3\): C, 79.02; H, 6.63; N, 0.00. Found: C, 78.87; H, 6.71; N, 0.00.

Synthesis of 5-H

To a solution of 4-H (0.846 g, 2.53 mmol) in dry CH\(_2\)Cl\(_2\) (12.3 mL) was added BBr\(_3\) (0.80 mL, 8.4 mmol) at 0 °C under an argon atmosphere. After being stirred at 0 °C for 1 h, the reaction mixture was quenched with brine (50 mL) and extracted with THF (50 mL \(\times 2\)). The combined organic layer was dried over Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo at 150 °C for 12 h to give 5-H (0.731 g, 2.50 mmol, 99%) as a colorless solid.

5-H: colorless solid; \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) \(\delta\) 9.25 (s, 3H), 7.07 (dd, \(J = 7.8, 7.8\) Hz, 3H), 6.58 (dd, \(J = 7.8, 1.8\) Hz, 3H), 6.53 (d, \(J = 7.8\) Hz, 3H), 6.50 (dd, \(J = 1.8, 1.8\) Hz, 3H), 5.29 (s, 1H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 157.1, 145.2, 129.0, 119.8, 116.0, 113.1, 55.6; Anal. Calcd for C\(_{19}\)H\(_{17}\)O\(_{3.5}\) (5-H·0.5H\(_2\)O): C, 75.73; H, 5.69; N, 0.00. Found: C, 75.92; H, 5.47; N, 0.00.
Synthesis of 1a

A suspension of 5-H (0.694 g, 2.37 mmol) and Cs$_2$CO$_3$ (2.32 g, 7.12 mmol) in dry DMF (25 mL) was stirred at 60 °C under an argon atmosphere. After 30 min, a solution of bpy-OMs (2.77 g, 7.16 mmol) in dry DMF (40 mL) was added to the reaction mixture, and the mixture was further stirred for 27 h. H$_2$O (200 mL) was added to the mixture, and the mixture was extracted with a mixed solvent of EtOAc/hexane = 1/1 (50 mL × 3). The combined organic layer was washed with H$_2$O (100 mL), dried over MgSO$_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on amine-functionalized silica gel (EtOAc/hexane = 1/2) to give 1a as a pale brown solid (0.853 g, 0.732 mmol, 31%).

1a: pale brown solid; $^1$H NMR (600 MHz, CDCl$_3$) δ 8.70 (d, $J = 2.4$ Hz, 3H), 8.60 (d, $J = 1.8$ Hz, 3H), 8.32 (d, $J = 8.4$ Hz, 3H), 8.29 (d, $J = 8.4$ Hz, 3H), 7.91 (dd, $J = 8.4$, 2.4 Hz, 3H), 7.45 (dd, $J = 8.2$, 1.8 Hz, 3H), 7.18 (dd, $J = 7.8$, 7.8 Hz, 3H), 6.76 (dd, $J = 7.8$, 1.8 Hz, 3H), 6.73–6.69 (m, 6H), 5.42 (s, 1H), 4.65 (s, 6H), 4.09 (t, 4.8 Hz, 6H), 3.82 (t, 4.8 Hz, 6H), $^{13}$C NMR (151 MHz, CDCl$_3$) δ 158.9, 154.8, 154.6, 150.3, 148.7, 145.3, 139.6, 136.6, 134.1, 129.4, 122.5, 122.4, 121.2, 120.8, 116.4, 112.3, 70.9, 69.2, 67.4, 57.0; ESI-MS: m/z calcd for C$_{58}$H$_{49}$Br$_3$N$_6$O$_6^+$ ([1a•H$^+$]): 1163.13; found: 1163.12.
Synthesis of 1b

A solution of 1a (0.227 g, 0.195 mmol), 4-ethynylbenzaldehyde (0.153 g, 1.17 mmol), Pd(PPh₃)₄ (0.169 g, 0.146 mmol), and CuI (28.4 mg, 0.146 mmol) in a mixed solvent of dry THF (20 mL) and Et₃N (20 mL) was refluxed under an argon atmosphere. After 15 h, the mixture was concentrated in vacuo. The residue was suspended in a solution of EDTA•4Na•4H₂O (0.689 g, 1.52 mmol) in H₂O (50 mL) and extracted with CHCl₃ (30 mL × 3). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by GPC (using CHCl₃ as an eluent) and reprecipitation from CHCl₃/diethyl ether to give 1b as a pale brown solid (0.0671 g, 51.1 µmol, 26%).

1b: pale brown solid; ¹H NMR (600 MHz, CDCl₃) δ 10.04 (s, 3H), 8.81 (br s, 3H), 8.64 (br s, 3H), 8.42 (d, J = 8.4 Hz, 3H), 8.40 (d, J = 8.4 Hz, 3H), 7.94 (dd, J = 8.4, 1.8 Hz, 3H), 7.89 (d, J = 7.8 Hz, 6H), 7.82 (dd, J = 8.4, 1.8 Hz, 3H), 7.71 (d, J = 7.8 Hz, 6H), 7.19 (dd, J = 7.8, 7.8 Hz, 3H), 6.78 (br d, J = 7.8 Hz, 3H), 6.74–6.71 (m, 6H), 5.43 (s, 1H), 4.68 (s, 6H), 4.11 (t, J = 4.2 Hz, 6H), 3.83 (t, J = 4.2 Hz, 6H); ¹³C NMR (151 MHz, CDCl₃) δ 191.3, 158.9, 155.5, 154.9, 151.9, 148.8, 145.3, 139.6, 136.5, 136.0, 134.2, 132.4, 129.7, 129.4, 128.9, 122.5, 121.3, 120.5, 119.6, 116.5, 112.4, 92.6, 90.4, 86.0, 70.9, 69.2, 67.5, 57.0.

Although we tried to characterize 1b by ESI-MS and MALDI-MS in various conditions, but 1b was not observed under any investigated conditions.
Synthesis of \([1\text{aFe}](\text{PF}_6)_2\):

A solution of 1a (0.122 g, 0.100 mmol) and Fe(BF$_4$)$_2$•6H$_2$O (41.5 mg, 0.123 mmol) in a mixed solvent of CH$_3$CN/CHCl$_3$ = 1/1 (30 mL) was sonicated for 5 min. A solution of KPF$_6$ (1.84 g, 10.0 mmol) in H$_2$O (100 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of CH$_3$CN/CHCl$_3$ = 1/2 (50 mL × 3). The combined organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (CH$_3$CN/CHCl$_3$ = 1/4) to give \([1\text{aFe}](\text{PF}_6)_2\) as a red solid (0.104 g, 0.068 mmol, 68%).

\([1\text{aFe}](\text{PF}_6)_2\): red solid; $^1$H NMR (600 MHz, CD$_3$CN, the signals for the fac-isomer are shown) δ 8.51 (d, $J$ = 8.4 Hz, 3H), 8.38 (d, $J$ = 8.4 Hz, 3H), 8.29 (dd, $J$ = 8.4, 2.4 Hz, 3H), 8.17 (dd, $J$ = 8.4, 1.2 Hz, 3H), 7.46 (d, $J$ = 2.4 Hz, 3H), 7.26 (dd, $J$ = 7.8, 7.8 Hz, 3H), 7.18 (d, $J$ = 1.2 Hz, 3H), 6.87 (d, $J$ = 7.8 Hz, 3H), 6.76 (dd, $J$ = 7.8, 1.8 Hz, 3H), 5.55 (s, 1H), 4.39 (dd, $J$ = 83.4, 12.6 Hz, 3H), 4.13 (dd, $J$ = 9.0, 9.0 Hz, 3H), 4.00–3.92 (m, 6H), 3.75–3.70 (m, 3H); $^{13}$C NMR (151 MHz, CD$_3$CN, the signals for the fac-isomer are shown) δ 159.5, 159.0, 158.6, 156.4, 153.4, 146.1, 142.9, 140.2, 139.4, 131.0, 125.7, 125.6, 123.8, 123.2, 117.6, 110.5, 70.9, 70.5, 68.8, 56.3; $^{19}$F NMR (376 MHz, CD$_3$CN) δ −73.0 (d, $^1J_{F-P}$ = 707 Hz); $^{31}$P NMR (243 MHz, CD$_3$CN) δ −144.6 (septet, $^1J_{F-P}$ = 707 Hz); HRMS (ESI-MS): m/z calcd for C$_{58}$H$_{46}$Br$_2$FeN$_6$O$_6^{2+}$ ([1aFe]$^{2+}$): 608.0324; found: 608.0335.
Synthesis of $[\text{1aFe}](\text{TFPB})_2$

A solution of $\text{1a}$ (0.122 g, 0.100 mmol) and $\text{FeCl}_2\cdot4\text{H}_2\text{O}$ (24.3 mg, 0.122 mmol) in a mixed solvent of CH$_3$CN/CHCl$_3$ = 1/1 (30 mL) was sonicated for 5 min. A solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) (0.806 g, 0.909 mmol) in H$_2$O (100 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of CH$_3$CN/CHCl$_3$ = 1/2 (50 mL × 3). The combined organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (CH$_3$CN/CHCl$_3$ = 1/4) to give $[\text{1aFe}](\text{TFPB})_2$ as a red solid (0.236 g, 80 µmol, 80%).

$[\text{1aFe}](\text{TFPB})_2$: red solid; $^1$H NMR (600 MHz, CD$_3$CN, the signals for the fac-isomer are shown) $\delta$ 8.50 (d, $J$ = 8.4 Hz, 3H), 8.38 (d, $J$ = 8.4 Hz, 3H), 8.28 (dd, $J$ = 8.4, 3.0 Hz, 3H), 8.16 (dd, $J$ = 8.4, 1.8 Hz, 3H), 7.69 (br s, 16H), 7.66 (s, 8H), 7.46 (d, $J$ = 1.8 Hz, 3H), 7.25 (dd, $J$ = 8.4, 8.4 Hz, 3H), 7.18 (d, $J$ = 1.8 Hz, 3H), 6.87 (br d, $J$ = 8.4 Hz, 3H), 6.83 (dd, $J$ = 8.4, 3.0 Hz, 3H), 6.39 (dd, $J$ = 3.0, 3.0 Hz, 3H), 5.55 (s, 1H), 4.31 (dd, $J$ = 8.5, 1.7 Hz, 6H), 4.16–4.09 (m, 3H) 4.01–3.91 (m, 6H), 3.75–3.68 (m, 3H), $^{13}$C NMR (151 MHz, CD$_3$CN, the signals for the fac-isomer are shown) $\delta$ 162.7 (q, $^1J_{\text{C-B}}$ = 49.8 Hz), 159.5, 159.0, 158.6, 153.5, 146.1, 142.9, 140.2, 139.4, 135.7 (br s), 131.0, 130.0 (qq, $^2J_{\text{C-F}}$ = 31.9 Hz, $^3J_{\text{C-F}}$ = 3.8 Hz), 125.7, 125.6, 125.5 (q, $^1J_{\text{C-F}}$ = 272 Hz), 123.8, 123.2, 118.7 (septet, $^1J_{\text{C-F}}$ = 3.8 Hz), 117.6, 110.4, 70.9, 70.5, 68.8, 56.4; $^{11}$B NMR (192 MHz, CD$_3$CN) $\delta$ -6.65; $^{19}$F NMR (376 MHz, CD$_3$CN) $\delta$ -63.3; HRMS (ESI-MS): $m/z$ calcd for C$_{58}$H$_{69}$Br$_3$FeN$_6$O$_5^{2+}$ ([$\text{1aFe}$]$^{2+}$): 608.0324; found: 608.0310.
Synthesis of $[1b\text{Fe}](\text{TFPB})_2$

A solution of $1b$ (0.104 g, 79.2 µmol) and FeCl$_2$·4H$_2$O (26.9 mg, 135 µmol) in a mixed solvent of CH$_3$CN/CHCl$_3$ = 1/1 (10 mL) was sonicated for 5 min. A solution of NaTFPB (0.489 g, 0.552 mmol) in H$_2$O (50 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of CH$_3$CN/CHCl$_3$ = 1/2 (20 mL × 3). The combined organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (CH$_3$CN/CHCl$_3$ = 1/4) to give $[1b\text{Fe}](\text{TFPB})_2$ as a purple solid (0.104 g, 33.6 µmol, 42%).

$[1b\text{Fe}](\text{TFPB})_2$: purple solid; $^{1}$H NMR (600 MHz, CD$_3$CN, the signals for the fac-isomer are shown) δ 10.00 (s, 3H), 8.56 (d, $J = 8.4$ Hz, 3H), 8.54 (d, $J = 8.4$ Hz, 3H), 8.25 (d, $J = 8.4$ Hz, 3H), 8.19 (d, $J = 8.4$ Hz, 3H), 7.89 (d, $J = 7.8$ Hz, 6H), 7.69 (br s, 16H), 7.68–7.62 (m, 17H), 7.30–7.32 (m, 6H), 6.88 (d, $J = 7.8$ Hz, 3H), 6.77 (d, $J = 7.8$ Hz, 3H), 6.41 (s, 3H), 5.56 (s, 1H), 4.42 (dd, $J = 8.52$, 12.6 Hz, 6H) 4.17–4.11 (m, 6H), 4.02–3.93 (m, 6H), 3.78–3.71 (m, 3H); $^{13}$C NMR (151 MHz, CD$_3$CN, the signals for the fac-isomer are shown) δ 192.8, 162.7 (q, $^{1}$J$_{C\cdot F} = 64.8$ Hz), 159.6, 159.5, 159.5, 158.8, 157.4, 153.7, 146.2, 142.2, 140.3, 139.4, 137.9, 135.7 (br s), 133.3, 131.0, 130.6, 130.1 (qq, $^{2}$J$_{C\cdot F} = 31.9$ Hz, $^{3}$J$_{C\cdot F} = 3.8$ Hz), 128.1, 125.8, 125.5 (q, $^{1}$J$_{C\cdot F} = 272$ Hz), 124.9, 124.1, 123.4, 118.7 (septet, $^{3}$J$_{C\cdot F} = 3.8$ Hz), 117.7, 110.6, 96.1, 88.2, 71.0, 70.6, 68.8, 56.5; $^{11}$B NMR (192 MHz, CD$_3$CN) δ −6.68; $^{19}$F NMR (376 MHz, CD$_3$CN) δ −63.2; HRMS (ESI): $m/z$ calcd for C$_{85}$H$_{64}$FeN$_6$O$_9^{2+}$ ([$1b\text{Fe}^2$]): 683.2060; found: 683.2072.
Synthesis of 4-TE

To a solution of 4-Ety\[^{[55]}\] (3.58 g, 9.98 mmol) in dry THF (100 mL) was added a solution of n-BuLi in hexane (1.57 M, 7.0 mL, 11.0 mmol) at \(-78^\circ\text{C}\) under an argon atmosphere. After the mixture was stirred at \(-78^\circ\text{C}\) for 1 h, triisopropylsilyl chloride (2.4 mL, 11.7 mmol) was added at r.t. After being stirred at r.t. for 18 h, the reaction mixture was diluted with H\(_2\)O (200 mL) and extracted with CHCl\(_3\) (100 mL \(\times 3\)). The combined organic layer was dried over MgSO\(_4\), filtered, and concentrated in vacuo. The crude product was recrystallized from methanol to give 4-TE (4.84 g, 9.42 mmol, 94%) as a colorless solid.

4-TE: colorless solid, m.p. 91.2–92.2 \(^{\circ}\text{C}\); \(^1\text{H}\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.16 (dd, \(J = 7.8, 7.8\) Hz, 3H), 6.93 (dd, \(J = 1.8, 1.8\) Hz, 3H), 6.82 (dd, \(J = 7.8, 7.8\) Hz, 3H), 6.77 (dd, \(J = 7.8, 1.8\) Hz, 3H), 3.73 (s, 9H), 1.10–1.09 (m, 21H); \(^13\text{C}\) NMR (151 MHz, CDCl\(_3\)) \(\delta\) 159.2, 146.6, 128.6, 121.8, 115.0, 113.3, 112.4, 85.7, 56.8, 55.1, 18.8, 11.4; Anal. Calcd for C\(_{33}\)H\(_{42}\)O\(_3\)Si: C, 77.00; H, 8.22; N, 0.00. Found: C, 76.93; H, 8.22; N, 0.00.

Synthesis of 5-TE

To a solution of 4-TE (9.30 g, 17.5 mmol) in dry CH\(_2\)Cl\(_2\) (78 mL) was added BBr\(_3\) (6.0 mL, 64.5 mmol) at 0 \(^{\circ}\text{C}\) under an argon atmosphere. After being stirred at 0 \(^{\circ}\text{C}\) for 1 h, the reaction mixture was quenched with H\(_2\)O (200 mL), and extracted with diethyl ether (100 mL \(\times 3\)). The combined organic layer was dried over Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo. The crude product was recrystallized from diethyl ether/hexane to give 5-TE (7.46 g, 15.8 mmol, 90%) as a colorless solid.

5-TE: colorless solid, m.p. 196–197 \(^{\circ}\text{C}\); \(^1\text{H}\) NMR (600 MHz, DMSO-\(d_6\)) \(\delta\) 9.35 (s, 3H), 7.10 (dd, \(J = 7.8, 7.8\) Hz, 3H), 6.68 (d, \(J = 7.8\) Hz, 3H), 6.65 (dd, \(J = 7.8, 1.8\) Hz, 3H), 6.60 (dd, \(J = 1.8, 1.8\) Hz, 3H), 1.08–1.04 (m, 21H); \(^13\text{C}\) NMR (151 MHz, DMSO-\(d_6\)) \(\delta\) 157.3, 146.6, 129.1, 119.8, 116.5, 114.3, 114.2, 84.9, 56.3, 19.0, 11.4; Anal. Calcd for C\(_{30}\)H\(_{36}\)O\(_{3}\)Si (5-TE·0.4H\(_2\)O): C, 75.08; H, 7.73; N, 0.00. Found: C, 75.05; H, 7.67; N, 0.00.
Synthesis of 2a

A suspension of 5-TE (1.18 g, 2.50 mmol) and Cs$_2$CO$_3$ (2.61 g, 8.00 mmol) in dry DMF (50 mL) was stirred at 60 °C under an argon atmosphere. After 30 min, a solution of bpy-OMs (3.10 g, 8.00 mmol) in dry DMF (40 mL) was added, and the reaction mixture was further stirred at 60 °C for 27 h. H$_2$O (200 mL) was added, and the mixture was extracted with a mixed solvent of ethyl acetate/hexane = 1/1 (50 mL × 3). The combined organic layer was washed with H$_2$O (100 mL), dried over MgSO$_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on amine-functionalized silica gel (ethyl acetate/hexane = 1/2) to give 2a as a pale brown solid (1.66 g, 1.23 mmol, 49%).

2a: pale brown solid; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.68 (d, $J = 1.8$ Hz, 3H), 8.59 (d, $J = 1.8$ Hz, 3H), 8.32 (d, $J = 8.4$ Hz, 3H), 8.27 (d, $J = 8.4$ Hz, 3H), 7.87 (dd, $J = 8.4$, 1.8 Hz, 3H), 7.76 (dd, $J = 8.4$, 1.8 Hz, 3H), 7.18 (dd, $J = 7.8$, 7.8 Hz, 3H), 6.98 (s, 3H), 6.89 (d, $J = 7.8$ Hz, 3H), 6.81 (dd, $J = 7.8$, 1.8 Hz, 3H), 4.63 (s, 6H), 4.09 (t, $J = 4.2$ Hz, 6H), 3.80 (t, $J = 4.2$ Hz, 6H), 1.12–1.07 (m, 21H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 158.3, 154.5, 154.3, 150.1, 148.5, 146.5, 139.4, 136.3, 133.9, 128.7, 122.2, 122.1, 121.0, 120.6, 115.7, 113.3, 113.1, 85.8, 70.6, 69.0, 67.3, 56.8, 18.8, 11.4; HRMS (ESI): m/z calcd for C$_{69}$H$_{70}$Br$_3$N$_6$O$_6$Si$^+$ ([2a•H]$^+$): 1343.2671; found:1343.2703.
Synthesis of 2b

A solution of 2a (0.686 g, 0.510 mmol), 4-ethynylbenzaldehyde\[^{[7]}\] (0.390 g, 3.00 mmol), Pd(PPh\(_3\))\(_4\) (0.200 g, 0.17 mmol), and Cul (68.0 mg, 0.350 mmol) in a mixed solvent of dry THF (50 mL) and Et\(_3\)N (50 mL) was refluxed under an argon atmosphere. After 20 h, the mixture was concentrated in vacuo. The residue was suspended in a solution of EDTA•4Na•4H\(_2\)O (2.32 g, 5.13 mmol) in H\(_2\)O (200 mL) and extracted with CHCl\(_3\) (50 mL × 3). The combined organic layer was dried over Na\(_2\)SO\(_4\), filtered, and concentrated in vacuo. The crude product was purified by GPC (using CHCl\(_3\) as eluent) to give 2b as a pale brown solid (0.602 g, 0.403 mmol, 79%).

2b: pale brown solid; \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 10.02 (s, 3H), 8.82 (d, \(J = 1.8\) Hz, 3H), 8.64 (d, \(J = 1.8\) Hz, 3H), 8.42 (d, \(J = 8.4\) Hz, 3H), 8.40 (d, \(J = 8.4\) Hz, 3H), 7.94 (dd, \(J = 8.4, 1.8\) Hz, 3H), 7.88 (d, \(J = 8.4\) Hz, 6H), 7.82 (dd, \(J = 8.4, 1.8\) Hz, 3H), 7.70 (d, \(J = 8.4\) Hz, 6H), 7.18 (dd, \(J = 7.8, 7.8\) Hz, 3H), 6.95 (br s, 3H), 6.87 (br d, \(J = 7.8\) Hz 3H), 6.82 (dd, \(J = 7.8, 1.8\) Hz, 3H), 4.67 (s, 6H), 4.10 (t, \(J = 4.8\) Hz, 6H), 3.83 (t, \(J = 4.8\) Hz, 6H), 1.09–1.80 (m, 21H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 191.4, 158.5, 155.4, 154.9, 151.9, 148.8, 146.7, 139.6, 136.5, 135.9, 134.2, 132.3, 129.7, 128.9, 122.8, 122.3, 121.3, 120.5, 119.6, 115.8, 113.4, 113.2, 92.6, 90.4, 86.0, 70.8, 69.1, 67.4, 56.9, 18.9, 11.6; HRMS (ESI): \(m/z\) calcd for C\(_{96}H_{83}N_{6}O_{9}Si\)\(^+\) ([2b•H]\(^+\)): 1493.6142; found: 1493.6138.
Synthesis of [2aFe](TFPB)$_2$

A solution of 2a (0.108 g, 80.2 µmol) and Fe(BF$_4$)$_2$·6H$_2$O (32.1 mg, 95.1 µmol) in a mixed solvent of CH$_3$CN/CHCl$_3$ = 1:1 (30 mL) was sonicated for 5 min. A solution of NaTFPB (0.408 g, 456 µmol) in H$_2$O (100 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of CH$_3$CN/CHCl$_3$ = 1/2 (30 mL × 3). The combined organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (CH$_3$CN/CHCl$_3$ = 1/4) to give [2aFe](TFPB)$_2$ as a red solid (0.123 g, 39.3 mmol, 49%).

[2aFe](TFPB)$_2$: red solid; $^1$H NMR (600 MHz, CD$_3$CN, the signals for the fac-isomer are shown) δ 8.49 (d, $J$ = 8.4 Hz, 3H), 8.37 (d, $J$ = 8.4 Hz, 3H), 8.28 (dd, $J$ = 8.4, 1.8 Hz, 3H), 8.13 (dd, $J$ = 8.4, 1.2 Hz, 3H), 7.69 (br s, 16H), 7.66 (s, 8H), 7.45 (d, $J$ = 1.8 Hz, 3H), 7.42 (dd, $J$ = 7.8, 1.8 Hz, 3H), 7.34 (dd, $J$ = 7.8, 7.8 Hz, 3H), 7.14 (d, $J$ = 1.2 Hz, 3H), 6.83 (dd, $J$ = 7.8, 1.8 Hz, 3H), 6.07 (dd, $J$ = 1.8, 1.8 Hz, 3H), 4.31 (dd, $J$ = 41.4, 12.0 Hz, 6H), 4.13–4.08 (m, 3H), 3.97–3.92 (m, 3H), 3.72–3.67 (m, 3H), 1.12–1.08 (m, 21H); $^{13}$C NMR (151 MHz, CD$_3$CN, the signals for the fac-isomer are shown) δ 162.6 (q, $^1$J$_{C,B}$ = 49.7 Hz), 159.0, 158.9, 158.6, 156.4, 153.4, 147.3, 142.9, 140.1, 139.6, 135.7 (br s), 130.9, 130.0 (qq, $^2$J$_{C,F}$ = 31.9 Hz, $^3$J$_{C,F}$ = 3.8 Hz), 125.7, 125.5, 125.5 (q, $^1$J$_{C,F}$ = 272 Hz), 123.9, 122.7, 118.7 (septet, $^3$J$_{C,F}$ = 3.8 Hz), 117.7, 113.6, 111.4, 87.0, 70.8, 70.1, 68.6, 57.1, 19.1, 12.3; $^{11}$B NMR (192 MHz, CD$_3$CN) δ −6.65; $^{19}$F NMR (376 MHz, CD$_3$CN) δ −63.2; HRMS (ESI): m/z calcd for C$_{69}$H$_{70}$Br$_3$FeN$_6$O$_6$Si$_2^{2+}$ ([2aFe]$_2^{2+}$): 698.6031; found: 698.6010.
Synthesis of $[2bFe](PF_6)_2$

A solution of $2b$ (0.337 g, 0.226 mmol) and Fe(BF$_4$)$_2$·6H$_2$O (50.7 mg, 0.254 mmol) in a mixed solvent of CH$_3$CN/CHCl$_3$ = 1/1 (30 mL) was sonicated for 5 min. A solution of KPF$_6$ (0.1898 g, 10.4 mmol) in H$_2$O (100 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of CH$_3$CN/CHCl$_3$ = 1/2 (30 mL × 3). The combined organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (CH$_3$CN/CHCl$_3$ = 1/4) to give $[2bFe](PF_6)_2$ as a purple solid (0.100 g, 54.4 µmol, 24%).

$[2bFe](PF_6)_2$: purple solid; $^1$H NMR (600 MHz, CD$_3$CN, the signals for the fac-isomer are shown) δ 10.00 (s, 3H), 8.55 (d, $J = 8.4$ Hz, 3H), 8.54 (d, $J = 8.4$ Hz, 3H), 8.25 (dd, $J = 8.4$, 2.4 Hz, 3H), 8.16 (dd, $J = 8.4$, 1.2 Hz, 3H), 7.90 (d, $J = 8.4$ Hz, 6H), 7.66–7.63 (m, 9H), 7.43 (dd, $J = 7.8$, 1.8 Hz, 3H), 7.34 (dd, $J = 7.8$, 7.8 Hz, 3H), 7.22 (d, $J = 1.2$ Hz, 3H), 6.84 (dd, $J = 7.8$, 1.8 Hz, 3H), 6.08 (dd, $J = 7.8$, 1.8 Hz, 3H), 4.34 (dd, $J = 30.6$, 12.6 Hz, 6H) 4.15–4.10 (m, 3H), 3.98–3.89 (m, 6H), 3.74–3.69 (m, 3H) 1.12–1.09 (m, 21H); $^{13}$C NMR (151 MHz, CD$_3$CN, the signals for the fac-isomer are shown) δ 192.8, 159.5, 159.1, 158.9, 157.4, 153.7, 147.4, 142.3, 140.2, 139.6, 137.9, 133.4, 130.9, 130.9, 128.2, 125.8, 124.9, 124.1, 122.8, 117.8, 113.8, 111.7, 96.2, 88.3, 88.0, 70.8, 70.2, 68.7, 57.3, 19.2, 12.4; $^{19}$F NMR (376 MHz, CD$_3$CN) δ –72.6 (d, $^1J_{F,P} = 706$ Hz); $^{31}$P NMR (243 MHz, CD$_3$CN) δ –144.6 (septet, $^1J_{P,F} = 706$ Hz); HRMS (ESI): m/z calcd for C$_{96}$H$_{34}$FeN$_6$O$_9$Si$_2$+: 773.2727; found: 773.2722.
Synthesis of [2Fe](TFPB)₂

A solution of 2b (0.167 g, 0.100 mmol) and FeCl₃·4H₂O (36.0 mg, 0.181 mmol) in a mixed solvent of CH₃CN/CHCl₃ = 1/1 (10 mL) was sonicated for 5 min. A solution of NaTFPB (0.8732 g, 0.985 mmol) in H₂O (100 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of CH₃CN/CHCl₃ = 1/2 (30 mL × 3). The combined organic layer was dried over Na₂SO₄, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (CH₃CN/CHCl₃ = 1/4) to give [2Fe](TFPB)₂ as a purple solid (0.241 g, 73.7 µmol, 74%).

[2Fe](TFPB)₂: purple solid; ¹H NMR (600 MHz, CD₃CN, the signals for the fac-isomer are shown) δ 9.98 (s, 3H), 8.57 (d, J = 8.4 Hz, 3H), 8.55 (d, J = 8.4 Hz, 3H), 8.25 (dd, J = 8.4, 2.4 Hz, 3H), 8.18 (dd, J = 8.4, 1.2 Hz, 3H), 7.87 (d, J = 7.8 Hz, 6H), 7.74 (br s, 16H), 7.71 (d, J = 2.4 Hz, 3H), 7.66 (br s, 8H), 7.63 (d, J = 7.8 Hz, 6H), 7.47 (dd, J = 7.8, 2.4 Hz, 3H), 7.36 (dd, J = 7.8, 7.8 Hz, 3H), 7.28 (d, J = 1.2 Hz, 3H), 6.85 (dd, J = 7.8, 2.4 Hz, 3H), 6.14 (dd, J = 2.4, 2.4 Hz, 3H), 4.38 (dd, J = 29.4, 12.6 Hz, 6H) 4.18–4.11 (m, 3H), 4.00–3.92 (m, 6H), 3.75–3.70 (m, 3H), 1.14–1.08 (m, 21H); ¹³C NMR (151 MHz, CD₃CN, the signals for the fac-isomer are shown) δ 192.7, 162.7 (q, ¹JC-Fe = 49.7 Hz), 159.4, 159.0, 158.9, 157.4, 153.7, 147.3, 142.2, 140.2, 139.6, 137.8, 135.8 (br s), 133.3, 130.9, 130.6, 130.0 (qq, ¹JC-Fe = 31.9 Hz, ¹JC-Fe = 3.8 Hz), 128.1, 125.7, 125.4 (q, ¹JC-Fe = 272 Hz), 124.9, 124.1, 122.9, 122.8, 118.7 (septet, ¹JC-Fe = 3.8 Hz), 117.8, 113.7, 111.4, 96.1, 88.2, 87.0, 70.8, 70.2, 68.6, 57.2, 19.1, 12.3; ¹¹B NMR (192 MHz, CD₃CN) δ −6.63; ¹⁹F NMR (376 MHz, CD₃CN) δ −63.2; HRMS (ESI): m/z calcd for C₉₀H₉₆Fe₄N₄O₄Si⁴⁺ ([2Fe]²⁺): 773.2727; found: 773.2747.
Synthesis of [2bZn](TFPB)$_2$

A solution of 2b (75.0 mg, 50.0 µmol) and Zn(NO$_3$)$_2$·6H$_2$O (16.2 mg, 52.2 µmol) in a mixed solvent of CH$_3$CN/CHCl$_3$ = 1/1 (10 mL) was sonicated for 5 min. A solution of NaTFPB (0.2248 g, 251 µmol) in H$_2$O (20 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of CH$_3$CN/CHCl$_3$ = 1/2 (20 mL × 3). The combined organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo to give [2bZn](TFPB)$_2$ as a brown solid (0.1763 g, quant.).

[2bZn](TFPB)$_2$: brown solid; $^1$H NMR (600 MHz, CD$_3$CN, the signals for the fac-isomer are shown) δ 10.00 (s, 3H), 8.51 (d, $J$ = 8.4 Hz, 3H), 8.51 (d, $J$ = 8.4 Hz, 3H), 8.35 (dd, $J$ = 8.4, 1.8 Hz, 3H), 8.26 (dd, $J$ = 8.4, 1.8 Hz, 3H), 8.21 (d, $J$ = 1.8 Hz, 63H), 7.90 (d, $J$ = 7.8 Hz, 6H), 7.84 (d, $J$ = 1.8 Hz, 3H), 7.69 (br s, 16H), 7.66 (s, 8H), 7.42 (d, $J$ = 7.8 Hz, 3H), 7.34 (dd, $J$ = 7.8, 7.8 Hz, 3H), 6.84 (dd, $J$ = 7.8, 1.8 Hz, 3H), 6.10 (s, 3H), 4.42 (dd, $J$ = 52.2, 11.4 Hz, 6H) 4.14–4.09 (m, 3H), 3.99–3.89 (m, 6H), 3.78–3.72 (m, 3H), 1.12–1.08 (m, 21H); $^{13}$C NMR (151 MHz, CD$_3$CN, the signals for the fac-isomer are shown) δ 192.7, 162.6 (q, $^1$J$_{C,B}$ = 49.8 Hz), 158.9, 151.4, 149.4, 149.1, 147.9, 147.3, 144.9, 142.5, 139.9, 135.7 (br s), 133.2, 130.8, 130.5, 130.0 (qq, $^2$J$_{C,F}$ = 31.9 Hz, $^3$J$_{C,F}$ = 3.8 Hz), 128.1, 125.4 (q, $^1$J$_{C,F}$ = 272 Hz), 125.0, 124.4, 124.2, 122.8, 118.7 (septet, $^3$J$_{C,F}$ = 3.8 Hz), 117.6, 113.8, 111.3, 96.0, 88.2, 86.8, 70.8, 70.1, 68.5, 57.2, 19.1, 12.2; $^{19}$B NMR (192 MHz, CD$_3$CN) δ −6.64; $^{19}$F NMR (376 MHz, CD$_3$CN) δ −63.2; HRMS (ESI): m/z calcd for C$_{96}$H$_{105}$Zn$_4$N$_6$O$_9$Si$_2$$^{2+}$ ([2bZn]$^2^+$): 778.7714; found: 778.7730.
Synthesis of 3a

A suspension of m-cresol (0.51 mL, 3.0 mmol) and Cs$_2$CO$_3$ (0.983 g, 3.02 mmol) in dry DMF (10 mL) was stirred at 60 °C under an argon atmosphere. After 30 min, a solution of bpy-OMs (1.16 g, 3.00 mmol) in DMF (17 mL) was added to the reaction mixture, and the reaction mixture was further stirred at 60 °C for 22 h. H$_2$O (100 mL) was added, and the mixture was extracted with a mixed solvent of EtOAc/hexane = 1/1 (50 mL × 2). The combined organic layer was washed with H$_2$O (100 mL), dried over MgSO$_4$, filtered, and concentrated in vacuo. The crude product was purified by GPC (using CHCl$_3$ as an eluent) to give 3a as a colorless solid (1.00 g, 2.51 mmol, 84%).

3a: colorless solid; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.71 (d, $J$ = 1.8 Hz, 3H), 8.64 (d, $J$ = 1.8 Hz, 1H), 8.36 (d, $J$ = 8.4 Hz, 1H), 8.31 (d, $J$ = 8.4 Hz, 1H), 7.92 (dd, $J$ = 8.4, 1.8 Hz, 1H), 7.63 (dd, $J$ = 8.4, 1.8 Hz, 1H), 7.16 (dd, $J$ = 7.8, 7.8 Hz, 1H), 6.78–6.75 (m, 2H), 6.73 (dd, $J$ = 7.8, 1.8 Hz, 1H), 4.70 (s, 2H), 4.18–4.14 (m, 2H), 3.89–3.86 (m, 2H), 2.32 (s, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 158.8, 154.8, 154.6, 150.3, 148.7, 139.6, 139.6, 136.6, 134.1, 129.3, 122.5, 122.0, 121.2, 120.8, 115.6, 111.6, 70.8, 69.2, 67.4, 21.6; HRMS (ESI): m/z calcd for C$_{20}$H$_{20}$BrN$_2$O$_2$*: [3a•H]*: 399.0703; found: 399.0686.

Synthesis of 3b

A solution of 3a (0.576 g, 1.44 mmol), 4-ethynylbenzaldehyde$^{[57]}$ (0.375 g, 2.88 mmol), Pd(PPh$_3$)$_4$ (0.168 g, 0.140 mmol), and Cul (62.3 mg, 0.330 mmol) in a mixed solvent of dry THF (50 mL) and Et$_3$N (50 mL) was refluxed under an argon atmosphere. After 19 h, the mixture was concentrated in vacuo. The residue was suspended in a solution of EDTA•4Na (2.32 g, 5.12 mmol) in H$_2$O (200 mL) and extracted with CHCl$_3$ (50 mL × 3). The combined organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The crude product was purified by GPC (using CHCl$_3$ as an eluent) to give 3b as a pale brown solid (0.137 g, 0.305 mmol, 21%).

3b: pale brown solid; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 10.04 (s, 1H), 8.67 (d, $J$ = 1.8 Hz, 1H), 8.68 (d, $J$ = 1.8 Hz, 1H), 8.42 (d, $J$ = 8.4 Hz, 1H), 8.40 (d, $J$ = 8.4 Hz, 1H), 7.96 (dd, $J$ = 8.4, 1.8 Hz, 1H), 7.90 (d, $J$ = 8.4 Hz, 2H), 7.86 (dd, $J$ = 8.4, 1.8 Hz, 1H), 7.72 (d, $J$ = 8.4 Hz, 1H), 7.16 (dd, $J$ = 7.8, 7.8 Hz, 3H), 6.79–6.76 (m, 2H), 6.74 (dd, $J$ = 7.8, 2.4 Hz, 1H), 4.73 (s, 2H), 4.19–4.16 (m, 2H), 3.91–3.87 (m, 2H), 2.33 (s, 3H); $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 191.4, 158.8, 155.4, 154.9, 151.9, 148.8, 139.6, 136.5, 135.9, 134.3, 132.3, 129.7, 129.3, 128.9, 121.9, 121.3, 120.5, 119.6, 115.6, 111.6, 92.5, 90.4, 70.8, 69.2, 67.4, 21.6; HRMS (ESI): m/z calcd for C$_{20}$H$_{20}$N$_2$O$_2$*: [3b•H]*: 449.1859; found: 449.1855.
Synthesis of [(3b)\textsubscript{3}Fe](TFPB)\textsubscript{2}

A solution of 3\textsubscript{b} (338.5 mg, 85.8 µmol) and FeCl\textsubscript{2}•4H\textsubscript{2}O (5.68 mg, 28.6 µmol) in a mixed solvent of CH\textsubscript{3}CN/CHCl\textsubscript{3} = 1:1 (6.0 mL) was sonicated for 5 min. A solution of NaTFPB (0.253 g, 0.286 mmol) in H\textsubscript{2}O (10.0 mL) was added to the reaction mixture, and the mixture was extracted with a mixed solvent of CH\textsubscript{3}CN/CHCl\textsubscript{3} = 1/2 (5.0 mL × 3). The combined organic layer dried over Na\textsubscript{2}SO\textsubscript{4}, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (CH\textsubscript{3}CN/CHCl\textsubscript{3} = 1/4) to give [(3b)\textsubscript{3}Fe](TFPB)\textsubscript{2} as a purple solid (56.5 mg, 24.9 µmol, 89%)

[(3b)\textsubscript{3}Fe](TFPB)\textsubscript{2}: purple solid; \textsuperscript{1}H NMR (600 MHz, CD\textsubscript{3}CN) and \textsuperscript{13}C NMR (151 MHz, CD\textsubscript{3}CN) spectra was shown in Fig. S61 and S62.

\textsuperscript{1}H NMR (600 MHz, CD\textsubscript{3}CN) and \textsuperscript{13}C NMR (151 MHz, CD\textsubscript{3}CN) spectra was shown in Fig. S61 and S62.
Figure S1. $^1$H NMR spectrum of bpy-OH (600 MHz, CDCl$_3$).

Figure S2. $^{13}$C NMR spectrum of bpy-OH (151 MHz, CDCl$_3$).
Figure S3. $^1$H NMR spectrum of bpy-OMs (600 MHz, CDCl$_3$).

Figure S4. $^{13}$C NMR spectrum of bpy-OMs (151 MHz, CDCl$_3$).
Figure S5. $^1$H NMR spectrum of 4-H (600 MHz, CDCl$_3$).

Figure S6. $^{13}$C NMR spectrum of 4-H (151 MHz, CDCl$_3$).
Figure S7. $^1$H NMR spectrum of 5-H (600 MHz, DMSO-$d_6$).

Figure S8. $^{13}$C NMR spectrum of 5-H (151 MHz, DMSO-$d_6$).
Figure S9. $^1$H NMR spectrum of 1a (600 MHz, CDCl$_3$).

Figure S10. $^{13}$C NMR spectrum of 1a (151 MHz, CDCl$_3$).
Figure S11. Simulated and observed isotopic pattern of [1a•H]$^+$ (ESI-MS, positive).

Figure S12. $^1$H NMR spectrum of 1b (600 MHz, CDCl$_3$).
Figure S13. $^{13}$C NMR spectrum of 1b (151 MHz, CDCl$_3$).

Figure S14. $^1$H NMR spectrum of [1aFe](PF$_6$)$_2$ (600 MHz, CD$_3$CN).
Figure S15. $^{13}$C NMR spectrum of $[\text{1aFe}]\text{(PF}_6\text{)}_2$ (151 MHz, CD$_3$CN).

Figure S16. $^{19}$F NMR spectrum of $[\text{1aFe}]\text{(PF}_6\text{)}_2$ (376 MHz, CD$_3$CN).
Figure S17. $^{31}$P NMR spectrum of [1aFe](PF$_6$)$_2$ (243 MHz, CD$_3$CN).

Figure S18. ESI mass spectrum of [1aFe](PF$_6$)$_2$ (solv. CD$_3$CN).
Figure S19. $^1$H NMR spectrum of [IaFe](TFPB)$_2$ (600 MHz, CD$_3$CN).

Figure S20. $^{13}$C NMR spectrum of [IaFe](TFPB)$_2$ (151 MHz, CD$_3$CN).
Figure S21. $^1$B NMR spectrum of [1aFe](TFPB)$_2$ (192 MHz, CD$_3$CN).

Figure S22. $^{19}$F NMR spectrum of [1aFe](TFPB)$_2$ (376 MHz, CD$_3$CN).
Figure S23. $^1$H NMR spectrum of $[1bFe](TFPB)_2$ (600 MHz, CD$_3$CN).

Figure S24. $^{13}$C NMR spectrum of $[1bFe](TFPB)_2$ (151 MHz, CD$_3$CN).
Figure S25. $^{11}$B NMR spectrum of [1bFe](TFPB)$_2$ (192 MHz, CD$_3$CN).

Figure S26. $^{19}$F NMR spectrum of [1bFe](TFPB)$_2$ (376 MHz, CD$_3$CN).
Figure S27. ESI mass spectrum of $[1bFe](\text{TFPB})_2$ (solv. CD$_3$CN).

Figure S28. $^1$H NMR spectrum of 4-TE (600 MHz, CDCl$_3$).
Figure S29. $^{13}$C NMR spectrum of 4-TE (151 MHz, CDCl$_3$).

Figure S30. $^1$H NMR spectrum of 5-TE (600 MHz, DMSO-$d_6$).
Figure S31. $^{13}$C NMR spectrum of 5-TE (151 MHz, DMSO-$d_6$).

Figure S32. $^1$H NMR spectrum of 2a (600 MHz, CDCl$_3$).
Figure S33. $^{13}$C NMR spectrum of 2a (151 MHz, CDCl$_3$).

Figure S34. $^1$H NMR spectrum of 2b (600 MHz, CD$_3$CN).
Figure S35. $^{13}$C NMR spectrum of 2b (151 MHz, CD$_3$CN).

Figure S36. $^1$H NMR spectrum of [2aFe](TFPB)$_2$ (600 MHz, CD$_3$CN).
Figure S37. $^{13}\text{C}$ NMR spectrum of $[2\text{aFe}](\text{TFPB})_2$ (151 MHz, CD$_3$CN).

Figure S38. $^{11}\text{B}$ NMR spectrum of $[2\text{aFe}](\text{TFPB})_2$ (192 MHz, CD$_3$CN).
Figure S39. $^{19}$F NMR spectrum of [2aFe](TFPB)$_2$ (376 MHz, CD$_3$CN).

Figure S40. ESI mass spectrum of [2aFe](TFPB)$_2$ (solv. CH$_3$CN).
Figure S41. $^1$H NMR spectrum of [2bFe](PF$_6$)$_2$ (600 MHz, CD$_3$CN).

Figure S42. $^{13}$C NMR spectrum of [2bFe](PF$_6$)$_2$ (151 MHz, CD$_3$CN).
Figure S43. $^{19}$F NMR spectrum of [2bFe](PF$_6$)$_2$ (376 MHz, CD$_3$CN).

Figure S44. $^{31}$P NMR spectrum of [2bFe](PF$_6$)$_2$ (243 MHz, CD$_3$CN).
Figure S45. ESI mass spectrum of $[2b\text{Fe}](\text{PF}_6)_2$ (solv. CH$_3$CN).

Figure S46. $^1$H NMR spectrum of $[2b\text{Fe}](\text{TFPB})_2$ (600 MHz, CD$_3$CN).
Figure S47. $^1$H–$^1$H ROESY spectrum of [2bFe](TFPB)$_2$ (600 MHz, CD$_3$CN. Signals of mer-isomer are numbered for each tripodal arm.).

Figure S48. $^{13}$C NMR spectrum of [2bFe](TFPB)$_2$ (151 MHz, CD$_3$CN).
Figure S49. Enlarged $^{13}$C NMR spectrum of [2bFe](TFPB)$_2$ (151 MHz, CD$_3$CN, 165–110 ppm).

Figure S50. $^{11}$B NMR spectrum of [2bFe](TFPB)$_2$ (192 MHz, CD$_3$CN).
Figure S51. $^{19}$F NMR spectrum of [2bFe](TFPB)$_2$ (376 MHz, CD$_3$CN).

Figure S52. $^1$H NMR spectrum of [2bZn](TFPB)$_2$ (600 MHz, CD$_3$CN).
Figure S53. $^{13}$C NMR spectrum of [2bZn](TFPB)$_2$ (151 MHz, CD$_3$CN).

Figure S54. $^{11}$B NMR spectrum of [2bZn](TFPB)$_2$ (192 MHz, CD$_3$CN).
Figure S55. $^{19}$F NMR spectrum of [2bZn](TFPB)$_2$ (376 MHz, CD$_3$CN).

Figure S56. ESI mass spectrum of [2bZn](TFPB)$_2$ (solv. CH$_3$CN).
Figure S57. $^1$H NMR spectrum of 3a (600 MHz, CDCl$_3$).

Figure S58. $^{13}$C NMR spectrum of 3a (151 MHz, CDCl$_3$).
Figure S59. $^1$H NMR spectrum of 3b (600 MHz, CDCl$_3$).

Figure S60. $^{13}$C NMR spectrum of 3b (151 MHz, CDCl$_3$).
Figure S61. $^1$H NMR spectrum of [(3b)$_2$Fe](TFPB)$_2$ (600 MHz, CD$_3$CN).

Figure S62. $^{13}$C NMR spectrum of [(3b)$_2$Fe](TFPB)$_2$ (151 MHz, CD$_3$CN).
Figure S63. $^{11}$B NMR spectrum of [(3b)$_2$Fe](TFPB)$_2$ (192 MHz, CD$_3$CN).

Figure S64. $^{19}$F NMR spectrum of [(3b)$_2$Fe](TFPB)$_2$ (376 MHz, CD$_3$CN).
Figure S65. ESI mass spectrum of [(3b)\textsubscript{3}Fe](TFPB)\textsubscript{2} (solv. CH\textsubscript{3}CN).
Solvent dependence in the fac/mer-isomerization of complexes

Figure S66. (Top) $^1$H NMR spectra of [2bFe](TFPB)$_2$ in various solvents. (Bottom) Enlarged $^1$H NMR spectra. Signals used for the determination of fac/mer ratios were denoted in the same way as Fig. 2a (600 MHz, 1.0 mM, measured in 12 h after dissolution).
Table S1. Solvent effects on the fac/mer-isomerization equilibrium of [2bFe](TFPB)₂ (298 K) and various parameters for solvents.

| Solvent      | fac/mer b | $\Delta G^c$ (kJ/mol) | $\varepsilon$ | $\mu$ (D) | DN (kcal/mol) | AN (kcal/mol) | $V_m$ (cm³/mol) | $\delta_d$ (MPa⁰/²) | $\delta_p$ (MPa⁰/²) | $\delta_h$ (MPa⁰/²) |
|--------------|-----------|-----------------------|---------------|----------|--------------|---------------|----------------|----------------|----------------|----------------|
| TCE-d₂       | 10:90     | 5.5                   | 8.0           | 1.31     | –            | –             | 105.2         | 18.8           | 5.1            | 5.3            |
| CDCl₃        | 10:90     | 5.5                   | 4.7           | 1.1      | 4            | 23.1          | 80.7          | 17.8           | 3.1            | 5.7            |
| o-DCB-d₄     | 13:87     | 4.8                   | 9.9           | 2.14     | 3            | –             | 112.8         | 19.0           | 6.3            | 3.3            |
| Dioxane-d₈   | 20:80     | 3.4                   | 2.2           | 0.4      | 14.8         | 10.8          | 85.7          | 17.5           | 1.8            | 7.4            |
| DMF-d₇       | 32:68     | 1.8                   | 36.7          | 3.86     | 26.6         | 16.0          | 77.4          | 17.4           | 13.7           | 11.3           |
| THF-d₈       | 34:66     | 1.7                   | 7.4           | 1.7      | 20           | 8.0           | 81.7          | 16.8           | 5.7            | 8.0            |
| CD₂Cl₂       | 40:60     | 1.1                   | 8.9           | 1.5      | 1            | 20.4          | 63.9          | 18.2           | 6.3            | 6.1            |
| CD₃CO₂D      | 53:47     | –0.31                 | 6.2           | 1.73     | 10           | 52.9          | 57.1          | 14.5           | 8.0            | 13.5           |
| CD₃NO₂       | 57:43     | –0.70                 | 36.7          | 3.57     | 2.7          | 20.5          | 54.3          | 15.8           | 18.8           | 5.1            |
| CD₃OD        | 64:36     | –1.5                  | 32.6          | 1.71     | 19           | 41.3          | 40.7          | 15.1           | 12.3           | 22.3           |
| Acetone-d₆   | 69:31     | –2.0                  | 20.7          | 2.88     | 17           | 12.5          | 74.0          | 15.5           | 10.4           | 7.0            |
| CD₃CN        | 71:29     | –2.2                  | 36            | 3.44     | 14.1         | 19.3          | 52.6          | 15.3           | 18.0           | 6.1            |

a: $\varepsilon$: dielectric constant[S8a]; $\mu$: dipole moment[S8a]; DN: donor number[S8a,b]; AN: accepter number[S8b]; $V_m$: molar volume[S8c]; $\delta_d$, $\delta_p$, and $\delta_h$: the terms of Hansen solubility parameters[S8e]. $\delta_d$: the dispersion term; $\delta_p$: the dipole interaction term; $\delta_h$: the hydrogen bonding term.

b: Determined from signals of proton $f$ (pivot unit) (For o-DCB-d₄ and dioxane-d₈, signals of proton $r$ (formyl group) were used. see Fig. S46).

c: $\Delta G = -RT \ln([fac]/[mer])$ ($R$: gas constant, $T$: temperature, [fac]: concentration of fac-isomer, [mer]: concentration of mer-isomer).
van’t Hoff analysis of the fac/mer-isomerization in various solvents

**Figure S67.** A van’t Hoff plot of the fac/mer ratio of [2bFe](TFPB)$_2$ in CDCl$_3$.

**Figure S68.** A van’t Hoff plot of the fac/mer ratio of [2bFe](TFPB)$_2$ in DMF-$d_7$. 

\[ y = 1105.5x - 5.7015 \quad R^2 = 0.9881 \]

\[ y = 503.11x - 2.4325 \quad R^2 = 0.9965 \]
Figure S69. A van’t Hoff plot of the fac/mer ratio of [2bFe](TFPB)$_2$ in THF-$d_6$.

Figure S70. A van’t Hoff plot of the fac/mer ratio of [2bFe](TFPB)$_2$ in acetone-$d_6$. 
Figure S71. A van’t Hoff plot of the fac/mer ratio of [2bFe](TFPB)$_2$ in CD$_3$CN.
DOSY NMR spectra of [2bFe](TFPB)_2 in CD_3CN or CDCl_3

The hydrodynamic radii of [2bFe](TFPB)_2 were evaluated by ^1^H DOSY measurements (Table S2, Fig. S72, S73). The hydrodynamic radii of the facial isomer and the meridional isomers in the same solvent were almost the same. However, the hydrodynamic radius of [2bFe]^2+ was approximately 9 Å in CD_3CN, but 14–15 Å in CDCl_3. Difference in hydrodynamic radius between CD_3CN and CDCl_3 was approximately 5 Å, which was roughly corresponding to the hydrodynamic radius of TFPB– in CD_3CN (5.7 Å). It was suggested that the ion pair of [2bFe]^2+ and TFPB– formed in CDCl_3, while it did not in CD_3CN. Thus, it must be cautioned that the solvent dependency of fac/mer isomerism discussed in this paper contains the effect of ion pair formation between [2bFe]^2+ and TFPB–, and should be treated as the result of ionic complex [2bFe](TFPB)_2 as a whole.

Figure S72. ^1^H DOSY NMR spectrum of [2bFe](TFPB)_2 (600 MHz, CD_3CN).
Figure S73. $^1$H DOSY NMR spectrum of [2bFe](TFPB)$_2$ (600 MHz, CDCl$_3$).

Table S2. Diffusion constants and hydrodynamic radii of [2bFe](TFPB)$_2$ in CD$_3$CN and CDCl$_3$.

| Solvent  | Species   | Diffusion constant (m$^2$/s) | Hydrodynamic radius (Å) |
|----------|-----------|------------------------------|-------------------------|
| CD$_3$CN | fac-isomer| $6.9 \times 10^{-10}$        | 9.3                     |
|          | mer-isomer| $7.2 \times 10^{-10}$        | 8.9                     |
|          | TFPB$^-$  | $1.1 \times 10^{-9}$         | 5.7                     |
| CDCl$_3$ | fac-isomer| $2.8 \times 10^{-10}$        | 15                      |
|          | mer-isomer| $2.9 \times 10^{-10}$        | 14                      |
|          | TFPB$^-$  | $2.9 \times 10^{-10}$        | 14                      |
Comparison of solvent dependence of $[2\text{bFe}](\text{TFPB})_2$ and the other complexes

Figure S74. $^1\text{H}$ NMR spectra of $[1\text{aFe}](\text{TFPB})_2$ (600 MHz).

Figure S75. $^1\text{H}$ NMR spectra of $[1\text{bFe}](\text{TFPB})_2$ (600 MHz).
**Figure S76.** $^1$H NMR spectra of [2aFe](TFPB)$_2$ (600 MHz).

**Figure S77.** $^1$H NMR spectra of [2bFe](PF$_6$)$_2$ (600 MHz).
Figure S78. $^1$H NMR spectra of [2bZn](TFPB)$_2$ (600 MHz).

Figure S79. $^1$H NMR spectra of [(3b)Fe](TFPB)$_2$ (600 MHz).
Regression analyses with various solvent parameters

Table S3. Results of regression analyses between $\Delta G$ of (mer to fac isomerization) of [2hFe](TFPB)$_2$ and thermodynamic parameters of solvents. See also Table S1.

| Parameter | (Multiple) correlation coefficient $R$ | adjusted $R$-squared $R_{adj}^2$ | Standard error $\sigma$(kJ/mol) |
|-----------|--------------------------------------|----------------------------------|-------------------------------|
| $\varepsilon$ | -0.64 | 0.34 | 2.3 |
| $\mu$ | -0.54 | 0.23 | 2.5 |
| DN | -0.29 | -0.015 | 2.7 |
| AN | 0.26 | -0.049 | 2.5 |
| $V_m$ | 0.83 | 0.66 | 1.6 |
| $\delta_d$ | 0.87 | 0.72 | 1.5 |
| $\delta_p$ | -0.73 | 0.48 | 2.0 |
| $\delta_h$ | -0.42 | 0.10 | 2.7 |
| $\varepsilon, \mu$ | 0.64 | 0.27 | 2.4 |
| DN, AN | 0.33 | -0.14 | 2.7 |
| $V_m, \delta_d$ | 0.89 | 0.75 | 1.4 |
| $\delta_d, \delta_p, \delta_h$ | 0.91 | 0.77 | 1.4 |
| $\delta_d, \delta_p$ | 0.91 | 0.79 | 1.3 |

$R_{adj}^2$ was defined as this equation ($R$: the correlation coefficient, $n$: the sample size, $p$: the total number of explanatory variables).

$$R_{adj}^2 = 1 - (1 - R^2) \frac{n - 1}{n - p - 1}$$

$R_{adj}^2$ is one of the extended coefficients of determination considered the number of explanatory variables and can be compared even when different numbers of variables are used.
X-ray diffraction analysis

A single crystal of [1aFe](PF₆)₂•4(CH₃)₂CO suitable for the X-ray diffraction analysis was obtained by the slow diffusion of diethyl ether vapor into an acetone solution of [1aFe](PF₆)₂.

Crystal data for [1aFe](PF₆)₂•4(CH₃)₂CO: C₇₀H₇₃Br₃FeN₁₆O₁₀P₂, Fw = 1743.86, hexagonal red plate, 0.14 × 0.17 × 0.02 mm³, rhombohedral, space group R-3, a = 13.982(3) Å, c = 67.108(15) Å, V = 11362(6) Å³, Z = 6, R₁ = 0.0643, wR₂ = 0.1997, GOF = 1.068. CCDC 2067281.

Figure S80. The structure of [1aFe](PF₆)₂•2(CH₃)₂CO•2PF₆ determined by X-ray diffraction analysis. Hydrogen atoms were omitted for clarity. a) An ellipsoidal model (50% probability). One of the disordered structures is shown. b) An ellipsoid model for [1aFe]²⁺ and a space-filling model for the included acetone. c) A stick model of [1aFe]²⁺.
Cycle characteristics of exchanging solvent

[2bFe](TFPB)$_2$ (2.32 mg, 1.25 µmol) was dissolved in CD$_3$CN (500 µL). The solution was heated at 50 °C for 12 h, cooled to r.t., and then $^1$H NMR spectrum was measured. After the measurement, the solution was concentrated in vacuo, and the residue was dissolved in CDCl$_3$ (500 µL). The solution was heated at 50 °C for 12 h, cooled to r.t., and then $^1$H NMR spectrum was measured. These operations were repeated for 5 times with the same sample.

![Figure S81](image1)

Figure S81. $^1$H NMR spectra of [2bFe](TFPB)$_2$ at 1st, 2nd, and 5th cycle in the solvent exchange experiment (600 MHz). (a) 1st cycle in CD$_3$CN. (b) 1st cycle in CDCl$_3$. (c) 2nd cycle in CD$_3$CN. (d) 2nd cycle in CDCl$_3$. (e) 5th cycle in CD$_3$CN. (f) 5th cycle in CDCl$_3$.

![Figure S82](image2)

Figure S82. Reversibility of the fac/mer isomerization of [2bFe](TFPB)$_2$. 

S65 / S74
Synthesis of imine-linked dimer and tetramer

Synthesis of D-PPD(PF₆)₄
To a solution of [2bFe](PF₆)₂ (0.92 mg, 0.50 µmol) in a mixed solvent of CD₂CN (250 µL) and CDCl₃ (250 µL) was added a solution of 1,3-propanediamine (60.0 mM, 12.5 µL) in a mixed solvent of CD₂CN/CDCl₃ = 1/1. The mixture was heated at 50 °C for 24 h, and then was subjected to the spectroscopic measurements. D-PPD(PF₆)₄: ¹H NMR (600 MHz, CD₂CN/CDCl₃ = 1/1) δ 8.53 (d, J = 8.4 Hz, 6H), 8.52 (d, J = 8.4 Hz, 6H), 8.31 (s, 6H), 8.22 (dd, J = 8.4, 1.8 Hz, 6H), 8.17 (d, J = 8.4 Hz, 6H), 7.71 (d, J = 7.8 Hz, 12H), 7.53–7.49 (m, 18H), 7.45 (d, J = 7.8 Hz, 6H), 7.32 (dd, J = 7.8, 7.8 Hz, 6H), 7.19 (br s, 6H), 6.80 (dd, J = 7.8, 1.8 Hz, 6H), 6.12 (br s, 6H), 4.39 (dd, J = 64.2, 12.6 Hz, 12H) 4.17–4.11 (m, 6H), 3.99–3.92 (m, 12H), 3.77–3.72 (m, 6H), 6.80 (t, J = 5.4 Hz, 12H), 1.15–1.09 (m, 42H); ¹³F NMR (376 MHz, CD₂CN/CDCl₃ = 1/1) δ −72.8 (d, ¹JF-P = 709 Hz); ³¹P NMR (243 MHz, CD₂CN/CDCl₃ = 1/1) δ −144.5 (d, ¹JP-P = 709 Hz); HRMS (ESI): m/z calced for (D-PPD⁺⁺): 801.8202; found: 801.8176.

Synthesis of D-CHZ(PF₆)₄
To a solution of [2bFe](PF₆)₂ (0.90 mg, 0.49 µmol) in a mixed solvent of CD₂CN (250 µL) and CDCl₃ (250 µL) was added a solution of carbohydrazide in water (375 mM, 2.0 µL). The mixture was heated at 50 °C for 24 h, and then was subjected to the spectroscopic measurements. D-CHZ(PF₆)₄: ¹H NMR (600 MHz, CD₂CN/CDCl₃ = 1/1) δ 9.36 (br s, 6H), 8.54–8.46 (m, 12H), 8.19–8.13 (m, 12H), 8.00 (br s, 6H), 7.73 (dd, J = 9.0, 9.0 Hz, 12H), 7.54 (s, 6H), 7.48 (dd, J = 45.6, 8.4 Hz, 12H), 7.43 (d, J = 7.8 Hz, 12H), 7.30 (d, J = 7.4 Hz, 6H), 7.17 (d, J = 18.6 Hz, 6H), 6.80–6.76 (m, 6H), 6.11 (td, J = 7.4, 2.4 Hz, 12H), 4.37 (ddd, J = 60.0, 12.6, 8.4 Hz, 12H), 4.14–4.01 (m, 12H), 3.96–3.89 (m, 12H), 3.75–3.70 (m, 12H), 1.16–1.04 (m, 42H); HRMS (ESI): m/z calced for (D-CHZ⁺⁺⁺): 813.7975; found: 813.7981.

Synthesis of T(PF₆)₈
To a solution of [2bFe](PF₆)₂ (4.60 mg, 2.50 µmol) in a mixed solvent of CD₂CN (250 µL) and CDCl₃ (250 µL) was added a solution of trans-1,4-cyclohexanediamine (37.5 mM, 10.0 µL) in a mixed solvent of CD₂CN/CDCl₃ = 1/1. The mixture was heated at 50 °C for 12 h, and then was subjected to the spectroscopic measurements. T(PF₆)₈: ¹H NMR (600 MHz, CD₂CN/CDCl₃ = 1/1) δ 8.55–8.46 (m, 24H), 8.33 (s, 12H), 8.21 (br dd, J = 7.2, 7.2 Hz, 12H), 8.15 (br d, J = 7.2 Hz, 12H), 7.70 (d, J = 7.2 Hz, 24H), 7.53–7.46 (m, 36H), 7.42 (d, J = 7.8 Hz, 12H), 7.29 (dd, J = 7.8, 7.8 Hz, 12H), 7.12–7.14 (m, 12H), 6.77 (d, J = 7.8 Hz, 12H), 6.11 (br s, 12H), 4.37 (dd, J = 66.0, 12.0 Hz, 24H) 4.15–4.07 (m, 12H), 3.97–3.88 (m, 24H), 3.76–3.69 (m, 12H), 3.28 (br s, 12H), 1.73 (d, J = 52.8 Hz, 48H), 1.15–1.09 (m, 84H); ¹⁹F NMR (376 MHz, CD₂CN/CDCl₃ = 1/1) δ −72.7 (d, ¹JF-P = 709 Hz); ³¹P NMR (243 MHz, CD₂CN/CDCl₃ = 1/1) δ −144.5 (d, ¹JP-P = 709 Hz); HRMS (ESI): m/z calced for (T⁺⁺⁺⁺): 832.2185; found: 832.2175.
Figure S83. $^1$H NMR spectrum of D-PPD(PF$_6$)$_4$ (600 MHz, CD$_3$CN/CDCl$_3$ = 1/1).

Figure S84. $^{19}$F NMR spectrum of D-PPD(PF$_6$)$_4$ (376 MHz, CD$_3$CN/CDCl$_3$ = 1/1).
Figure S85. $^{31}$P NMR spectrum of D-PPD(PF$_6$)$_4$ (162 MHz, CD$_3$CN/CDCl$_3$ = 1/1).

Figure S86. ESI mass spectrum of D-PPD(PF$_6$)$_4$ (solv. CH$_3$CN).
Figure S87. $^1$H DOSY spectrum of D-PPD(PF$_6$)$_4$ (400 MHz, CD$_3$CN/CDCl$_3$ = 1/1).

Figure S88. $^1$H NMR spectrum of D-CHZ(PF$_6$)$_4$ (600 MHz, CD$_3$CN/CDCl$_3$ = 1/1).
Figure S89. ESI mass spectrum of D-CHZ(PF$_6$)$_4$ (solv. CH$_3$CN).

![ESI mass spectrum of D-CHZ(PF$_6$)$_4$ (solv. CH$_3$CN).]

Figure S90. $^1$H NMR spectrum of T(PF$_6$)$_8$ (600 MHz, CD$_3$CN/CDCl$_3$ = 1/1).

![$^1$H NMR spectrum of T(PF$_6$)$_8$ (600 MHz, CD$_3$CN/CDCl$_3$ = 1/1).]
Figure S91. $^{19}$F NMR spectrum of T(PF$_6$)$_8$ (376 MHz, CD$_3$CN/CDCl$_3$ = 1/1).

Figure S92. $^{31}$P NMR spectrum of T(PF$_6$)$_8$ (162 MHz, CD$_3$CN/CDCl$_3$ = 1/1).
Figure S93. ESI mass spectrum of $\text{T}(\text{PF}_6)_8$ (solv. CH$_3$CN).

Figure S94. $^1$H DOSY spectrum of $\text{T}(\text{PF}_6)_8$ (400 MHz, CD$_3$CN/CDCl$_3$ = 1/1).
**Table S4.** Diffusion constants determined by $^1$H DOSY measurements and the hydrodynamic radii calculated by the Stokes-Einstein Equation.

| Structure          | Diffusion constant (m$^2$/s) | Hydrodynamic radius (Å) |
|--------------------|------------------------------|-------------------------|
| [2bFe](PF$_6$)$_2$ | $4.0 \times 10^{-10}$       | 12                      |
| D-PPD(PF$_6$)$_4$ | $2.8 \times 10^{-10}$       | 17                      |
| T(PF$_6$)$_8$     | $1.8 \times 10^{-10}$       | 25                      |
References for the Supporting Information

S1. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112–122.
S2. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3–8.
S3. (a) K. Wakita, *Yadokari-XG, Software for Crystal Structure Analyses*, 2001; (b) C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218–224.
S4. T. Nakamura, H. Kimura, T. Okuhara, M. Yamamura and T. Nabeshima, *J. Am. Chem. Soc.*, 2016, **138**, 794–797.
S5. J. E. Nunez, T.-A. V. Khuong, L. M. Campos, N. Farfan, H. Dang, S. D. Karlen and M. A. Garcia-Garibay, *Cryst. Growth Des.*, 2006, **6**, 866–873.
S6. S. T. Bowden, *J. Chem. Soc.*, 1957, 4235–4239.
S7. W. B. Austin, N. Bilow, W. J. Kelleghan and K. S. Y. Lau, *J. Org. Chem.*, 1981, **46**, 2280–2286.
S8. (a) U. Mayer, V. Gutmann and W. Gerger, *Monatsh. Chem.*, 1975, **106**, 1235–1257; (b) F. Cataldo, *Eur. Chem. Bull.*, 2015, **4**, 92–97; (c) C. M. Hansen, *Hansen Solubility Parameters: A User’s Handbook, 2nd ed.*; CRC Press LLC: Boca Raton, Florida, USA, 2007.