Advanced Study of Switchable Spin Crossover Compounds

Gavin Craig

ADVANCED STUDY OF SWITCHABLE SPIN CROSSOVER COMPOUNDS

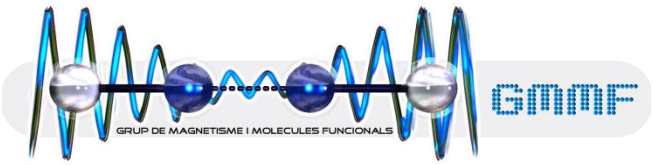
Universitat de Barcelona

Facultat de Química

Departament de Química Inorgànica

Programa de Doctorat: Química Inorgànica Molecular

Grup de Magnetisme i Molècules Funcionals



Gavin Craig

Director: Dr. Guillem Aromí Bedmar, Departament de Química Inorgànica

Tutor: Dr. Santiago Alvarez Reverter, Departament de Química Inorgànica

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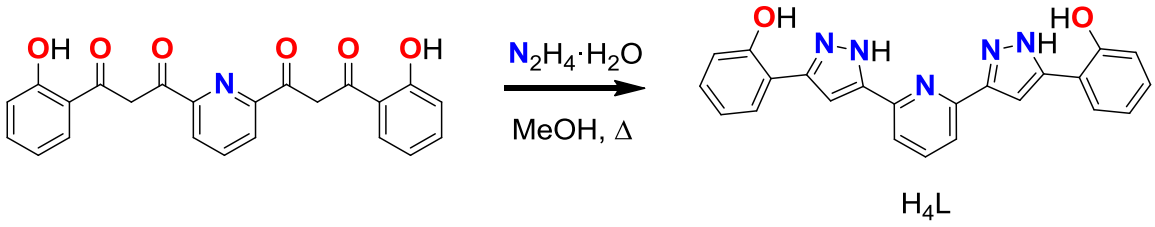
2.1 Synthesis

2.1.1 Ligands

1,3-Bis-(3-oxo-3-(2-hydroxyphenyl)-propionyl)benzene was synthesised following a procedure that was previously described in the literature,[1] as was the ligand 3-bpp.[2] 1,3-bis-(3-oxo-3-(2-hydroxyphenyl)-propionyl)pyridine was synthesised following a route that had been developed in the group prior to this thesis.[3]

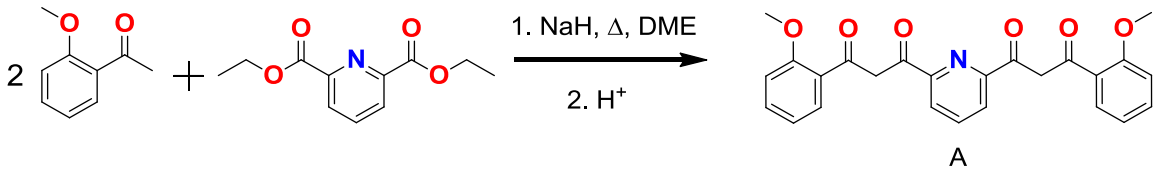
2,6-Bis(5-(2-hydroxyphenyl)-pyrazol-3-yl)pyridine (H_4L): (Scheme 2.1) The compound 1,3-bis-(3-oxo-3-(2-hydroxyphenyl)-propionyl)pyridine (4.06 g, 10 mmol) was refluxed for 16 h with hydrazine monohydrate (5.15 g, 103 mmol) in MeOH (150 mL). After cooling to room temperature, the resulting white suspension was filtered. A white precipitate of **H_4L** was then collected and dried in air. The yield was 71% (2.832 g). IR (KBr disc, υ = cm^{-1}) = 3383 (s), 3350 (s), 1557 (m), 1509 (m), 1473 (s), 1393 (s), 1257 (m), 1190 (s), 827 (m); ^{1}H-NMR (400 MHz, ppm, d_6-DMSO): 10.7 (very broad, s, 2H), 8.01 (broad, t, 1H), 7.88 (d, 2H), 7.78 (d, 2H), 7.61 (s, 2H), 7.19 (t, 2H), 6.95 (d, 2H), 6.92 (t, 2H); elemental analysis calcd (%) for $C_{23}H_{17}N_5O_2$: C 69.86, H 4.33, N 17.71; found: C 69.81, H 4.30, N 17.63.



Scheme 2.1: Synthesis of H_4L

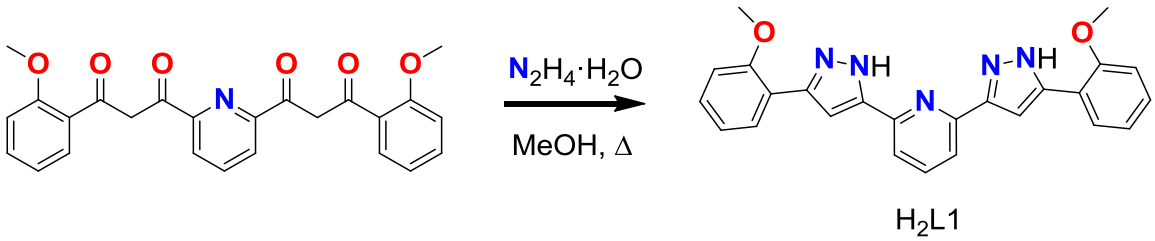
1,3-Bis(3-oxo-3-(2-methoxyphenyl)-propionyl)-2-pyridine (A): (see Scheme 2.2) 2-methoxyacetophenone (5.44 g, 36.2 mmol) and ethyl-2,6-pyridinedicarboxylate (4.04 g, 18.1 mmol) were dissolved in DME (200 mL) under N_2. Separately, a 60% oil dispersion of NaH (8.35 g total mass, for 5.01 g of NaH, 208.8 mmol) was washed in hexane under N_2 for 10 minutes. The solvent was then extracted and replaced with DME (50 mL),

giving a suspension. This suspension was then added dropwise with stirring to the first solution. The resulting yellow suspension was then heated to reflux, which was maintained overnight. The resulting orange suspension was left to cool to RT, before EtOH (20 mL) was added dropwise with stirring to quench any remaining NaH. To this mix, H_2O (100 mL) was added, before glacial acetic acid was added dropwise with stirring until a pH of 5 was attained. During the course of addition, the orange suspension changed to a more viscous yellow suspension, before becoming a brown solution at pH = 5. Diethyl ether was then used to extract the organic phase. The combined organic phases were then dried over $MgSO_4$, and reduced in volume using a rotary evaporator. On reaching ~10 mL, a yellow solid precipitated in the form of needle-like fibres (3.910 g, 50%). ^{1}H-NMR (400 MHz, δ ppm in $CDCl_3$): 16.30 (s, 2H, C(O)-CH), 8.30 (d, 2H, C-CH-CH), 8.06 (t, 1H, CH-CH-CH), 7.96 (dd, 2H, C(OH)-C-CH), 7.72 (s, 2H, C(O)-CH), 7.48 (td, 2H, C-CH-CH-CH), 7.06 (dd, 2H, $C(OCH_3)$-CH), 6.95 (dt, 2H, $C(OCH_3)$-CH-CH), 3.80 (s, 6H, O-CH_3). Mass $(M+H)^+$ 432.2; elemental analysis calcd (%) for $C_{25}H_{21}N_1O_6 \cdot H_2O$: C 69.60, H 4.91, N 3.25; found: C 69.15, H 4.91, N 3.27.



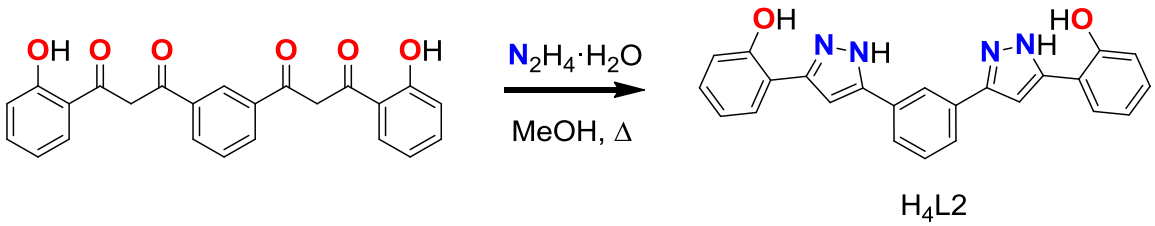
Scheme 2.2 Synthesis of 1,3-Bis(3-oxo-3-(2-methoxyphenyl)-propionyl)-2-pyridine (A).

2,6-Bis(5-(2-methoxyphenyl)-pyrazol-3-yl)pyridine (H_2L1): (Scheme 2.3) The compound 1,3-bis-(3-oxo-3-(2-methoxyphenyl)-propionyl)pyridine (2.00 g, 4.64 mmol) was refluxed for 16 h with hydrazine monohydrate (0.44 g, 9.27 mmol) in MeOH (120 mL). After cooling to room temperature, the resulting white suspension was filtered. A white precipitate of **H_2L1** was then collected and dried in air. The yield was 1.726 g (88%). IR (KBr disc, υ = cm^{-1}) = 3313 (m), 3097 (m), 1602 (m), 1574 (s), 1472 (s), 1255 (s), 1120 (m), 798 (m); ^{1}H-NMR (400 MHz, ppm, d_6-DMSO): 13.55 (broad, s, 1H), 13.10 (broad, s, 1H), 7.98 (broad t, 1H), 7.90 (broad m, 2H), 7.79 (broad m, 2H), 7.36 (m, 4H), 7.14 (dd, 2H), 7.04 (m, 2H), 3.93 (d, 6);). Mass $(M+H)^+$ 424.2; elemental analysis calcd (%) for $C_{25}H_{23}N_5O_3$ ($H_2L \cdot H_2O$): C 68.01, H 5.25, N 15.86; found: C 67.60, H 5.23, N 15.86.



Scheme 2.3: Synthesis of the ligand H_2L1

2,6-Bis(5-(2-hydroxyphenyl)-pyrazol-3-yl)benzene (H_4L2): (Scheme 2.4) 1,3-bis-(3-oxo-3-(2-hydroxyphenyl)-propionyl)benzene (3.00 g, 7.46 mmol) and hydrazine monohydrate (4.12 g, 103 mmol) were refluxed overnight in MeOH (100 mL). The suspension was left to cool to room temperature, was filtered, and the white solid **H_4L2** obtained was dried in air. Yield: 2.338 g (79%). IR (KBr disc) = 3379 (s), 3284 (s), 1627 (m), 1590 (s), 1476 (s), 1300 (w), 1120 (m), 965 (m), 738 (s); ^{1}H-NMR (400 MHz, δ ppm in d_6-acetone): 8.58 (s, 1H), 7.94 (dd, 2H), 7.80 (dd, 2H), 7.65 (t, 1H), 7.39 (s, 2H), 7.23 (td, 2H), 6.97 (d, 2H), 6.93 (d, 2H); elemental analysis calcd (%) for $C_{24}H_{18}N_4O_2$: C 73.08, H 4.60, N 14.20; found: C 73.14, H 4.67, N 14.44.



Scheme 2.4: Synthesis of H_4L2

2.1.2 Coordination compounds containing iron

The iron salts were bought from Sigma Aldrich and used without further purification, with the exception of iron (II) triflate monohydrate and iron (II) thiocyanate, which were prepared following literature procedures.[4] The composition of iron (II) triflate was tested by elemental analysis. **Caution:** Although no problems were experienced during the course of this thesis, perchlorate salts of metal complexes are potentially explosive. Only small quantities of material should be prepared and the samples should be handled with care.

[Fe(3-bpp)$_2$](ClO$_4$)$_2$·1.75 C$_3$H$_6$O·1.5 C$_4$H$_{10}$O (i): A solution of 3-bpp (0.0504 g, 0.238 mmol) in acetone was added dropwise with stirring to a suspension of Fe(ClO$_4$)$_2$·H$_2$O (0.0307 g, 0.121 mmol) and ascorbic acid (approx. 3 mg) in acetone (10 mL), giving a red/brown solution that was stirred at RT. After 1 hour, stirring was stopped, the solution filtered, and layers with diethyl ether were made. Crystals suitable for X-ray diffraction formed after a few days (yield: 14.2 mg, 14%). IR (KBr disc, υ = cm^{-1}) = 3398 (m), 3098 (m), 2923 (m), 1615 (m), 1438 (m), 1354 (m), 1279 (w), 1145 (s), 1122 (s), 1082 (s), 767 (m); elemental analysis calcd (%) for C$_{23.5}$H$_{21}$FeN$_{10}$O$_{8.5}$Cl$_2$ (**i**-1.25C$_3$H$_6$O-1.5C$_4$H$_{10}$O): C 39.97, H 3.00, N 19.83; found: C 39.75, H 2.60, N 20.16.

[Fe(H$_4$L)$_2$](ClO$_4$)$_2$·H$_2$O·2(CH$_3$)$_2$CO (**1**): A suspension of H$_4$L (0.0504 g, 0.128 mmol) in acetone (10 mL) was added dropwise with continuous stirring to a solution of Fe(ClO$_4$)$_2$·H$_2$O (0.0165 g, 0.065 mmol) in acetone (5 mL) in the presence of ascorbic acid (approx. 3 mg). The orange solution that formed was stirred for 1 h at RT before being filtered to remove excess ascorbic acid. The filtrate was used to prepare layers with diethyl ether (volume 1:1). Large, dark orange, polycrystalline aggregates were obtained after a week, which gave crystals suitable for single-crystal X-ray diffraction (yield: 12.3 mg, 16%). IR (KBr disc, υ = cm^{-1}) = 3414 (s), 3319 (s), 1690 (w), 1613 (s), 1486 (m), 1467 (s), 1355 (w), 1290 (m), 1114 (s), 1087 (s), 755 (s); elemental analysis calcd (%) for C$_{52}$H$_{48}$FeN$_{10}$O$_{15}$Cl$_2$: C 52.94, H 4.10, N 11.87; found: C 52.79, H 4.08, N 11.87.

[Fe(H$_4$L)$_2$](ClO$_4$)$_2$·(C$_2$H$_5$)$_2$O·3(CH$_3$)$_2$CO (**2**): The same procedure is followed as for compound **1**, however a drop of water is added to the layers or the crystallisation tubes are gently moved. Small orange crystals form after a few hours (yield: 36.1 mg, 44%). IR (KBr disc, υ = cm^{-1}) = 3414 (s), 3319 (s), 1690 (w), 1613 (s), 1486 (m), 1467 (s), 1355 (w), 1290 (m), 1114 (s), 1087 (s), 755 (s); elemental analysis calcd (%) for C$_{50}$H$_{48}$FeN$_{10}$O$_{15}$Cl$_2$ (**2**·2H$_2$O-(C$_2$H$_5$)$_2$O-2(CH$_3$)$_2$CO): C 51.96, H 4.19, N 12.12; found: C 51.93, H 3.82, N 12.03.

[Fe(H$_4$L)$_2$](ClO$_4$)$_2$·H$_2$O·2(CH$_3$)$_2$CO (**3**): The same procedure is followed as for compound **1**, however layers are prepared with dichloromethane (1:1 volume). Crystals suitable for X-ray diffraction formed after around 2 months (13.5 mg, 18%). IR (KBr disc, υ = cm^{-1}) = 3414 (s), 3319 (s), 1690 (w), 1613 (s), 1486 (m), 1467 (s), 1355 (w),

1290 (m), 1114 (s), 1087 (s), 755 (s); elemental analysis calcd (%) for $C_{52}H_{52}FeN_{10}O_{17}Cl_2$ (**3**·$2H_2O$): C 51.37, H 4.31, N 11.52; found: C 51.48, H 3.93, N 11.66.

$[Fe(H_4L)_2](ClO_4)_2·4C_2H_5OH$ (4): H_4L (0.0502 g, 0.127 mmol) was suspended in ethanol (10 mL) and added dropwise with stirring to a solution of $Fe(ClO_4)_2·H_2O$ (0.0172 g, 0.0631 mmol) and ascorbic acid (approx. 3 mg) in ethanol (10 mL). This gave a yellow suspension that was left to stir for 2 hours at RT. The suspension very quickly turned orange, and on filtering was very nearly a clean solution. The filtrate was layered with hexane (volume 1:1), and crystals suitable for X-ray diffraction formed after a day or so (yield: 9.7 mg, 13.5%). IR (KBr disc, υ = cm^{-1}) = 3421 (s), 2923 (m), 2852 (m), 1613 (s), 1561 (m), 1471 (s), 1270 (m), 1190 (w), 1022 (s), 1015 (s), 808 (m), 754 (m); elemental analysis calcd (%) for $C_{46}H_{40}FeN_{10}O_{15}Cl_2$ (**4**·$3H_2O$-$4C_2H_5OH$): C 50.24, H 3.67, N 12.74; found: C 49.73, H 3.34, N 12.56.

$[Fe(H_4L)_2](ClO_4)_2·2C_3H_7OH$ (5): A suspension of H_4L (0.0499 g, 0.126 mmol) in propan-2-ol (10 mL) was added dropwise with stirring to a solution of $Fe(ClO_4)_2·H_2O$ (0.0172 g, 0.0631 mmol) and ascorbic acid (approx. 3 mg) in propan-2-ol (10 mL). This gave a yellow suspension that after a few minutes turned dark orange. After 2 hours stirring, this orange suspension was filtered and layered with diethyl ether (volume 1:1). Crystals suitable for X-ray diffraction formed after 2 days (yield: 7.0 mg, 10%). IR (KBr disc, υ = cm^{-1}) = 3367 (s), 1613 (s), 1560 (w), 1472 (s), 1270 (m), 1192 (w), 1121 (s), 1086 (s), 1015 (m), 780 (w), 752 (m), 725 (w); elemental analysis calcd (%) for $C_{46}H_{40}FeN_{10}O_{15}Cl_2$ (**5**·$3H_2O$-$2C_3H_7OH$): C 50.24, H 3.67, N 12.73; found: C 50.11, H 3.57, N 12.92.

$[Fe(H_4L)_2](ClO_4)_2·2CH_3NO_2·2H_2O$ (6): H_4L (0.0504 g, 0.128 mmol) was suspended in nitromethane (10 mL) and added dropwise with stirring to a solution of $Fe(ClO_4)_2·H_2O$ (0.0186 g, 0.0682 mmol) and ascorbic acid (approx. 3 mg) in nitromethane (10 mL). This gave an orange suspension that was left to stir for an hour at RT. The resulting yellow solution was filtered, and the filtrate left to slowly evaporate. Crystals suitable for X-ray diffraction formed after 3 weeks (yield: 18.5 mg, 24%). IR (KBr disc, υ = cm^{-1}) = 3410 (m), 3310 (m), 1614 (m), 1556 (m), 1467 (s), 1443 (m), 1275 (m), 1190 (w), 1091 (s), 1014 (m), 807 (m), 758 (m); elemental analysis calcd (%) for $C_{48}H_{44}FeN_{12}O_{18}Cl_2$: C 47.90, H 3.68, N 13.96; found: C 48.06, H 3.59, N 13.83.

[Fe(H_4L)$_2$](ClO_4)$_2$·2THF·H_2O (7): H_4L (0.0500 g, 0.128 mmol) was dissolved in THF (10 mL) and added dropwise with stirring to a suspension of Fe(ClO_4)$_2$·H_2O (0.019 g, 0.068 mmol) and ascorbic acid (approx. 3 mg) in THF (10 mL). The resulting dark orange solution was left to stir at room temperature for 45 minutes. This was then filtered, and the filtrate left to slowly evaporate at 4 ºC, yielding large orange crystals of **1** after 4-5 days (yield: 24.4 mg, 24%). IR (KBr disc, υ = cm^{-1}) = 3410 (m), 3323 (m), 1613 (m), 1468 (m), 1442 (m), 1288 (m), 1273 (m), 1121 (s), 1108 (s), 1015 (m), 804 (m), 757 (m); elemental analysis calcd (%) for $C_{50}H_{47}FeN_{10}O_{15.5}Cl_2$ (**7**·1.5H_2O-C_4H_8O): C 51.65, H 4.07, N 12.05; found: C 51.52, H 3.91, N 12.07.

[Fe(H_4L)(H_2LBF_2)](BF_4)·5C_3H_6O·2H_2O (8): A suspension of H_4L (0.0509 g, 0.129 mmol) in acetone (10 mL) was added dropwise with stirring to a solution of Fe(BF_4)$_2$·4H_2O (0.0224 g, 0.0742 mmol) and ascorbic acid (approx. 3 mg) in acetone (10 mL). The resulting orange solution was stirred for 5 minutes at RT, before being filtered and layered with hexane (volume 1:1). Crystals suitable for X-ray diffraction formed after 3-4 days (yield: 11.4 mg, 14%). IR (KBr disc, υ = cm^{-1}) = 3363 (m), 1614 (m), 1573 (w), 1469 (s), 1440 (m), 1268 (m), 1083 (s), 1015 (s), 809 (w), 753 (s); elemental analysis calcd (%) for $C_{46}H_{40}FeN_{10}O_8B_2F_6$ (**8**·2H_2O-5C_3H_6O): C 52.50, H 3.83, N 13.31; found: C 52.47, H 3.56, N 12.81.

[Fe(H_4L)$_2$](CF_3SO_3)$_2$·3$(CH_3)_2CO$ (9): H_4L (0.0504 g, 0.128 mmol) was suspended in acetone (10 mL) and added dropwise with stirring to a solution of Fe(CF_3SO_3)$_2$·H_2O (0.0201 g, 0.0540 mmol) and ascorbic acid (approx. 3 mg) in acetone (10 mL). This gave an orange solution that was left to stir for 1 hour at RT. The filtrate was layered with hexane (volume 1:1), and crystals suitable for X-ray diffraction formed after 4-5 days (yield: 18.2 mg, 22%). IR (KBr disc, υ = cm^{-1}) = 3387 (m), 1614 (m), 1471 (m), 1443 (m), 1279 (s), 1224 (s), 1173 (s), 1029 (s), 755 (m), 638 (m); elemental analysis calcd (%) for $C_{57}H_{52}FeN_{10}O_{13}S_2F_6$: C 51.90, H 3.97, N 10.62; found: C 51.71, H 3.85, N 10.49.

[Fe$_2$(H_4L)$_2$(ox)($NCS)_4$]·MeOH (10)

Method 1. A 0.006 M methanolic solution of [Fe($NCS)_2$] was prepared as described in the literature. To 10 mL of this solution (10 mg, 0.06 mmol of [Fe($NCS)_2$]) was added ascorbic acid (~5 mg). A white suspension of H_4L (53.1 mg, 0.134 mmol) in MeOH (10

mL) was added dropwise with stirring to the above mixture. After 1 h stirring, the light orange suspension was filtered and the filtrate was left unperturbed for slow evaporation. The filtrate turns progressively darker and black crystals of **10**, suitable for X-ray diffraction, form after two days. Additional powder of the compound precipitates after two to three more days. The combined yield based on Fe is 30%. IR (KBr disc, υ = cm^{-1}) = 3358 (m), 2029 (m), 1648 (s), 1613 (s), 1481 (s), 1466 (s), 1444 (s), 1186 (s), 1018 (s), 789 (s), 757 (s); elemental analysis calcd (%) for $Fe_2C_{53}H_{38}N_{14}O_9S_4$: C 50.73, H 3.05, N 15.63; found: C 50.34, H 2.95, N 15.73.

Method 2. To 10 mL of a 0.006M methanolic solution of [$Fe(NCS)_2$] (10 mg, 0.06 mmol) was added oxalic acid dihydrate (4 mg, 0.032 mmol). A white suspension of H_4L (25 mg, 0.063 mmol) in MeOH (10 mL) was added dropwise to the above mixture with stirring. After 1 h, the resulting light orange suspension was filtered and the filtrate was left unperturbed for slow evaporation. Black crystals of **10** were obtained by filtration. Yield of crystalline material, 11%. The IR spectrum was identical to that obtained *via* method 1; elemental analysis calcd (%) for $Fe_2C_{53}H_{38}N_{14}O_9S_4$: C 50.73, H 3.05, N 15.63; found: C 50.65, H 2.71, N 15.35.

[$Fe(H_2L1)_2$]$(ClO_4)_2$·$(CH_3)_2CO$ (11) A suspension of H_2L (0.0514 g, 0.121 mmol) in acetone (10 mL) was added dropwise with stirring to a solution of $Fe(ClO_4)_2·H_2O$ (0.0194 g, 0.064 mmol) in acetone (5 mL) with a spatula tip of ascorbic acid. The resulting orange mix was left to stir for 1 h at room temperature. The reaction was filtered and layered with hexane. The first crystals suitable of X-ray diffraction formed after 2 days (yield: 27.8 mg, 37%). IR (KBr disc, υ = cm^{-1}) = 3408 (m), 1626 (m), 1577 (m), 1478 (s), 1448 (s), 1383 (m), 1257 (m), 1092 (s), 1022 (s); elemental analysis calcd (%) for $C_{56}H_{56}FeN_{10}O_{15}Cl_2$ (**11**·H_2O·$(CH_3)_2CO$): C 54.42, H 4.57, N 11.33; found: C 54.42, H 4.57, N 11.33.

[$Fe(H_2L1)_2$]$(BF_4)_2$·3$(CH_3)_2CO·H_2O$ (12) A suspension of H_2L (0.0505 g, 0.119 mmol) in acetone (10 mL) was added dropwise with stirring to a solution of $Fe(BF_4)_2·4H_2O$ (0.0212 g, 0.070 mmol) in acetone (5 mL) with a spatula tip of ascorbic acid. The resulting orange mix was left to stir for 90 minutes at room temperature. The reaction was filtered and layered with hexane. The first crystals suitable of X-ray diffraction appeared after one day (yield: 19.4 mg, 30%). IR (KBr disc, υ = cm^{-1}) = 3408 (m), 1606 (m), 1586

(m), 1478 (s), 1448 (s), 1260 (m), 1073 (s), 1015 (s); elemental analysis calcd (%) for $C_{50}H_{48.5}FeN_{10}O_{7.25}B_2F_8$ (**12**·3H_2O-3$(CH_3)_2CO$): C 52.75, H 3.54, N 12.30; found: C 52.56, H 3.95, N 12.32.

[Fe(H_2L1)$_2$](BF_4)$_2$·2.5(EtOH) (13): A suspension of H_2L (0.0505 g, 0.119 mmol) in EtOH (10 mL) was added dropwise with stirring to a solution of Fe$(BF_4)_2$·4H_2O (0.0212 g, 0.070 mmol) in EtOH (5 mL) with a spatula tip of ascorbic acid. The resulting red solution was left to stir for 90 minutes at room temperature. The reaction was filtered and the filtrate left to slowly evaporate. The first crystals suitable of X-ray diffraction appeared after three days (yield: 11.2 mg, 30%). IR (KBr disc, υ = cm^{-1}) = 3411 (m), 3309 (m), 1607 (m), 1577 (s), 1479 (s), 1448 (s), 1287 (w), 1128 (m), 1022 (s), 1082 (s), 1013 (s), 810 (m), 756 (s); elemental analysis calcd (%) for $C_{52}H_{48}FeN_{10}O_5B_2F_8$ (**13**-1.5C_2H_5OH): C 55.64, H 4.31, N 12.48; found: C 55.19, H 3.90, N 12.18.

[Fe(H_2L1)$_2$](CF_3SO_3)$_2$·$C_4H_{10}O$ (14): (The formulation is partial, because one of the solvent molecules in the crystal lattice couldn't be fully assigned due to disorder). A suspension of H_2L1 (0.0513 g, 0.0570 mmol) in propan-2-ol (10 mL) was added dropwise with stirring to a solution of Fe$(CF_3SO_3)_2$·H_2O (0.0212 g,) in propan-2-ol (10 mL) to give a yellow suspension that was stirred at room temperature. After 90 minutes, the resulting orange solution was filtered and layers with diethyl ether were prepared. After 10-12 days, crystals suitable for X-ray crystallography were formed. IR (KBr disc, υ = cm^{-1}) = 3410 (m), 3156 (m), 1607 (m), 1574 (m), 1477 (s), 1448 (s), 1292 (m), 1248 (s), 1030 (s), 757 (m).

[Fe(H_2L1)$_2$](CF_3SO_3)$_2$·5H_2O (15): A suspension of H_2L (0.0504 g, 0.119 mmol) in acetone (10 mL) was added dropwise with stirring to a solution of Fe$(CF_3SO_3)_2$·H_2O (0.0203 g, 0.0540 mmol) in acetone (10 mL) with a spatula tip of ascorbic acid. This gave an initially dark orange solution that turned lighter over several minutes. After 45 minutes, the reaction was filtered and layers with hexane were prepared. Crystals appeared after a week. (yield: 19.5 mg, 30%). IR (KBr disc, υ = cm^{-1}) = 3403 (w), 1607 (m), 1576 (m), 1449 (s), 1260 (s), 1155 (m), 1032 (s), 1016 (s), 754 (m); elemental analysis calcd (%) for $C_{52}H_{52}FeN_{10}O_{14}S_2F_6$: C 48.38, H 4.06, N 10.85; found: C 48.32, H 3.90, N 10.93.

2.2 Physical Techniques

2.2.1 Infrared Spectroscopy

IR spectra for all compounds were recorded on KBr pellets, in the range 4000-400 cm^{-1}, with a Thermo Nicolet Avatar 330 FT-IR spectrometer.

2.2.2 Elemental Analysis

Elemental analyses of compounds **H_4L**, **H_4L2**, **1**, **2**, **3**, **6**, **7**, **9**, and **10**, were performed with a Perkin-Elmer Series II CHNS/O Analyser 2400 at the Servei de Microanàlisi of the CSIC, Barcelona. For compounds **A**, **H_2L1**, **i**, **4**, **5**, **8**, **11**, **12**, **13**, and **15**, they were performed with an EA-1108 CE Instruments (Thermo Fisher Scientific) Analyser at the Servei Cientificotècnics in the Parc Científic of the Universitat de Barcelona.

2.2.3 SQUID Magnetometry

Variable-temperature magnetic susceptibility data for all coordination compounds were obtained with a Quantum Design MPMS-XL SQUID magnetometer at the "Unitat de Mesures Magnètiques" of the Universitat de Barcelona. The correction for the diamagnetism was applied by subtracting one half of the molecular mass from the χ_m measurement, which had already been corrected for the sample holder. The rate of temperature change was generally 1 $Kmin^{-1}$, and is mentioned where relevant in the discussion of the measurements. Some additional measurements were made for compounds **i**, **1**, and **8** using the same apparatus at the SAI Physical Measurements unit at the Universidad de Zaragoza. A series of iso-thermal kinetics experiments for compound **1** were made at the Universitat de Barcelona, although those presented in the thesis were made at the Universidad de Zaragoza.

In the case of the LIESST measurements discussed in Chapter 5, experiments were performed using either a Quantum Design MPMS-5S or MPMS-XL SQUID magnetometers and the Quantum Design fiber optics setup (FOSH). The applied field was 1 T throughout the whole study. The light source was a Xenon lamp equipped with sets of short-pass and long-pass filters (SPF or LPF). For the thick sample case (see Chapter 5 for details), orange block crystals (4-5 rather large crystals) were taken out of their mother liquor, put in the FOSH holder with some solution, and left to fall to the bottom part of the holder. The remaining solvent was then removed by absorbing it with a small piece of

absorbing paper. The mass was ca. 1.72 mg. For the thin sample case, two sets of measurements were performed with orange polycrystalline samples weighing approximately 0.30 and 0.40 mg, which had been covered with some Paraton N grease. Extended relaxation studies were made on the former due to the comparatively longer excitation times required in the latter. Data have been corrected for the signal of the empty FOSH, measured prior to these measurements in the same applied field, and for diamagnetism of the sample (7×10^{-4} cm^3mol^{-1}).

2.2.4 Differential Scanning Calorimetry

DSC experiments were performed with a differential scanning calorimeter Q1000 with the LNCS accessory from TA Instruments. The temperature and enthalpy scales were calibrated with a standard sample of indium, using its melting transition (156.6 ºC, 3296 $Jmol^{-1}$). Measurements were carried out using aluminium pans. For the trapping experiment of **1** (see Chapter 5) a few crystals (ca. 0.5 mg) were covered with a little Paraton N grease within the Al pan, which was simply covered and not crimped. An empty pan in the same un-crimped geometry was used as reference. The measurements in Chapter 4 were carried out at 10 or 2 $Kmin^{-1}$ scanning rate on several batches using 3 to 8 mg of undamaged crystals directly taken out of their mother liquor and sealed in aluminium pans with mechanical crimp, with an empty pan as reference. The same procedure was performed for compound **i** as presented in Chapter 3.

2.2.5 Nuclear Magnetic Resonance Spectroscopy

^{1}NMR spectra were recorded with a Varian Mercury 400 MHz or Varian Inova 300 MHz instrument at the Unitat de RMN at the Universitat de Barcelona. Chemical shifts are reported in δ (parts per million) relative to an internal standard of tetramethylsilane.

2.2.6 X-ray Crystallography

Data for compound **H_4L** were collected on a colourless block with a Bruker APEX II CCD diffractometer on Advanced Light Source beamline 11.3.1 at Lawrence Berkeley National Laboratory, using a silicon 111 monochromator (T = 100 K, λ = 0.7749 A).The structure was solved by SIR97[5] and refined on $F2$ with SHELXTL.[6] All hydrogens were found in difference Fourier maps.

Data for compound **i** were collected at 250 and 90 K on a Bruker APEX II CCD diffractometer at station 11.3.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory, with λ = 0.7749 Å from a silicon 111 monochromator, and the structure solved with SIR97.[5]

Data for compound **1** were collected on a block crystal that was orange (HS) or purple (LS) depending on the temperature, at λ = 0.7515 Å using a single-axis HUBER diffractometer at station BM16 of the European Synchrotron Radiation Facility, Grenoble, France. Measurements were performed at 200 K (HS), 150 K (HS) and 100 K (LS) cooling from 200 K at 5 K/min, at 150 K (LS) after warming from 100 K at 5 K/min and at 100 K (HS) mounting the crystal directly at 100 K from room temperature. Cell refinement, data reduction and absorption corrections were performed with the HKL-2000 suite.[7] The structure was solved by SIR92[8] and the refinement and all further calculations were carried out using SHELXTL[6] suite. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found in difference Fourier maps except those of the disordered methyl groups. Water and phenol hydrogen atoms were refined with their thermal parameters 1.5 times that of their carrier oxygen and distance restraints. The rest of the hydrogen atoms were placed geometrically on their carrier atom and refined with a riding model. Monitoring of the cell parameters variation with temperature was done on a block crystal of 1 using a Bruker APEX II CCD diffractometer at station 11.3.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory, at 0.7749 Å, from a silicon 111 monochromator. Datasets were also acquired at both 200 and 100 K to confirm the similarity of the structure.

For the photo-trapped structure of compound **1**, single crystal X-ray diffraction data were collected on a Bruker SMART-CCD 1K diffractometer (ω-scan, 0.3°/frame) equipped with a Helix (Oxford Cryosystems) open-flow helium cryostat using graphite monochromated MoKα radiation (λ = 0.71073 Å) in the Chemical Crystallography Group at the University of Durham. A green laser (λ = 0.532 nm) mounted on a special attachment[9] was used for *in situ* irradiation (1 h) of the crystal without changing the temperature. The structure was solved by direct methods and refined by full-matrix least squares on F^2 for all data using SHELXTL[6] and OLEX2[10] software. All non-hydrogen

atoms were refined with anisotropic displacement parameters, H-atoms were placed in the calculated positions and refined in riding mode.

Data for compounds **2** and **6** were collected on an Oxford XCalibur diffractometer at the Universidad de Zaragoza. The structure of **2** and **6** was resolved using SHELXS.[11]

Data for compounds **3**, **4**, **5**, **8**, **9**, **11**, **12**, and **14** were collected at 100 K on a Bruker APEX II CCD diffractometer at station 11.3.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory, with λ = 0.7749 Å from a silicon 111 monochromator, and the structures solved with SIR97,[5] except for **3** and **12** which were resolved with SHELXS.[11]

The data were collected with an orange block crystal of **7** with a Bruker APEX II CCD diffractometer at the Advanced Light Source beamline 11.3.1 at Lawrence Berkeley National Laboratory from a silicon (111) monochromator (T = 90 and 250 K, λ = 0.7749 Å). The crystal was taken directly from its solution, mounted with a drop of Paratone-N oil and immediately put into the cold stream of dry N_2 on the goniometer. The structure was solved by direct methods and the refinement on $F2$ and all further calculations were carried out with the SHELXTL[6] suite. All non-hydrogen atoms were refined anisotropically. The perchlorate ions exhibit two and three of their oxygen atoms disordered over two positions. The lattice THF molecules and one of the phenol oxygen atoms are disordered over two positions with relative occupancies that vary with temperature. All these were refined with both displacement parameter (SIMU and DELU) and positional (SAME for THF molecules, SADI for perchlorate ions) restraints. Hydrogen atoms were placed geometrically on their carrier atoms and were refined with a riding model where possible, except that on the phenol oxygen atom O1, which was found in a difference Fourier map and refined with its thermal parameter 1.2 times that of O1. Hydrogen atoms on the lattice water molecule could not be found nor fixed and were omitted in the structural model, although hydrogen bonds indicate the presence of these missing atoms.

After preliminary X-ray diffraction on a laboratory diffractometer showed the small crystals to be weakly diffracting, data for compound **10** were collected on a black needle at 150 K and λ= 0.7515 Å using a single-axis HUBER diffractometer on station BM16 of

the European Synchrotron Radiation Facility, Grenoble, France. Cell refinement, data reduction and absorption corrections were made with the HKL-2000 suite.[7] The structure was solved by direct methods and the refinement and all further calculations were carried out using the SHELXTL[6] suite. Hydrogen atoms were found in difference Fourier maps, except those on the methanol molecule.

Data for compound **13** were collected at 100 K on a SuperNova Dual Atlas CCD diffractometer at Agilent Technologies with λ = 0.7107 Å and the structure solved with SIR97.

2.2.7 Raman Spectroscopy

All of the Raman spectra presented in the thesis for compound **1** were collected at the Laboratoire de Chimie de Coordination in Toulouse, France, during the course of several placements in the Switchable Molecular Materials Group. The spectra were collected using a Labram HR microspectrometer. The excitation source was either an HeNe laser (632.8 nm, 15 mW) or an Ar^+ laser (532 nm, 50 mW), as specified in the text. The sample was located using a 10× long-working-distance objective, and the spectra acquired through a 50× long-working-distance objective. The spectra were recorded using an 1800 grooves mm^{-1} grating. The filters used are specified in the text, depending on the measurement.

For the variable temperature measurements, the sample was placed on a glass slide, and the slide was then put on top of a sample stage within a Linkam THMS600 liquid nitrogen cryostat. The cryostat was then closed, and the sample irradiated through the glass windows of the apparatus. The cooling rate employed was 5 $Kmin^{-1}$ to cool down to 170 K, and then 2 $Kmin^{-1}$ below that when outwith the hysteresis loop. Within the hysteresis loop, the heating and cooling rate was 1 $Kmin^{-1}$, and the cryostat was left for 2 minutes to stabilise the temperature before the measurements were performed. Although the HS→LS transition was always found to begin around 150 K, and the LS→HS transition began around 165 K, the exact width of the hysteresis loop was found to vary with the monocrystal.

In the case of the variable pressure measurements, a small screw-driven Diamond Anvil Cell (DAC) was used to generate pressure (at ambient temperature). The sample chamber was filled with a single crystal sample of **1**, together with some ruby chips needed for the calibration of the applied pressure, and Fluorinert (FC-77) oil, which serves as the

pressure transmitting medium. To increase the pressure, the screws are turned, and the applied pressure determined via the displacement of the ruby's fluorescence signal.[12] Due to a design flaw, the pressure could not be gradually released, and the return to atmospheric pressure was abrupt. The spectra for the sample were recorded using a 600 grooves mm^{-1} grating, and the ruby signal was recorded using an 1800 grooves mm^{-1} grating.

2.3 References

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