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A Synthetic Molecular Pentafoil Knot

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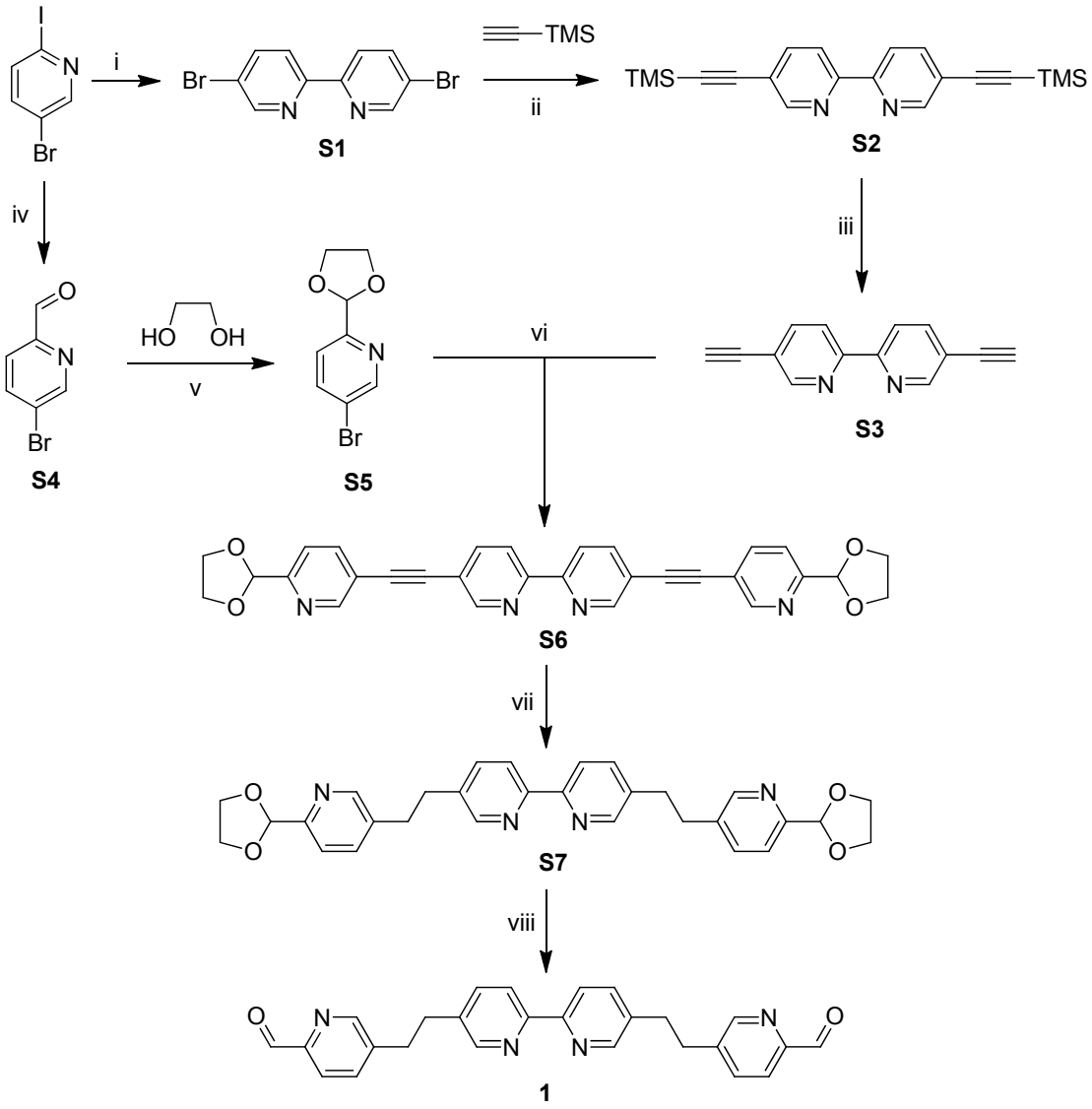
1. General Experimental Section

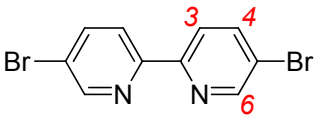
Unless stated otherwise, all reagents and solvents were purchased from Aldrich Chemicals and used without further purification. Column chromatography was carried out using Silica 60A (particle size 35-70 μm, Fisher, UK) as the stationary phase, and TLC was performed on precoated silica gel plates (0.25 mm thick, 60 F_{254}, Merck, Germany) and observed under UV light. NMR spectra were recorded on Bruker AV 400, and Bruker DMX 500 instruments. Chemical shifts are reported in parts per million (ppm) from low to high frequency and referenced to the residual solvent resonance. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet, b = broad, ddd = doublet of double doublets. ^{1}H and ^{13}C NMR assignments were made using 2D-NMR methods (COSY, ROESY, TOCSY, HSQC, HMBC) and are unambiguous unless stated otherwise. Melting points (m.p.) were determined using a Sanyo Gallenkamp apparatus and are reported uncorrected. Low resolution ESI mass spectrometry was performed with a Finnigan LCQ-MS, Micromass Platform II or Waters Quattro Ultima LC-*MS*/*MS* mass spectrometers. High resolution ESI and FAB mass spectrometry were carried out by the mass spectrometry services at the University of Edinburgh and the EPSRC National Mass Spectrometry Service Centre, Swansea, UK. Circular dichroism (CD) spectra were collected on a JASCO J-810 spectropolarimeter with a 2mm cell length.

2. Synthesis and Experimental Section

2.1 Synthesis of dialdehyde 1



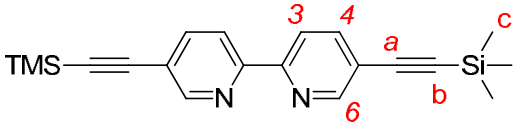
Scheme S1. Preparation of dialdehyde **1.** Reagents and conditions: (i) $Pd(PPh_3)_4$, *n*-Bu_6Sn_2, toluene, 125 °C, 3 days, 74%; (ii) $Pd(PPh_3)_4$, CuI, toluene, NEt_3, 50 °C, overnight, 87%; (iii) K_2CO_3, MeOH, THF, overnight, 85%; (iv) a) *i*-PrMgCl, THF, -10 °C, 1 hour, b) DMF, -10 °C, 1 hour, 90%; (v) *p*-TsOH, toluene, reflux, 44h, 97%; (vi) $Pd(PPh_3)_4$, THF, NEt_3, 60 °C, 2d, 58%; (vii) H_2, $Pd(OH)_2$/C, THF/methanol, 48h, 80%; (viii) 10% HCl, reflux, 1 hour, 82%.



S1

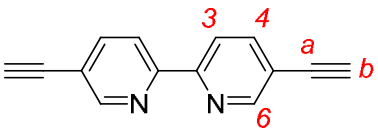
S1 was prepared by a modified literature procedure.[1]

5-Bromo-2-iodopyridine (6.60 g, 23.2 mmol) was dissolved in anhydrous toluene (120 mL) and N_2 was bubbled through the solution for 15 min. $Pd(PPh_3)_4$ (0.72 g, 0.62 mmol) and *n*-Bu_6Sn_2 (7.25 g, 12.5 mmol) were added and the solution was degassed. The mixture was stirred at reflux for 3 days. The reaction mixture was cooled down and diethylether (about 200 mL) was added. The white-brown precipitate that formed was filtered and washed consecutively with distilled water and diethylether. The precipitate was dissolved in $CHCl_3$ and the solution was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure to afford **S1** as a colorless solid (2.71 g, 8.6 mmol, 74%). NMR in agreement with literature.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, J = 2.2 Hz, 2H, H^6), 8.29 (d, J = 8.5 Hz, 2H, H^3), 7.94 (dd, J = 8.5, 2.4 Hz, 2H, H^4). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8 (C^2), 150.4 (C^6), 139.8 (C^4), 122.4 (C^3), 121.6 (C^5). HREI-MS: *m/z* = 312.8974, $C_{10}H_7N_2Br_2$ requires 312.8971 *m/z*. m.p. 212-214 °C, literature[2] 224–225 °C).



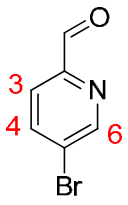
S2

Trimethylsilylacetylene (4 mL, 28.1 mmol) was added to a degassed solution of **S1** (3.0 g, 9.5 mmol) in a mixture of toluene (200 mL) and NEt_3 (75 mL) and N_2 was bubbled through the solution for 5 min. $Pd(PPh_3)_4$ (1.11 g, 0.96 mmol, 10%) and CuI (0.27 g, 1.42 mmol, 15%) were added and the solution was degassed again. The mixture was stirred at 60 °C overnight under nitrogen. The solution was concentrated under reduced pressure, the residue dissolved in CH_2Cl_2 and washed with an aqueous saturated solution of NH_4Cl, then brine, dried ($MgSO_4$) and absorbed onto SiO_2 and the solvent removed. Flash chromatography (SiO_2, CH_2Cl_2:MeOH 100:0 to 99:1) afforded **S2** as a pale yellow solid (2.9 g, 8.3 mmol, 87%). NMR in agreement with literature.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, J = 2.0, 0.7 Hz, 2H, H^6), 8.35 (dd, J = 8.3, 0.7 Hz, 2H, H^3), 7.86 (dd, J = 8.3, 2.1 Hz, 2H, H^4), 0.28 (s, 18H, H^c). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 154.3 (C^2), 152.2 (C^6), 139.9 (C^4), 120.6 (C^3), 120.5 (C^5), 101.9 ($C^{a/b}$), 99.6 ($C^{a/b}$), -0.02 (C^c). HRESI-MS: *m/z* = 349.1552 $[M+H]^+$ (calcd. for $C_{20}H_{25}N_2Si_2$ 349.1551). m.p. 162-164 °C, literature[4] 176-8 °C.



S3

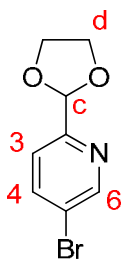
S2 (2.9 g, 8.3 mmol) was dissolved in methanol : THF (1:1, 150 mL) and powdered K_2CO_3 (1 g, 7 mmol) was added. The mixture was stirred overnight at room temperature and the solvent reduced to 50 mL, CH_2Cl_2 (150mL) was added and the mixture was washed with brine (2 x 100 mL). The organic fraction was treated with activated charcoal, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Flash chromatography (CH_2Cl_2:EtOH 100:0 to 95:5) afforded **S3** as a beige solid (1.4 g, 7.0 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) 8.77 (d, J = 1.5 Hz, 2H, H^6), 8.39 (d, J = 8.2 Hz, 2H, H^3), 7.91 (dd, J = 8.2, 2.1 Hz, 2H, H^4), 3.31 (s, 2H, H^b). ^{13}C NMR (100 MHz, $CDCl_3$) δ =154.7 (C^2), 152.4 (C^6), 140.2 (C^3), 120.7 (C^4), 119.6 (C^5), 81.8 ($C^{a/b}$), 80.7 ($C^{a/b}$). NMR assignments differ from literature.[3,4]



S4

S4 was prepared by a literature procedure.[5]

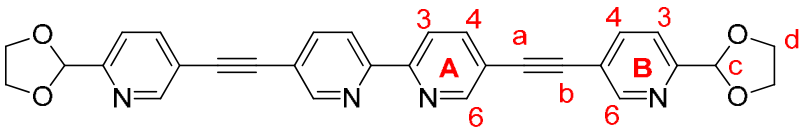
In a 250 mL, two-neck, round-bottom flask 10 g (35 mmol) of 5-bromo-2-iodopyridine was dissolved in 60 mL of THF. The solution was cooled to -10 °C and 2 M *i*-PrMgCl (19 mL, 38 mmol) was added over 30 min at a rate to maintain the temperature below 0 °C. The reaction mixture became a brown suspension. After the reaction mixture was stirred between -15 to 0 °C for 1 h, anhydrous DMF (4 mL, 51 mmol) was slowly (temperature maintained below 0 °C). The reaction mixture was stirred at 0 °C for 30 min and allowed to warm to room temperature over 1 h. The reaction mixture was then cooled to 0 °C, and 2M HCl (40 mL) was added with the internal temperature maintained below 25 °C and stirred for 30 min. The pH was adjusted to pH 6-7 by addition of 2 M NaOH. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3x 100 mL). The combined organic phases were washed with water (2x 100 mL), dried over $MgSO_4$ and the solvent removed to give **S4** as a brownish-yellow solid (5.9 g, 31 mmol, 90% yield) which was used in the subsequent step without further purification.



S5

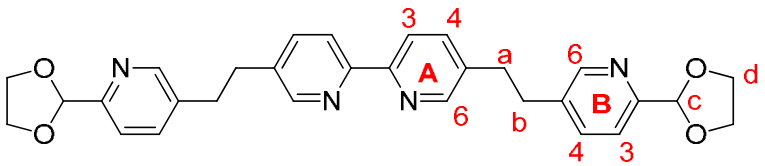
S5 was prepared by a modified procedure.[6]

S4 (1.1 g, 5.9 mmol) and ethylene glycol (0.66 mL, 11.8 mmol) were dissolved in toluene (60 mL) and TsOH (0.12 g, 0.63 mmol) was added. The mixture was stirred under reflux using a Dean-Stark for 44 hours. A 1% aqueous solution of Na_2CO_3 (60 mL) was added and the two phases were separated. The aqueous layer was extracted with $CHCl_3$ and the organic phases were combined, dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography (petroleum ether : EtOAc 95:5 to 80:20) afforded **S5** as a colorless solid (1.33 g, 5.8 mmol 97%). ^{1}H NMR ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (dd, J = 2.3, 0.5 Hz, 1H, H^6), 7.85 (dd, J = 8.3, 2.3 Hz, 1H, H^4), 7.43 (d, J = 8.3 Hz, 1H, H^3), 5.81 (s, 1H, H^c), 4.20–3.99 (m, 4H, H^d). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.8 (C^2), 150.6 (C^6), 139.5 (C^4), 122.2 (C^3), 121.2 (C^5), 103.2 (C^c), 65.7 (C^d). HRESI-MS: *m/z* = 229.9815 $[M+H]^+$ (calcd. for $C_8H_9O_2N_1Br$, 229.9811). m.p. 50-52 °C.



S6

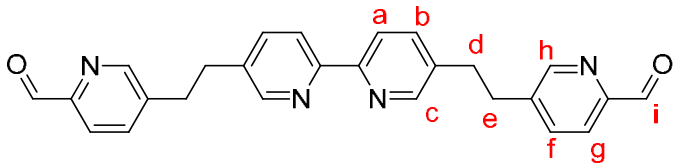
S3 (1.25 g, 6.1 mmol) and **S5** (3.08 g, 13.4 mmol) were dissolved in a mixture of THF (150 mL) and NEt_3 (30 mL). Then N_2 was bubbled through the solution for 10 minutes and $Pd(PPh_3)_4$ (2.82 g, 2.4 mmol, 40%) was added and the solution was degassed again for 10 minutes. The solution was stirred at 60 °C for 2 days and then cooled down to room temperature. Activated carbon was added and the mixture was filtered over celite. The filtrate was absorbed onto SiO_2 and flash chromatography (CH_2Cl_2:CH_3OH 100:0 to 96:4, product fluorescent blue under UV light) afforded crude **S6** as a slightly yellow solid which was dissolved in a minimum of CH_2Cl_2 and petroleum ether (100 mL) added to precipitate pure **S6** as a colorless solid (1.80 g, 3.5 mmol, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, J = 1.5 Hz, 2H, H^{A6}), 8.81 (d, J = 1.4 Hz, 2H, H^{B6}), 8.47 (d, J = 8.3 Hz, 2H, H^{A3}), 7.98 (dd, J = 8.3, 2.1 Hz, 2H, H^{A4}), 7.91 (dd, J = 8.1, 2.0 Hz, 2H, H^{B4}), 7.57 (d, J = 8.1 Hz, 2H, H^{B3}), 5.89 (s, 2H, H^c), 4.24 – 4.06 (m, 8H, H^d). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.6 (C^{B2}), 154.6 (C^{A2}), 152.0 x 2 (C^{A6}, C^{B6}), 139.7 (C^{A4}), 139.5 (C^{B4}), 120.9 (C^{B3}), 120.4 (C^{A3}), 120.2 (C^{B5}), 120.0 (C^{A5}), 103.4 (C^c), 90.3 (C^b), 90.0 (C^a), 65.8 (C^d). HRESI-MS: *m/z* = 503.1706 $[MH]^+$ (calcd. for $C_{30}H_{23}N_4O_4$, 503.1714). m.p. 264-266 °C (dec.).



S7

S6 (1.80 g, 3.5 mmol) was dissolved in THF:MeOH 2:1 (300 mL) and 20% w/w $Pd(OH)_2$/C (0.51 g) was added. The mixture was stirred under H_2 for 48 hours. The mixture was filtered through Celite and the residue washed with CH_2Cl_2. The filtrate fractions were combined and the solvent removed under reduced pressure. The resulting yellow solid was purified by flash chromatography (SiO_2,

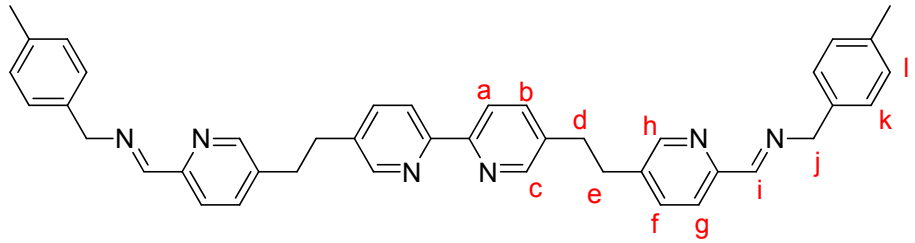
CH_2Cl_2:CH_3OH:NEt_3 100:0:0 to 95:4:1) to yield to **S7** as a colorless solid (1.47 g, 2.8 mmol, 80%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.47 (d, J = 1.7 Hz, 2H, H^{B6}), 8.46 (d, J = 2.0 Hz, 2H, H^{A6}), 8.26 (d, J = 8.1 Hz, 2H, H^{A3}), 7.57 (dd, J = 8.1, 2.3 Hz, 2H, H^{A4}), 7.49 (dd, J = 8.0, 2.2 Hz, 2H, H^{B4}), 7.44 (d, J = 8.0 Hz, 2H, H^{B3}), 5.84 (s, 2H, H^{c}), 4.24 – 4.03 (m, 8H, H^{d}), 2.99 (s, 8H, H^{a+b}). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2 (C^{B2}), 154.5 (C^{A2}), 149.7 (C^{B6}), 149.4 (C^{A6}), 137.1 (C^{A4}), 136.9 (C^{B4}), 136.6 (C^{B5}), 136.1 (C^{A5}), 120.8 (C^{A3}), 120.6 (C^{B3}), 103.7 (C^{c}), 65.7 (C^{d}), 34.5 ($C^{a/b}$), 34.4 ($C^{a/b}$). HRESI-MS: *m/z* = 511.2335 $[M+H]^+$ (calcd. for $C_{30}H_{31}N_4O_4$, 511.2340). m.p. 278-280 °C (dec.).



1

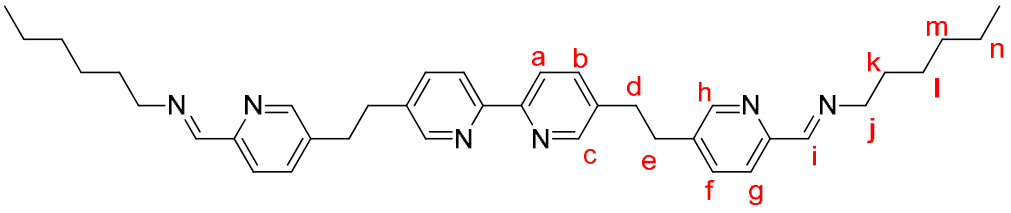
S7 (1.06 g, 2.1 mmol) was dissolved in 10% aqueous HCl (250 mL) and refluxed for 1 hour, cooled to room temperature and neutralized by slow addition of solid $NaHCO_3$. The mixture was extracted with CH_2Cl_2 and the organic fraction was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Flash chromatography (SiO_2, CH_2Cl_2 to CH_2Cl_2 : CH_3OH : NEt_3 94:4:2) afforded **1** as a colorless solid (0.727 g, 1.7 mmol , 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.05 (d, J = 0.7 Hz, 2H, H^{i}), 8.58 (d, J = 1.6 Hz, 2H, H^{c}), 8.43 (d, J = 1.8 Hz, 2H, H^{h}), 8.27 (d, J = 8.1 Hz, 2H, H^{a}), 7.89 (dd, J = 7.9, 0.6 Hz, 2H, H^{g}), 7.63 (dd, J = 7.9, 1.6 Hz, 2H, H^{f}), 7.56 (dd, J = 8.1, 2.3 Hz, 2H, H^{b}), 3.27 – 2.85 (m, 8H, $H^{d+}H^{e}$). ^{1}H NMR (500 MHz, CD_3CN) δ 9.96 (d, J = 0.7 Hz, 2H, CHO), 8.60 (d, J = 1.6 Hz, 2H, H^{c}), 8.42 (d, J = 1.9 Hz, 2H, H^{h}), 8.27 (d, J = 8.1 Hz, 2H, H^{a}), 7.85 (dd, J = 7.9, 0.6 Hz, 2H, H^{g}), 7.78 (dd, J = 7.9, 1.7 Hz, 2H, H^{f}), 7.67 (dd, J = 8.1, 2.3 Hz, 2H, H^{b}), 3.14–3.00 (m, 10H, H^{d}+H^{e}). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.94 (d, J = 0.7 Hz, 2H, C^{c}), 8.68 (d, J = 1.4 Hz, 2H, H^{c}), 8.49 (d, J = 1.7 Hz, 2H, H^{h}), 8.25 (d, J = 8.1 Hz, 2H, H^{a}), 7.92 (dd, J = 7.9, 1.6 Hz, 2H, H^{f}), 7.87 (dd, J = 7.9, 0.7 Hz, 2H, H^{g}), 7.79 (dd, J = 8.2, 2.3 Hz, 2H, H^{b}), 3.13–3.02 (m, 8H, H^{d}+H^{e}). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2 (C^{i}), 154.6 (N-C-C^{g}), 151.5 (N-C-C^{a}), 150.6 (C^{c}), 149.4 (C^{h}), 141.3 (C^{f}-C-C^{h}), 137.1 x 2 (C^{b} + C^{f}), 135.6 (C^{c}-C-C^{b}), 121.7 (C^{g}), 120.8 (C^{a}), 34.7 (C^{d}/C^{e}), 34.1 (C^{d}/C^{e}). HRESI-MS: *m/z* = 423.1812 $[M+H]^+$ (calcd. for $C_{26}H_{23}N_4O_2$, 423.1816). m.p. 212-214 °C.

2.2 Synthesis of bis(imino) ligands S8 and S9



S8

Dialdehyde **1** (50 mg, 120 µmol) was dissolved in hot MeOH (20 mL) and two drops of glacial acetic acid were added. 4-Methylbenzylamine (30 µL) was added and the mixture was refluxed for 3h. The solution was cooled to room temperature and the white precipitate was collected and washed with EtOH (~ 2mL) to give **S8** as a colorless powder (55 mg, 87 µmol, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48–8.38 (m, 6H, $H^c + H^h + H^i$), 8.25 (d, J = 8.1 Hz, 2H, H^a/H^g), 7.96 (d, J = 8.1 Hz, 2H, H^a/H^g), 7.55 (dd, J = 8.1, 2.2 Hz, 2H, H^b/H^f), 7.50 (dd, J = 8.1, 2.1 Hz, 2H, H^b/H^f), 7.23 (d, J = 7.9 Hz, 4H, H^k/H^l), 7.16 (d, J = 7.9 Hz, 4H, H H^k/H^l), 4.82 (s, 2H, H^j), 3.01 (s, 4H, H^d+H^e), 2.34 (s, 6H, CH_3). ^{1}H NMR (500 MHz, DMSO) δ 8.52–8.45 (m, 4H, H^c+H^h), 8.42 (s, 2H, H^i), 8.24 (d, J = 8.1 Hz, 2H, H^a/H^g), 7.89 (d, J = 8.1 Hz, 2H, H^a/H^g), 7.76 (m, 4H, H^b+H^f), 7.21 (d, J = 8.0 Hz, 4H, H^k/H^l), 7.15 (d, J = 7.9 Hz, 4H, H^k/H^l), 4.77 (s, 4H, H^j), 3.01 (s, 4H, H^d+H^e), 2.28 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (C^i), 154.5 (N-C-C^a/N-C-C^g), 153.0 (N-C-C^a/N-C-C^g), 149.6 (C^c/C^h), 149.4 (C^c/C^h), 137.6 (C^c-C-C^b)/C^f-C-C^h), 137.1 (C^b/C^f), 136.9 (C^c-C-C^b)/C^f-C-C^h), 136.8 (C^b/C^f), 135.9 (C^k-C-C^k/C-Me), 135.7 (C^k-C-C^k/C-Me), 129.4 (C^l), 128.3 (C^k), 121.2 (C^a/C^g), 120.8 (C^a/C^g), 64.8 (C^j), 34.6 (C^d/C^e), 34.4 (C^d/C^e), 21.3 (CH_3). HRESI-MS: m/z = 629.3382 $[M+H]^+$ (calcd. for $C_{42}H_{41}N_6$, 629.3387). m..p. 224-226 °C



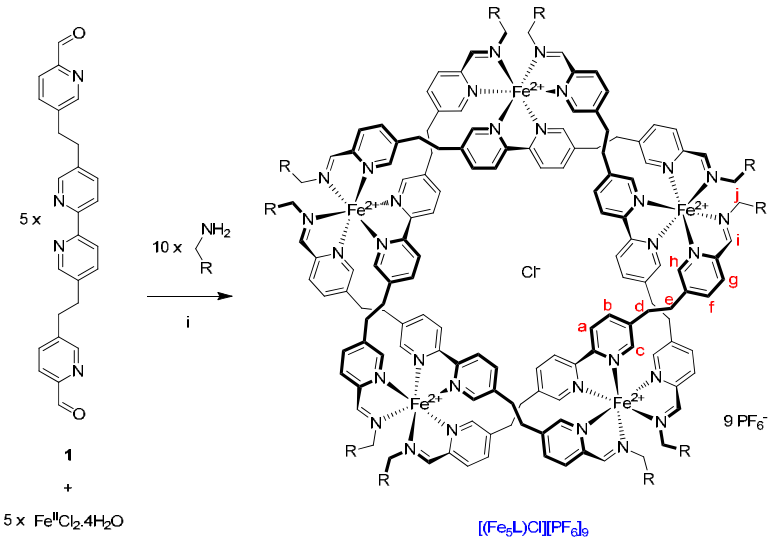
S9

Dialdehyde **1** (10 mg, 24 µmol) was dissolved in hot MeOH (50 mL) and two drops of glacial acetic acid were added. 1-Hexylamine (10 µL, 75 µmol, 3 eq) was added and the mixture was refluxed for 3h. The solution was cooled to room temperature and the volume reduced to precipitate **S9** as a fine colorless powder which was collected and washed with chilled MeOH (~5mL) (17mg, 29 umol, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47–8.41 (m, 4H, H^c/H^h), 8.34 (t, J = 1.5 Hz, 2H, H^i), 8.26 (dd, J = 8.2, 0.5 Hz, 2H, H^a), 7.89 (dd, J = 8.1, 0.6 Hz, 2H, H^g), 7.56 (dd, J = 8.2, 2.3 Hz, 2H, H^b), 7.50 (dd, J = 8.1, 2.1 Hz, 2H, H^f), 3.65 (td, J = 7.0, 1.1 Hz, 4H, H^j), 3.01 (s, 8H, H^d+H^e), 1.71 (p, J = 7.1 Hz, 4H, H^k) 1.45 – 1.24 (m, 12H, $H^l + H^m + H^n$), 0.89 (t, J = 7.0 Hz, 6H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6 (C^i), 154.5 (N-C-C^a), 153.1 (N-C-C^g), 149.7 (C^c), 149.4 (C^h), 137.4 (C^f-C-C^h), 137.1 (C^e), 136.8 (C^f), 136.0 (C^c-C-C^b), 121.1 (C^g), 120.8 (C^a), 61.8 (C^j), 34.6 (C^d/C^e), 34.4 (C^d/C^e), 31.8 (C^m), 30.9 (C^k),

27.2 (C^l), 22.8 (C^n), 14.2 (CH_3). HRESI-MS: *m/z* = 589.3997 $[M+H]^+$ (calcd. for $C_{38}H_{49}N_6$, 589.4013). m.p. 256-258 °C.

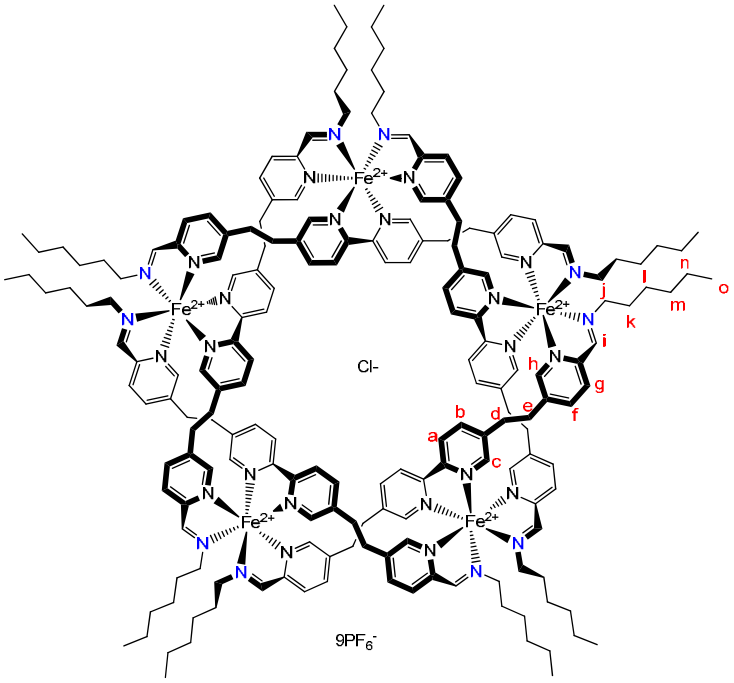
2.3 Synthesis of cyclic helicates

The general synthetic procedure for forming circular helicates is shown in Scheme S2.



Scheme S2. Preparation of helicates [**3a-g**]Cl$(PF_6)_9$ and knot [**6**]Cl$(PF_6)_9$. Reagents and conditions: (i) a) DMSO, 60 °C, 24 h (48 h for [**3g**]Cl$(PF_6)_9$), b) Excess saturated aqueous KPF_6.

2.3.1 Preparation of helicate [3a]Cl$(PF_6)_9$



[**3a**]Cl$(PF_6)_9$

A DMSO-d_6 solution of anhydrous $FeCl_2$ (250 µL of 210 mM, 52 µmol, 1.1 eq.) was added to dialdehyde **1** (20 mg, 47 µmol, 1 eq) in DMSO-d_6 (10 mL) The resulting purple solution was treated in an ultrasonic bath for 10 min and heated at 60°C for 30 min to ensure complete dissolution of the dialdehyde. A DMSO-d_6 solution of hexylamine (1.00 mL of a 100 mM DMSO-d_6 solution, 100 µmol, 2.2 equivalents) was added to the mixture. The resulting dark purple purple mixture was heated at 60 °C for one day. After cooling to room temperature, excess saturated aqueous KPF_6 was added (~5 mL). A fine suspension of a purple material formed which was collected on Celite, thoroughly washed with water, EtOH, DCM and diethylether. The purple solid was dissolved in acetonitrile and concentrated under reduced pressure to give [**3a**]$Cl(PF_6)_9$ as a purple powder (27 mg, 5.9 µmol, 63%). ^{1}H NMR: (500 MHz, CD_3CN) δ 9.93 (d, J = 8.3 Hz, 10H, H^a), 9.06 (s, 10H, H^i), 7.98 (d, J = 8.1 Hz, 10H, H^g), 7.82 (d, J = 8.0 Hz, 10H, H^f), 7.54 (d, J = 8.3 Hz, 10H, H^b), 7.17 (s, 10H, H^c), 6.42 (s, 10H, H^h), 3.55–3.34 (m, 10H, C^jH_A), 3.20–3.10 (m, 10H, C^dH_B), 3.10–3.01 (m, 20H, C^eH_A + C^jH_B), 3.01–2.92 (m, 10H, C^eH_B), 2.92–2.78 (m, 10H, C^dH_A), 1.62–1.39 (m, 20H, H^e), 1.19 (dq, J = 13.9, 7.1 Hz, 20H, H^n), 1.15–1.03 (m, 40H, H^l + H^m), 0.84 (t, J = 7.3 Hz, 30H, CH_3). ^{13}C NMR: (126 MHz, CD_3CN) δ 171.4 (C^i), 157.5 (N-C-C^a/N-C-C^g), 156.8 (N-C-C^a/N-C-C^g), 153.8 (C^h) 153.4 (C^c), 140.7 (C^c-C-C^b)/C^f-C-C^h), 140.3 (C^e), 140.1 (C^c-C-C^b)/C^f-C-C^h), 138.9 (C^f), 129.2 (C^g) 125.5 (C^a), 60.8 (C^j), 31.8 (C^l/C^m), 31.0 (C^e), 30.3 (C^d), 29.9 (C^k), 27.0 (C^l/C^m), 23.1 (C^n), 14.3 (CH_3). ESI-MS: *m/z* 1377.4 $[M\text{-}3PF_6]^{3+}$ requires 1376.8 ; 996.1 $[M\text{-}4PF_6]^{4+}$ requires 996.6; 767.8 $[M\text{-}5PF_6]^{5+}$ requires 768.5; 615.8 $[M\text{-}6PF_6]^{6+}$ requires 616.4, 507.1 $[M\text{-}6PF_6]^{7+}$ requires 507.8 *m/z*. . HRESI-MS: *m/z* 767.7143 $[M\text{-}4(PF_6)]^{5+}$ (calcd. for $C_{190}H_{240}ClF_{24}Fe_5N_{30}P_4$, 767.6946).

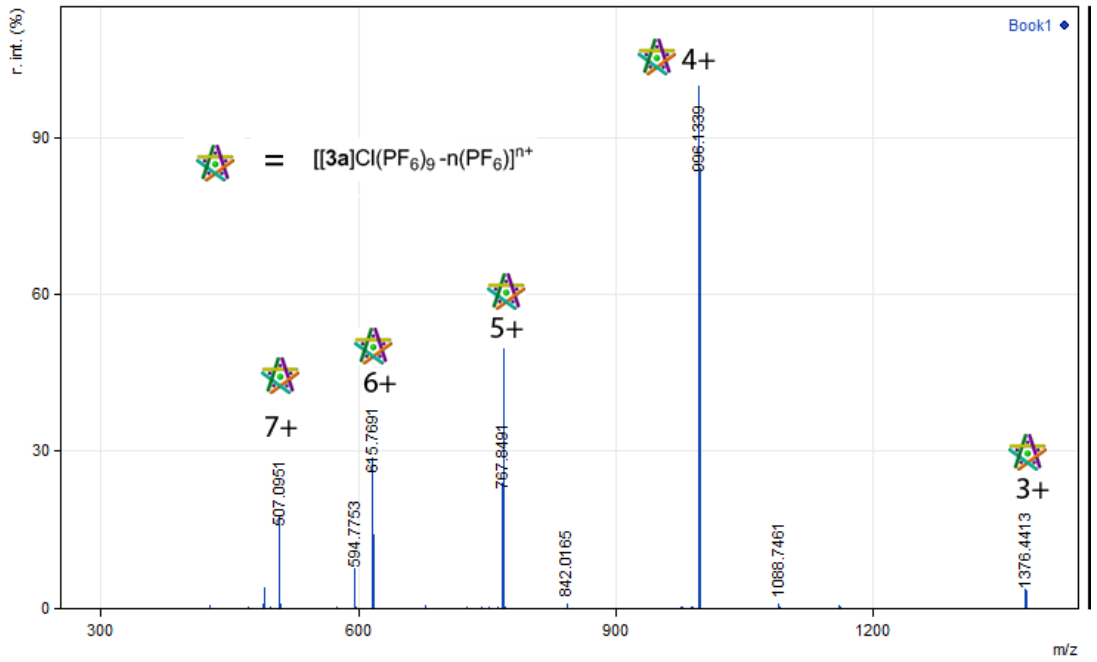
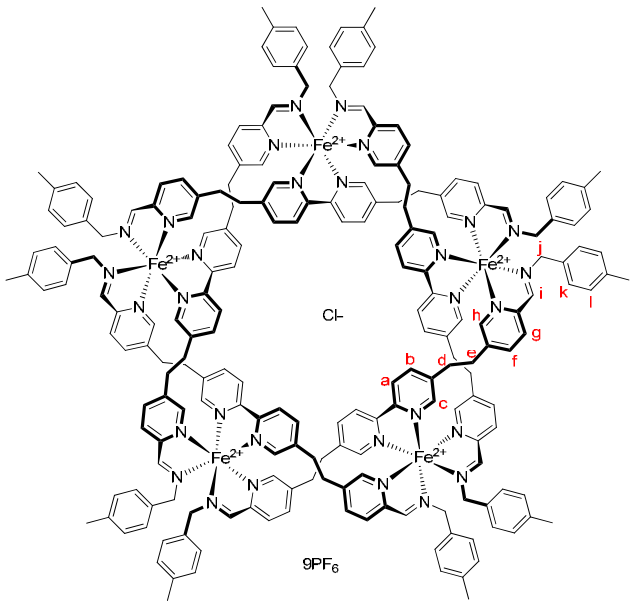


Figure S1 Low-resolution ESI-MS of helicate [**3a**]Cl(PF_6)$_9$. Calculated peaks (*m*/*z*): 1376.8 [M-3PF_6]$^{3+}$; 996.6 [M-4PF_6]$^{4+}$; 768.5 [M-5PF_6]$^{5+}$; 616.4 [M-6PF_6]$^{6+}$, 507.8 [M-6PF_6]$^{7+}$.

2.3.2 Preparation of helicate [3b]Cl(PF_6)$_9$



[3b]Cl(PF_6)$_9$

A DMSO-d_6 solution of anhydrous $FeCl_2$ (250 µL of 210 mM, 52 µmol, 1.1 eq.) was added to dialdehyde **1** (20 mg, 47 µmol, 1 eq) in DMSO-d_6 (10 mL). The resulting purple solution was treated in an ultrasonic bath for 10 min and heated at 60°C for 30 min to ensure complete dissolution of the dialdehyde. A DMSO-d_6 solution of 4-methylbenzylamine (1.00 mL of a 100 mM DMSO-d_6 solution, 100 µmol, 2.2 equivalents) was added to the mixture. The resulting dark purple purple mixture was heated at 60 °C for one day. After cooling to room temperature, excess saturated aqueous KPF_6 was added (~5 mL). A fine suspension of a purple material formed which was collected on Celite, thoroughly washed with water, EtOH, DCM and diethylether. The purple solid was dissolved in

acetonitrile and concentrated under reduced pressure to give **[3b]**Cl$(PF_6)_9$ as a purple powder (25 mg, 5.3 μmol, 56%). ^{1}H NMR: (500 MHz, CD_3CN) δ 9.85 (d, J = 8.3 Hz, 10H, H^a), 8.57 (s, 10H, H^i), 7.74 (d, J = 8.1 Hz, 10H, H^g), 7.59 (d, J = 8.1 Hz, 10H, H^f), 7.48 (d, J = 8.2 Hz, 10H, H^b), 7.16 (d, J = 7.8 Hz, 20H, H^{C3}), 7.14 (d, J = 8.0 Hz, 10H, H^c), 6.71 (d, J = 7.9 Hz, 20H, H^{C2}), 6.30 (s, 10H, H^h), 4.60 (d, J = 15.2 Hz, 10H, H^j), 4.24 (d, J = 15.4 Hz, 10H, C^jH_B), 3.16–3.09 (m, 10H, C^dH_B), 3.01 (dd, J = 10.4, 6.6 Hz, 20H, H^e), 2.88–2.80 (m, 10H, H^a), 2.37 (s, 30H, CH_3). ^{13}C NMR: (126 MHz, CD_3CN) δ 171.8 (C^j), 157.5 (N-C-C^g), 156.8 (N-C-C^a), 153.8 (C^h), 153.2 (C^c), 140.6 (C^c-C-C^b)/C^f-C-C^h), 140.3 (C^e), 140.1 x 2 (C^c-C-C^b)/C^f-C-C^h + C^l-C-C^l/C_k-C-C_k), 138.8 (C^f), 131.0 (C^l-C-C^l/C_k-C-C_k), 130.8 (C^l), 130.2 (C^k), 129.6 (C^g), 125.4 (C^a), 64.9 (C^j), 31.2 (C^e), 30.2 (C^d), 21.3 (CH_3). HRESI-MS: *m/z* = 807.6309 $[M\text{-}4(PF_6)]^{5+}$ (calcd. for $C_{210}H_{200}ClF_{24}Fe_5N_{30}P_4$, 807.6323).

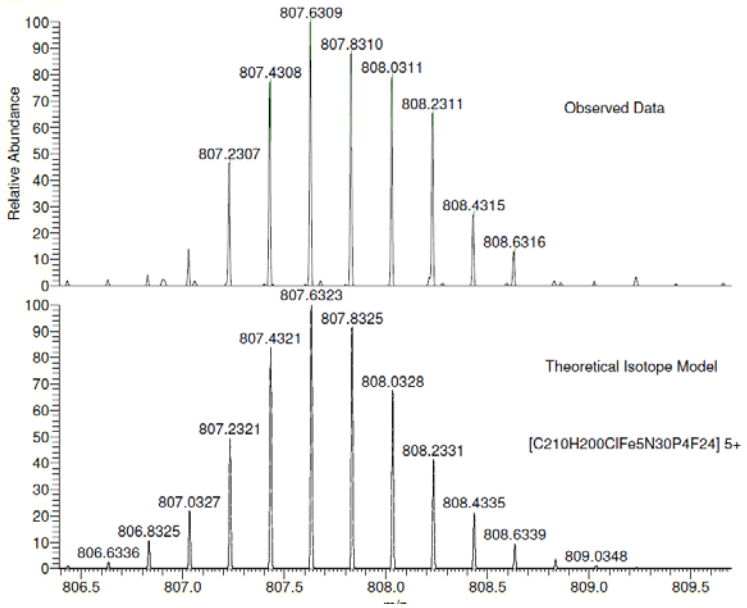


Figure S2 High-resolution ESI-MS of $[M\text{-}4PF_6]^{5+}$ peak of **[3b]**Cl$(PF_6)_9$**.** Experimental spectrum (top) and calculated (bottom).

2.3.3 Preparation of helicates [3c-f]Cl$(PF_6)_9$

Helicates **3c-f** were prepared using the follow procedure.

Dialdehyde **1** (2mg, 4.7 μ mmol) was dissolved in 1.7 mL of DMSO-d_6 and $FeCl_2$ (20 μL of 260 μM DMSO-d_6 solution, 5.2 μmol) was added. The mixture was treated in an ultrasonic bath for 10 mins. The appropriate amine was added (2.2 eq in 20 μL DMSO-d_6) and the sample was heated at 60 °C for 24 h. Excess $KPF_{6(aq)}$ was added and the resulting precipitate was collected on Celite and washed well with water, EtOH and diethylether; and redissolved in MeCN. Removal of the solvent gave helicates **3c-f** as purple powders which were dissolved in CD_3CN and the ^{1}H NMR spectra collected (Figure S3).

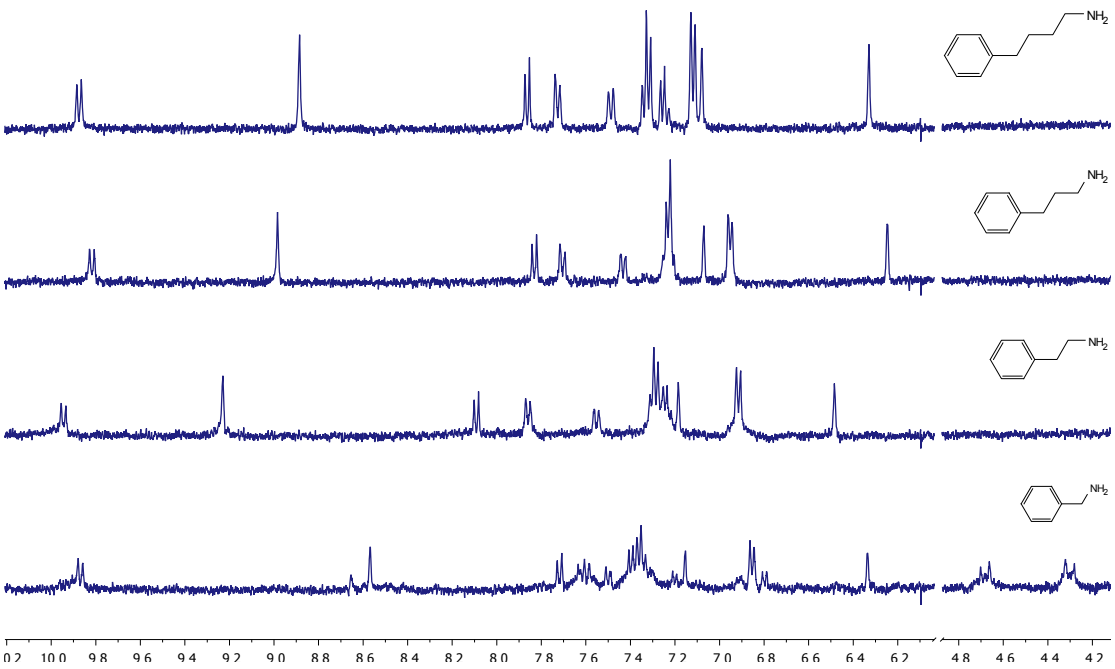
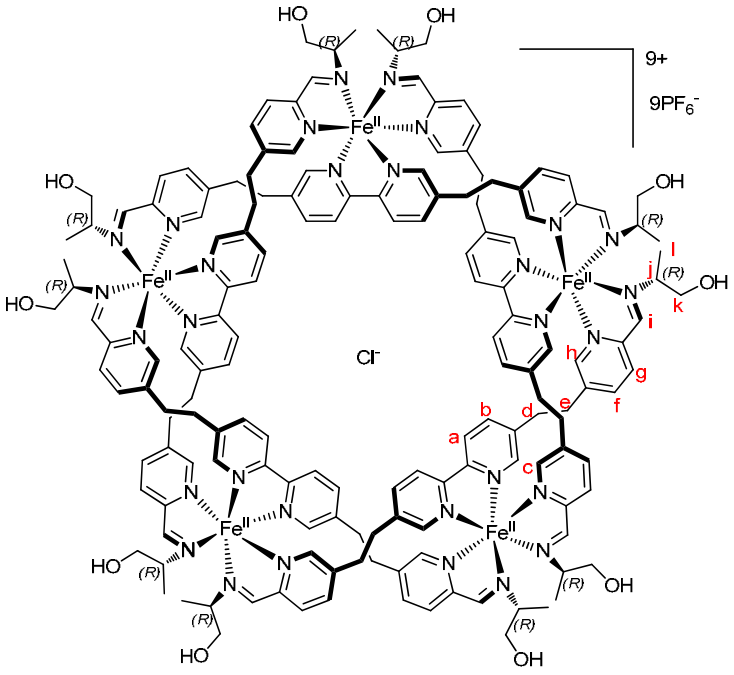


Figure S3 ^{1}H NMR (CD_3CN, 500 MHz) of helicates **3c-f**.

2.3.4 Preparation of diastereoselective helicate [3g]Cl$(PF_6)_9$



***M*-(ΔΔΔΔΔ)-[3g]Cl$(PF_6)_9$**

(*R*)-2-Amino-1-propanol (430 µL of a 240 µM DMSO solution, 100 µmol, 2.2 equivalents) was added to a solution of dialdehyde **1** (20 mg, 47 µmol) in 20 mL of DMSO-d_6 with anhydrous $FeCl_2$ (220 µl of 240 µM DMSO-d_6 solution, 52 mmol, 1.1 eq). The mixture was heated at 60 °C for 48 h. After cooling to room temperature the mixture was added to excess aqueous KPF_6 (~100 mL). A fine suspension of a purple material formed which was collected on Celite, thoroughly washed with water, little EtOH

(complex is soluble) and diethyl ether. The purple solid was dissolved in acetonitrile and concentrated under reduced pressure to give *M*-(ΔΔΔΔΔ)-[**3g**]Cl$(PF_6)_9$ as a purple powder (14 mg, 3.2 μmol, 34%). ^{1}H NMR (500 MHz, CD_3CN) δ 9.88 (d, *J* = 8.3 Hz, 10H, H^a), 9.04 (s, 10H, H^i), 8.04 (d, *J* = 8.0 Hz, 10H, H^g), 7.80 (s, 10H, H^c), 7.69 (d, *J* = 8.0 Hz, 10H, H^f), 7.52 (d, *J* = 8.3 Hz, 10H, H^b), 6.52 (s, 10H, H^h), 3.80–3.52 (m, 30H, C^kH_A + OH), 3.38–3.29 (m, 10H, C^kH_B), 3.22 (ddd, *J* = 14.8, 8.2, 5.4 Hz, 10H, H^d+H^e), 3.19–3.02 (m, 20H, H^j + H^d+H^e), 2.96 – 2.81 (m, 20H, H^d+H^e), 1.08 (d, *J* = 6.7 Hz, 30H, Me). ^{13}C NMR (126 MHz, CD_3CN) δ 171.9 (C^i), 158.0 (N-C-C^g), 156.9 (N-C-C^a), 154.7 (C^i), 153.8 (C^h), 140.7 (C^c-C-C^b)/C^f-C-C^h), 140.6 (C^c-C-C^b)/C^f-C-C^h), 140.0 (C^e), 138.9 (C^f), 129.9 (C^g), 125.2 (C^a), 64.7 (C^j), 62.3 (C^k), 30.4 (C^d/C^e), 30.3 (C^d/C^e), 18.4 (Me). ESI-MS: *m/z* 1288.8, $[M\text{-}3PF_6]^{3+}$ requires 1288.6; 930.4 $[M\text{-}4PF_6]^{4+}$ requires 930.2; 715.4, $[M\text{-}5PF_6]^{5+}$ requires 715.2; 571.8, $[M\text{-}6PF_6]^{6+}$ requires 571.8 *m*/*z*.

An identical procedure using (*S*)-2-amino-1-propanol gave *P*-(ΛΛΛΛΛ)-[**3g**]Cl$(PF_6)_9$ with identical ^{1}H and ^{13}C NMR.

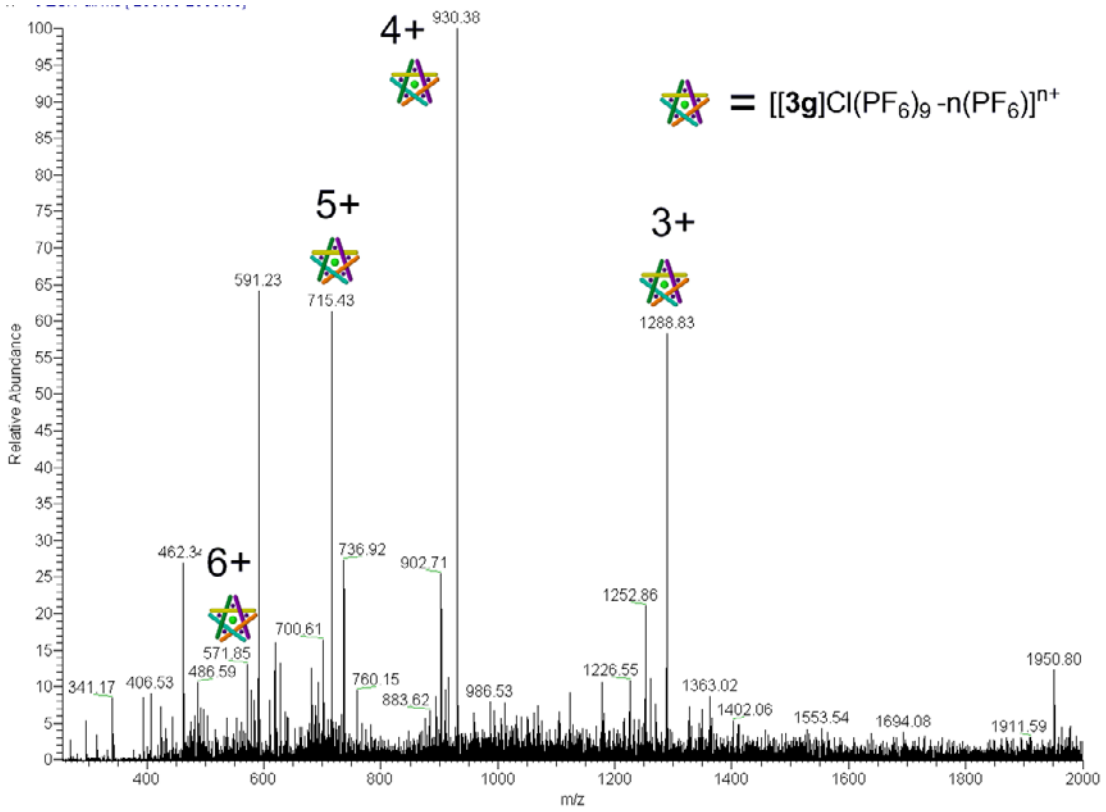
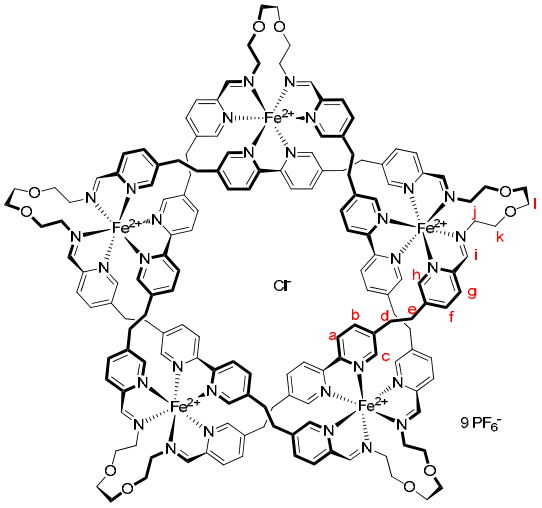


Figure S4 Low-resolution ESI-MS spectrum of enantiopure helicate [**3g**]Cl$(PF_6)_9$. Calculated peaks (*m*/*z*): 1288.6 $[M\text{-}3PF_6]^{3+}$; 930.2 $[M\text{-}4PF_6]^{4+}$; 715.2 $[M\text{-}5PF_6]^{5+}$; 571.8 $[M\text{-}6PF_6]^{6+}$.

2.3.5 Preparation of pentafoil knot [6]Cl$(PF_6)_9$



[**6**]Cl$(PF_6)_9$

A DMSO-d_6 solution of anhydrous $FeCl_2$ (250 µL of 210 mM, 52 µmol, 1.1 eq.) was added to dialdehyde **1** (20 mg, 47 µmol, 1 eq) 10 mL of DMSO-d_6. The resulting purple solution was treated in an ultrasonic bath for 10 min and heated at 60°C for 30 min to ensure complete dissolution of the dialdehyde. A DMSO-d_6 solution of 2,2′-(ethylenedioxy)bis(ethylamine) (1.00 mL of a 52 mM DMSO-d_6 solution, 52 µmol, 1.1 equivalents) was added to the mixture. The resulting dark purple purple mixture was heated at 60 °C for 2 days. After cooling to room temperature, excess saturated aqueous KPF_6 was added (~5 mL). A fine suspension of a purple material formed which was collected on Celite, thoroughly washed with water, EtOH, DCM and diethylether. The purple solid was dissolved in acetonitrile and concentrated under reduced pressure to give [**6**]Cl$(PF_6)_9$ as a purple powder (18 mg, 4.2 µmol, 44%). ^{1}H NMR (500 MHz, CD_3CN) δ 9.90 (d, J = 8.2 Hz, 10H, H^a), 9.04 (s, 10H, H^i), 8.03 (d, J = 7.9 Hz, 10H, H^g), 7.86 (d, J = 7.7 Hz, 10H, H^f), 7.50 (d, J = 7.9 Hz, 10H, H^b), 7.20 (s, 10H, H^c), 6.43 (s, 10H, H^h), 4.15–4.06 (m, 10H, C^jH_A), 3.66 (d, J = 9.6 Hz, 20H, C^kH_A + C^lH_A), 3.32 (d, J = 9.3 Hz, 10H, C^lH_B), 3.23 (d, J = 13.9 Hz, C^jH_B), 3.19–3.15 (m, 10H, C^dH_B), 3.15–3.07 (m, 10H, C^eH_A), 3.03 – 2.89 (m, 20H, C^kH_B + C^eH_B), 2.88–2.80 (m, 10H, C^dH_A). ^{13}C NMR (126 MHz, CD_3CN) δ 174.0 (C^i), 157.2 (N-C-C^a), 156.8 (N-C-C^g), 154.1 (C^h), 153.4 (C^c), 140.9 (C^c-C-C^b)/C^f-C-C^h), 140.7 (C^c-C-C^b)/C^f-C-C^h), 140.3 (C^e), 138.9 (C^f), 129.5 (C^g), 125.5 (C^a), 71.4 (C^l), 68.9 (C^k), 61.4 (C^j), 31.0 (C^e), 30.2 (C^d). HRESI-MS: m/z = 713.5736 $[M\text{-}4(PF_6)]^{5+}$ (calcd. for $C_{160}H_{170}ClF_{24}Fe_5N_{30}O_{10}P_4$, 713.5750).

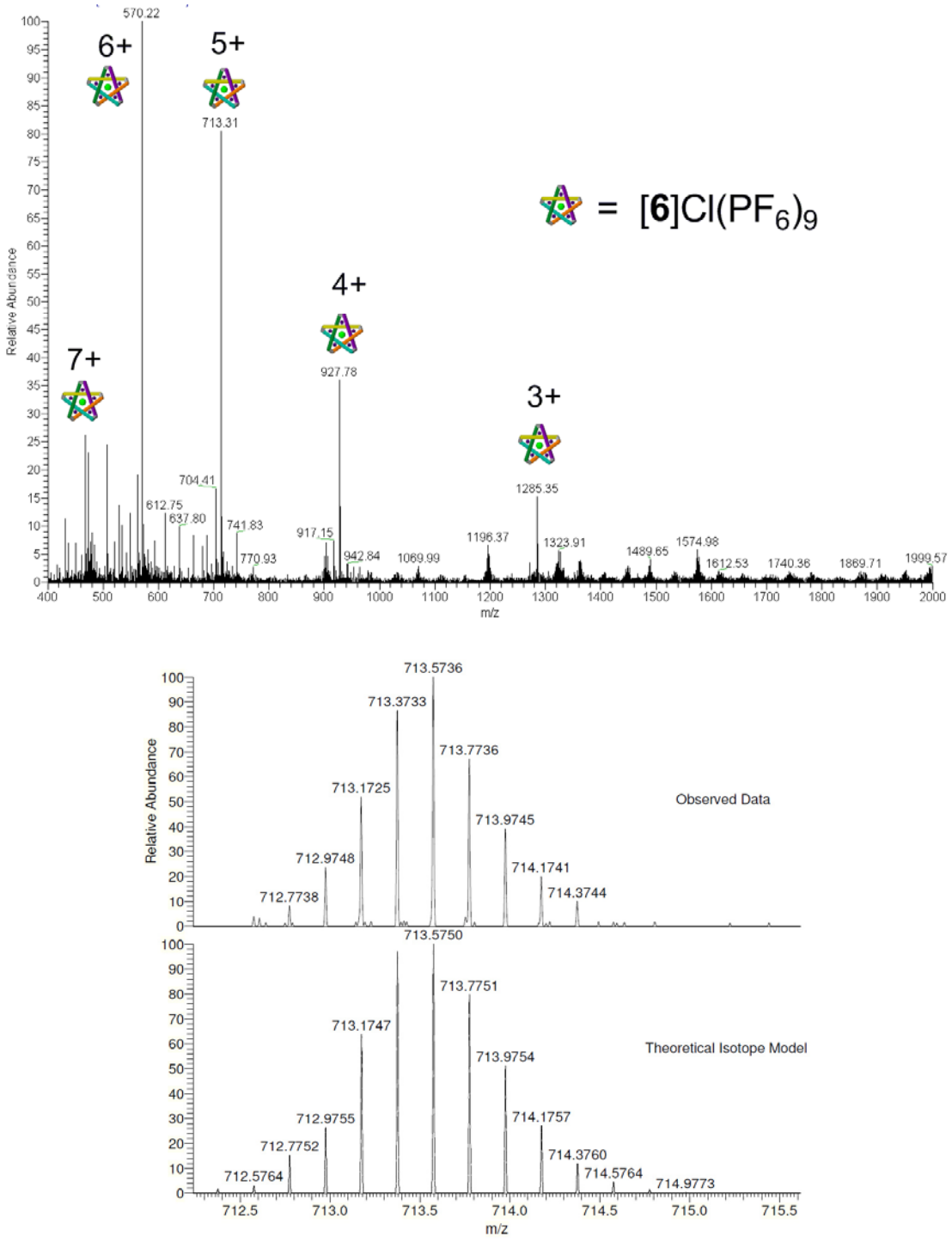
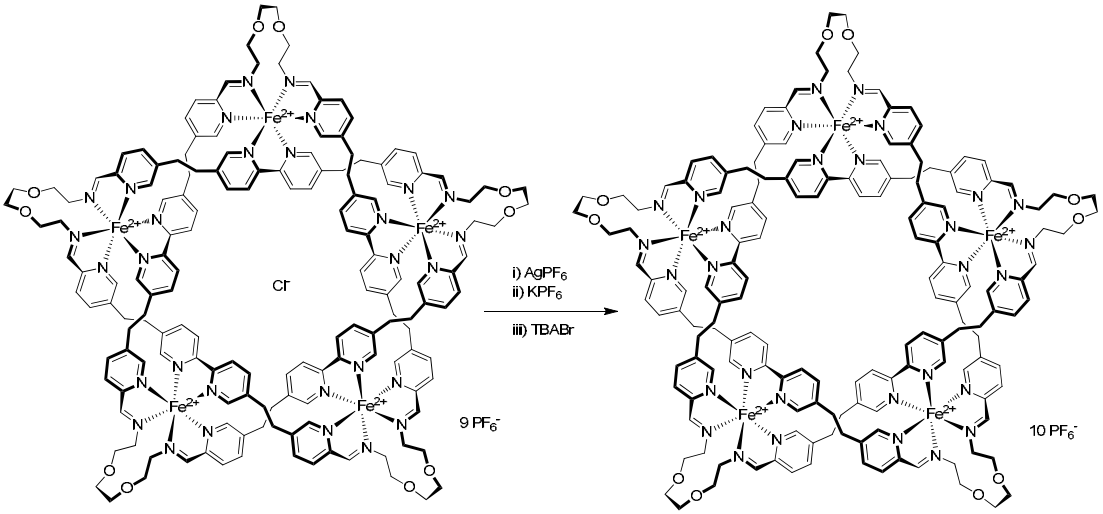


Figure S5 Low-resolution ESI-MS of pentafoil knot [**6**]Cl(PF_6)$_9$ (top), and high-resolution isotope pattern (bottom) of [M-4PF_6]$^{5+}$ peak**.**

2.3.6 Removal of Cl^- from the central cavity of $[6]^{10+}$



Scheme S3 Removal of central chloride ion from [**6**]$Cl(PF_6)_9$ with $AgPF_6$

Pentafoil knot [**6**]$Cl(PF_6)_9$ was dissolved in CD_3CN and 90 eq of $AgPF_6$ in CD_3CN was added and the mixture treated in an ultrasonic bath for 30 min. Although no precipitate was apparent - unsurprising considering the amount of $AgCl_{(s)}$ expected to be formed - ^1H NMR indicated complete removal of the Cl^- anion. Excess $KPF_{6(aq)}$ was added. The addition of Bu_4NBr in CD_3CN did not change the ^1H NMR spectrum, however, the addition of Bu_4NCl restored the ^1H signals due to [**6**]$Cl(PF_6)_9$. [**6**]$(PF_6)_{10}$ (in the presence of excess $AgPF_6$): ^1H NMR (500 MHz, CD_3CN) δ 9.11 (s, 2H, H^i), 8.95 (d, J = 8.0 Hz, 2H, H^a), 8.08 (d, J = 8.0 Hz, 2H, H^g), 7.91 (d, J = 7.7 Hz, 2H, H^f), 7.50 (d, J = 7.9 Hz, 2H, H^b), 7.31 (s, 2H, H^c), 6.58 (s, 2H, H^h), 4.12 (t, J = 10.2 Hz, 2H, C^jH_A/H_B), 3.79–3.60 (m, 4H, C^kH_A/H_B+ C^lH_A/H_B), 3.34 (d, J = 9.7 Hz, 2H, C^lH_A/H_B), 3.29–3.16 (m, 4H, C^eH_A/H_B+C^jH_A/H_B), 3.08 (m, 2H, C^dH_A/H_B), 3.00 (t, J = 8.9 Hz, 4H, C^kH_A/H_B+ C^dH_A/H_B), 2.91–2.77 (m, 2H, C^eH_A/H_B). ESI-MS (m/z): $[[\mathbf{6}]Cl(OH)(H_2O)(PF_6)_6]^{3+}$ requires 1285.96, found 1285.93; $[[\mathbf{6}](OH)(H_2O)(PF_6)_5]^{4+}$ requires 928.23, found 928.21.

2.4 Circular Dichroism of [3g]$Cl(PF_6)_9$

The CD spectra of (*R*)-[**3g**]$Cl(PF_6)_2$ and (*S*)-[**3g**]$Cl(PF_6)_2$ are shown in Figure S6. Using exciton theory[7-9] to analyse the π-π* transitions around 300 nm, (*R*)-$[\mathbf{3g}]^{10+}$ corresponds to ΔΔΔΔΔ-$[\mathbf{3g}]^{10+}$ and (*S*)- $[\mathbf{3g}]^{10+}$ corresponds to ΛΛΛΛΛ-$[\mathbf{3g}]^{10+}$. This is in agreement with both previous simple pyridyl-imine complexes[10] and a triple-stranded dinuclear Fe(II)-containing helicate.[11] Additionally, the CD

band for the MLCT transition of (*S*)-**3g** also corresponds to sign of that of Λ-[Fe(bpy)$_3$][9,12] and Λ-[Ru(phen)$_3$].[7]

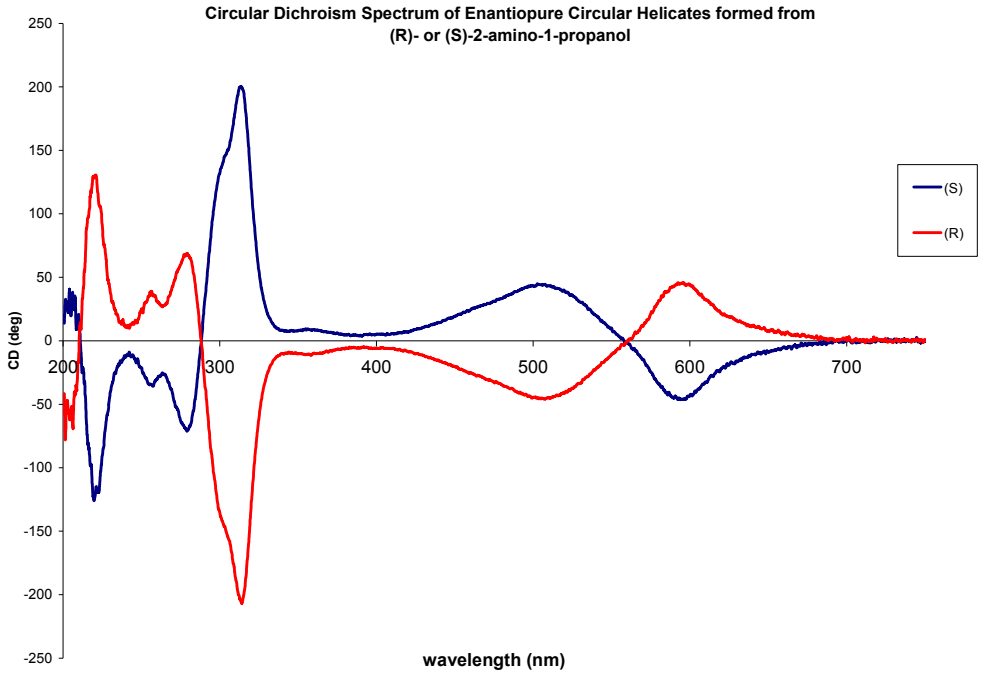


Figure S8 Circular dichroism spectra of (*R*)-[**3g**]Cl(PF$_6$)$_9$ and (*S*)-[**3g**]Cl(PF$_6$)$_9$ in MeCN.

By comparison with the X-ray crystal structure of [**6**]Cl(PF$_6$)$_9$, (*R*)-[**3g**]$^{10+}$ and (*S*)-[**3g**]$^{10+}$ correspond to *M*-(ΔΔΔΔΔ)-[**3g**]Cl(PF$_6$)$_9$ and *P*-(ΛΛΛΛ)-[**3g**]Cl(PF$_6$)$_9$. All these assignments are also supported by 2D-ROESY NMR data.

3. Knot assembly process: additional data

3.1 Monitoring of crude reaction mixture of $[6](Cl)_{10}$

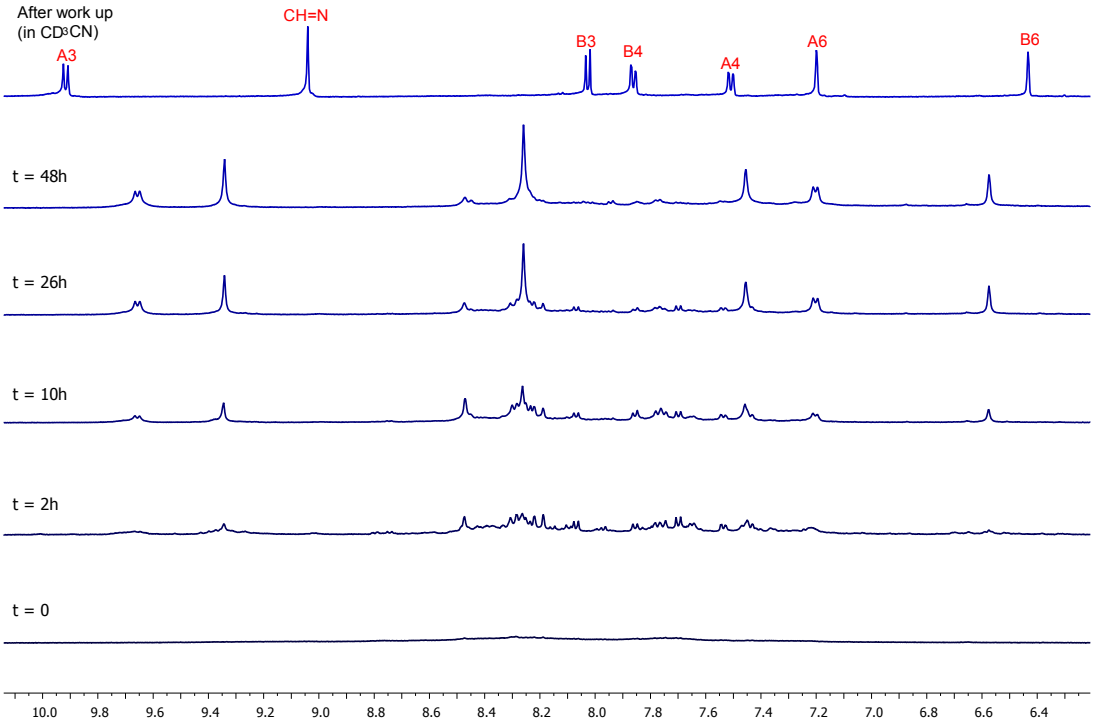


Figure S9 Formation of pentafoil knot $[\mathbf{6}]^{10+}$ monitored by ^{1}H NMR (DMSO-d_6, 500 MHz), aromatic region of spectrum shown. Spectra were collected of the crude reaction mixture after t = 0 (bottom), 2h, 10h, 26h and 48h. The top spectra is of the same sample after work-up (^{1}H NMR in CD_3CN) with ^{1}H NMR assignments indicated.

3.2 Effect of reaction stoichiometry on knot yield

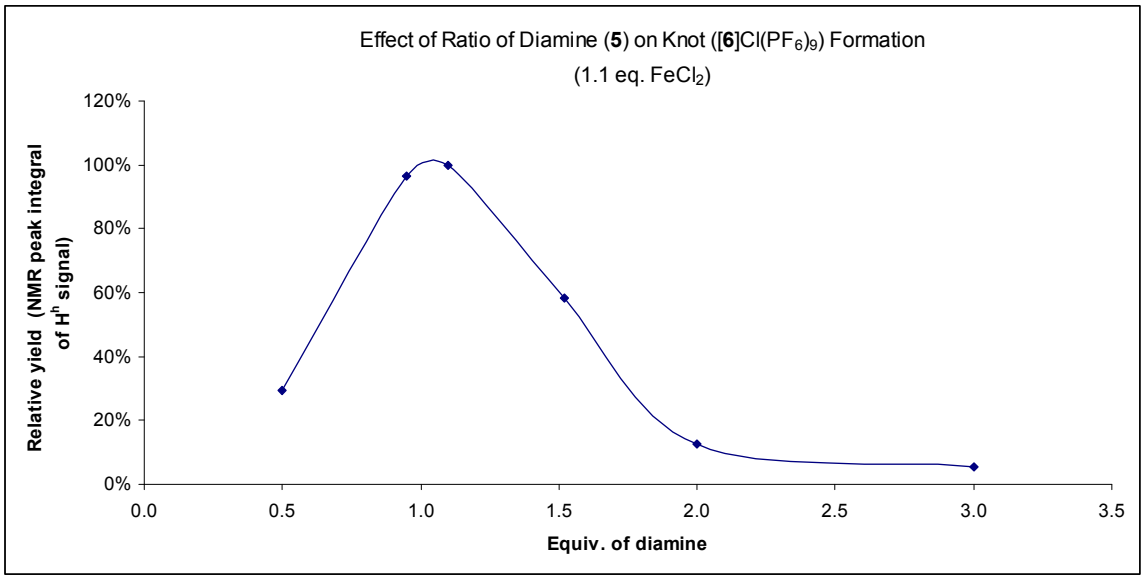


Figure S11 Effect on relative isolated yield of increasing the ratio of diamine (**5**) to dialdehyde **1**, with 1.1 equiv. of $FeCl_2$ in all cases. Relative yields measured from ^1H NMR peak integrals (CD_3CN, 500 MHz). As the equivalents of amine is increased above 1.1 equivalents, the yield drops rapidly.

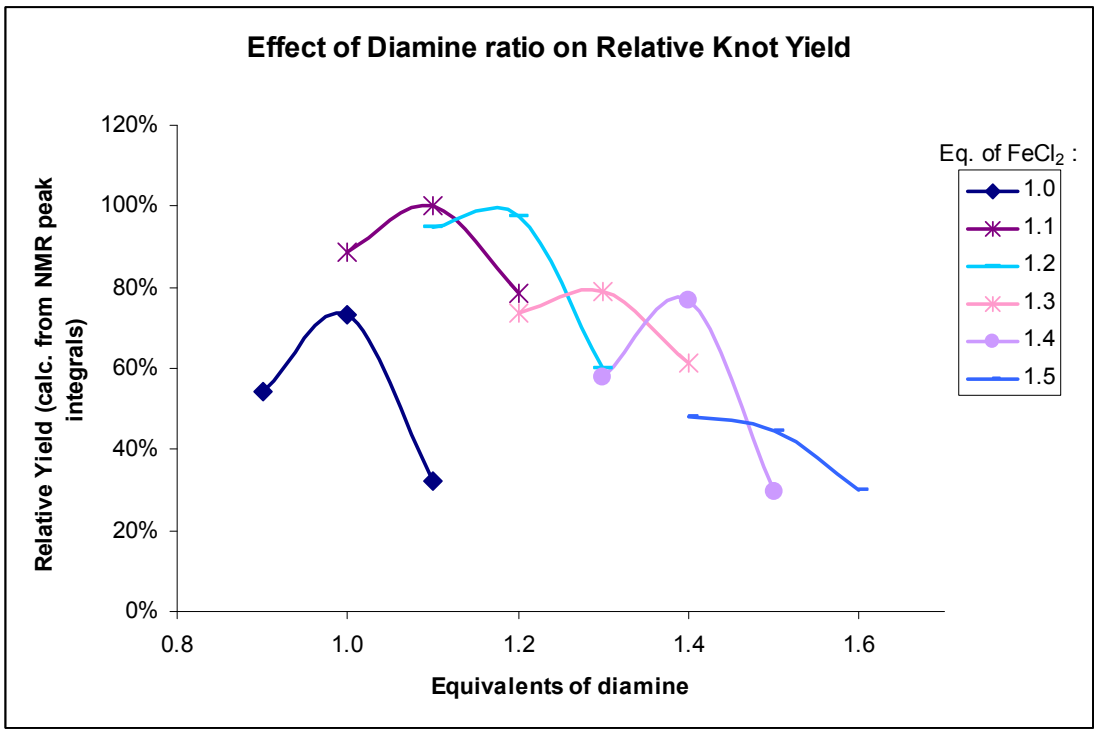


Figure S12 Effect on relative isolated yield of increasing the ratio of $FeCl_2$ and diamine (**5**) to dialdehyde **1**. ^1H NMR peak integrals (CD_3CN, 500 MHz). For any given ratio of $FeCl_2$, an equimolar amount of diamine gave the highest yield, with yields steadily decreasing as the ratio of $FeCl_2$ and diamine to dialdehyde increase. Estimated errors ±4%.

4. X-Ray crystal structure of [6]Cl(PF_6)$_9$·xSolvent

4.1 Experimental details

Purple crystals pentafoil knot [**6**]Cl(PF_6)$_9$·xSolvent were obtained by slow vapor diffusion of diethyl ether into a MeCN:Toluene (3:2) solution of [**6**]Cl(PF_6)$_9$ over 1 month. The structural analysis was performed using single crystal synchrotron X-ray diffraction data collected on beamline I19 at Diamond Light Source (UK) (l = 0.6889Å) at 100K. The CrystalClear-SM Expert 2.0 r5 suite of programs[13] was used for the data measurement and reduction. The structure were solved by charge flipping method using SUPERFLIP[14] and refined by full-matrix least-squares methods using the WinGX-software,[15] which utilizes the SHELXL-97 module.[16] Multi-scan absorption correction was applied.[13] All C-H hydrogen positions were calculated using a riding atom model with U_H = 1.2 x U_C. The crystal lattice contains a lot of disordered solvents and anions. Only eight of the nine PF_6 anions could be located, one of them severely disordered, also some of the ethylene glycol loops showed very large thermal motion (maybe due positional disorder, which however could not be modeled) and thus a few bond distance restraints between the loop atoms (C-O and C-C) had to be applied in order to avoid chemically unreasonable bond distances. All atoms, except some of the disordered O- and C-atoms with occupancy 1/3 and H-atoms, were refined anisotropically, with only a few thermal parameter restraints (EADP). The helicate [**6**]Cl(PF_6)$_9$ is solvated by a large number of badly disordered solvent molecules, only two acetonitrile molecules could be modeled (one with full occupancy, the second divided into three positions with occupancy 0.33) resulting in a moderate quality structure solution. One of the PF_6 anion that could not be located and all unresolved solvate molecules were modeled as isolated carbon or oxygen atoms with partial occupancies until plateau of ca. 1 e/Å^3 was reached. The crystal lattice contains very large voids filled with a lot of scattered electron density, the SQUEEZE protocol inside PLATON[17] was used to remove the void electron density.

Due to the poor crystal quality and diffraction power of the knot crystal, the checkcif gives 12 A and 46 B level alerts. Nearly all of these alerts (both A and B level) result from the large and deformed/ill-balanced thermal movement of the ethylene glycol atoms, the high value of weighted R and the ratio of the observed/unique reflections. The use of restrains for the thermal parameters was kept to a minimum in order to retain reasonable R-values. Very large voids (residual electron density SQUEEZED) of the crystal lattice also give an A alert. The bond distance alerts result from the large thermal movement of the atoms.

Crystal data for [**6**]Cl(PF_6)$_9$: M = 4432.87 [$C_{168}H_{176}ClF_{49}Fe_5N_{32}O_{18.5}P_8$], purple needles, 3 x 40 x 50 μm^3 [0.003 x 0.040 x 0.050 mm^3], monoclinic, space group $P2_1/c$, a = 23.444(5) Å, b = 36.333(7) Å, c = 29.094(7) Å, β = 105.335(5)º, V = 23900(9) Å^3, Z = 4, D_c = 1.232 g/cm^3, F000 = 9056, μ= 0.455 mm^{-1} , T = 100.0(1) K, $2\theta_{max}$ = 48.42°, 40213 reflections, 13300 with $I_o > 2\sigma(I_o)$, Ri_{nt} = 0.1218, 2431 parameters, 7 restraints, GoF = 1.022, R = 0.138 [$I_o > 2\sigma(I_o)$], wR= 0.422 (all reflections), 1.207 < Δρ < -0.609 e/Å^3. CCDC- 845599 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif;

4.2 Additional X-ray structure picture

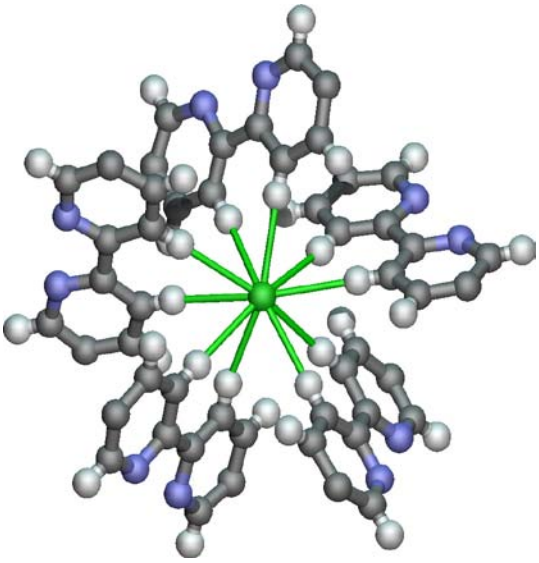


Figure S13 Chloride ion binding in the center of the helicate. The 10 CH···Cl contacts are shown.

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