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

Radu Custelcean,* Peter V. Bonnesen, Benjamin D. Roach, and Nathan C. Duncan

Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

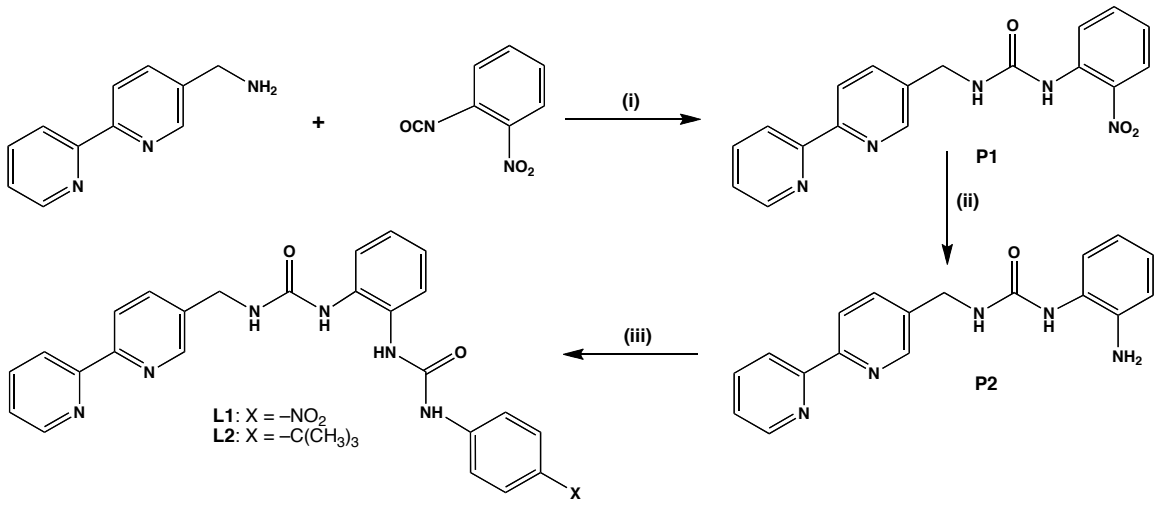
Email: custelceanr@ornl.gov

1. Materials and methods

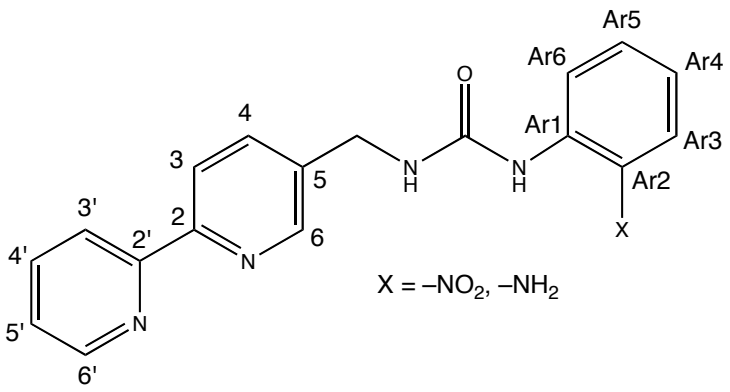
All reagents were used as received from the suppliers without further purification unless otherwise noted. The compound 5-aminomethyl-2,2'-bipyridine was prepared as previously described [Panetta, 1999; Custelcean, 2009]. Proton, carbon, gCOSY, HSQCAD, and APT Nuclear Magnetic Resonance spectra were 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 **L1** and **L2** were synthesized according to Scheme S1.



Scheme S1. Synthesis of **L1** and **L2**, (*i*) CH_2Cl_2, RT, 2h, 82%; (*ii*) $NH_2NH_2{\bullet}H_2O$, 10% Pd/C catalyst, abs. EtOH, reflux 18 h, 76%; (*iii*) (**L1**) 4-nitrophenyl isocyanate, $CHCl_3$, reflux 19h, quant; (**L2**) 4-*t*-butylphenyl isocyanate, $CHCl_3$, reflux 19h, 89%.



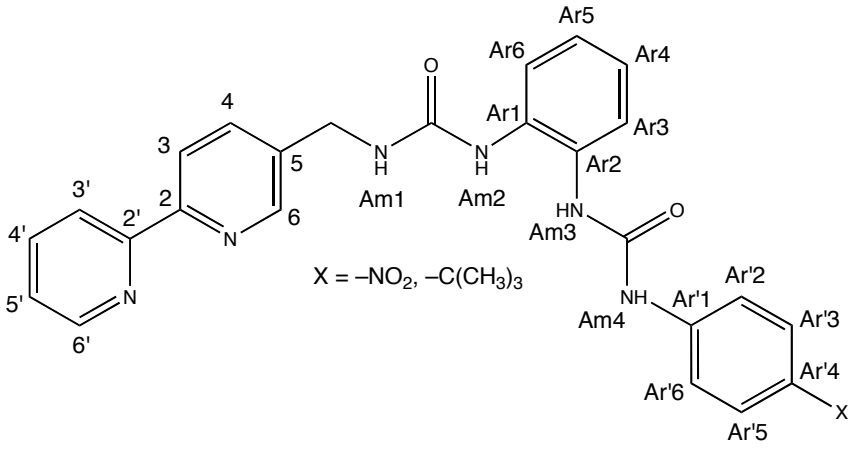
Scheme S2. Numbering scheme for the synthetic intermediates.

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 ºC. ^{1}H NMR (DMSO-d_6): δ 9.49 (s, 1H, 2-NO_2Ar-N*H*), 8.67 (dd, $J_{6'4'}$ = 1.7 Hz, $J_{6'5'}$ = 4.7 Hz, 1H, H6'), 8.64 (d, J_{64} = 2.2 Hz, 1H, H6), 8.37 (overlapping dd and d, 2H, H3' + H3), 8.30 (dd, J_{Ar64} = 1.2 Hz, J_{Ar65} = 8.4 Hz, 1H, ArH6), 8.10 (t, J = 5.7 Hz, 1H, –N*H*CH_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_{46} = 2.2 Hz, J_{43} = 8.3 Hz, 1H, H4), 7.65 (ddd, J_{Ar53} = 1.5 Hz,

J_{Ar54} = 7.4 Hz, J_{Ar56} = 8.4, Hz, 1H, ArH5), 7.44 (ddd, $J_{5'3'}$ = 0.7 Hz, $J_{5'6'}$ = 4.7 Hz, $J_{5'4'}$ = 7.4 Hz 1H, H5'), 7.14 (ddd, J_{Ar46} = 1.2 Hz, J_{Ar45} = 7.4 Hz, J_{Ar43} = 8.3 Hz, 1H, ArH4), 4.42 (d, J = 5.7 Hz, 2H, –CH_2–). $^{13}C\{^1H\}$ 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'), 122.1 (Ar6), 121.6 (Ar4), 120.3 (C3'), 120.2 (C3), 40.5 (CH_2). Anal. Calc. for $C_{18}H_{15}N_5O_3$ (%): C, 61.9; H, 4.3; N, 20.05; Found: C, 61.5; H, 4.3; N, 20.2.

1-(2,2'-bipyridin-5-ylmethyl)-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 ºC. ^1H NMR (DMSO-d_6): ^1H NMR (DMSO-d_6): δ 8.68 (dd, $J_{6'4'}$ = 1.7 Hz, $J_{6'5'}$ = 4.7 Hz, 1H, H6'), 8.63 (d, J_{64} = 2.2 Hz, 1H, H6), 8.36 (overlapping dd and d, 2H, H3' + H3), 7.94 (ddd, $J_{4'6'}$ = 1.8 Hz, $J_{4'5'}$ = 7.3, $J_{4'3'}$ = 8.1 Hz, 1H, H4'), 7.87 (dd, J_{46} = 2.2 Hz, J_{43} = 8.2 Hz, 1H, H4), 7.69 (s, 1H, 2-NH_2Ar-N*H*), 7.44 (ddd, $J_{5'3'}$ = 1.1 Hz, $J_{5'6'}$ = 4.7 Hz, $J_{5'4'}$ = 7.3 Hz, 1H, H5'), 7.27 (dd, J_{Ar64} = 1.3 Hz, J_{Ar65} = 7.9 Hz, 1H, ArH6), 6.80 (ddd, J_{Ar46} = 1.3 Hz, J_{Ar45} = 7.2 Hz, J_{Ar43} = 7.9 Hz, 1H, ArH4), 6.76 (t, J = 5.9 Hz, 1H, –N*H*CH_2–), 6.70 (dd, J_{Ar35} = 1.3 Hz, J_{Ar34} = 7.9 Hz, 1H, ArH3), 6.54 (ddd, J_{Ar53} = 1.3 Hz, J_{Ar54} = 7.3 Hz, J_{Ar56} = 7.9, Hz, 1H, ArH5), 4.73 (br s, 2H, –NH_2), 4.38 (d, J = 5.9 Hz, 2H, –CH_2–). $^{13}C\{^1H\}$ 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 (CH_2). Anal. Calc. for $C_{18}H_{17}N_5O$ (%): 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 ºC. ^{1}H NMR (DMF-d_7): 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, $J_{5',6'}$ = 4.9 Hz, $J_{5',4'}$ = 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, –CH_2–). $^{13}C\{^1H\}$ NMR (DMF-d_7): (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 (CH_2). Anal. Calc. for $C_{25}H_{21}N_5O_4 \cdot 0.1CHCl_3$ (%): 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 ºC. ^1H NMR (DMF-d_7): 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, $J_{5'6'}$ = 5.1 Hz, $J_{5'4'}$ = 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, $-CH_2-$), 1.29 (s, 9H, $-CH_3$). $^{13}C\{^1H\}$ 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 ($-CH_2-$), 34.2 ($-C(CH_3)_3$), 31.3 ($-C(CH_3)_3$), Anal. Calc. for $C_{29}H_{30}N_6O_2 \cdot 0.05CHCl_3$ (%): 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 $[Ni(\mathbf{L1})_3SO_4](DMF)(H_2O)_2$ (%): 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

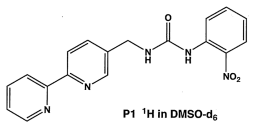
[Ni(**L1**)$_3$SO$_4$](DMF)$_3$(dioxane) (%): C, 55.3; H, 4.85; N, 17.6; Found: C, 54.85; H, 4.5, N, 17.2.

H2a. To a solution of **L1** (0.06 mmol, 0.030 g) in 2 mL DMF was added an aqueous solution of $FeSO_4$ (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**)$_3$SO$_4$](DMF)(H_2O) (%): 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 $NiSO_4$ (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 7 days and dried under vacuum. Yield 0.018 g (48%). Anal. Calc. for [Ni(**L1**)$_3$SO$_4$](DMF)$_2$(H_2O)$_4$ (%): C, 60.2; H, 6.1; N, 15.1; Found: C, 60.2; H, 5.8, N, 15.3.

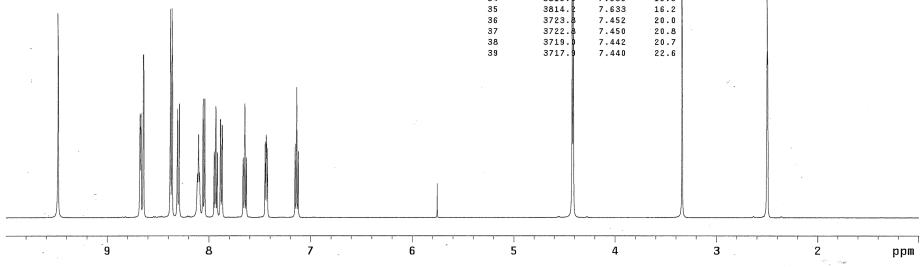
M2a. To a solution of **L2** (0.03 mmol, 0.015 g) in 1 mL DMF was added an aqueous solution of $FeSO_4$ (0.01 mmol, 0.1 mL, 0.1 M). Vapor diffusion of 1,4-dioxane into the resulting solution led to the formation of red crystals, which were filtered after 4 days and dried under vacuum. Yield 0.008 g (41%). Anal. Calc. for [Fe(**L1**)$_3$SO$_4$](DMF)$_2$(dioxane)$_2$ (%): C, 61.95; H, 6.2; N, 14.3; Found: C, 61.9; H, 5.8, N, 14.1.

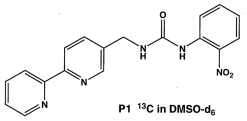
3. NMR Spectra of P1, P2, L1, and L2



P1 ^{1}H in DMSO-d_6

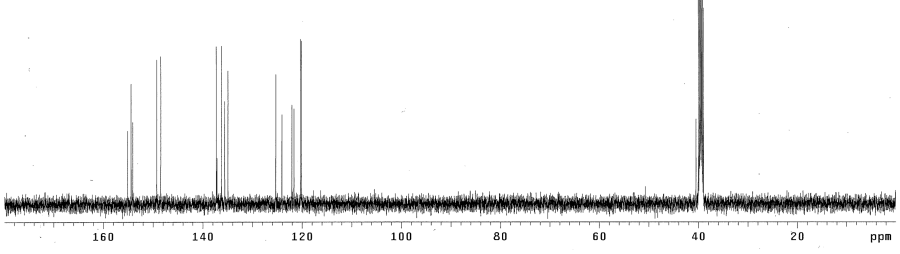
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	4740.3	9.486	56.1	40	3716.4	7.437	22.0
2	4338.0	8.681	27.4	41	3715.3	7.435	20.3
3	4337.2	8.679	28.4	42	3711.6	7.428	19.1
4	4336.3	8.678	25.1	43	3710.5	7.425	18.9
5	4333.2	8.671	28.7	44	3576.1	7.156	19.1
6	4332.5	8.670	28.1	45	3574.8	7.154	20.2
7	4321.3	8.647	44.6	46	3567.7	7.139	35.8
8	4319.6	8.644	44.8	47	3560.5	7.125	18.1
9	4188.5	8.382	44.5	48	3559.2	7.123	18.1
10	4187.4	8.380	57.1	49	2211.3	4.425	64.2
11	4180.6	8.366	46.1	50	2205.6	4.414	64.2
12	4179.1	8.363	57.4	51	1668.8	3.339	211.6
13	4153.3	8.311	29.9	52	1251.0	2.503	45.3
14	4145.4	8.296	31.3	53	1249.3	2.500	61.2
15	4144.7	8.294	31.2	54	1247.5	2.496	45.8
16	4050.0	8.105	22.9				
17	4028.7	8.062	31.0				
18	4027.3	8.059	32.6				
19	4020.5	8.046	32.7				
20	4018.8	8.042	32.6				
21	3974.1	7.953	17.5				
22	3972.3	7.949	18.1				
23	3966.2	7.937	30.5				
24	3964.6	7.934	30.5				
25	3958.5	7.922	17.9				
26	3956.9	7.918	17.5				
27	3943.3	7.891	27.0				
28	3941.1	7.887	26.9				
29	3935.0	7.875	25.4				
30	3932.8	7.870	25.3				
31	3831.4	7.667	16.0				
32	3829.9	7.664	16.4				
33	3822.8	7.650	31.3				
34	3815.6	7.636	16.5				
35	3814.2	7.633	16.2				
36	3723.8	7.452	20.0				
37	3722.0	7.450	20.8				
38	3719.1	7.442	20.7				
39	3717.9	7.440	22.6				

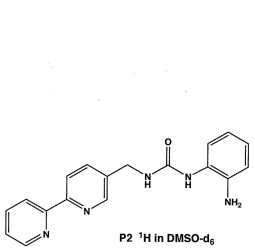




P1 ^{13}C in DMSO-d_6

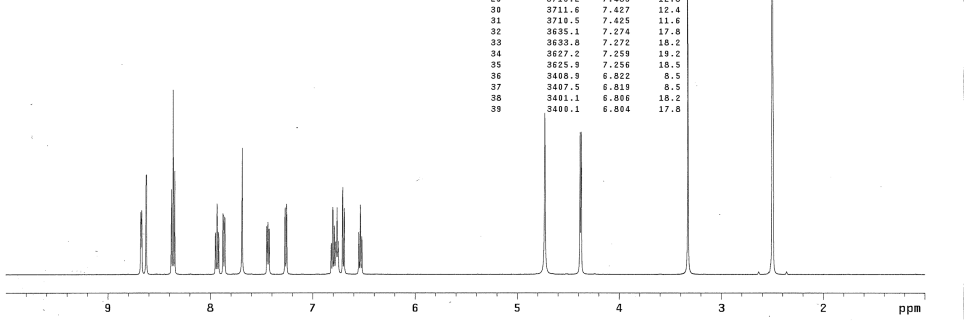
INDEX	FREQUENCY	PPM	HEIGHT
1	19492.1	155.126	29.6
2	19403.6	154.422	33.7
3	19363.8	154.105	23.0
4	18755.1	149.261	40.5
5	18656.1	148.472	41.5
6	17251.9	137.298	44.3
7	17234.9	137.162	12.9
8	17122.9	136.271	44.4
9	17042.5	135.631	28.9
10	17036.0	135.580	22.4
11	16957.3	134.953	37.4
12	15748.0	125.329	36.5
13	15591.3	124.082	25.2
14	15340.5	122.086	27.8
15	15286.1	121.653	26.8
16	15121.4	120.342	46.3
17	15087.8	120.155	45.8
18	5092.0	40.524	23.9
19	5027.9	40.014	57.7
20	5006.8	39.846	175.1
21	4997.8	39.768	16.9
22	4985.7	39.678	347.6
23	4964.5	39.510	410.3
24	4943.4	39.342	345.7
25	4922.3	39.174	168.5
26	4902.1	39.013	55.1

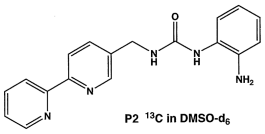




P2 ^{1}H in DMSO-d_6

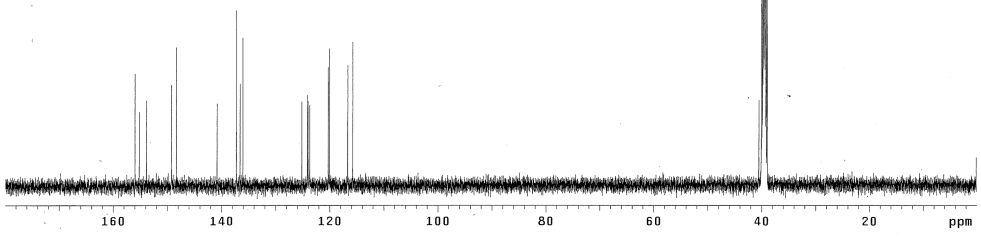
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	4339.0	8.683	14.3	40	3393.9	6.792	13.3
2	4338.0	8.681	16.7	41	3392.4	6.789	12.9
3	4337.3	8.680	17.0	42	3386.0	6.776	8.9
4	4336.4	8.678	14.5	43	3380.2	6.764	18.2
5	4334.2	8.673	15.5	44	3374.3	6.752	9.1
6	4333.3	8.672	17.4	45	3353.4	6.711	22.9
7	4332.5	8.670	16.8	46	3352.1	6.708	23.7
8	4312.2	8.629	27.1	47	3345.5	6.695	18.0
9	4310.5	8.626	27.2	48	3344.2	6.692	17.0
10	4188.2	8.381	23.1	49	3274.5	6.553	11.5
11	4180.3	8.365	50.4	50	3273.2	6.550	11.1
12	4172.4	8.350	28.1	51	3266.8	6.537	18.9
13	3974.4	7.953	11.4	52	3265.9	6.536	18.2
14	3972.5	7.950	11.2	53	3259.5	6.523	10.3
15	3966.7	7.938	19.2	54	3258.0	6.520	9.6
16	3965.0	7.935	18.7	55	2364.7	4.732	44.0
17	3959.0	7.922	11.5	56	2191.9	4.386	38.8
18	3957.1	7.919	11.2	57	2185.9	4.374	38.9
19	3937.5	7.880	16.6	58	1663.7	3.329	382.2
20	3935.3	7.875	16.3	59	1251.1	2.504	95.7
21	3929.3	7.863	15.7	60	1249.2	2.500	127.6
22	3927.1	7.859	15.5	61	1247.6	2.497	93.5
23	3843.8	7.692	34.4				
24	3723.8	7.452	13.1				
25	3722.7	7.450	12.9				
26	3719.1	7.442	13.4				
27	3718.0	7.440	14.2				
28	3716.5	7.437	13.8				
29	3715.2	7.435	12.3				
30	3711.6	7.427	12.4				
31	3710.5	7.425	11.6				
32	3635.1	7.274	17.8				
33	3633.8	7.272	18.2				
34	3627.2	7.259	19.2				
35	3625.9	7.256	18.5				
36	3408.9	6.822	8.5				
37	3407.5	6.819	8.5				
38	3401.1	6.806	18.2				
39	3400.1	6.804	17.8				

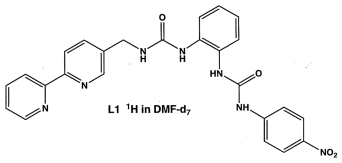




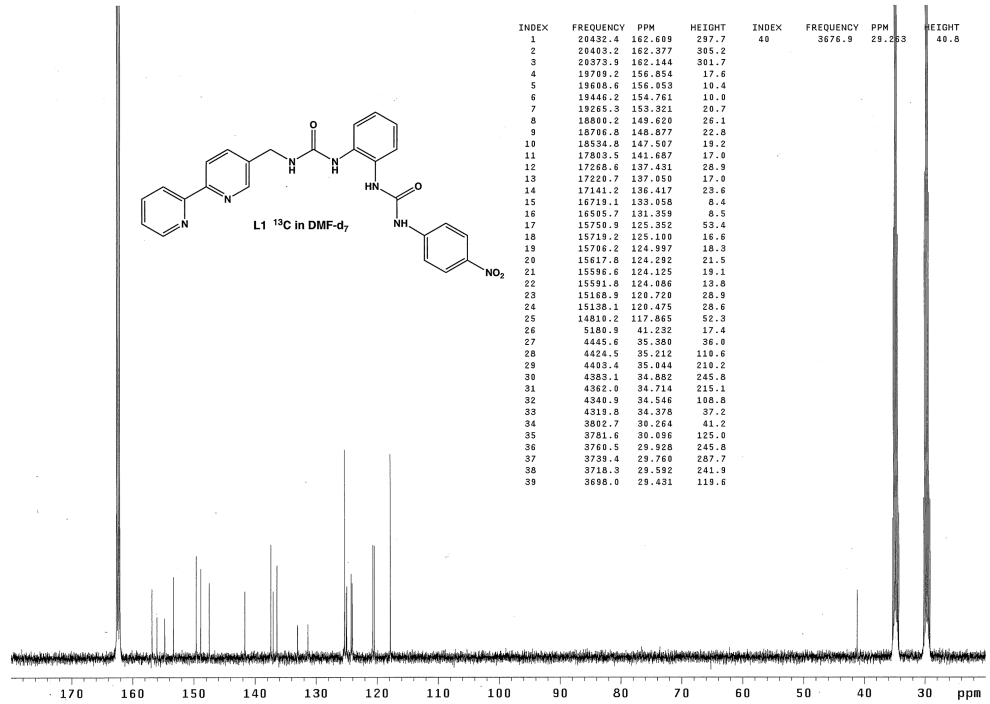
P2 ^{13}C in DMSO-d_6

INDEX	FREQUENCY	PPM	HEIGHT
1	19600.0	155.985	28.9
2	19501.8	155.203	19.0
3	19333.8	153.866	21.9
4	18753.4	149.247	26.0
5	18639.0	148.337	35.7
6	17687.5	140.844	21.1
7	17249.5	137.278	45.1
8	17163.4	136.594	26.2
9	17098.5	136.077	38.1
10	15729.3	125.180	21.6
11	15598.6	124.140	23.3
12	15584.0	124.024	21.8
13	15546.7	123.727	20.7
14	15116.5	120.303	30.6
15	15086.5	120.064	35.4
16	14663.6	116.699	31.0
17	14547.5	115.775	37.1
18	5092.8	40.530	22.0
19	5027.0	40.007	142.6
20	5018.1	39.936	25.7
21	5005.9	39.839	428.4
22	4996.2	39.762	43.2
23	4985.6	39.678	842.5
24	4975.9	39.600	44.6
25	4964.5	39.510	1007.4
26	4943.4	39.342	868.1
27	4922.3	39.174	437.5
28	4901.2	39.006	139.9

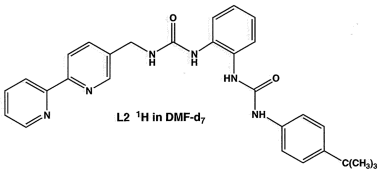




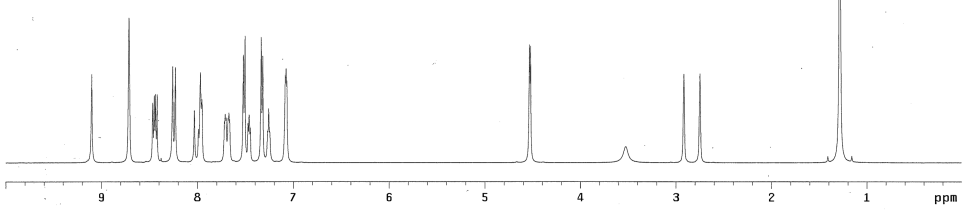
INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	5002.3	10.010	38.7	40	3565.7	7.136	40.9
2	4350.3	8.706	55.0	41	3562.1	7.128	46.8
3	4344.5	8.694	27.5	42	3558.4	7.121	39.4
4	4253.5	8.512	45.1	43	3556.6	7.117	26.8
5	4216.1	8.437	29.8	44	2268.0	4.539	55.1
6	4208.2	8.421	32.6	45	2262.1	4.527	54.4
7	4199.9	8.405	36.1	46	1754.3	3.511	45.4
8	4191.7	8.388	82.0	47	1462.7	2.927	39.0
9	4115.0	8.235	62.0	48	1461.1	2.924	67.7
10	4105.7	8.216	67.2	49	1459.2	2.920	85.7
11	4013.6	8.032	51.2	50	1457.4	2.916	62.5
12	3987.6	7.980	14.9	51	1455.7	2.913	32.9
13	3985.9	7.976	14.7	52	1378.0	2.758	39.7
14	3978.2	7.961	46.6	53	1376.1	2.754	68.9
15	3972.0	7.948	21.7	54	1374.3	2.750	88.4
16	3970.1	7.945	33.0	55	1372.3	2.746	64.0
17	3967.9	7.940	22.3	56	1370.5	2.742	33.9
18	3922.1	7.849	68.2				
19	3912.7	7.830	62.4				
20	3851.1	7.707	28.1				
21	3849.1	7.703	15.6				
22	3845.1	7.695	17.6				
23	3841.8	7.688	21.2				
24	3832.2	7.669	28.8				
25	3829.5	7.663	17.3				
26	3827.1	7.659	15.5				
27	3824.7	7.654	16.5				
28	3822.9	7.650	20.6				
29	3733.8	7.470	16.8				
30	3732.1	7.468	16.5				
31	3728.2	7.461	18.6				
32	3727.3	7.459	19.7				
33	3725.7	7.456	19.4				
34	3720.9	7.446	16.0				
35	3720.0	7.444	14.7				
36	3620.6	7.245	12.9				
37	3614.5	7.233	24.6				
38	3608.7	7.221	13.0				
39	3567.6	7.139	29.6				

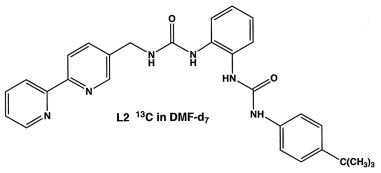


INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	20432.4	162.609	297.7	40	3676.9	29.263	40.8
2	20403.2	162.377	305.2				
3	20373.9	162.144	301.7				
4	19709.2	156.854	17.6				
5	19608.6	156.053	10.4				
6	19446.2	154.761	10.0				
7	19265.3	153.321	20.7				
8	18800.2	149.620	26.1				
9	18706.8	148.877	22.8				
10	18534.8	147.507	19.2				
11	17803.5	141.687	17.0				
12	17268.6	137.431	28.9				
13	17220.7	137.050	17.0				
14	17141.2	136.417	23.6				
15	16719.1	133.058	8.4				
16	16505.7	131.359	8.5				
17	15750.9	125.352	53.4				
18	15719.2	125.100	16.6				
19	15706.2	124.997	18.3				
20	15617.8	124.292	21.5				
21	15596.6	124.125	19.1				
22	15591.8	124.086	13.8				
23	15168.9	120.720	28.9				
24	15138.1	120.475	28.6				
25	14810.2	117.865	52.3				
26	5180.9	41.232	17.4				
27	4445.6	35.380	36.0				
28	4424.5	35.212	110.6				
29	4403.4	35.044	210.2				
30	4383.1	34.882	245.8				
31	4362.0	34.714	215.1				
32	4340.9	34.546	108.8				
33	4319.8	34.378	37.2				
34	3802.7	30.264	41.2				
35	3781.6	30.096	125.0				
36	3760.5	29.928	245.8				
37	3739.4	29.760	287.7				
38	3718.3	29.592	241.9				
39	3698.0	29.431	119.6				



INDEX	FREQUENCY	PPM	HEIGHT
1	4549.6	9.104	23.1
2	4355.9	8.717	37.9
3	4231.0	8.467	15.6
4	4223.1	8.451	17.5
5	4216.5	8.438	17.9
6	4208.5	8.422	17.9
7	4128.0	8.261	25.2
8	4113.8	8.232	25.0
9	4014.3	8.033	13.7
10	3992.3	7.989	8.8
11	3984.0	7.973	23.5
12	3975.7	7.956	16.6
13	3858.0	7.721	10.9
14	3853.9	7.712	12.7
15	3849.0	7.702	11.8
16	3839.5	7.683	11.7
17	3834.6	7.674	13.0
18	3830.4	7.665	11.4
19	3760.0	7.524	28.2
20	3751.4	7.507	33.1
21	3734.8	7.474	10.4
22	3729.4	7.463	12.5
23	3723.1	7.450	9.2
24	3667.1	7.338	32.8
25	3658.8	7.322	27.9
26	3632.8	7.270	8.3
27	3627.2	7.259	14.2
28	3621.6	7.247	8.3
29	3542.1	7.088	22.9
30	3537.5	7.079	24.6
31	3532.8	7.070	21.4
32	2267.1	4.537	30.9
33	2261.3	4.525	30.5
34	1458.5	2.919	23.2
35	1374.3	2.750	23.3
36	642.9	1.287	297.7





INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	20432.1	162.607	197.1	40	3718.0	29.589	159.7
2	20402.0	162.368	203.0	41	3697.7	29.428	80.8
3	20372.8	162.135	203.5	42	3676.6	29.260	29.4
4	19704.0	156.813	21.0				
5	19613.1	156.089	14.1				
6	19443.5	154.739	15.2				
7	19344.5	153.951	20.2				
8	18801.5	149.630	32.3				
9	18709.8	148.900	32.0				
10	18170.8	144.611	19.5				
11	17369.8	138.236	17.5				
12	17270.7	137.448	27.9				
13	17231.0	137.131	19.0				
14	17146.6	136.459	33.3				
15	16660.4	132.590	11.8				
16	16612.5	132.209	10.8				
17	15795.2	125.705	56.9				
18	15623.9	124.342	18.0				
19	15615.8	124.277	29.3				
20	15611.8	124.245	20.6				
21	15602.8	124.174	21.7				
22	15584.2	124.025	19.8				
23	15170.2	120.731	28.6				
24	15138.6	120.479	34.3				
25	14877.2	118.399	53.9				
26	5179.8	41.223	23.9				
27	4445.2	35.377	23.0				
28	4424.1	35.209	70.1				
29	4403.0	35.041	141.0				
30	4381.9	34.873	162.3				
31	4361.6	34.712	138.1				
32	4340.5	34.544	71.4				
33	4319.4	34.376	23.1				
34	4296.7	34.195	28.2				
35	3930.7	31.282	103.6				
36	3802.4	30.261	26.3				
37	3781.3	30.093	81.7				
38	3760.2	29.925	159.9				
39	3739.1	29.757	188.1				

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 $FeSO_4$•$7H_2O$ (11.7 mmol) as a solution in 36 microliters of D_2O. 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 ≥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_2O. 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): δ 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, –CH_aH$_b$–), 3.50 (d, J = 17.6 Hz, 1H, –CH$_a$$H_b$–). The residual proton signals (low intensity due to exchange with deuterium) from the urea amides are present at δ 9.74, 9.18, 8.47, and 8.34.

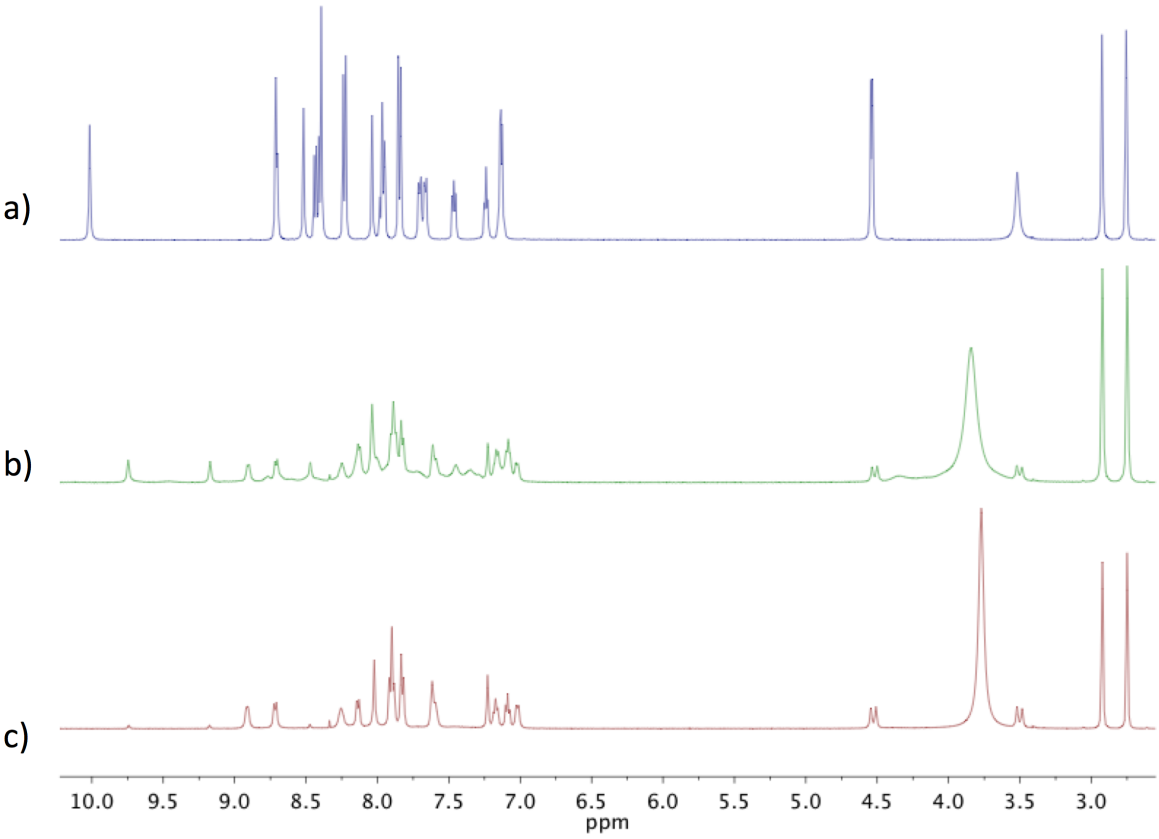


Figure S1. Monitoring the self-assembly of **H2** by ^{1}H NMR: a) initial **L1**; b) reaction mixture 10 min after the addition of $FeSO_4$; c) final **H2**, 3.5 h after the addition of $FeSO_4$.

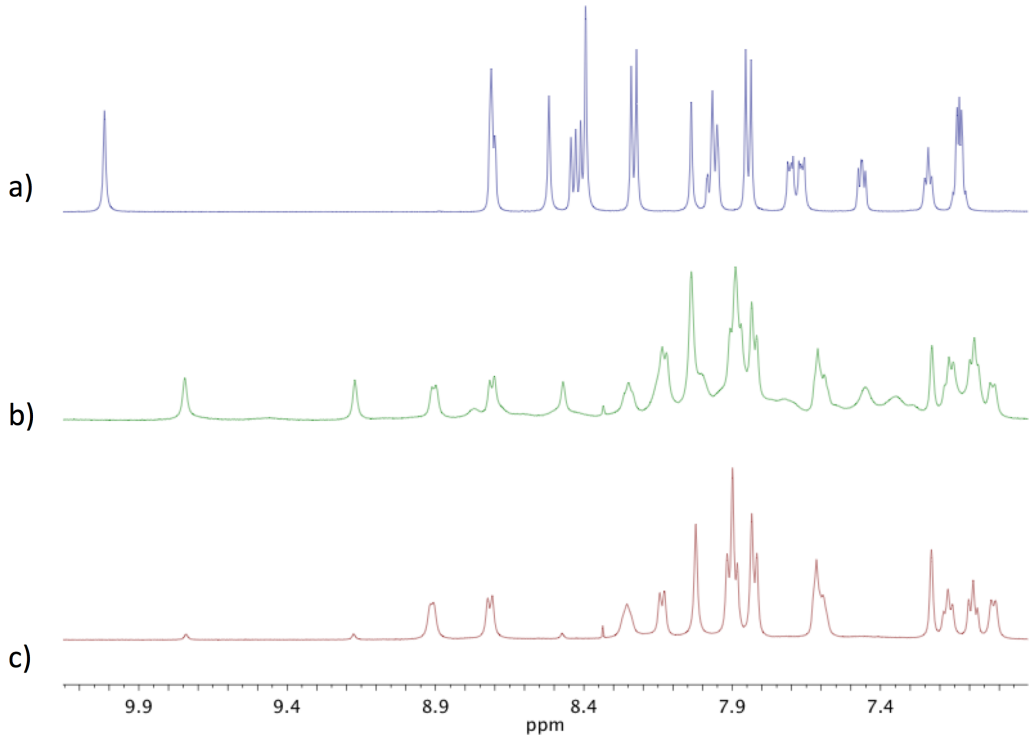


Figure S2. Monitoring the self-assembly of **H2** by ^{1}H NMR (aromatic region): a) initial **L1**; b) reaction mixture 10 min after the addition of $FeSO_4$; c) final **H2**, 3.5 h after the addition of $FeSO_4$.

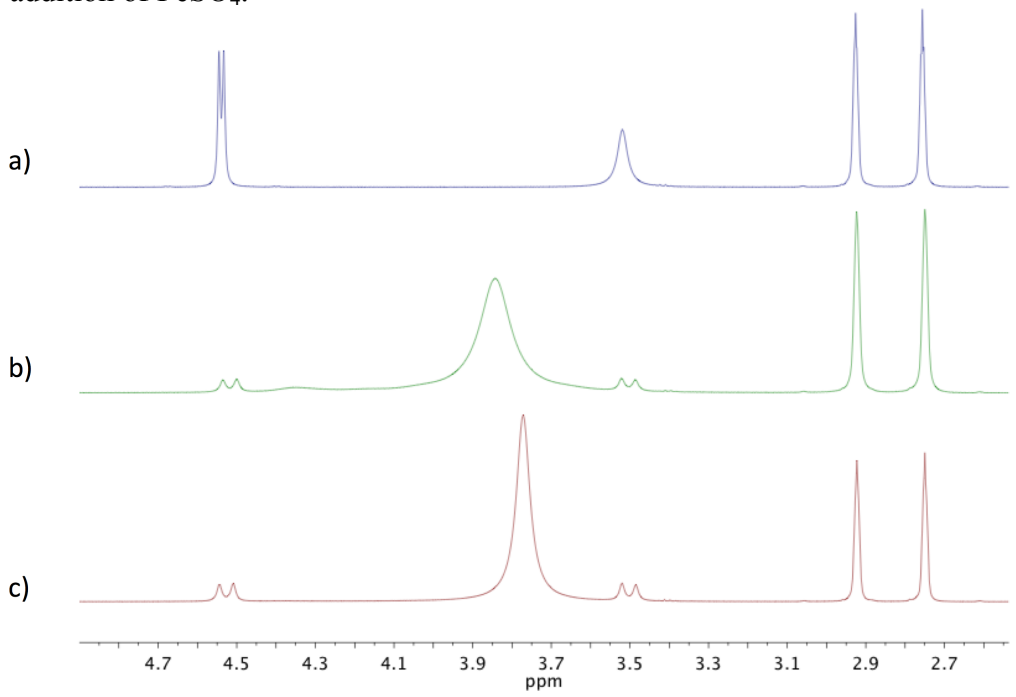


Figure S3. Monitoring the self-assembly of **H2** by ^{1}H NMR (aliphatic region): a) initial **L1**; b) reaction mixture 10 min after the addition of $FeSO_4$; c) final **H2**, 3.5 h after the addition of $FeSO_4$.

M2. To 12.1 mg (24.5 mmol) of **L2** dissolved in 0.75 mL DMF-d_7 was added a slight excess of $FeSO_4$•$7H_2O$ (11.7 mmol) as a solution in 36 microliters of D_2O. 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 D_2O, 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): δ 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, –CH_aH$_b$–), 3.40 (d, J = 17.7 Hz, 1H, –CH$_a$$H_b$–), 1.15 (s, 9H, –CH$_3$). The residual proton signals (low intensity due to exchange with deuterium) from the urea amides are present at δ 9.08, 8.99, 8.48, and 8.34.

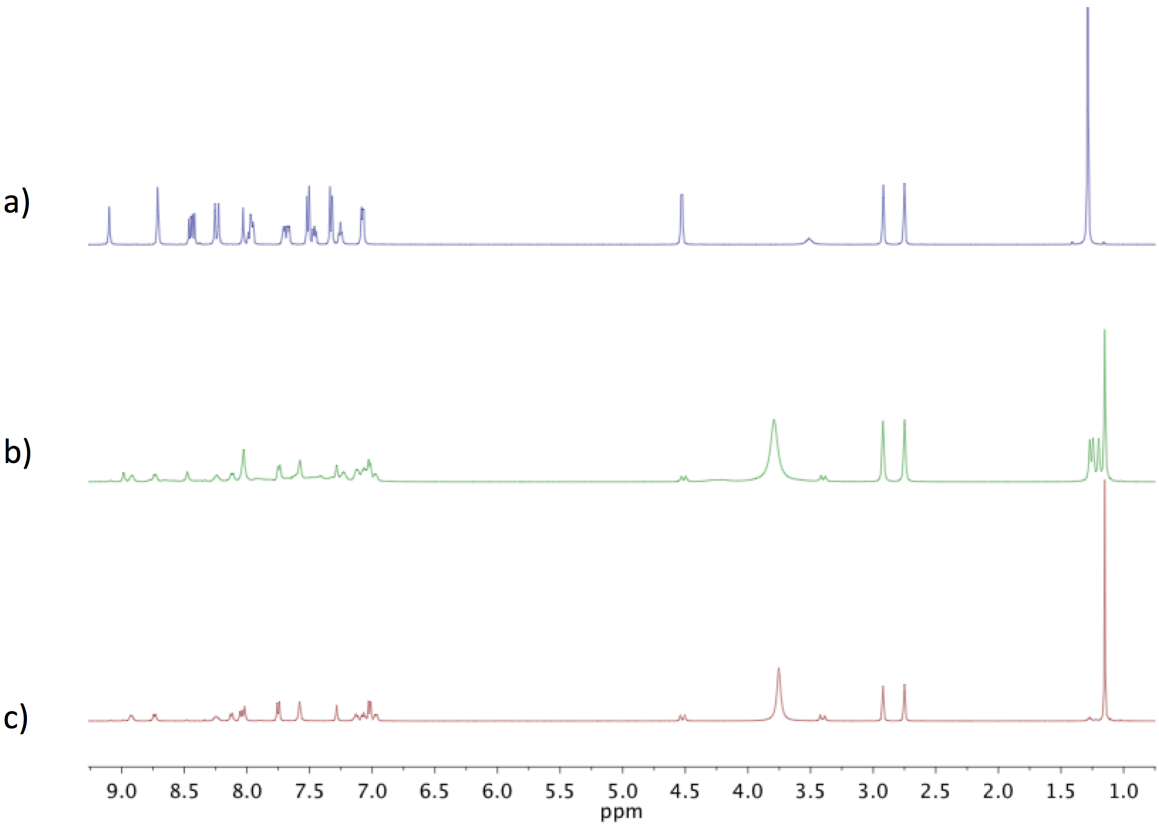


Figure S4. Monitoring the self-assembly of **M2** by ^{1}H NMR: a) initial **L1**; b) reaction mixture 12 min after the addition of $FeSO_4$; c) final **M2**, 5 h after the addition of $FeSO_4$.

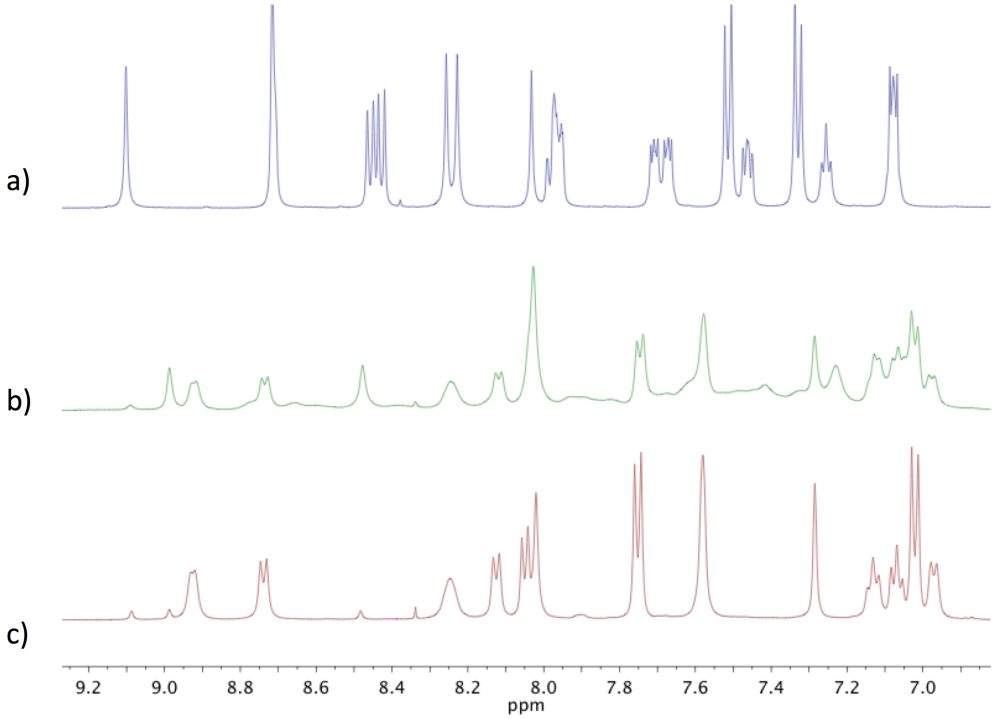


Figure S5. Monitoring the self-assembly of **M2** by ^{1}H NMR (aromatic region): a) initial **L1**; b) reaction mixture 12 min after the addition of $FeSO_4$; c) final **M2**, 5 h after the addition of $FeSO_4$.

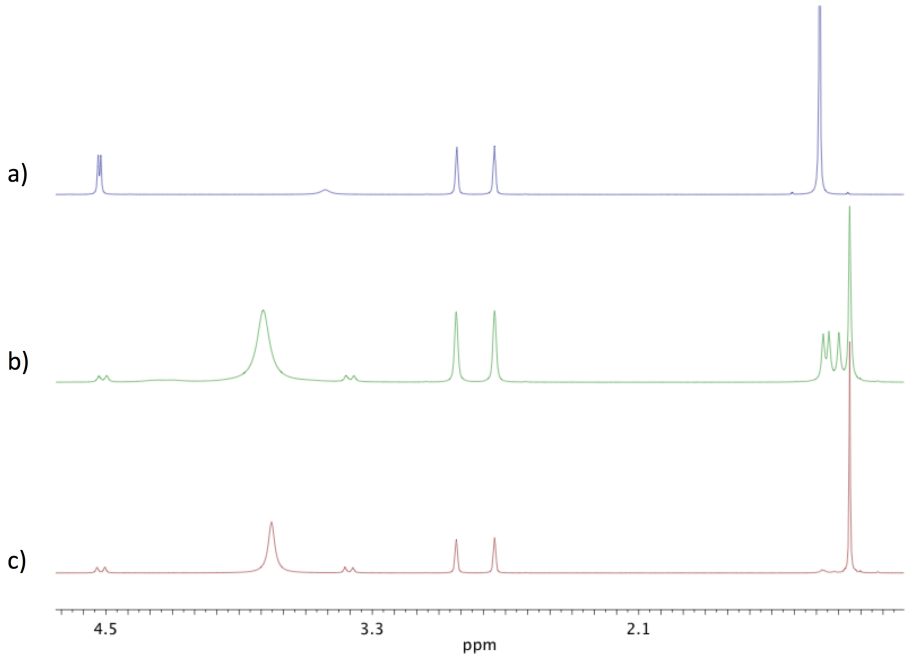


Figure S6. Monitoring the self-assembly of **M2** by ^{1}H NMR (aliphatic region): a) initial **L1**; b) reaction mixture 12 min after the addition of $FeSO_4$; c) final **M2**, 5 h after the addition of $FeSO_4$.

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 (Δ) was set at 75 ms and the gradient length (δ) was set at 3.6 ms. For the **H2** and **M2** measurements, Δ and δ values were set at 100 ms and 4.0 ms, respectively. The diffusion coefficients were determined using the Simfit algorithm from Bruker Biospin.

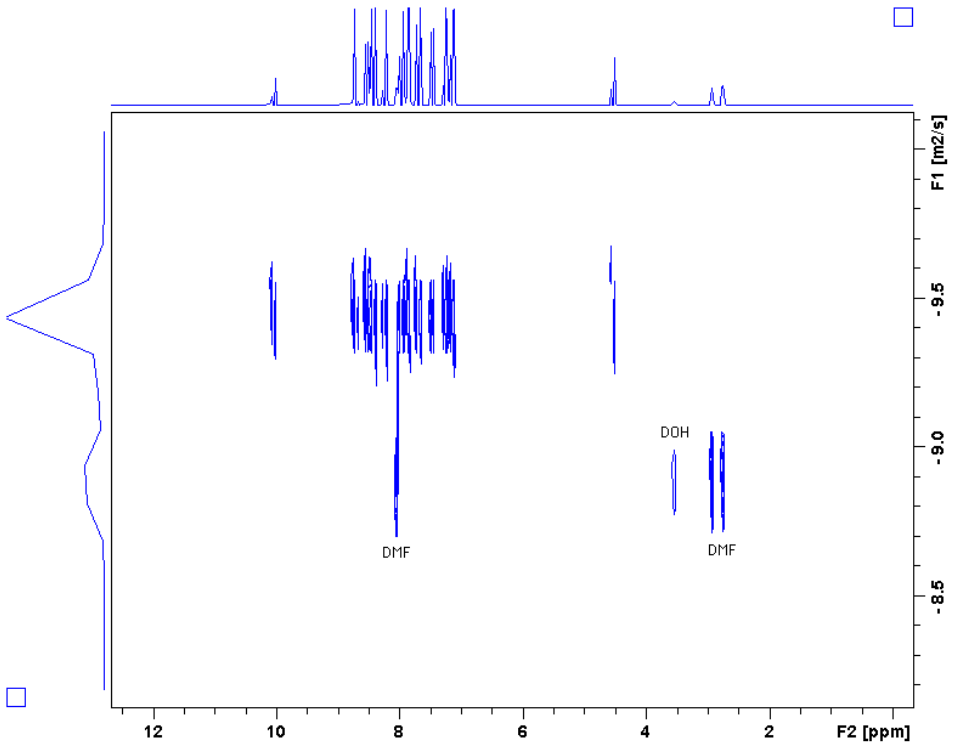


Figure S7. ^{1}H 2D DOSY NMR spectrum of **L1**.

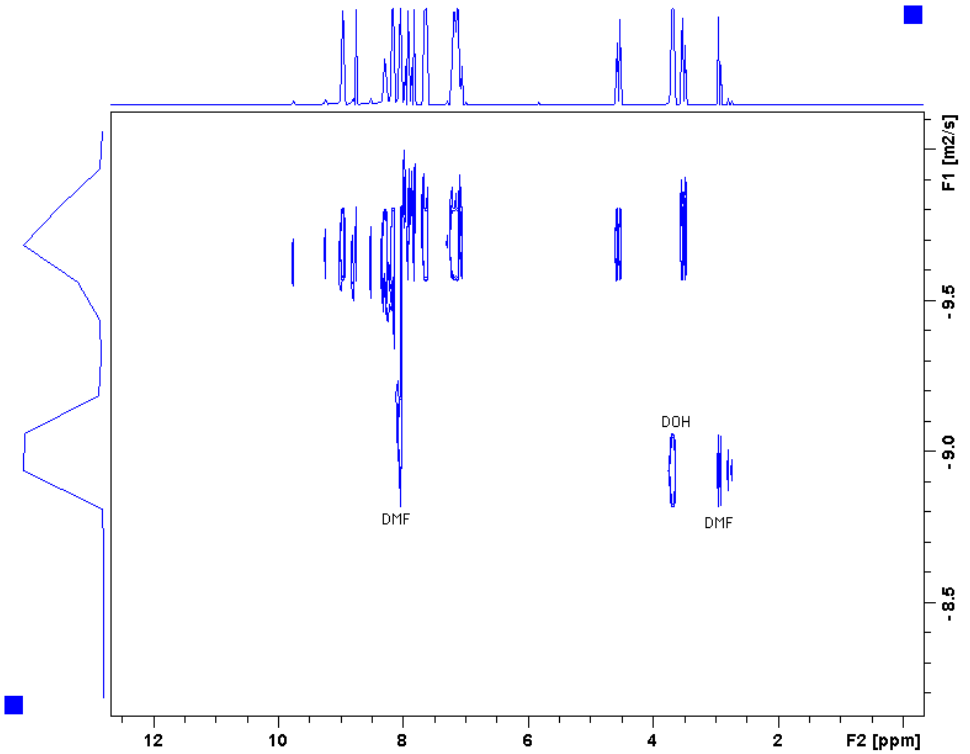


Figure S8. ^{1}H 2D DOSY NMR spectrum of **H2**.

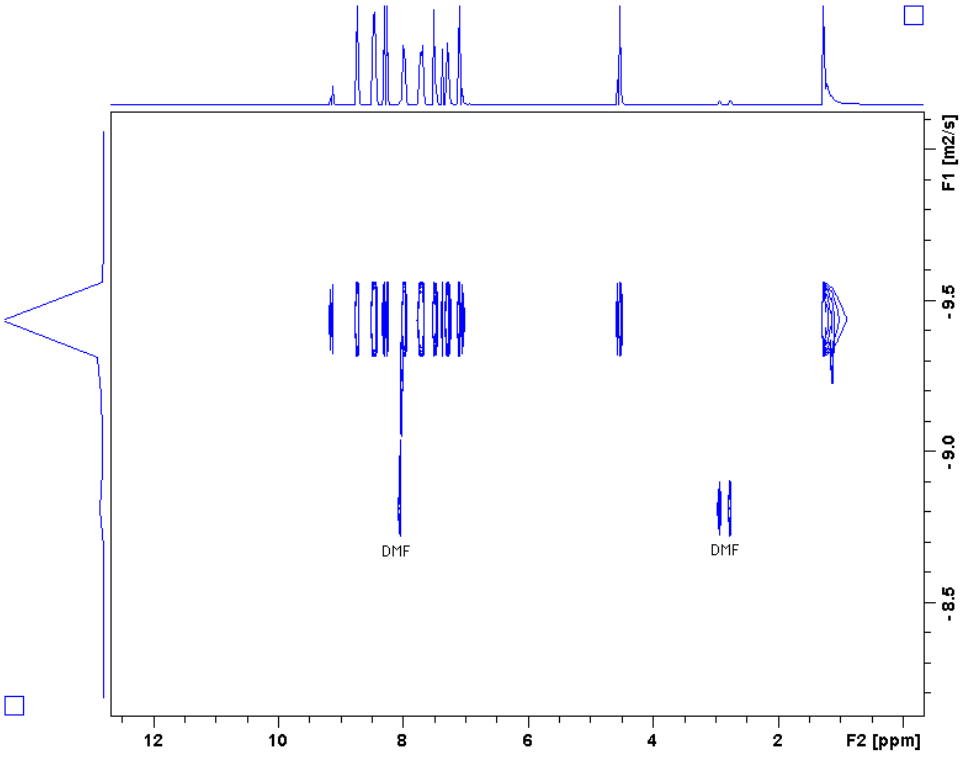


Figure S9. ^{1}H 2D DOSY NMR spectrum of **L2**.

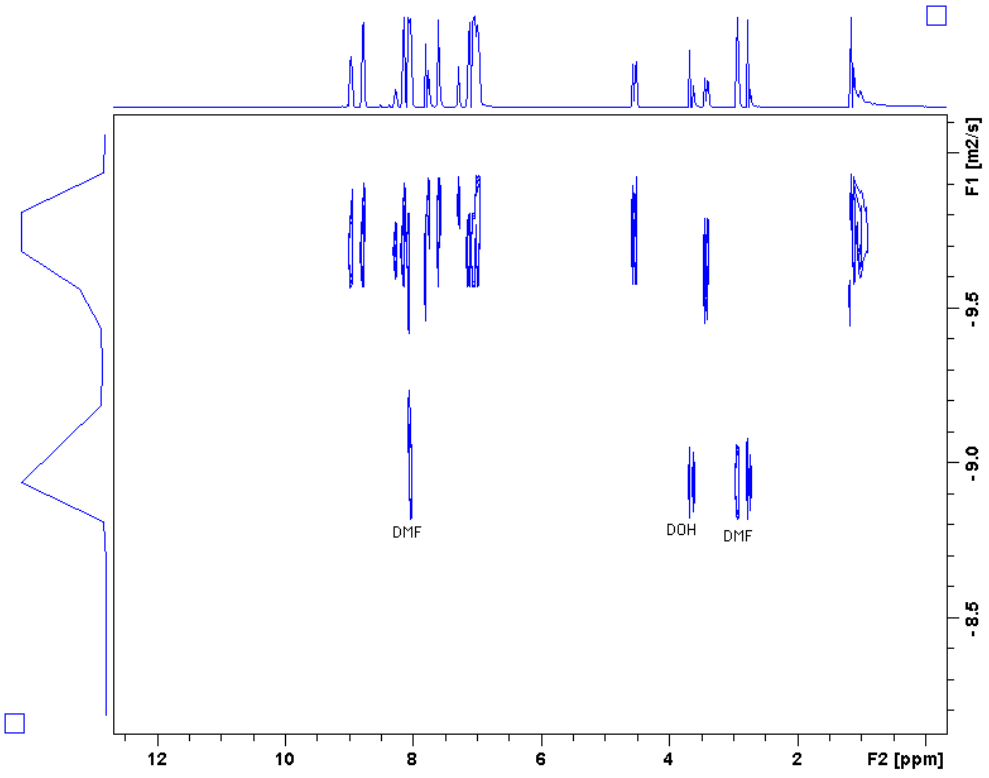


Figure S10. ^{1}H 2D DOSY NMR spectrum of **M2**.

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.

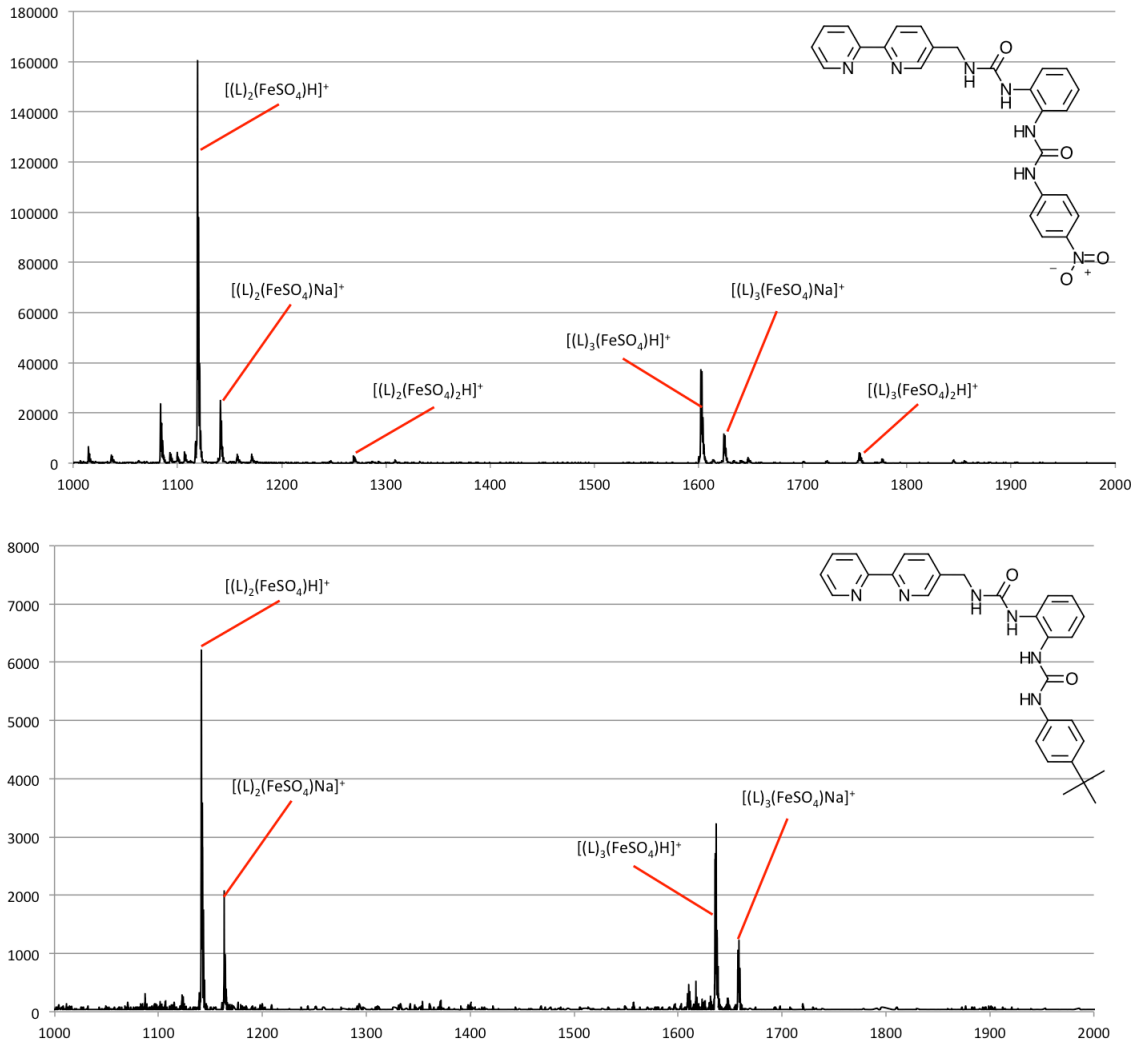


Figure S11. ESI-MS spectra of **H2** (top) and **M2** (bottom).

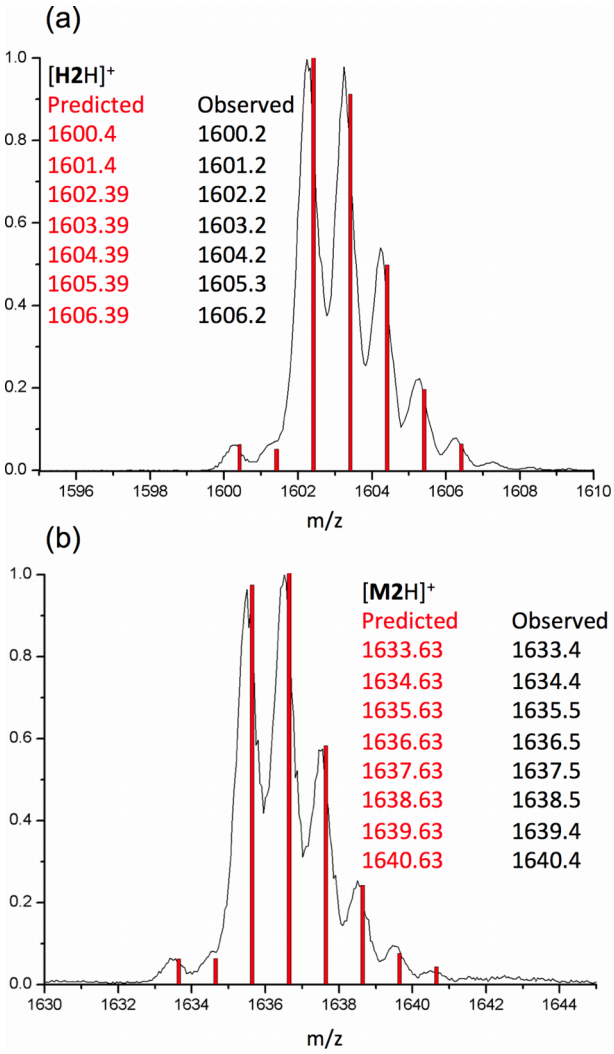


Figure S12. Observed (black) and predicted (red) peaks for the protonated cations of **H2** (a) and **M2** (b).

7. Single-crystal X-ray crystallography

Diffraction quality single crystals of **H1a**, **H2a**, **M1a**, and **M2a** were obtained by diffusion of CH_3CN vapors into solutions containing 0.03 mmol of **L1** or **L2** and 0.01 mmol $NiSO_4$ or $FeSO_4$ (0.1 mL aqueous solution, 0.1M) in 2 mL DMF. Single crystals of **H1b** were obtained as above, but using 1,4-dioxane instead of CH_3CN. 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 $2\theta = 40\text{-}45°$.

Single-crystal X-ray data were collected on a Bruker SMART APEX CCD diffractometer with fine-focus Mo Kα radiation (λ = 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 **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**)$_3$SO$_4$](DMF)$_1$(CH$_3$CN) (**H1a**): $C_{83}H_{80}N_{24}NiO_{18}S$, M = 1792.48, orange prism, 0.29 × 0.20 × 0.19 mm^3, triclinic, space group P-1 (No. 2), a = 13.867(3), b = 18.673(4), c = 18.691(4) Å, α = 74.412(4), β = 77.467(4), γ = 69.753(4)°, V = 4332.2(15) Å^3, Z = 2, D_c = 1.374 g/cm^3, F_{000} = 1868, MoKα radiation, λ = 0.71073 Å, T = 173(2)K, $2\vartheta_{max}$ = 50.0º, 41988 reflections collected, 15248 unique (R_{int} = 0.0672). Final *GooF* = 1.005, R_1 = 0.0901, wR_2 = 0.2471, R indices based on 8114 reflections with I >2σ(I) (refinement on F^2), 1139 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.331 mm^{-1}.

Crystal data for [Ni(**L1**)$_3$SO$_4$](DMF)$_2$(1,4-dioxane)$_{1.5}$ (**H1b**): $C_{87}H_{89}N_{23}NiO_{21}S$, M = 1883.58, orange prism, 0.20 × 0.16 × 0.15 mm^3, triclinic, space group P-1 (No. 2), a = 13.7888(11), b = 19.1350(15), c = 19.5872(16) Å, α = 95.997(2), β = 104.132(2), γ = 108.688(2)°, V = 4652.6(6) Å^3, Z = 2, D_c = 1.345 g/cm^3, F_{000} = 1968, MoKα radiation, λ = 0.71073 Å, T = 173(2)K, $2\theta_{max}$ = 50.0º, 45983 reflections collected, 16391 unique (R_{int} = 0.0342). Final *GooF* = 1.072, R_1 = 0.0667, wR_2 = 0.1967, R indices based on 11542 reflections with I >2sigma(I) (refinement on F^2), 1200 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.313 mm^{-1}.

Crystal data for $[Fe(\mathbf{L1})_3SO_4]_2(DMF)_{11}(H_2O)_3$ (**H2a**): $C_{183}H_{209}Fe_2N_{53}O_{46}S_2$, M = 4062.85, red prism, 0.35 × 0.22 × 0.20 mm^3, 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) Å^3, Z = 2, D_c = 1.222 g/cm^3, F_{000} = 4260, MoKα radiation, λ = 0.71073 Å, T = 120(2)K, $2\theta_{max}$ = 50.0º, 103522 reflections collected, 38898 unique (R_{int} = 0.0725). Final *GooF* = 0.971, R_1 = 0.1014, wR_2 = 0.2794, R indices based on 17827 reflections with I >2sigma(I) (refinement on F^2), 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 $[Ni(\mathbf{L2})_3SO_4](DMF)_2(CH_3CN)$ (**M1a**): $C_{95}H_{107}N_{21}NiO_{12}S$, M = 1825.79, orange prism, 0.28 × 0.10 × 0.10 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 17.7602(16), b = 14.4780(13), c = 40.446(4) Å, β = 99.418(2)°, V = 10259.8(16) Å^3, Z = 4, D_c = 1.182 g/cm^3, F_{000} = 3856, MoKα radiation, λ = 0.71073 Å, T = 173(2)K, $2\theta_{max}$ = 50.0º, 95762 reflections collected, 18056 unique (R_{int} = 0.0825). Final *GooF*

= 1.022, R_1 = 0.0706, wR_2 = 0.1903, R indices based on 11678 reflections with I >2sigma(I) (refinement on F^2), 1185 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.275 mm^{-1}.

Crystal data for [Fe(**L2**)$_3$SO$_4$] (**M2a**): $C_{87}H_{90}FeN_{18}O_{10}S$, M = 1635.68, red prism, 0.17 × 0.14 × 0.12 mm^3, triclinic, space group P-1 (No. 2), a = 15.318(2), b = 18.423(3), c = 19.119(3) Å, α = 85.524(3), β = 85.020(3), γ = 78.522(3)°, V = 5257.3(13) Å^3, Z = 2, D_c = 1.033 g/cm^3, F_{000} = 1720, MoKα radiation, λ = 0.71073 Å, T = 120(2)K, 2θ_{max} = 50.0º, 37150 reflections collected, 18476 unique (R_{int} = 0.0604). Final *GooF* = 0.878, *R1* = 0.0929, *wR2* = 0.2409, R indices based on 7737 reflections with I >2sigma(I) (refinement on F^2), 1019 parameters, 4 restraints. Lp and absorption corrections applied, μ = 0.219 mm^{-1}.

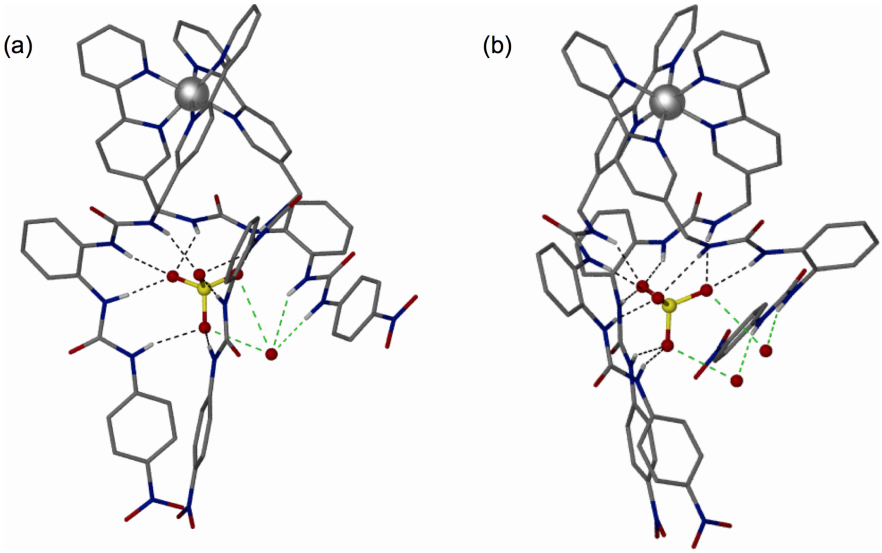


Figure S13. Crystal structure of **H2a**, showing the two unique helicate structures. Urea hydrogen bonds to sulfate are shown as black dashed lines. Hydrogen bonds involving water molecules are shown in green dashed lines.

8. References

[Panetta, 1999]. Panetta, C.A.; Kumpaty, H.J.; Heimer, N.E.; Leavy, M.C.; Huusy, C.L. *J. Org. Chem.* **1999**, *64*, 1015-1021.

[Custelcean, 2009]. Custelcean, R.; Bosano, J.; Bonnesen, P.V.; Kertesz, V.; Hay, B.P. "Computer-Aided Design of a Sulfate-Encapsulating Receptor," *Angew. Chem. Int. Ed.* **2009**, *48*, 4025-4029.

[Spek, 2003] Spek, A. L. *J. Appl. Cryst.* **2003**, *36*, 7.