Supplementary information:

Solvent Effects on the Spin-Transition in a Series of Fe(II) Dinuclear Triple Helicate Compounds

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Single-Crystal X-ray diffraction:

Table S1. Crystal data and structure refinement for **1** at 298 K:

Empirical formula	$C_{63}H_{54}B_4F_{16}Fe_2N_{18}(CH_3CN)_{1.25}$
Formula weight	1572.49
Temperature/K	298(2)
Crystal system	triclinic
Space group	P-1
a/Å	13.018(3)
b/Å	14.202(3)
c/Å	21.191(4)
α/°	73.79(3)
β/°	79.44(3)
γ/°	77.23(3)
Volume/Å^3	3638.1(15)
Z	2
ρ_{calc}g/cm^3	1.435
μ/mm^{-1}	0.495
F(000)	1601.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.018 to 49.998
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -25 ≤ l ≤ 25
Reflections collected	42752
Independent reflections	11357 [R_{int} = 0.0373, R_{sigma} = 0.0325]
Data/restraints/parameters	11357/291/1141
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0717, wR_2 = 0.1966
Final R indexes [all data]	R_1 = 0.0880, wR_2 = 0.2121
Largest diff. peak/hole / e Å^{-3}	0.61/-0.69

Experimental

A suitable crystal was selected and run on beamline MX1 of the Australian Synchrotron. The crystal was kept at 298(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.

2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of **1** at 298 K:

Crystal Data for $C_{63}H_{54}B_4F_{16}Fe_2N_{18}(CH_3CN)_{1.25}$ (*M* =1572.49 g/mol): triclinic, space group P-1 (no. 2), *a* = 13.018(3) Å, *b* = 14.202(3) Å, *c* = 21.191(4) Å, *α* = 73.79(3)°, *β* = 79.44(3)°, *γ* = 77.23(3)°, *V* = 3638.1(15) Å^3, *Z* = 2, *T* = 298(2) K, μ(MoKα) = 0.495 mm^{-1}, *Dcalc* = 1.435 g/cm^3, 42752 reflections measured (2.018° ≤ 2Θ ≤ 49.998°), 11357 unique (R_{int} = 0.0373, R_{sigma} = 0.0325) which were used in all calculations. The final R_1 was 0.0717 (I > 2σ(I)) and wR_2 was 0.2121 (all data).

Refinement model description

Number of restraints - 291, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All N(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Restrained distances
 C3-N2
 1.137 with sigma of 0.01
 C3-C4
 1.456 with sigma of 0.01
 C4-N2
 2.593 with sigma of 0.02
 C2-C5
 1.456 with sigma of 0.01
 N1C-C2
 1.15 with sigma of 0.02
 C5-C2
 1.4 with sigma of 0.02
 F3-F4 ≈ F4-F1 ≈ F3-F1
 with sigma of 0.04
 B1-F2 ≈ B1-F7 ≈ B1-F8 ≈ B1-F9
 with sigma of 0.02
 F2-F7 ≈ F7-F8 ≈ F8-F9 ≈ F9-F2 ≈ F7-F9 ≈ F2-F8
 with sigma of 0.04
 F01Q-B02S ≈ F01R-B02S
 with sigma of 0.02
 F02D-B02S ≈ F02E-B02S
 with sigma of 0.02
 F02L-B02S ≈ F02M-B02S
 with sigma of 0.02
 B02S-F5 ≈ B02S-F4AA
 with sigma of 0.02
 F00R-B02Q ≈ F00S-B02Q
 with sigma of 0.02
 F019-B02Q ≈ F0-B02Q
 with sigma of 0.02
 F02C-B02Q ≈ F5AA-B02Q
 with sigma of 0.02
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B02Q-F02U ≈ B02Q-F02V
with sigma of 0.02
C2-C5 ≈ C0AA-C1AA
with sigma of 0.02
C4-C3 ≈ C5-C2 ≈ C1AA-C0AA
with sigma of 0.02
F01Q-F02D ≈ F01Q-F5 ≈ F02D-F02L ≈ F02L-F5
with sigma of 0.04
B02S-F01Q ≈ B02S-F02D ≈ B02S-F02L ≈ B02S-F5
with sigma of 0.02
F01Q-F02D ≈ F01Q-F5 ≈ F02D-F02L ≈ F02L-F5 ≈ F02M-F02E ≈ F02M-F01R ≈ F02E-F4AA
≈ F02E-F01R ≈ F4AA-F01R
with sigma of 0.04
B02S-F01Q ≈ B02S-F02D ≈ B02S-F02L ≈ B02S-F5 ≈ B02S-F02M ≈ B02S-F02E ≈ B02S-
F4AA ≈ B02S-F01R
with sigma of 0.02
3. Rigid bond restraints
F3, F4, F1, B1, F2, F7, F8, F9, F2AA, F1AA, F3AA, F6, F11
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
F01Q, F02D, F02L, B02S, F5, F02M, F02E, F4AA, F01R
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
F00R, F019, F02C, B02Q, F02U, F5AA, F00S, F0, F02V
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
4. Uiso/Uaniso restraints and constraints
F3 ≈ F4 ≈ F1: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
B1 ≈ F2 ≈ F7 ≈ F8 ≈ F9: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
N2 ≈ C3 ≈ C4: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
C2 ≈ C5: within 2A with sigma of 0.04 and sigma for terminal atoms of 0.08
Uanis(F5) = Uanis(F4AA)
5. Rigid body (RIGU) restrains
F3, F4, F1
with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
B1, F2, F7, F8, F9
with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
N2, C3, C4
with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
C2, C5
with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
6. Others
Sof(F02M)=Sof(F02E)=Sof(F4AA)=Sof(F01R)=1-FVAR(1)
Sof(F01Q)=Sof(F02D)=Sof(F02L)=Sof(F5)=FVAR(1)
Sof(F5AA)=Sof(F00S)=Sof(F0)=Sof(F02V)=1-FVAR(2)
Sof(F00R)=Sof(F019)=Sof(F02C)=Sof(F02U)=FVAR(2)
Fixed Sof: F3(0.33333) F4(0.33333) F1(0.33333) F2(0.33333) F7(0.33333)
F8(0.33333) F9(0.33333) F2AA(0.33333) F1AA(0.33333) F3AA(0.33333) F6(0.33333)
F11(0.33333) N2(0.5) C3(0.5) C4(0.5) H4D(0.5) H4E(0.5) H4F(0.5) C2(0.25)
C5(0.25) H5A(0.25) H5B(0.25) H5C(0.25) C0AA(0.5) C1AA(0.5) H1AA(0.5) H1AB(0.5)
H1AC(0.5) N0AA(0.5) N1C(0.25)
7.a Free rotating group:
B1(F2,F7,F8,F9), N2(C3,C4)
7.b Secondary CH2 refined with riding coordinates:
C10A(H10A,H10C), C11B(H11A,H11B), C11C(H11C,H11D)
7.c Aromatic/amide H refined with riding coordinates:
N10(H10), C4B(H4B), C6B(H6B), C17B(H17B), C9A(H9A), N00S(H00S), C9C(H9C),

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 C17A(H17A), C16B(H16B), N00X(H00X), C10B(H10B), C7B(H7B), C4A(H4A),
C9B(H9B),
 C12A(H12A), C4C(H4C), C8A(H8A), N01A(H01A), N01D(H01D), C18B(H18B),
C13A(H13A),
  C15A(H15A), C16A(H16A), C6A(H6A), C13B(H13B), C10C(H10D), C01U(H01U),
 N01W(H01W), C14B(H14B), C1C(H1C), C2B(H2B), C15C(H15C), C22(H22),
C6C(H6C),
 C17C(H17C), C20A(H20A), C16C(H16C), C21B(H21B), C1A(H1A), C20C(H20C),
 C20B(H20B), C13C(H13C), C12C(H12C), C1B(H1B), C7C(H7C), C2A(H2A),
C19C(H19C)
7.d Idealised Me refined as rotating group:
 C4(H4D,H4E,H4F), C5(H5A,H5B,H5C), C1AA(H1AA,H1AB,H1AC)
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Discussion of Issues with Crystallographic Data:

Anion and solvent molecules were quite disordered, and for this reason some thermal ellipsoids remain quite large.

One acetonitrile molecule was assigned in two parts of 0.25 and 0.5 occupancy respectively, while the other was assigned 0.5 occupancy.

Table S2. Crystal data and structure refinement for **2** at 155 K.

Empirical formula	$C_{60}H_{48}B_4F_{16}Fe_2N_{18}S_3(CH_3CN)_2$
Formula weight	1658.39
Temperature/K	155(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.4960(19)
b/Å	16.709(3)
c/Å	23.605(5)
α/°	95.07(3)
β/°	100.27(3)
γ/°	92.96(3)
Volume/Å^3	3662.3(13)
Z	2
ρ_{calc}g/cm^3	1.504
μ/mm^{-1}	0.578
F(000)	1684.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.452 to 49.426
Index ranges	−11 ≤ h ≤ 11, −19 ≤ k ≤ 19, −27 ≤ l ≤ 27
Reflections collected	39131
Independent reflections	11544 [R_{int} = 0.0389, R_{sigma} = 0.0359]
Data/restraints/parameters	11544/225/1062
Goodness-of-fit on F^2	1.633
Final R indexes [I>=2σ (I)]	R_1 = 0.1103, wR_2 = 0.3529
Final R indexes [all data]	R_1 = 0.1215, wR_2 = 0.3729
Largest diff. peak/hole / e Å^{-3}	1.54/−0.98

Experimental

A suitable crystal was selected and run on a Bruker APEX-II CCD diffractometer. The crystal was kept at 155(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339–341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3–8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3–8.

Crystal structure determination of **2** at 155 K

Crystal Data for $C_{60}H_{48}B_4F_{16}Fe_2N_{18}S_3(CH_3CN)_2$ M =1650.28 g/mol): triclinic, space group P-1 (no. 2), a = 9.4960(19) Å, b = 16.709(3) Å, c = 23.605(5) Å, α = 95.07(3)°, β = 100.27(3)°, γ = 92.96(3)°, V = 3662.3(13) Å^3, Z = 2, T = 155(2) K, μ(MoKα) = 0.578 mm^{-1}, *Dcalc* = 1.497 g/cm^3, 39131 reflections measured (2.452° ≤ 2Θ ≤ 49.426°), 11544 unique (R_{int} = 0.0389, R_{sigma} = 0.0359) which were used in all calculations. The final R_1 was 0.1108 (I > 2σ(I)) and wR_2 was 0.3751 (all data).

Refinement model description

Number of restraints – 225, number of constraints – unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All N(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Restrained distances
 F1-B2
 1.40225 with sigma of 0.01
 F0AA-B2
 1.40225 with sigma of 0.02
 F0AA-F1
 2.28987 with sigma of 0.02
 F13-B10 = F1AA-B10
 1.4 with sigma of 0.02
 F1AA-F13
 2.28987 with sigma of 0.02
 F1AA-F6
 2.28987 with sigma of 0.02
 F6-F13
 2.28987 with sigma of 0.02
 F3-B10
 1.4 with sigma of 0.02
 F3-F13
 2.28987 with sigma of 0.02
 F3-F1AA
 2.28987 with sigma of 0.02
 F3-F6
 2.28987 with sigma of 0.02
 F3AA-F5AA
 2.28987 with sigma of 0.02
 F3AA-F2AA
 2.28987 with sigma of 0.02
 F3AA-F4AA
 2.28987 with sigma of 0.02
 F2AA-F5AA
 2.28987 with sigma of 0.02
 F2AA-F4AA
 2.28987 with sigma of 0.02
 F4AA-F5AA
 2.28987 with sigma of 0.02
 F3AA-B0AA
 1.4 with sigma of 0.02
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 F5AA-B0AA = F4AA-B0AA = F2AA-B0AA
 1.4 with sigma of 0.02
 F7AA-B0AA
 1.4 with sigma of 0.02
 F8AA-B0AA
 1.4 with sigma of 0.02
 B0AA-F2AA = B0AA-F3AA = B0AA-F4AA = B0AA-F5AA = B0AA-F6AA = B0AA-F7AA =
B0AA-
 F2 = B0AA-F8AA
 1.4 with sigma of 0.02
 N1-C20
 1.2 with sigma of 0.02
3. Rigid body (RIGU) restrains
 F02Q, F00R, F010, F029, B02Y
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 F1, F5, F4, F0AA
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 F8AA, F2AA, B0AA, F3AA, F6AA, F4AA, F2, F7AA, F5AA
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C20
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 C1
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 F1, B2, F4, F5, F6, B10, F3, F0AA, F1AA, F13
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
 F009, F006, B02O, F007, F00B
 with sigma for 1-2 distances of 0.004 and sigma for 1-3 distances of 0.004
4. Others
 Fixed Sof: B2(0.75) F4(0.5) F5(0.5) F1(0.5) F0AA(0.5) F1AA(0.5) F6(0.5)
 B10(0.25) F13(0.5) F3(0.5) F2AA(0.75) F3AA(0.75) F4AA(0.75) F5AA(0.25)
 F6AA(0.75) F7AA(0.25) F2(0.25) F8AA(0.25)
5.a Free rotating group:
 B2(F4,F5)
5.b Aromatic/amide H refined with riding coordinates:
 N00G(H00G), N00J(H00J), C00L(H00L), N27(H27), C00S(H00S), N00T(H00T),
 C013(H013), C014(H014), C015(H015), C016(H016), C017(H017), C01A(H01A),
 C01B(H01B), C01C(H01C), C01D(H01D), C01E(H01E), C01F(H01F), N01G(H01G),
 N01I(H01I), C01K(H01K), C01L(H01L), C01N(H01N), C01O(H01O), C01P(H01P),
 C01Q(H01Q), C01R(H01R), C01S(H01S), C01T(H01T), C01U(H01U), C01V(H01V),
 C01W(H01W), C01X(H01X), C01Y(H01Y), C01Z(H01Z), C023(H023), C025(H025),
 C29(H29), C027(H027), C028(H028), C02A(H02A), C02E(H02E), C02H(H02H),
 C02I(H02I), C02J(H02J), C02K(H02K), C02L(H02L), C02N(H02N), C02P(H02P)
5.c Idealised Me refined as rotating group:
 C02V(H02B,H02C,H02D), C1(H1A,H1B,H1C)
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Discussion of Issues with crystallographic data:

Large R1, wR2 and GoF values were obtained, although the wR2 and GoF are more severe. Disorder in BF_4^- counter ions and the acetonitrile molecule containing C1 in particular may be responsible for these high values.

Table S3. Crystal data and structure refinement for **3** at 298 K.

Empirical formula	$C_{60}H_{48}B_4F_{16}Fe_2N_{18}O_3.(CH_3CN)_{1.5}$
Formula weight	1589.68
Temperature/K	298(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	20.420(4)
b/Å	19.394(4)
c/Å	20.836(4)
α/°	90
β/°	107.68(3)
γ/°	90
Volume/$Å^3$	7862(3)
Z	4
$\rho_{calc}g/cm^3$	1.343
μ/mm^{-1}	0.461
F(000)	3228.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.966 to 46.494
Index ranges	−20 ≤ h ≤ 20, −19 ≤ k ≤ 19, −20 ≤ l ≤ 20
Reflections collected	33555
Independent reflections	4808 [R_{int} = 0.0735, R_{sigma} = 0.0385]
Data/restraints/parameters	4808/0/506
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0804, wR_2 = 0.2429
Final R indexes [all data]	R_1 = 0.1043, wR_2 = 0.2640

Experimental

A suitable crystal was selected and run on a Bruker APEX-II CCD diffractometer. The crystal was kept at 298 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339–341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3–8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3–8.

Crystal structure determination of **3** at 298 K

Crystal Data for $C_{60}H_{48}B_4F_{16}Fe_2N_{18}O_3.(CH_3CN)_{1.5}$ (*M* =1589.68 g/mol): monoclinic, space group C2/c (no. 15), *a* = 20.420(4) Å, *b* = 19.394(4) Å, *c* = 20.836(4) Å, *β* = 107.68(3)°, *V* = 7862(3) Å^3, *Z* = 4, *T* = 298(2) K, μ(MoKα) = 0.461 mm^{-1}, *Dcalc* = 1.343 g/cm^3, 33555 reflections measured (2.966° ≤ 2Θ ≤ 46.494°), 4808 unique (R_{int} = 0.0735, R_{sigma} = 0.0385) which were used in all calculations. The final R_1 was 0.0804 (I > 2σ(I)) and wR_2 was 0.2640 (all data).

Refinement model description

Number of restraints – 0, number of constraints – unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All N(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Others
 Fixed Sof: C1(0.5) H1C(0.5) H1D(0.5) H1E(0.5) C2AA(0.5) N2(0.5) N1AA(0.25)
 C0AA(0.25) H0AA(0.25) H0AB(0.25) H0AC(0.25) C3(0.25)
3.a Aromatic/amide H refined with riding coordinates:
 N2A(H2A), N5A(H5A), N2B(H2B), C1A(H1A), C2A(H2AA), C4A(H4A), C6A(H6A),
 C7A(H7A), C9A(H9A), C10A(H10A), C12A(H12A), C13A(H13A), C15A(H15A),
C16A(H16A),
  C17A(H17A), C19A(H19A), C20A(H20A), C1B(H1B), C2B(H2BA), C4B(H4B),
C6B(H6B),
 C7B(H7B), C9B(H9B), C10B(H10B)
3.b Idealised Me refined as rotating group:
 C1(H1C,H1D,H1E), C0AA(H0AA,H0AB,H0AC)
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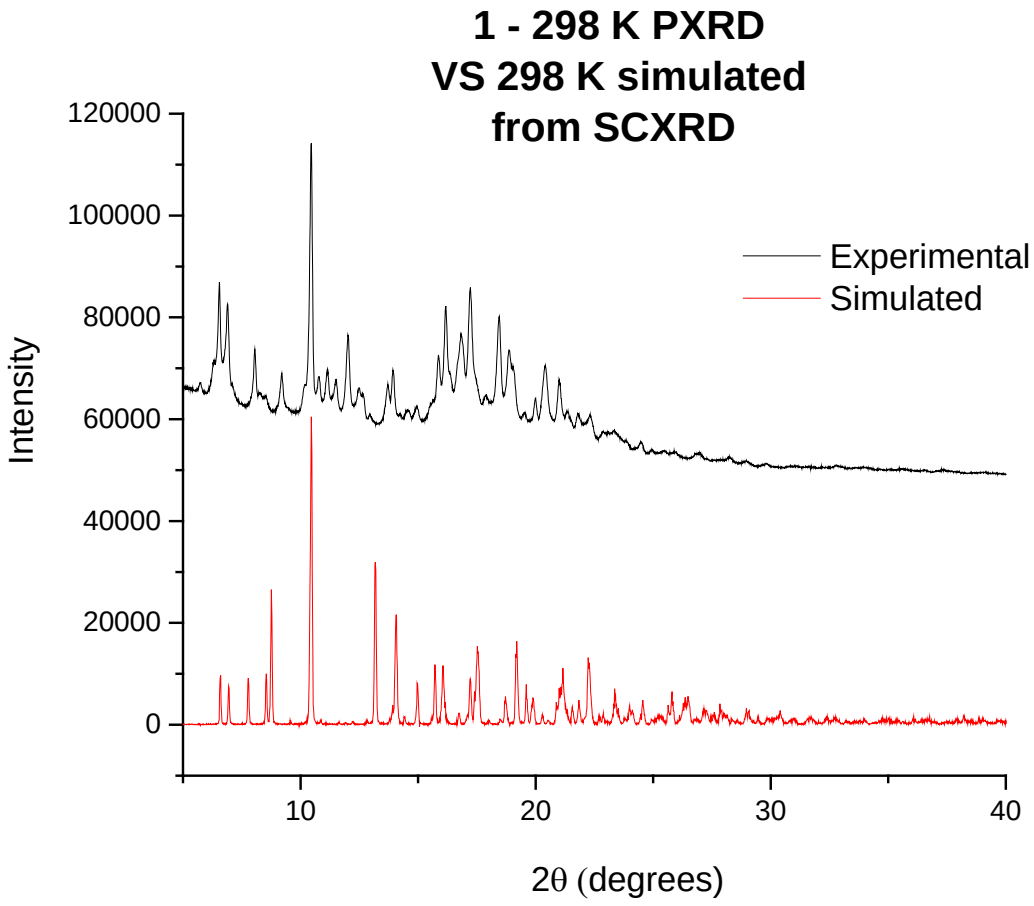
Discussion of Issues with crystallographic data:

The acetonitrile molecule containing N1AA was modelled with a site occupancy of 0.25 and was, as a result of such a small degree of electron density, unable to be modelled anisotropically and was accordingly modelled isotropically.

Due to the Australian synchrotron being a single circle instrument, completeness fell of steeply at resolutions between 0.8 and 0.85 Å. A balance was thus attempted to be made between the resolution and the completeness, using a SHEL command to remove some high angle data that was greatly affecting the completeness values. As such, the d min is slightly high and the completeness slightly low.

The wR2 value of 26.4 is also slightly high, possibly a result of the larger thermal ellipsoids observed during the room temperature measurement.



Powder X-ray Diffraction:

Figure S1. PXRD pattern of **1**, with the 298 K PXRD pattern in black on top and simulated spectrum from 298 K SCXRD data in red on the bottom.

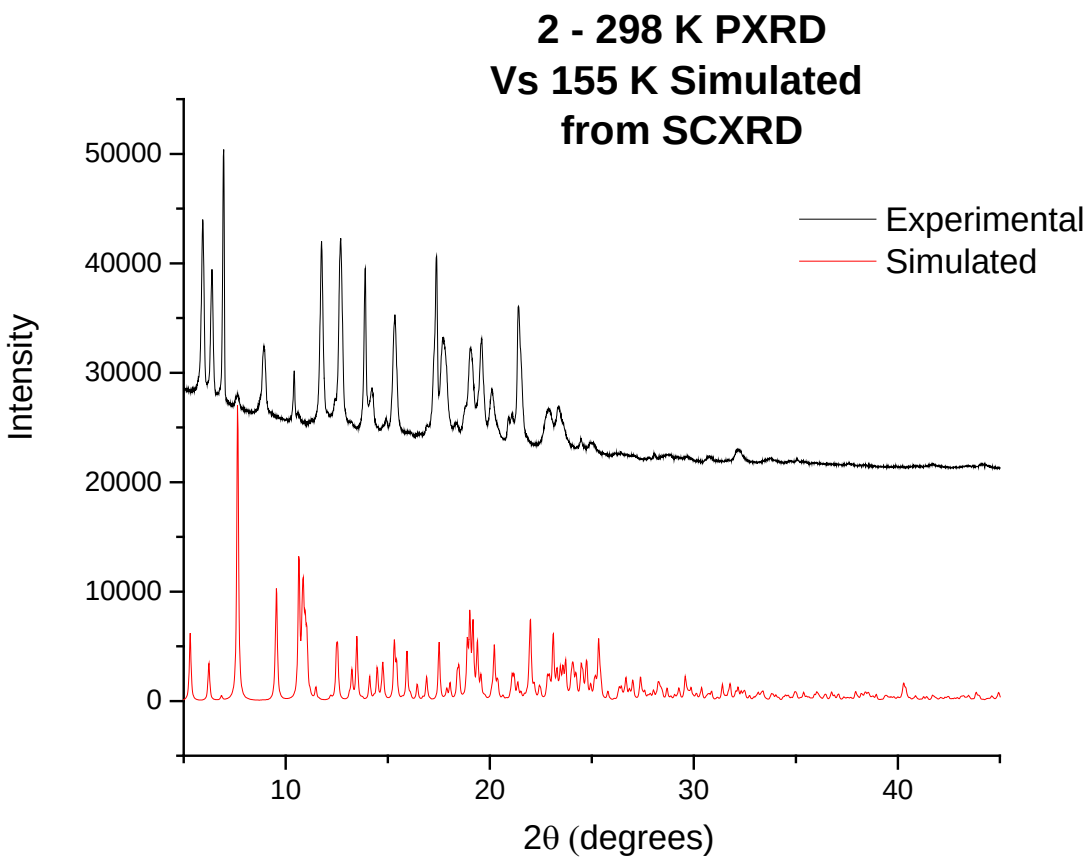


Figure S2. PXRD pattern of **2**, with the 298 K PXRD pattern in black on top and simulated spectrum from 155 K SCXRD data in red on the bottom. No 298 K SCXRD structure could be obtained.

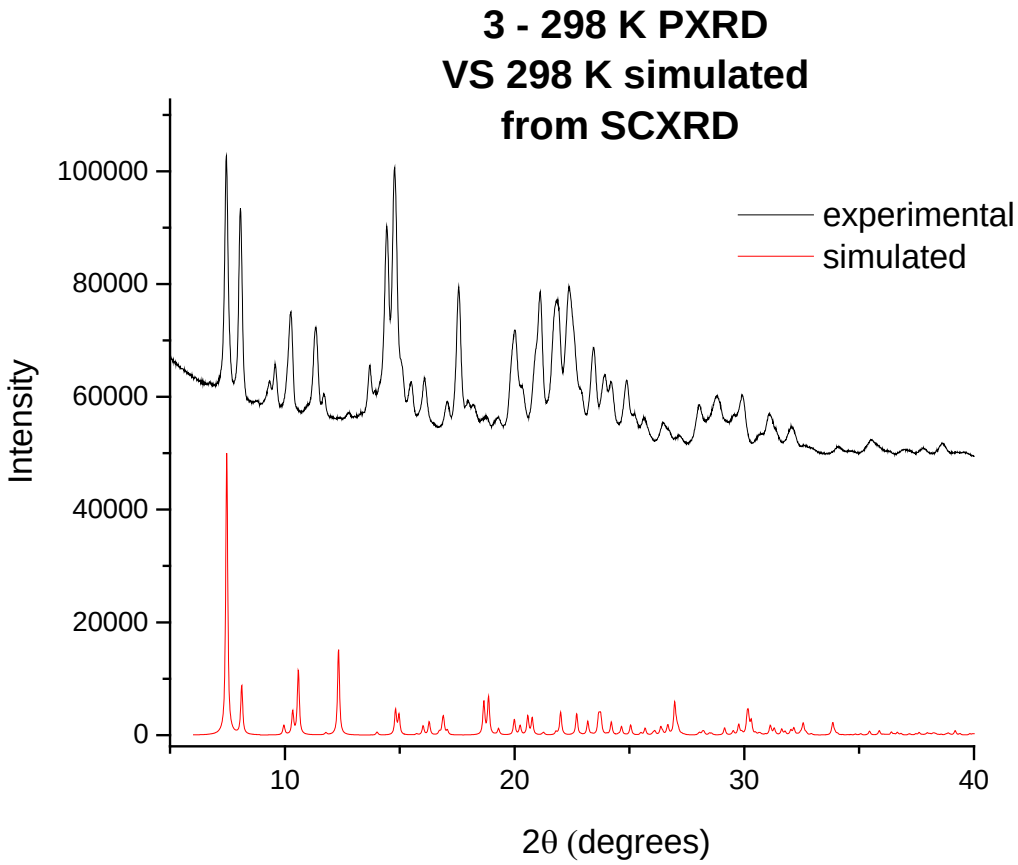


Figure S3. PXRD pattern of **3**, with the 298 K PXRD pattern in black on top and simulated spectrum from 298 K SCXRD data in red on the bottom.

Thermal Gravimetric Analysis (TGA):

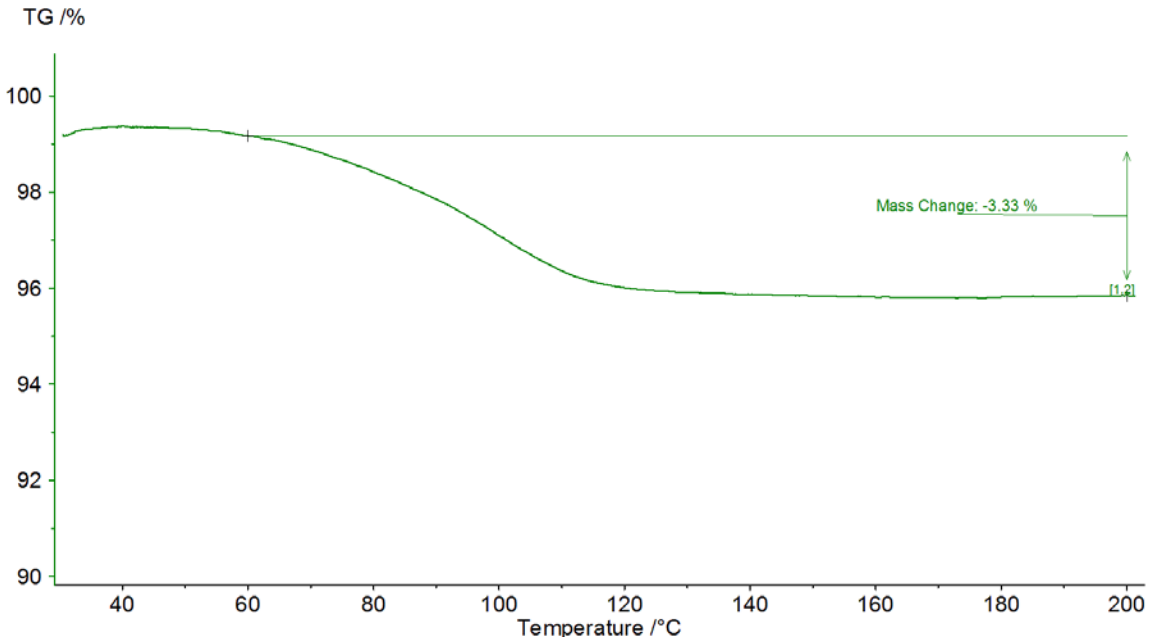


Figure S4. TGA analysis of filtered samples of **1**.

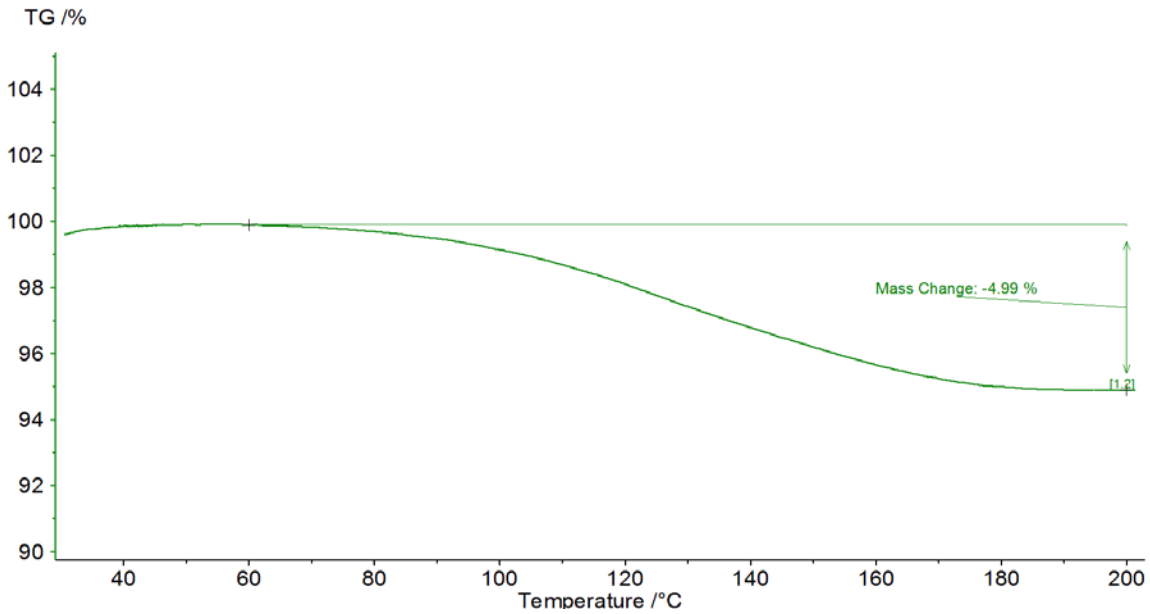


Figure S5. TGA analysis of filtered samples of **2.**

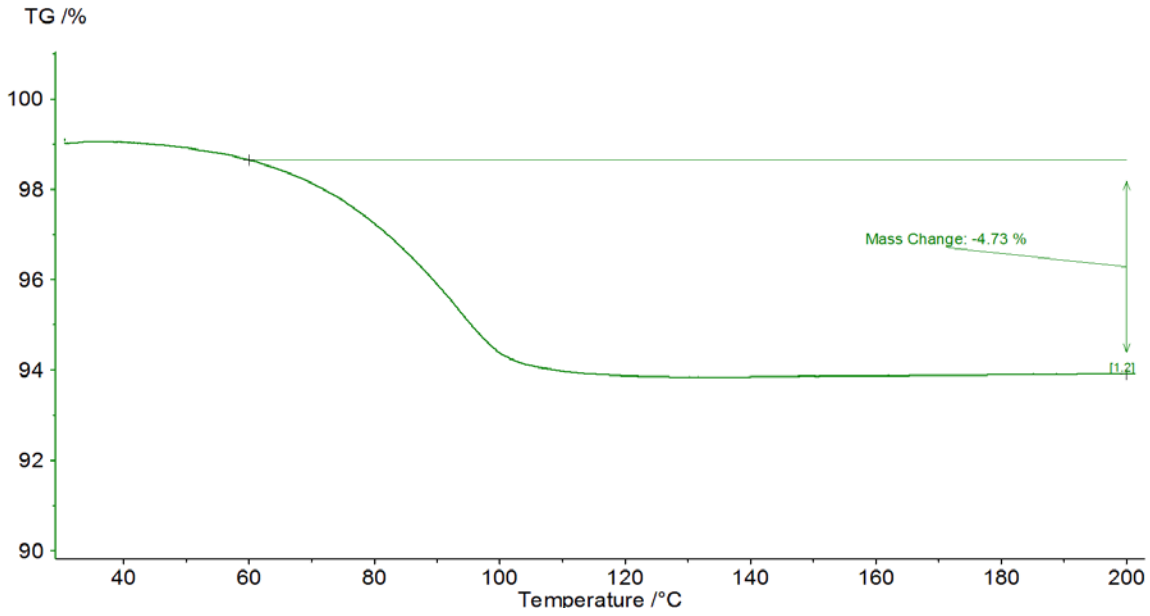


Figure S6. TGA analysis of filtered samples of **3**.