Supporting Information

Subcomponent Self-Assembly of a Cyclic Tetranuclear Fe" Helicate in a Highly Diastereoselective Self-Sorting Manner

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Abstract: An enantiomerically pure diamine based on the 4,15-difunctionalized [2.2]paracyclophane scaffold and 2-formylpyridine self-assemble into an optically pure cyclic metallosupramolecular Fe₄L₆ helicate upon mixing with iron(II) ions in a diastereoselective subcomponent self-assembly process. The cyclic assembly results from steric strain that prevents the formation of a smaller linear dinuclear triple-stranded helicate, and hence, leads to the larger strain-free assembly that fulfills the maximum occupancy rule. Interestingly, use of the racemic diamine also leads to a racemic mixture of the homochiral cyclic helicates as the major product in a highly diastereoselective narcissistic chiral self-sorting manner given the fact that the assembly contains ten stereogenic elements which can in principle give rise to 149 different diastereomers. The metallosupramolecular aggregates could be characterized by NMR, UV-Vis and CD spectroscopy, mass spectrometry and X-ray crystallography.

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General experimental information

All reactions with air and moisture sensitive compounds were performed under argon atmosphere using standard Schlenk techniques, oven-dried glassware and dry solvents.

The following chemicals were obtained commercially from Alfa Aesar, Sigma-Aldrich, Carbolution, Fluorochem or abcr and used as received: tert-butyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate, cesium fluoride, tetrakis(triphenylphosphine)-palladium(0), trifluoroacetic acid.

The following chemicals were synthesized according to known literature synthesis procedures: 4,15-diiodo[2.2]paracyclophane (rac)-A,[1] iron(II) triflate hexahydrate.[2]

All solvents were obtained from commercial sources. Dry solvents were obtained from the solvent purification system MS-SPS 800 from MBraun. Other reaction solvents and solvents for specific rotation value, UV-Vis or CD measurements were solvents of p.a. grade. For flash column chromatography freshly destilled solvents of technical grade and for high performance liquid chromatography solvents of HPLC grade were used.

Thin-layer chromatography was performed on silica gel-coated aluminum plates with fluorescent indicator F254 from Merck. Detection was done by UV-light (254 and 366 nm).

Products were purified by flash column chromatography on silica gel 60 (particle size 0.040-0.063 mm) from Merck or on reversed phase silica gel (C18-RP, 17% C, 0.048-0.065 mm) from Acros Organics.

\[ D = \frac{k_B T}{6 \pi \eta f R_h} \]

**Equation S1: Stokes-Einstein equation.** \( D \) = diffusion constant, \( k_B \) = Boltzmann constant, \( T \) = temperature, \( \eta \) = viscosity of solvent, \( f \) = correction factor for ellipsoids, \( R_h \) = hydrodynamic radius.

(High-resolution) electrospray ionization mass spectra in positive mode (ESI(+)-MS) were measured on an Orbitrap XL mass spectrometer from Thermo Fisher Scientific or a micrOTOF-Q time-of-flight mass spectrometer from Bruker Daltonik.

Elementary analyses were performed on a Vario EL elemental analyzer from Heraeus.

Melting points were determined with a DigiMelt MPA 161 instrument from Stanford Research Systems.

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[2] K. S. Hagen, Inorg. Chem. 2000, 39, 5867-5869.
[3] a) K. E. Van Holde, Physical Biochemistry, Prentice-Hall, Englewood Cliffs, 1971; b) A. Macchioni, G. Ciancaleoni, C. Zuccaccia, D. Zuccaccia, Chem. Soc. Rev., 2008, 37, 479-489.
UV-Vis spectra were measured on a Specord 200 instrument from Analytik Jena and analyzed using the software WinASPECT 1.7.2.0. Quartz glass cuvettes from Hellma Analytics with a layer thickness of 10 mm (solutions of ligand precursors/ligands) and 0.01 mm (complex solutions) were used.

Circular dichroism (CD) spectra were measured on a J-810 spectrometer from Jasco. Quartz glass cuvettes from Hellma Analytics with a layer thickness of 1 mm (solutions of ligand precursors/ligands) and 0.01 mm (complex solutions) were used.

Specific rotation values were measured on an Anton Paar Model MCP 150 polarimeter with a standard wavelength of 589 nm using a cuvette with a layer thickness of 100 mm.

High performance liquid chromatography on analytical scale was performed on a PLATINblue HPLC system from Knauer, equipped with two pumps, an online degasser and a photodiode array detector PDA-1 with a deuterium and tungsten-halogen lamp (190-1000 nm), and a CHIRALPAK® IB column (4.6 mm Ø, 250 mm) by Daicel was used. High performance liquid chromatography on semi-preparative scale was performed on an Azura HPLC system from Knauer, equipped with a binary HPG pump P 6.1L, an online degasser, a multi wavelength detector MWL 2.1L with deuterium lamp (190-700 nm) and a fraction collector, and a CHIRALPAK® IB column (20 mm Ø, 250 mm) by Daicel was used.

**Synthetic Scheme**

![Synthetic Scheme](image)

**Scheme S1**: Synthetic route to diamine (rac)-1.
Synthesis and characterization of ligand precursors

(rac)-4,15-Bis-((4,1-phenylene)-N-(tert-butyloxy carbonyl)amine)[2.2]paracyclophane ((rac)-B)

Under an atmosphere of argon, (rac)-A$^{[1]}$ (790 mg, 1.72 mmol, 1.00 eq.), tert-butyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxoborolan-2-yl)phenyl)carbamate (1.15 g, 3.61 mmol, 2.10 eq.), cesium fluoride (1.75 g, 10.3 mmol, 6.00 eq.), tetrakis(triphenylphosphine)palladium(0) (199 mg, 0.172 mmol, 10.0 mol%) were dissolved in dry tetrahydrofuran (80 mL). The reaction mixture was degased at room temperature and then heated to reflux for 48 h. After cooling to room temperature the solution was quenched by the addition of saturated aqueous ethylenediaminetetraacetic acid disodium salt solution and dichloromethane. The mixture was extracted with dichloromethane. The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The crude product was subjected to flash column chromatography on silica gel (cyclohexane/ethyl acetate 10:1) and reversed phase silica gel (acetonitrile/water 3:2) to give (rac)-B (469 mg, 0.794 mmol, 46%) as a white solid.

1H NMR (499.1 MHz, CDCl$_3$, 298 K): $\delta$[ppm] = 7.49-7.45 (m, 4 H, H-19), 7.44-7.40 (m, 4 H, H-18), 6.67 (d, 2 H, H-8, H-13, $^3J_{8,7} = ^3J_{13,12} = 7.8$ Hz), 6.66 (d, 2 H, H-5, H-16, $^4J_{5,7} = ^4J_{16,12} = 1.9$ Hz), 6.56 (s, 2 H, NH), 6.54 (dd, 2 H, H-7, H-12, $^3J_{7,8} = ^3J_{12,13} = 7.8$ Hz, $^4J_{7,5} = ^4J_{12,16} = 1.9$ Hz), 3.25-3.00 (m, 6 H, H-1, H-2, H-9, H-10), 2.52-2.42 (m, 2 H, H-1, H-2), 1.55 (s, 18 H, H-23).

13C NMR (125.5 MHz, CDCl$_3$, 298 K): $\delta$ [ppm] = 153.0 (C-21), 142.0 (C-4, C-15), 139.7 (C-6, C-11), 137.5 (C-3, C-14), 137.4 (C-20), 136.3 (C-17), 132.3 (C-8, C-13), 131.8 (C-5, C-16), 131.1 (C-7, C-12), 130.3 (C-18, C-12), 118.8 (C-19), 80.8 (C-22), 35.3 (C-9, C-10), 33.5 (C-1, C-2), 28.5 (C-23).

MS (ESI+) m/z: 590.3137 [(rac)-B]$^{+*}$, HR-MS (ESI+) m/z: calculated for C$_{38}$H$_{42}$N$_2$O$_4$ [(rac)-B]$^{+*}$: 590.3139, found: 590.3137.

Elementary analysis: calculated for C$_{38}$H$_{42}$N$_2$O$_4$ $\cdot \frac{1}{3}$CH$_2$Cl$_2$: C: 74.37, H: 6.95, N: 4.53, found: C: 74.55, H: 7.12, N: 4.51.

Melting point: 195 °C

R$_f$ (cyclohexane/ethyl acetate 4:1): 0.47

UV-Vis (CH$_3$CN, c = 1.69 µM): $\lambda$ [nm] = 253, 289.
Figure S1: $^1$H NMR spectrum (499.1 MHz, CDCl$_3$, 298 K) of (rac)-B.

Figure S2: $^{13}$C NMR spectrum (125.5 MHz, CDCl$_3$, 298 K) of (rac)-B.

Figure S3: $^1$H, $^{13}$C-HSQC NMR spectrum (499.1 MHz, 125.5 MHz, CDCl$_3$, 298 K) of (rac)-B.
**Figure S4:** $^1$H, $^{13}$C-HMBC NMR spectrum (499.1 MHz, 125.5 MHz, CDCl$_3$, 298 K) of (rac)-B.

**Figure S5:** ESI positive mass spectrum of (rac)-B.
Figure S6: Non-normalized UV-Vis spectrum of (rac)-B (c = 1.69 µM, CH$_3$CN).

(R$_p$)-, (S$_p$)- and (rac)-4,15-Bis-(4-aminophenyl)[2.2]paracyclophane ((R$_p$)-, (S$_p$)- and (rac)-1)

Under an atmosphere of argon, (rac)-B (200 mg, 339 µmol, 1.00 eq.) was dissolved in dry dichloromethane (10 mL) and trifluoroacetic acid (5.22 mL, 7.73 g, 67.8 mmol, 200 eq.) was added. The reaction solution was stirred at room temperature for 18 h. Then, it was concentrated under reduced pressure, the residue was dissolved in ethyl acetate and neutralized with saturated potassium hydrogen carbonate solution. The mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The crude product was dissolved in warm acetonitrile and precipitated as hydrochloride by adding hydrochloric acid (37%, 60.0 µL, 70.8 mg, 678 µmol, 2.00 eq.). The white solid was filtered off, washed with acetonitrile and dissolved in water. After the addition of saturated potassium hydrogen solution, the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried with anhydrous magnesium sulfate and the solvent was removed under reduced pressure to give (rac)-1 (110 mg, 282 µmol, 83%) as a yellow solid.

$^1$H NMR (700.4 MHz, CD$_3$CN, 298 K): $\delta$ [ppm] = 7.26-7.23 (m, 4 H, H-18), 6.76-6.73 (m, 4 H, H-19), 6.63 (d, 2 H, H-8, H-13), $^{3}J_{8,7} = ^{3}J_{13,12} = 7.6$), 6.61 (d, 2 H, H-5, H-16), $^{4}J_{5,7} = ^{4}J_{16,12} = 1.9$ Hz), 6.54 (dd, 2 H, H-7, H-12), $^{3}J_{7,8} = ^{3}J_{12,13} = 7.6$ Hz, $^{4}J_{7,5} = ^{4}J_{12,16} = 1.9$ Hz), 4.23 (s, 4 H, H-21), 3.20-3.12 (m, 2 H, H-9, H-10), 2.39-2.33 (m, 2 H, H-2, H-1, H-2, H-9, H-10), 3.04-2.99 (m, 2 H, H-9, H-10), 2.39-2.33 (m, 2 H, H-1, H-2).
\(^{13}\)C NMR (176.1 MHz, CD\(_2\)CN, 298 K): \(\delta\) [ppm] = 148.1 (C-20), 143.5 (C-4, C-15), 140.7 (C-6, C-11), 137.8 (C-3, C-14), 133.0 (C-8, C-13), 132.3 (C-5, C-16), 131.5 (C-17), 131.4 (C-18), 131.2 (C-7, C-12), 115.5 (C-19), 35.6 (C-9, C-10), 34.4 (C-1, C-2).

MS (ESI+) \textit{m/z}: 391.2173 \([1+H]^+\), 196.1125 \([1+2H]^+\); HR-MS (ESI+) \textit{m/z}: calculated for [C\(_{28}\)H\(_{26}\)N\(_2\)H\(_2\)]\(^+\): 391.2169, found: 391.2173.

Elementary analysis: calculated for C\(_{28}\)H\(_{26}\)N\(_2\) \(\cdot\) \(\frac{1}{2}\) C\(_4\)H\(_8\)O\(_2\): C: 82.91, H: 6.96, N: 6.45, found: C: 83.28, H: 6.88, N: 6.40.

Melting point: 245 °C (decomposition)

\(R\) \(_f\) (cyclohexane/ethyl acetate 2:1+ 5% triethylamine): 0.19

UV-Vis (CH\(_3\)CN, \(c = 25.6\) µM): \(\lambda\) [nm] = 265, 296.

HPLC analytical (CHIRALPAK\(^\text{®}\) IB, methanol/water (95:5 v/v), flow rate 1 mL min\(^{-1}\)): (\(R\)_p)-1 \(t_R = 8.38\) min, (\(S\)_p)-1 \(t_R = 10.82\) min.

HPLC semi-preparative (CHIRALPAK\(^\text{®}\) IB, methanol/water (95:5 v/v), 18 mL min\(^{-1}\)): (\(R\)_p)-1 > 99% ee, (\(S\)_p)-1 97% ee.

Specific rotation: (\(-\)-(\(R\)_p)-1: \([\alpha]^{25}_D = -615^\circ\) (\(c = 1.00\) mg mL\(^{-1}\) = 2.56 mM, CH\(_2\)Cl\(_2\)), (+)-(\(S\)_p)-1: \([\alpha]^{25}_D = +646^\circ\) (\(c = 1.00\) mg mL\(^{-1}\) = 2.56 mM, CH\(_2\)Cl\(_2\)).

CD (CH\(_3\)CN, \(c = 256\) µM): \(\lambda\) [nm] (\(\Delta\varepsilon\) [L mol\(^{-1}\) cm\(^{-1}\)]): (\(R\)_p)-1: 217 (−69), 235 (+59), 248 (+13), 261 (+64), 271 (+35), 276 (+36), 313 (−110); (\(S\)_p)-1: 217 (+79), 235 (−65), 248 (−12), 261 (−70), 271 (−37), 276 (−38), 313 (+126).

**Figure S7:** \(^1\)H NMR spectrum (700.4 MHz, CD\(_2\)CN, 298 K) of 1.

**Figure S8:** \(^{13}\)C NMR spectrum (176.1 MHz, CD\(_2\)CN, 298 K) of 1.
**Figure S9:** $^1$H, $^{13}$C-HSQC NMR spectrum (700.4 MHz, 176.1 MHz, CD$_3$CN, 298 K) of 1.

**Figure S10:** $^1$H, $^{13}$C-HMBC NMR spectrum (700.4 MHz, 176.1 MHz, CD$_3$CN, 298 K) of 1.
**Figure S11**: ESI positive mass spectrum of 1.

**Figure S12**: Non-normalized UV-Vis spectrum of 1 (c = 25.6 µM, CH₃CN).
Figure S13: Chromatogram of chiral resolution of (rac)-1 via analytical HPLC (chiral stationary phase: CHIRALPAK® IB column, eluent: methanol/water (95:5 v/v), flow rate: 1 mL min⁻¹). When upscaling to semi-preparative mode, the flow rate was increased to 18 mL min⁻¹.

Figure S14: CD spectra of (R)-1 and (S)-1 (c = 256 μM, CH₂CN).
Self-assembly and characterization of iron(II) complexes

Cyclic [Fe₄L₆]([OTf]₈ helicates in acetonitrile

(Δ,Δ,Δ,Δ)-(Fe₄((R)₆-L)₆)(OTf)₈ or (Δ,Δ,Δ,Δ)-(Fe₄((S)₆-L)₆)(OTf)₈ obtained from (R)₆ or (S)₆-1

(R)₆- or (S)₆-1 (3.01 mg, 7.71 μmol, 3.00 eq.) was dissolved in acetonitrile (0.6 mL) and 2-formylpyridine (1.47 μL, 1.65 mg, 15.4 μmol, 6.00 eq.) was added. The mixture was stirred at 70 °C for 30 min. After cooling to room temperature, a solution of iron(II) triflate hexahydrate (2.41 mg, 5.22 μmol, 2.03 eq.) in acetonitrile (0.1 mL) was added. The violet solution was stirred at 70 °C for 15 h. After cooling to room temperature, the solution was poured into diethyl ether (4 mL). The violet precipitate was collected and washed with diethyl ether as well as n-hexane and dissolved in deuterated acetonitrile (0.6 mL).

(Δ,Δ,Δ,Δ)-(Fe₄((R)₆-L)₆)(OTf)₈ and (Δ,Δ,Δ,Δ)-(Fe₄((S)₆-L)₆)(OTf)₈ obtained from (rac)-1

(rac)-1 (4.08 mg, 10.4 μmol, 3.00 eq.) was dissolved in acetonitrile (0.6 mL) and 2-formylpyridine (1.98 μL, 2.23 mg, 20.8 μmol, 6.00 eq.) was added. The mixture was stirred at 70 °C for 30 min. After cooling to room temperature, a solution of iron(II) triflate hexahydrate (3.25 mg, 7.03 μmol, 2.03 eq.) in acetonitrile (0.6 mL) was added. The violet solution was stirred at 70 °C for 15 h. After cooling to room temperature, the solution was poured into diethyl ether (4 mL). The violet precipitate was collected and washed with diethyl ether as well as n-hexane and dissolved in deuterated acetonitrile (0.6 mL).

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enantiomerically pure (Δ,Δ,Δ,Δ)-(Fe₄((R)₆-L)₆)(OTf)₈ and (Δ,Δ,Δ,Δ)-(Fe₄((S)₆-L)₆)(OTf)₈ obtained from (R)₆-1 or (S)₆-1, respectively

^1H NMR (700.4 MHz, CD₃CN, 298 K): δ [ppm] = 9.46 (s, 4 H, H-21), 9.43 (s, 4 H, H-21), 9.11 (s, 4 H, H-21), 8.78-8.73* (m, 4 H), 8.70-8.66* (m, 4 H), 8.44-8.24* (m, 20 H), 7.86-7.71* (m, 24 H), 7.67-7.62* (m, 6 H), 7.47-7.40* (m, 14 H), 7.18-7.06* (m, 12 H), 6.98-6.95* (m, 6 H), 6.83-6.79* (m, 6 H), 6.71-6.66* (m, 14 H), 6.63-6.58* (m, 8 H), 6.55-6.52* (m, 4 H), 6.45-6.37* (m, 10 H), 3.37-3.20* (m, 16 H), 3.08-2.95* (m, 12 H), 2.87-2.82* (m, 4 H), 2.80-2.74* (m, 4 H), 2.50-2.45* (m, 4 H), 2.08-2.05* (m, 4 H), 1.90-1.84* (m, 4 H).

^13C NMR (176.1 MHz, CD₃CN, 298 K): δ [ppm] = 174.7 (C-21), 173.9 (C-21), 173.4 (C-21), 163.4* (C-21), 160.0*, 159.8*, 159.0*, 158.5*, 157.9*, 157.2*, 152.9*, 152.2*, 147.3*, 146.2*, 143.2*, 143.1*, 142.2*, 141.8*, 141.8*, 141.7*, 141.4*, 141.3*, 141.2*, 140.1*, 139.9*, 139.1*, 138.4*, 137.5*, 137.3*, 133.5*, 133.4*, 133.2*, 133.2*, 133.1*, 132.8*, 132.7*, 132.3*, 132.2*, 131.8*, 131.3*, 131.1*, 130.0*, 129.7*, 129.7*, 126.0*, 124.1*, 124.1*, 123.2*, 35.5*, 35.4*, 35.2*, 34.3*, 34.2*, 33.5*.

*signals could not be unambiguously assigned.
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\[^1\text{H}-2\text{D}-\text{DOSY NMR}\] (700.4 MHz, CD\(_3\)CN, 298 K): \(D = 4.94 \times 10^{-10}\) m\(^2\) s\(^{-1}\), \(R_H = 13.7\) Å.

**MS (ESI+)** \(m/z\): 374.1656 [1 + 4 formylpyridine – 4 H\(_2\)O + 4 H\(^+\)]\(^{2+}\); C\(_{50}\)H\(_{40}\)N\(_6\)\(^{2+}\), 540.6048 [Fe\(_4\)((R\(_\text{p}\))-L\(_6\))(OTf)\(^8\)], 655.5365 [Fe\(_4\)((R\(_\text{p}\))-L\(_6\))(OTf)\(^6\)], 773.1460 [Fe\(_4\)((R\(_\text{p}\))-L\(_6\))(OTf)\(^4\)], 816.6298 [Fe\(_4\)((R\(_\text{p}\))-L\(_6\))(OTf)\(^2\)], 844.9554 [Fe\(_4\)((R\(_\text{p}\))-L\(_6\))(OTf)\(^0\)], 1057.7751 [Fe\(_2\)((R\(_\text{p}\))-L\(_2\))(OTf)\(^2\)], 1460.0054 [Fe\(_2\)((R\(_\text{p}\))-L\(_2\))(OTf)\(^0\)].

**UV-Vis** (CH\(_3\)CN, \(c = 2.14\) mM): \(\lambda\) [nm] = 224, 290, 362, 580.

**CD** (CH\(_3\)CN, \(c = 2.14\) mM): \(\lambda\) [nm] (\(\Delta\varepsilon\) [L mol\(^{-1}\) cm\(^{-1}\)]): (\(\Delta\),\(\Delta\),\(\Delta\),\(\Delta\))-Fe\(_4\)((R\(_\text{p}\))-L\(_6\))(OTf)\(^8\): 214 (-116), 247 (+183), 288 (-180), 323 (-117), 357 (-149), 438 (-12), 510 (-96), 608 (+160); (\(\Lambda\),\(\Lambda\),\(\Lambda\),\(\Lambda\))-Fe\(_4\)((S\(_\text{p}\))-L\(_6\))(OTf)\(^8\): 214 (+77), 247 (-126), 288 (+128), 325 (+90), 348 (+110), 438 (+29), 515 (+78), 606 (-85).

**Figure S15:** \(^1\text{H} NMR spectrum (700.4 MHz, CD\(_3\)CN, 298 K) of (\(\Delta\),\(\Delta\),\(\Delta\),\(\Delta\))-Fe\(_4\)((R\(_\text{p}\))-L\(_6\))(OTf)\(^8\).

**Figure S16:** \(^{13}\text{C} NMR spectrum (176.1 MHz, CD\(_3\)CN, 298 K) of (\(\Delta\),\(\Delta\),\(\Delta\),\(\Delta\))-Fe\(_4\)((R\(_\text{p}\))-L\(_6\))(OTf)\(^8\).
Figure S17: $^1$H, $^1$H-COSY NMR spectrum (700.4 MHz, CD$_3$CN, 298 K) of ($\Delta,\Delta,\Delta,\Delta$)-[Fe$_4$((R)$_p$-L)$_6$](OTf)$_8$.

Figure S18: $^1$H, $^{13}$C-HSQC NMR spectrum (700.4 MHz, 176.1 MHz, CD$_3$CN, 298 K) of ($\Delta,\Delta,\Delta,\Delta$)-[Fe$_4$((R)$_p$-L)$_6$](OTf)$_8$. 
Figure S19: $^1$H, $^{13}$C-HMBC NMR spectrum (700.4 MHz, 176.1 MHz, CD$_3$CN, 298 K) of $(\Delta,\Delta,\Delta,\Delta)$-[Fe$_4$(($R_p$)-L)$_6$](OTf)$_8$.

Figure S20: $^1$H-2D-DOSY NMR spectrum (700.4 MHz, CD$_3$CN, 298 K) of $(\Delta,\Delta,\Delta,\Delta)$-[Fe$_4$(($R_p$)-L)$_6$](OTf)$_8$. 
**Figure S21**: ESI positive mass spectrum of \((\Delta,\Delta,\Delta,\Delta)-[\text{Fe}_4((R_p)-\text{L})_6](\text{OTf})_8\) in CD$_3$CN measured on a micrOTOF-Q quadrupole/time-of-flight spectrometer with ESI parameters tuned to very soft ionization conditions. An accurate mass determination of \(m/z\) 374.16 at the Orbitrap XL spectrometer resulted in \(m/z\) 374.1656. A putative structure is given below. The ESI response of this stable dication is supposed to be extremely high and thus a strong signal is expected even if the ion is present in very low concentration. According to CID-MS$^2$ experiments, the signals at \(m/z\) 773 and \(m/z\) 845 marked with \(x\) are gas-phase fragments of the very labile \([\text{Fe}_4((R_p)-\text{L})_6](\text{OTf})_3]^{5+}\) at \(m/z\) 816.
Figure S22: Experimental and calculated high resolution ESI positive mass spectra of $(\Delta,\Delta,\Delta,\Delta)$-[Fe$_4$((R$_p$)-L)$_6$](OTf)$_8$ in CD$_3$CN measured on an Orbitrap XL mass spectrometer (OT) or a micrOTOF-Q time-of-flight spectrometer (TOF).

Figure S23: Non-normalized UV-Vis spectrum of [Fe$_4$L$_6$](OTf)$_8$ ($c = 2.14$ mM in CH$_3$CN).
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**Figure S24:** CD spectra of \((\Delta,\Delta,\Delta,\Delta)\text{-}[\text{Fe}_4\text{(R}_p\text{-L})_6]\text{(OTf)}_8\text{ and } (\Lambda,\Lambda,\Lambda,\Lambda)\text{-}[\text{Fe}_4\text{(S}_p\text{-L})_6]\text{(OTf)}_8\text{ (c = 2.14 mM in } \text{CH}_3\text{CN).}

**Figure S25:** \(^1\text{H} \text{NMR spectrum (700.4 MHz, CD}_3\text{CN, 298 K) of the product of the subcomponent self-assembly process of (rac)-1, 2-formylpyridine and iron(II) triflate hexahydrate.} \)
Figure S26: \(^1\)H 2D-DOSY NMR spectrum (700.4 MHz, CD\(_3\)CN, 298 K) of the product of the subcomponent self-assembly process of (rac)-1, 2-formylpyridine and iron(II) triflate hexahydrate.
Figure S27: ESI positive mass spectrum of a 3:6:2 mixture of (rac)-1, 2-formylpyridine and Fe(OTf)_2 in CD_3CN measured on a microTOF-Q quadrupole/time-of-flight spectrometer with ESI parameters tuned to very soft ionization conditions. A putative structure for the signal at m/z 374.2^2+ is given in Figure S21. The signals marked with X (m/z 504.4^4+, 722.2^3+, 1157.8^2+) belong to a dinuclear iron complex with triflate anions.

Figure S28: Experimental and calculated high resolution ESI positive mass spectra of a 3:6:2 mixture of (rac)-1, 2-formylpyridine and Fe(OTf)_2 in CD_3CN measured on an Orbitrap XL spectrometer.
**Table S1**: Schematic drawings of possible aggregates formed from enantiomerically pure starting material

| Experimentally observed product | 1 (6.25%) | 1 (6.25%) | 4 (25%) | 4 (25%) |
|---------------------------------|-----------|-----------|---------|---------|
| statistically expected relative |          |           |         |         |
| ratio (yield)                   | 2 (12.5%) | 2 (12.5%) | 2 (12.5%) | 2 (12.5%) |
Table S2: Schematic drawings of possible aggregates formed from racemic starting material

Possible diastereomers with (A,A,A,A)- or (A,A,A,A)-configured metal centers (only the (A,A,A,A)-enantiomer is shown)

| Possible diastereomers | Statistically expected relative ratio (yield) of the racemic diastereomer |
|------------------------|-------------------------------------------------------------------------|

| 1 (0.2%) | 4 (0.8%) | 2 (0.4%) | 1 (0.2%) | 2 (0.4%) |
|-----------|----------|----------|----------|----------|
| 2 (0.4%) | 4 (0.8%) | 4 (0.8%) | 4 (0.8%) | 4 (0.8%) |
| 4 (0.8%) | 2 (0.4%) | 2 (0.4%) | 2 (0.4%) | 4 (0.8%) |
| 4 (0.8%) | 2 (0.4%) | 4 (0.8%) | 1 (0.2%) | 4 (0.8%) |

Σ = 21 possible diastereomers with (A,A,A,A)- or (A,A,A,A)-configured metal centers
(combined statistically expected ratio 56/512 (ca. 11% yield))

Possible diastereomers with (A,A,A,A)- or (A,A,A,A)-configured metal centers (only the (A,A,A,A)-enantiomer is shown)

| Possible diastereomers | Statistically expected relative ratio (yield) of the racemic diastereomer |
|------------------------|-------------------------------------------------------------------------|

| 4 (0.8%) | 4 (0.8%) | 4 (0.8%) | 4 (0.8%) | 4 (0.8%) |
|-----------|----------|----------|----------|----------|
| 4 (0.8%) | 4 (0.8%) | 4 (0.8%) | 4 (0.8%) | 4 (0.8%) |
| 4 (0.8%) | 4 (0.8%) | 4 (0.8%) | 4 (0.8%) | 4 (0.8%) |
| 4 (0.8%) | 4 (0.8%) | 4 (0.8%) | 4 (0.8%) | 4 (0.8%) |
| 4 (0.8%) | 4 (0.8%) | 4 (0.8%) | 4 (0.8%) | 4 (0.8%) |
$\sum = 68$ possible diastereomers with

$\langle \Lambda, \Lambda, \Lambda, \Lambda \rangle$- or $\langle \Lambda, \Lambda, \Lambda, \Lambda \rangle$-

configured metal centers

(combined statistically expected ratio
272/512 (ca. 53% yield))
Possible diastereomers with \((\Lambda,\Lambda,\Lambda,\Lambda,\Lambda)-\) or \((\Lambda,\Lambda,\Lambda,\Lambda,\Lambda)-\) configured metal centers
(only one enantiomer or the meso-isomer is shown)

\[ \sum = 30 \text{ possible diastereomers with } (\Lambda,\Lambda,\Lambda,\Lambda,\Lambda)-\text{ or } (\Lambda,\Lambda,\Lambda,\Lambda,\Lambda)-\text{ configured metal centers} \]
(combined statistically expected ratio 104/512 (ca. 20% yield))
\[ \Sigma = 30 \text{ possible diastereomers with } (\Lambda,\Lambda,\Lambda,\Lambda)- \text{ or } (\Lambda,\Lambda,\Lambda,\Lambda)- \text{ configured metal centers} \]

(combined statistically expected ratio 80/512 (ca. 16% yield))
X-ray crystallography

X-Ray crystal structure experimental details for (S)p-1, enantiomerically pure (\(\Delta,\Delta,\Delta,\Delta\))-[Fe4((R)p)-L]6(OTf)8 and (\(\Lambda,\Lambda,\Lambda,\Lambda\))-[Fe4((S)p)-L]6(OTf)8 and the racemate of (\(\Delta,\Delta,\Delta,\Delta\))-[Fe4((R)p)-L]6(OTf)8 and (\(\Lambda,\Lambda,\Lambda,\Lambda\))-[Fe4((S)p)-L]6(OTf)8 are given below. The single-crystal X-ray data for all structures were measured using a dual-source Rigaku SuperNova diffractometer equipped with an Atlas detector using mirror-monochromated Cu-Kα (\(\lambda = 1.54184\) Å) radiation. The data collection and reduction were performed using the program CrysAlisPro and Gaussian face index absorption correction method was applied. All structures were solved using direct methods (SHELXS) and refined by sole full-matrix least squares based on \(F^2\) using the OLEX2 software that utilizes the SHELXL-2015 module.

Crystal structure refinement details: In Fe(II)-complexes, not all triflate anions to balance the metal ion positive charge could be found using electron Fourier difference map. This is due to weakly diffracting power of the crystals and severely disordered solvent molecules or electron residuals. Attempts to squeeze triflate anions and acetonitrile solvent molecules leaves Q-peaks ranging between 3.0 and 7.0 e/Å\(^3\) in the final refinement. Therefore, restrains/constraints are applied to give roughly tetrahedral geometry for -SO\(_3\) and CF\(_3\) groups in the triflate counterions.

Crystal data for (S)p-1: CCDC-1919439, C\(_{25}\)H\(_{30}\)O\(_2\)N\(_2\), M = 422.55, colourless plate, 0.115x0.108x0.08 mm\(^3\), orthorhombic, space group P2\(_1\)2\(_1\)2\(_1\), \(a = 8.06940(10)\) Å, \(b = 12.71500(10)\) Å, \(c = 22.9022(2)\) Å, \(\alpha = 90^\circ\), \(\beta = 90^\circ\), \(\gamma = 90^\circ\), \(V = 2349.82(4)\) Å\(^3\), \(Z = 4\), \(Dc = 1.194\) g/cm\(^3\), \(F000 = 904\), \(\mu = 0.558\) mm\(^{-1}\), \(T = 120.0(1)\) K, \(\theta_{max} = 76.908^\circ\), 42957 total reflections, 4777 with \(I_o > 2\sigma(I_o)\), \(R_{int} = 0.0322\), 4927 data, 291 parameters, 0 restraints, \(GooF = 1.041\), \(R = 0.0297\) and \(wR = 0.0791\) \([I_o > 2\sigma(I_o)]\), \(R = 0.0309\) and \(wR = 0.0801\) (all reflections), \(0.174 < \Delta d < 0.140\) Å\(^3\), Flack = -0.04(8).

Crystal data for (\(\Delta,\Delta,\Delta,\Delta\))-[Fe4((R)p)-L]6(OTf)8: CCDC-1919440, C\(_{24}\)H\(_{195}\)F\(_{15}\)Fe\(_{4}\)N\(_{25}\)O\(_{15}\)S\(_{5}\), M = 4421.97, purple block, 0.222x0.123x0.116 mm\(^3\), orthorhombic, space group P2\(_1\)2\(_1\)2\(_1\), \(a = 28.0369(12)\) Å, \(b = 35.6387(7)\) Å, \(c = 41.0905(10)\) Å, \(\alpha = 90^\circ\), \(\beta = 90^\circ\), \(\gamma = 90^\circ\), \(V = 41058(2)\) Å\(^3\), \(Z = 4\), \(Dc = 0.715\) g/cm\(^3\), \(F000 = 9164\), \(\mu = 1.710\) mm\(^{-1}\), \(T = 128(12)\) K, \(\theta_{max} = 56.021^\circ\), 270876 total reflections, 26113 with \(I_o > 2\sigma(I_o)\), \(R_{int} = 0.1085\), 52293 data, 2555 parameters, 90 restraints, \(GooF = 1.007\), \(R = 0.0883\) and \(wR = 0.2543\) \([I_o > 2\sigma(I_o)]\), \(R = 0.1520\) and \(wR = 0.3016\) (all reflections), \(0.558 < \Delta d < 0.482\) e/Å\(^3\), Flack = 0.045(5).

Crystal data for (\(\Lambda,\Lambda,\Lambda,\Lambda\))-[Fe4((S)p)-L]6(OTf)8: CCDC-1919441, C\(_{24}\)H\(_{195}\)F\(_{15}\)Fe\(_{4}\)N\(_{25}\)O\(_{15}\)S\(_{5}\), M = 3825.69, purple block, 0.11x0.09x0.09 mm\(^3\), orthorhombic, space group P2\(_1\)2\(_1\)2\(_1\), \(a = 28.6877(5)\) Å, \(b = 35.6914(6)\) Å, \(c = 41.3557(7)\) Å, \(\alpha = 90^\circ\), \(\beta = 90^\circ\), \(\gamma = 90^\circ\), \(V = 42344.3(13)\) Å\(^3\), \(Z = 4\), \(Dc = 0.600\) g/cm\(^3\), \(F000 = 7996\), \(\mu = 1.376\) mm\(^{-1}\), \(T = 120.0(1)\) K, \(\theta_{max} = 55.731^\circ\), 503946 total reflections, 27281 with \(I_o > 2\sigma(I_o)\), \(R_{int} = 0.1206\), 54068 data, 2033 parameters, 96 restraints, \(GooF = 1.033\), \(R = 0.0885\) and \(wR = 0.2642\) \([I_o > 2\sigma(I_o)]\), \(R = 0.1539\) and \(wR = 0.3125\) (all reflections), \(0.560 < \Delta d < 0.483\) e/Å\(^3\), Flack = 0.061(5).

Crystal data for the racemic mixture of (\(\Delta,\Delta,\Delta,\Delta\))-[Fe4((R)p)-L]6(OTf)8 and (\(\Lambda,\Lambda,\Lambda,\Lambda\))-[Fe4((S)p)-L]6(OTf)8: CCDC-1919442, C\(_{24}\)H\(_{192}\)F\(_{12}\)Fe\(_{4}\)N\(_{24}\)O\(_{12}\)S\(_{5}\), M = 4231.84, purple block, 0.147x0.145x0.041 mm\(^3\), tetragonal, space group I4/\(\bar{a}\)cd, \(a = 24.8852(3)\) Å, \(b = 24.8852(3)\) Å, \(c = 95.426(2)\) Å, \(\alpha = 90^\circ\), \(\beta = 90^\circ\), \(\gamma = 90^\circ\), \(V = 59095(2)\) Å\(^3\), \(Z = 8\), \(Dc = 0.951\) g/cm\(^3\), \(F000 = 17568\), \(\mu = 2.270\) mm\(^{-1}\), \(T = 120.0(1)\) K, \(\theta_{max} = 38.216^\circ\), 23669 total reflections, 2747 with \(I_o > 2\sigma(I_o)\), \(R_{int} = 0.0502\), 3912 data, 289 parameters, 50 restraints, \(GooF = 2.091\), \(R = 0.1795\) and \(wR = 0.4825\) \([I_o > 2\sigma(I_o)]\), \(R = 0.2082\) and \(wR = 0.5100\) (all reflections), \(0.736 < \Delta d < 0.880\) e/Å\(^3\).

[4] Rigaku Oxford Diffraction, 2017, CrysAlisPro Software system, version 38.46, Rigaku Corporation, Oxford, UK.
[5] a) G. M. Sheldrick, Acta Crystallogr. Sect. C, 2015, 71, 3-8; b) G. M. Sheldrick, Acta Crystallogr. Sect. A, 2015, 71, 3-8.
[6] O. V Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Crystallogr., 2009, 42, 339-341.
Figure S29. X-ray crystal structure of \((S_p)-1\) in ball and stick model. Black broken lines represent hydrogen bonding interactions.

Figure S30. X-ray crystal structures of \((\Delta,\Delta,\Delta,\Delta)-[Fe_4{(R_p)-L}_6](OTf)_8\) and \((\Lambda,\Lambda,\Lambda,\Lambda)-[Fe_4{(S_p)-L}_6](OTf)_8\) in capped-stick model. Counterions were omitted for viewing clarity.
**Figure S31.** X-ray crystal structure of the racemic mixture of \((\Delta,\Delta,\Delta,\Delta)\)-[Fe\(_4\)\((R_p)-L\)\(_6\)](OTf)\(_8\) and \((\Lambda,\Lambda,\Lambda,\Lambda)\)-[Fe\(_4\)\((S_p)-L\)\(_6\)](OTf)\(_8\) depicted in isomeric forms using capped-stick model. Counterions were omitted for viewing clarity.