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SUPPLEMENTARY INFORMATION

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Optically pure, water-stable, metallo-helical 'flexicate' assemblies with antibiotic activity

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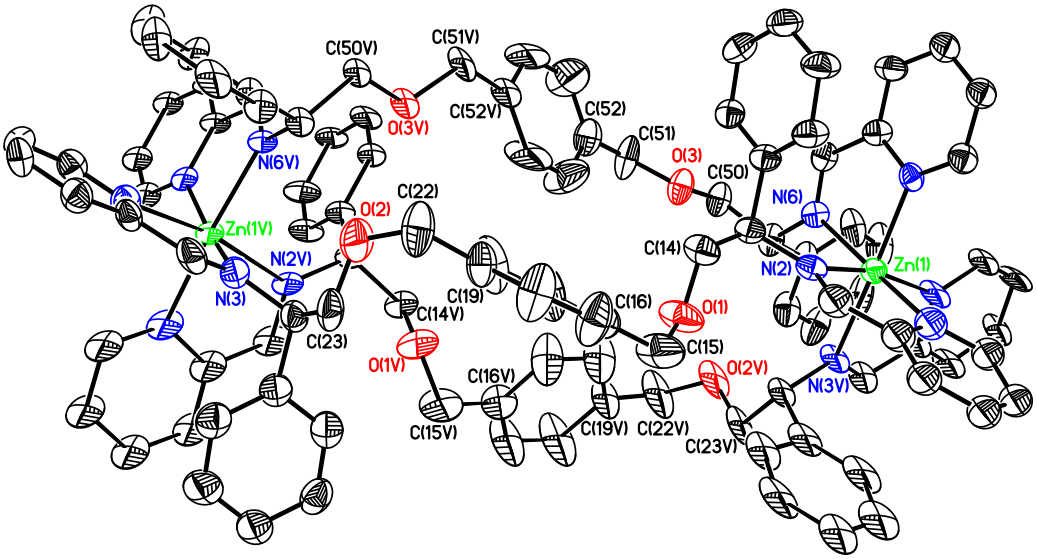
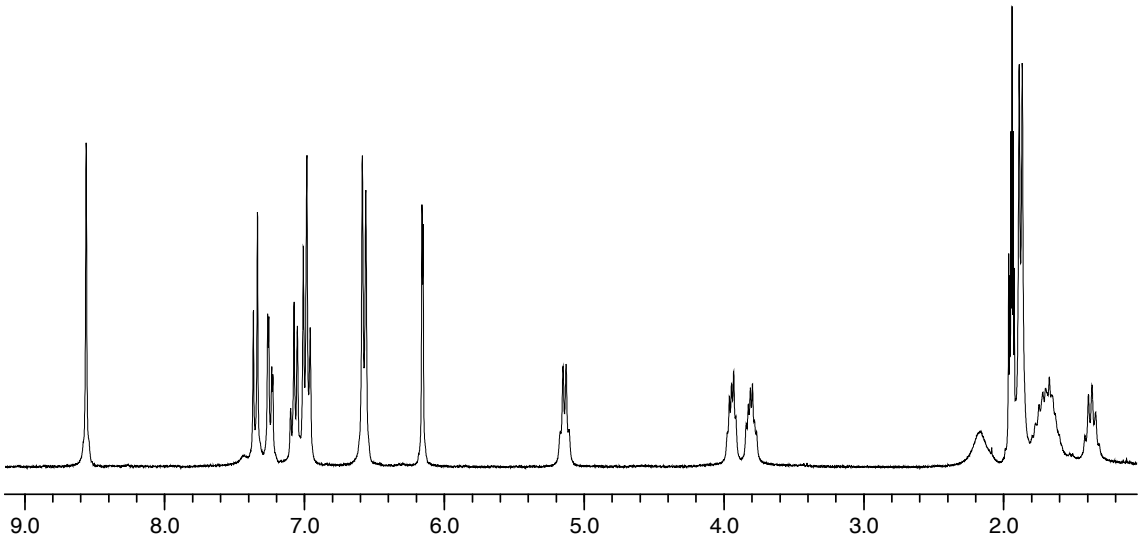
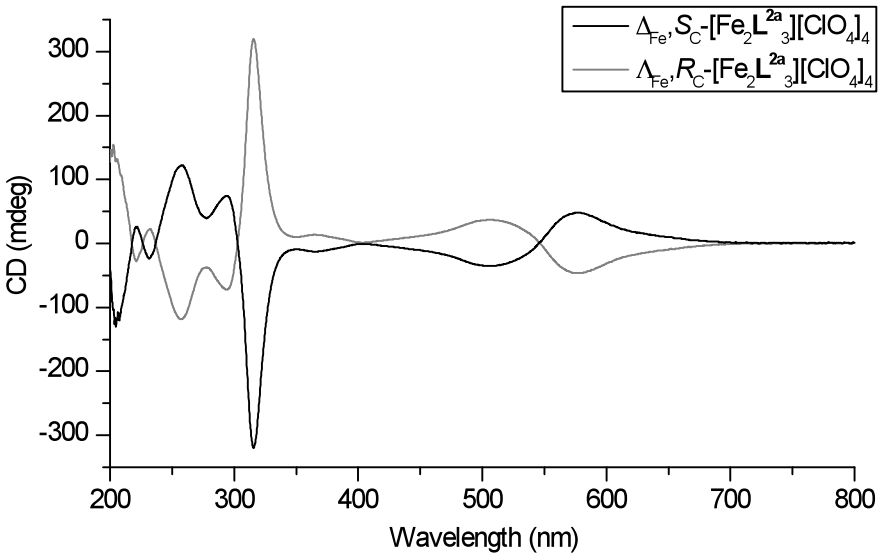
Supplementary Figures



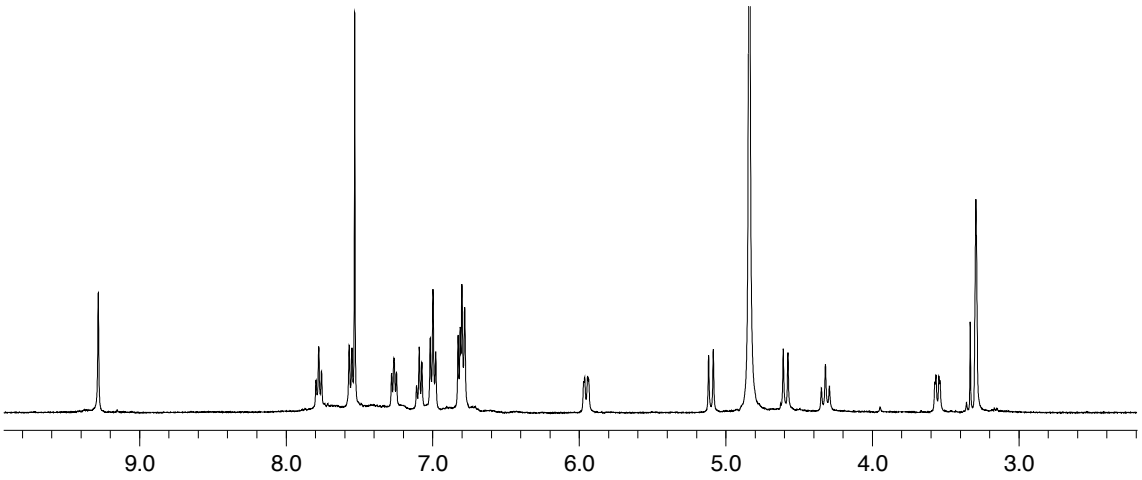
Supplementary Figure S1 | Structure of the cation unit in Δ_{Zn},R_C-$[Zn_2\mathbf{L}^{1a}{}_3][ClO_4]_4{\cdot}2CH_3CN{\cdot}3H_2O{\cdot}½MeOH$. (**Δ4a**) CCDC reference number 847378. Ellipsoids modelled at 50% probability. Hydrogen atoms, solvent molecules and counterions removed for clarity. Zinc(II) ions are shown in green, nitrogen atoms are shown in blue, oxygen atoms are shown in red, and cardon atoms are shown in black. The observed solid state structure has two distinct bridge orientations as follows: (i) the units containing O(1) and O(2) contain acute torsion angles at C(19)–C(22)–O(2)–C(23) and C(16)–C(15)–O(1)–C(14) of 69.4° and 61.1° respectively, creating a zig-zag chain; (ii) in contrast, the bridge containing O(3) traces an essentially linear route between the Zn centres with a torsion angle at C(52)–C(51)–O(3)–C(50) of 173.9°. Despite this, the overall assembly is only slightly "bent" along the nominal C_3 axis, and the angle between the two imine N atom planes N(2)–N(3)–N(6) and N(2)–N(3)–N(6) is 8.6°.



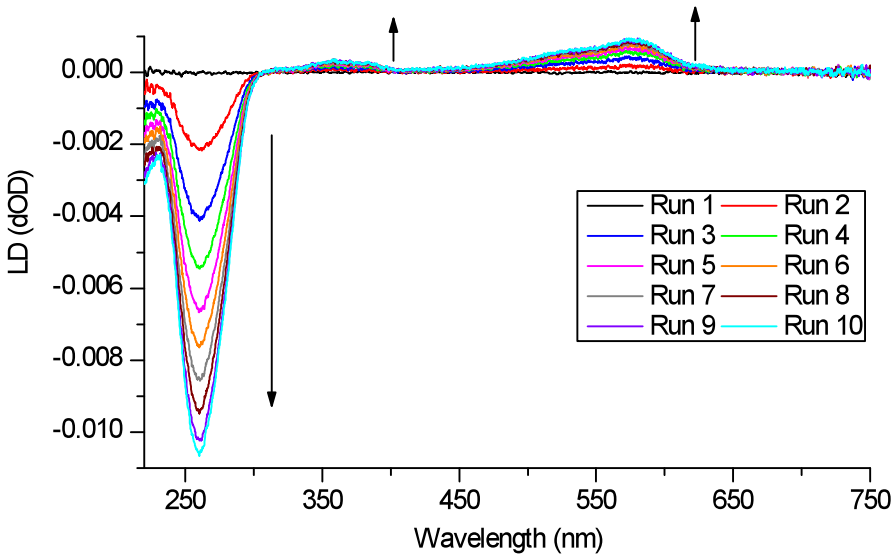
Supplementary Figure S2 | ^{1}H NMR spectrum of Δ_{Fe},S_C-$[Fe_2\mathbf{L}^{\mathbf{2a}}{}_3][ClO_4]_4$ (**Δ5a**) in CD_3CN.



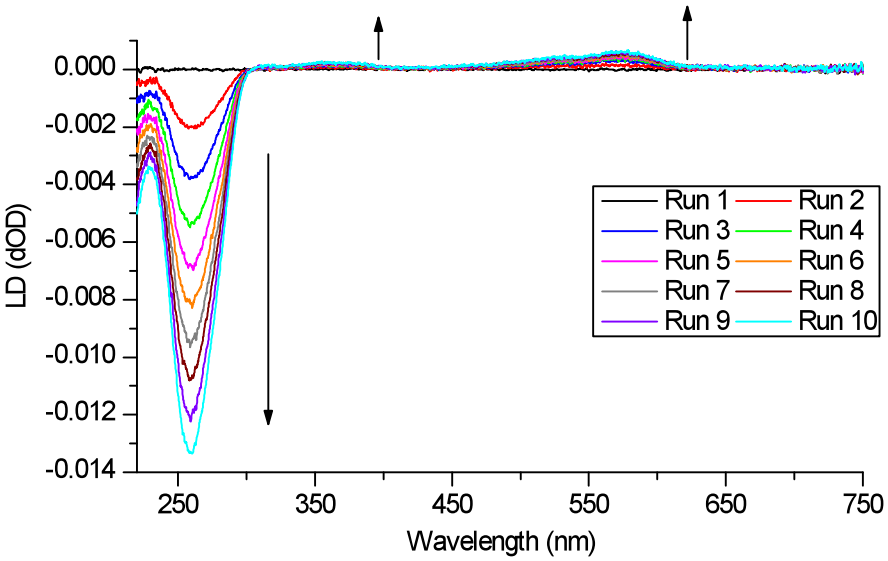
Supplementary Figure S3 | CD spectra of Δ_{Fe},S_C-$[Fe_2\mathbf{L}^{\mathbf{2a}}{}_3][ClO_4]_4$ (**Δ5a**) and its enantiomer Λ_{Fe},R_C-$[Fe_2\mathbf{L}^{\mathbf{2a}}{}_3][ClO_4]_4$ in acetonitrile at concentration 0.03 mM and path length 1.0 cm.



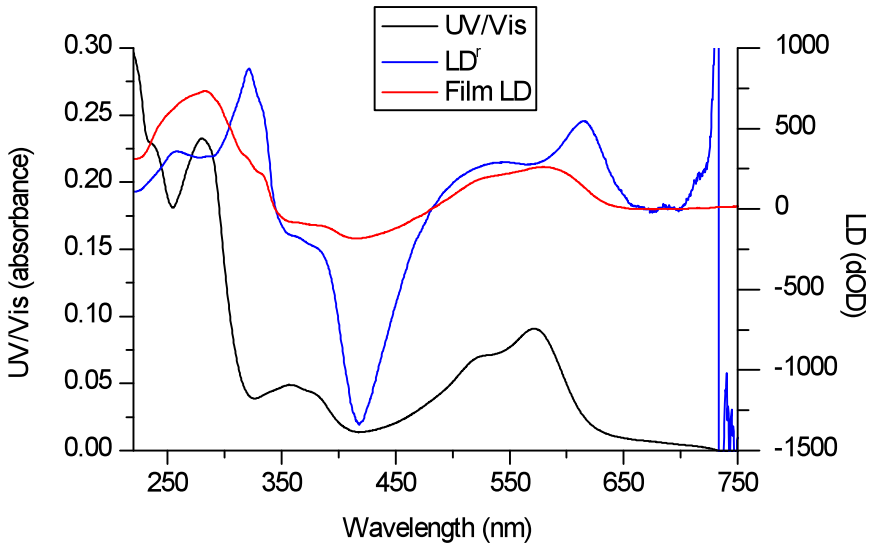
Supplementary Figure S4 | ^{1}H NMR spectrum of Δ_{Fe},R_{C}-[Fe_2**L**$^{1a}_3$]Cl_4 (**Δ7a**) in CD_3OD.



Supplementary Figure S5 | LD titration series for Λ_{Fe},S_{C}-[Fe_2**L**$^{1a}_3$]Cl_4 (**Λ7a**) at constant flexicate concentration 15 μM, TRIZMA® base buffer (1 mM, pH 7.2), and increasing concentrations of ct-DNA. The positive LD signals between 440 nm and 640 nm and between 325 nm and 400 nm correspond to MLCT transitions in **Λ7a**. Any peaks between 300 nm and 200 nm arising from the alignment of **Λ7a** are overlaid by the strong negative LD signal at 260 nm from ct-DNA.



Supplementary Figure S6 | LD titration series for Δ_{Fe},R_C-[Fe_2**L**$^{1a}{}_3$]Cl_4 (**Δ7a**) at constant flexicate concentration 15 μM, TRIZMA® base buffer (1 mM, pH 7.2), and increasing concentrations of ct-DNA. The positive LD signals between 440 nm and 640 nm and between 325 nm and 400 nm correspond to MLCT transitions in **Δ7a**. Any peaks between 300 nm and 200 nm arising from the alignment of **Δ7a** are overlaid by the strong negative LD signal at 260 nm from ct-DNA.



Supplementary Figure S7 | UV-Vis absorbance, LD^r and film LD spectra for Δ_{Fe},R_C-[Fe_2**L**$^{1a}{}_3$]Cl_4 (**Δ7a**)

General Experimental Considerations

All solvents and chemicals purchased from commercial sources (Sigma-Aldrich, Acros, Fisher Scientific or Alfa Aesar) were used without further purification. Deuterated solvents were purchased from Sigma-Aldrich and Cambridge Isotope Laboratories. Sodium hydride dispersions in mineral oil were placed in a Schlenk vessel under an inert atmosphere and washed three times with diethyl ether to remove the oil. The sodium hydride powder was then dried and stored in the glove box. Where appropriate, reactions were carried out under argon using a dual manifold argon/vacuum line and standard Schlenk techniques. THF was pre-dried over sodium wire and then heated to reflux for 3 d under dinitrogen over potassium, and degassed before use. The dried solvent was stored in glass ampoules under argon. All glassware and cannulae were stored in an oven at > 375 K.

NMR spectra were recorded on Bruker Spectrospin 300/400/700 spectrometers. Routine NMR assignments were confirmed by ^{1}H-^{1}H (COSY) and ^{13}C-^{1}H (HMQC) correlation experiments where necessary. The spectra were internally referenced using the residual protio solvent ($CDCl_3$, CD_3CN *etc.*) resonance relative to tetramethylsilane (δ = 0 ppm). ESI mass spectra were recorded on Bruker Esquire 2000 and Bruker MicroTOF spectrometers. Infra-Red spectra were measured using a Perkin-Elmer FTIR spectrometer. Elemental analyses were performed by Warwick Analytical Services, Coventry, UK and MEDAC Ltd, Surrey, UK.

CD spectra were measured on a Jasco J-815 spectrometer, which was calibrated conventionally using 0.060% ACS for intensity and a holmium filter for wavelength, and also against our recently introduced Na[Co(EDDS)] system.[1] Measurements were collected using a 1 cm path-length quartz cuvette and the standard parameters used were: bandwidth 1 nm, response time 1 sec, wavelength scan range 200 – 800 nm, data pitch 0.2 nm, scanning speed 100 nm/min and accumulation 4.

The crystal data were collected using a Siemens SMART CCD single crystal diffractometer using MoKα (λ = 0.71073 Å) radiation source. The structure was solved by direct methods using SHELX (TREF)[2,3] with additional light atoms found by Fourier methods. Crystal refinement was performed using SHELX97.[3]

Optical rotation measurements were performed on a Perkin Elmer Polarimeter 341 by Warwick Analytical Services, Coventry, UK. The following parameters were used: solvent methanol, temperature 20°C, pathlength 100 mm, wavelength 589 nm.

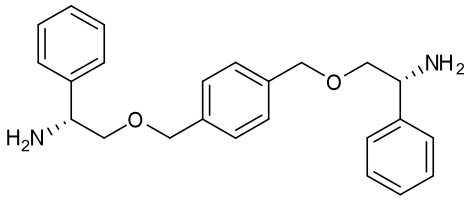
Synthesis and Characterisation

Previously reported compounds

The following compounds were synthesised as previously described:

- (*R*)- and (*S*)-2-Phenylglycinol [4,5]
- 5-(Hydroxy)picolinaldehyde [6]
- 1,5-Bis(2-pyridinaldehyd-5-oxy)pentane (**2**) [7]
- 2-(Propargyloxy)-1-phenylethanamine [4]

(*R*,*R*)-1,4-Bis{(2-amino-2-phenylethoxy)methyl}benzene (1)



(*R*)-2-Phenylglycinol (2.00 g, 14.6 mmol, 2.0 eq.) was dissolved in dry THF (20 ml) and was added dropwise to a stirred suspension of sodium hydride (0.72 g, 30.0 mmol, 4.1 eq) in dry THF (10 ml). The solution was stirred for 1 hour at ambient temperature. α,α′-Dibromo-*p*-xylene (1.73 g, 6.6 mmol, 0.9 eq.) dissolved in dry THF (10 ml) was added dropwise and the solution was stirred for 1 hour at ambient temperature under argon. At this point, the solution was heated to reflux (65°C) under partial vacuum overnight. The solution was then cooled to ambient temperature, followed by the addition of brine (40 ml). The product was extracted into diethyl ether (4 × 60 ml), dried over sodium sulfate and the solvent was removed under reduced pressure to leave a yellow oil. This crude product was purified by Kügelrohr distillation to remove the unreacted excess (*R*)-2-phenylglycinol (bp 130°C under high vacuum) and then by column chromatography first eluting with ethyl acetate/10% triethylamine followed by ethyl acetate/10% methanol. Purified yield = 1.88 g, 5.0 mmol, 76%.

^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ_H 7.35-7.22 (14H, m, Ph), 4.51 (4H, s, CH_2Ph), 4.20 (2H, dd, $^{3}J_{HH}$ = 4.0 Hz, 9.0 Hz, CH), 3.57 (2H, dd, $^{2}J_{HH}$ = 9.0 Hz, $^{3}J_{HH}$ = 4.0 Hz, CH_2CHPh), 3.41 (2H, t, $^{2}J_{HH}$ / $^{3}J_{HH}$ = 9.0 Hz, CH_2CHPh), 1.73 (4H, s, NH_2).

^{13}C{^{1}H} NMR (75 MHz, 298 K, $CDCl_3$) δ_C 142.5 (Ph), 137.6 (Ph), 128.4 (Ph), 127.8 (Ph), 127.4 (Ph), 126.9 (Ph), 76.6 (*C*H_2CHPh), 73.0 (*C*H_2Ph), 55.6 (*C*HPh).

MS (ESI) m/z 377.2 $[M+H]^+$, 399.2 $[M+Na]^+$.

IR ν cm^{-1} 3289 w, 2855 w, 1603 w, 1493 w, 1452 m, 1354 m, 1083 s, 1020 m, 843 m, 757 s, 699 s.

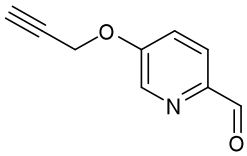
Elemental Analysis found (Calculated for $C_{24}H_{28}N_2O_2$) % C 76.19 (76.56), H 7.41 (7.50), N 7.12 (7.44).

Optical Rotation -24.19° (6.667 g/100 ml).

(*S*,*S*)-1,4-Bis{(2-amino-2-phenylethoxy)methyl}benzene

This compound was synthesised analogously to (*R*,*R*)-1,4-bis{(2-amino-2-phenylethoxy)methyl}benzene (**1**) described above using (*S*)-2-phenylglycinol.

5-(Propargyloxy)picolinaldehyde



Potassium carbonate (0.59 g, 4.26 mmol, 1.05 eq.) was added to a solution of 5-(hydroxy)picolinaldehyde (0.50 g, 4.06 mmol, 1.0 eq.) in DMF (15 ml). Propargyl bromide (80% wt. in toluene, 0.475 ml, 4.26 mmol, 1.05 eq.) was added to the reaction. The solution was stirred at 100°C for 4 hours before allowing to cool to ambient temperature with stirring for an additional 1 hour. The solvent was then removed under reduced pressure. The crude solid was taken up in chloroform (150 ml) and filtered. This process was repeated a further two times (2 × 40 ml). The chloroform was then removed from the filtrate under reduced pressure to leave an orange solid, which was dried overnight *in vacuo*. Yield = 0.32 g, 1.99 mmol, 49%.

^{1}H NMR (400 MHz, 298 K, DMSO) δ_H 9.90 (1H, s, HC=O), 8.53 (1H, d, $^4J_{HH}$ = 3.0 Hz, Py), 7.97 (1H, d, $^3J_{HH}$ = 8.5 Hz, Py), 7.64 (1H, dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 3.0 Hz, Py), 5.05 (2H, d, $^4J_{HH}$ = 2.5 Hz, CH_2-C≡C), 3.71 (1H, t, $^4J_{HH}$ = 2.5 Hz, C≡CH).

^{13}C{^{1}H} NMR (100 MHz, 298K, DMSO) δ_C 191.9 (C=O), 156.7 (Py), 146.1 (Py), 138.8 (Py), 123.3 (Py), 121.7 (Py), 79.4 (*C*≡CH), 78.9 (C≡*C*H), 56.3 (CH_2).

MS (ESI) m/z 162.2 $[M+H]^+$, 184.1 $[M+Na]^+$.

IR ν cm^{-1} 3213 w, 2127 w, 1692 s, 1569 s, 1490 w, 1474 w, 1379 w, 1308 m, 1282 w, 1259 s, 1203 s, 1132 m, 1006 s, 975 m, 916 w, 835 s, 800 s, 762 m, 732 m, 694 s, 659 s.

Elemental Analysis found (Calculated for $C_9H_7NO_2$) % C 66.85 (67.07), H 4.02 (4.38), N 8.52 (8.69).

General procedure for $[Fe_2L^1{}_3][ClO_4]_4$ flexicates

The appropriate pyridinecarboxaldehyde (2.20 mmol, 6.0 eq.) and (*R*,*R*)-1,4-bis{(2-amino-2-phenylethoxy)methyl}benzene (**1**) (0.41 g, 1.10 mmol, 3.0 eq.) were dissolved in acetonitrile (30 ml). Iron(II) perchlorate hexahydrate (0.26 g, 0.73 mmol, 2.0 eq.) in acetonitrile (10 ml) was added and immediately the solution turned intense purple ($\mathbf{L^{1a}}$) / pink ($\mathbf{L^{1b,1c}}$) in colour. The solution was heated to reflux (85°C) for 24 hours. After cooling the solvent was removed under reduced pressure to leave a crude purple or pink solid. The product, $[Fe_2\mathbf{L}^{n}{}_3][ClO_4]_4$, was purified by recrystallisation from acetonitrile and ethyl acetate, and the resulting purple or pink crystals were filtered, washed with ethyl acetate and dried *in vacuo*.

Δ_{Fe},R_C-$[Fe_2L^{1a}{}_3][ClO_4]_4$ (Δ3a)

Yield = 0.48 g, 0.22 mmol, 60%.

^{1}H NMR (300 MHz, 298 K, CD_3CN) δ_H 8.96 (6H, s, HC=N), 7.70 (6H, t, $^3J_{HH}$ = 7.0 Hz, Py), 7.45-7.41 (18H, m, Ph/Py), 7.17 (6H, t, $^3J_{HH}$ = 6.5 Hz, Py), 7.07 (6H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 6.95 (12H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 6.73-6.69 (18H, m, Ph/Py), 5.83 (6H, dd, $^3J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 3.5 Hz, CH), 5.05 (6H, d, $^2J_{HH}$ = 13.0 Hz, C*H*$_2$Ph), 4.51 (6H, d, $^2J_{HH}$ = 13.0 Hz, C*H*$_2$Ph), 4.23 (6H, t, $^2J_{HH}$ / $^3J_{HH}$ = 11.0 Hz, C*H*$_2$CHPh), 3.49 (6H, dd, $^2J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 3.5 Hz, C*H*$_2$CHPh).

^{13}C{^{1}H} NMR (100 MHz, 298 K, CD_3CN) δ_C 172.2 (C=N), 159.5 (Ph/Py), 154.5 (Ph/Py), 138.3 (Py), 135.8 (Ph/Py), 130.2 (Ph/Py), 130.0 (Ph/Py), 129.0 (Ph/Py), 128.9 (Ph/Py), 128.6 (Ph/Py), 126.7 (Ph/Py), 126.6 (Ph/Py), 73.4 (*C*H$_2$Ph), 73.1 (*C*H$_2$CHPh), 72.5 (*C*HPh).

MS (ESI) m/z 443.92 $[Fe_2\mathbf{L^{1a}}_3]^{4+}$, 582.23 $[Fe\mathbf{L^{1a}}_2]^{2+}$, 305.10 $[Fe\mathbf{L^{1a}}]^{2+}$.

IR ν cm^{-1} 1738 w, 1615 w, 1495 w, 1474 w, 1455 w, 1239 m, 1078 s, 839 m, 757 s, 700 s.

Elemental Analysis found (Calculated for $C_{108}H_{102}Cl_4Fe_2N_{12}O_{22}$) % C 59.17 (59.68), H 4.88 (4.73), N 7.27 (7.73).

Δ_{Fe},R_C-$[Fe_2L^{1b}{}_3][ClO_4]_4$ (Δ3b)

Yield = 0.57 g, 0.25 mmol, 68%.

^{1}H NMR (400 MHz, 298 K, CD_3CN) δ_H 8.80 (6H, s, HC=N), 8.15 (6H, br s, OH), 7.43 (12H, s, Ph), 7.30 (6H, d, $^{3}J_{HH}$ = 8.5 Hz, Py), 7.11-6.98 (24H, m, Py/Ph), 6.76 (12H, d, $^{3}J_{HH}$ = 7.5 Hz, Ph), 6.31 (6H, d, $^{4}J_{HH}$ = 2.0 Hz, Py), 5.70 (6H, dd, $^{3}J_{HH}$ = 11.0 Hz, $^{3}J_{HH}$ = 3.0 Hz, CH), 5.01 (6H, d, $^{2}J_{HH}$ = 12.5 Hz, C*H*$_2$Ph), 4.50 (6H, d, $^{2}J_{HH}$ = 12.5 Hz, C*H*$_2$Ph), 4.18 (6H, t, $^{2}J_{HH}$ / $^{3}J_{HH}$ = 11.0 Hz, C*H*$_2$CHPh), 3.47 (6H, dd, $^{2}J_{HH}$ = 11.0 Hz, $^{3}J_{HH}$ = 3.0 Hz, C*H*$_2$CHPh).

^{13}C{^{1}H} NMR (100 MHz, 298 K, CD_3CN) δ_C 170.5 (C=N), 156.9 (Ph/Py), 152.3 (Ph/Py), 142.7 (Py), 138.4 (Ph/Py), 136.6 (Ph/Py), 131.0 (Py), 129.6 (Ph/Py), 129.0 (Ph/Py), 128.9 (Ph/Py), 126.8 (Ph/Py), 124.8 (Ph/Py), 73.4 (*C*H$_2$Ph), 73.1 (*C*H$_2$CHPh), 71.4 (*C*HPh).

MS (ESI) m/z 467.91 $[Fe_2\mathbf{L}^{\mathbf{1b}}{}_3]^{4+}$, 641.19 $[Fe(\mathbf{L}^{\mathbf{1b}}\text{-H})]^{+}$.

IR ν cm^{-1} 3056 w, 2867 w, 1593 w, 1560 w, 1492 w, 1452 m, 1284 m, 1218 m, 1075 s, 928 m, 839 m, 757 m, 699 s.

Elemental Analysis found (Calculated for $C_{108}H_{102}Cl_4Fe_2N_{12}O_{28}$) % C 57.69 (57.16), H 4.67 (4.53), N 7.20 (7.41).

Δ_{Fe},*R*$_C$-$[Fe_2\mathbf{L}^{\mathbf{1c}}{}_3][ClO_4]_4$ (Δ3c)

Yield = 0.55 g, 0.22 mmol, 60%.

^{1}H NMR (400 MHz, 298 K, CD_3CN) δ_H 8.87 (6H, s, HC=N), 7.44 (12H, s, Ph), 7.41 (6H, d, $^{3}J_{HH}$ = 8.5 Hz, Py), 7.25 (6H, dd, $^{3}J_{HH}$ = 8.5 Hz, $^{4}J_{HH}$ = 2.5 Hz, Py), 7.10 (6H, t, $^{3}J_{HH}$ = 7.5 Hz, Ph), 7.01 (12H, t, $^{3}J_{HH}$ = 7.5 Hz, Ph), 6.77 (12H, d, $^{3}J_{HH}$ = 7.5 Hz, Ph), 6.38 (6H, d, $^{4}J_{HH}$ = 2.5 Hz, Py), 5.74 (6H, dd, $^{3}J_{HH}$ = 11.0 Hz, $^{3}J_{HH}$ = 3.0 Hz, CH), 5.03 (6H, d, $^{2}J_{HH}$ = 12.5 Hz, C*H*$_2$Ph), 4.68 (6H, dd, $^{2}J_{HH}$ = 16.5 Hz, $^{4}J_{HH}$ = 2.0 Hz, CH$_2$-C≡C), 4.61 (6H, dd, $^{2}J_{HH}$ = 16.5 Hz, $^{4}J_{HH}$ = 2.0 Hz, CH$_2$-C≡C), 4.51 (6H, d, $^{2}J_{HH}$ = 12.5 Hz, C*H*$_2$Ph), 4.21 (6H, t, $^{2}J_{HH}$ / $^{3}J_{HH}$ = 11.0 Hz, C*H*$_2$CHPh), 3.48 (6H, dd, $^{2}J_{HH}$ = 11.0 Hz, $^{3}J_{HH}$ = 3.0 Hz, C*H*$_2$CHPh), 2.92 (6H, t, $^{4}J_{HH}$ = 2.0 Hz, C≡CH).

^{13}C{^{1}H} NMR (100 MHz, 298 K, CD_3CN) δ_C 170.9 (C=N), 156.4 (Ph/Py), 153.3 (Ph/Py), 142.7 (Py), 138.3 (Ph/Py), 136.2 (Ph/Py), 130.9 (Ph/Py), 129.9 (Ph/Py), 129.2 (Ph/Py), 129.0 (Ph/Py), 126.8 (Ph), 124.5 (Py), 79.0 (C≡*C*H), 77.7 (*C*≡CH), 73.4 (*C*H$_2$Ph), 73.1 (CH*C*H$_2$), 71.7 (CH), 57.3 (*C*H$_2$C≡C).

MS (ESI) m/z 524.94 $[Fe_2\mathbf{L}^{\mathbf{1c}}{}_3]^{4+}$, 359.11 $[Fe\mathbf{L}^{\mathbf{1c}}]^{2+}$.

IR ν cm^{-1} 3255 w, 2863 w, 1592 w, 1560 m, 1496 m, 1453 w, 1364 w, 1279 m, 1229 m, 1075 s, 1003 s, 930 m, 842 m, 758 m, 699 s.

Elemental Analysis found (Calculated for $C_{126}H_{114}Cl_4Fe_2N_{12}O_{28}$) % C 61.05 (60.59), H 4.74 (4.60), N 6.62 (6.73).

Δ_{Zn},*R*$_C$-[$Zn_2\mathbf{L}^{\mathbf{1a}}_3$][$ClO_4$]$_4$ (Δ4a)

2-Pyridinecarboxaldehyde (0.23 g, 2.15 mmol, 6 eq.) and (*R*,*R*)-1,4-bis{(2-amino-2-phenylethoxy)methyl}benzene (**1**) (0.40 g, 1.08 mmol, 3 eq.) were dissolved in acetonitrile (30 ml) and stirred for 2 hours. Zinc(II) perchlorate hexahydrate (0.26 g, 0.72 mmol, 2 eq.) in acetonitrile (10 ml) was added and the yellow solution was stirred overnight at ambient temperature. The pure product, [$Zn_2\mathbf{L}^{\mathbf{1a}}_3$][$ClO_4$]$_4$, was isolated by the addition of a few drops of ethyl acetate to the acetonitrile solution. The resulting white crystals were filtered, washed with ethyl acetate and dried *in vacuo*. Yield = 0.37 g, 0.17 mmol, 47%.

^{1}H NMR (400 MHz, 298 K, CD_3CN) δ_H 8.71 (6H, s, HC=N), 7.90 (6H, t, $^3J_{HH}$ = 8.0 Hz, Py), 7.66 (6H, d, $^3J_{HH}$ = 5.5 Hz, Py), 7.59 (12H, s, Ph), 7.42-7.35 (12H, m, Py), 7.05 (6H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 6.92 (12H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 6.69 (12H, d, $^3J_{HH}$ = 7.5 Hz, Ph), 5.69 (6H, dd, $^3J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 3.5 Hz, CH), 5.04 (6H, d, $^2J_{HH}$ = 13.0 Hz, C*H*$_2$Ph), 4.58 (6H, d, $^2J_{HH}$ = 13.0 Hz, C*H*$_2$Ph), 4.11 (6H, t, $^2J_{HH}$ / $^3J_{HH}$ = 11.0 Hz, C*H*$_2$CHPh), 3.54 (6H, dd, $^2J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 3.5 Hz, C*H*$_2$CHPh).

^{13}C{^{1}H} NMR (100 MHz, 298 K, CD_3CN) δ_C 163.7 (*C*=N), 148.9 (Ph), 147.2 (Ph/Py), 142.7 (Ph/Py), 138.7 (Ph/Py), 136.1 (Ph/Py), 130.6 (Ph/Py), 129.8 (Ph/Py), 129.7 (Ph/Py), 129.2 (Ph/Py), 128.9 (Ph/Py), 127.3 (Ph/Py), 73.4 (*C*H$_2$Ph), 72.2 (*C*H$_2$CH), 68.3 (CH).

MS (ESI) m/z 448.67 [$Zn_2\mathbf{L}^{\mathbf{1a}}_3$]$^{4+}$, 586.23 [$Zn\mathbf{L}^{\mathbf{1a}}_2$]$^{2+}$, 309.10 [$Zn\mathbf{L}^{\mathbf{1a}}$]$^{2+}$.

IR ν cm^{-1} 1646 w, 1598 m, 1495 w, 1446 m, 1361 w, 1309 w, 1226 w, 1080 s, 838 m, 759 s, 700 s.

Elemental Analysis found (Calculated for $C_{108}H_{102}Cl_4N_{12}O_{22}Zn_2$) % C 59.41 (59.16), H 4.62 (4.69), N 7.38 (7.67).

Crystallography:

Δ_{Zn},*R*$_C$-[$Zn_2\mathbf{L}^{\mathbf{1a}}_3$][$ClO_4$]$_4$·2$CH_3CN$·3$H_2O$·½$CH_3OH$ $C_{112.5}H_{116}Cl_4N_{14}O_{25.5}Zn_2$, M = 2344.73, trigonal, $P3_112$, colourless plate 0.48 × 0.24 × 0.06 mm, a = 12.4175(18), b = 12.4175(18), c = 66.702(13) Å, α = 90°, β = 90°, γ = 120°, U = 8907(3) Å^3, Z = 3, T = 120(2) K, radiation Mo-Kα (λ = 0.71073 Å), 47232 total reflections, 12877 unique (R_{int} = 0.1086), R_1 = 0.0826 (obs. data), wR_2 = 0.2528 (all data), GooF 1.053, Flack 0.023(17).

General procedure for $[Fe_2L^2{}_3][ClO_4]_4$ flexicates

1,5-Bis(2-pyridinaldehyd-5-oxy)pentane (**2**) (0.31 g, 1.00 mmol, 3 eq.) and the appropriate α-phenylamine (2.00 mmol, 6 eq.) were dissolved in acetonitrile to form a yellow solution, which was stirred for approximately 1 hour at ambient temperature. Iron(II) perchlorate hexahydrate (0.24 g, 0.67 mmol, 2 eq.) was added and immediately the solution turned from yellow to deep pink. This solution was stirred under reflux (85°C) for 24 hours before ethyl acetate was added dropwise until signs of crystallisation. The dark pink crystals were filtered and dried *in vacuo*. Yields are unoptimised – analysis of crude reaction mixtures indicates that reactions are essentially complete.

Δ_{Fe},*S*$_C$-$[Fe_2L^{2a}{}_3][ClO_4]_4$ (Δ5a)

Yield = 0.51 g, 0.25 mmol, 76%.

^{1}H NMR (300 MHz, 298 K, CD_3CN) δ_H 8.56 (6H, s, HC=N), 7.35 (6H, d, $^3J_{HH}$ = 9.0 Hz, Py), 7.24 (6H, dd, $^3J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 2.5 Hz, Py), 7.08 (6H, t, $^3J_{HH}$ = 7.0 Hz, Ph), 6.98 (12H, t, $^3J_{HH}$ = 7.0 Hz, Ph), 6.57 (12H, d, $^3J_{HH}$ = 7.0 Hz, Ph), 6.16 (6H, d, $^4J_{HH}$ = 2.5 Hz, Py), 5.14 (6H, quartet, $^3J_{HH}$ = 7.5 Hz, CH), 3.98-3.92 (6H, m, OCH_2), 3.84-3.77 (6H, m, OCH_2), 1.88 (18H, d, $^3J_{HH}$ = 7.5 Hz, CH_3), 1.80-1.63 (12H, m, OCH_2CH_2), 1.42-1.32 (6H, m, $OCH_2CH_2CH_2$).

$^{13}C\{^1H\}$ NMR (75 MHz, 298 K, CD_3CN) δ_C 170.2 (C=N), 158.9 (Py/Ph), 151.9 (Py/Ph), 143.3 (Py), 141.1 (Py/Ph), 130.9 (Py), 129.9 (Ph), 128.3 (Ph), 125.4 (Ph), 122.4 (Py), 69.9 (OCH_2), 69.1 (CH), 29.3 (OCH_2CH_2), 26.3 (CH_3), 22.8 ($OCH_2CH_2CH_2$).

MS (ESI) m/z 418.43 $[Fe_2L^{2a}{}_3]^{4+}$, 548.25 $[FeL^{2a}{}_2]^{2+}$.

IR ν cm^{-1} 2939 w, 1592 w, 1558 m, 1495 m, 1452 w, 1382 w, 1302 m, 1279 m, 1237 m, 1081 s, 1008 m, 928 m, 837 m, 761 m, 701 s.

Elemental Analysis found (Calculated for $C_{99}H_{108}Cl_4Fe_2N_{12}O_{22}$) % C 57.12 (57.40), H 5.33 (5.26), N 7.99 (8.11).

Δ_{Fe},*R*$_C$-$[Fe_2L^{2b}{}_3][ClO_4]_4$ (Δ5b)

Yield = 0.60 g, 0.28 mmol, 85%.

^{1}H NMR (300 MHz, 298 K, CD_3CN) δ_H 8.79 (6H, s, HC=N), 7.34 (6H, d, $^{3}J_{HH}$ = 9.0 Hz, Py), 7.12 (6H, dd, $^{3}J_{HH}$ = 9.0 Hz, $^{4}J_{HH}$ = 2.5 Hz, Py), 7.07 (6H, d, $^{3}J_{HH}$ = 7.0 Hz, Ph), 6.99 (12H, t, $^{3}J_{HH}$ = 7.0 Hz, Ph), 6.81 (12H, d, $^{3}J_{HH}$ = 7.0 Hz, Ph), 6.22 (6H, d, $^{4}J_{HH}$ = 2.5 Hz, Py), 5.54 (6H, d, $^{3}J_{HH}$ = 7.0 Hz, CH), 4.17 (6H, m, C*H*$_2$CH), 3.92-3.72 (24H, m, OH, C*H*$_2$CH, OC*H*$_2$CH$_2$), 1.78-1.58 (12H, m, OCH$_2$C*H*$_2$), 1.39-1.29 (6H, m, OCH$_2$CH$_2$C*H*$_2$).

^{13}C{^{1}H} NMR (75 MHz, 298 K, CD_3CN) δ_C 170.9 (C=N), 158.5 (Py/Ph), 152.4 (Py/Ph), 143.0 (Py), 136.8 (Py/Ph), 130.6 (Py), 129.5 (Ph), 128.7 (Ph), 126.8 (Ph), 122.5 (Py), 73.4 (CH), 69.8 (O*C*H$_2$CH$_2$), 65.6 (*C*H$_2$CH), 29.2 (OCH$_2$*C*H$_2$), 22.8 (OCH$_2$CH$_2$*C*H$_2$).

MS (ESI) m/z 405.14 [Fe$_2$**L**^{2b}(**L**^{2b}-H)]$^{3+}$, 607.20 [Fe(**L**^{2b}-H)]$^{+}$.

IR ν cm^{-1} 3494 w, 1592 w, 1558 m, 1495 w, 1453 w, 1381 w, 1308 w, 1281 w, 1237 m, 1082 s, 929 w, 844 w, 759 m, 701 m.

Elemental Analysis found (Calculated for $C_{99}H_{108}Cl_4Fe_2N_{12}O_{28}$) % C 54.90 (54.86), H 5.01 (5.02), N 7.52 (7.75).

Δ_{Fe},*R*$_C$-[Fe$_2$L$^{2c}_3$][ClO$_4$]$_4$ (Δ5c)

Yield = 0.63 g, 0.26 mmol, 79%.

^{1}H NMR (300 MHz, 298 K, CD_3CN) δ_H 8.82 (6H, s, HC=N), 7.36 (6H, d, $^{3}J_{HH}$ = 8.0 Hz, Py), 7.12-7.09 (12H, m, Py, Ph), 7.03 (12H, t, $^{3}J_{HH}$ = 7.0 Hz, Ph), 6.82 (12H, d, $^{3}J_{HH}$ = 7.0 Hz, Ph), 6.20 (6H, d, $^{4}J_{HH}$ = 1.5 Hz, Py), 5.65 (6H, dd, $^{3}J_{HH}$ = 10.0 Hz, 3.5 Hz, CH), 4.55 (6H, dd, $^{2}J_{HH}$ = 16.0 Hz, $^{4}J_{HH}$ = 2.0 Hz, CH$_2$-C≡C), 4.46 (6H, dd, $^{2}J_{HH}$ = 16.0 Hz, $^{4}J_{HH}$ = 2.0 Hz, CH$_2$-C≡C), 4.33 (6H, t, $^{2}J_{HH}$ / $^{3}J_{HH}$ = 10.5 Hz, C*H*$_2$CHPh), 3.86 (6H, m, OCH$_2$), 3.74 (6H, m, OCH$_2$), 3.63 (6H, dd, $^{2}J_{HH}$ = 10.5 Hz, $^{3}J_{HH}$ = 3.5 Hz, C*H*$_2$CHPh), 2.91 (6H, t, $^{4}J_{HH}$ = 2.0 Hz, C≡CH), 1.78-1.54 (12H, m, OCH$_2$C*H*$_2$), 1.38-1.27 (6H, m, OCH$_2$CH$_2$C*H*$_2$).

^{13}C{^{1}H} NMR (75 MHz, 298 K, CD_3CN) δ_C 170.7 (C=N), 158.6 (Py/Ph), 152.2 (Py/Ph), 143.1 (Py), 136.0 (Py/Ph), 131.0 (Py), 129.7 (Py/Ph), 129.2 (Py/Ph), 126.9 (Ph), 122.6 (Py/Ph), 80.0 (C≡*C*H), 77.2 (*C*≡CH), 72.1 (CH*C*H$_2$), 70.6 (CH), 69.8 (O*C*H$_2$CH$_2$), 59.2 (OCH$_2$C≡CH), 29.2 (OCH$_2$*C*H$_2$), 22.7 (OCH$_2$CH$_2$*C*H$_2$).

MS (ESI) m/z 499.45 [Fe$_2$**L**$^{2c}_3$]$^{4+}$, 656.27 [Fe**L**$^{2c}_2$]$^{2+}$.

IR ν cm^{-1} 3266 w, 2871 w, 1592 w, 1558 m, 1496 m, 1453 w, 1381 w, 1358 w, 1309 m, 1281 m, 1237 m, 1078 s, 1001 m, 840 m, 760 m, 699 s.

Elemental Analysis found (Calculated for $C_{117}H_{120}Cl_4Fe_2N_{12}O_{28}$) % C 58.17 (58.66), H 4.87 (5.05), N 7.00 (7.02).

Δ_{Zn},*S*$_C$-[$Zn_2L^{2a}_3$][ClO_4]$_4$ (Δ6a)

1,5-Bis(2-pyridinaldehyd-5-oxy)pentane (**2**) (0.31 g, 1.00 mmol, 3 eq.) and (*S*)-α-methylbenzylamine (0.24 g, 2.00 mmol, 6 eq.) were dissolved in acetonitrile to form a yellow solution, which was stirred for around 1 hour at ambient temperature. Zinc(II) perchlorate hexahydrate (0.25 g, 0.67 mmol, 2 eq.) was added and the solution remained yellow in colour. This was stirred for 7 hours before ethyl acetate was added dropwise until signs of crystallisation. The white crystals were filtered and dried *in vacuo*. Yield = 0.61 g, 0.29 mmol, 87%.

^{1}H NMR (300 MHz, 298 K, CD_3CN) δ_H 8.09 (6H, s, HC=N), 7.50 (6H, dd, $^3J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 3.0 Hz, Py), 7.39 (6H, d, $^3J_{HH}$ = 9.0 Hz, Py), 7.09 (6H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 6.95 (12H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 6.87 (6H, d, $^4J_{HH}$ = 3.0 Hz, Py), 6.65 (12H, d, $^3J_{HH}$ = 7.5 Hz, Ph), 5.35 (6H, quartet, $^3J_{HH}$ = 6.5 Hz, CH), 4.07-4.00 (6H, m, OCH_2), 3.94-3.86 (6H, m, OCH_2), 1.84-1.66 (12H, m, OCH_2CH_2), 1.57 (18H, d, $^3J_{HH}$ = 6.5 Hz, CH_3), 1.52-1.41 (6H, m, $OCH_2CH_2CH_2$).

^{13}C{^{1}H} NMR (75 MHz, 298 K, CD_3CN) δ_C 161.6 (C=N), 160.4 (Py/Ph), 141.7 (Py/Ph), 140.0 (Py/Ph), 137.5 (Py), 132.1 (Py), 129.6 (Ph), 128.5 (Ph), 126.5 (Ph), 124.6 (Py), 70.0 (OCH_2), 64.7 (CH), 29.4 (OCH_2CH_2), 23.7 (CH_3), 22.9 ($OCH_2CH_2CH_2$).

MS (ESI) m/z 292.11 [Zn**L**^{2a}]$^{2+}$, 552.25 [Zn**L**$^{2a}_2$]$^{2+}$, 597.22 [Zn_2**L**$^{2a}_3$][ClO4]$^{3+}$.

IR *v* cm^{-1} 2939 w, 1641 w, 1591 w, 1568 s, 1494 w, 1454 w, 1385 w, 1314 m, 1263 m, 1227 m, 1079 s, 1028 m, 925 m, 843 m, 762 m, 702 s.

Elemental Analysis found (Calculated for $C_{99}H_{108}Cl_4N_{12}O_{22}Zn_2$) % C 56.40 (56.88), H 5.09 (5.21), N 7.83 (8.04).

General procedure for [$Fe_2L^1_3$]Cl_4 flexicates

2-Pyridinecarboxaldehyde (0.28 g, 2.66 mmol, 6.0 eq.) and the appropriate optically pure 1,4-bis{(2-amino-2-phenylethoxy)methyl}benzene (**1**) (0.50 g, 1.33 mmol, 3.0 eq.) were dissolved in methanol (50 ml) and were stirred for 2 hours at ambient temperature. Anhydrous iron(II) chloride (0.11 g, 0.89 mmol, 2.0 eq.) was added as a solid and the solution turned intense purple in colour as the solid dissolved. The solution was stirred

under reflux (80°C) for 24 hours. After cooling, the solvent was removed under reduced pressure to leave a purple solid, which was dried *in vacuo*.

Δ_{Fe},*R*$_C$-[Fe$_2$L$^{1a}_3$]Cl$_4$ (Δ7a)

Yield = 0.85 g, 0.44 mmol, 100%.

^{1}H NMR (400 MHz, 298 K, CD_3OD) δ_H 9.30 (6H, s, HC=N), 7.80 (6H, t, $^3J_{HH}$ = 7.0 Hz, Py), 7.58 (6H, d, $^3J_{HH}$ = 7.0 Hz, Py), 7.55 (12H, s, Ph), 7.29 (6H, t, $^3J_{HH}$ = 7.0 Hz, Py), 7.11 (6H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 7.02 (12H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 6.85-6.80 (18H, m, Py/Ph), 5.97 (6H, dd, $^3J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 3.5 Hz, CH), 5.12 (6H, d, $^2J_{HH}$ = 13.0 Hz, C*H*$_2$Ph), 4.61 (6H, d, $^2J_{HH}$ = 13.0 Hz, C*H*$_2$Ph), 4.34 (6H, t, $^2J_{HH}$ / $^3J_{HH}$ = 11.0 Hz, C*H*$_2$CHPh), 3.58 (6H, dd, $^2J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 3.5 Hz, C*H*$_2$CHPh).

^{13}C{^{1}H} NMR (100 MHz, 298 K, CD_3CN) δ_C 173.3 (C=N), 160.5 (Ph/Py), 154.7 (Py), 139.9 (Py), 138.8 (Ph/Py), 136.5 (Ph/Py), 130.5 (Ph/Py), 129.7 (Ph/Py), 129.6 (Ph/Py), 129.5 (Ph/Py), 128.9 (Ph/Py), 127.1 (Ph), 73.8 (*C*H$_2$Ph), 73.1 (*C*H$_2$CHPh), 73.0 (CH).

MS (ESI) m/z 443.92 [Fe$_2$**L**$^{1a}_3$]$^{4+}$, 582.24 [Fe**L**$^{1a}_2$]$^{2+}$, 305.10 [Fe**L**^{1a}]$^{2+}$.

IR *v* cm^{-1} 3366 w, 2861 w, 1613 w, 1494 w, 1472 m, 1452 m, 1362 w, 1299 w, 1242 w, 1075 s, 1019 m, 836 m, 757 s, 700 s.

Elemental Analysis found (Calculated for $C_{108}H_{102}Cl_4Fe_2N_{12}O_6$) % C 66.63 (67.65), H 5.52 (5.36), N 8.23 (8.77).

Λ_{Fe},*S*$_C$-[Fe$_2$L$^{1a}_3$]Cl$_4$ (Λ7a)

Yield = 0.85 g, 0.44 mmol, 100%.

^{1}H NMR (400 MHz, 298 K, CD_3OD) δ_H 9.30 (6H, s, HC=N), 7.79 (6H, t, $^3J_{HH}$ = 7.0 Hz, Py), 7.58 (6H, d, $^3J_{HH}$ = 7.0 Hz, Py), 7.55 (12H, s, Ph), 7.28 (6H, t, $^3J_{HH}$ = 7.0 Hz, Py), 7.10 (6H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 7.01 (12H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 6.84-6.79 (18H, m, Py/Ph), 5.97 (6H, dd, $^3J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 3.5 Hz, CH), 5.12 (6H, d, $^2J_{HH}$ = 13.0 Hz, C*H*$_2$Ph), 4.61 (6H, d, $^2J_{HH}$ = 13.0 Hz, C*H*$_2$Ph), 4.34 (6H, t, $^2J_{HH}$ / $^3J_{HH}$ = 11.0 Hz, C*H*$_2$CHPh), 3.57 (6H, dd, $^2J_{HH}$ = 11.0 Hz, $^3J_{HH}$ = 3.5 Hz, C*H*$_2$CHPh).

^{13}C{^{1}H} NMR (100 MHz, 298 K, CD_3CN) δ_C 173.3 (C=N), 160.5 (Ph/Py), 154.7 (Py), 139.9 (Py), 138.8 (Ph/Py), 136.5 (Ph/Py), 130.5 (Ph/Py), 129.7 (Ph/Py), 129.6 (Ph/Py), 129.5 (Ph/Py), 128.9 (Ph/Py), 127.1 (Ph), 73.8 (*C*H$_2$Ph), 73.1 (*C*H$_2$CHPh), 73.0 (CH).

MS (ESI) m/z 443.92 [Fe$_2$**L**$^{1a}_3$]$^{4+}$, 582.24 [Fe**L**$^{1a}_2$]$^{2+}$, 305.10 [Fe**L**^{1a}]$^{2+}$.

IR ν cm^{-1} 3364 w, 2860 w, 1613 w, 1494 w, 1472 m, 1452 m, 1361 w, 1241 w, 1074 s, 1019 m, 836 m, 757 s, 699 s.

Elemental Analysis found (Calculated for $C_{108}H_{102}Cl_4Fe_2N_{12}O_6$) % C 66.57 (67.65), H 5.49 (5.36), N 8.07 (8.77).

General procedure for $[Fe_2L^2{}_3]Cl_4$ flexicates

1,5-Bis(2-pyridinaldehyd-5-oxy)pentane (**2**) (0.40 g, 1.27 mmol, 3.0 eq.) and the appropriate α-phenylamine (2.55 mmol, 6.0 eq.) were dissolved in methanol (50 ml) and were stirred for 2 hours at ambient temperature. Anhydrous iron(II) chloride (0.11 g, 0.85 mmol, 2.0 eq.) was added as a solid and the solution turned deep pink in colour as the solid dissolved. The solution was stirred at reflux (80°C) for 24 hours. After cooling the solvent was removed under reduced pressure to leave a pink solid, which was dried *in vacuo*.

Δ_{Fe},*S*$_C$-$[Fe_2L^{2a}{}_3]Cl_4$ (Δ8a)

Yield = 0.77 g, 0.42 mmol, 100%.

^{1}H NMR (400 MHz, 298 K, CD_3OD) δ_H 8.83 (6H, s, HC=N), 7.52-7.40 (12H, m, Py), 7.11 (6H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 7.02 (12H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 6.66 (12H, d, $^3J_{HH}$ = 7.5 Hz, Ph), 6.26 (6H, s, Py), 5.23 (6H, q, $^3J_{HH}$ = 6.0 Hz, CH), 4.05-3.99 (6H, m, OCH_2), 3.91-3.83 (6H, m, OCH_2), 1.97 (18H, d, $^3J_{HH}$ = 6.0 Hz, CH_3), 1.89-1.76 (6H, m, OCH_2CH_2), 1.74-1.63 (6H, m, OCH_2CH_2), 1.50-1.40 (6H, m, $OCH_2CH_2CH_2$).

$^{13}C\{^1H\}$ NMR (100 MHz, 298 K, CD_3OD) δ_C 171.3 (C=N), 159.5 (Ph/Py), 152.8 (Ph/Py), 143.8 (Py), 141.7 (Ph/Py), 131.4 (Py), 130.3 (Ph), 128.8 (Ph), 125.8 (Ph), 122.6 (Py), 70.5 (OCH_2), 69.9 (CH), 29.8 (OCH_2CH_2), 26.4 (CH_3), 23.4 ($OCH_2CH_2CH_2$).

MS (ESI) m/z 418.3 $[Fe_2L^{2a}{}_3]^{4+}$, 288.2 $[Fe_2L^{2a}{}_2]^{4+}$.

IR ν cm^{-1} 3372 w, 2934 w, 1591 w, 1557 s, 1493 m, 1452 m, 1382 w, 1299 m, 1277 m, 1235 s, 1133 w, 1069 m, 1009 m, 921 m, 834 m, 760 s, 700 s.

Elemental Analysis found (Calculated for $C_{99}H_{108}Cl_4Fe_2N_{12}O_6$) % C 64.45 (65.50), H 6.05 (6.00), N 8.71 (9.26).

Λ_{Fe},*R*$_C$-$[Fe_2L^{2a}{}_3]Cl_4$ (Λ8a)

Yield = 0.77 g, 0.42 mmol, 100%.

^{1}H NMR (400 MHz, 298 K, CD_3OD) δ_H 8.83 (6H, s, HC=N), 7.52-7.40 (12H, m, Py), 7.11 (6H, t, $^{3}J_{HH}$ = 7.5 Hz, Ph), 7.02 (12H, t, $^{3}J_{HH}$ = 7.5 Hz, Ph), 6.66 (12H, d, $^{3}J_{HH}$ = 7.5 Hz, Ph), 6.26 (6H, s, Py), 5.23 (6H, q, $^{3}J_{HH}$ = 6.0 Hz, CH), 4.04-3.99 (6H, m, OCH_2), 3.92-3.84 (6H, m, OCH_2), 1.97 (18H, d, $^{3}J_{HH}$ = 6.0 Hz, CH_3), 1.88-1.76 (6H, m, OCH_2CH_2), 1.74-1.63 (6H, m, OCH_2CH_2), 1.50-1.40 (6H, m, $OCH_2CH_2CH_2$).

^{13}C{^{1}H} NMR (100 MHz, 298 K, CD_3OD) δ_C 171.3 (C=N), 159.5 (Ph/Py), 152.8 (Ph/Py), 143.8 (Py), 141.7 (Ph/Py), 131.4 (Py), 130.3 (Ph), 128.8 (Ph), 125.8 (Ph), 122.6 (Py), 70.5 (OCH_2), 69.9 (CH), 29.8 (OCH_2CH_2), 26.4 (CH_3), 23.4 ($OCH_2CH_2CH_2$).

MS (ESI) m/z 418.4 $[Fe_2\mathbf{L}^{\mathbf{2a}}{}_3]^{4+}$, 288.2 $[Fe_2\mathbf{L}^{\mathbf{2a}}{}_2]^{4+}$.

IR ν cm^{-1} 3361 w, 2935 w, 1591 w, 1557 s, 1493 m, 1452 m, 1382 w, 1299 m, 1276 m, 1234 s, 1127 w, 1069 m, 1008 m, 926 m, 839 m, 760 s, 700 s.

Elemental Analysis found (Calculated for $C_{99}H_{108}Cl_4Fe_2N_{12}O_6$) % C 64.52 (65.50), H 5.91 (6.00), N 8.65 (9.26).

Δ_{Fe},R_C-$[Fe_2\mathbf{L}^{\mathbf{2b}}{}_3]Cl_4$ (Δ8b)

Yield = 0.81 g, 0.42 mmol, 100%.

^{1}H NMR (400 MHz, 298 K, CD_3OD) δ_H 9.04 (6H, s, HC=N), 7.48 (6H, d, $^{3}J_{HH}$ = 8.5 Hz, Py), 7.26 (6H, dd, $^{3}J_{HH}$ = 8.5 Hz, $^{4}J_{HH}$ = 2.0 Hz, Py), 7.10 (6H, t, $^{3}J_{HH}$ = 7.5 Hz, Ph), 7.02 (12H, t, $^{3}J_{HH}$ = 7.5 Hz, Ph), 6.93 (12H, d, $^{3}J_{HH}$ = 7.5 Hz, Ph), 6.32 (6H, d, $^{4}J_{HH}$ = 2.0 Hz, Py), 5.77 (6H, dd, $^{3}J_{HH}$ = 10.0 Hz, $^{3}J_{HH}$ = 3.0 Hz, CH), 4.28 (6H, t, $^{2}J_{HH}$ / $^{3}J_{HH}$ = 10.0 Hz, CH_2), 3.98-3.93 (6H, m, OCH_2), 3.84-3.78 (12H, m, CH_2/OCH_2), 1.86-1.74 (6H, m, OCH_2CH_2), 1.72-1.61 (6H, m, OCH_2CH_2), 1.47-1.38 (6H, m, $OCH_2CH_2CH_2$).

^{13}C{^{1}H} NMR (100 MHz, 298 K, CD_3OD) δ_C 171.6 (C=N), 159.1 (Ph/Py), 153.3 (Ph/Py), 143.5 (Py), 137.6 (Ph/Py), 131.1 (Py), 129.8 (Ph), 129.1 (Ph), 127.3 (Ph), 122.6 (Py), 74.1 (CH), 70.4 (OCH_2), 66.0 (CH_2), 29.7 (OCH_2CH_2), 23.4 ($OCH_2CH_2CH_2$).

MS (ESI) m/z 607.1 $[Fe(\mathbf{L}^{\mathbf{2b}}\text{-H})]^{+}$, 405.2 $[Fe_2\mathbf{L}^{\mathbf{2b}}(\mathbf{L}^{\mathbf{2b}}\text{-H})]^{3+}$, 304.1 $[Fe_2\mathbf{L}^{\mathbf{2b}}{}_2]^{4+}$.

IR ν cm^{-1} 3246 w, 2933 w, 1591 w, 1557 s, 1494 m, 1452 w, 1381 w, 1304 m, 1278 m, 1234 s, 1133 w, 1057 m, 1020 m, 930 m, 844 m, 758 m, 700 s.

Elemental Analysis found (Calculated for $C_{99}H_{108}Cl_4Fe_2N_{12}O_{12}$) % C 61.01 (62.21), H 5.65 (5.69), N 8.31 (8.79).

Λ_{Fe},S_C-[$Fe_2L^{2b}_3$]Cl_4 (Λ8b)

Yield = 0.81 g, 0.42 mmol, 100%.

^{1}H NMR (400 MHz, 298 K, CD_3OD) δ_H 9.04 (6H, s, HC=N), 7.48 (6H, d, $^3J_{HH}$ = 8.5 Hz, Py), 7.26 (6H, dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.5 Hz, Py), 7.10 (6H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 7.02 (12H, t, $^3J_{HH}$ = 7.5 Hz, Ph), 6.93 (12H, d, $^3J_{HH}$ = 7.5 Hz, Ph), 6.32 (6H, d, $^4J_{HH}$ = 1.5 Hz, Py), 5.77 (6H, dd, $^3J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 3.5 Hz, CH), 4.28 (6H, t, $^2J_{HH}$ / $^3J_{HH}$ = 10.0 Hz, CH_2), 3.97-3.93 (6H, m, OCH_2), 3.83-3.78 (12H, m, CH_2/OCH_2), 1.84-1.75 (6H, m, OCH_2CH_2), 1.73-1.61 (6H, m, OCH_2CH_2), 1.47-1.39 (6H, m, $OCH_2CH_2CH_2$).

$^{13}C\{^1H\}$ NMR (100 MHz, 298 K, CD_3OD) δ_C 171.6 (C=N), 159.1 (Ph/Py), 153.3 (Ph/Py), 143.5 (Py), 137.6 (Ph/Py), 131.1 (Py), 129.8 (Ph), 129.1 (Ph), 127.3 (Ph), 122.6 (Py), 74.1 (CH), 70.4 (OCH_2), 66.0 (CH_2), 29.7 (OCH_2CH_2), 23.4 ($OCH_2CH_2CH_2$).

MS (ESI) m/z 607.2 [Fe(**L**^{2b}-H)]$^+$, 405.2 [Fe_2**L**^{2b}(**L**^{2b}-H)]$^{3+}$, 304.1 [Fe_2**L**$^{2b}_2$]$^{4+}$.

IR ν cm^{-1} 3273 w, 2935 w, 1591 m, 1557 s, 1494 m, 1452 m, 1380 w, 1303 m, 1278 m, 1234 s, 1131 w, 1057 m, 1021 m, 930 m, 844 m, 758 m, 700 s.

Elemental Analysis found (Calculated for $C_{99}H_{108}Cl_4Fe_2N_{12}O_{12}$) % C 61.12 (62.21), H 5.61 (5.69), N 8.27 (8.79).

Ethidium bromide displacement experiments

Fluorescence measurements were performed on a Varian Cary Eclipse spectrofluorophotometer using a 0.5 cm quartz cell at ambient temperature. The DNA–ethidium bromide complexes were excited at 546 nm and the fluorescence was measured at 595 nm. Aliquots of a 1 mM stock solution of the flexicate were added to a solution of ethidium bromide and DNA (10 mM Tris pH 7.4, 1 mM EDTA, 1.3 μM EB, and 3.9 mM DNA) and the fluorescence was measured after each addition until the fluorescence was reduced to 50%.

DNA binding studies using spectroscopic methods

Flow LD spectra were recorded using a Jasco J815 spectrometer adapted for LD spectroscopy. The LD measurements were collected using a large volume (1 ml) Couette flow cell built by Crystal Precision Optics based on the design by A. Rodger[8] and is now available from Dioptica Scientific Ltd. The standard parameters used were: bandwidth 1 nm, response time 1 sec, wavelength scan range 200 – 800 nm, data pitch 0.2 nm, scanning speed 200 nm/min and accumulation 1.

UV-Visible absorbance spectra were recorded using a Jasco V-660 spectrometer. The UV-Vis measurements were collected in a 1 cm path-length quartz cuvette and the standard parameters used were: bandwidth 1 nm, response time 1 sec, wavelength scan range 200 – 800 nm, data pitch 0.2 nm, scanning speed 100 nm/min and accumulation 2.

The film LD spectrum was recorded using a Jasco J600 spectrometer. The flexicate Δ_{Fe},R_C-$[Fe_2\mathbf{L}^{\mathbf{1a}}{}_3]Cl_4$ (**Δ7a**) was adsorped onto a stretched polyethylene film. The standard parameters used were: bandwidth 1 nm, response time 1 sec, wavelength scan range 200 – 800 nm, data pitch 0.2 nm, scanning speed 100 nm/min and accumulation 2.

UV melting experiments

The stability of DNA in the presence of the flexicates was monitored by measuring the absorbance at 260 nm as a function of temperature using the following parameters: bandwidth 1 nm, average time 10 s, heating rate 0.4°C/min. The experiments were run simultaneously on six masked 1 cm pathlength cuvettes of 1.2 mL volume using a Peltier controlled 6-sample cell-changer in a Varian Cary 4000 UV-Visible spectrophotometer. T_m was calculated within the thermal heating program by applying a first derivative calculation. The concentration of ct-DNA was 7.5×10^{-5} M (per base) and buffer conditions were 10 mM sodium phosphate buffer (pH 7.0) and 10 mM NaCl. The DNA three-way and four-way junctions were measured at a concentration of 3×10^{-6} M (per strand) in a buffer containing 10 mM sodium phosphate (pH 7.0), 100 mM NaCl and 5 mM $MgCl_2$. The melting of bulge oligonucleotides were carried out in 10 mM sodium phosphate (pH 7.0) and 100 mM NaCl at a concentration of 3×10^{-6} M.

Antimicrobial experiments

The procedure is described in the main article. The bacterial strains used were *Escherichia coli* MC4100[9] and *Staphylococcus aureus* MRSA252.[10] The minimal inhibitory concentration (MIC) values of the flexicates were determined with a macrobroth dilution method as previously described.[11]

Analysis of toxicity in *Caenorhabditis elegans*

The procedure is described in the main article. *C. elegans* Bristol (N2) nematodes were maintained on nematode growth medium, using *E. coli* OP50 as a source of food.[12] Nematodes were age-synchronised as previously described.[13]

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