Electronic Supplementary Information

for

Ion-pair triple helicates and mesocates self-assembled from ditopic 2,2’-bipyridine-bis(urea) ligands and Ni(II) or Fe(II) sulfate salts

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1. Materials and methods

All reagents were used as received from the suppliers without further purification unless otherwise noted. The compound 5-aminomethyl-2,2’-bipyridine was prepared as previously described [Panetta, 1999; Custelcean, 2009]. Proton, carbon, gCOSY, HSQCAD, and APT Nuclear Magnetic Resonance spectra were obtained on a Varian VNMRS 500 NMR spectrometer. Proton and carbon NMR spectra were recorded at room temperature in either DMSO-\(d_6\) (referenced to 2.50 ppm and 39.51 ppm, respectively) or DMF-\(d_7\) (referenced to 2.75 ppm and 29.76 ppm, respectively, for the upfield methyl group), unless otherwise noted. Melting points were obtained on a Thomas Hoover capillary melting point apparatus and are uncorrected.

2. Synthesis

Ligands \(\text{L1}\) and \(\text{L2}\) were synthesized according to Scheme S1.

\[ \text{Scheme S1. Synthesis of } \text{L1 and L2, (i) CH}_2\text{Cl}_2, \text{RT, 2h, 82%; (ii) NH}_2\text{NH}_2\cdot\text{H}_2\text{O, 10% Pd/C catalyst, abs. EtOH, reflux 18 h, 76%; (iii) L1 4-nitrophenyl isocyanate, CHCl}_3, \text{reflux 19h, quant; (L2) 4-t-butylphenyl isocyanate, CHCl}_3, \text{reflux 19h, 89%.} \]
**Scheme S2.** Numbering scheme for the synthetic intermediates.

1-(2,2'-bipyridin-5-ylmethyl)-3-(2-nitrophenyl)urea (P1). A solution of 5-aminomethyl-2,2'-bipyridine (6.00 g, 32.3 mmol) in 100 mL dichloromethane was added dropwise to a rapidly stirred solution of 2-nitrophenyl isocyanate (5.30 g, 32.3 mmol) in 100 mL dichloromethane at laboratory temperature in a 500-mL flask. Yellow precipitates formed immediately, and after 2 h the thick yellow slurry was filtered, and the yellow solid washed with a small portion of dichloromethane, followed by 3 x 20 mL diethyl ether. After suction and vacuum drying, 8.626 g of analytically pure product as a yellow solid was obtained. An additional 0.604 g of analytically pure material was obtained by concentration of the filtrate, and washing the resultant precipitate with diethyl ether. The combined yield was 9.230 g (82%). M.p. 207-208 °C. $^1$H NMR (DMSO-$d_6$): δ 9.49 (s, 1H, 2-NO$_2$Ar-NH), 8.67 (dd, $J_{6'4'} = 1.7$ Hz, $J_{6'5'} = 4.7$ Hz, 1H, H6’), 8.64 (d, $J_{6d} = 2.2$ Hz, 1H, H6), 8.37 (overlapping dd and d, 2H, H3’ + H3), 8.30 (dd, $J_{Ar6d} = 1.2$ Hz, $J_{Ar65} = 8.4$ Hz, 1H, ArH6), 8.10 (t, $J = 5.7$ Hz, 1H, –NHCH$_2$–), 8.05 (dd, $J_{Ar35} = 1.5$ Hz, $J_{Ar34} = 8.3$ Hz, 1H, ArH3), 7.93 (ddd, $J_{4'6'} = 1.7$ Hz, $J_{4'5'} = 7.4$ Hz, $J_{4'3'} = 8.2$ Hz, 1H, H4’), 7.88 (dd, $J_{4d} = 2.2$ Hz, $J_{43} = 8.3$ Hz, 1H, H4), 7.65 (ddd, $J_{Ar53} = 1.5$ Hz, $J_{Ar54} = 7.4$ Hz, 1H, H5).
\( J_{Ar54} = 7.4 \text{ Hz}, J_{Ar56} = 8.4 \text{ Hz}, 1\text{H, ArH5}) \), 7.44 (ddd, \( J_{5'3'} = 0.7 \text{ Hz}, J_{5'6'} = 4.7 \text{ Hz}, J_{5'4'} = 7.4 \text{ Hz} 1\text{H, H5'} \)), 7.14 (ddd, \( J_{Ar46} = 1.2 \text{ Hz}, J_{Ar45} = 7.4 \text{ Hz}, J_{Ar43} = 8.3 \text{ Hz}, 1\text{H, ArH4}) \), 4.42 (d, \( J = 5.7 \text{ Hz}, 2\text{H, } –\text{CH}_2–) \). \(^{13}\text{C}\{^1\text{H}\} \) NMR DMSO-\( d_6 \) (assignments using APT and HSQCAD) δ 155.1 (C2'), 154.4 (CO), 154.1 (C2), 149.3 (C6'), 148.5 (C6), 137.3 (C4'), 137.2 (Ar2), 136.3 (C4), 135.63 (Ar1 or C5), 135.58 (Ar1 or C5), 135.0 (Ar5), 125.3 (Ar3), 124.0 (C5'), 121.6 (Ar4), 120.3 (C3'), 120.2 (C3), 40.5 (CH2). Anal. Calc. for C18H15N5O3 (%): C, 61.9; H, 4.3; N, 20.05; Found: C, 61.5; H, 4.3; N, 20.2.

1-(2,2'-bipyridin-5-yilmethyl)-3-(2-aminophenyl)urea (P2). To a stirred solution of P1 (3.50 g, 10.0 mmol) in 750 mL refluxing absolute ethanol in a 1-L recovery flask under nitrogen was added 0.50 g of 10% Pd/C, followed by 5.0 mL of hydrazine monohydrate. After 18 hours, the slurry was allowed to cool, and was then filtered through Celite, followed by 0.2 micron filter, to remove the catalyst. The colorless filtrate was concentrated to ca. 10 mL, and the white solid that formed was collected by filtration, washed with ether, and dried under vacuum to afford 2.438 g (76%) of analytically pure material. M.p. 188-192 °C. \(^1\text{H} \) NMR (DMSO-\( d_6 \)): \(^1\text{H} \) NMR (DMSO-\( d_6 \)): δ 8.68 (dd, \( J_{6'4'} = 1.7 \text{ Hz}, J_{6'5'} = 4.7 \text{ Hz}, 1\text{H, H6'}) \)), 8.63 (d, \( J_{64} = 2.2 \text{ Hz}, 1\text{H, H6}) \), 8.36 (overlapping dd and d, 2\text{H, } H3'+ H3), 7.94 (ddd, \( J_{4'6'} = 1.8 \text{ Hz}, J_{4'5'} = 7.3, J_{4'3'} = 8.1 \text{ Hz}, 1\text{H, H4'}) \), 7.87 (dd, \( J_{46} = 2.2 \text{ Hz}, J_{43} = 8.2 \text{ Hz}, 1\text{H, H4}) \), 7.69 (s, 1\text{H, 2-NH}_2\text{Ar-NH}) ), 7.44 (ddd, \( J_{5'3'} = 1.1 \text{ Hz}, J_{5'6'} = 4.7 \text{ Hz}, J_{5'4'} = 7.3 \text{ Hz}, 1\text{H, H5'}) \), 7.27 (dd, \( J_{Ar64} = 1.3 \text{ Hz}, J_{Ar65} = 7.9 \text{ Hz}, 1\text{H, ArH6}) \), 6.80 (ddd, \( J_{Ar46} = 1.3 \text{ Hz}, J_{Ar45} = 7.2 \text{ Hz}, J_{Ar43} = 7.9 \text{ Hz}, 1\text{H, ArH4}) \), 6.76 (t, \( J = 5.9 \text{ Hz}, 1\text{H, }–\text{NHCH}_2–) \), 6.70 (dd, \( J_{Ar35} = 1.3 \text{ Hz}, J_{Ar34} = 7.9 \text{ Hz}, 1\text{H, ArH3}) \), 6.54 (ddd, \( J_{Ar53} = 1.3 \text{ Hz}, J_{Ar54} = 7.3 \text{ Hz}, J_{Ar56} = 7.9 \text{ Hz}, 1\text{H, ArH5}) \), 4.73 (br s, 2\text{H, }–\text{NH}_2) \), 4.38 (d, \( J = 5.9 \text{ Hz}, 2\text{H, }–\text{CH}_2–) \). \(^{13}\text{C}\{^1\text{H}\} \) NMR DMSO-\( d_6 \) (assignments using APT and
HSQCAD) δ 156.0 (CO), 155.2 (C2’), 153.9 (C2), 149.3 (C6’), 148.4 (C6), 140.8 (Ar2), 137.3 (C4’), 136.6 (C5), 136.1 (C4), 125.2 (Ar1), 124.1 (Ar4), 124.0 (C5’), 123.7 (Ar6), 120.3 (C3’), 120.2 (C3), 116.7 (Ar5), 115.8 (Ar3), 40.5 (CH2). Anal. Calc. for C18H17N3O (%): C, 67.7; H, 5.4; N, 21.9; Found: C, 67.5; H, 5.3; N, 22.3.

Scheme S3. Numbering scheme for L1 and L2.

**L1.** To a stirred solution of P2 (0.402 g, 1.26 mmol) in 150 mL refluxing chloroform in a 200-mL recovery flask under nitrogen was added slowly dropwise a solution of 4-nitrophenyl isocyanate (0.213 g, 1.30 mmol) in 3 mL chloroform. A yellow precipitate was observed to form within 3 minutes. The turbid solution was refluxed for 19 h and allowed to cool to room temperature, whereupon a yellow solid was observed suspended near the top of the nearly colorless solution. The mixture was filtered and the precipitate washed with small portions of cold chloroform. After drying under vacuum, 0.608 g (1.26 mmol, quantitative) of a bright yellow solid was obtained. M.p. 202-204 °C. 1H NMR (DMF-d7): δ 10.0 (s, 1H, Am4), 8.71-8.69 (overlapping multiplets, 2H, H6 + H6’), 8.51 (s, 1H, Am3 or Am2), 8.44-8.39 (overlapping dd and d, 2H, H3’ + H3), 8.39 (s, 1H,
Am3 or Am2), 8.22 (d, J = 8.4 Hz, 2H, Ar’3,5), 7.99-7.93 (overlapping ddd and dd, 2H, H4’ + H4), 7.83 (d, J = 8.4 Hz, 2H, Ar’2,6), 7.67 (m, 2H, Ar3,6), 7.46 (dd, J5’6’ = 4.9 Hz, J5’4’ = 6.6 Hz, 1H, H5’), 7.23 (t, J = 5.9 Hz, 1H, Am1), 7.13 (m, 2H, Ar4,5), 4.53 (d, J = 5.9 Hz, 2H, –CH2–).

13C{1H} NMR (DMF-d7): (assignments using APT and HSQCAD)
δ 156.8 (CO), 156.1 (C2’), 154.8 (C2), 153.3 (CO), 149.6 (C6’), 148.9 (C6), 147.5 (Ar’1), 141.7 (Ar’4), 137.4 (C4’), 137.0 (C5), 136.4 (C4), 133.0 (Ar1), 131.4 (Ar2), 125.4 (Ar’3,5), 125.1 (Ar4 or Ar5), 125.0 (Ar3 or Ar6), 124.3 (C5’), 124.12 (Ar4 or Ar5), 124.09 (Ar3 or Ar6), 120.7 (C3’), 120.5 (C3), 117.9 (Ar’2,6), 41.2 (CH2). Anal. Calc. for C25H21N3O4⋅0.1CHCl3 (%): C, 60.85; H, 4.3; N, 19.8; Found: C, 60.4; H, 4.35; N, 20.15.

**L2.** To a stirred solution of P2 (0.800 g, 2.50 mmol) in 300 mL refluxing chloroform in a 500-mL recovery flask under nitrogen was added slowly dropwise a solution of 4-t-butylphenyl isocyanate (0.468 g, 2.67 mmol) in 8 mL chloroform. The colorless solution was refluxed for 19 h during which a thick gelatinous flocculent mass formed. After cooling to room temperature, filtration was attempted by the gel was too difficult to filter. The material from the initial filtration was washed with ether to afford after vacuum drying 0.151 g of a first crop as a white flaky solid. For the bulk reaction mixture, the solvent volume was concentrated to ca. 40 mL, and 300 mL of diethyl ether was then added to break up the gel. The solid mass that formed was collected by filtration, and washed with ether to afford after vacuum drying 0.948 g of pale pink solid. Both crops were analytically pure by NMR. The combined yield was 1.099 g (2.22 mmol, 89%). M.p. 184-185 °C. 1H NMR (DMF-d7): δ 9.10 (s, 1H, Am4), 8.72 (overlapping multiplets, 2H, H6 + H6’), 8.47-8.42 (overlapping dd and d, 2H, H3’ + H3), 8.26 (s, 1H, Am3 or Am2),
8.23 (s, 1H, Am3 or Am2), 7.99-7.94 (overlapping ddd and dd, 2H, H4' + H4), 7.69 (m, 2H, Ar3,6), 7.51 (d, J = 8.4 Hz, 2H, Ar’2,6), 7.46 (dd, J5,6' = 5.1 Hz, J5',4' = 6.4 Hz, 1H, H5'), 7.33 (d, J = 8.4 Hz, 2H, Ar’3,5), 7.26 (t, J = 5.7 Hz, 1H, Am1), 7.08 (m, 2H, Ar4,5), 4.53 (d, J = 5.8 Hz, 2H, –CH2–), 1.29 (s, 9H, –CH3). $^{13}$C{$^1$H} NMR (DMF-$d_7$): (assignments using HSQCAD) δ 156.8 (CO), 156.1 (C2’), 154.7 (C2), 153.9 (CO), 149.6 (C6’), 148.9 (C6), 144.6 (Ar’4), 138.2 (Ar’1), 137.4 (C4’), 137.1 (C5), 136.5 (C4), 132.6 (Ar1 or Ar2), 132.2 (Ar1 or Ar2), 125.7 (Ar’3,5), 124.34 (Ar3 or Ar6), 124.28 (C5’), 124.25 (Ar3 or Ar6), 124.18 (Ar4 or Ar5), 124.03 (Ar4 or Ar5), 120.7 (C3’), 120.5 (C3), 118.4 (Ar’2,6), 41.2 (–CH2–), 34.2 (–C(CH3)3), 31.3 (–C(CH3)3), Anal. Calc. for C$_{29}$H$_{30}$N$_6$O$_2$ ⋅ 0.05CHCl$_3$ (%): C, 69.7; H, 6.05; N, 16.8; Found: C, 69.4; H, 6.1, N, 17.0.

**Synthesis of the Ni and Fe helicate/mesocate complexes**

**H1a.** To a solution of L1 (0.06 mmol, 0.030 g) in 2 mL DMF was added an aqueous solution of NiSO$_4$ (0.02 mmol, 0.2 mL, 0.1 M). Vapor diffusion of acetonitrile into the resulting solution led to the formation of orange crystals, which were filtered after 4 days and dried under vacuum. Yield 0.015 g (44%). Anal. Calc. for [Ni(L1)$_3$SO$_4$](DMF)(H$_2$O)$_2$ (%): C, 54.65; H, 4.35; N, 18.0; Found: C, 54.6; H, 4.3, N, 18.1.

**H1b.** To a solution of L1 (0.06 mmol, 0.030 g) in 2 mL DMF was added an aqueous solution of NiSO$_4$ (0.02 mmol, 0.2 mL, 0.1 M). Vapor diffusion of 1,4-dioxane into the resulting solution led to the formation of orange crystals, which were filtered after 4 days and dried under vacuum. Yield 0.011 g (29%). Anal. Calc. for
[Ni(L1)3SO4](DMF)3(dioxane) (%): C, 55.3; H, 4.85; N, 17.6; Found: C, 54.85; H, 4.5, N, 17.2.

**H2a.** To a solution of L1 (0.06 mmol, 0.030 g) in 2 mL DMF was added an aqueous solution of FeSO4 (0.02 mmol, 0.2 mL, 0.1 M). Vapor diffusion of acetonitrile into the resulting solution led to the formation of red crystals, which were filtered after 3 days and dried under vacuum. Yield 0.028 g (83%). Anal. Calc. for [Fe(L1)3SO4](DMF)(H2O) (%): C, 55.3; H, 4.3; N, 18.2; Found: C, 55.6; H, 4.0, N, 18.5.

**M1a.** To a solution of L2 (0.06 mmol, 0.030 g) in 2 mL DMF was added an aqueous solution of NiSO4 (0.02 mmol, 0.2 mL, 0.1 M). Vapor diffusion of acetonitrile into the resulting solution led to the formation of orange crystals, which were filtered after 7 days and dried under vacuum. Yield 0.018 g (48%). Anal. Calc. for [Ni(L1)3SO4](DMF)2(H2O)4 (%): C, 60.2; H, 6.1; N, 15.1; Found: C, 60.2; H, 5.8, N, 15.3.

**M2a.** To a solution of L2 (0.03 mmol, 0.015 g) in 1 mL DMF was added an aqueous solution of FeSO4 (0.01 mmol, 0.1 mL, 0.1 M). Vapor diffusion of 1,4-dioxane into the resulting solution led to the formation of red crystals, which were filtered after 4 days and dried under vacuum. Yield 0.008 g (41%). Anal. Calc. for [Fe(L1)3SO4](DMF)2(dioxane)2 (%): C, 61.95; H, 6.2; N, 14.3; Found: C, 61.9; H, 5.8, N, 14.1.
3. NMR Spectra of P1, P2, L1, and L2
4. Study of H2 and M2 self-assembly by $^1$H NMR

**H2.** To 11.9 mg (24.6 mmol) of L1 dissolved in 0.75 mL DMF-$d_7$ was added a slight excess of FeSO$_4$$\cdot$7H$_2$O (11.7 mmol) as a solution in 36 microliters of D$_2$O. The solution started to turn red immediately, and a proton NMR taken in the time interval 6.5-10 minutes after addition revealed the formation of a set of resonances associated with a major species of high symmetry representing about 50% of the ligand (Figures S1-S3). A major feature is the change in the methylene resonances from a single doublet at 4.53 ppm, to two doublets of 1H each, centered at 4.52 and 3.50 ppm. There was evidence of several smaller doublets between 4.4 and 4.0 ppm, associated with complexes of perceived lower symmetry, but these were somewhat obscured by a broad peak due to DHO. The aromatic region was extremely complex, but it was evident that distinct resonances of the complex were present. Proton NMR spectra were recorded approximately every half-hour over a 3.5 hour period, during which time the resonances of the major species grew in, with the concomitant reduction in the intensity of other resonances, so that by 3.5 hours the major complex comprised $\geq$95% of the resonances (Figures S1-S3). The 3 and 3’ protons on the bipyridyl moiety exhibit a downfield chemical shift, and the 6 and 6’ protons exhibit an upfield chemical shift, relative to the free ligand, upon metal-ion coordination. The amide resonances were reduced in intensity via exchange with deuterium from the added D$_2$O. No precipitates were observed after 24 hours, but by 44 hours, some material had crystallized out at the bottom of the NMR tube. $^1$H NMR of the major complex at 3.5 hours (DMF-$d_7$, assignments made using COSY): $\delta$

8.91 (br doublet, $J = 5.5$ Hz, 1H, H3’), 8.71 (br doublet, $J = 7.5$ Hz, 1H, H3), 8.26 (br
triplet, 1H, H4’), 8.13 (doublet, $J = 7.7$ Hz, 1H, Ar3 or 6), 7.92-7.88 (overlapping doublets, 3H, Ar’3,5, and Ar3 or 6), 7.82 (d, $J = 8.4$ Hz, Ar’2,6), 7.62 (br m, 2H, overlapping H5’ and H6’), 7.23 (br s, 1H, H6), 7.17 (br dd, $J = 7.1, 7.3$ Hz, 1H, Ar4 or Ar5), 7.09 (br dd, $J = 7.1, 7.3$ Hz, 1H, Ar4 or Ar5), 7.01 (br doublet, $J = 7.5$ Hz, 1H, H4), 4.52 (d, $J = 17.6$ Hz, 1H, $-\text{CH}_2\text{H}_b$), 3.50 (d, $J = 17.6$ Hz, 1H, $-\text{CH}_3\text{H}_b$). The residual proton signals (low intensity due to exchange with deuterium) from the urea amides are present at $\delta$ 9.74, 9.18, 8.47, and 8.34.

**Figure S1.** Monitoring the self-assembly of H2 by $^1$H NMR: a) initial L1; b) reaction mixture 10 min after the addition of FeSO4; c) final H2, 3.5 h after the addition of FeSO4.
Figure S2. Monitoring the self-assembly of H2 by $^1$H NMR (aromatic region): a) initial L1; b) reaction mixture 10 min after the addition of FeSO$_4$; c) final H2, 3.5 h after the addition of FeSO$_4$.

Figure S3. Monitoring the self-assembly of H2 by $^1$H NMR (aliphatic region): a) initial L1; b) reaction mixture 10 min after the addition of FeSO$_4$; c) final H2, 3.5 h after the addition of FeSO$_4$. 
M2. To 12.1 mg (24.5 mmol) of L2 dissolved in 0.75 mL DMF-d7 was added a slight excess of FeSO₄•7H₂O (11.7 mmol) as a solution in 36 microliters of D₂O. The solution started to turn red immediately, and a proton NMR taken in the time interval 8.5-12 minutes after addition revealed the formation of a set of resonances associated with a major species of high symmetry representing about 45-47% of the ligand (Figures S4-S6). As with the nitro ligand above, the methylene resonances change from a single doublet at 4.53 ppm, to two coupled doublets of 1H each, centered at 4.52 and 3.40 ppm. There was a very broad peak between 4.4 and 4.0 ppm, somewhat obscured by a broad peak due to DHO, which is believed to be associated with complexes of perceived lower symmetry. In addition, the single peak for the t-Butyl group, at 1.29 ppm for the free ligand, was observed as a group of four peaks. The peaks were comprised of a new major peak at 1.15 ppm (the major species, comprising 45-47% of the total t-Butyl methyl group peak area), and three peaks of approximately equal intensity at 1.27, 1.24, and 1.20. As with L1 above, the aromatic region was extremely complex, but it was again evident that distinct resonances due to the complex were present, with the bipyridyl 3 and 3’ protons, and 6 and 6’ protons, respectively experiencing chemical shifts in the expected directions. Proton NMR spectra were recorded over a 5 hour period, during which time the resonances of the major species grew in, with the concomitant reduction in the intensity of other resonances, so that by 5 hours the major complex comprised ≥95% of the resonances (Figures S4-S6). The rate to equilibrium for the complex formed between ferrous sulfate and the t-Butyl ligand appears to be ca. 40% slower than for the nitro ligand. As with the complex with the nitro ligand, the amide resonances were reduced in intensity via exchange with deuterium from the added D₂O, and no precipitates were
observed after 24 hours, but over time, crystals form on the walls and bottom of the NMR tube. $^1$H NMR of the major complex at 5.0 hours (DMF-$d_7$, assignments made using COSY): $\delta$ 8.92 (br doublet, $J = 5.7$ Hz, 1H, H3’), 8.74 (br doublet, $J = 8.0$ Hz, 1H, H3), 8.25 (br singlet, 1H, H4’), 8.12 (doublet, $J = 7.7$ Hz, 1H, Ar3 or Ar6), 8.05 (doublet, $J = 7.7$ Hz, 1H, Ar3 or Ar6), 7.75 (d, $J = 8.4$ Hz, Ar’2,6), 7.58 (br s, 2H, overlapping H5’ and H6’), 7.28 (br s, 1H, H6), 7.13 (br dd, $J = 7.2, 7.7$ Hz, 1H, Ar4 or Ar5), 7.07 (br dd, $J = 7.2, 7.7$ Hz, 1H, Ar4 or Ar5), 7.02 (d, $J = 8.4$ Hz, Ar’3,5), 6.97 (br doublet, $J = 8.0$ Hz, 1H, H4), 4.52 (d, $J = 17.7$ Hz, 1H, $-\text{CH}_a\text{H}_b$), 3.40 (d, $J = 17.7$ Hz, 1H, $-\text{CH}_a\text{H}_b$), 1.15 (s, 9H, $-\text{CH}_3$). The residual proton signals (low intensity due to exchange with deuterium) from the urea amides are present at $\delta$ 9.08, 8.99, 8.48, and 8.34.

Figure S4. Monitoring the self-assembly of M2 by $^1$H NMR: a) initial L1; b) reaction mixture 12 min after the addition of FeSO$_4$; c) final M2, 5 h after the addition of FeSO$_4$. 

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Figure S5. Monitoring the self-assembly of $\textbf{M2}$ by $^1\text{H}$ NMR (aromatic region): a) initial $\textbf{L1}$; b) reaction mixture 12 min after the addition of FeSO$_4$; c) final $\textbf{M2}$, 5 h after the addition of FeSO$_4$.

Figure S6. Monitoring the self-assembly of $\textbf{M2}$ by $^1\text{H}$ NMR (aliphatic region): a) initial $\textbf{L1}$; b) reaction mixture 12 min after the addition of FeSO$_4$; c) final $\textbf{M2}$, 5 h after the addition of FeSO$_4$. 
5. Diffusion NMR spectroscopy

Diffusion NMR measurements were carried out at 294 ± 1 K on a Bruker Avance 400 spectrometer using a gradient amplifier with a maximum gradient of 54.1 G/cm. Reference $^1$H NMR spectra of the samples were taken prior to diffusion experiments. In the case of H2 and M2, the diffusion measurements were done after the self-assembly reactions had reached equilibrium. The Stebpgp1s (STimulated Echo BiPolar Gradient Pulse) program from Bruker Biospin was used for the DOSY NMR using gradients varied linearly from 5% up to 95% in 16 steps, with 64 scans per step. For the L1 and L2 measurements, the diffusion time ($\Delta$) was set at 75 ms and the gradient length ($\delta$) was set at 3.6 ms. For the H2 and M2 measurements, $\Delta$ and $\delta$ values were set at 100 ms and 4.0 ms, respectively. The diffusion coefficients were determined using the Simfit algorithm from Bruker Biospin.
Figure S7. $^1$H 2D DOSY NMR spectrum of L1.

Figure S8. $^1$H 2D DOSY NMR spectrum of H2.
Figure S9. $^1$H 2D DOSY NMR spectrum of L2.

Figure S10. $^1$H 2D DOSY NMR spectrum of M2.
6. ESI-MS

Electrospray (ESI) mass spectrometry was used to investigate the solution speciation of the iron containing species. A PE-SCIEX API-150MCA quadrupole mass spectrometer was used in conjunction with a Harvard PhD Ultra external syringe pump for this study. 10 µM Solutions of each complex (solvent DMF: MeCN: MeOH, 1:10:100, HPLC Grade, >99.9 %) were injected into the API-150MCA via the ESI source (syringe pump flow rate set to 25 µL min⁻¹) with a spray voltage of 4.5 kV. Desolvation occurred with assistance from the nitrogen sheath gas, together with a heated turbo-ion curtain gas (maintained at 150°C). Fifty scans were acquired for each sample.

**Instrument settings.** Nebulizing gas: 10, Curtain gas: 10, Needle Voltage: +3500 V, Orifice plate voltage: +60.0 V, Focusing ring voltage: +24.00 V, RF-only Quadrupole voltage: -10.00 V, Interquad lens voltage: -11.00 V, Stubbies voltage: -15.00 V Mass Filter voltage: -11.00 V, Deflector voltage: +200.0 V, Ion Detector voltage: +2300.0 V.

**Acquisition settings.** Step size: 0.1 amu, Dwell time: 10.0 msec, pause time: 5.0 msec.
Figure S11. ESI-MS spectra of H2 (top) and M2 (bottom).
Figure S12. Observed (black) and predicted (red) peaks for the protonated cations of H2 (a) and M2 (b).
7. Single-crystal X-ray crystallography

Diffraction quality single crystals of \( \text{H1a}, \text{H2a}, \text{M1a}, \) and \( \text{M2a} \) were obtained by diffusion of CH\(_3\)CN vapors into solutions containing 0.03 mmol of \( \text{L1} \) or \( \text{L2} \) and 0.01 mmol NiSO\(_4\) or FeSO\(_4\) (0.1 mL aqueous solution, 0.1M) in 2 mL DMF. Single crystals of \( \text{H1b} \) were obtained as above, but using 1,4-dioxane instead of CH\(_3\)CN. All crystals included relatively large amounts of solvent, and were extremely unstable once removed from solutions. The crystals were mounted quickly in inert oil and then transferred immediately into the cryostream of the diffractometer. Although this transfer from solution to the cryostream was typically done in less than 30 seconds, the quality of the crystals deteriorated, diffracting relatively poorly with no or very few reflections observed above \( 2\theta = 40-45^\circ \).

Single-crystal X-ray data were collected on a Bruker SMART APEX CCD diffractometer with fine-focus Mo K\( \alpha \) radiation (\( \lambda = 0.71073 \) Å), operated at 50 kV and 30 mA. The structures were refined on \( F^2 \) using the SHELXTL 6.12 software package (Bruker AXS, Inc., Madison, WI, 1997). Absorption corrections were applied using SADABS. Hydrogen atoms were placed in idealized positions and refined isotropically, except for the water H atoms in \( \text{H2a} \), which were not included in the final model. Some included solvent molecules could be located from the Fourier difference maps and could be reasonably refined anisotropically, with a few exceptions where the solvent molecules were too disordered and were therefore refined isotropically. The remaining diffuse electron density could not be unambiguously assigned, and was therefore treated with the SQUEEZE routine in PLATON [Spek, 2003], which removed the contribution of this
electron density from the $hkl$ reflections data prior to final refinement. As a result, all crystals appear to contain large voids. There was some moderate to severe disorder in some parts of the ligand molecule in M2a, leading to unreasonably large anisotropic displacement parameters. These atoms were therefore refined isotropically.

Crystal data for [Ni(L1)3SO4](DMF)1(CH3CN) (H1a): C83H80N24NiO18S, $M = 1792.48$, orange prism, $0.29 \times 0.20 \times 0.19$ mm$^3$, triclinic, space group $P$-1 (No. 2), $a = 13.867(3)$, $b = 18.673(4)$, $c = 18.691(4)$ Å, $\alpha = 74.412(4)$, $\beta = 77.467(4)$, $\gamma = 69.753(4)^\circ$, $V = 4332.2(15)$ Å$^3$, $Z = 2$, $Dc = 1.374$ g/cm$^3$, $F_{000} = 1868$, MoK$\alpha$ radiation, $\lambda = 0.71073$ Å, $T = 173(2)$K, $2\theta_{\text{max}} = 50.0^\circ$, 41988 reflections collected, 15248 unique ($R_{\text{int}} = 0.0672$).

Final $GooF = 1.005$, $R_1 = 0.0901$, $wR_2 = 0.2471$, $R$ indices based on 8114 reflections with $I > 2\sigma(I)$ (refinement on $F^2$), 1139 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.331$ mm$^{-1}$.

Crystal data for [Ni(L1)3SO4](DMF)$_2$(1,4-dioxane)$_{1.5}$ (H1b): C87H89N23NiO21S, $M = 1883.58$, orange prism, $0.20 \times 0.16 \times 0.15$ mm$^3$, triclinic, space group $P$-1 (No. 2), $a = 13.7888(11)$, $b = 19.1350(15)$, $c = 19.5872(16)$ Å, $\alpha = 95.997(2)$, $\beta = 104.132(2)$, $\gamma = 108.688(2)^\circ$, $V = 4652.6(6)$ Å$^3$, $Z = 2$, $Dc = 1.345$ g/cm$^3$, $F_{000} = 1968$, MoK$\alpha$ radiation, $\lambda = 0.71073$ Å, $T = 173(2)$K, $2\theta_{\text{max}} = 50.0^\circ$, 45983 reflections collected, 16391 unique ($R_{\text{int}} = 0.0342$). Final $GooF = 1.072$, $R_1 = 0.0667$, $wR_2 = 0.1967$, $R$ indices based on 11542 reflections with $I > 2\sigma(I)$ (refinement on $F^2$), 1200 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.313$ mm$^{-1}$.
Crystal data for [Fe(L1)2SO4]2(DMF)11(H2O)3 (H2a): C183H209Fe2N53O46S2, M = 4062.85, red prism, 0.35 × 0.22 × 0.20 mm³, triclinic, space group P-1 (No. 2), a = 18.2186(16), b = 19.1483(17), c = 35.531(3) Å, α = 85.896(2), β = 88.045(2), γ = 63.311(2)°, V = 11046.2(17) Å³, Z = 2, Dc = 1.222 g/cm³, F000 = 4260, MoKα radiation, λ = 0.71073 Å, T = 120(2)K, 2θmax = 50.0º, 103522 reflections collected, 38898 unique (Rint = 0.0725). Final Goof = 0.971, R1 = 0.1014, wR2 = 0.2794, R indices based on 17827 reflections with I >2sigma(I) (refinement on F²), 2300 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.232 mm⁻¹.

There are two unique helicate complexes in the crystal. The first helicate binds sulfate with 5 of the 6 urea groups, involving 10 hydrogen bonds. The sixth urea donates 2 hydrogen bonds to an included water solvent, with observed N---O distances of 2.78(1) and 3.48(1) Å. In turn, the water molecule donates 2 hydrogen bonds to sulfate, with observed O---O distances of 2.82(1) and 3.27(1) Å. In the second helicate there are 2 water molecules accepting 2 hydrogen bonds from one urea group (N---O = 2.85(1), 2.90(1) Å) and donating 2 hydrogen bonds to sulfate (O---O = 2.89(1)1, 3.33(1) Å) (Figure 12S).

Crystal data for [Ni(L2)3SO4](DMF)2(CH3CN) (M1a): C95H107N21NiO12S, M = 1825.79, orange prism, 0.28 × 0.10 × 0.10 mm³, monoclinic, space group P21/c (No. 14), a = 17.7602(16), b = 14.4780(13), c = 40.446(4) Å, β = 99.418(2)°, V = 10259.8(16) Å³, Z = 4, Dc = 1.182 g/cm³, F000 = 3856, MoKα radiation, λ = 0.71073 Å, T = 173(2)K, 2θmax = 50.0º, 95762 reflections collected, 18056 unique (Rint = 0.0825). Final Goof
= 1.022, \( R_1 = 0.0706, wR_2 = 0.1903 \), \( R \) indices based on 11678 reflections with \( I > 2\sigma(I) \) (refinement on \( F^2 \)), 1185 parameters, 0 restraints. Lp and absorption corrections applied, \( \mu = 0.275 \text{ mm}^{-1} \).

Crystal data for [Fe(\text{L2})_3\text{SO}_4] (\text{M2a}): \( \text{C}_{87}\text{H}_{90}\text{FeN}_{18}\text{O}_{10}\text{S} \), \( M = 1635.68 \), red prism, 0.17 \( \times \) 0.14 \( \times \) 0.12 mm\(^3\), triclinic, space group \( P-1 \) (No. 2), \( a = 15.318(2), b = 18.423(3), c = 19.119(3) \text{ Å}, \alpha = 85.524(3), \beta = 85.020(3), \gamma = 78.522(3)° \), \( V = 5257.3(13) \text{ Å}^3, Z = 2, \)
\( D_c = 1.033 \text{ g/cm}^3, F_{000} = 1720, \text{MoK}\alpha \text{ radiation, } \lambda = 0.71073 \text{ Å}, T = 120(2)\text{K, } 2\theta_{\text{max}} = 50.0°, \) 37150 reflections collected, 18476 unique (\( R_{\text{int}} = 0.0604 \)). Final \( Goof = 0.878, R1 = 0.0929, wR2 = 0.2409 \), \( R \) indices based on 7737 reflections with \( I > 2\sigma(I) \) (refinement on \( F^2 \)), 1019 parameters, 4 restraints. Lp and absorption corrections applied, \( \mu = 0.219 \text{ mm}^{-1} \).

**Figure S13.** Crystal structure of \text{H2a}, showing the two unique helicate structures. Urea hydrogen bonds to sulfate are shown as black dashed lines. Hydrogen bonds involving water molecules are shown in green dashed lines.
8. References

