

Supporting Information

Chiral Hexanuclear Ferric Wheels

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1. Experimental

General. Ligand synthesis was carried out under ambient atmosphere, and all coordination chemistry was performed under a dry argon atmosphere. Enantiomerically pure (*R*)-, (*S*)-1-Phenylethylamine (99+% ee) and the racemic mixture (*R/S*)-1-Phenylethylamine were purchased from Alfa Aesar. THF was dried by refluxing over Na/benzophenone or using a drying column.¹ All other reagents were obtained commercially (analytical grade) and used without further purification. ¹H and ¹³C-NMR spectra were acquired on Bruker DRX-400, Bruker Avance 400, and Varian INOVA 400 spectrometers, positive-mode electrospray mass spectra (ES⁺-MS) on a Finnigan TSQ mass spectrometer, IR spectra on a Bruker TENSOR 27 spectrometer, UV-vis data on an Analytik Jena Specord S600 spectrophotometer, and circular dichroism data on a JASCO J-710 CD spectrophotometer. Single crystal X-ray diffraction data were obtained using the molybdenum source (Mo K_α, λ = 0.71073 Å) of an Oxford Diffraction Supernova dual-source diffractometer with an Oxford Diffraction Atlas CCD detector. C/H/N analyses were performed by Chemical Instrumentation Facility (Iowa State University) and Zentralabteilung für Chemische Analysen (Forschungszentrum Jülich). Magnetic measurements were performed in the range of 2 to 290 K at 0.1 Tesla using a Quantum Design MPMS-5XL SQUID magnetometer.

Synthesis of (*R*)- and (*S*)-H₂pedea [(*R*)-1, (*S*)-1] and (*R/S*)-H₂pedea [(*R/S*)-1]. Excess, dry ice-cooled ethylene oxide (4 to 6 mL) was added to a solution of 1-phenylethylamine (1.00 g, 1.055 mmol, 8.25 mmol) in ethanol (20 mL) at −78 °C. Once the dry ice had evaporated, it was replaced with an ice bath before the mixture was finally allowed to warm to room temperature and stirred for 4 days. After removal of solvent *in vacuo*, the resulting oil was purified by column chromatography over silica (EtOAc/hexane (1:1), then ⁱPrOH/EtOAc (1:9) and ⁱPrOH/EtOAc (1:4)), yielding the target phenylethyldiethanolamine as a viscous, pale yellow oil (1.589 g, 7.64 mmol, 93% yield). ¹H-NMR (400 MHz, D₂O): δ = 7.43–7.30 (m, 5H, 5ArH), 3.97 (q, 1H, PhCHMeN), 3.61 (t, 4H, 2CH₂OH), 2.83–2.53 (dm, 4H, 2NCH₂), 1.41 (d, 3H, CH₃) ppm. ¹³C-NMR (100 MHz, D₂O): δ 142.173 (Ar, C), 128.46 (Ar, CH), 128.39 (Ar, CH), 127.52 (Ar, CH), 60.16 (CH), 59.24 (CH₂), 51.95 (CH₂), 16.75 (CH₃) ppm. ES⁺-MS: m/z 254 [M-C₂H₄OH]⁺, 210

[MH]⁺. FTIR (KBr pellet): 3385 (s), 3085 (w), 3060 (w), 3028 (w), 2969 (s), 2937 (s), 2878 (s), 1583 (m), 1493 (m), 1451 (m), 1405 (m), 1374 (m), 1271 (w), 1202 (m), 1046 (s), 911 (w), 875 (m), 735 (s) cm⁻¹. Elemental analysis for C₁₂H₁₉NO₂·0.1H₂O, calcd. (found): C 68.28 (68.27), H 9.17 (9.15), N 6.64 (6.68) %.

Synthesis of [Fe₆((S)-pedea)₆Cl₆] [(S)-2]. (S)-H₂pedea [(S)-1] (1.605 g, 7.67 mmol) was added to a suspension of calcium hydride (0.401 g, 9.54 mmol) in dry THF (100 mL). After stirring at room temperature for approximately 1 hour, a solution of anhydrous FeCl₃ (1.245 g, 7.68 mmol) in dry THF (ca. 20 mL) was added dropwise over 45 minutes, resulting in precipitation of an orange solid. After stirring at room temperature for a further 48 hours, the orange precipitate was recovered by filtration and extracted with dichloromethane. This dichloromethane solution was evaporated to dryness yielding crude (S)-2 as an orange, microcrystalline solid (0.814 g, 0.44 mmol, 35 % yield): ES⁺-MS: m/z 1792.0 [Fe₆(pedea)₆Cl₆-H]⁺, 1754.1 [Fe₆(pedea)₆Cl₅]⁺. Elemental analysis for C₇₂H₁₀₈Cl₆Fe₆N₆O₁₃ ([(S)-2]·3H₂O), calcd. (found): C 46.86 (46.43), H 5.90 (5.84), N 4.55 (4.86) %. For magnetic analysis this material (55 mg, 0.030 mmol) was redissolved in dichloromethane (4 mL), filtered through a Whatman microfiltration membrane and re-precipitated as a yellow solid (20 mg, 0.011 mmol, 37%) by addition of THF (12 mL).

Elemental analysis for C₇₂H₁₀₆Cl₁₂Fe₆N₆O₁₄ ((S)-2·H₂O), calcd. (found) %: C 47.79 (47.85), H 5.79 (6.08), N 4.64 (4.62). FTIR (KBr pellet): 3385(s), 3085 (w), 3060 (w), 3028 (w), 2931 (s), 2869 (s), 1626 (m), 1495 (m), 1454 (s), 1390 (s), 1358 (w), 1293 (w), 1259 (w), 1238 (m), 1204 (m), 1152 (w), 1070 (vs), 1031 (w), 909 (s), 881 (w), 768 (s), 741 (w), 705 (s), 662 (w), 617 (m), 597 (w), 572 (m), 555 (m), 529 (w), 470 (w), 438 (m), 403 (m) cm⁻¹. UV-vis (DCM): λ_{max} = 280 nm (ε = 30300 M⁻¹ cm⁻¹).

Synthesis of [Fe₆{(S)-pedea}₃{(R)-pedea}₃Cl₆] [(R/S)-2 and (RSRSRS)-2]. (R/S)-2 was synthesized in a similar fashion to (S)-2, using (R/S)-H₂pedea [(R/S)-1] (0.797 g, 3.81 mmol), CaH₂ (0.20 g, 4.77 mmol), anhydrous FeCl₃ (0.650 g, 4.00 mmol) and anhydrous THF (50 mL). Crude (R/S)-2 was recovered as an orange solid (0.554 g, 0.280 mmol, 44% yield).

ES⁺-MS: m/z 1792.0 [Fe₆(pedea)₆Cl₆-H]⁺, 1754.1 [Fe₆(pedea)₆Cl₅]⁺. Elemental analysis for C₇₂H₁₀₈Cl₁₀Fe₆N₆O₁₃ ([(R/S)-2]·H₂O·2CH₂Cl₂), calcd. (found): C 44.90 (44.80), H 5.50 (5.56), N

4.25 (4.32) %. Re-dissolution of crude (*R/S*)-**2** (0.200 g, 0.126 mmol) in DCM (17 mL), filtration through a Whatman microfiltration membrane and addition of THF (51 mL) produced a pale yellow crystalline sample of (*RSRSRS*)-**2**·2CH₂Cl₂·9THF which was used for magnetic analysis and X-ray diffraction. Solvent is rapidly lost from the crystals before weighing (60 mg, 0.021 mmol, 30%): Elemental analysis for C₇₂H₁₀₂Cl₆Fe₆N₆O₁₂ [(*RSRSRS*)-**2**], calcd. (found): C 48.27 (48.33), H 5.74 (5.70), N 4.69 (4.67) %. FTIR (KBr pellet): 3439 (m), 3084 (w), 3061 (w), 3024 (w), 2924 (s), 2907 (s), 2864 (s), 1710 (w), 1601 (w), 1580 (w), 1496 (m), 1451 (m), 1388 (m), 1302 (m), 1270 (w), 1234 (w), 1192 (w), 1152 (w), 1084 (vs), 1043 (m), 1032 (m), 921 (vs), 898 (m), 880 (m), 764 (s), 740 (m), 707 (vs), 652 (w), 625 (s), 574 (s), 547 (m), 507 (m), 473 (m), 444 (m), 413 (m) cm⁻¹. UV-vis (DCM): λ_{max} = 297 nm (ε = 36400 M⁻¹ cm⁻¹).

Synthesis of [Fe₆((*R*)-pedea)₆Cl₆] [(*R*)-2**] and co-crystallization with (*S*)-**2**.** A small sample of (*R*)-**2** was synthesized in analogous fashion to (*S*)-**2**. The UV-vis absorption profile, CD and IR spectra were checked against those of (*S*)-**2**. (*R*)-**2** (0.085 g, 0.046 mmol) was then combined with an equal quantity of (*S*)-**2** in dichloromethane (16 mL) and THF (48 mL) was added. After 10 days at room temperature, followed by 7 days at -10 °C, yellow crystals were observed. IR, UV-vis and X-ray crystallographic measurements indicated formation of (*RSRSRS*)-**2** (0.012 g, 0.0065 mmol, 7% yield).

UV-vis monitored reaction of (*R*)-2** and (*S*)-**2**.** Equal quantities of (*R*)-**2** and (*S*)-**2** (estimated using the absorbances of the starting solutions) were combined in dichloromethane in a 1 cm path length quartz cuvette. The concentration of the resulting solution was *ca.* 1.75 × 10⁻⁵ M in each {Fe₆} wheel. After recording an initial spectrum, further UV-vis spectra were obtained at 45–60 minute intervals until 340 minutes.

2. Crystal structure solution and refinement of [Fe₆{(*S*)-pedea}₃{(*R*)-pedea}₃Cl₆]·9THF·2DCM ((*RSRSRS*)-**2**·9THF·2DCM)

Suitable single crystals of (*RSRSRS*)-**2**·9THF·2DCM were selected under ambient conditions, from two different samples: (i) crystallization of (*RSRSRS*)-**2** produced by direct synthesis from (*R/S*)-H₂pedea and (ii) (*RSRSRS*)-**2** produced from co-crystallization of enantiomerically pure

(*R*)-2 and (*S*)-2 (rearrangement to (*RSRSRS*)-2 occurs during the crystallization process). The crystals were rapidly mounted on a cryoloop using Dow Corning High Vacuum Grease or Paratone-N oil, and placed under the cryostream at 173 K. Crystal evaluation and collection of X-ray diffraction intensity data were performed using an Oxford Diffraction Supernova dual-source diffractometer (Mo K_{α} , $\lambda = 0.71073$ Å) with Atlas CCD detector, and data reduction was performed using Oxford Diffraction CrysAlisPro software.² Correction for incident and diffracted beam absorption effects were applied using empirical methods.³ (*RSRSRS*)-2·9THF·2DCM crystallized in the space group *P*-1 as determined by systematic absences in the intensity data, intensity statistics and the successful solution and refinement of the structure. The sample produced by co-crystallization showed significant twinning in all of the crystals tested, however the obtained data set could be integrated, solved and refined satisfactorily without special treatment. Structure solution and refinement was carried out using the Bruker SHELXTL software package.⁴ The structure was solved by direct methods and refined against F^2 by the full matrix least-square technique. All non-H atoms were refined anisotropically and H atoms were included in calculated positions except on one THF molecule disordered over a symmetry position. Restraints were applied to all of the solvent molecules, which are subject to thermal disorder. The final CIF file was validated using the IUCr CheckCIF online service. Crystal data, data collection parameters and refinement statistics for both structures are listed in Table 1. Bond lengths and angles in Table 2 refer to the higher quality structure.

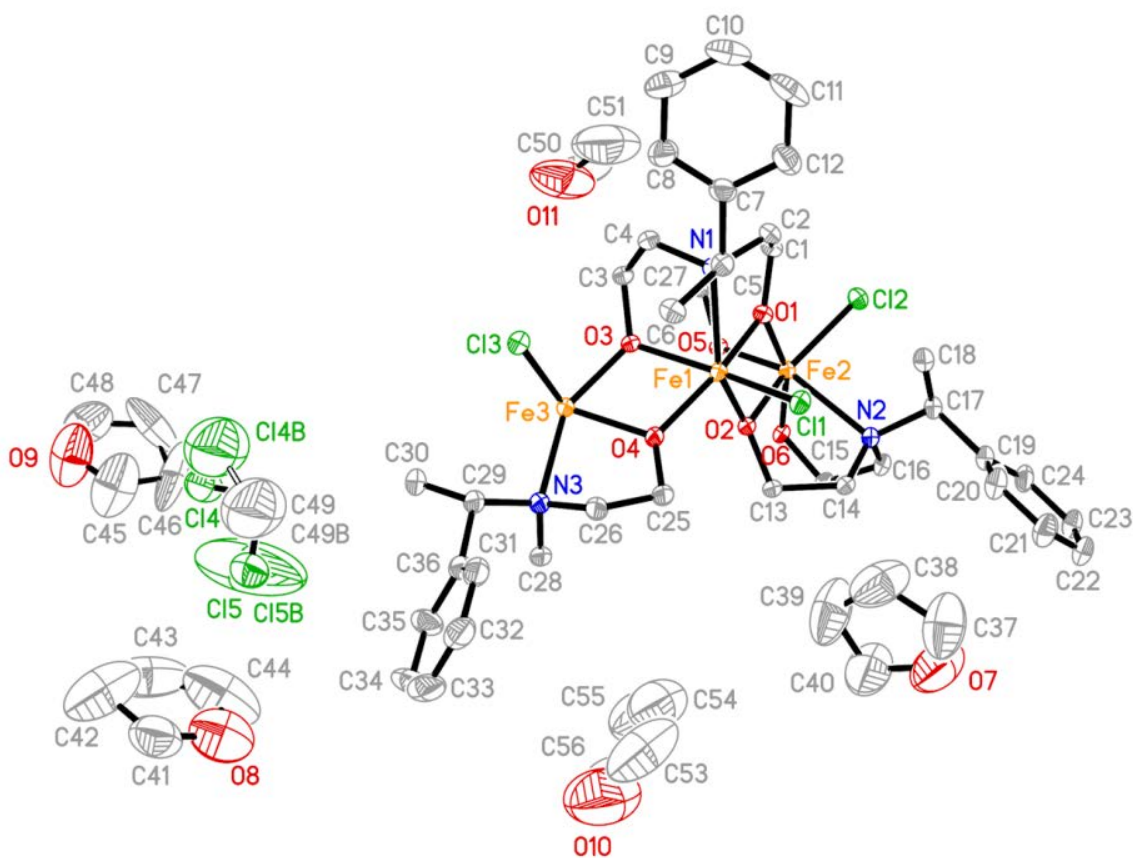


Figure S1. ORTEP representation of the asymmetric unit of (RSRSRS)-2·9THF·2DCM. ADP ellipsoids are drawn at the 30% probability level, H atoms omitted for clarity, color scheme as for Figure 2. C50, C51 and O11 are one-half of a disordered THF molecule.

Table S1. Crystal Data, Data Collection Parameters and Refinement Statistics for (RSRSRS)-[Fe₆(pedea)₆Cl₆]·9THF·2DCM ((RSRSRS)-2·9THF·2DCM)

	Direct Synthesis from (R/S)-H ₂ pedea	Co-crystallization of (R)-2 and (S)-2
Empirical formula	C ₁₁₀ H ₁₇₈ Cl ₁₀ Fe ₆ N ₆ O ₂₁	C ₁₁₀ H ₁₇₈ Cl ₁₀ Fe ₆ N ₆ O ₂₁
<i>F_w</i> / g mol⁻¹	2610.18	2610.18
<i>T</i> / K	173(2)	173(2)
<i>λ</i> / Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> / Å	12.948(3)	13.018(1)
<i>b</i> / Å	16.650(3)	16.644(1)
<i>c</i> / Å	17.224(3)	17.233(1)
<i>α</i> / °	63.96(3)	63.65(1)
<i>β</i> / °	81.05(3)	80.87(1)
<i>γ</i> / °	68.75(3)	68.78(1)
<i>V</i> / Å³	3109.5(2)	3119.0(3)
<i>Z</i>	1	1
<i>ρ</i>_{calc} / g cm⁻³	1.394	1.390
<i>μ</i> / mm⁻¹	0.961	0.959
Crystal size / mm³	0.30 × 0.20 × 0.15	0.28 × 0.20 × 0.12
No. reflections (unique)	24531 (12693)	22334 (10961)
<i>R</i>_{int}	0.0191	0.0644
<i>θ</i>_{max}	26.37	25.03
Completeness to <i>θ</i>_{max}	99.7%	99.4%
Data / restraints / parameters	12693 / 725 / 177	10961 / 725 / 168
Goodness-of-fit on <i>F</i>²	1.093	1.209
Residuals: <i>R</i>₁; <i>wR</i>₂	0.0537; 0.1775	0.1039; 0.3212
Final difference peak and hole / eÅ⁻³	1.124; -0.834	2.420 (1.10 Å from Fe3); -0.899 (0.91 Å from Fe1)

Table S2. Coordinate Bond Lengths (Å) and Angles (°) for (*RSRSRS*)-2·9THF·2DCM.

Fe(1)-Cl(1)	2.313(1)	O(2)-Fe(1)-(O3)	103.65(9)
Fe(1)-N(1)	2.332(3)	O(2)-Fe(1)-O(4)	96.19(9)
Fe(1)-O(1)	2.020(2)	O(3)-Fe(1)-O(4)	72.97(8)
Fe(1)-O(2)	1.981(2)	Cl(2)-Fe(2)-N(2)	88.82(7)
Fe(1)-O(3)	1.994(2)	Cl(2)-Fe(2)-O(1)	91.57(7)
Fe(1)-O(4)	1.998(2)	Cl(2)-Fe(2)-O(5)	97.23(9)
Fe(2)-Cl(2)	2.314(1)	Cl(2)-Fe(2)-O(6)	105.59(7)
Fe(2)-N(2)	2.340(3)	N(2)-Fe(2)-O(1)	112.2(1)
Fe(2)-O(1)	2.004(2)	N(2)-Fe(2)-O(2)	78.77(9)
Fe(2)-O(2)	1.995(2)	N(2)-Fe(2)-O(6)	77.13(9)
Fe(2)-O(5)	1.988(2)	O(1)-Fe(2)-O(2)	72.97(9)
Fe(2)-O(6)	2.018(2)	O(1)-Fe(2)-O(5)	97.23(9)
Fe(3)-Cl(3)	2.303(2)	O(2)-Fe(2)-O(5)	104.36(9)
Fe(3)-N(3)	2.347(3)	O(2)-Fe(2)-O(6)	93.51(9)
Fe(3)-O(3)	1.986(2)	O(5)-Fe(2)-O(6)	72.67(9)
Fe(3)-O(4)	2.023(2)	Cl(3)-Fe(3)-N(3)	88.91(8)
Fe(3)-O(5)	1.994(2)	Cl(3)-Fe(3)-O(3)	97.17(7)
Fe(3)-O(6)	2.002(2)	Cl(3)-Fe(3)-O(4)	105.81(7)
Cl(1)-Fe(1)-N(1)	88.64(7)	Cl(3)-Fe(3)-O(6)A	90.95(7)
Cl(1)-Fe(1)-O(1)	105.68(7)	N(3)-Fe(3)-O(4)	76.83(9)
Cl(1)-Fe(1)-O(2)	98.27(7)	N(3)-Fe(3)-O(5)A	78.7(1)
Cl(1)-Fe(1)-O(4)	91.59(7)	N(3)-Fe(3)-O(6)A	112.53(9)
N(1)-Fe(1)-O(1)	77.13(1)	O(3)-Fe(3)-O(4)	72.58(8)
N(1)-Fe(1)-O(3)	79.08(9)	O(3)-Fe(3)-O(5)A	105.48(9)
N(1)-Fe(1)-O(4)	112.82(9)	O(3)-Fe(3)-O(6)A	97.46(9)
O(1)-Fe(1)-O(2)	72.92(9)	O(4)-Fe(3)-O(5)A	94.12(9)
O(1)-Fe(1)-O(3)	93.60(9)	O(5)A-Fe(3)-O(6)A	72.87(9)

3. Additional Notes on the Synthesis and Structure of the {Fe₆} Wheels

As well as enforcing a strong chirality transfer, the steric bulk provided by the phenyl and methyl groups of the pedea ligand appears to influence the structure of the wheels and the ease of their synthesis. As stated in the main text, the Fe···Fe distances observed in the structure of (*RSRSRS*)-2 are longer than those of comparable wheel and the alternation of stereocenters around the ring appears to avoid a steric clash. To model what would occur with adjacent (*R*) or (*S*)-stereocenters, we have used Accelrys *DS Visualizer 3.0*⁵ to construct a simple model based on the structure of (*RSRSRS*)-2, switching the methyl and hydrogen positions of the (*R*)-pedea ligands to construct (*S*)-2 (Fig. S2). Based on a C–CH₃ distance of 1.54 Å this suggests three

unfavourable H $\cdots$ Cl contacts of *ca.* 1.63 Å and a C $\cdots$ Cl distance of *ca.* 2.69 Å, situated in the Fe $\cdots$ Fe pairs where methyl groups face each other across the Fe–O–Fe bridge. This should force three longer Fe $\cdots$ Fe distances and/or other structural distortions. Where H atoms face each other across an Fe $\cdots$ Fe pair, much less steric repulsion should occur and shorter Fe $\cdots$ Fe distances are possible. The slightly stronger antiferromagnetic coupling observed in homochiral (*S*)-**2** vs. (*RSRSRS*)-**2** implies that overall, this results in average Fe $\cdots$ Fe distances that are longer than those in (*RSRSRS*)-**2**. The shift of the LMCT bands in the UV-vis (see below) is also consistent with a change in the Fe(III) coordination geometry. The model below also suggests that the initial dissociation pathway of the homochiral wheels is into [Fe₂(pedea)₂Cl₂] dimers in which H-atoms face each other across the Fe–O–Fe bridge.

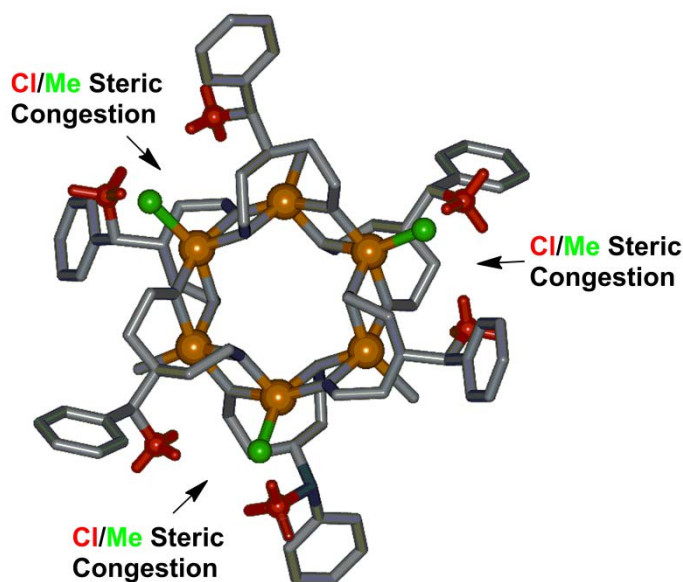


Figure S2. Model of [Fe₆{(*S*)-pedea}₆Cl₆], (*S*)-**2**. The red methyl groups and three green chloro ligands highlight the sterically congested faces of the wheel. Fe atoms shown as gold spheres; all other atoms are grey with H (other than methyl H) omitted for clarity.

These steric factors have a dramatic effect on the yield of the homochiral wheels when the reaction is performed in less than perfectly dry THF. The quoted (35%) yields of enantiomerically pure products could only be achieved with sodium-dried THF, and THF produced from a drying column or bought in SureSeal bottles resulted in much less efficient reaction (*ca.* 10% yield). The reaction of (*R/S*)-pedea with FeCl₃ consistently gave a yield of

mixed diastereomers of 44%, regardless of the nature of the THF. This indicates that the steric clash described above significantly reduces the ability of the ligand to compete with adventitious water in the homochiral system, and suggests that homochiral wheels are probably only formed in very small quantities when racemic ligand is used.

4. UV-visible Spectra

The UV-vis spectra of (S)-2/(R)-2, crude (R/S)-2 and crystalline (RSRSRS)-2 were recorded at concentrations of *ca.* 3×10^{-5} M in dichloromethane. The strong absorption at around 280–300 nm is assigned to ligand N,O,O $\rightarrow$ Fe^{III} charge transfer, and red shifts from 280 nm in the enantiomerically pure compounds, to 290 nm in crude (R/S)-2 (mixture of diastereomers) and 297 nm in the crystallized (RSRSRS)-2. The spectrum of the pro-ligand (S)-H₂pedea was also recorded in dichloromethane (*ca.* 10^{-4} M). The weak absorption of the ligand ($\epsilon < 1000$ M⁻¹ cm⁻¹) between 280 and 300 nm confirms that the peaks in the wheel compounds must be primarily associated with charge transfer processes, rather than phenyl $\pi \rightarrow \pi^*$ transitions.

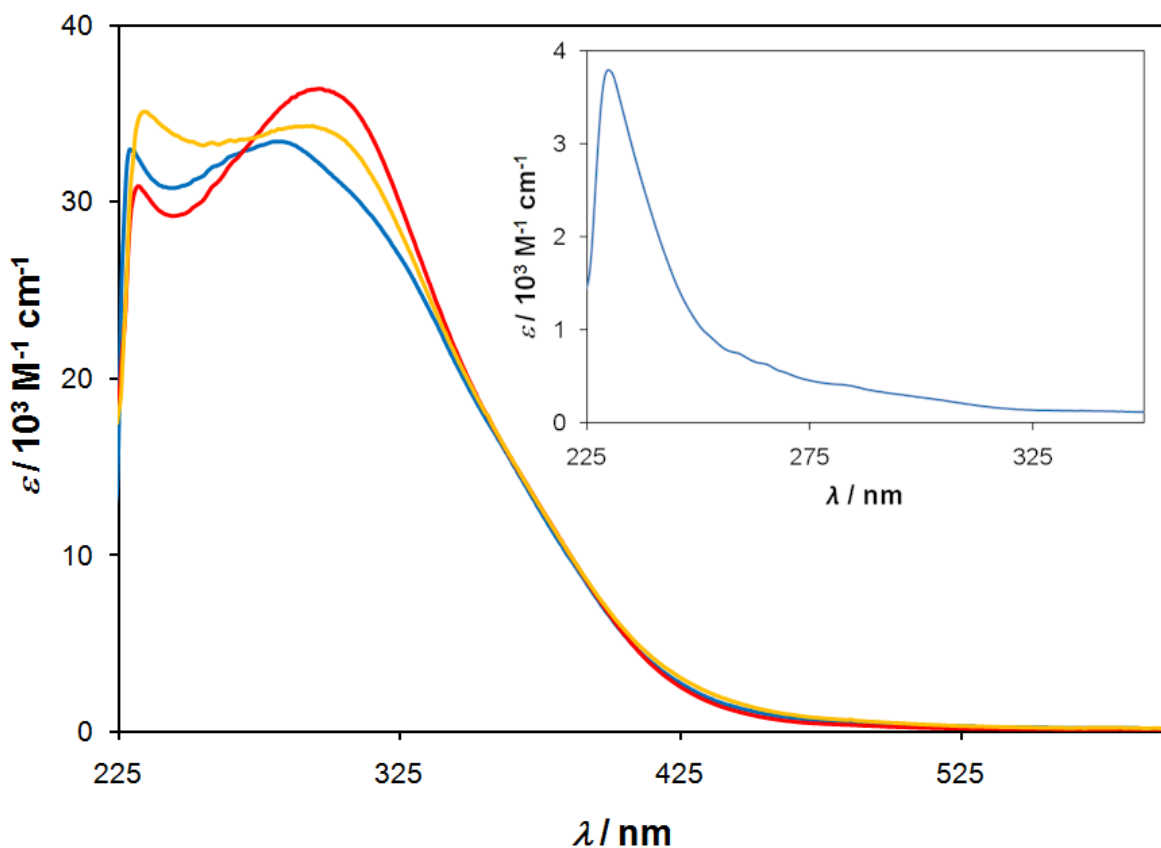


Figure S3. UV-vis spectra of enantiomerically pure (S)-2 (blue), crude (R/S)-2 (orange) and crystalline, diastereomerically pure (RSRSRS)-2 (red). For comparison, the inset shows the ligand (S)-1 in the range of 225 to 350 nm. Spectra were recorded at 293 K in dichloromethane.

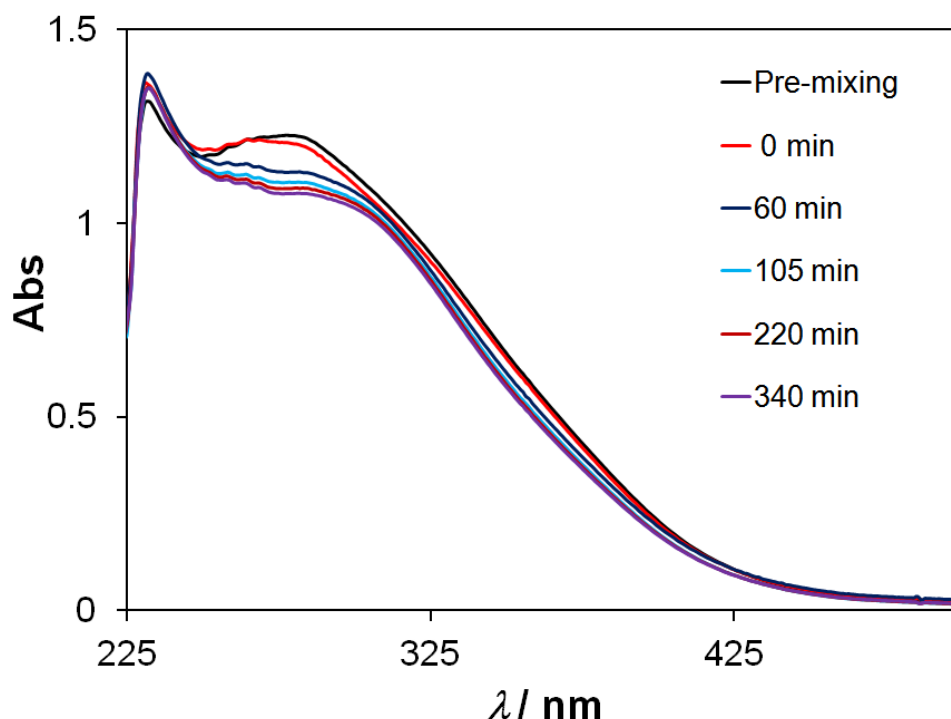


Figure S4. Evolution of the UV-spectrum of a mixture of (S)-2 and (R)-2 in DCM at 298 K. The ‘pre-mixing’ spectrum is an average of the spectra of pure (unreacted) (S)-2 and (R)-2 solutions.

5. Magnetic Measurements and Fitting of (S)-2 and (RSRSRS)-2

The low-field magnetic susceptibilities of (S)-2 and (RSRSRS)-2 were determined in the temperature range of 2.0–290 K in a static applied field of 0.1 Tesla. The data were corrected for diamagnetic contributions ($\chi_{\text{dia}} = -0.8967 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ for both compounds). The octahedrally coordinated Fe(III) centers ($^6S_{5/2}$) in both compounds represent spin-only sites. Our computational framework CONDON 2.0⁶ was used to evaluate the Heisenberg-type spin Hamiltonian

$$\hat{H}_{\text{ex}} = -2 \left[J \left(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4 + \hat{S}_4 \cdot \hat{S}_5 + \hat{S}_5 \cdot \hat{S}_6 + \hat{S}_6 \cdot \hat{S}_1 \right) \right]$$

where a common exchange energy J quantizes the coupling between nearest-neighbor $S = 5/2$ centers in the hexagonal spin rings. Impurities (mononuclear Fe(III) complexes) were assessed by the impurity fraction ρ defined as $\chi_{\text{total}} = (1-\rho) \times \chi(\{\text{Fe}_6\}) + \rho \times \chi_{\text{impurity}}$, where $\chi(\{\text{Fe}_6\})$ represents the susceptibility of the $\{\text{Fe}_6\}$ wheel and χ_{impurity} the Curie susceptibility of an $S = 5/2$ center (i.e. a [Fe(pedeac)Cl] monomer). Least-squares fitting to this model yields $J = -14.34 \text{ cm}^{-1}$ for (S)-2 and $J = -13.71 \text{ cm}^{-1}$ for (RSRSRS)-2.

6. Paramagnetic ^1H -NMR

^1H -NMR spectra of paramagnetic species (*S*)-**2**, (*RSRSRS*)-**2** and the crude mixture of diastereomers (*R/S*)-**2** were acquired at 400 MHz in d_2 -DCM, and also d_6 -benzene for (*R/S*)-**2**; using a relaxation delay of 0.15 s, an acquisition time of 0.5 s and processing with an exponential line broadening factor of 2 Hz. Although we used a wide sweep width (initially 48000, then 32000 Hz), we found that the signals observed were confined to the displayed range of -2 to 14 ppm, in common with other ferric wheels.⁷ Typically, 5 to 12 mg of the compound was dissolved in 0.75 mL of solvent: concentrations are noted under the spectra displayed below. Spectra, and some additional notes in the form of extended captions, are displayed on the following pages.

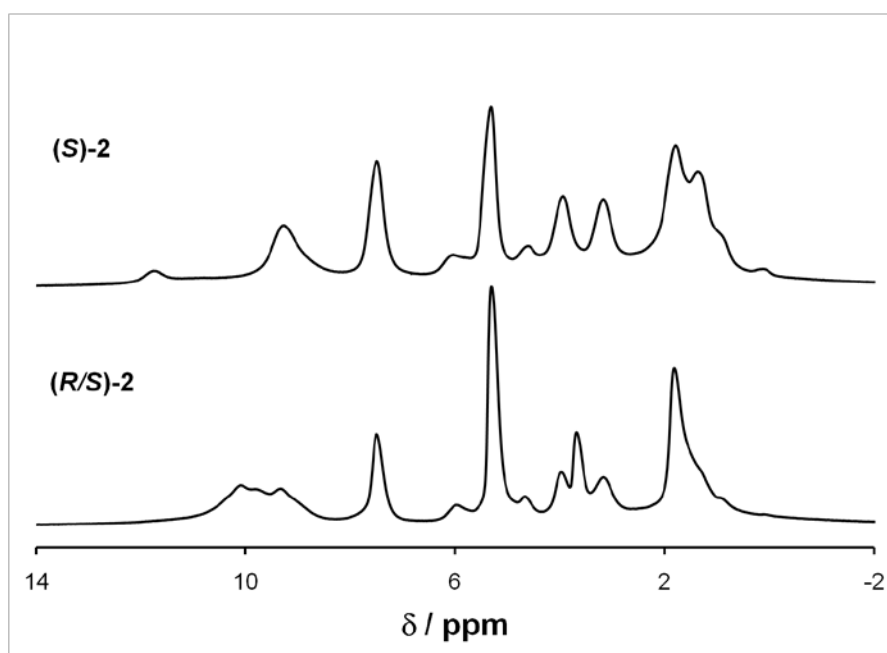


Figure S5. ^1H -NMR spectra of (*S*)-**2** and crude (*R/S*)-**2** acquired at 400 MHz in CD_2Cl_2 at 293 K; concentration: 8.8×10^{-3} M. Although the overall form of the spectra is very similar, the absence of the small peaks at 11.74 and 0.11 ppm suggests that the enantiomerically pure (*S*)-**2** and (*R*)-**2** are not significant components in the (*R/S*)-**2** mixture of diastereomers.

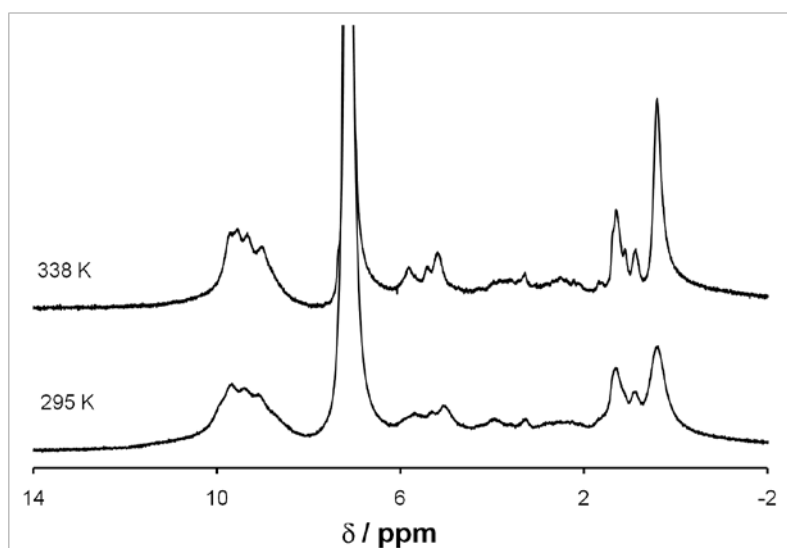


Figure S6. ¹H-NMR spectra of crude (R/S)-2 acquired at 400 MHz in C₆D₆ at 295 and 338 K; concentration: 8.8×10^{-3} M. The continued observation of three peaks between 8 and 10 ppm upon heating to 338 K indicates that exchange processes in the heterochiral wheels are still slow at this temperature.

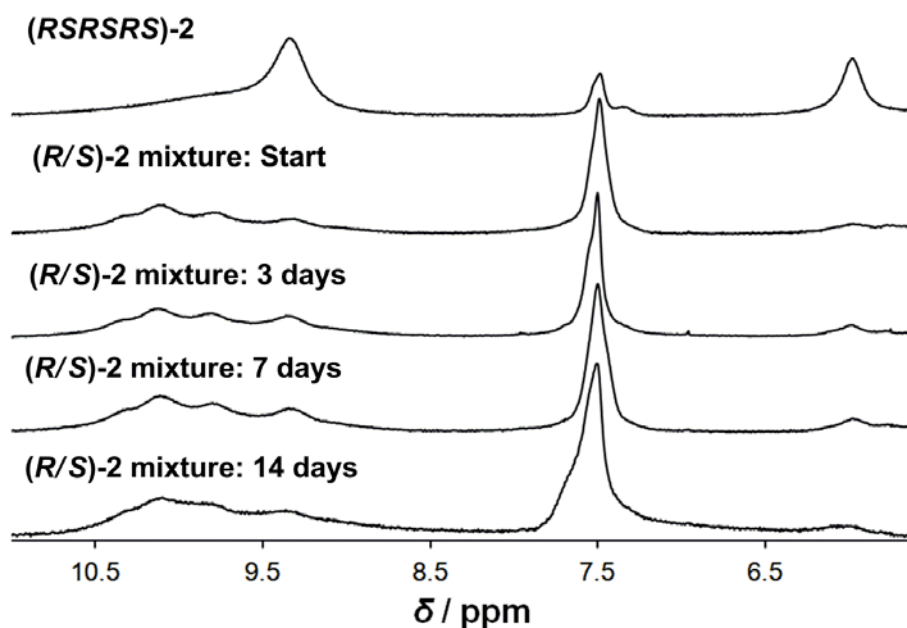


Figure S7. ¹H-NMR spectra of (RSRSRS)-2 and crude (R/S)-2 acquired at 400 MHz in CD₂Cl₂, at 298 K, concentration: 3.6×10^{-3} M. The most diagnostic chemical shift range is selected: the three or four peaks observed in (R/S)-2 in the range of 9.3 to 10.5 ppm appear to result from the different diastereomers, since (S)-2 and (RSRSRS)-2 have only one peak in this range. The relative intensities of these peaks do not appear to change significantly over time.

7. FTIR Spectra

IR spectra of enantiomerically pure (*S*)-**2**, centrosymmetric diastereomer (*RSRSRS*)-**2** and crude (*R/S*)-**2**, recorded as KBr pellets, are displayed below in Figure S8. Overall, the spectra are very similar, but there are clear differences between the spectrum of (*S*)-**2** and the heterochiral materials, and more subtle ones between crystallized (*RSRSRS*)-**2** and the crude (*R/S*)-**2**.

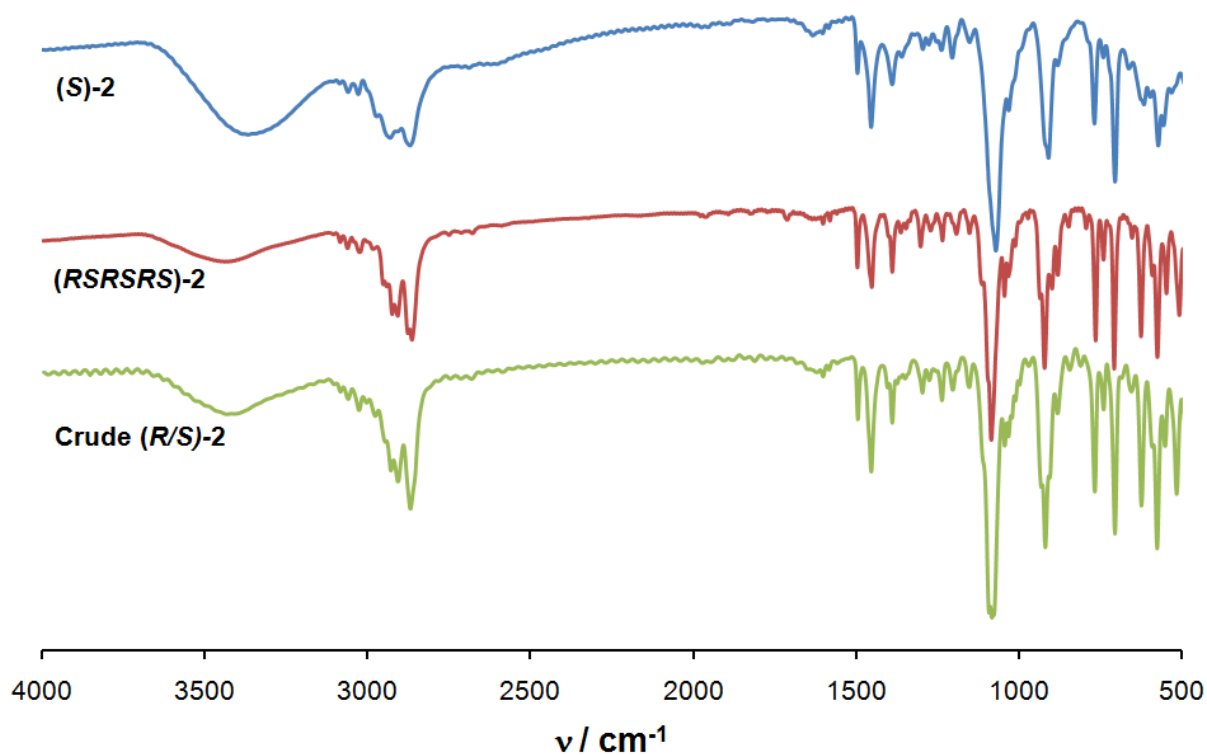


Figure S8. FTIR spectra (KBr pellets) of (*S*)-**2**, (*RSRSRS*)-**2**, and crude (*R/S*)-**2**.

8. FTIR and UV-vis comparison of (*RSRSRS*)-2 produced by co-crystallization with directly synthesized material

To ensure that all of the solid material produced by co-crystallization of (*R*)- and (*S*)-2 was (*RSRSRS*)-2, we compared its FTIR and UV-vis spectra with those obtained for the directly synthesized material, and crude (*R/S*)-2. Although the three IR spectra in Figure S9 are very similar, it can be seen that the form of the CH stretching region in the two (*RSRSRS*)-2 samples is slightly different to the crude material. More significantly, expansion of the range from 1200–800 cm^{-1} indicates that the strong peak at 1084 cm^{-1} is broad in crude (*R/S*)-2, and appears to have two or three contributing vibrations. Both crystallized materials show a much sharper peak.

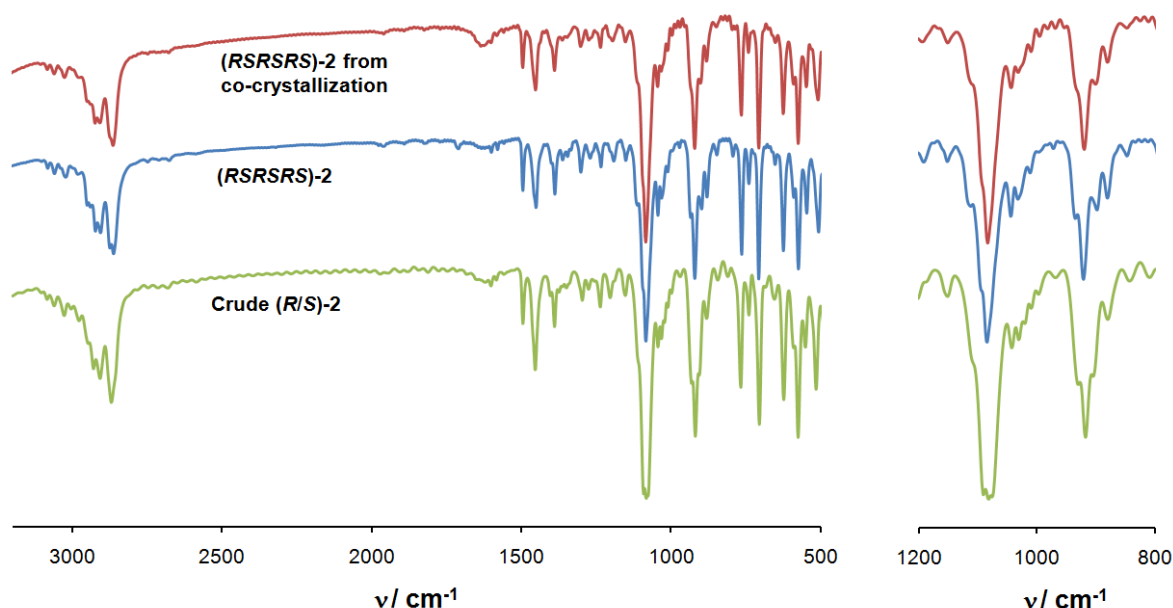


Figure S9. Comparison of IR spectra (KBr disc) from crude (*R/S*)-2 and two crystalline batches of (*RSRSRS*)-2: Left, full range; Right, expansion of the 1200–800 cm^{-1} region.

Comparison of the UV-vis data indicates that the spectra of directly synthesized and co-crystallized (*RSRSRS*)-2 are near identical (Fig. S10), showing λ_{max} red-shifted by *ca.* 7 nm from the crude material, and very similar extinction coefficients.

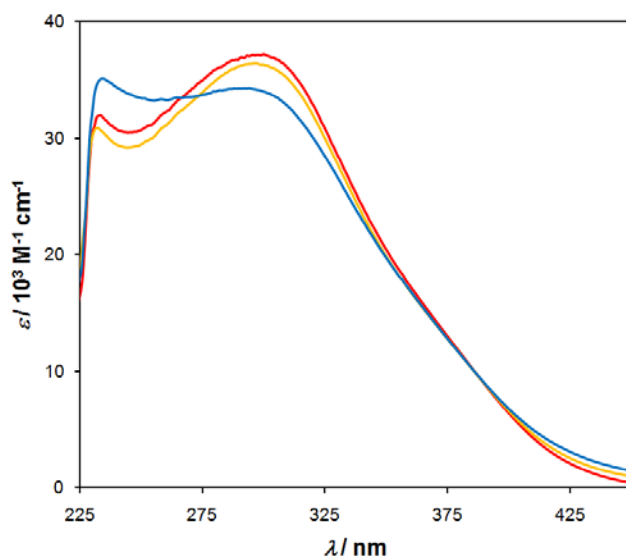


Figure S10. UV-vis spectra of co-crystallized (*RSRSRS*)-2 (red) and directly synthesized (*RSRSRS*)-2 (orange) and crude (*R/S*)-2 (blue), at 293 K in dichloromethane.

10. Notes and References

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