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Synthesis and Characterization of Ferrocene Based Hemicages

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Supporting Information Placeholder

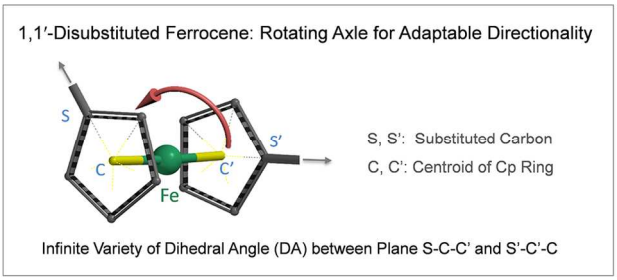
ABSTRACT: We present a series of tripodal ligands **L1-3**, which fold into hemicages **C1-3** by using coordination-driven dynamic combinational chemistry. The identities of these hemicages were characterized using ^{1}H NMR, ^{1}H-^{1}H COSY, DOSY, and ESI-TWIM-MS. Free rotation of the ferrocene structural units in the ligands affords an adaptable directionality, which is essential for the construction of these hemicages. Encapsulation of adamantane by **C2** indicates the presence of a well-defined inner cavity as the binding pocket.

Metal-organic cages (MOCs) have attracted considerable interests for their potential utilizations in fields such as molecular recognition,[1-7] catalysis in small space,[8-13] and stabilization of reactive species.[14-17] Construction of such discrete MOCs relies on directional bonding interactions encoded in their building blocks,[18-24] and matching of the geometry requirements for different structural subunits is crucial for the successful delivery of a specific target MOC.[25-27] Metal-organic hemicage is a kind of MOC, which is prepared by assembling of metal ion with a multidentate ligand, normally in a 1:1 mole ratio.[28] For instance, Raymond and his coworkers have prepared a series of hemicages by assembling Fe^{3+} with the enterobactin or catecholate-based tripodal ligands.[29-34] Over the years, various tripodal ligands, derived from 8-hydroxyquinoline,[35] 2-phenylpyridine,[36,37] and 2,2′-bipyridine[38-43] had been utilized to build metal-organic hemicages. However, most of these ligands use highly flexible linkers to provide the desired angularity in favor of cage formation. Therefore, in these hemicages, it is difficult to generate a well-defined inner cavity, which is highly important for their applications.

Ferrocene (Fc) has been utilized as a key structural unit in different molecular systems for its reversible redox property.[44-47] In addition, free rotation about the Fc axle (Scheme 1) was utilized to facilitate dynamic response in molecular machines.[48-50] Specifically, the adaptable directionality of the Fc axle was employed for the construction of metal-organic macrocycles.[51] But, to the best of our knowledge, previous attempt to utilize the adaptable directionality of the Fc axle for the construction of MOCs was unsuccessful.[52]

Herein, we show that adaptable directionality from the Fc units can be utilized to build metal-organic hemicages with defined inner cavity. As shown in Figure 1, we designed three tripodal precursors **L1-3** incorporated with the Fc-axles. These precursors can fold into hemicages **C1-3** (Figure 1), in the presence of one equivalent of iron (Ⅱ) and three equivalents of 2-formylpyridine, using a coordination-driven dynamic combinational chemistry (DCC).[14,53] To satisfy the spatial arrangement of the octahedral coordination of iron (Ⅱ) as well as that of the trigonal bottom panels, the Fc-axle functions as an adaptable structural unit in the final hemicages **C1-3** by manifesting a dihedral angle (DA), ranging from ca. 54° to 86°. This approach is highly modular. Metal-organic hemicages of varied size and shape can be rationally designed and efficiently assembled. Study on guest encapsulation indicates a well-defined inner cavity present in the obtained metal-organic hemicages.

Scheme 1. Adaptable directionality of the 1,1′-disubstituted ferrocene unit.



The synthesis and characterization of precursors **L1-3** are described in the Experimental Section. To demonstrate the feasibility of this approach, hemicage **C1** was synthesized using Nitschke's DCC condition (Figure 1).[14,53] Upon addition of 1.0 equivalent of iron (Ⅱ) tetrafluoroborate to a mixture of **L1** and 2-formylpyridine (3.0 equivalents), the color of the solution immediately turns from yellow to deep burgundy (Figure 1B, inset), indicating the formation of an iron complex.

In the ^{1}H NMR spectrum, typical resonance signals of the iron (Ⅱ)–iminopyridine complexes,[54] at 5.15 and 5.40 ppm, assigned to the aromatic protons H^f and H^h (Figure 2A) in the ortho-position of the imine substituent, were observed. These two protons undergo a significant upfield shift, due to strong shielding effect from the adjacent phenyl rings in the octahedral iron (Ⅱ) coordination unit.[54] Moreover, a group of eight well-resolved resonance signals, assigned to the cyclopentadienyl protons of the Fc-axle unit, appears in the spectrum.[55] This spectral feature is in sharp contrast to the corresponding tetrad resonance signals for the Fc-axle unit in precursor **L1** (Figure 2A, inset). Apparently,

restricted rotation of the Fc-unit in **C1** results in a magnetic inequivalence, which is not observed in **L1** with the free-rotating Fc-unit. All the signals can be assigned using a combination of ^{1}H NMR, ^{1}H-^{1}H correlation spectroscopy (COSY) and ^{1}H-^{1}H rotating-frame Overhauser spectroscopy (ROESY) (Figure S2-5).

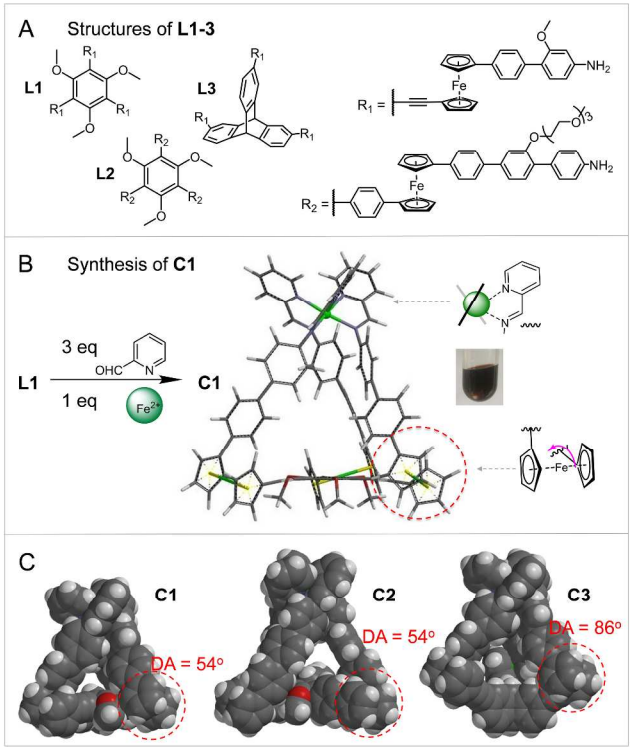


Figure 1. Molecular structures of the tripodal precursors **L1-3** (A), representative preparation of hemicage (B), and the molecular models of **C1-3** (C). The octahedral iron (□)–iminopyridine coordination center, the ferrocene moiety, and the visualized image of a solution of **C1** are shown beside the synthetic scheme (B). Molecular models are optimized with molecular mechanics using SPARTAN software. Methoxy group or the triethylene glycol monomethyl ether chains, appended on the phenylene edge of the cage, and counterions are omitted for clarity. Note, in **C1-3**, both the octahedral vertices and the ferrocene moiety are chiral, and only the low-energy isomer of each hemicage is presented.

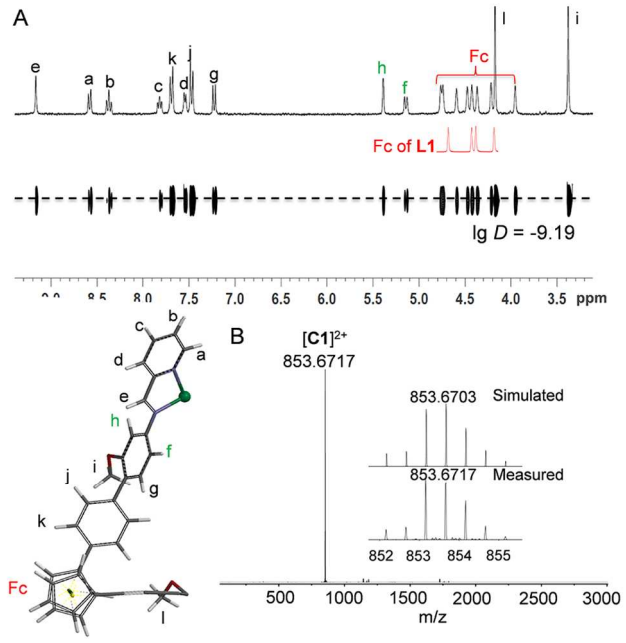


Figure 2. ^{1}H DOSY (300 MHz, CD_3CN, 293 K) spectrum (A) and ESI-TOF mass spectrum (B) of **C1**. Protons are indicated on a partial stick model of **C1**. Inset of (A), the ^{1}H NMR spectrum of the ferrocene part of **L1**. Inset of (B), the measured mass spectrum of $[\mathbf{C1}]^{2+}$ and the simulated spectrum.

All signals in the ^{1}H diffusion ordered spectroscopy (DOSY) share a common diffusion coefficient, which indicates the formation of only one discrete species (Figure 2A, for full DOSY NMR spectrum, see Figure S6). A hydrodynamic radius of 9.2 Å, derived from the diffusion coefficient (D, 6.46 × 10^{-10} m^2s^{-1}) in CD_3CN, is consistent with the computed molecular model (Figure S1). High-resolution electrospray ionization mass spectrometry (ESI-MS) reveals a clean ionic species of $[\mathbf{C1}]^{2+}$ (HRMS (ESI-TOF) m/z: $[\mathbf{C1}]^{2+}$ Calcd. for $C_{102}H_{78}Fe_4N_6O_6$ 853.6703; Found 853.6717, Figure 2B and S7). The isotopic pattern matches that of the theoretical one. All these data support an efficient synthesis of **C1**, in which the Fc-axle functions as a ca. 54° corner, as indicated by the molecular model (Figure 1C).

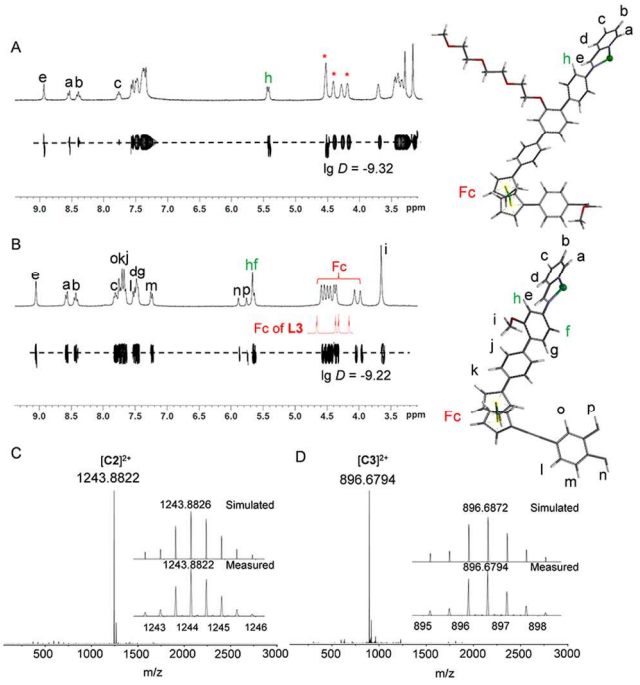


Figure 3. Partial ^{1}H-NMR spectra (300 MHz, CD_3CN, 293 K) of **C2** (A) and **C3** (B). Protons from the Fc-axle are marked with asterisks (A). ESI-MS data of **C2** (C) (HRMS (ESI-TOF) m/z: $[\mathbf{C2}]^{2+}$ Calcd. for $C_{150}H_{138}Fe_4N_6O_{15}$ 1243.8826; Found 1243.8822) and **C3** (D) (HRMS (ESI-TOF) m/z: $[\mathbf{C3}]^{2+}$ Calcd. for $C_{174}H_{150}Fe_4N_6O_{15}$ 896.6872; Found 896.6794) are consistent with the theoretical values.

We then tested the modularity of this approach by changing the size and shape of the target hemicages. As shown in Figure 1A, the edge of the precursor was extended from two phenylene rings, in **L1**, to three phenylene rings in **L2**. The bottom panel in the precursor was also extended, concurrently, to meet the structural requirement. These variations are expected to result in an enlarged hemicage **C2** (Figure 1C). In addition, precursor **L3** was designed, which uses triptycene as the bottom panel (Figure 1A). Molecular modeling study reveals that the Fc-axle would accommodate the cage formation by manifesting a DA of around 54° for **C2**, and 86° for **C3**, respectively (Figure 1C).

Despite a significant change in the structure of the precursor, **L2** and **L3** assemble into hemicage **C2** and **C3** in a highly efficient manner. In situ ^{1}H NMR spectra demonstrated that **C2** and **C3** were formed quantitatively, after subjecting the precursors to a mixture of iron and 2-formylpyridine (precursor/Fe^{2+}/2-formylpyridine, 1/1/3, mole ratio). Spectroscopic analysis, using a combination of ^{1}H NMR, ^{1}H-^{1}H COSY, DOSY, and ESI-MS,

confirmed the structure of hemicages **C2** (Figure 3A, 3C and S10-14) and **C3** (Figure 3B, 3D and S17-21). The D value of **C1** (6.46 × 10^{-10} m^2s^{-1}) and **C3** (6.03 × 10^{-10} m^2s^{-1}) are larger than that of **C2** (4.90 × 10^{-10} m^2s^{-1}), which is consistent with the size of these hemicages (Figure S1, S9 and S16).

C1-3 were further analyzed using electrospray ionization traveling wave ion mobility mass spectrometry (ESI-TWIM-MS), in which the drift time of the sample is dependent on the average collision cross-section (CCS).[56] As shown in Figure 4, the drift times of these cages were found to be 9.4 (**C1**), 14.8 (**C2**), and 10.8 ms (**C3**), respectively (Figure S8, S15 and S22). The corresponding CCS values (**C1**, 336.2 Å^2, **C2**, 444.2 Å^2, **C3**, 364.7 Å^2), derived from the drift times, are highly consistent with the theoretical ones (Mobcal TM: 322.1 ± 5.8 Å^2, 437.3 ± 15.3 Å^2, and 363.0 ± 6.2 Å^2 for **C1**, **C2,** and **C3**, respectively, See Table S1-3). We also tried different conditions to grow single crystals to characterize these hemicages by X-ray analysis, but unfortunately, these endeavors were failed.

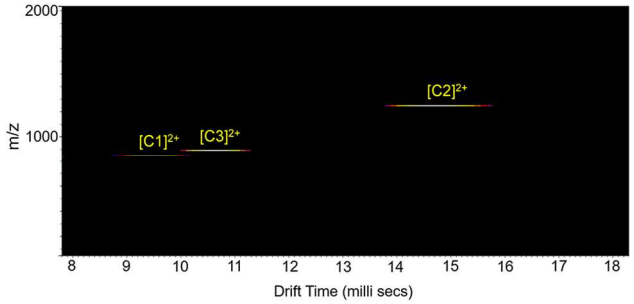


Figure 4. ESI-TWIM-MS plot of **C1-3** (A-C).

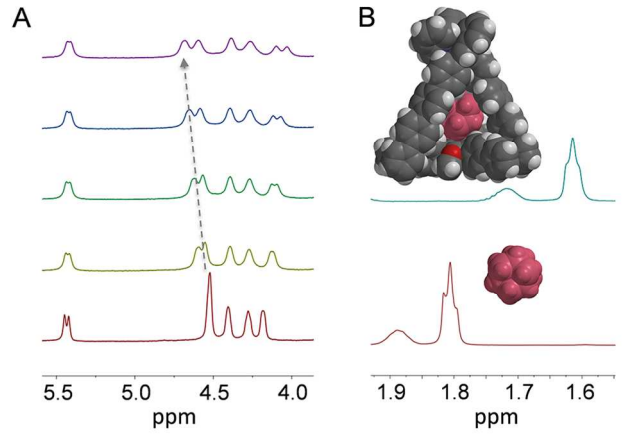


Figure 5. (A) Partial ^{1}H NMR spectral changes of **C2** (2.0 mM, 500 μL) upon addition of adamantane from 0 to 16 mM (300 MHz, CD_3CN, 293 K). (B) The adamantane resonance signals shift to upfield upon encapsulation, inset: models of adamantane and its complex with **C2**.

To prove that the hemicage obtained has a well-defined inner cavity, we carried out an encapsulation study (Figure 5). Molecular modeling indicates that **C2** has an inner cavity which may bind adamantane, a pseudo-spherical guest (Figure 5B, inset). This expectation is proven by the experimental observation that the resonance signals of adamantane undergo an evident shift to high field, from 1.78 to 1.63 ppm, in the present of 1.4 equivalent **C2** (Figure 5B). We attribute this spectral change to a shielding effect resulting from host-guest encapsulation. An association constant K_a of 320 ± 30 M^{-1} is determined by fitting the titration curve (Figure S24).

In conclusion, we have demonstrated that Fc-axle could accommodate the construction of hemicages **C1-3** by providing adaptable directionality. The structure of the obtained hemicages were confirmed using ^{1}H NMR, ^{1}H-^{1}H COSY, DOSY, and ESI-TWIM-MS. Host-guest complexation with adamantane suggests that **C2** has a well-defined inner cavity. In principle, Fc-axle can provide on-demand directionality without inducing structural strains, greatly expanding the potential combinations of various structural units for building MOCs with more sophisticated functions, such as molecular recognition and catalysis in a confined small space. Moreover, given the pivotal roles that macroscopic axles play in various dynamic structures, axle units, in the molecular scale, are expected to be utilized in the construction of MOCs featuring stimulus responsive structures and properties.

EXPERIMENTAL SECTION

All chemicals and solvents were purchased from commercial sources, and used without further purification unless otherwise noted. Compounds below were synthesized according to literatures: 1,1′-diiodoferrocene,[57] 1,1′-dibromoferrocene,[57] 1-iodo-1′-(trimethylsilylethynyl)ferrocene (**1a**),[58] triptycene,[59] 1,3,5-triiodo-2,4,6-trimethoxybenzene (**5a**),[60] 1-iodo-2-methoxy-4-nitrobenzene (**7a**),[61] 2,7,14-triiodotriptycene (**1c**),[62] triethyleneglycol monomethyl ether tosylate.[63] Et_2O and THF were purified by distillation from Na/benzophenone under a nitrogen atmosphere. Et_3N was dried with KOH powder overnight prior to use. All reactions were performed using either standard Schlenk technique or in a glove box with dry solvents under nitrogen atmosphere. Column chromatography was carried out using silica gel (200-300 mesh). ^{1}H NMR (300 MHz), ^{13}C{^{1}H} NMR (75 MHz), ^{1}H-^{1}H COSY, ^{1}H-^{1}H ROESY, and ^{1}H DOSY spectra were recorded in $CDCl_3$, CD_2Cl_2 or CD_3CN on a Bruker AVANCE III-300 spectrometer (TOPSPIN 3.2 software version). Chemical shifts (δ) were given in parts per million (ppm) using the residual solvent peaks as internal standards: $CHCl_3$ (δ 7.26 ppm) or CHD_2CN (δ 1.94 ppm) for ^{1}H NMR; $CDCl_3$ (δ 77.16 ppm) or CD_3CN (δ 118.26 ppm) for ^{13}C{^{1}H} NMR. The coupling constants (J) were reported as Hertz (Hz). Splitting patterns are shown as s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), and br (broad signal). Melting points (mp) were measured on a YUHUA X-5 micro-melting point apparatus without correction.

Diffusion Ordered Spectroscopy (DOSY) Experiments. The DOSY experiments were acquired using the standard Bruker pulse program ledbpgp2s (2D LED experiment using bipolar gradients). DOSY spectra were processed using the Bruker Topspin software (version 3.2). Assuming that the cage is a spherical molecule, the diffusion coefficient D is described using the Stokes-Einstein equation

$$D = \frac{kT}{6\pi\eta r_H}$$

where k is the Boltzmann constant, T is the temperature, η is the viscosity of the solvent and r_H is the hydrodynamic radius.

Mass Spectrometry and Traveling Wave Ion-Mobility Experiments. Low-resolution electrospray ionization mass spectra (LRMS-ESI) were obtained using TSQ Quantum Ultra mass spectrometer (Thermofisher). Electron ionization (EI) mass spectra were obtained on a DSQ mass spectrometer (Thermofisher). High-resolution electrospray ionisation mass spectra (HRMS-ESI) were obtained on either a Bruker maXis 4G (electrospray ionization time-of-flight mass spectrometry, ESI-TOF-MS), or a LTQ Orbitrap Elite (Thermofisher) spectrometer.

HR-MS and traveling wave ion-mobility (TWIM) experiments of the cages were conducted on a Waters Synapt HDMS G2 with a LockSpray ESI source, using the same measurement conditions in the literature.[64] The experimental collision cross-sections (CCSs) and molecular modeling were obtained according to the literature.[64,65]

General Procedure for the Suzuki-Miyaura Coupling.[66] A mixture of halogenated reactant, 1.2-1.5 equivalents of the corresponding boronic acid pinacol ester, Pd catalyst (3-5 mol %) and 3 equivalents of base in toluene/MeOH = 3:1 (v/v) solution was refluxed for the appropriate time under a nitrogen atmosphere. The reaction was monitored by thin layer chromatography. The reaction mixture was then allowed to cool to 25 °C and filtered through Celite with CH_2Cl_2 as eluent. Then the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel.

General Procedure for the Sonogashira Coupling.[67] A mixture of aryl halide, 1.2-1.5 equivalents of the corresponding terminal alkyne, Pd catalyst (3-5 mol %), and CuI (6-10 mol %) in Et_3N solution was refluxed for the appropriate time under a nitrogen atmosphere, and the reaction was monitored by thin layer chromatography. The reaction mixture was then allowed to cool to 25 °C and filtered through Celite with CH_2Cl_2 as eluent. Then the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel.

Synthesis of C1 (Scheme S1)**.**

*Synthesis of **2a***.[68] In a 100 mL Schlenk flask, a THF (60 mL) solution of **1a** (2.13 g, 5.22 mmol) was stirred at -78 °C for 15 min. Then *n*-BuLi (4.3 mL, 6.88 mmol, 1.6 M in *n*-hexane) was added and the mixture was stirred for 30 min at -78 °C. After warming to 0 °C, anhydrous zinc chloride (1.00 g, 7.35 mmol) in 10 mL THF was added and the solution was stirred at 0 °C for 120 min. Then the pre-reduced $Pd(PPh_3)_2Cl_2$ (294 mg, 0.42 mmol) with DIBAL-H (600 μL, 0.90 mmol, 1.5 M in toluene) in 10 mL THF and the 1-bromo-4-iodobenzene (1.92 g, 6.78 mmol) in 10 mL THF were added sequentially. The resulting mixture was stirred at 70 °C for 17 h. The mixture was cooled to 25 °C. Dilute aqueous NaOH and CH_2Cl_2 were added and the organic phase was separated, washed with water, dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, petroleum ether/ CH_2Cl_2, 15:1, v/v, $R_f \approx 0.3$) to afford a red-brown solid (1.17 g, yield 51%). mp 102.2 – 104.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.41 (s, 4H), 4.55 (s, 2H), 4.37 (s, 2H), 4.20 (s, 2H), 4.08 (s, 2H), 0.24 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 137.7, 131.6, 128.0, 119.9, 103.7, 91.3, 85.5, 73.8, 71.3, 70.4, 69.0, 66.0, 0.4. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd. for $C_{21}H_{21}BrFeSi$ 435.9942 and 437.9920; Found 435.9946 and 437.9925.

*Synthesis of **3a***. In a 50 mL Schlenk flask, **2a** (1.16 g, 2.65 mmol) was dissolved in 15 mL THF and the solution was cooled to -78 °C. *n*-BuLi (2.2 mL, 3.52 mmol, 1.6 M in *n*-hexane) was added dropwise. After 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (900 μL, 4.41 mmol) was added. The mixture was stirred at -78 °C for 4 h, then warmed to 25 °C and further stirred overnight. The reaction mixture was quenched with water and filtered through Celite with CH_2Cl_2 as eluent. The organic layer was dried over anh. Na_2SO_4 and evaporated. The residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether 1/5 ($R_f \approx 0.4$) to 3/2, v/v) to afford the product (820 mg, yield 63%) as a yellow solid. mp 91.6 – 94.4 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.75 (d, *J* = 7.8 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 4.63 (s, 2H), 4.38 (s, 2H), 4.19 (s, 2H), 4.05 (s, 2H), 1.36 (s, 12H), 0.24 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 141.8, 135.0, 125.7, 103.8, 91.1, 86.2, 83.8, 73.8, 71.4, 70.5, 69.2, 65.8, 25.0, 0.4. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd. for $C_{27}H_{33}BFeO_2Si$ 484.1692; Found 484.1711.

*Synthesis of **4a***. A mixture of **3a** (2.0 g, 4.13 mmol) and K_2CO_3 (1.14 g, 8.25 mmol) in THF (20 mL) and MeOH (50 mL) was stirred at 25 °C overnight. Then the reaction mixture was filtered through a pad of Celite with CH_2Cl_2 as eluent, and the filtrate was concentrated in vacuo. The crude residue was purified by flash chromatography (silica gel, CH_2Cl_2/petroleum ether 1/3, v/v, $R_f \approx 0.25$) to afford **4a** (1.29 g, yield 76%) as a yellow solid. mp 126.8 – 130.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.75 (d, *J* = 8.2 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 4.73 – 4.66 (m, 2H), 4.42 – 4.36 (m, 2H), 4.27 – 4.20 (m, 2H), 4.08 – 4.02 (m, 2H), 2.67 (s, 1H), 1.36 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 141.5, 135.0, 125.6, 86.1, 83.8, 82.1, 74.2, 73.6, 71.5, 70.7, 68.7, 64.9, 25.0. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd. for $C_{24}H_{25}BFeO_2$ 412.1296; Found 412.1304.

*Synthesis of **6a***. Following the general procedure of Sonogashira coupling, a mixture of 1,3,5-triiodo-2,4,6-trimethoxybenzene **5a** (300 mg, 0.55 mmol), **4a** (780 mg, 1.89 mmol), $Pd(PPh_3)_2Cl_2$ (150 mg, 0.21 mmol), CuI (75 mg, 0.39 mmol), and Et_3N (50 mL) was refluxed for 22 h. The residue was purified by column chromatography (silica gel, EtOAc/petroleum ether 1/8, v/v, $R_f \approx 0.2$) to afford **6a** (331 mg, yield 43%) as a red-brown solid. mp 113.1 – 116.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.74 (d, *J* = 8.2 Hz, 6H), 7.55 (d, *J* = 8.1 Hz, 6H), 4.75 (pseudo-t, *J* = 1.9 Hz, 6H), 4.48 (pseudo-t, *J* = 1.9 Hz, 6H), 4.35 (pseudo-t, *J* = 1.9 Hz, 6H), 4.13 (s, 9H), 4.11 (pseudo-t, *J* = 1.9 Hz, 6H), 1.34 (s, 36H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 163.0, 141.9, 135.0, 125.7, 108.5, 96.0, 86.2, 83.8, 77.5, 73.2, 71.7, 71.1, 68.8, 66.4, 61.4, 25.0. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd. for $C_{81}H_{81}B_3Fe_3O_9$ 1398.4241; Found 1398.4227.

*Synthesis of **8a***. Following the general procedure of Suzuki-Miyaura coupling, a mixture of **6a** (331 mg, 0.24 mmol), 1-iodo-2-methoxy-4-nitrobenzene **7a** (290 mg, 1.04 mmol), $Pd(PPh_3)_4$ (110 mg, 0.095 mmol), K_2CO_3 (690 mg, 5.00 mmol), toluene (36 mL) and MeOH (12 mL) was refluxed overnight. The residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether 4/1, v/v, $R_f \approx 0.5$) to afford **8a** (330 mg, yield 95%) as a brick red solid. mp 117.1 – 118.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.87 (dd, *J* = 8.4, 2.2 Hz, 3H), 7.77 (d, *J* = 2.2 Hz, 3H), 7.60 (d, *J* = 8.3 Hz, 6H), 7.46 (d, *J* = 8.3 Hz, 6H), 7.40 (d, *J* = 8.4 Hz, 3H), 4.69 (pseudo-t, *J* = 1.9 Hz, 6H), 4.45 (pseudo-t, *J* = 1.9 Hz, 6H), 4.35 (pseudo-t, *J* = 1.9 Hz, 6H), 4.22 (pseudo-t, *J* = 1.9 Hz, 6H), 4.06 (s, 9H), 3.88 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.7, 156.8, 147.8, 138.7, 137.2, 134.2, 130.8, 129.6, 126.4, 116.3, 108.5, 106.3, 96.1, 86.4, 77.7, 73.3, 71.2, 70.7, 68.9, 66.5, 61.3, 56.2. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd. for $C_{84}H_{63}Fe_3N_3O_{12}$ 1473.2464; Found 1473.2478.

*Synthesis of **L1***. To a 100 mL Schlenk flask were added **8a** (261 mg, 0.176 mmol), $SnCl_2 \cdot 2H_2O$ (1.78 g, 7.89 mmol), THF (50 mL) and MeOH (15 mL). The mixture was stirred at 65 °C for 12 h. The reaction mixture was neutralized by $NaHCO_3$ (aq) and extracted with CH_2Cl_2. The organic layer was dried over anh. Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc 100/3, v/v, $R_f \approx 0.2$) to afford **L1** (242 mg, yield 99%) as an orange-red solid. mp 115.0 – 117.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.54 (d, *J* = 8.2 Hz, 6H), 7.43 (d, *J* = 8.1 Hz, 6H), 7.12 (d, *J* = 8.0 Hz, 3H), 6.34 (d, *J* = 8.0 Hz, 3H), 6.31 (s, 3H), 4.67 (s, 6H), 4.42 (s, 6H), 4.37 (s, 6H), 4.18 (s, 6H), 4.10 (s, 9H), 3.77 (s, 9H), 3.70 (s, 6H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 163.3, 158.0, 148.1, 137.5,

136.3, 131.7, 129.8, 126.5, 120.9, 109.1, 107.8, 99.1, 96.6, 87.7, 78.0, 73.5, 71.5, 71.3, 69.0, 66.6, 61.8, 55.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{84}H_{70}Fe_3N_3O_6$ 1384.3317; Found 1384.3220.

*Synthesis of **C1***. In a 25 mL Schlenk tube, to a $CHCl_3$ solution (1000 µL) of **L1** (21.55 mg, 0.0147 mmol), 2-pyridinecarboxaldehyde (5.2 mg, 0.0486 mmol) in 460 µL $CHCl_3$ was added. After stirring for 3 minutes, an MeCN solution (1500 µL) of iron (II) tetrafluoroborate hexahydrate (5.75 mg, 0.0170 mmol) was added. The reaction mixture was stirred at 50 °C for 8 h. After cooling to 25 °C, Et_2O (30 mL) was added to the reaction mixture. The resulted flocculent precipitate was collected by centrifugation, washed three times with Et_2O (3 × 20 mL) and dried in vacuo to afford the product (20.0 mg, yield 69%) as a black brown solid. ^{1}H NMR (300 MHz, CD_3CN) δ 9.16 (s, 3H), 8.58 (d, *J* = 7.7 Hz, 3H), 8.37 (t, *J* = 7.7 Hz, 3H), 7.82 (t, *J* = 6.7 Hz, 3H), 7.69 (d, *J* = 8.1 Hz, 6H), 7.54 (d, *J* = 5.6 Hz, 3H), 7.47 (d, *J* = 8.1 Hz, 6H), 7.23 (d, *J* = 8.1 Hz, 3H), 5.39 (d, *J* = 1.9 Hz, 3H), 5.14 (d, *J* = 7.9 Hz, 3H), 4.76 (s, 3H), 4.74 (s, 3H), 4.59 (s, 3H), 4.47 (s, 3H), 4.43 (s, 3H), 4.37 (s, 3H), 4.22 (s, 3H), 4.17 (s, 9H), 3.95 (s, 3H), 3.38 (s, 9H). HRMS (ESI-TOF) m/z: $[M]^{2+}$ Calcd. for $C_{102}H_{78}Fe_4N_6O_6$ 853.6703; Found 853.6717,

*In situ synthesis of **C1***. To a 4 mL glass bottle, **L1** (1.38 mg, 1.00 µmol) and then 2-pyridine-carboxaldehyde (0.33 mg, 3.05 µmol) in 150 µL $CDCl_3$ were added. After stirring for 3 minutes, a CD_3CN solution (450 µL) of iron (II) tetrafluoroborate hexahydrate (0.37 mg, 1.10 µmol) was added. The reaction mixture was stirred at 25 °C for 10 h. The deep burgundy solution was used for the NMR experiments.

Synthesis of C2 (Scheme S2)**.**

*5-Bromo-2-iodo-phenol (**2b**).* A 2 M solution of boron tribromide in CH_2Cl_2 (9.6 mL, 19.2 mmol) was added dropwise to 4-bromo-1-iodo-2-methoxybenzene (3.0 g, 9.59 mmol) in CH_2Cl_2 (100 ml) at -78 °C. The resulting mixture was stirred at -78 °C for 2 h, then allowed to warm to 25 °C, and stirred overnight. The reaction was then quenched by pouring in ice bath with caution. The organic phase was extracted with water (2 × 200 mL), brine (100 mL), dried over anh. Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether 1/5, v/v, $R_f \approx 0.2$) to afford **2b** (2.15 g, yield 75%) as a white solid. mp 57.1 – 58.1 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.50 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 2.2 Hz, 1H), 6.83 (dd, *J* = 8.4, 2.2 Hz, 1H), 5.32 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 155.7, 139.1, 125.8, 123.6, 118.6, 84.1. The characterization data were in agreement with the data previously reported.[69]

*4-Bromo-1-iodo-2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (**3b**).* A mixture of 5-bromo-2-iodophenol (1.69 g, 5.65 mmol), 2-(2-(2-methoxyethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (5.4 g, 16.98 mmol), K_2CO_3 (2.34 g, 16.96 mmol), NaI (117 mg, 0.78 mmol), and butanone (50 mL) was refluxed for 17 h. The reaction mixture was filtered through a pad of Celite with CH_2Cl_2 as eluent and evaporated to dryness. The residue was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc 10/1, v/v, $R_f \approx 0.5$) to afford **3b** (1.14 g, yield 45%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.59 (d, *J* = 8.3 Hz, 1H), 6.96 (d, *J* = 2.0 Hz, 1H), 6.85 (dd, *J* = 8.3, 2.0 Hz, 1H), 4.21 – 4.10 (m, 2H), 3.97 – 3.86 (m, 2H), 3.84 – 3.76 (m, 2H), 3.71 – 3.62 (m, 4H), 3.58 – 3.50 (m, 2H), 3.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 158.4, 140.3, 125.9, 122.9, 116.0, 85.0, 72.1, 71.4, 70.9, 70.7, 69.6, 69.5, 59.2. HRMS (ESI-TOF) m/z: $[M+K]^+$ Calcd. for $C_{13}H_{18}BrIO_4K$ 482.9065 and 484.9045; Found 482.9087 and 484.9068.

*4'-Bromo-2'-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-[1,1'-biphenyl]-4-amine (**4b**).* Following the general procedure of Suzuki-Miyaura coupling, a mixture of **3b** (2.33 g, 5.24 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (1.5 g, 6.9 mmol), $Pd(PPh_3)_4$ (300 mg, 0.26 mmol), K_2CO_3 (2.16 g, 15.65 mmol), toluene (80 mL), and MeOH (20 mL) was refluxed overnight. The residue was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc 5/1, v/v, $R_f \approx 0.3$) to afford **4b** (1.35 g, yield 63%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.35 (d, *J* = 8.4 Hz, 2H), 7.19 – 7.06 (m, 3H), 6.70 (d, *J* = 8.5 Hz, 2H), 4.09 (t, *J* = 4.8 Hz, 2H), 3.78 (t, *J* = 4.9 Hz, 2H), 3.67 – 3.58 (m, 6H), 3.57 – 3.50 (m, 2H), 3.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 156.5, 145.7, 131.5, 130.5, 130.2, 127.7, 124.3, 120.7, 116.5, 114.8, 72.1, 71.0, 70.8, 70.7, 69.7, 68.6, 59.2. LRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. 410.1; Found 410.1.

*1,1'-Bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ferrocene (**5b**).* In a 100 mL Schlenk flask, 1,1'-di(4-bromophenyl)ferrocene (2.0 g, 4.03 mmol) was dissolved in 50 mL dry THF, then *n*-BuLi (4.8 mL, 12 mmol, 2.5 M in *n*-hexane) was added dropwise at -78 °C. The solution was stirred at -78 °C for 1 h. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.7 mL, 13.2 mmol) was added, and the solution was stirred for additional 4 h at -78 °C. After that, the resulting mixture was warmed to 25 °C and stirred overnight. The reaction was quenched with water and filtered through a pad of Celite with CH_2Cl_2 as eluent, then extracted with CH_2Cl_2. The organic layer was dried over anh. Na_2SO_4 and evaporated. The residue was purified by column chromatography (silica gel, CH_2Cl_2 / petroleum ether, 2/3 ($R_f \approx 0.17$) to 1/1, v/v) to afford **5b** (1.6 g, 67%) as a brick red solid. mp 163.7 – 165.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.71 (d, *J* = 8.0 Hz, 4H), 7.37 (d, *J* = 8.1 Hz, 4H), 4.45 (pseudo-t, *J* = 1.9 Hz, 4H), 4.20 (pseudo-t, *J* = 1.9 Hz, 4H), 1.37 (s, 24H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 142.1, 134.9, 125.4, 85.5, 83.8, 71.2, 68.6, 25.1. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd. for $C_{34}H_{40}B_2FeO_4$ 590.2469; Found 590.2500.

*Synthesis of **6b***. Following the general procedure of Suzuki-Miyaura coupling, a mixture of **4b** (957 mg, 2.33 mmol), **5b** (2.75 g, 4.66 mmol), $Pd(PPh_3)_4$ (135 mg, 0.117 mmol), K_2CO_3 (1000 mg, 7.25 mmol), toluene (50 mL), and MeOH (18 mL) was refluxed overnight. The residue was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc 4/1, v/v, $R_f \approx 0.4$) to afford **6b** (1.0 g, yield 54%) as a brick red oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.67 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 4H), 7.42 – 7.32 (m, 5H), 7.29 (d, *J* = 1.6 Hz, 1H), 7.20 (d, *J* = 1.7 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 2H), 4.53 (pseudo-t, *J* = 1.9 Hz, 2H), 4.49 (pseudo-t, *J* = 1.8 Hz, 2H), 4.30 – 4.18 (m, 6H), 3.84 (t, *J* = 4.9 Hz, 2H), 3.72 – 3.60 (m, 6H), 3.57 – 3.49 (m, 2H), 3.37 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 156.1, 145.5, 141.8, 140.8, 138.5, 137.5, 134.9, 130.8, 130.6, 130.0, 128.6, 127.0, 126.4, 125.4, 119.9, 114.8, 111.7, 85.8, 85.6, 83.8, 72.1, 71., 71.0, 70.9, 70.9, 70.7, 69.9, 68.5, 68.3, 68.2, 59.2, 25.0. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd. for $C_{47}H_{52}BFeNO_6$ 793.3240; Found 793.3264.

*Synthesis of **L2***. Following the general procedure of Suzuki-Miyaura coupling, a mixture of **6b** (358 mg, 0.45 mmol), **5a** (70 mg, 0.13 mmol), $Pd(PPh_3)_4$ (31 mg, 0.026 mmol), K_2CO_3 (108 mg, 0.78 mmol), toluene (18 mL), and MeOH (6 mL) was refluxed overnight. The residue was purified by column chromatography (silica gel, CH_2Cl_2/MeOH 80/1, v/v, $R_f \approx 0.2$) to afford **L2** (110 mg, yield 39%) as an orange-red solid. mp 75.1 – 75.9 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.56 – 7.40 (m, 30H), 7.38

(d, *J* = 7.9 Hz, 3H), 7.30 – 7.24 (m, 3H), 7.20 (d, *J* =1.7 Hz, 3H), 6.73 (d, *J* = 8.4 Hz, 6H), 4.54 (pseudo-t, *J* = 1.9 Hz, 6H), 4.49 (pseudo-t, *J* = 1.9 Hz, 6H), 4.29 – 4.16 (m, 18H), 3.81 (t, *J* = 4.9 Hz, 6H), 3.72 – 3.58 (m, 18H), 3.56 – 3.47 (m, 6H), 3.36 (s, 9H), 3.22 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 156.2, 156.0, 145.5, 140.7, 138.6, 138.1, 137.4, 132.1, 130.9, 130.7, 130.7, 130.1, 128.5, 127.0, 126.6, 126.0, 125.7, 119.9, 114.8, 111.8, 85.9, 85.7, 72.1, 71.1, 71.1, 71.0, 70.9, 70.7, 69.9, 68.6, 68.4, 68.3, 60.7, 59.2. HRMS (ESI-TOF) m/z: $[M+2Na]^{3+}$ Calcd. for $C_{132}H_{129}Fe_3N_3O_{15}Na_2$ 736.9097; Found 736.9107.

*Synthesis of **C2***. In a 25 mL Schlenk tube, to a $CHCl_3$ solution (1500 μL) of **L2** (30.40 mg, 0.014 mmol), 2-pyridinecarboxaldehyde (4.96 mg, 0.046 mmol) in 500 μL $CHCl_3$ was added. After stirring for 3 minutes, an MeCN solution (2000 μL) of iron (II) tetrafluoroborate hexahydrate (6.16 mg, 0.018 mmol) was added. The reaction mixture was stirred at 50 °C for 8 h. After cooling to 25 °C, Et_2O (30 mL) was added to the reaction mixture. The resulted flocculent precipitate was collected by centrifugation, washed three times with Et_2O (3 × 20 mL) and dried in vacuo to afford the product (26.6 mg, yield 73%) as a black brown solid. ^{1}H NMR (300 MHz, CD_3CN) δ 8.95 (s, 3H), 8.56 (d, *J* = 7.7 Hz, 3H), 8.41 (t, *J* = 7.9 Hz, 3H), 7.77 (t, *J* = 6.6 Hz, 3H), 7.62 – 7.26 (m, 42H), 5.41 (d, *J* = 8.0 Hz, 6H), 4.49 (s, 12H), 4.38 (s, 6H), 4.25 (s, 6H), 4.15 (s, 6H), 3.66 (s, 6H), 3.46 – 3.17 (m, 33H), 3.12 (s, 9H). HRMS (ESI-TOF) m/z: $[M]^{2+}$ Calcd. for $C_{150}H_{138}Fe_4N_6O_{15}$ 1243.8826; Found 1243.8822.

*In situ synthesis of **C2***. To a 4 mL glass bottle, **L2** (2.16 mg, 1.00 μmol), and 2-pyridine-carboxaldehyde (0.33 mg, 3.05 μmol) in 150 μL $CDCl_3$ were added. After stirring for 3 minutes, a CD_3CN solution (450 μL) of iron (II) tetrafluoroborate hexahydrate (0.37 mg, 1.10 μmol) was added. The reaction mixture was stirred at 25 °C for 10 h. The deep burgundy solution was used for the NMR experiments.

Synthesis of C3 (Scheme S3)**.**

*Synthesis of **2c***. Following the general procedure of Sonogashira coupling, a mixture of **4a** (990 mg, 2.40 mmol), 2,7,14-triiodotriptycene **1c** (430 mg, 0.68 mmol), $Pd(PPh_3)_2Cl_2$ (180 mg, 0.26 mmol), CuI (90 mg, 0.47 mmol), and Et_3N (60 mL) was refluxed for 18 h. The residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether 3/2, v/v, $R_f \approx 0.4$) to afford **2c** (820 mg, yield 84%) as a red-brown solid. mp 169.6 – 172.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.75 (d, *J* = 7.7 Hz, 6H), 7.59 (s, 3H), 7.52 (d, *J* = 7.9 Hz, 6H), 7.37 (d, *J* = 7.6 Hz, 3H), 7.15 (d, *J* = 7.6 Hz, 3H), 5.51 (s, 1H), 5.44 (s, 1H), 4.67 (s, 6H), 4.39 (s, 6H), 4.24 (s, 6H), 4.08 (s, 6H), 1.37 (s, 36H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 144.8, 144.1, 141.9, 135.0, 128.8, 127.0, 125.6, 123.8, 121.1, 87.3, 86.4, 86.0, 83.9, 73.4, 71.5, 70.7, 68.9, 66.3, 53.8, 53.3, 25.1. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd. for $C_{92}H_{83}B_3Fe_3O_6$ 1484.4554; Found 1484.4543.

*Synthesis of **3c***. Following the general procedure of Suzuki-Miyaura coupling, a mixture of **2c** (445 mg, 0.31 mmol), 1-iodo-2-methoxy-4-nitrobenzene **7a** (312 mg, 1.12 mmol), $Pd(PPh_3)_4$ (72 mg, 0.06 mmol), K_2CO_3 (445 mg, 3.22 mmol), toluene (30 mL) and MeOH (10 mL) was refluxed overnight. The residue was purified by column chromatography (silica gel, CH_2Cl_2/petroleum ether 2/1, v/v, $R_f \approx 0.4$) to afford **3c** (434 mg, yield 90%) as a red-brown solid. mp 142.6 – 145.3 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.80 – 7.75 (m, 6H), 7.55 (d, *J* = 8.6 Hz, 6H), 7.41 (d, *J* = 8.5 Hz, 9H), 7.29 – 7.22 (m, 6H), 7.08 (dd, *J* = 7.6, 1.6 Hz, 3H), 5.34 (s, 1H), 5.23 (s, 1H), 4.68 (pseudo-t, *J* = 1.9 Hz, 6H), 4.41 (pseudo-t, *J* = 1.9 Hz, 6H), 4.32 (pseudo-t, *J* = 1.9 Hz, 6H), 4.17 (pseudo-t, *J* = 1.9 Hz, 6H), 3.85 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 156.8, 147.8, 144.6, 144.0, 138.4, 137.2, 134.0, 130.7, 129.5, 128.8, 126.6, 126.2, 123.7, 121.1, 116.2, 106.3, 87.2, 86.5, 86.2, 73.1, 71.1, 70.5, 68.6, 66.8, 56.2, 53.5, 53.5. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd. for $C_{95}H_{65}Fe_3N_3O_9$ 1560.2799; Found 1560.2833.

*Synthesis of **L3***. A mixture of **3c** (347 mg, 0.22 mmol), $SnCl_2 \cdot 2H_2O$ (2.8 g, 12.4 mmol), THF (60 mL), and MeOH (20 mL) was stirred at 65 °C for 12 h. After the reaction mixture had been neutralized by $NaHCO_3$ (aq) and extracted with CH_2Cl_2, the organic layer was dried over anh. Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc 100/3 to 100/10, v/v, $R_f \approx 0.3$) to afford **L3** (300 mg, yield 92%) as a yellow solid. mp 152.7 – 154.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.53 (d, *J* = 8.5 Hz, 6H), 7.44 (d, *J* = 8.5 Hz, 6H), 7.41 (d, *J* = 1.3 Hz, 3H), 7.31 (d, *J* = 7.6 Hz, 3H), 7.18 – 7.08 (m, 6H), 6.36 – 6.28 (m, 6H), 5.39 (s, 1H), 5.16 (s, 1H), 4.66 (pseudo-t, *J* = 1.9 Hz, 6H), 4.37 (pseudo-t, *J* = 1.9 Hz, 6H), 4.32 (pseudo-t, *J* = 1.9 Hz, 6H), 4.16 (pseudo-t, *J* = 1.9 Hz, 6H), 3.76 (s, 9H), 3.51 – 3.94 (br, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 157.6, 147.3, 144.7, 144.1, 136.7, 135.8, 131.5, 129.4, 128.8, 126.9, 126.1, 123.7, 121.1, 121.0, 107.7, 99.0, 87.4, 87.2, 86.5, 73.2, 70.8, 70.5, 68.6, 66.4, 55.6, 53.7, 53.3. HRMS (ESI-TOF) m/z: $[M]^+$ Calcd. for $C_{95}H_{71}Fe_3N_3O_3$ 1470.3573; Found 1470.3613.

*Synthesis of **C3***. In a 10 mL Schlenk tube, to a $CHCl_3$ solution (800 μL) of **L3** (16.10 mg, 0.011 mmol), 2-pyridinecarboxaldehyde (3.88 mg, 0.036 mmol) in 335 μL $CHCl_3$ was added. After stirring for 3 minutes, an MeCN solution (1150 μL) of iron (II) tetrafluoroborate hexahydrate (4.80 mg, 0.014 mmol) was added. The reaction mixture was stirred at 50 °C for 8 h. After cooling to 25 °C, Et_2O (30 mL) was added to the reaction mixture. The resulted flocculent precipitate was collected by centrifugation, washed three times with Et_2O (3 × 20 mL) and dried in vacuo to afford the product (15.3 mg, yield 74%) as a black brown solid. ^{1}H NMR (300 MHz, CD_3CN) δ 9.03 (s, 3H), 8.55 (d, *J* = 7.4 Hz, 3H), 8.41 (t, *J* = 7.7 Hz, 3H), 7.91 – 7.56 (m, 18H), 7.55 – 7.37 (m, 9H), 7.23 (d, *J* = 7.6 Hz, 3H), 5.86 (s, 1H), 5.74 (s, 1H), 5.63 (d, *J* = 8.7 Hz, 6H), 4.60 – 4.28 (m, 18H), 4.05 (s, 3H), 3.96 (s, 3H), 3.63 (s, 9H). HRMS (ESI-TOF) m/z: $[M]^{2+}$ Calcd. for $C_{174}H_{150}Fe_4N_6O_{15}$ 896.6872; Found 896.6794.

*In situ synthesis of **C3***. To a 4 mL glass bottle, **L3** (1.75 mg, 1.2 μmol) and then 2-pyridine-carboxaldehyde (0.39 mg, 3.66 μmol) in 165 μL $CDCl_3$ were added. After stirring for 3 minutes, a CD_3CN solution (435 μL) of iron (II) tetrafluoroborate hexahydrate (0.44 mg, 1.32 μmol) was added. The reaction mixture was stirred at 25 °C for 10 h. The deep burgundy solution was used for the NMR experiments.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.

Synthetic routes, molecular models, and characterizations of **C1**-**3**, ^{1}H NMR titration experiment, spectroscopic data (^{1}H NMR and ^{13}C NMR) of new compounds and cartesian coordinates of the optimized hemicages.

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Notes

The authors declare no competing financial interest.

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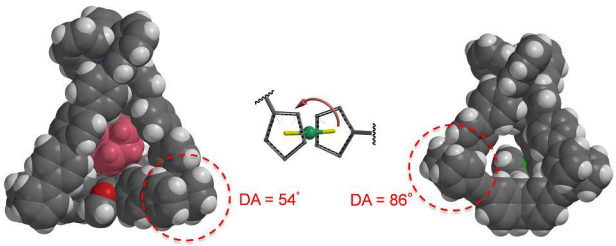
REFERENCES

(1) Takezawa, H.; Murase, T.; Resnati, G.; Metrangolo, P.; Fujita, M. *J. Am. Chem. Soc.* **2014**, *136*, 1786.
(2) Frischmann, P. D.; Kunz, V.; Würthner, F. *Angew. Chem., Int. Ed.* **2015**, *54*, 7285.
(3) Takezawa, H.; Akiba, S.; Murase, T.; Fujita, M. *J. Am. Chem. Soc.* **2015**, *137*, 7043.
(4) Meng, W.; Breiner, B.; Rissanen, K.; Thoburn, J. D.; Clegg, J. K.; Nitschke, J. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 3479.
(5) Rizzuto, F. J.; Wu, W.-Y.; Ronson, T. K.; Nitschke, J. R. *Angew. Chem., Int. Ed.* **2016**, *55*, 7958.
(6) Zarra, S.; Wood, D. M.; Roberts, D. A.; Nitschke, J. R. *Chem. Soc. Rev.* **2015**, *44*, 419.
(7) García-Simón, C.; Costas, M.; Ribas, X. *Chem. Soc. Rev.* **2016**, *45*, 40.
(8) Smulders, M. M. J.; Nitschke, J. R. *Chem. Sci.* **2012**, *3*, 785.
(9) Yoshizawa, M.; Klosterman, J. K.; Fujita, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 3418.
(10) Wang, Q.-Q.; Gonell, S.; Leenders, S. H. A. M.; Dürr, M.; Ivanović-Burmazović, I.; Reek, J. N. H. *Nat. Chem.* **2016**, *8*, 225.
(11) Zhang, D.; Martinez, A.; Dutasta, J.-P. *Chem. Rev.* **2017**, *117*, 4900.
(12) Brown, C. J.; Toste, F. D.; Bergman, R. G.; Raymond, K. N. *Chem. Rev.* **2015**, *115*, 3012.
(13) Sadjadi, S. *Organic Nanoreactors*; Academic Press: Boston, 2016, 257-303.
(14) Mal, P.; Breiner, B.; Rissanen, K.; Nitschke, J. R. *Science* **2009**, *324*, 1697.
(15) Yamashina, M.; Sei, Y.; Akita, M.; Yoshizawa, M. *Nat. Commun.* **2014**, *5*, 4662.
(16) Yang, D.; Zhao, J.; Yu, L.; Lin, X.; Zhang, W.; Ma, H.; Gogoll, A.; Zhang, Z.; Wang, Y.; Yang, X.-J.; Wu, B. *J. Am. Chem. Soc.* **2017**, *139*, 5946.
(17) Jiao, T.; Chen, L.; Yang, D.; Li, X.; Wu, G.; Zeng, P.; Zhou, A.; Yin, Q.; Pan, Y.; Wu, B.; Hong, X.; Kong, X.; Lynch, V. M.; Sessler, J. L.; Li, H. *Angew. Chem., Int. Ed.* **2017**, *56*, 14545.
(18) Smulders, M. M.; Riddell, I. A.; Browne, C.; Nitschke, J. R. *Chem. Soc. Rev.* **2013**, *42*, 1728.
(19) Han, M.; Engelhard, D. M.; Clever, G. H. *Chem. Soc. Rev.* **2014**, *43*, 1848.
(20) Ward, M. D. *Chem. Commun.* **2009**, 4487.
(21) Bivaud, S.; Goeb, S.; Croue, V.; Dron, P. I.; Allain, M.; Salle, M. *J. Am. Chem. Soc.* **2013**, *135*, 10018.
(22) Ye, Y.; Cook, T. R.; Wang, S. P.; Wu, J.; Li, S.; Stang, P. J. *J. Am. Chem. Soc.* **2015**, *137*, 11896.
(23) Chakraborty, S.; Hong, W.; Endres, K. J.; Xie, T.-Z.; Wojtas, L.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *J. Am. Chem. Soc.* **2017**, *139*, 3012.
(24) Frischmann, P. D.; MacLachlan, M. J. *Chem. Soc. Rev.* **2013**, *42*, 871.
(25) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810.
(26) Cook, T. R.; Stang, P. J. *Chem. Rev.* **2015**, *115*, 7001.
(27) Young, N. J.; Hay, B. P. *Chem. Commun.* **2013**, *49*, 1354.
(28) Zysman-Colman, E.; Denis, C. *Coord. Chem. Rev.* **2012**, *256*, 1742.
(29) Harris, W. H.; Raymond, K. N. *J. Am. Chem. Soc.* **1979**, *101*, 6534.
(30) Tor, Y.; Libman, J.; Shanzer, A.; Lifson, S. *J. Am. Chem. Soc.* **1987**, *109*, 6517.
(31) Karpishin, T. B.; Raymond, K. N. *Angew. Chem., Int. Ed.* **1992**, *31*, 466.
(32) Karpishin, T. B.; Stack, T. D. P.; Raymond, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 6115.
(33) Hay, B. P.; Dixon, D. A.; Vargas, R.; Garza, J.; Raymond, K. N. *Inorg. Chem.* **2001**, *40*, 3922.
(34) Raymond, K. N.; Dertz, E. A.; Kim, S. S. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 3584.
(35) Wang, J.; Oyler, K. D.; Bernhard, S. *Inorg. Chem.* **2007**, *46*, 5700.
(36) St-Pierre, G.; Ladouceur, S.; Fortin, D.; Zysman-Colman, E. *Dalton Trans.* **2011**, *40*, 11726.
(37) Schaffner-Hamann, C.; von Zelewsky, A.; Barbieri, A.; Barigelletti, F.; Muller, G.; Riehl, J. P.; Neels, A. *J. Am. Chem. Soc.* **2004**, *126*, 9339.
(38) De Cola, L.; Belser, P.; Ebmeyer, F.; Barigelletti, F.; Voegtle, F.; Von Zelewsky, A.; Balzani, V. *Inorg. Chem.* **1990**, *29*, 495.
(39) Amendola, V.; Boiocchi, M.; Colasson, B.; Fabbrizzi, L.; Rodriguez Douton, M.-J.; Ugozzoli, F. *Angew. Chem., Int. Ed.* **2006**, *45*, 6920.
(40) Oyler, K. D.; Coughlin, F. J.; Bernhard, S. *J. Am. Chem. Soc.* **2007**, *129*, 210.
(41) Beeston, R. F.; Larson, S. L.; Fitzgerald, M. C. *Inorg. Chem.* **1989**, *28*, 4187.
(42) Hamann, C.; von Zelewsky, A.; Neels, A.; Stoeckli-Evans, H. *Dalton Trans.* **2004**, 402.
(43) Coughlin, F. J.; Oyler, K. D.; Pascal, R. A.; Bernhard, S. *Inorg. Chem.* **2008**, *47*, 974.
(44) Fukino, T.; Joo, H.; Hisada, Y.; Obana, M.; Yamagishi, H.; Hikima, T.; Takata, M.; Fujita, N.; Aida, T. *Science* **2014**, *344*, 499.
(45) Yamagishi, H.; Fukino, T.; Hashizume, D.; Mori, T.; Inoue, Y.; Hikima, T.; Takata, M.; Aida, T. *J. Am. Chem. Soc.* **2015**, *137*, 7628.
(46) Obana, M.; Fukino, T.; Hikima, T.; Aida, T. *J. Am. Chem. Soc.* **2016**, *138*, 9246.
(47) Xu, L.; Wang, Y.-X.; Chen, L.-J.; Yang, H.-B. *Chem. Soc. Rev.* **2015**, *44*, 2148.
(48) Muraoka, T.; Kinbara, K.; Kobayashi, Y.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 5612.
(49) Muraoka, T.; Kinbara, K.; Aida, T. *Nature* **2006**, *440*, 512.
(50) Scottwell, S. O.; Crowley, J. D. *Chem. Commun.* **2016**, *52*, 2451.
(51) Das, N.; Arif, A. M.; Stang, P. J.; Sieger, M.; Sarkar, B.; Kaim, W.; Fiedler, J. *Inorg. Chem.* **2005**, *44*, 5798.
(52) Mugridge, J. S.; Fiedler, D.; Raymond, K. N. *J. Coord. Chem.* **2010**, *63*, 2779.
(53) Mal, P.; Schultz, D.; Beyeh, K.; Rissanen, K.; Nitschke, J. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 8297.
(54) Young, M. C.; Johnson, A. M.; Gamboa, A. S.; Hooley, R. J. *Chem. Commun.* **2013**, *49*, 1627.
(55) Curran, T. P.; Lawrence, A. P.; Murtaugh, T. S.; Ji, W.; Pokharel, N.; Gober, C. B.; Suitor, J. *J. Organomet. Chem.* **2017**, *846*, 24.
(56) Chan, Y.-T.; Li, X.; Yu, J.; Carri, G. A.; Moorefield, C. N.; Newkome, G. R.; Wesdemiotis, C. *J. Am. Chem. Soc.* **2011**, *133*, 11967.
(57) Inkpen, M. S.; Du, S.; Driver, M.; Albrecht, T.; Long, N. J. *Dalton Trans.* **2013,** *42*, 2813.
(58) Ma, J.; Vollmann, M.; Menzel, H.; Pohle, S.; Butenschön, H. *J. Inorg. Organomet. Polym.* **2007,** *18*, 41.
(59) Friedman, L.; Logullo, F. M. *J. Org. Chem.* **1969,** *34*, 3089.
(60) Muraki, T.; Togo, H.; Yokoyama, M. *J. Org. Chem.* **1999,** *64*, 2883.
(61) Sato, M.; Kawakami, H.; Motomura, T.; Aramaki, H.; Matsuda, T.; Yamashita, M.; Ito, Y.; Matsuzaki, Y.; Yamataka, K.; Ikeda, S.; Shinkai, H. *J. Med. Chem.* **2009,** *52*, 4869.
(62) Zhang, C.; Chen, C.-F. *J. Org. Chem.* **2006,** *71*, 6626.
(63) Roy, R. K.; Gowd, E. B.; Ramakrishnan, S. *Macromolecules* **2012,** *45*, 3063.
(64) Liang, Y.-P.; He, Y.-J.; Lee, Y.-H.; Chan, Y.-T. *Dalton Trans.* **2015,** *44*, 5139.
(65) Wang, Y.-C.; Liang, Y.-P.; Cai, J.-Y.; He, Y.-J.; Lee, Y.-H.; Chan, Y.-T. *Chem. Commun.* **2016,** *52*, 12622.
(66) N. Miyaura, T. Yanagi, A. Suzuki, *Synth. Commun.* **1981**, *11*, 513.
(67) K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *16*, 4467.
(68) Baumgardt, I.; Butenschön, H. *Eur. J. Org. Chem.* **2010,** *2010*, 1076.
(69) Terao, J.; Konoshima, Y.; Matono, A.; Masai, H.; Fujihara, T.; Tsuji, Y. *Beilstein J. Org. Chem.* **2014,** *10*, 2800.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