Co-crystallization as a modular approach to the discovery of novel spin-crossover materials.

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Contents

Instrumentation....2
Materials....2
Experimental....2
$[Fe(3\text{-bpp})_2][BF_4]_2$ (**1a**) (Solution synthesis)....2
Recrystallisation:....3
$[Fe(3\text{-bpp})_2][BF_4]_2$ (**1a**) (Mechanochemical synthesis – Neat Grinding)....4
$[Fe(3\text{-bpp})_2][PF_6]_2$ (**1b**)....5
$[Fe(3\text{-bpp})_2][BF_4]_2$·2(bpe) (**1a·bpe**)....5
$[Fe(3\text{-bpp})_2][BF_4]_2$·2(azp) (1) (**1a·azp(α)**)....7
$[Fe(3\text{-bpp})_2][BF_4]_2$·2(azp) (2) (**1a·azp(β)**)....8
$[Fe(3\text{-bpp})_2][BF_4]_2$·2(bipy) (**1a·bipy**)....9
$[Fe(3\text{-bpp})_2][BF_4]_2$·2(bpa) (**1a·bpa**)....12
$[Fe(3\text{-bpp})_2][PF_6]_2$·2(bpe) (**1b·bpe**)....13
$[Fe(3\text{-bpp})_2][PF_6]_2$·2(azp) (1) (**1b·azp(α)**)....15
Repeat experiment with seeding:....15
$[Fe(3\text{-bpp})_2][PF_6]_2$·2(azp) (2) (**1b·azp(β)**)....17
$[Fe(3\text{-bpp})_2][PF_6]_2$·2(bipy) (**1b·bipy**)....18
$[Fe(3\text{-bpp})_2][PF_6]_2$·2(bpa) (**1b·bpa**)....20
$[Fe(3\text{-bpp})_2][PF_6]_2$·2(dpds) (**1b·dpds**)....23
Crystallographic tables....24
1a·EtOH....24
1a·bpe....25
1a·azp(α)....26
1a·azp(β)....26

1a·bipy 27
1a.bpa 28
1b·bpe 29
1b·azp(α) 29
1b·azp(β) 30
1b·bipy 31
1b·bpa 32
1b·dpds 32
Distortion parameters 33
References 34

Instrumentation

Single crystal XRD data were collected on a Rigaku Oxford Diffraction SuperNova A S2 single crystal diffractometer using a Cu radiation source. Sample specific details can be found in the CIF files.

Using Olex2,[1] the structures were solved with either the ShelXS or ShelXT structure solution programs using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation.[2–4]

Powder XRD data were collected on a Rigaku Miniflex 600 using a Cu radiation source and measurements were performed at room temperature.

Magnetic susceptibility measurements were performed using a Quantum Design MPMS SQUID magnetometer. Temperature dependent measurements were made using a 1000 Oe magnetic field across the stated temperature ranges (in sweep mode), while ramping the temperature at the rates specified (vide infra).

Elemental analyses were conducted through the Elemental Analysis Service at London Metropolitan University using a ThermoFlash 2000 analyser.

Materials

3-bpp was synthesised according to a slightly modified literature procedure, where the product was recrystallised from ethyl acetate rather than chloroform.[5] The Fe^{II} salts, $NaPF_6$ and co-formers were commercially available and were used without further purification.

Experimental

$[Fe(3\text{-bpp})_2][BF_4]_2$ (1a) (Solution synthesis)

3-bpp (150 mg, 0.71 mmol, 2 eq) was added to ethanol (10 mL) and the solution was heated until all solid had dissolved. In a separate flask, $Fe(BF_4)_2{\cdot}6H_2O$ (120 mg, 0.355 mmol, 1 eq) was added to ethanol (10 mL) and heated until all solid had dissolved. The iron salt solution was added to the 3-bpp solution slowly over a few minutes whilst stirring and upon mixing the solutions, the colour changed from

colorless to red. The solvent was removed *in vacuo*, yielding the product as a red powder, **1a·EtOH***,* (208 mg, 90%), which was analyzed by PXRD.

Recrystallisation:

A small amount of **1a·EtOH** was dissolved in ethanol in a small vial. This vial was placed into a larger vial containing toluene and the larger vial was sealed to allow the solvents to slowly diffuse. Dark red crystals grew in 1-2 weeks which were analyzed by SCXRD, including variable temperature measurements.

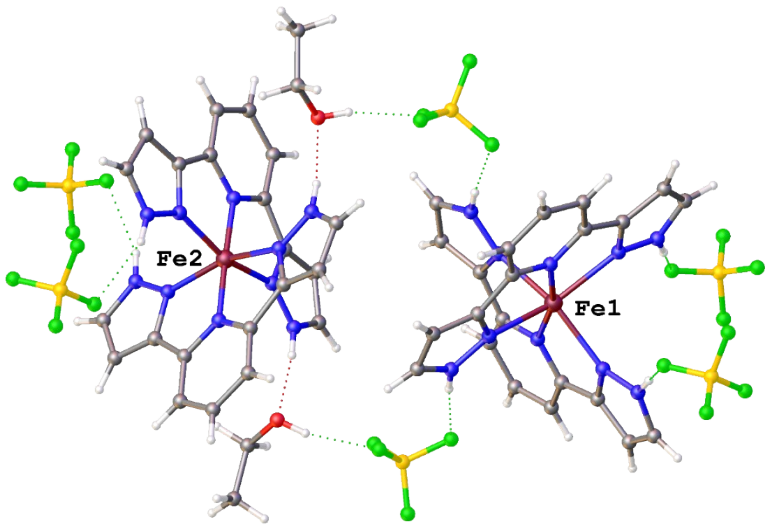

Figure S1 ***1a·EtOH*** *crystal structure which has been grown to show the hydrogen bonding of each N-H on the 3-bpp ligands.*

The crystal structure (Figure S1) contains two distinct Fe centers, where the complex containing Fe1 is hydrogen bonded only to BF_4 counter ions and the complex containing Fe2 is hydrogen bonded to both ethanol and BF_4. The average volume of the FeN_6 octahedra within the structure suggest that at 150 K, Fe1 is in the HS state (12.31239(9) $Å^3$) and Fe2 is in the LS state (9.54733(7) $Å^3$). Variable temperature SCXRD measurements were performed to determine if either of the Fe centers display SCO activity upon a change in temperature (Figure S2).

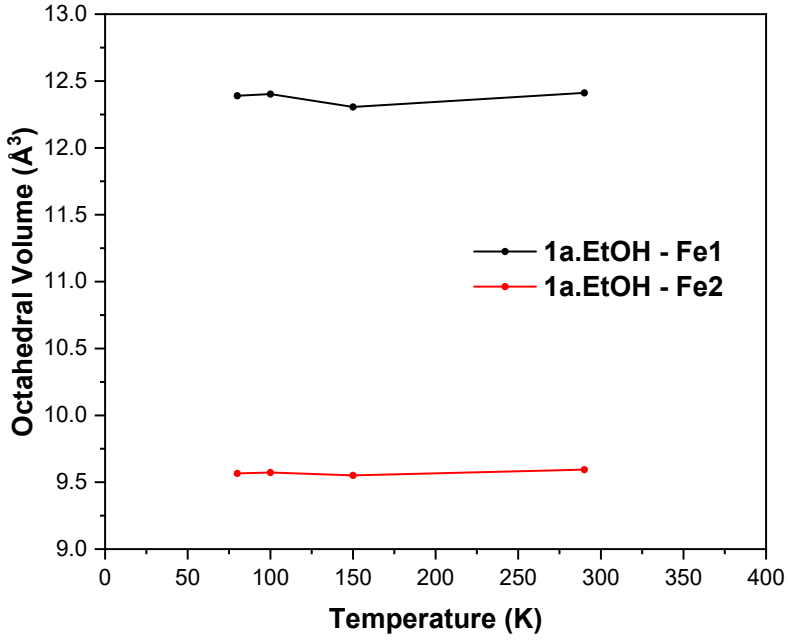

*Figure S2 Change in average octahedral volume of the Fe1 and Fe2 centers with temperature in the **1a·EtOH** crystal structure.*

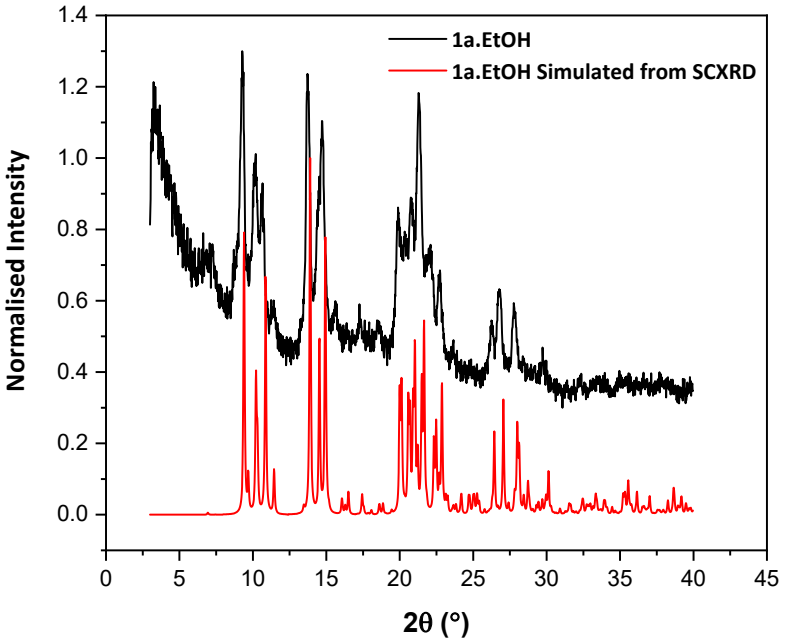

*Figure S3 Powder pattern comparison of the as-synthesised **1a·EtOH** (black) from solution synthesis with the pattern simulated (red) from the **1a·EtOH** crystal structure.*

From Figure S3, it can be seen that from the solution synthesis of $[Fe(3\text{-bpp})_2][BF_4]_2$, an ethanol solvate is formed.

$[Fe(3\text{-bpp})_2][BF_4]_2$ (1a) (Mechanochemical synthesis – Neat Grinding)

$Fe(BF_4)_2{\cdot}6H_2O$ (24 mg, 0.071 mmol, 1 eq) and 3-bpp (30 mg, 0.142 mmol, 2 eq) were ground together using a pestle & mortar (3 x 5 min) where the color changed from white to yellow-orange to orange-red as the reaction proceeded. The resulting product, $[Fe(3\text{-bpp})_2][BF_4]_2$, was collected and analyzed by PXRD. The powder pattern matched well with the pattern from a previous report of the anhydrous complex.[6]

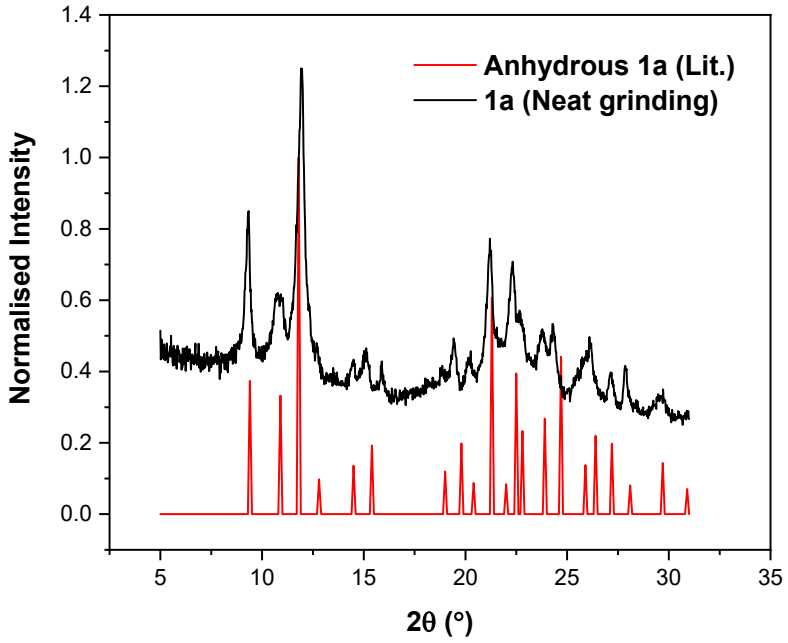

*Figure S4 Powder pattern comparison of the as-synthesised powder, **1a** (black), from mechanochemical synthesis, with the pattern reported in literature for the anhydrous **[Fe(3-bpp)$_2$][BF$_4$]$_2$** complex, **1a** (red).[6] The literature pattern was re-plotted using WebPlotDigitizer.[7]*

$[Fe(3\text{-bpp})_2][PF_6]_2$ (1b)

$FeCl_2.4H_2O$ (47 mg, 0.24 mmol) was dissolved in distilled water (15 mL) containing a very small amount of ascorbic acid. This was added to a warm solution of 3-bpp (100 mg, 0.47 mmol) in ethanol (15 mL) causing a colour change from colourless to red-orange. To this solution was added a solution of $NaPF_6$ (80 mg, 0.48 mmol) in distilled water (3 mL). The solution was gently heated (5 min) and the solvent was then removed *in vacuo*, resulting in a red solid, which was washed with distilled water and dried by vacuum filtration. The product, **1b**, was a red-orange powder (142 mg, 78%).

$[Fe(3\text{-bpp})_2][BF_4]_2{\cdot}2(bpe)$ (1a·bpe)

$[Fe(3\text{-bpp})_2][BF_4]_2$ (30 mg, 0.046 mmol, 1 eq) and 1,2-di(4-pyridyl)ethylene (bpe) (16.8 mg, 0.092 mmol, 2 eq) were dissolved in methanol (approx. 2mL). The solution was transferred to a vial by filtering through cotton wool and the vial was covered with parafilm. A small hole was pierced into the parafilm, and the solution was left to evaporate slowly to dryness, yielding the co-crystalline product, **1a·bpe**, as yellow/orange crystalline solid, which was analysed by SCXRD (Figure S5a), SQUID magnetometry (Figure S5b) and PXRD (Figure S6). Anal. Calcd. for $FeC_{46}H_{38}N_{14}B_2F_8$ (1016.27 g mol^{-1}): C 54.36 %, H 3.77 %, N 19.29 %. Found: C 52.96 %, H 3.40 %, N 18.29 %.

SQUID magnetometry details:

- The weight of the sample was 10.73 mg.

- 290 K to 20 K cooled at 2 K/min.
- 20 K to 290 K heated at 2 K/min.

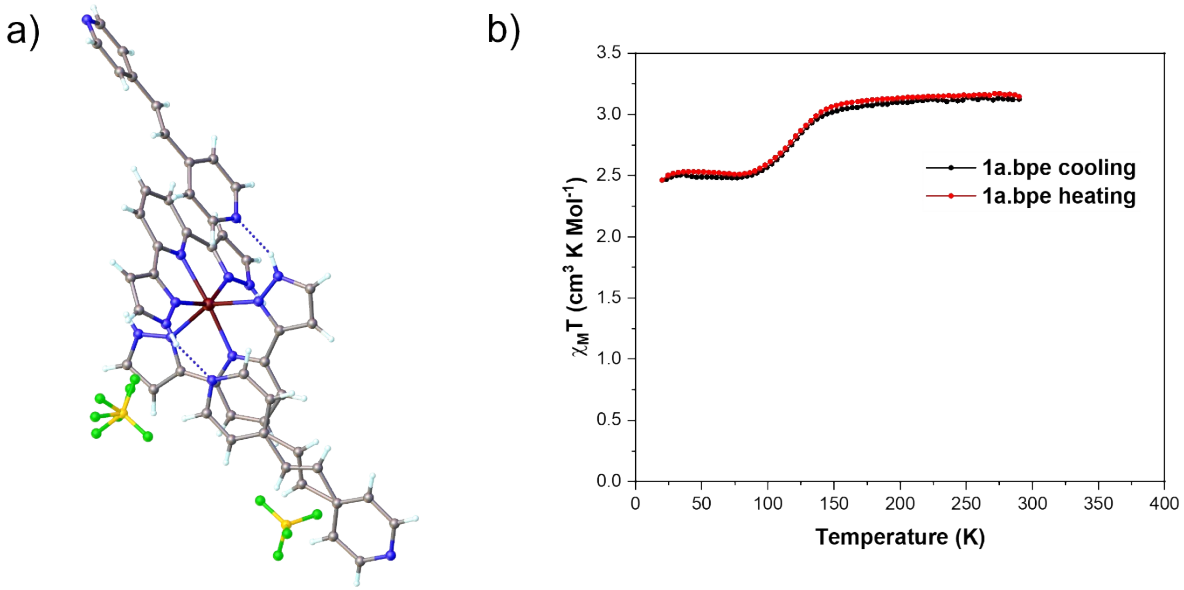

*Figure S5 a) Asymmetric unit of the $[Fe(3\text{-}bpp)_2][BF_4]_2 \cdot 2(bpe)$ crystal structure at room temperature, where thermal ellipsoids have not been shown for clarity. b) Magnetic susceptibility curves obtained from a sample of **1a·bpe**, measured using SQUID magnetometry, showing both the cooling (black) and heating (red) curves.*

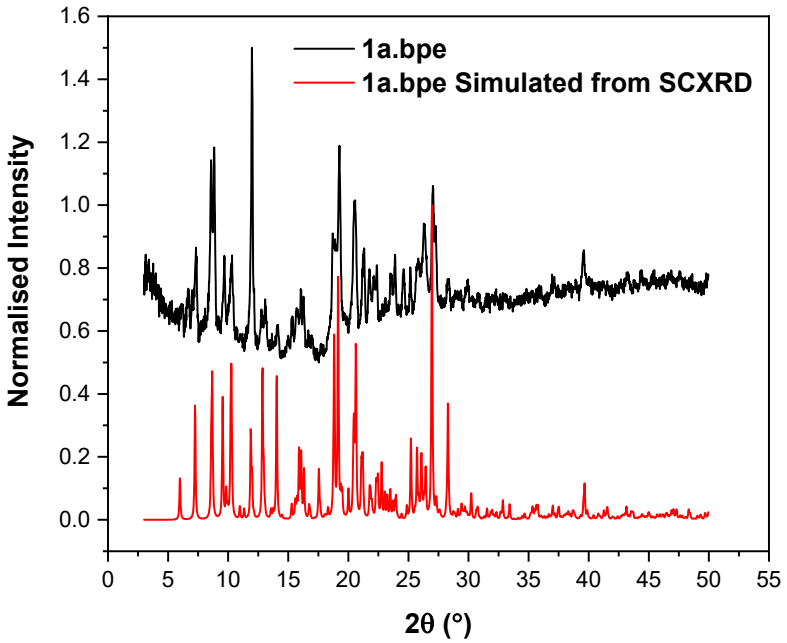

*Figure S6 Powder pattern comparison of the as-synthesised **1a·bpe** (black) with the pattern simulated (red) from the **1a·bpe** crystal structure.*

*Table S1 Unit cell parameters and average FeN_6 octahedral volume values as collected from VT-SCXRD measurements for **1a·bpe**.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å^3)
Room Temp	10.4294(5)	18.5284(11)	24.7378(8)	90	99.669(4)	90	12.470 (12)

150	10.238(2)	18.273(3)	24.895(4)	90	98.592(17)	90	11.49(3)

$[Fe(3\text{-}bpp)_2][BF_4]_2 \cdot 2(azp)$ (1) (1a·azp(α))

$[Fe(3\text{-}bpp)_2][BF_4]_2$ (30 mg, 0.046 mmol) and 4,4'-azopyridine (azp) (17 mg, 0.092 mmol) were dissolved in methanol (approx. 2 mL). The solution was filtered through cotton wool into a vial which was then covered on top with parafilm. A small hole was pierced into the parafilm, and the vial was left for the solution to evaporate slowly to dryness, yielding two types of crystals that could be distinguished by colour. The **1a·azp(α)** co-crystals were yellow and plate-like. It was extremely difficult to separate the polymorphs to obtain enough sample for SQUID or PXRD analysis, but VT-SCXRD analysis was performed (Figure S7). Anal. Calcd. for $FeC_{42}H_{34}N_{18}B_2F_8$ (1020.22 g mol^{-1}): C 49.44 %, H 3.36 %, N 24.71 %. Found: C 49.17 %, H 3.42 %, N 22.71 %.

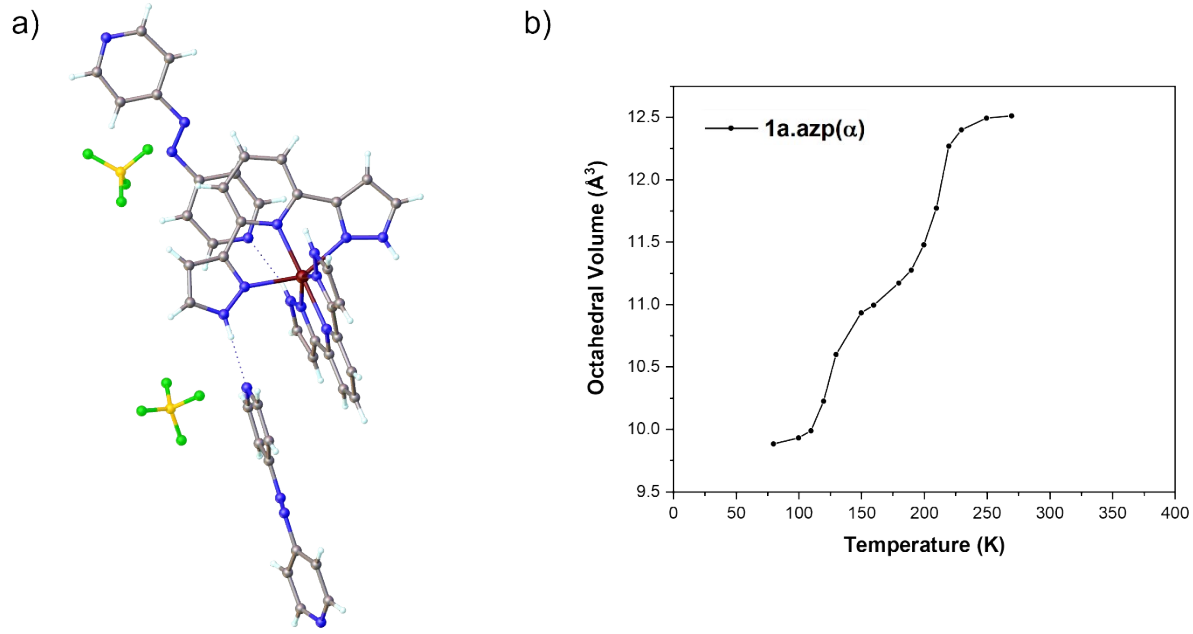

*Figure S7 a) Asymmetric unit of the **1a·azp(α)** co-crystal at 270 K, where thermal ellipsoids have not been shown for clarity. b) SCO cooling curve for the **1a·azp(α)** co-crystal, plotted by measuring the volume of the FeN_6 octahedron in the asymmetric unit upon decreasing temperature.*

*Table S2 Unit cell parameters and average FeN_6 octahedral volume values as collected from VT-SCXRD measurements for **1a·azp(α)**.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
80	9.7998(6)	10.0426(4)	22.5627(12)	92.809(4)	99.956(5)	94.715(4)	9.867(11)
100	9.8088(5)	10.0591(4)	22.5537(12)	92.699(4)	100.001(4)	94.636(4)	9.911(11)
110	9.8200(4)	10.0724(4)	22.5535(12)	92.684(4)	100.135(4)	94.567(3)	9.987(10)
130	9.8871(7)	10.2008(7)	22.487(2)	81.578(7)	79.712(7)	85.838(5)	10.58(2)
150	9.9194(5)	10.2308(4)	22.3927(14)	81.840(4)	79.947(5)	85.881(4)	10.924(10)
160	9.9373(5)	10.2410(4)	22.3677(14)	81.920(4)	80.061(5)	85.898(4)	10.988(10)
180	9.9713(4)	10.2652(4)	22.3055(11)	82.076(4)	80.118(4)	86.058(3)	11.169(10)
190	9.9891(3)	10.2817(3)	22.276(1)	82.142(3)	80.329(3)	86.138(3)	11.268(10)

200	10.0147(4)	10.3091(4)	22.2333(9)	82.156(3)	80.535(3)	86.265(3)	11.466(10)
210	10.0545(3)	10.3485(4)	22.1265(7)	82.255(3)	80.806(3)	86.482(3)	11.771(10)
220	10.1224(3)	10.4094(3)	21.9384(7)	82.302(3)	81.399(3)	86.857(3)	12.273(10)
230	10.1527(3)	10.4289(4)	21.8764(7)	82.311(3)	81.644(3)	87.037(3)	12.40(1)
250	10.1837(4)	10.4500(4)	21.8487(8)	82.380(3)	81.835(3)	87.233(3)	12.495(10)
270	10.2090(4)	10.4618(5)	21.8559(10)	82.284(4)	82.051(4)	87.374(3)	12.506(11)

$[Fe(3\text{-}bpp)_2][BF_4]_2 \cdot 2(azp)$ (2) (1a·azp(β))

$[Fe(3\text{-}bpp)_2][BF_4]_2$ (30 mg, 0.046 mmol) and 4,4'-azopyridine (azp) (17 mg, 0.092 mmol) were dissolved in methanol (approx. 2 mL). The solution was filtered through cotton wool into a vial which was then covered on top with parafilm. A small hole was pierced into the parafilm, and the vial was left for the solution to evaporate slowly to dryness, yielding two types of crystals that could be distinguished by colour. The **1a·azp(β)** co-crystals were orange in colour. The as-synthesised **1a·azp** co-crystals, which contain a mix of polymorphs, were found to mostly contain the **1a·azp(β)** polymorph through PXRD (Figure S8a). This was further evidenced through the good agreement between the magnetic data from SQUID measurements (Figure S8b) and the structural data from VT-SCXRD measurements (Figure S8c). Anal. Calcd. for $FeC_{42}H_{34}N_{18}B_2F_8$ (1020.22 g mol^{-1}): C 49.44 %, H 3.36 %, N 24.71 %. Found: C 49.17 %, H 3.42 %, N 22.71 %.

SQUID magnetometry details:

- The weight of the sample was 11.98 mg.
- 290 K to 5 K cooled at 1 K/min.
- 5 K to 290 K heated at 1 K/min.
- 290 K to 5 K cooled at 1 K/min.

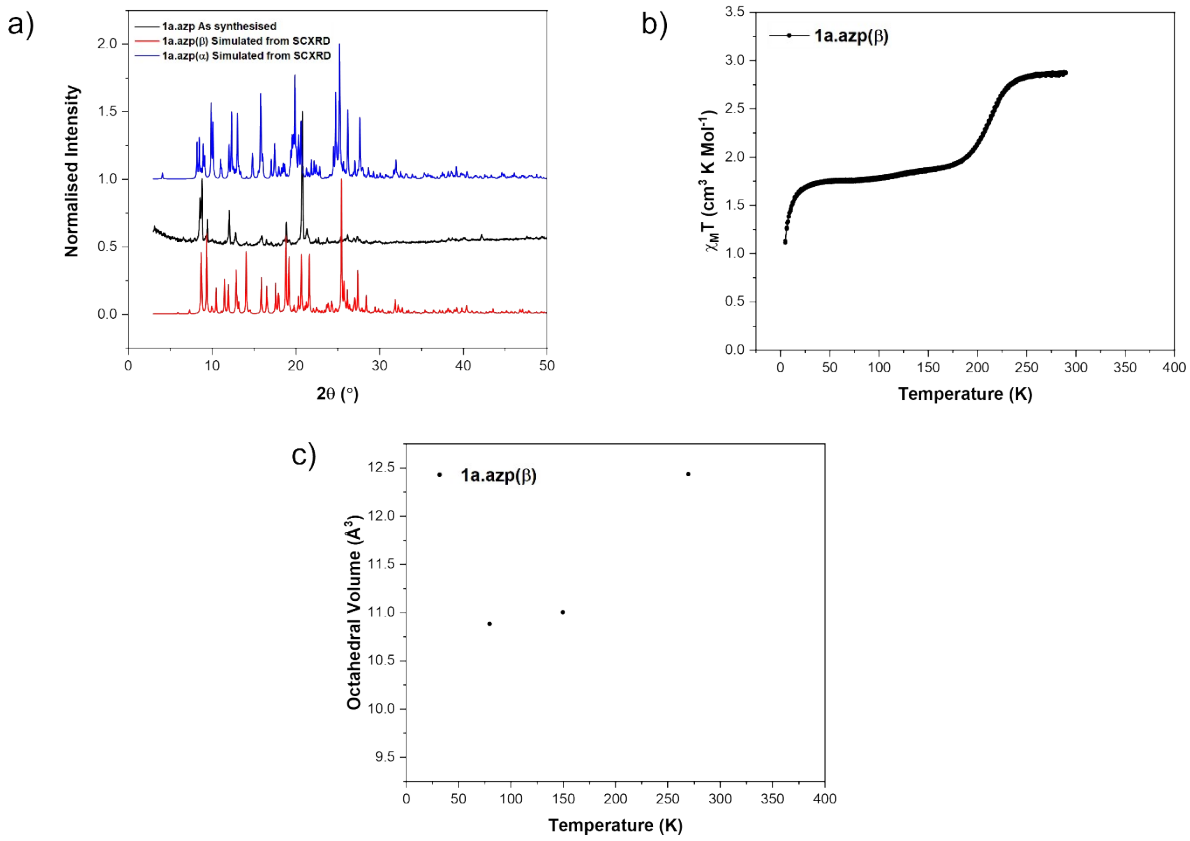

*Figure S8 a) PXRD pattern of the as-synthesised **1a·azp** co-crystals (mix of polymorphs), the simulated pattern from the **1a·azp(α)** SCXRD data, and the simulated pattern from the **1a·azp(β)** SCXRD data. The as-synthesised **1a·azp** co-crystals match best with the **1a·azp(β)** pattern. b) Magnetic susceptibility curve obtained from a sample of the as-synthesised **1a·azp** co-crystals, measured using SQUID magnetometry, where the heating and cooling curves have both been shown in black as they match very well. c) SCO curve obtained for the **1a·azp(β)** co-crystal, plotted by measuring the volume of the FeN_6 octahedron in the asymmetric unit upon decreasing temperature.*

*Table S3 Unit cell parameters and average FeN_6 octahedral volume values as collected from VT-SCXRD measurements for **1a·azp(β)**.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
80	9.9764(2)	18.0458(3)	24.6253(4)	90	97.592(2)	90	10.884(8)
150	10.0201(2)	18.1481(3)	24.6417(4)	90	97.959(2)	90	10.998(8)
270	10.1555(2)	18.7976(6)	24.3818(5)	90	99.376(2)	90	12.432(10)

$[Fe(3\text{-}bpp)_2][BF_4]_2 \cdot 2(bipy)$ (1a·bipy)

$[Fe(3\text{-}bpp)_2][BF_4]_2$ (30.3 mg, 0.046 mmol, 1 eq) and 4,4'-bipyridine (bipy) (14.4 mg, 0.092 mmol, 2 eq) were dissolved in methanol (approx. 2mL). The solution was transferred to a vial by filtering through cotton wool and the vial was covered with parafilm. A small hole was pierced into the parafilm, and the solution was left to evaporate slowly to dryness, yielding the co-crystalline product, **1a·bipy**, as a dark red crystalline solid, which was analysed by VT-SCXRD (Figure S9), SQUID magnetometry (Figure S10) and PXRD. PXRD analysis was carried out on the fresh sample (Figure S11) as well as the sample that had been used for magnetic measurements (Figure S12). Anal. Calcd. for $FeC_{42}H_{34}N_{14}B_2F_8$ (964.20 g mol^{-1}): C 52.31 %, H 3.55 %, N 20.34 %. Found: C 49.93 %, H 3.55 %, N 20.04 %.

SQUID magnetometry details:

- The weight of the sample was 17.15 mg.
- 290 K to 100 K cooled at 2 K/min.
- 100 K to 400 K heated at 2 K/min.
- 400 K to 100 K cooled at 2 K/min.
- 100 K to 400 K heated at 2 K/min.

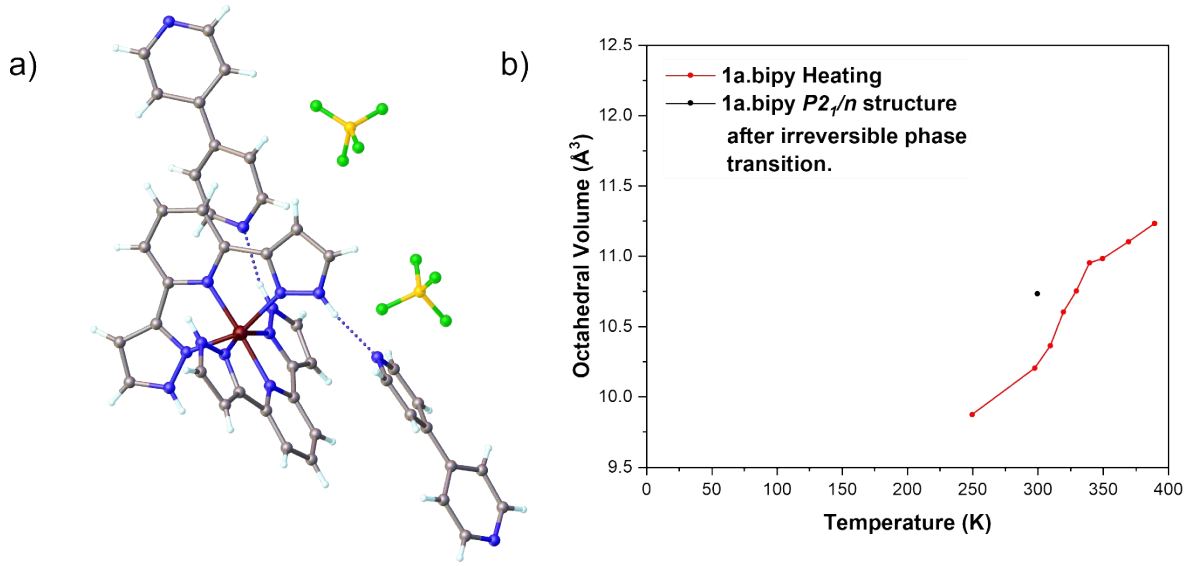

*Figure S9 a) Asymmetric unit of the $[Fe(3\text{-}bpp)_2][BF_4]_2 \cdot 2(bipy)$ crystal structure at 298 K, where thermal ellipsoids have not been shown for clarity. b) SCO curve obtained by measuring the average FeN_6 octahedral volume at different temperatures. The point shown in black is the average FeN_6 octahedral volume of the **1a·bipy** co-crystal after it has been cooled down from 400 K, showing the irreversible nature of the phase transition that occurs around 340 K.*

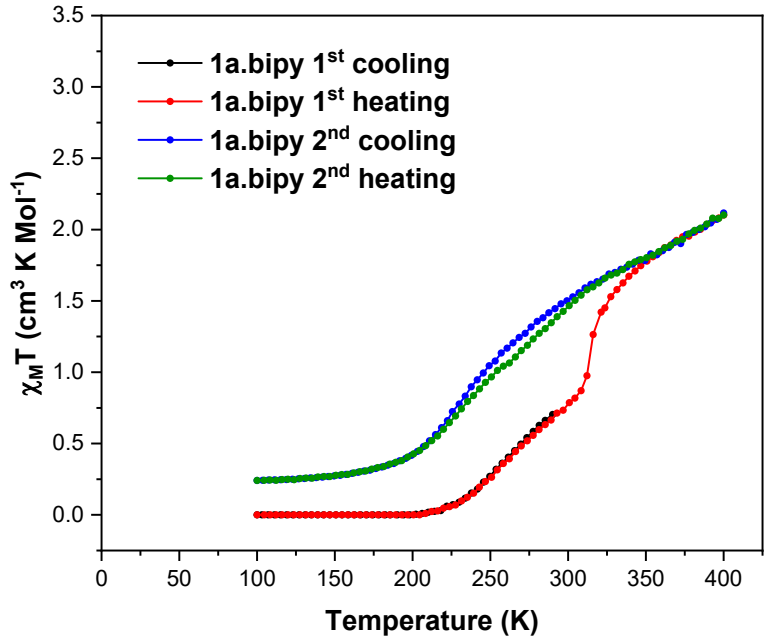

*Figure S10 Magnetic susceptibility curves obtained from a sample of **1a·bipy** measured using SQUID magnetometry, where the heating and cooling curves from the 2 cycles are shown by different colours.*

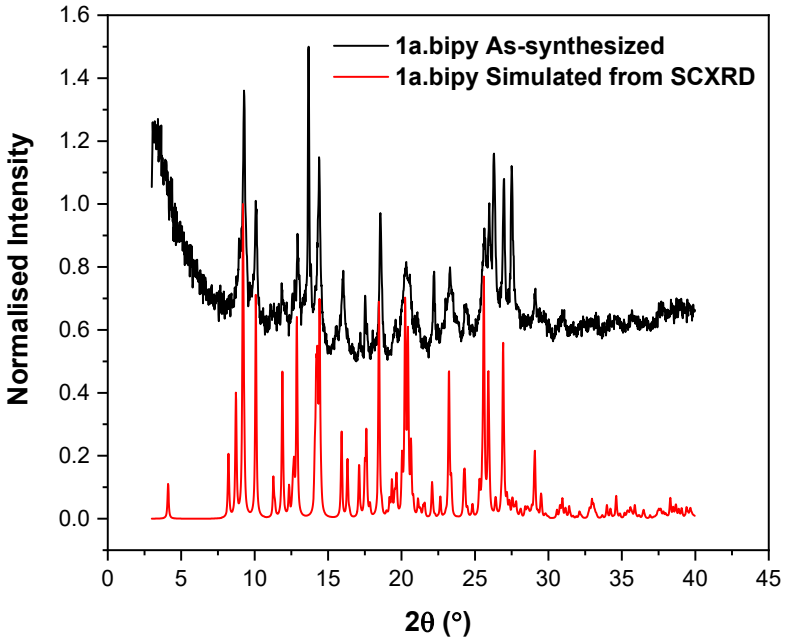

*Figure S11 Powder pattern comparison of the as-synthesised **1a·bipy** (black) with the pattern simulated (red) from the **1a·bipy** crystal structure at 298 K.*

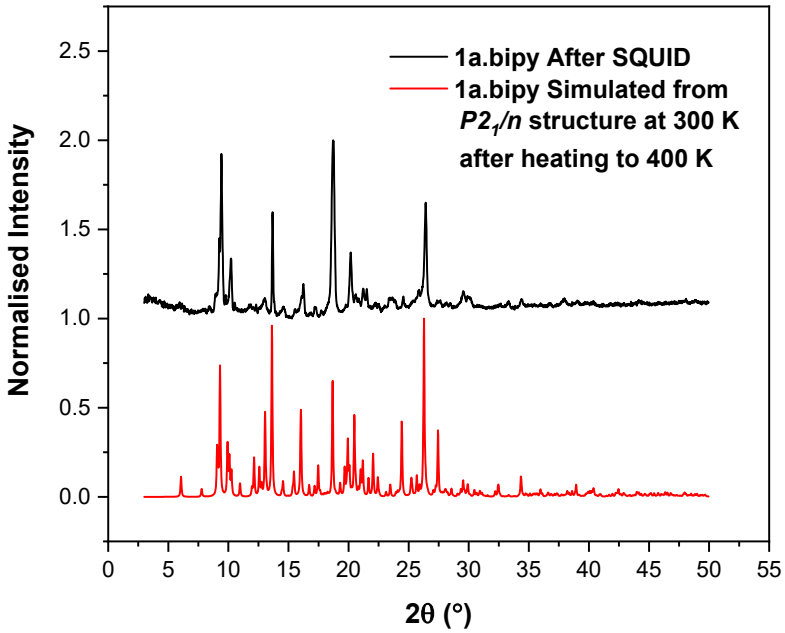

*Figure S12 Comparison of the PXRD pattern of **1a·bipy** after SQUID magnetometry and the pattern simulated from SCXRD data of the $P2_1/n$ phase obtained at 300 K after the crystal had been heated to 400 K. The patterns match well apart from intensities, which is due to the lack of grinding of the sample and shows that the crystallographic phase transition during the 1st heating cycle is irreversible.*

*Table S4 Unit cell parameters and average FeN_6 octahedral volumes as collected from VT-SCXRD measurements for **1a·bipy**.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
250	10.0861(3)	10.1542(3)	21.8490(6)	96.262(2)	96.200(2)	93.852(2)	9.873(9)
298	10.1441(4)	10.2185(4)	21.7492(5)	96.263(2)	95.635(3)	93.859(3)	10.202(10)
310	10.1645(5)	10.2047(4)	21.7294(6)	96.328(3)	95.314(3)	93.836(4)	10.358(11)
320	10.1951(3)	10.1790(4)	21.6800(5)	96.335(2)	95.000(2)	93.874(3)	10.595(9)
330	10.2254(4)	10.1492(6)	21.6116(6)	96.133(3)	94.628(3)	93.979(4)	10.75(1)
340	10.2756(6)	18.9626(12)	22.8808(10)	90	95.903(5)	90	10.949(17)
350	10.2889(5)	18.9461(11)	22.8834(9)	90	95.792(4)	90	10.982(16)
370	10.3119(5)	18.9471(11)	22.8937(9)	90	95.620(4)	90	11.101(15)
390	10.3414(5)	18.9725(12)	22.8949(10)	90	95.411(4)	90	11.225(15)

*Table S5 Unit cell parameters and average FeN_6 octahedral volume as collected by SCXRD at 300 K on a **1a·bipy** crystal which had been heated to 400 K and undergone an irreversible phase transition.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
300	10.2076(3)	18.9941(9)	22.8634(8)	90	96.403(3)	90	10.729(13)

$[Fe(3\text{-}bpp)_2][BF_4]_2 \cdot 2(bpa)$ (1a·bpa)

$[Fe(3\text{-}bpp)_2][BF_4]_2$ (20 mg, 0.031 mmol, 1 eq) and 1,2-bis(4-pyridyl)ethane (bpa) (11.30 mg, 0.061 mmol, 2 eq) were ground together in the presence of methanol (15 µL) using a pestle & mortar (3 min). Additional methanol (18 µL) was added, and liquid assisted grinding (LAG) was done (3 min). During the reaction, the powder changed from orange-red to a yellow-orange color and the product, **1a·bpa**, was analyzed by PXRD (Figure S13a) and SQUID magnetometry (Figure S13b). A small amount of solid was recrystallized from methanol, affording yellow crystals, which were analyzed by SCXRD (Figure S14). Anal. Calcd. for $FeC_{46}H_{42}N_{14}B_2F_8$ (1020.30 g mol^{-1}): C 54.14 %, H 4.15 %, N 19.22 %. Found: C 54.81 %, H 4.18 %, N 18.03 %.

SQUID magnetometry details:

- The sample weight was 9.90 mg.
- 290 K to 5 K cooled at 2 K/min.

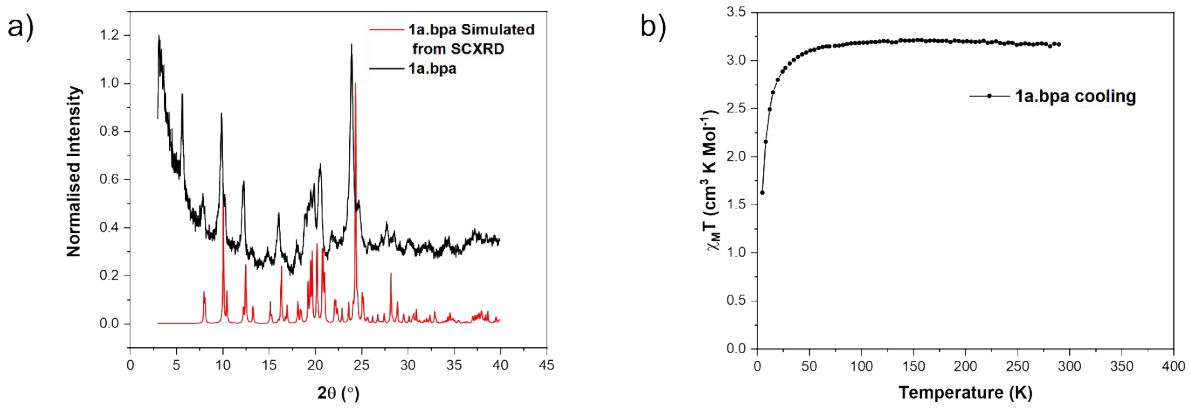

*Figure S13 a) Powder pattern comparison of the as-synthesised **1a·bpa** (black) from LAG (methanol) with the pattern simulated (red) from the **1a·bpa** crystal structure. b) Magnetic susceptibility curve obtained from a sample of **1a·bpa**, measured using SQUID magnetometry.*

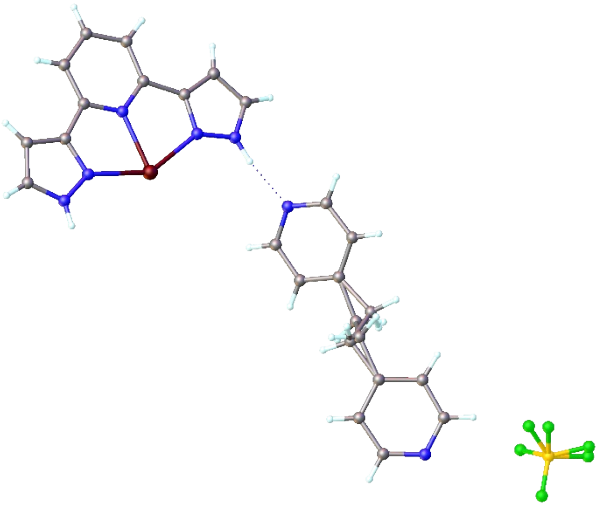

*Figure S14 Asymmetric unit of the **1a·bpa** co-crystal at 150 K, where thermal ellipsoids have not been shown for clarity.*

*Table S6 Unit cell parameters and average FeN_6 octahedral volume as collected from a SCXRD measurements of **1a·bpa** at 150 K.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
150	22.0537(2)	9.5781(1)	22.3969(3)	90	98.891(1)	90	13.061(6)

$[Fe(3\text{-}bpp)_2][PF_6]_2 \cdot 2(bpe)$ (1b·bpe)

$[Fe(3\text{-}bpp)_2][PF_6]_2$ (30.5 mg, 0.040 mmol) and 1,2-di(4-pyridyl)ethylene (bpe) (14.3 mg, 0.078 mmol) were dissolved in methanol (approx. 2mL). The solution was filtered through cotton wool into a vial which was then covered with parafilm. A small hole was pierced into the parafilm to allow the solution to evaporate slowly to dryness, yielding the product, **1b·bpe**, as small yellow crystals. These crystals were analysed using PXRD (Figure S15a), SQUID magnetometry (Figure S15b) and VT-SCXRD (Figure S15c). Anal. Calcd. for $FeC_{46}H_{38}N_{14}P_2F_{12}$ (1132.60 g mol^{-1}): C 48.78 %, H 3.38 %, N 17.31 %. Found: C 49.00 %, H 3.37 %, N 15.48 %.

SQUID magnetometry details:

- The weight of the sample was 10.69 mg.
- 290 K to 250 K cooled at 1 K/min.
- 250 K to 140 K cooled at 0.25 K/min.
- 140 K to 100 K cooled at 1 K/min.
- 100 K to 140 K heated at 1 K/min.
- 140 K to 270 K heated at 0.25 K/min.
- 270 K to 290 K heated at 1 K/min.

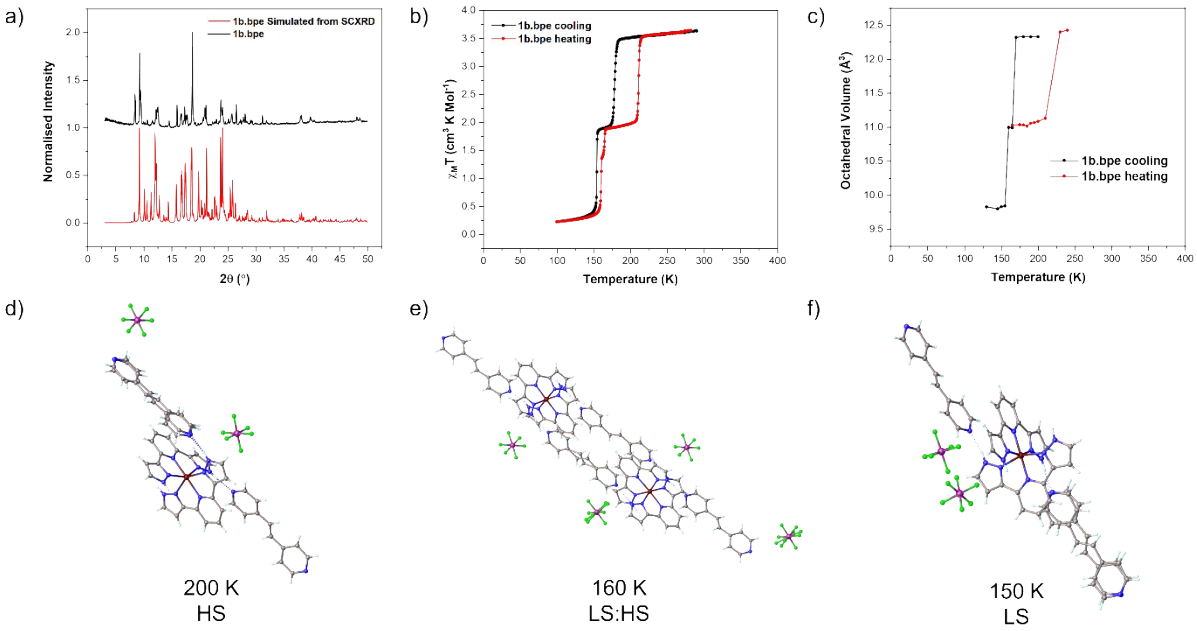

*Figure S15 a) Comparison of the PXRD pattern of the as-synthesised **1b·bpe** co-crystals with the pattern simulated from the **1b·bpe** SCXRD data. b) Magnetic susceptibility curves obtained from a sample of **1b·bpe**, measured using SQUID magnetometry, showing both the cooling (black) and heating (red) curves. c) SCO cooling and heating curves obtained for the **1b·bpe** co-crystal, plotted by measuring the volume of the FeN_6 octahedron in the asymmetric unit upon varying*

*temperature, where each point represents a full SCXRD measurement. d) Asymmetric unit of the **1b·bpe** co-crystal in the HS state at 200 K. e) Asymmetric unit of the **1b·bpe** co-crystal in the 50:50 LS:HS state at 160 K, where there is ordering of the LS and HS $[Fe(3\text{-}bpp)_2]^{2+}$ complexes within the 1D chains. f) Asymmetric unit of the **1b·bpe** co-crystal in the fully LS state at 150 K. Thermal ellipsoids have not been shown for clarity.*

*Table S7 Unit cell parameters and average FeN_6 octahedral volume values as collected from VT-SCXRD measurements for **1b·bpe** on cooling.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
200	10.2078(2)	11.4083(2)	21.4035(4)	97.221(2)	96.811(2)	93.568(2)	12.330(6)
190	10.2082(3)	11.4002(3)	21.3691(5)	97.097(2)	96.908(2)	93.566(2)	12.327(6)
180	10.2032(3)	11.3967(3)	21.3443(6)	96.999(2)	96.955(2)	93.544(2)	12.329(6)
170	10.2048(4)	11.3986(4)	21.3016(6)	96.914(3)	97.065(3)	93.509(3)	12.308(8)
165	9.8369(5)	22.4078(6)	22.3273(8)	79.398(3)	89.315(4)	89.203(3)	Fe1 = 9.776(10) Fe2 = 12.460(13) Avg = 11.12
160	9.8294(6)	22.3967(7)	22.3209(10)	79.439(3)	89.335(4)	89.190(4)	Fe1 = 9.773(11) Fe2 = 12.460(14) Avg = 11.12
155	9.8659(5)	10.9609(5)	22.6019(9)	100.457(4)	91.375(4)	93.322(4)	9.838(10)
150	9.8626(4)	10.9527(4)	22.6007(8)	100.390(3)	91.401(3)	93.390(3)	9.826(9)
145	9.8592(5)	10.9499(5)	22.6132(11)	100.426(4)	91.409(4)	93.448(4)	9.793(9)
130	9.8578(5)	10.9436(6)	22.5607(12)	100.287(4)	91.451(4)	93.522(4)	9.822(8)

*Table S8 Unit cell parameters and average FeN_6 octahedral volume values as collected from VT-SCXRD measurements for **1b·bpe** on heating.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
165	9.8556(7)	22.4124(9)	22.3512(10)	79.374(4)	89.415(5)	89.185(5)	Fe1 = 9.882(12) Fe2 = 12.415(15) Avg = 11.15
175	9.8628(6)	22.4227(12)	22.3337(11)	79.268(4)	89.418(4)	89.158(4)	Fe1 = 9.801(9) Fe2 = 12.460(11) Avg = 11.13
180	9.8708(6)	22.4260(12)	22.3674(12)	79.152(4)	89.413(4)	89.093(4)	Fe1 = 9.831(9) Fe2 = 12.455(12) Avg = 11.14
185	9.8690(5)	22.4100(8)	22.3765(10)	79.177(3)	89.421(4)	89.137(3)	Fe1 = 9.854(10) Fe2 = 12.393(13) Avg = 11.12
190	9.8766(6)	22.4211(8)	22.3907(11)	79.115(4)	89.420(4)	89.141(4)	Fe1 = 9.876(10) Fe2 = 12.411(13) Avg = 11.14
195	9.8792(6)	22.4178(13)	22.4028(13)	79.070(5)	89.458(5)	89.124(5)	Fe1 = 9.901(10) Fe2 = 12.426(12) Avg = 11.16

200	9.8898(5)	22.4177(7)	22.4003(9)	79.064(3)	89.471(4)	89.155(3)	Fe1 = 9.935(10) Fe2 = 12.382(12) Avg = 11.16
210	9.9079(6)	22.4260(12)	22.4143(11)	78.939(4)	89.501(4)	89.169(4)	Fe1 = 10.122(11) Fe2 = 12.245(13) Avg = 11.18
230	10.2167(10)	11.4170(8)	21.5491(13)	97.805(5)	96.452(7)	93.527(7)	12.396(12)
240	10.2181(11)	11.4218(9)	21.5858(14)	97.939(6)	96.353(7)	93.519(7)	12.424(13)

$[Fe(3\text{-}bpp)_2][PF_6]_2 \cdot 2(azp)$ (1) (1b·azp(α))

$[Fe(3\text{-}bpp)_2][PF_6]_2$ (30 mg, 0.039 mmol) and 4,4'-azopyridine (azp) (14.4 mg, 0.078 mmol) were dissolved in methanol (approx. 2mL). The solution was filtered through cotton wool into a vial which was then covered with parafilm. A small hole was pierced into the parafilm to allow the solution to evaporate slowly to dryness, yielding two polymorphic co-crystals; **1b·azp(α)** and **1b·azp(β)**.

Repeat experiment with seeding:

The co-crystallisation was repeated, where $[Fe(3\text{-}bpp)_2][PF_6]_2$ (30.5 mg, 0.040 mmol) and 4,4'-azopyridine (azp) (14.6 mg, 0.079 mmol) were dissolved in methanol (approx. 2mL). The solution was filtered through cotton wool into a vial and a **1b·azp(α)** seed crystal was dropped in. The vial was then covered with parafilm, and a small hole was pierced into it to allow the solution to evaporate slowly to dryness. Upon investigation of the crystals under the microscope, the **1b·azp(α)** polymorph was the dominant polymorph present and so these crystals were analysed by PXRD (Figure S16), SQUID magnetometry (Figure S17a) and VT-SCXRD (Figure S17b). Anal. Calcd. for $FeC_{42}H_{34}N_{18}P_2F_{12}$ (1136.55 g mol^{-1}): C 44.38 %, H 3.01 %, N 22.18 %. Found: C 43.41 %, H 2.90 %, N 19.43 %.

SQUID magnetometry details:

- The weight of the sample was 7.00 mg.
- 400 K to 195 K cooled at 1 K/min.
- 195 K to 400 K heated at 1 K/min.

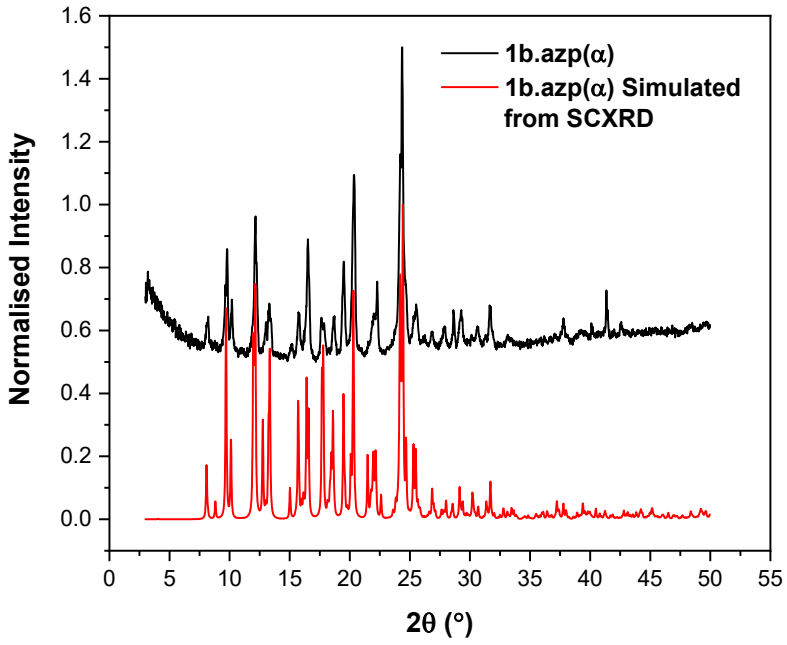

*Figure S16 Comparison of the PXRD pattern of the as-synthesised **1b·azp(α)** co-crystals from the seeded crystallisation, with the pattern simulated from the **1b·azp(α)** SCXRD data.*

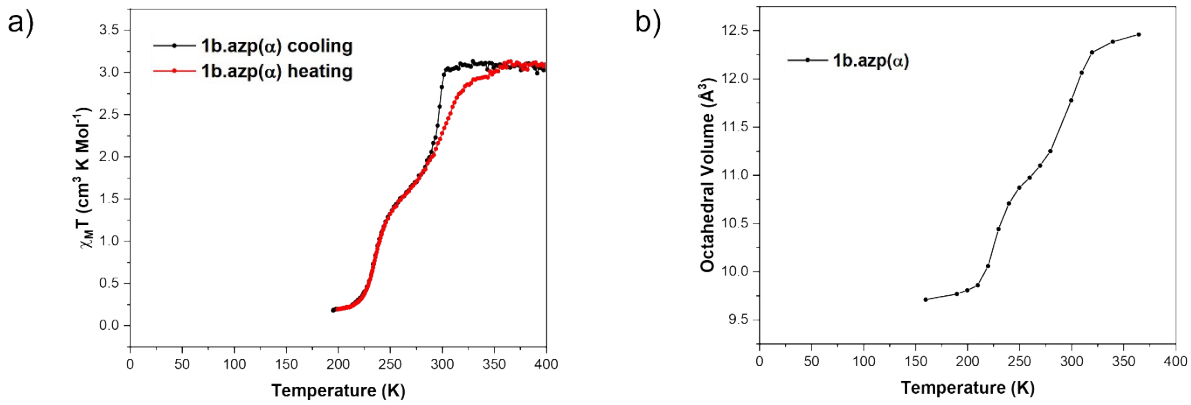

*Figure S17 a) Magnetic susceptibility curves obtained from a sample of **1b·azp(α)**, measured using SQUID magnetometry, showing the 1st heating (orange), 1st cooling (blue) and 2nd heating (red) curves. b) SCO curve obtained for the **1b·azp(α)** co-crystal, plotted by measuring the volume of the FeN_6 octahedron in the asymmetric unit upon varying temperature, where each point represents a full SCXRD measurement.*

*Table S9 Unit cell parameters and average FeN_6 octahedral volume values as collected from VT-SCXRD measurements for **1b·azp(α)**.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
160	9.8259(4)	10.8645(4)	22.6056(10)	101.980(3)	91.870(3)	91.858(3)	9.705(6)
190	9.8596(3)	10.8693(3)	22.6191(7)	102.011(2)	91.773(2)	91.794(2)	9.721(6)
205	9.8788(3)	10.8821(3)	22.6364(7)	102.093(3)	91.663(3)	91.701(2)	9.763(6)
220	9.9043(3)	10.9002(3)	22.6267(8)	102.194(3)	91.481(3)	91.565(2)	9.881(7)

235	9.9474(3)	10.9573(3)	22.5424(8)	102.490(3)	90.926(3)	91.146(3)	10.348(7)
250	9.9827(4)	11.0082(4)	22.5053(8)	102.782(3)	90.438(3)	90.847(3)	10.752(8)
265	9.9994(4)	11.0389(4)	22.5035(9)	102.939(3)	90.267(3)	90.662(3)	10.952(8)
280	10.0259(4)	11.0754(3)	22.4756(7)	103.162(3)	90.003(3)	90.504(3)	11.172(8)
300	10.0731(4)	11.1516(3)	22.4071(9)	103.519(3)	89.501(3)	89.995(3)	11.666(9)
320	10.1221(4)	11.2487(4)	22.3176(9)	103.908(3)	88.876(3)	89.376(3)	12.236(9)
340	10.1407(5)	11.2900(4)	22.3314(10)	104.116(3)	88.638(4)	89.213(3)	12.373(9)
365	10.1721(5)	11.3235(3)	22.3862(7)	104.374(3)	88.492(3)	88.975(3)	12.455(10)

$[Fe(3\text{-}bpp)_2][PF_6]_2 \cdot 2(azp)$ (2) (1b·azp(β))

$[Fe(3\text{-}bpp)_2][PF_6]_2$ (30 mg, 0.039 mmol) and 4,4'-azopyridine (azp) (14.4 mg, 0.078 mmol) were dissolved in methanol (approx. 2mL). The solution was filtered through cotton wool into a vial which was then covered with parafilm. A small hole was pierced into the parafilm to allow the solution to evaporate slowly to dryness, yielding two polymorphic co-crystals; **1b·azp(α)** and **1b·azp(β)**.

It was not possible to separate the polymorphs sufficiently to obtain enough **1b·azp(β)** crystals for PXRD and SQUID magnetometry analyses. Instead, the SCO behaviour of the **1b·azp(β)** polymorph was assessed using SCXRD (Figure S18). A measurement was carried out at 250 K where the material was found to be in the HS state though the large octahedral volume (12.5 $Å^3$). After cooling slowly to 100 K, a single crystal diffraction experiment was carried out and the material was still found to be in the HS state with a large octahedral volume (12.5 $Å^3$). Anal. Calcd. for $FeC_{42}H_{34}N_{18}P_2F_{12}$ (1136.55 g mol^{-1}): C 44.38 %, H 3.01 %, N 22.18 %. Found: C 43.41 %, H 2.90 %, N 19.43 %.

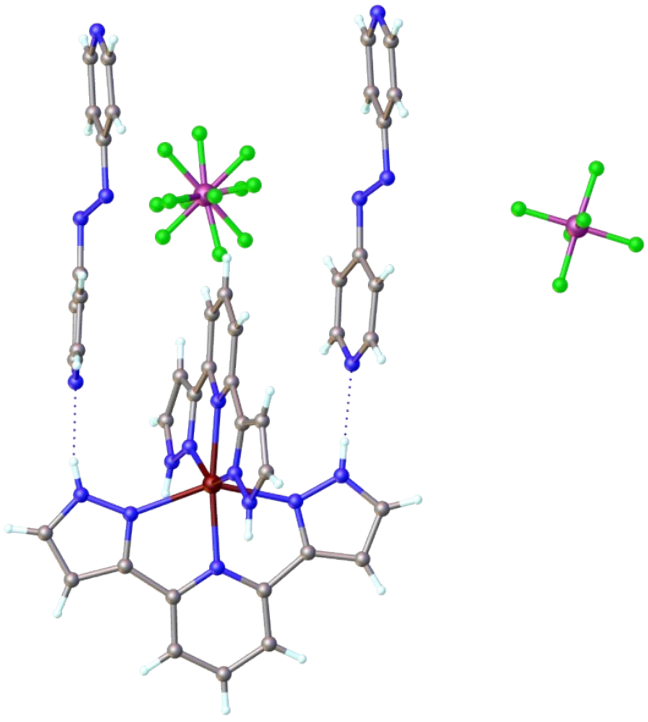

*Figure S18 Asymmetric unit of the **1b·azp(β)** co-crystal where thermal ellipsoids have not been shown for clarity.*

*Table S10 Unit cell parameters and average FeN_6 octahedral volume values as collected from VT-SCXRD measurements for **1b·azp(β)**.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
250	12.4569(2)	16.5431(3)	23.9335(4)	90	98.279(2)	90	12.518(9)
100	12.4566(3)	16.191(5)	23.7533(4)	90	98.4865(19)	90	12.451(16)

$[Fe(3\text{-}bpp)_2][PF_6]_2 \cdot 2(bipy)$ (1b·bipy)

$[Fe(3\text{-}bpp)_2][PF_6]_2$ (10 mg, 0.013 mmol) and 4,4'-bipyridine (bipy) (5 mg, 0.032 mmol) were dissolved in methanol (approx. 2mL). The solution was filtered through cotton wool into a vial which was then covered with parafilm. A small hole was pierced into the parafilm to allow the solution to evaporate slowly to dryness, yielding the product, **1b·bipy**, as small dark red crystals. These crystals were collected and analysed by PXRD (Figure S19), SCXRD (Figure S20a) and SQUID magnetometry (Figure S20b). VT-SCXRD measurements were carried out and the structure remained fully in the LS state up to 400 K and remained in the C2/m space group. Anal. Calcd. for $FeC_{42}H_{34}N_{14}P_2F_{12}$ (1080.53 g mol^{-1}): C 46.68 %, H 3.17 %, N 18.15 %. Found: C 43.22 %, H 2.43 %, N 15.62 %.

SQUID magnetometry details:

- The weight of the sample was 8.97 mg.
- 290 K to 5 K cooled at 2 K/min.
- 5 K to 400 K heated at 2 K/min.

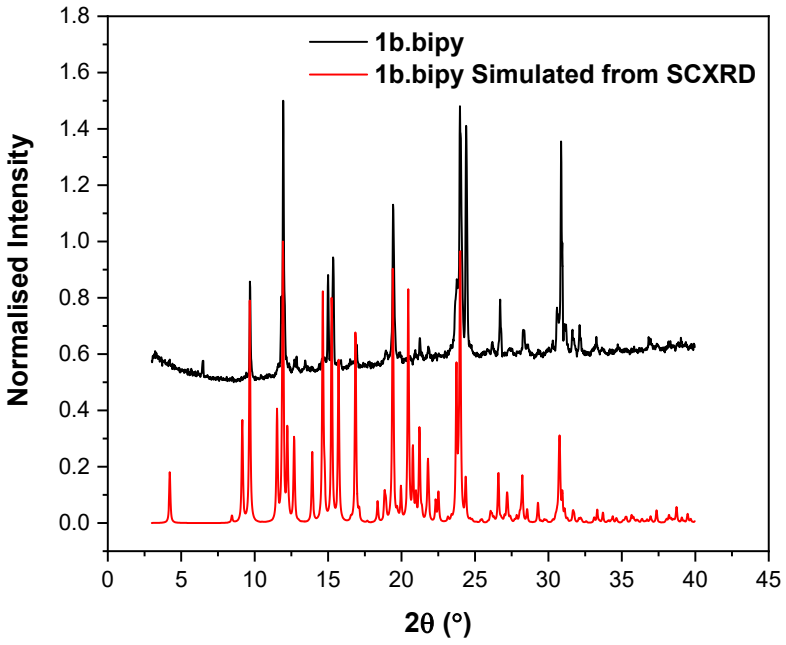

*Figure S19 Comparison of the PXRD pattern of the **1b·bipy** co-crystal sample after SQUID analysis, with the pattern simulated from the **1b·bipy** SCXRD data.*

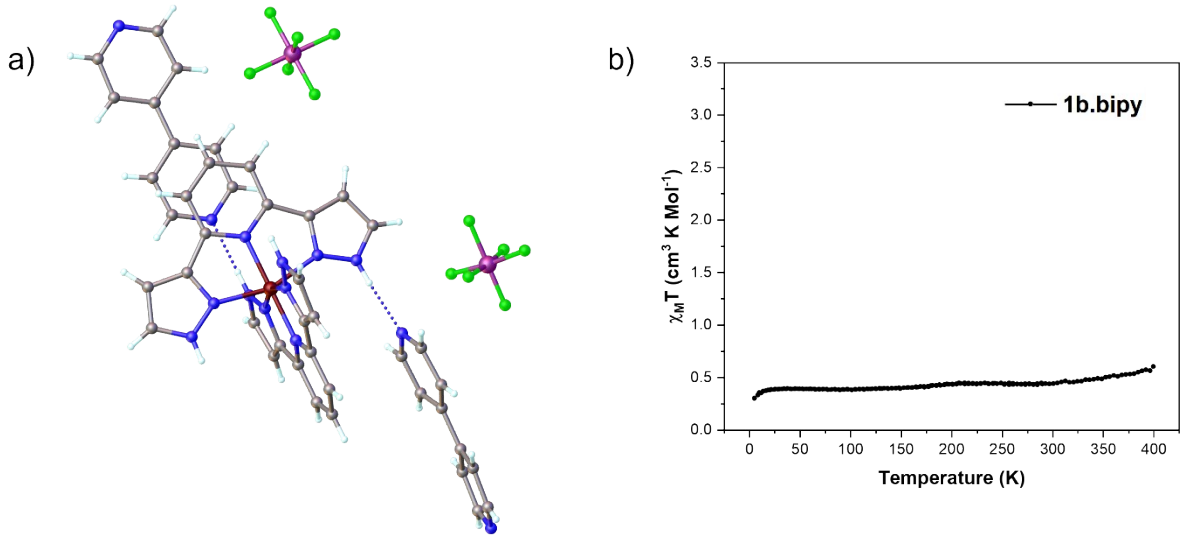

*Figure S20 a) Structure of the **1b·bipy** co-crystal, where thermal ellipsoids have not been shown for clarity. b) Magnetic susceptibility curve of the **1b·bipy** co-crystal, obtained using SQUID magnetometry, showing that the material remains in the LS state between 0 K and 400 K.*

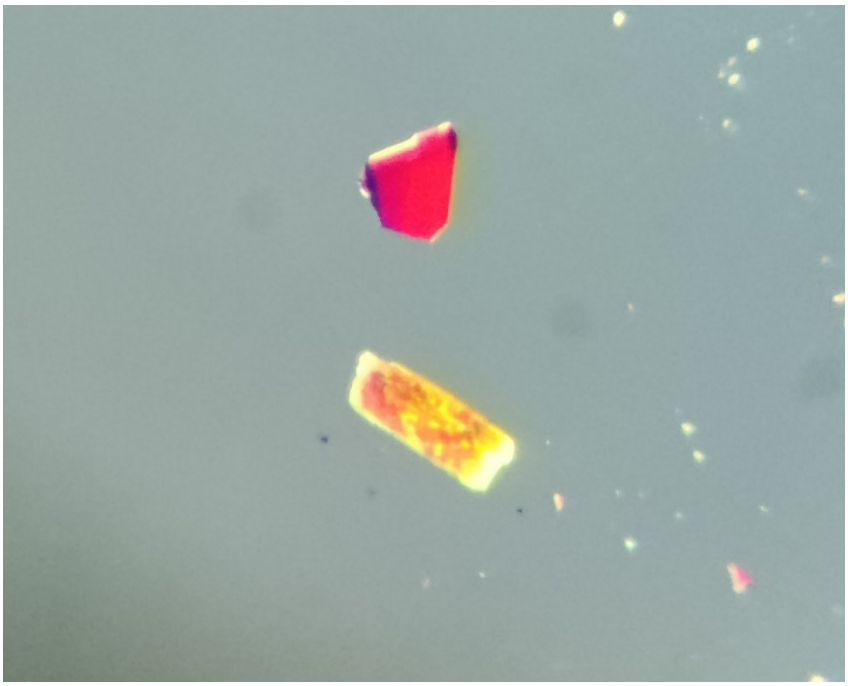

*Figure S21 Crystals of **1b.bipy**, where the top, red crystal had been kept at room temperature and the bottom, yellow crystal had been heated to 430 K and then cooled back down to room temperature.*

*Table S11 Unit cell parameters and average FeN_6 octahedral volume values as collected from VT-SCXRD measurements for **1b·bipy**.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
298	14.9529(3)	14.8247(3)	21.0093(3)	90	95.4899(17)	90	9.596(9)

320	14.9920(6)	14.8523(7)	20.9906(6)	90	95.382(3)	90	9.507(19)
340	15.0435(5)	14.8868(7)	20.9911(6)	90	95.295(3)	90	9.54(2)
360	15.0869(6)	14.9194(7)	20.9836(6)	90	95.183(3)	90	9.51(2)
380	15.1190(7)	14.9411(8)	20.9538(8)	90	95.062(4)	90	9.52(2)
400	15.1692(7)	14.9803(9)	20.9353(8)	90	94.939(4)	90	9.56(3)
411	15.191(3)	14.9759(13)	20.9141(16)	90	94.928(10)	90	9.55(4)

$[Fe(3\text{-}bpp)_2][PF_6]_2 \cdot 2(bpa)$ (1b·bpa)

$[Fe(3\text{-}bpp)_2][PF_6]_2$ (30 mg, 0.039 mmol) and 1,2-bis(4-pyridyl)ethane (bpa) (14.3 mg, 0.078 mmol) were dissolved in methanol (approx. 2mL). The solution was filtered through cotton wool into a vial which was then covered with parafilm. A small hole was pierced into the parafilm to allow the solution to evaporate slowly to dryness, yielding the product, **1b·bpa**, as small yellow crystals. These crystals were analysed by PXRD (Figure S22a), SQUID magnetometry (Figure S22b) and VT-SCXRD (Figure S22c). Anal. Calcd. for $FeC_{46}H_{42}N_{14}P_2F_{12}$ (1136.63 g mol^{-1}): C 48.60 %, H 3.72 %, N 17.25 %. Found: C 49.21 %, H 2.66 %, N 17.35 %.

SQUID magnetometry details:

- The weight of the sample was 11.82 mg.
- 290 K to 200 K cooled at 2 K/min.
- 200 K to 100 K cooled at 0.25 K/min.
- 100 K to 20 K cooled at 2 K/min.
- 20 K to 120 K heated at 2 K/min.
- 120 K to 220 K heated at 0.25 K/min.
- 220 K to 275 K heated at 2 K/min.

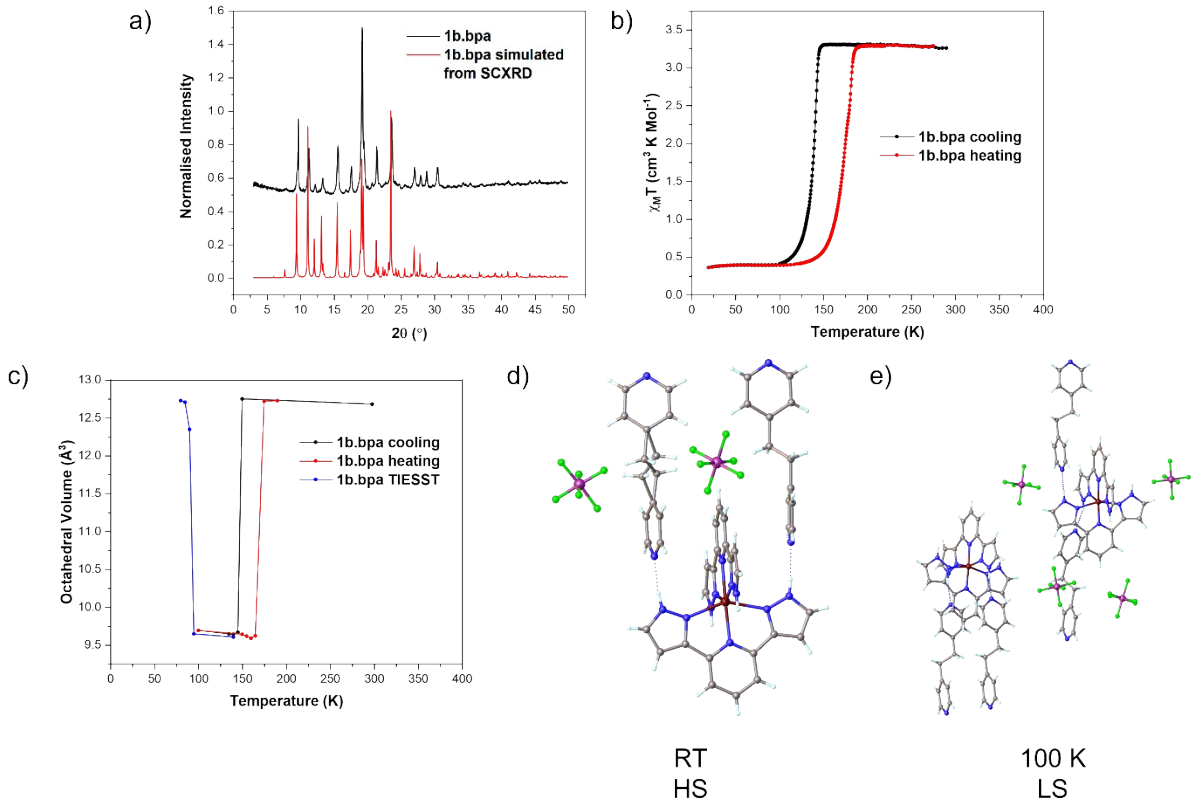

*Figure S22 a) Comparison of the PXRD pattern of the as-synthesised **1b·bpa** co-crystals with the pattern simulated from the **1b·bpa** SCXRD data. b) Magnetic susceptibility curves of the as-synthesised **1b·bpa** co-crystals, obtained using SQUID magnetometry, where both the cooling (black) and heating (red) curves are shown. c) SCO cooling (black) and heating (red) curves for the **1b·bpa** co-crystal, along with the TIESST curve (blue), obtained by performing VT-SCXRD measurements and plotting the average FeN_6 octahedral volume at each temperature. d) Asymmetric unit of the **1b·bpa** co-crystal, measured at room temperature where the material is in the fully HS state. e) Asymmetric unit of the **1b·bpa** co-crystal, measured at 100 K where the material is in the fully LS state and the structure is Z' = 2.*

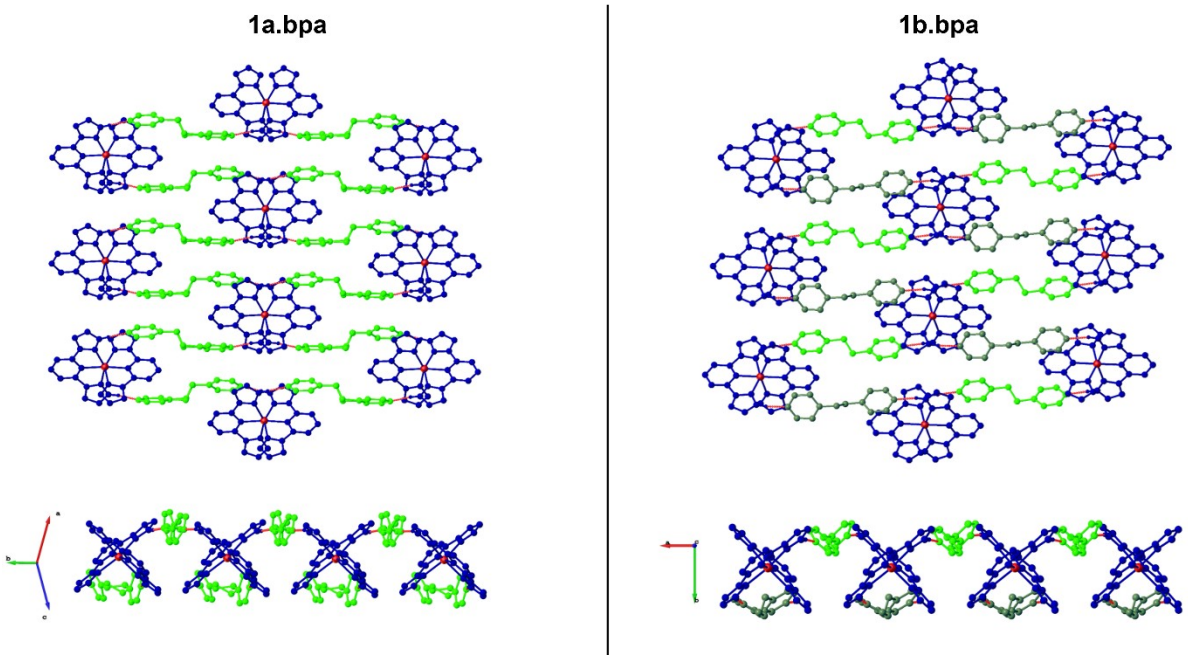

*Figure S23 Structures showing the differences between the 2D supramolecular sheets in the **1a·bpa** co-crystal and the **1b·bpa** co-crystal from the perspective of looking onto the sheets (top) and down the sheets (bottom). Different shades of green were used for the co-formers in the **1b·bpa** structure to represent that the bpa co-formers are crystallographically distinct.*

*Table S12 Unit cell parameters and average FeN_6 octahedral volume values as collected from VT-SCXRD measurements for **1b·bpa** on cooling.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
Room Temperature	9.5962(2)	18.5839(4)	15.0131(2)	90	102.499(2)	90	12.703(18)
150	9.5209(1)	18.0371(2)	14.9810(2)	90	101.851(1)	90	12.748(11)
145	9.0628(3)	30.8027(8)	18.3171(6)	90	102.671(3)	90	Fe1 = 9.65(2) Fe2 = 9.68(2) Avg = 9.67
140	9.0578(3)	30.7994(8)	18.3149(7)	90	102.662(4)	90	Fe1 = 9.64(2) Fe2 = 9.63(2) Avg = 9.64
135	9.0523(3)	30.8080(9)	18.3037(9)	90	102.668(4)	90	Fe1 = 9.69(2) Fe2 = 9.59(2) Avg = 9.64
100	9.0158(3)	30.8171(9)	18.2814(7)	90	102.704(4)	90	Fe1 = 9.71(2) Fe2 = 9.67(3) Avg = 9.69

*Table S13 Unit cell parameters and average FeN_6 octahedral volume values as collected from VT-SCXRD measurements for **1b·bpa** on heating.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
155	9.0799(4)	30.7779(9)	18.3263(9)	90	102.704(5)	90	Fe1 = 9.64(2) Fe2 = 9.58 (2) Avg = 9.61
160	9.0847(4)	30.7926(11)	18.3338(11)	90	102.641(5)	90	Fe1 = 9.60(2) Fe2 = 9.57(2) Avg = 9.59
165	9.0956(4)	30.7943(10)	18.3364(9)	90	102.688(5)	90	Fe1 = 9.63(2) Fe2 = 9.60(2) Avg = 9.62
175	9.5480(2)	18.1019(4)	14.9987(2)	90	102.054(2)	90	12.718(12)
190	9.55236(16)	18.1504(3)	15.00388(19)	90	102.1107(14)	90	12.723(13)

*Table S14 Unit cell parameters and average FeN_6 octahedral volume values as collected from VT-SCXRD measurements for **1b·bpa** after thermal trapping (TIESST) at 80 K.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
80	9.45496(9)	17.98580(15)	14.95322(14)	90	101.5451(9)	90	12.728(10)
85	9.4661(2)	17.9850(3)	14.9587(3)	90	101.616(2)	90	12.706(17)
90	9.4764(7)	17.9735(8)	14.9664(7)	90	101.627(6)	90	12.35(6)
95	9.0149(5)	30.8160(11)	18.3004(8)	90	102.818(5)	90	Fe1 = 9.61(3) Fe2 = 9.67(3) Avg = 9.64
140	9.0643(7)	30.7963(13)	18.3265(10)	90	102.812(7)	90	Fe1 = 9.61(3) Fe2 = 9.60(3) Avg = 9.61

$[Fe(3\text{-}bpp)_2][PF_6]_2 \cdot 2(dpds)$ (1b·dpds)

$[Fe(3\text{-}bpp)_2][PF_6]_2$ (20 mg, 0.026 mmol) and 2,2'-dipyridyl disulfide (dpds) (12 mg, 0.054 mmol) were ground together in the presence of methanol (15 µL) using a pestle and mortar (3 min). More methanol (15 µL) was added, and grinding was continued (3 min). A sample of the powder was recrystallised from methanol, where the product was obtained as small yellow crystals. These crystals were analysed by SCXRD at 80 K and 250 K, where the structure was found to be in the HS state for both measurements. Anal. Calcd. for $FeC_{42}H_{34}N_{14}P_2F_{12}S_4$ (1208.77 g mol^{-1}): C 41.73 %, H 2.83 %, N 16.22 %. Found: C 43.61 %, H 3.75 %, N 14.33 %.

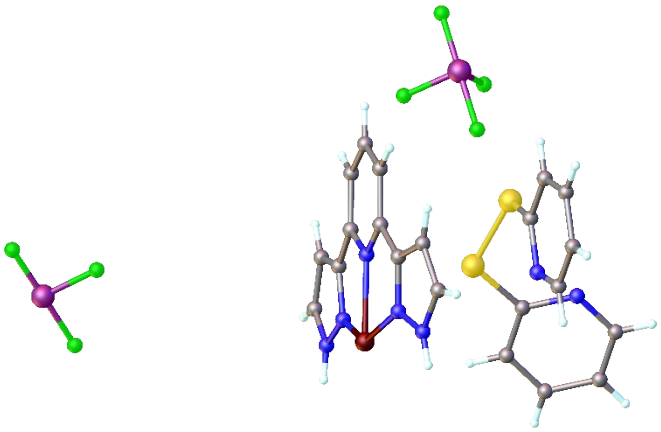

*Figure S24 Asymmetric unit of the **1b·dpds** co-crystal where thermal ellipsoids have not been shown for clarity.*

*Table S15 Unit cell parameters and average FeN_6 octahedral volume values as collected from VT-SCXRD measurements for **1b·dpds**.*

Temperature (K)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Octahedral Volume (Å³)
80	14.8052(7)	14.8052(7)	19.695(2)	90	90	120	12.48(5)
250	14.9913(8)	14.9913(8)	19.7406(16)	90	90	120	12.59(3)

Crystallographic tables

1a·EtOH

Identification code	**1a·EtOH**
Empirical formula	$C_{24}H_{24}B_2F_8FeN_{10}O$
Formula weight	698.00
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	20.4712(2)
b/Å	17.30860(10)
c/Å	18.6657(2)
α/°	90
β/°	113.2860(10)
γ/°	90
Volume/Å³	6075.04(10)
Z	8
ρ_{calc}g/cm³	1.526

μ/mm^{-1}	4.777
F(000)	2832.0
Crystal size/mm^3	0.261 × 0.153 × 0.146
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.942 to 143.94
Index ranges	-22 ≤ h ≤ 25, -14 ≤ k ≤ 21, -22 ≤ l ≤ 22
Reflections collected	17359
Independent reflections	5876 [R_{int} = 0.0188, R_{sigma} = 0.0188]
Data/restraints/parameters	5876/154/464
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0315, wR_2 = 0.0832
Final R indexes [all data]	R_1 = 0.0334, wR_2 = 0.0847
Largest diff. peak/hole / e Å^{-3}	0.48/-0.37

1a·bpe

Identification code	**1a·bpe**
Empirical formula	$C_{46}H_{38}B_2F_8FeN_{14}$
Formula weight	1016.37
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.4294(5)
b/Å	18.5284(11)
c/Å	24.7378(8)
α/°	90
β/°	99.669(4)
γ/°	90
Volume/Å^3	4712.4(4)
Z	4
ρ_{calc}g/cm^3	1.433
μ/mm^{-1}	3.281
F(000)	2080.0
Crystal size/mm^3	0.097 × 0.062 × 0.037
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.25 to 143.892
Index ranges	-12 ≤ h ≤ 12, -21 ≤ k ≤ 22, -25 ≤ l ≤ 30
Reflections collected	25171
Independent reflections	9068 [R_{int} = 0.0583, R_{sigma} = 0.0611]
Data/restraints/parameters	9068/112/657
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0614, wR_2 = 0.1417
Final R indexes [all data]	R_1 = 0.1088, wR_2 = 0.1710
Largest diff. peak/hole / e Å^{-3}	0.46/-0.33

1a·azp(α)

Identification code	**1a·azp(α)** 110 K	**1a·azp(α)** 160 K	**1a·azp(α)** 270 K
Empirical formula	$C_{42}H_{34}B_2N_{18}F_8Fe$	$C_{42}H_{34}B_2N_{18}F_8Fe$	$C_{42}H_{34}B_2F_8FeN_{18}$
Formula weight	1020.34	1020.34	1020.34
Temperature/K	110.00(10)	159.98(11)	270.00(17)
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	9.8200(4)	9.9373(5)	10.2090(4)
b/Å	10.0724(4)	10.2410(4)	10.4618(5)
c/Å	22.5535(12)	22.3677(14)	21.8559(10)
α/°	92.684(4)	81.920(4)	82.284(4)
β/°	100.135(4)	80.061(5)	82.051(4)
γ/°	94.567(3)	85.898(4)	87.374(3)
Volume/Å^3	2184.79(17)	2217.3(2)	2290.06(18)
Z	2	2	2
ρ_{calc}g/cm^3	1.551	1.528	1.480
μ/mm^{-1}	3.568	3.516	3.404
F(000)	1040.0	1040.0	1040.0
Crystal size/mm^3	0.319 × 0.181 × 0.051	0.324 × 0.18 × 0.038	0.322 × 0.191 × 0.037
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.98 to 143.932	8.096 to 143.916	8.238 to 144.372
Index ranges	-6 ≤ h ≤ 12, -12 ≤ k ≤ 12, -27 ≤ l ≤ 27	-12 ≤ h ≤ 6, -12 ≤ k ≤ 12, -27 ≤ l ≤ 27	-12 ≤ h ≤ 8, -12 ≤ k ≤ 12, -26 ≤ l ≤ 21
Reflections collected	15714	16372	16932
Independent reflections	8279 [R_{int} = 0.0379, R_{sigma} = 0.0535]	8454 [R_{int} = 0.0299, R_{sigma} = 0.0404]	8758 [R_{int} = 0.0291, R_{sigma} = 0.0384]
Data/restraints/parameters	8279/37/640	8454/166/640	8758/166/640
Goodness-of-fit on F^2	1.032	1.041	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0693, wR_2 = 0.1818	R_1 = 0.0676, wR_2 = 0.1844	R_1 = 0.0732, wR_2 = 0.2090
Final R indexes [all data]	R_1 = 0.0796, wR_2 = 0.1936	R_1 = 0.0791, wR_2 = 0.1968	R_1 = 0.0854, wR_2 = 0.2253
Largest diff. peak/hole / e Å^{-3}	1.58/-0.90	1.50/-0.66	1.11/-0.61

1a·azp(β)

Identification code	**1a·azp(β)** 80 K	**1a·azp(β)** 270 K
Empirical formula	$C_{42}H_{34}B_2N_{18}F_8Fe$	$C_{42}H_{34}B_2N_{18}F_8Fe$
Formula weight	1020.34	1020.34
Temperature/K	80.0(6)	269.98(12)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	9.9764(2)	10.1555(2)
b/Å	18.0458(3)	18.7976(6)
c/Å	24.6253(4)	24.3818(5)

α/°	90	90
β/°	97.592(2)	99.376(2)
γ/°	90	90
Volume/Å^3	4394.48(14)	4592.3(2)
Z	4	4
ρ_{calc}g/cm^3	1.542	1.476
μ/mm^{-1}	3.548	3.395
F(000)	2080.0	2080.0
Crystal size/mm^3	0.389 × 0.204 × 0.133	0.521 × 0.253 × 0.193
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.244 to 144.886	7.35 to 144.048
Index ranges	-8 ≤ h ≤ 12, -22 ≤ k ≤ 17, -28 ≤ l ≤ 30	-4 ≤ h ≤ 12, -23 ≤ k ≤ 21, -30 ≤ l ≤ 29
Reflections collected	18282	19401
Independent reflections	8412 [R_{int} = 0.0309, R_{sigma} = 0.0389]	8801 [R_{int} = 0.0291, R_{sigma} = 0.0355]
Data/restraints/parameters	8412/169/677	8801/8/714
Goodness-of-fit on F^2	1.023	1.018
Final R indexes [I>=2σ (I)]	R_1 = 0.0530, wR_2 = 0.1418	R_1 = 0.0602, wR_2 = 0.1683
Final R indexes [all data]	R_1 = 0.0623, wR_2 = 0.1501	R_1 = 0.0829, wR_2 = 0.1898
Largest diff. peak/hole / e Å^{-3}	1.82/-0.30	1.45/-0.26

1a·bipy

Identification code	**1a·bipy** 250 K	**1a·bipy** 330 K	**1a·bipy** 350 K	**1a·bipy** 300 K After heating to 400 K.
Empirical formula	$C_{42}H_{34}B_2N_{14}F_8Fe$	$C_{42}H_{34}B_2F_8FeN_{14}$	$C_{42}H_{34}B_2F_8FeN_{14}$	$C_{42}H_{34}B_2F_8FeN_{14}$
Formula weight	964.30	964.30	964.30	964.30
Temperature/K	249.99(15)	330.00(15)	349.98(18)	300.0(2)
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	P-1	P-1	$P2_1/n$	$P2_1/n$
a/Å	10.0861(3)	10.2254(4)	10.2889(5)	10.2076(3)
b/Å	10.1542(3)	10.1492(6)	18.9461(11)	18.9941(9)
c/Å	21.8490(6)	21.6116(6)	22.8834(9)	22.8634(8)
α/°	96.262(2)	96.133(3)	90	90
β/°	96.200(2)	94.628(3)	95.792(4)	96.403(3)
γ/°	93.852(2)	93.979(4)	90	90
Volume/Å^3	2204.26(11)	2215.84(16)	4438.0(4)	4405.2(3)
Z	2	2	4	4
ρ_{calc}g/cm^3	1.453	1.445	1.443	1.454
μ/mm^{-1}	3.474	3.456	3.451	3.477
F(000)	984.0	984.0	1968.0	1968.0
Crystal size/mm^3	0.369 × 0.127 × 0.095	0.366 × 0.348 × 0.246	0.378 × 0.315 × 0.259	0.375 × 0.205 × 0.143
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data	8.198 to 143.976	8.262 to 144.124	7.766 to 144.214	7.782 to 143.946

collection/°				
Index ranges	-12 ≤ h ≤ 7, -12 ≤ k ≤ 12, -25 ≤ l ≤ 26	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -22 ≤ l ≤ 26	-12 ≤ h ≤ 12, -23 ≤ k ≤ 21, -27 ≤ l ≤ 24	-10 ≤ h ≤ 12, -23 ≤ k ≤ 22, -28 ≤ l ≤ 22
Reflections collected	20325	16626	32038	25065
Independent reflections	8465 [R_{int} = 0.0219, R_{sigma} = 0.0267]	8476 [R_{int} = 0.0398, R_{sigma} = 0.0457]	8629 [R_{int} = 0.0645, R_{sigma} = 0.0460]	8525 [R_{int} = 0.0476, R_{sigma} = 0.0408]
Data/restraints/parameters	8465/0/604	8476/0/604	8629/0/604	8525/0/604
Goodness-of-fit on F^2	1.077	1.056	1.204	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0717, wR_2 = 0.2196	R_1 = 0.0719, wR_2 = 0.2011	R_1 = 0.1138, wR_2 = 0.3034	R_1 = 0.0982, wR_2 = 0.2572
Final R indexes [all data]	R_1 = 0.0739, wR_2 = 0.2237	R_1 = 0.0819, wR_2 = 0.2128	R_1 = 0.1379, wR_2 = 0.3377	R_1 = 0.1197, wR_2 = 0.2914
Largest diff. peak/hole / e $Å^{-3}$	3.40/-0.95	0.91/-0.45	2.73/-0.35	2.81/-0.38

1a.bpa

Identification code	**1a·bpa**
Empirical formula	$C_{46}H_{42}B_2F_8FeN_{14}$
Formula weight	1020.40
Temperature/K	149(1)
Crystal system	monoclinic
Space group	I2/a
a/Å	22.0537(2)
b/Å	9.57810(10)
c/Å	22.3969(3)
α/°	90
β/°	98.8910(10)
γ/°	90
Volume/$Å^3$	4674.11(9)
Z	4
ρ_{calc}g/cm^3	1.450
μ/mm^{-1}	3.308
F(000)	2096.0
Crystal size/mm^3	0.21 × 0.093 × 0.065
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.992 to 146.288
Index ranges	-27 ≤ h ≤ 24, -11 ≤ k ≤ 11, -24 ≤ l ≤ 27
Reflections collected	25568
Independent reflections	4647 [R_{int} = 0.0325, R_{sigma} = 0.0192]
Data/restraints/parameters	4647/200/363
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0349, wR_2 = 0.0900

Final R indexes [all data]	R_1 = 0.0360, wR_2 = 0.0908
Largest diff. peak/hole / e Å^{-3}	0.32/-0.39

1b·bpe

Identification code	**1b·bpe** 130 K	**1b·bpe** 160 K	**1b·bpe** 200 K
Empirical formula	$C_{46}H_{38}N_{14}F_{12}P_2Fe$	$C_{46}H_{38}N_{14}F_{12}P_2Fe$	$C_{46}H_{38}F_{12}FeN_{14}P_2$
Formula weight	1132.69	1132.69	1132.69
Temperature/K	130.00(10)	160.00(10)	200.00(10)
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	9.8578(5)	9.8294(6)	10.2078(2)
b/Å	10.9457(6)	22.3967(7)	11.4083(2)
c/Å	22.5606(12)	22.3209(10)	21.4035(4)
α/°	100.301(4)	79.439(3)	97.221(2)
β/°	91.468(4)	89.335(4)	96.811(2)
γ/°	93.516(4)	89.190(4)	93.568(2)
Volume/Å^3	2388.9(2)	4829.9(4)	2447.76(8)
Z	2	4	2
ρ_{calc}g/cm^3	1.575	1.558	1.537
μ/mm^{-1}	4.045	4.002	3.948
F(000)	1152.0	2304.0	1152.0
Crystal size/mm^3	0.276 × 0.255 × 0.221	0.275 × 0.203 × 0.199	0.288 × 0.184 × 0.178
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.972 to 144.104	8.032 to 144.136	7.836 to 144.062
Index ranges	-11 ≤ h ≤ 12, -12 ≤ k ≤ 13, -20 ≤ l ≤ 27	-12 ≤ h ≤ 11, -25 ≤ k ≤ 27, -27 ≤ l ≤ 25	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -25 ≤ l ≤ 19
Reflections collected	17689	35116	27568
Independent reflections	9136 [R_{int} = 0.0494, R_{sigma} = 0.0596]	18380 [R_{int} = 0.0567, R_{sigma} = 0.0774]	9383 [R_{int} = 0.0223, R_{sigma} = 0.0209]
Data/restraints/parameters	9136/66/641	18380/125/1432	9383/33/641
Goodness-of-fit on F^2	1.054	1.064	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0693, wR_2 = 0.1744	R_1 = 0.0740, wR_2 = 0.1818	R_1 = 0.0412, wR_2 = 0.1082
Final R indexes [all data]	R_1 = 0.0815, wR_2 = 0.1905	R_1 = 0.1111, wR_2 = 0.2099	R_1 = 0.0436, wR_2 = 0.1106
Largest diff. peak/hole / e Å^{-3}	1.44/-0.52	1.16/-0.43	0.79/-0.46

1b·azp(α)

Identification code	**1b·azp(α)** 160 K	**1b·azp(α)** 265 K	**1b·azp(α)** 365 K
Empirical formula	$C_{42}H_{34}N_{18}F_{12}P_2Fe$	$C_{42}H_{34}N_{18}F_{12}P_2Fe$	$C_{42}H_{34}N_{18}F_{12}P_2Fe$
Formula weight	1136.66	1136.66	1136.66
Temperature/K	159.99(11)	264.98(18)	365.0(3)

Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	9.8259(4)	9.9994(4)	10.1721(5)
b/Å	10.8645(4)	11.0389(4)	11.3235(3)
c/Å	22.6056(10)	22.5035(9)	22.3862(7)
α/°	101.980(3)	102.939(3)	104.374(3)
β/°	91.870(3)	90.267(3)	88.492(3)
γ/°	91.858(3)	90.662(3)	88.975(3)
Volume/Å^3	2357.51(16)	2420.69(17)	2496.15(16)
Z	2	2	2
ρ_{calc}g/cm^3	1.601	1.559	1.512
μ/mm^{-1}	4.127	4.019	3.898
F(000)	1152.0	1152.0	1152.0
Crystal size/mm^3	0.577 × 0.122 × 0.122	0.563 × 0.134 × 0.117	0.484 × 0.256 × 0.105
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.002 to 144	8.062 to 144	8.062 to 144.16
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 9, -26 ≤ l ≤ 27	-11 ≤ h ≤ 12, -13 ≤ k ≤ 12, -25 ≤ l ≤ 27	-12 ≤ h ≤ 12, -8 ≤ k ≤ 13, -27 ≤ l ≤ 27
Reflections collected	14001	14363	21239
Independent reflections	8804 [R_{int} = 0.0209, R_{sigma} = 0.0308]	9056 [R_{int} = 0.0220, R_{sigma} = 0.0322]	9565 [R_{int} = 0.0229, R_{sigma} = 0.0256]
Data/restraints/parameters	8804/87/657	9056/87/657	9565/219/712
Goodness-of-fit on F^2	1.037	1.039	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0458, wR_2 = 0.1185	R_1 = 0.0529, wR_2 = 0.1439	R_1 = 0.0554, wR_2 = 0.1615
Final R indexes [all data]	R_1 = 0.0487, wR_2 = 0.1215	R_1 = 0.0605, wR_2 = 0.1516	R_1 = 0.0713, wR_2 = 0.1778
Largest diff. peak/hole / e Å^{-3}	1.00/-0.81	0.58/-0.46	0.56/-0.30

1b·azp(β)

Identification code	**1b·azp(β)** 250 K
Empirical formula	$C_{42}H_{34}F_{12}FeN_{18}P_2$
Formula weight	1136.66
Temperature/K	249.99(11)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.4569(2)
b/Å	16.5431(3)
c/Å	23.9335(4)
α/°	90
β/°	98.279(2)
γ/°	90
Volume/Å^3	4880.71(15)
Z	4

ρ_{calc}g/cm^3	1.547
μ/mm^{-1}	3.987
F(000)	2304.0
Crystal size/mm^3	0.293 × 0.146 × 0.142
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.466 to 143.81
Index ranges	-14 ≤ h ≤ 15, -20 ≤ k ≤ 11, -29 ≤ l ≤ 28
Reflections collected	20354
Independent reflections	9365 [R_{int} = 0.0295, R_{sigma} = 0.0358]
Data/restraints/parameters	9365/163/731
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0564, wR_2 = 0.1539
Final R indexes [all data]	R_1 = 0.0688, wR_2 = 0.1654
Largest diff. peak/hole / e Å^{-3}	0.86/-0.58

1b·bipy

Identification code	**1b·bipy**
Empirical formula	$C_{42}H_{34}N_{14}F_{12}P_2Fe$
Formula weight	1080.62
Temperature/K	298.00(13)
Crystal system	monoclinic
Space group	C2/m
a/Å	14.9529(3)
b/Å	14.8247(3)
c/Å	21.0093(3)
α/°	90
β/°	95.4899(17)
γ/°	90
Volume/Å^3	4635.81(15)
Z	4
ρ_{calc}g/cm^3	1.548
μ/mm^{-1}	4.138
F(000)	2192.0
Crystal size/mm^3	0.321 × 0.256 × 0.134
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.418 to 144.086
Index ranges	-18 ≤ h ≤ 15, -17 ≤ k ≤ 18, -25 ≤ l ≤ 25
Reflections collected	17455
Independent reflections	4687 [R_{int} = 0.0287, R_{sigma} = 0.0224]
Data/restraints/parameters	4687/60/361
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0623, wR_2 = 0.1888
Final R indexes [all data]	R_1 = 0.0686, wR_2 = 0.1981
Largest diff. peak/hole / e Å^{-3}	1.04/-0.76

1b·bpa

Identification code	**1b·bpa** TIESST 80 K	**1b·bpa** 135 K	**1b·bpa** 190 K
Empirical formula	$C_{46}H_{42}F_{12}FeN_{14}P_2$	$C_{46}H_{42}F_{12}FeN_{14}P_2$	$C_{46}H_{42}F_{12}FeN_{14}P_2$
Formula weight	1136.72	1136.72	1136.72
Temperature/K	80.0(5)	135.00(13)	189.99(15)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$
a/Å	9.45496(9)	9.0523(3)	9.55236(16)
b/Å	17.98580(15)	30.8080(9)	18.1504(3)
c/Å	14.95322(14)	18.3037(9)	15.00388(19)
α/°	90	90	90
β/°	101.5451(9)	102.668(4)	102.1107(14)
γ/°	90	90	90
Volume/Å^3	2491.42(4)	4980.3(3)	2543.46(7)
Z	2	4	2
ρ_{calc}g/cm^3	1.515	1.516	1.484
μ/mm^{-1}	3.879	3.881	3.800
F(000)	1160.0	2320.0	1160.0
Crystal size/mm^3	0.378 × 0.242 × 0.2	0.261 × 0.201 × 0.179	0.277 × 0.196 × 0.195
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.784 to 143.924	7.58 to 144.214	7.748 to 144.048
Index ranges	-11 ≤ h ≤ 11, -21 ≤ k ≤ 21, -18 ≤ l ≤ 17	-6 ≤ h ≤ 11, -37 ≤ k ≤ 37, -22 ≤ l ≤ 22	-8 ≤ h ≤ 11, -22 ≤ k ≤ 21, -18 ≤ l ≤ 17
Reflections collected	21379	21662	18071
Independent reflections	9538 [R_{int} = 0.0278, R_{sigma} = 0.0324]	21662 [R_{int} = ?, R_{sigma} = 0.0569]	9158 [R_{int} = 0.0225, R_{sigma} = 0.0285]
Data/restraints/parameters	9538/118/690	21662/1/1352	9158/118/689
Goodness-of-fit on F^2	1.039	0.997	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0355, wR_2 = 0.0918	R_1 = 0.0512, wR_2 = 0.1307	R_1 = 0.0442, wR_2 = 0.1178
Final R indexes [all data]	R_1 = 0.0358, wR_2 = 0.0923	R_1 = 0.0614, wR_2 = 0.1367	R_1 = 0.0477, wR_2 = 0.1216
Largest diff. peak/hole / e Å^{-3}	0.33/-0.30	0.56/-0.32	0.56/-0.34
Flack parameter	0.011(3)	-0.002(4)	-0.005(4)

1b·dpds

Identification code	**1b·dpds**
Empirical formula	$C_{42}H_{34}N_{14}F_{12}P_2S_4Fe$
Formula weight	1208.86
Temperature/K	80.1(7)
Crystal system	trigonal
Space group	$P3_221$

a/Å	14.8052(7)
b/Å	14.8052(7)
c/Å	19.695(2)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	3738.7(5)
Z	3
ρ_{calc}g/cm^3	1.611
μ/mm^{-1}	5.443
F(000)	1836.0
Crystal size/mm^3	0.172 × 0.128 × 0.103
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.228 to 143.382
Index ranges	-15 ≤ h ≤ 17, -15 ≤ k ≤ 18, -13 ≤ l ≤ 22
Reflections collected	8959
Independent reflections	4454 [R_{int} = 0.0484, R_{sigma} = 0.0698]
Data/restraints/parameters	4454/49/318
Goodness-of-fit on F^2	1.130
Final R indexes [I>=2σ (I)]	R_1 = 0.0609, wR_2 = 0.1481
Final R indexes [all data]	R_1 = 0.0763, wR_2 = 0.1571
Largest diff. peak/hole / e Å^{-3}	0.69/-0.32
Flack parameter	0.001(12)

Distortion parameters

Table S16 Distortion parameters for the co-crystal structures that were deposited to the CSD. Parameters ϑ and φ were calculated within the Olex2 software.[1] Parameters Σ and Θ were calculated using the OctaDist software.[8]

Structure	Spin State	θ (°)	ϕ (°)	Σ (°)	Θ (°)
1a·bpe	**HS**	89.56	171.01	144.81	497.81
1a·azp(α) 110 K	**LS**	85.30	174.51	100.48	345.66
1a·azp(α) 160 K	**mixed**	87.893	173.34	119.50	402.91
1a·azp(α) 270 K	**HS**	89.65	170.57	141.52	478.25
1a·azp(β) 80 K	**mixed**	85.38	172.20	116.18	407.51
1a·azp(β) 270 K	**HS**	83.38	169.48	140.13	488.92
1a·bipy 250 K	**mixed (mostly LS)**	87.84	176.53	96.91	326.20
1a·bipy 330 K	**mixed**	88.65	175.38	112.81	380.17
1a·bipy 350 K	**mixed**	88.27	174.88	115.26	391.44
1a·bipy 300 K	**mixed**	88.33	175.40	111.80	378.04

P2$_1$/n					
1a·bpa	**HS**	84.46	173.93	148.76	491.99
1b·bpe 130 K	**LS**	87.41	176.56	94.05	313.53
1b·bpe 160 K Fe1 / Fe2	**50% HS 50% LS**	89.69 / 87.55	175.87 / 163.90	94.40 / 142.03	319.86 / 487.66
1b·bpe 200 K	**HS**	79.64	165.07	148.35	540.45
1b·azp(α) 160 K	**LS**	87.102	177.29	94.29	311.83
1b·azp(α) 265 K	**mixed**	88.84	174.69	117.22	393.51
1b·azp(α) 365 K	**HS**	88.82	171.37	141.33	483.71
1b·azp(β)	**HS**	76.93	172.00	161.96	523.29
1b·bipy	**LS**	90.00	179.87	88.94	289.30
1b·bpa TIESST 80 K	**HS**	88.77	174.50	145.82	477.27
1b·bpa 135 K Fe1 / Fe2	**LS**	87.04 / 89.08	177.40 / 177.90	93.20 / 94.09	308.71 / 320.64
1b·bpa 190 K	**HS**	88.56	175.06	145.68	475.71
1b·dpds	**HS**	73.74	166.70	176.45	598.61

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