Supporting Information for:

From isolated to 2D Coordination Polymers based on 6-aminonicotinate and 3d-Metal Ions: Towards Field-Induced Single-Ion-Magnets

Antonio Rodríguez-Diéguez,[a] Sonia Pérez-Yáñez,[b] Leire Ruiz-Rubio,[c] Jose M. Seco,*[d] Javier Cepeda*[d,e]

[a]Departamento de Química Inorgánica, Facultad de Ciencias, University of Granada, 18071 Granada, Spain. [b] Departamento de Química Inorgánica, Facultad de Farmacia, Universidad del País Vasco (UPV/EHU), 01006Vitoria, Spain. [c] Departamento de Química Física, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Apdo. 644 48080 Bilbao, Spain. [d]Departamento de Química Aplicada, Facultad de Química, Universidad del País Vasco (UPV/EHU), 20080 Donostia, Spain. [e] Departamento de Ciencia y Tecnología de Polímeros, Facultad de Química, Universidad del País Vasco (UPV/EHU), 20080 Donostia, Spain.

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S1. Additional figures of compounds.

(a) **(b)**
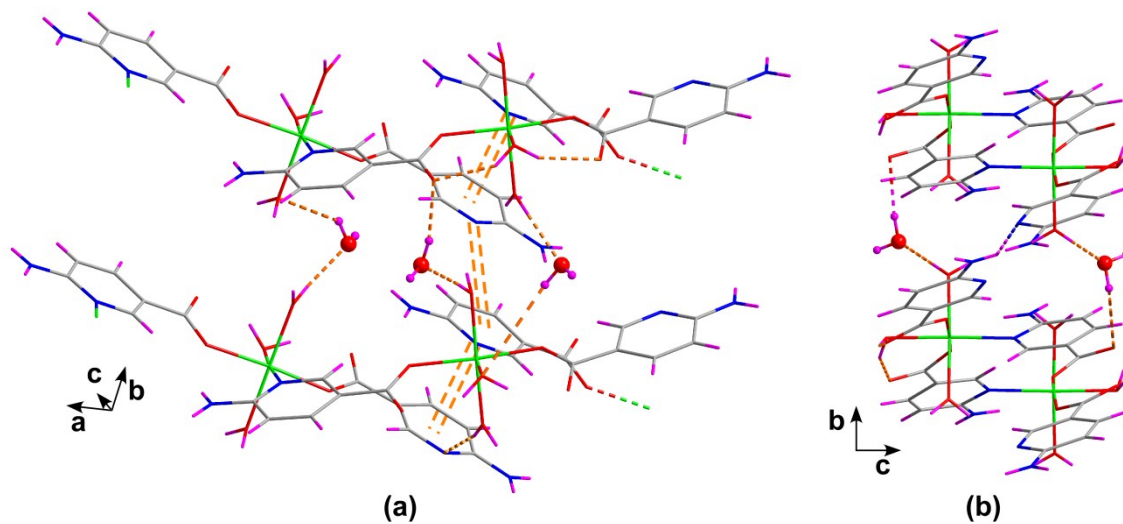
Figure S1. Supramolecular interactions in **3**joining broken ladder-like chains along **(a)**c and **(b)**a axes.

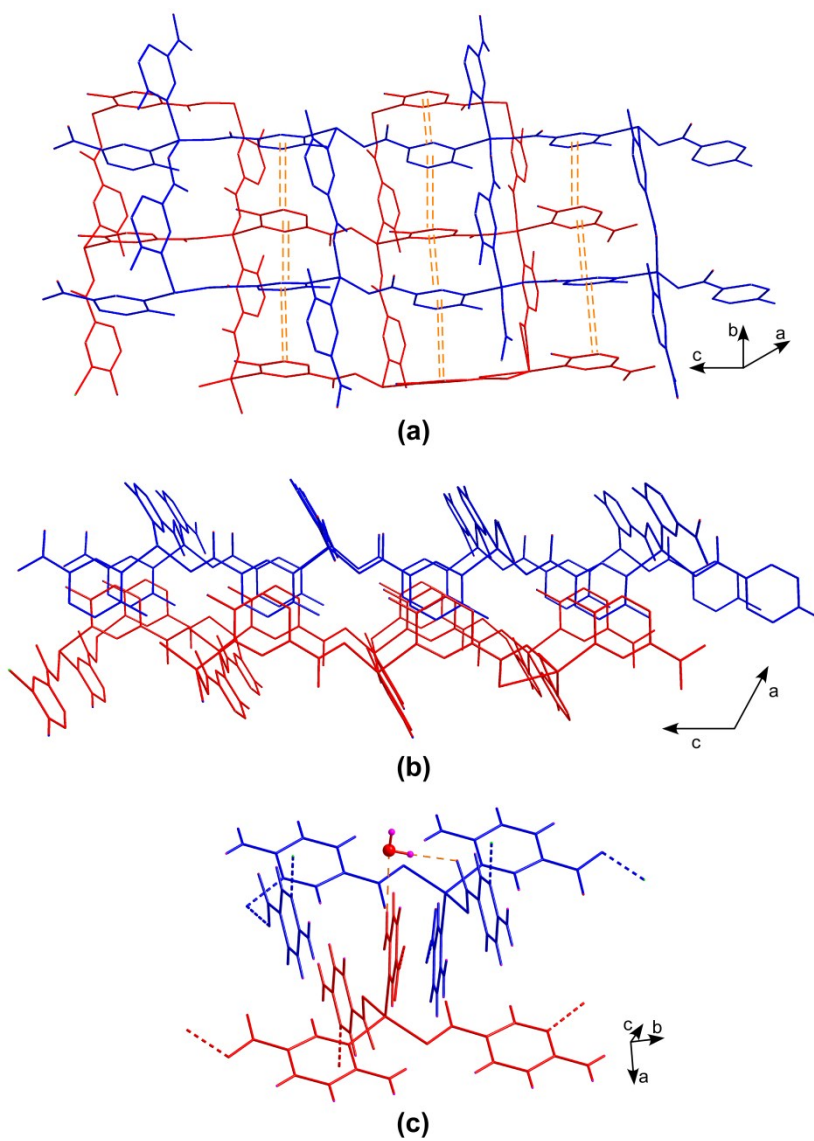**(a)**

(b)

(c)

Figure S2. Supramolecular interactions among layers of **5**showing **(a-b)**π–π and hydrogen bonding interactions **(c)** Interactions involving the coordination water molecule.

S2. Additional structural data.

Table S1. Structural parameters (Å, º) of hydrogen bonds (Å, º) in compound **1**.[a]

D–H⋯A[b]	D–H	H⋯A	D⋯A	D–H⋯A
O1w–H11w⋯O72B(ii)	0.85	2.05	2.905(2)	175.7
O1w–H12w⋯O72A	0.86	1.78	2.634(2)	174.5
O2w–H21w⋯O72B(iii)	0.86	1.97	2.796(2)	162.2
O2w–H22w⋯N1B(i)	0.85	2.00	2.825(2)	164.6
O3w–H31w⋯O71B(iv)	0.86	1.85	2.694(2)	164.9
O3w–H32w⋯O1w(v)	0.85	1.97	2.816(2)	170.1
O4w–H41w⋯O72B(iv)	0.85	1.99	2.831(2)	16.6
O4w–H42w⋯O71B(ii)	0.85	1.87	2.709(2)	170.6
N8A–H81A⋯O72A(vi)	0.86	2.05	2.896(3)	169.0
N8A–H81A...O72A(i)	0.86	2.32	3.054(3)	142.8
N8A–H81A...O72A	0.86	2.40	3.255(2)	173.5
N8A–H81A⋯O72A(i)	0.86	2.55	3.188(2)	132.2

[a]Symmetry codes: (i) –x + 1, –y, –z ; (ii) x + 1/2, –y – 1/2, z + 1/2; (iii) –x + 3/2, y + 1/2, –z + 1/2; (iv) –x + 1/2, y + 1/2, –z + 1/2; (v) –x + 2, –y, –z + 1; (vi) x – 1/2, –y – 1/2, z – 1/2. [b]D: donor. A: acceptor.

Table S2. Structural parameters (Å, º) of π–π interactions of compound **1**.[a]

Ring⋯Ring[b]	α	DC	β	DZ	Dist.
1A–2B	7.26	3.483(1)	12.89	3.34	3.30–3.67
1A–2B(vi)	5.93	4.629(1)	44.55	3.261	
2B–1A	7.26	3.483(1)	16.72	3.40	3.30–3.67
2B–1A(vii)	5.93	4.629(1)	45.21	3.30	

[a] α: dihedral angle between mean planes of the rings (°), DC: distance between ring centroids (Å), β: angle between DC vector and normal to plane(I) (°), DZ: perpendicular distance of the centroids of ring(I) on plane of ring(II) (Å), Dist.: shorter distances between non-hydrogen atoms of rings (I) and (II). [b] Rings: **1A**: N1A, C2A, C3A, C4A, C5A, C6A; **2B**: N1B, C2B, C3B, C4B, C5B, C6B. Symmetries: (vi) x + 1/2, –y – 1/2, z – 1/2; (vii) x – 1/2, –y – 1/2, z – 1/2.

Table S3. Structural parameters (Å, º) of hydrogen bonds (Å, º) in compound **2**.[a]

$D–H···A$[b]	$D–H$	$H···A$	$D···A$	$D–H···A$
O1w–H11w···N1A(i)	0.86	1.90	2.753(4)	172.0
O1w–H12w···O8w(ii)	0.86	1.87	2.715(4)	171.0
O2w–H21w···O4w	0.90	1.91	2.678(4)	143.0
O2w–H22w···O5w(iii)	0.89	1.92	2.719(4)	149.1
O3w–H31w···O5w	0.86	1.82	2.671(4)	168.5
O3w–H32w···O72A	0.86	1.82	2.668(4)	168.9
O4w–H41w···O7w	0.93	1.84	2.729(5)	161.1
O4w–H42w···O3w(iii)	0.93	2.02	2.870(4)	151.8
O5w–H51w···N10C(iv)	0.85	1.90	2.744(5)	171.3
O5w–H52w···O6w	0.85	1.90	2.738(5)	168.1
O6w–H61w···O71B(v)	0.86	1.89	2.721(7)	160.5
O6w–H62w···O72A(vi)	0.92	1.94	2.848(5)	169.0
O7w–H71w···O72A(i)	0.86	1.95	2.776(5)	162.2
O7w–H72w···O6w(i)	0.87	1.94	2.785(7)	162.9
O8w–H81w···N10D(vii)	0.95	1.91	2.785(5)	152.1
O8w–H82w···O71A	0.93	2.01	2.894(4)	156.8

[a]Symmetry codes: (i) x − 1, y, z ; (ii) −x + 1, −y, −z + 1; (iii) −x + 1, −y, −z; (iv) x, y − 1, z; (v) −x, −y − 1, −z; (vi) −x + 2, −y, −z; (vii) x, y + 1, z. [b]D: donor. A: acceptor.

Table S4. Structural parameters (Å, º) of π–π interactions of compound **2**.[a]

Ring···Ring[b]	α	DC	β	DZ	Dist.
1A–1A(viii)	0.03	3.940(2)	29.71	3.422	3.52–3.95
2A–3A(ix)	3.29	4.130(3)	32.45	3.509	4.08–4.17
2A–3B(vii)	0.89	4.323(3)	33.89	3.625	4.29–4.35
3A–3B(i)	5.17	4.151(4)	31.01	3.367	3.68–4.12
2B–2B(x)	6.16	4.049(3)	27.82	3.736	3.92–4.17
3A–3A(xi)	0.00	4.275(3)	34.05	3.542	3.69–4.17
3A–3B(viii)	3.14	4.091(3)	29.31	3.575	3.63–4.34

[a] α: dihedral angle between mean planes of the rings (°), DC: distance between ring centroids (Å), β: angle between DC vector and normal to plane(I) (°), DZ: perpendicular distance of the centroids of ring(I) on plane of ring(II) (Å), Dist.: shorter distances between non-hydrogen atoms of rings (I) and (II). [b] Rings: **1A**: N1C, C2C, C3C, C4C, C5C, C6C; **2B**: N1D, C2D, C3D, C4D, C5D, C6D; **3A**: C7C, C8C, C9C, N10C, C11C, C12C; **3B**: C7D, C8D, C9D, N10D, C11D, C12D. Symmetries: (viii): −x + 2, −y, −z; (ix) −x + 1, −y, −z; (x) −x + 1, −y + 1, −z + 1; (xi) −x + 1, −y + 1, −z.

Table S5. Structural parameters (Å, °) of hydrogen bonds (Å, °) in compound **3**.[a]

D–H⋯A[b]	D–H	H⋯A	D⋯A	D–H⋯A
O1w–H11w⋯O5w(i)	0.85	1.90	2.719(4)	160.8
O1w–H12w⋯N1B(ii)	0.85	2.06	2.897(4)	168.1
O2w–H21w⋯O72B	0.85	1.95	2.721(4)	149.5
O2w–H22w⋯O72A	0.85	1.99	2.708(4)	141.8
O3w–H31w⋯N1B(iii)	0.85	2.05	2.870(4)	161.0
O3w–H32w⋯O4w	0.85	1.87	2.723(4)	173.4
O4w–H41w⋯O72A(iv)	0.85	1.97	2.811(4)	167.0
O4w–H42w⋯O72A(v)	0.85	1.95	2.801(4)	174.7
O5w–H51w⋯O72B(vi)	0.85	1.93	2.773(4)	168.8
O5w–H52w⋯O71B	0.85	2.51	3.220(4)	141.7
O5w–H52w⋯O3w	0.85	2.51	3.206(4)	140.0
N18–H8A1⋯O71A	0.86	2.12	2.897(4)	149.4
N18–H8A2⋯O5w(vii)	0.86	2.29	3.149(4)	174.4
N28–H8B2⋯O4w(viii)	0.86	2.28	3.093(4)	158.4

[a]Symmetry codes: (i) x, y − 1, z ; (ii) x − 1/2, −y + 1/2, −z − 2; (iii) x − 1/2, −y + 3/2, −z −2; (iv) x, y + 1, z; (v) −x + 2, y + 1/2, −z − 3/2; (vi) −x + 3, y + 1/2, −z − 3/2; (vii) x − 1/2, −y + 3/2, −z − 2; (viii) x + 1, y, z. [b]D: donor. A: acceptor.

Table S6. Structural parameters (Å, °) of π–π interactions of compound **3**.[a]

Ring⋯Ring[b]	α	DC	β	DZ	Dist.
1A–2B(ii)	3.11	3.482(2)	10.24	3.391	3.45–3.63
1A–2B(iii)	3.11	4.202(2)	36.22	3.369	3.83–4.03
2B–1A(ix)	3.11	3.482(2)	13.13	3.427	3.83–4.33
2B–1A(x)	3.11	4.202(2)	36.68	3.390	3.46–4.63

[a] α: dihedral angle between mean planes of the rings (°), DC: distance between ring centroids (Å), β: angle between DC vector and normal to plane(I) (°), DZ: perpendicular distance of the centroids of ring(I) on plane of ring(II) (Å), Dist.: shorter distances between non-hydrogen atoms of rings (I) and (II). [b] Rings: **1A**: N1A, C2A, C3A, C4A, C5A, C6A; **2B**: N1B, C2B, C3B, C4B, C5B, C6B. Symmetries: (ix) x + 1/2, −y −1/2, −z − 2; (x) x + 1/2, −y −3/2, −z − 2.

Table S7. Structural parameters (Å, °) of hydrogen bonds (Å, °) in compound **5**.[a]

D–H⋯A[b]	D–H	H⋯A	D⋯A	D–H⋯A
O1w–H12w⋯O72B(iii)	0.87	2.03	2.891(13)	170.9
N8A–H8A1⋯O71A(i)	0.86	1.92	2.733(11)	157.8
N8A–H8A2⋯O72B(iv)	0.86	2.07	2.862(11)	153.7
N8B–H8B1⋯O1w	0.86	2.42	3.256(14)	163.2
N8B–H8B2⋯O71B(ii)	0.86	2.12	2.904(12)	150.5

[a]Symmetry codes: (i) x, y + 1, z; (ii) x, −y, z − 1/2; (iii) −x + 1/2, y + 1/2, −z + 1/2; (iv) −x + 1, −y, −z + 1.[b]D: donor. A: acceptor.
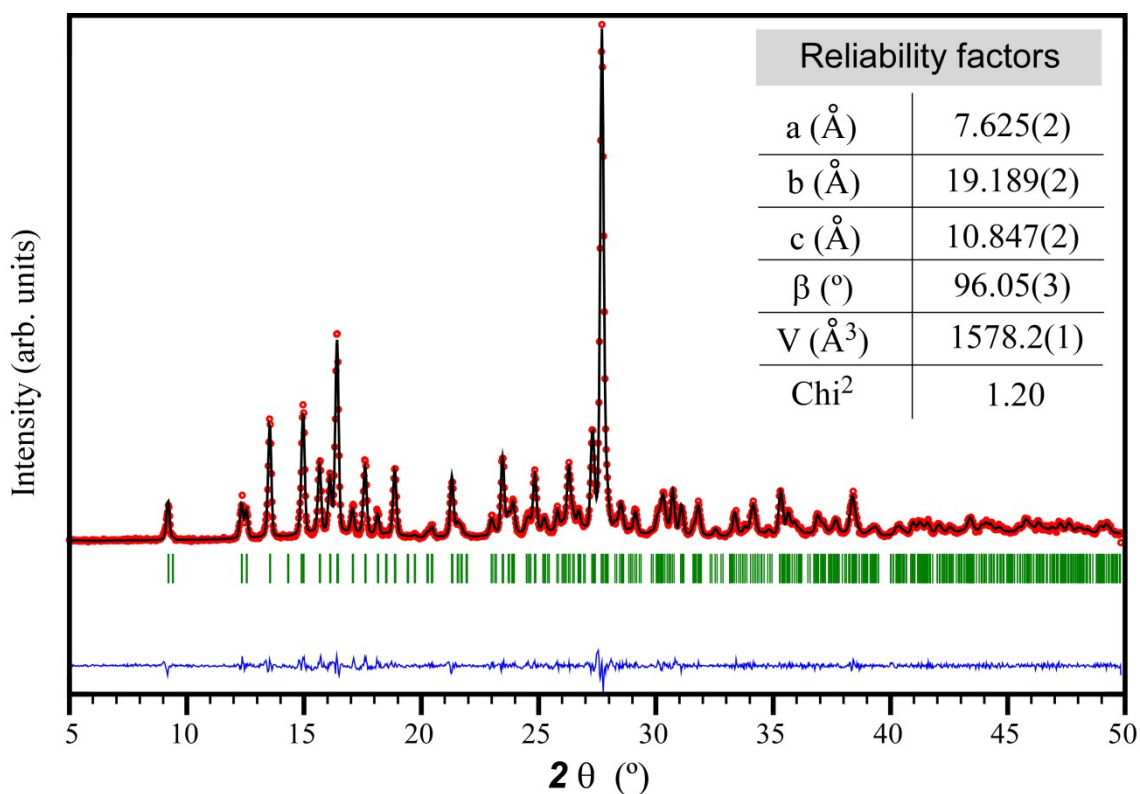
Table S8. Structural parameters (Å, º) of π–π interactions of compound **5**.[a]

Ring···Ring[b]	α	DC	β	DZ	Dist.
1A–1A(v)	0.66	3.481(7)	20.37	3.26	3.45–3.53
2B–2B(vi)	14.80	4.176(7)	12.71	3.72	3.86–4.48
2B–2B(iii)	14.80	4.177(7)	27.04	4.07	3.86–4.48

[a] α: dihedral angle between mean planes of the rings (°), DC: distance between ring centroids (Å), β: angle between DC vector and normal to plane(I) (°), DZ: perpendicular distance of the centroids of ring(I) on plane of ring(II) (Å), Dist.: shorter distances between non-hydrogen atoms of rings (I) and (II). [b] Rings: **1A**: N1A, C2A, C3A, C4A, C5A, C6A; **2B**: N1B, C2B, C3B, C4B, C5B, C6B. Symmetries: (v) –x + 1, y, –z + 1/2; (vi) –x + 1/2, y – 1/2, –z + 1/2.

S3. Pattern-matching analyses of Powder X-ray diffraction Data.

Pattern-matching analyses confirm the purity of the polycrystalline samples.

Reliability factors	
a (Å)	7.625(2)
b (Å)	19.189(2)
c (Å)	10.847(2)
β (°)	96.05(3)
V (Å^3)	1578.2(1)
Chi^2	1.20

Figure S3. Full profile pattern-matching analysis of **1**.

Reliability factors	
a (Å)	9.819(2)
b (Å)	14.165(2)
c (Å)	14.273(2)
α (°)	73.15(3)
β (°)	74.16(3)
γ (°)	86.88(3)
V (Å^3)	1827.1(1)
Chi^2	1.70
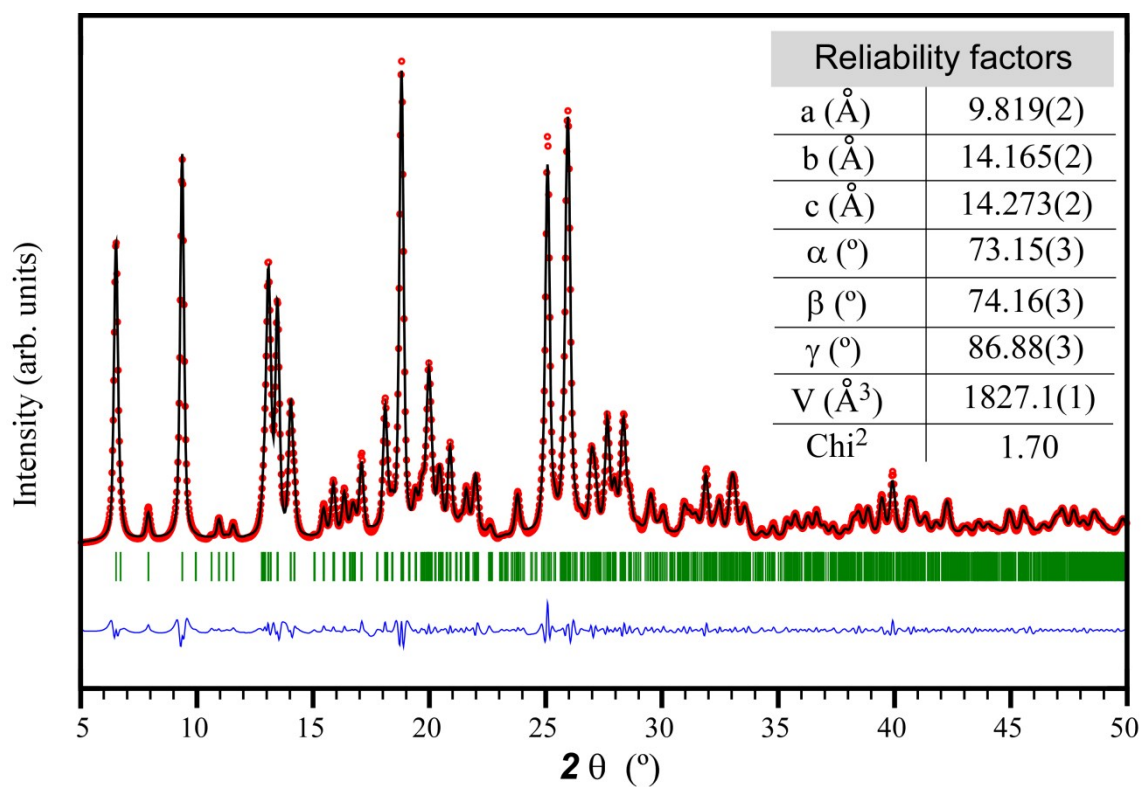
Figure S4. Full profile pattern-matching analysis of **2**.

Reliability factors	
a (Å)	11.886(2)
b (Å)	7.468(2)
c (Å)	18.919(2)
V (Å^3)	1679.3(1)
Chi^2	2.87
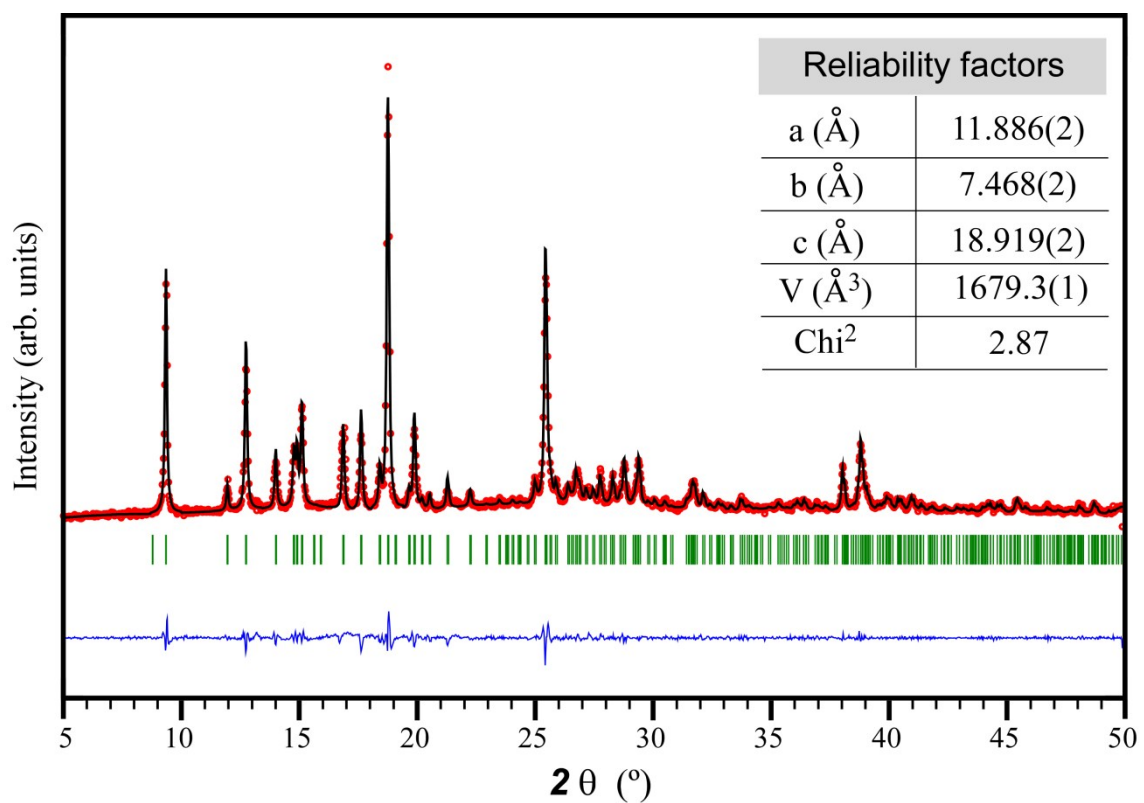
Figure S5. Full profile pattern-matching analysis of **3**.

Reliability factors	
a (Å)	11.873(2)
b (Å)	7.434(2)
c (Å)	18.792(2)
V (Å³)	1658.7(1)
Chi²	1.54
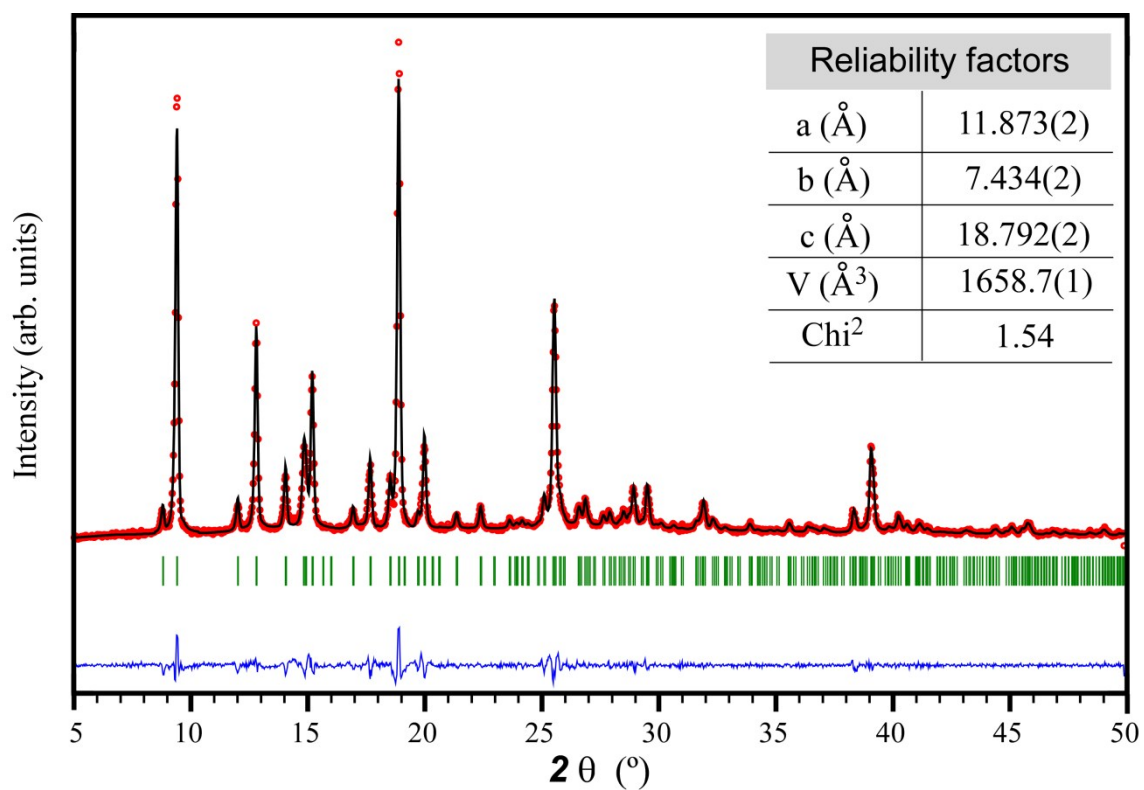
Figure S6. Full profile pattern-matching analysis of **4**.

Reliability factors	
a (Å)	26.772(2)
b (Å)	7.866(2)
c (Å)	15.667(2)
β (º)	117.52(3)
V (Å³)	2926.3(2)
Chi²	1.70
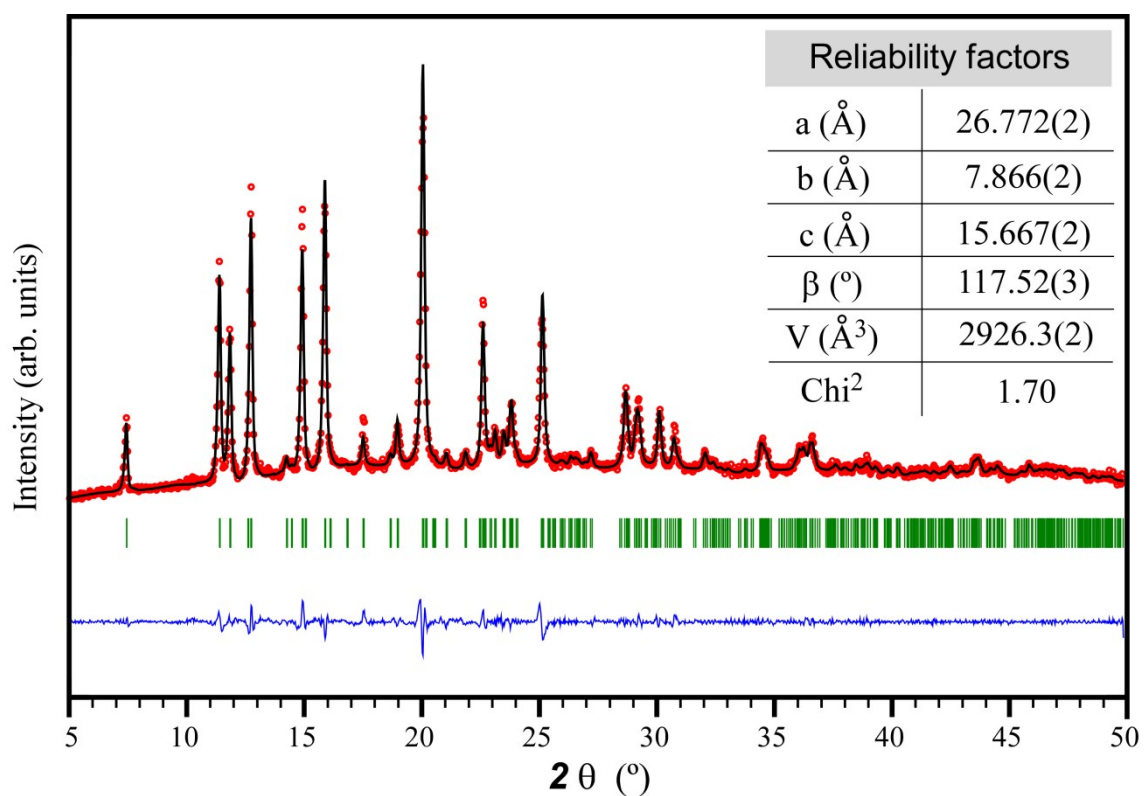
Figure S7. Full profile pattern-matching analysis of **5**.

Reliability factors	
a (Å)	26.874(2)
b (Å)	7.918(2)
c (Å)	15.880(2)
β (º)	117.84(3)
V (Å^3)	2988.1(2)
Chi^2	2.20
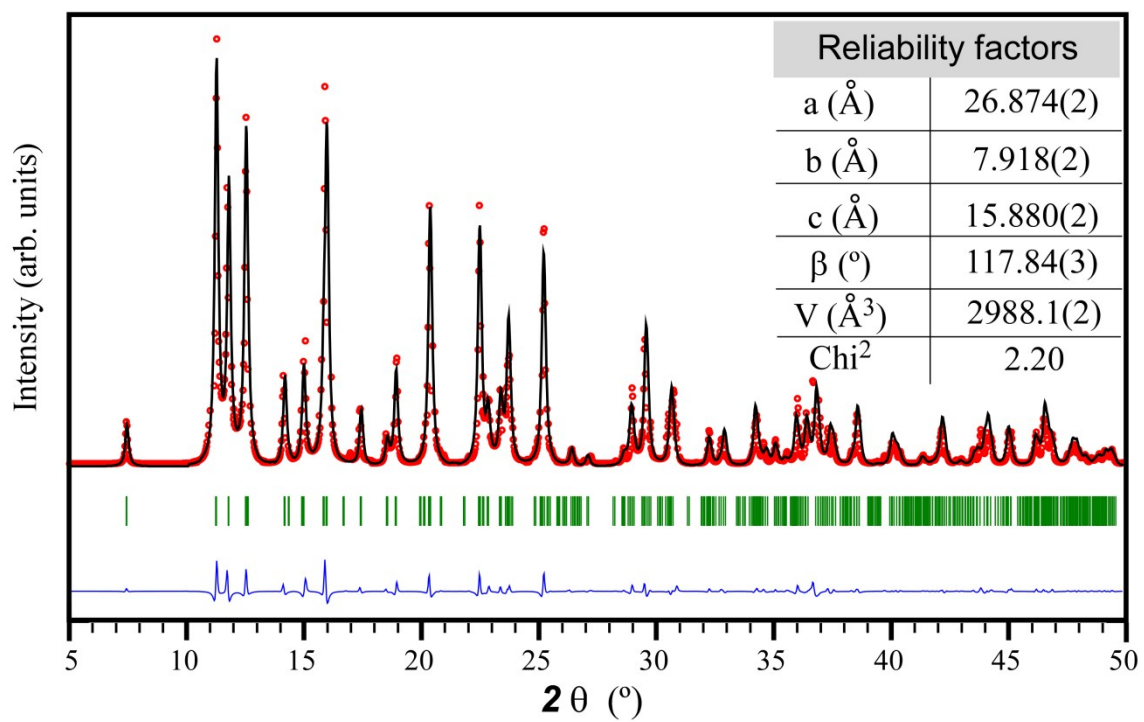
Figure S8. Full profile pattern-matching analysis of **6**.

S4. Thermogravimetric Analysis.
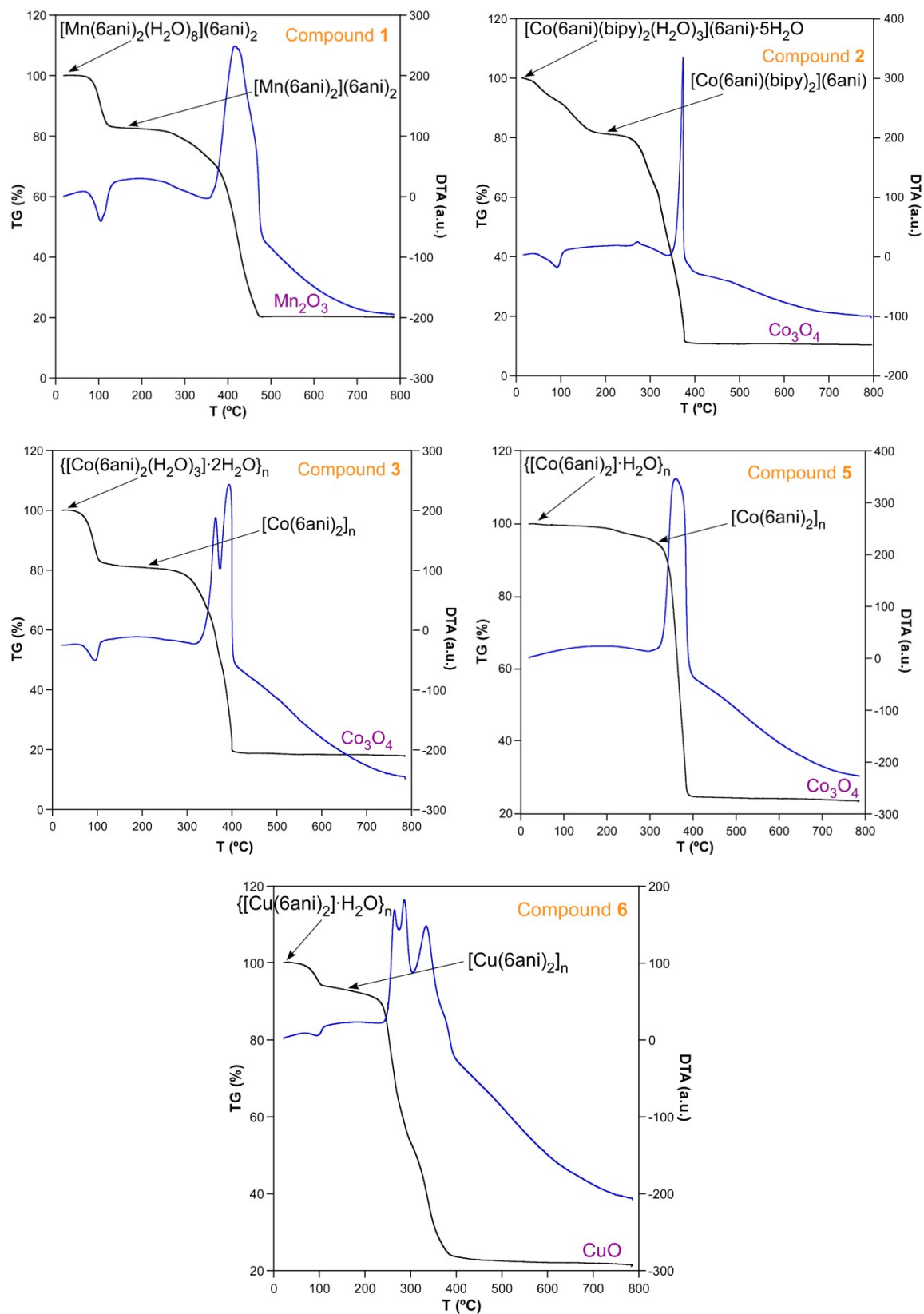
Figure S9. TG/DTA analysis for compounds **1–3**, **5**, and **6**.

S5. FT-IR spectroscopy.

All compounds show the presence of the bands assigned to the vibrations and displacements of the coordinated 6ani ligand. In compound **2**, there are additional bands attributed to 4,4'-bipyridine ligand. Assignations of the spectra were performed according to bibliography of compounds based on 6ani ligands. At high frequencies, all spectra exhibitan intense band at 3400 cm^{-1} that corresponds to the vibration of the O–H bond of coordinated and lattice watermolecules of the compounds, followed by a strong vibration at 3310–3280 cm^{-1}range related with N–H vibrations of the exocyclic amino group of 6ani. Weak shoulders between 3100 and 2900 cm^{-1}are attributed to C–H vibrations of the pyridinic ring of 6aniligand and 4,4'-bipyridine ligand in the spectrum of **2**. The intense vibrations in the 1670–1520 cm^{-1} region correspond to both the asymmetric stretching vibrations of the carboxylate groups and the aromatic C–C and C–N bonds, while the symmetric stretching vibrations of the carboxylate groups occur in the lower range of 1410–1270cm^{-1}. It is worth noting the presence of strong band peaking at 1540 cm^{-1}and a very wide band at 1385 cm^{-1}corresponding to the stretching vibrations of aromatic C–C and C–N bonds of 4,4'-bipyridine in compound **2**. At lower frequencies, the remaining bands are assigned to the distortions originated in the aromatic ring and the carboxylate groups of the 6ani ligand. The vibration bands of the M–O and M–N bonds are observed around 560–530 cm^{-1} and around 400 cm^{-1}.

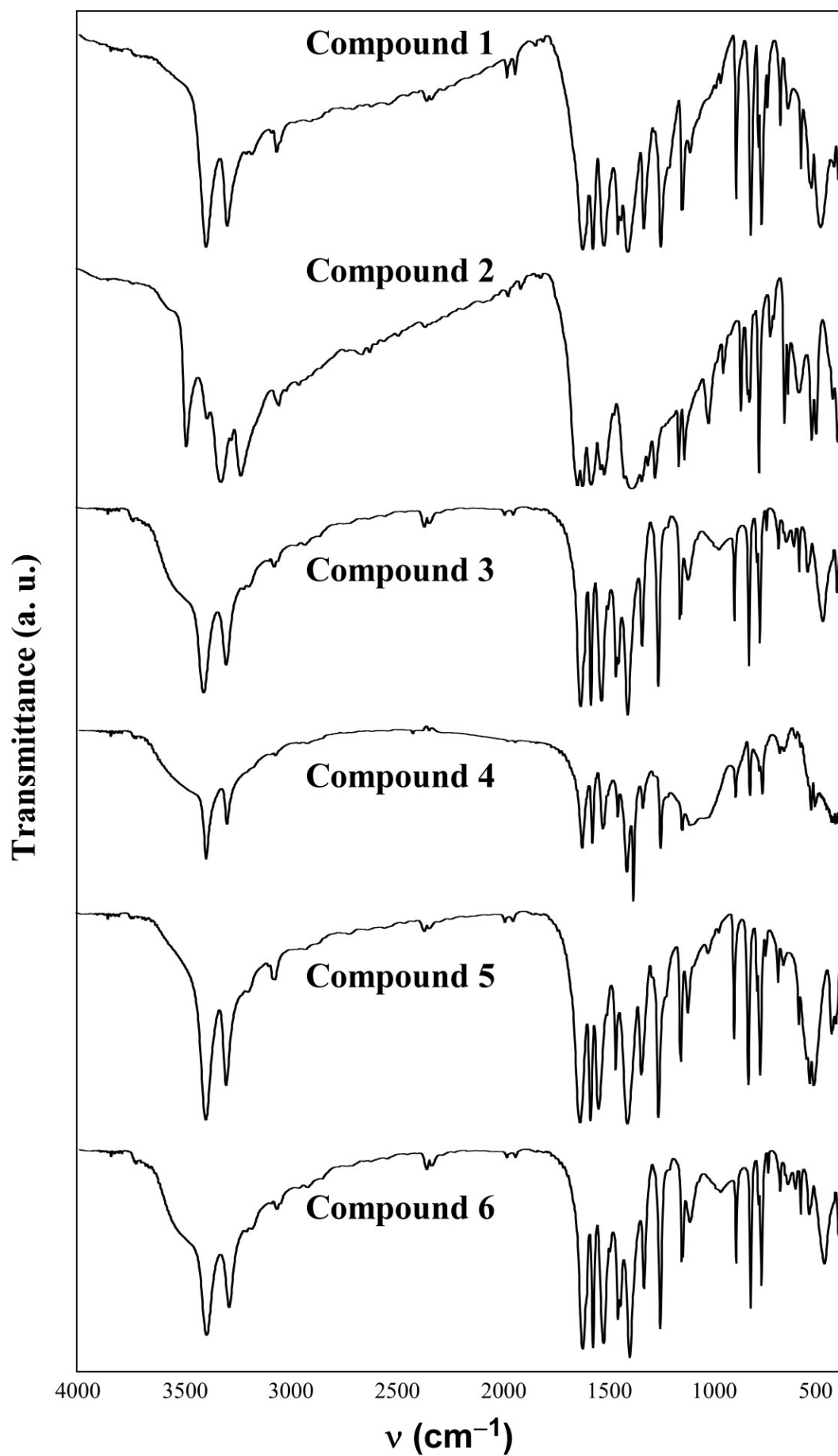**Figure S10.** FTIR spectra of all compounds.

S6. *Ac* magnetic susceptibility measurements.

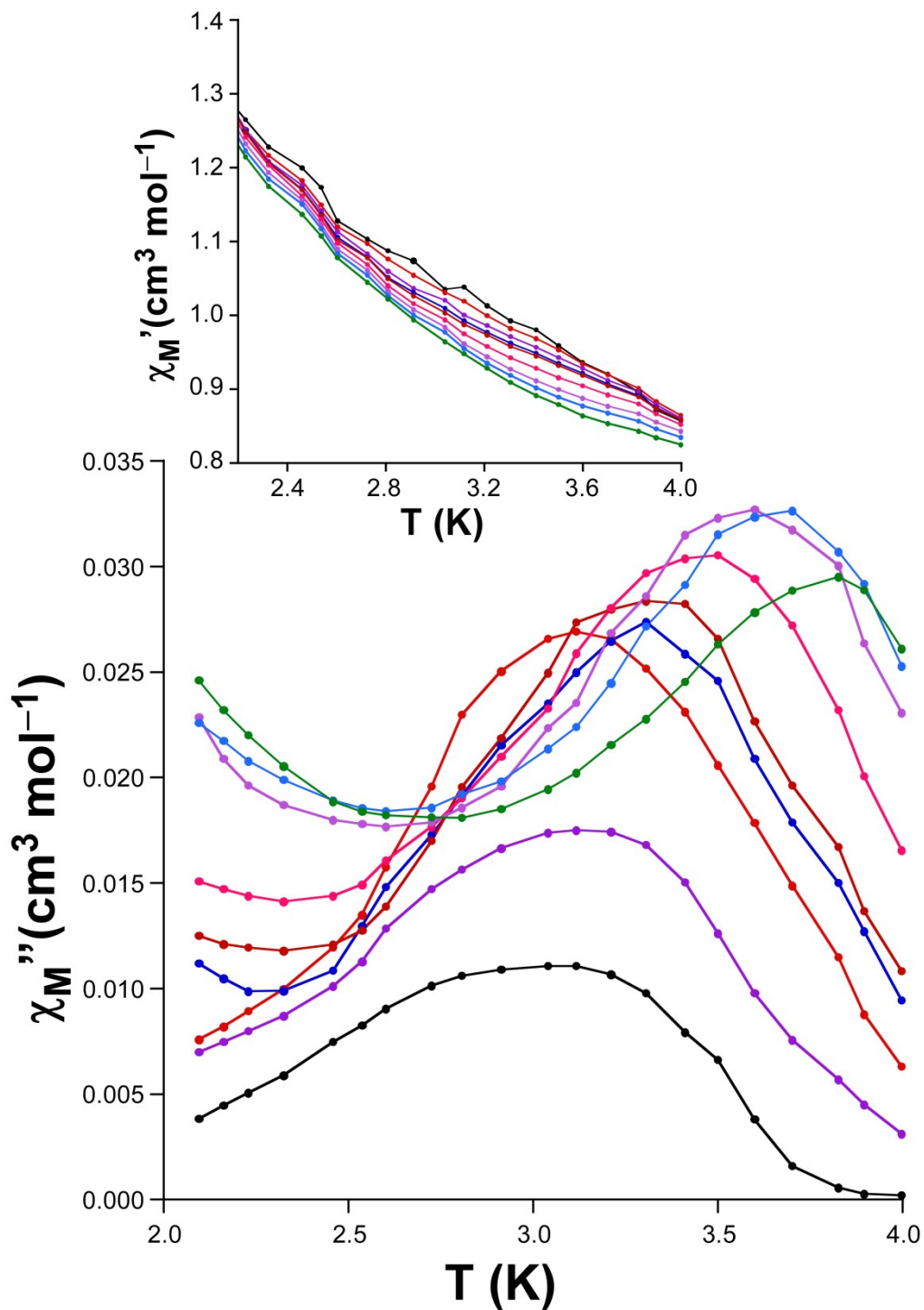**Figure S11.** Temperature dependence of the χ_M' and χ_M'' signals for compound **2** under an applied field of 1000 Oe.
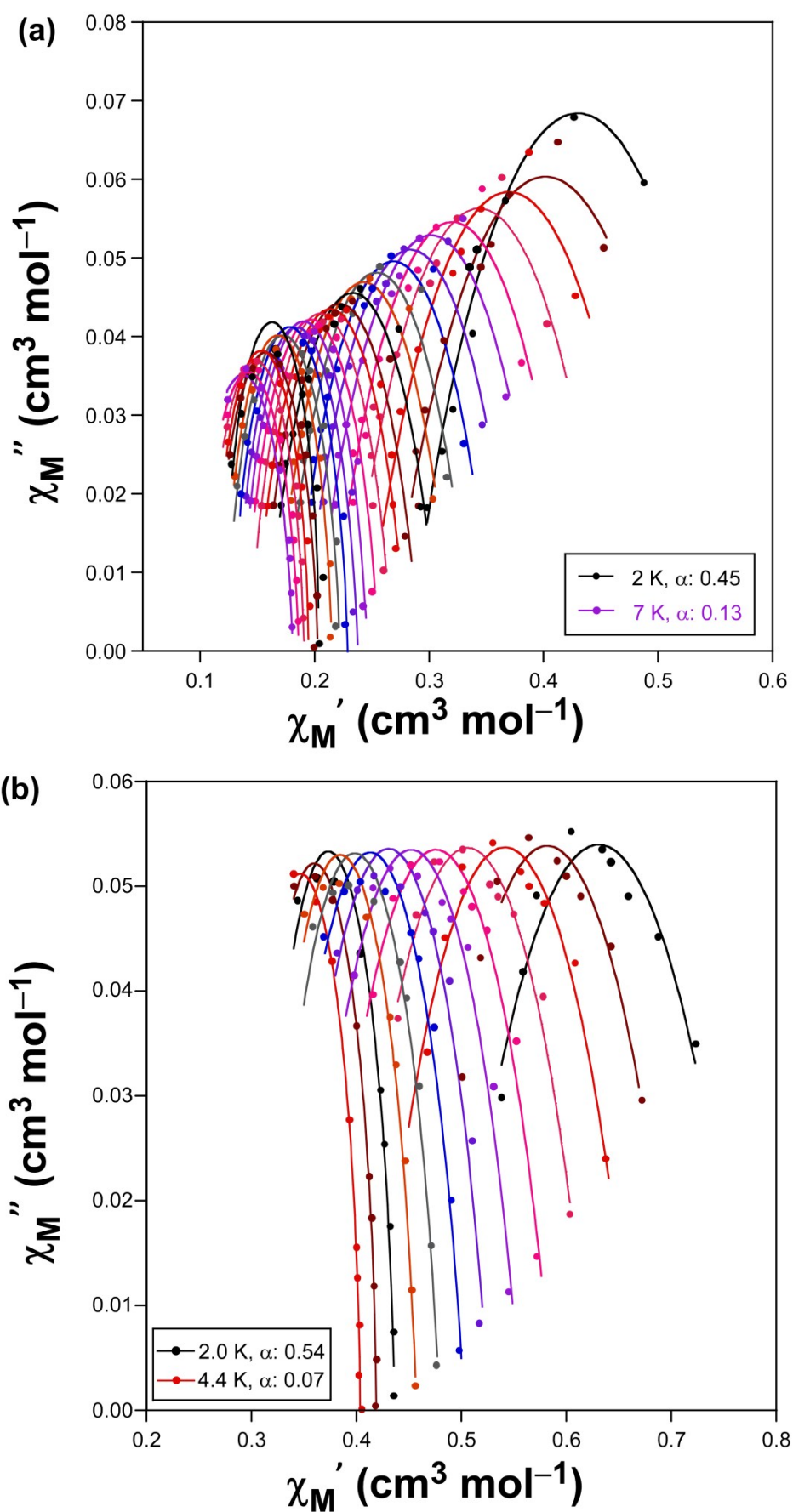
Figure S12. Cole-Cole plots for compounds **(a) 3** and **(b) 5** with an applied field of 1 KOe.
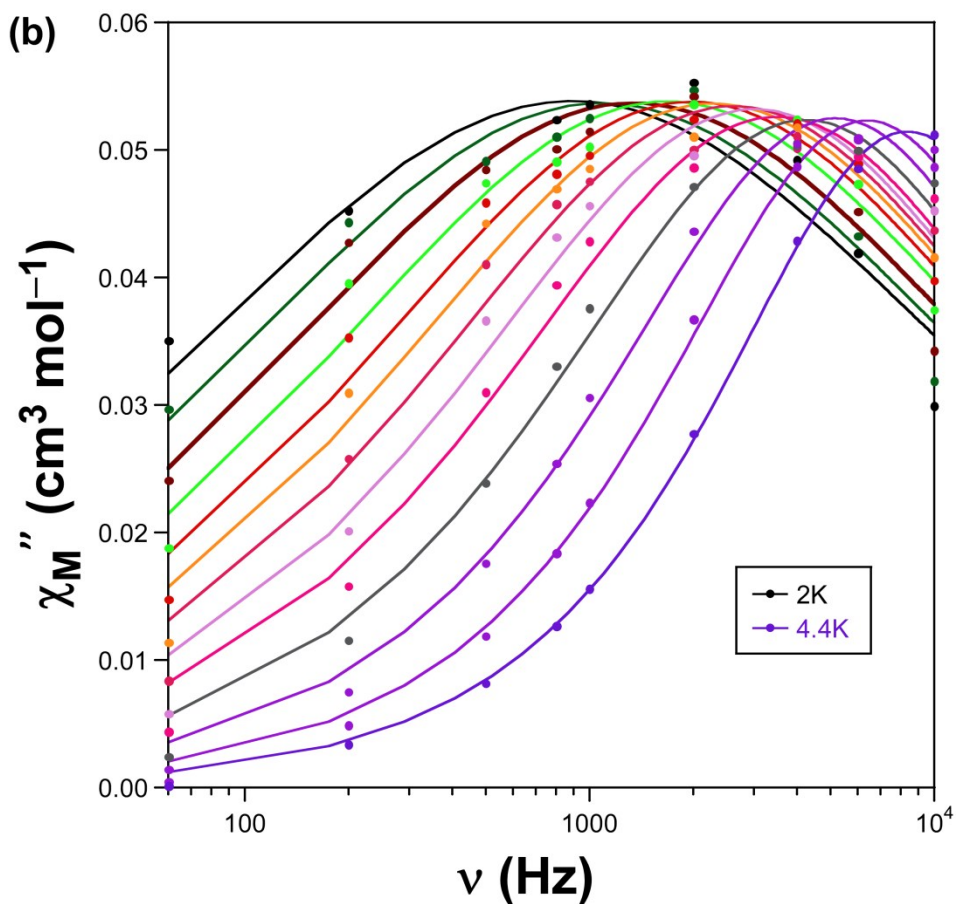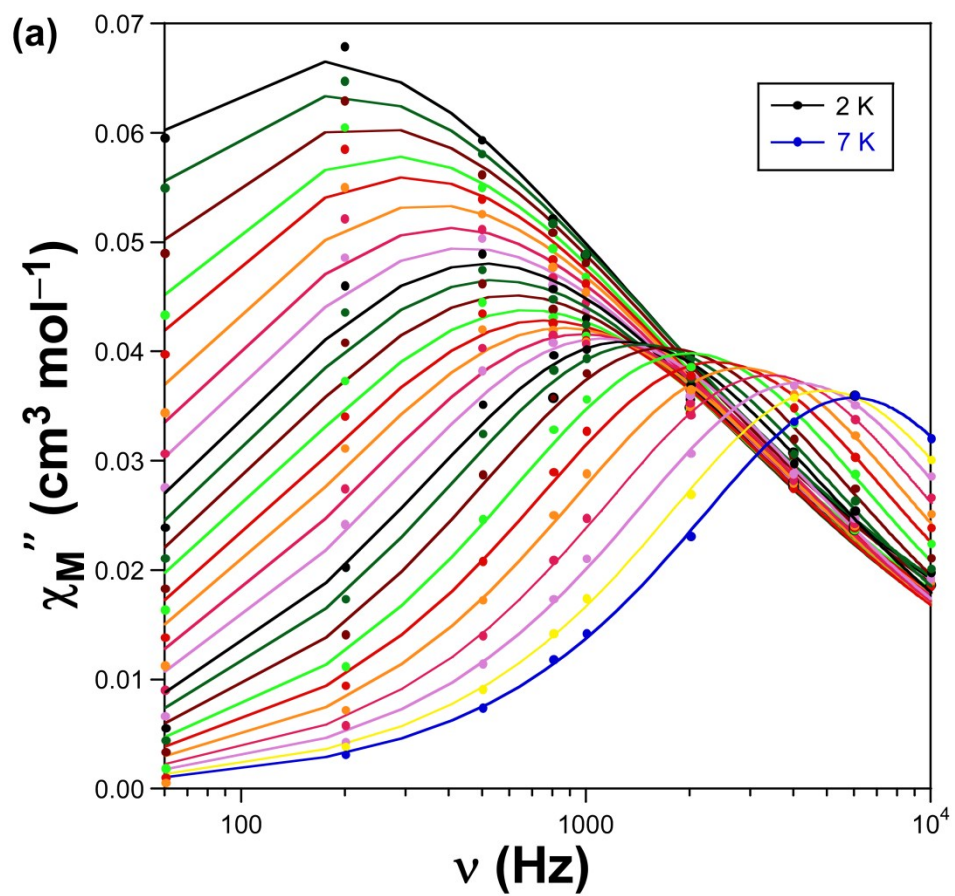
Figure S13. Variable-temperature frequency dependence of the χ_M'' signal for compounds **(a) 3** and **(b) 5** with an applied field of 1 KOe.

S7. *Dc* magnetic susceptibility measurements.
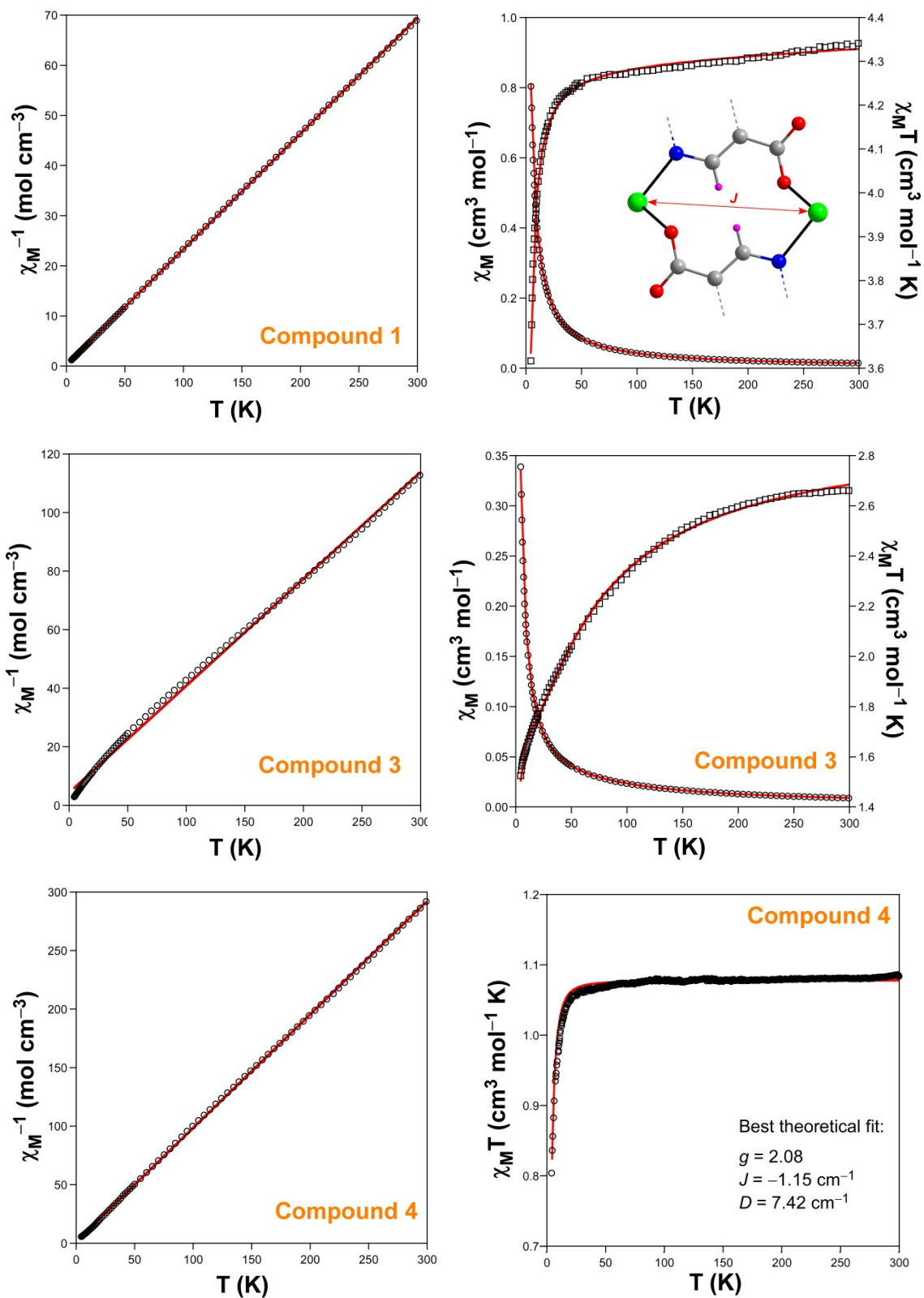
Figure S14. χ_M^{-1} vs T and $\chi_M T$ vs T plots of compounds **1**, **3**, and **4** showing best theoretical fits (red line).
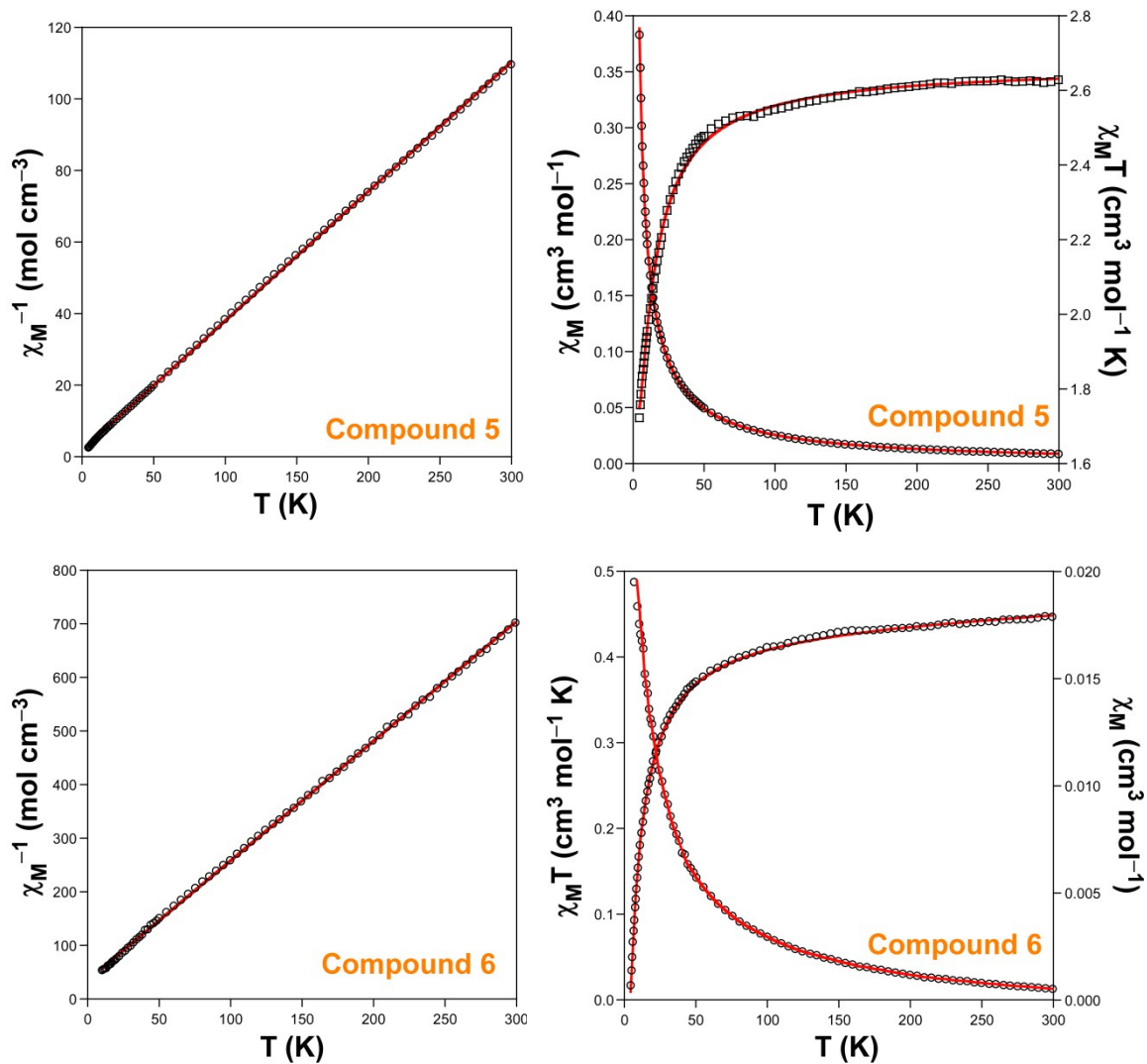
Figure S15. χ_M^{-1} vs T and $\chi_M T$ vs T plots of compounds **5** and **6** showing best theoretical fits (red line).

S8. Spin densities of broken symmetry calculations.

Calculations of the coupling constants through the broken symmetry strategy for all compounds have been performed upon models based on dimeric entities grown from crystallographic coordinates of X-ray crystal structures. Bridging and terminal ligands have been simplified replacing them by simpler molecules. For instance, bridging carboxylate 6ani ligands have been replaced by acetate ligands and aromatic nitrogen atoms of 6ani ligands by ammonium molecules.
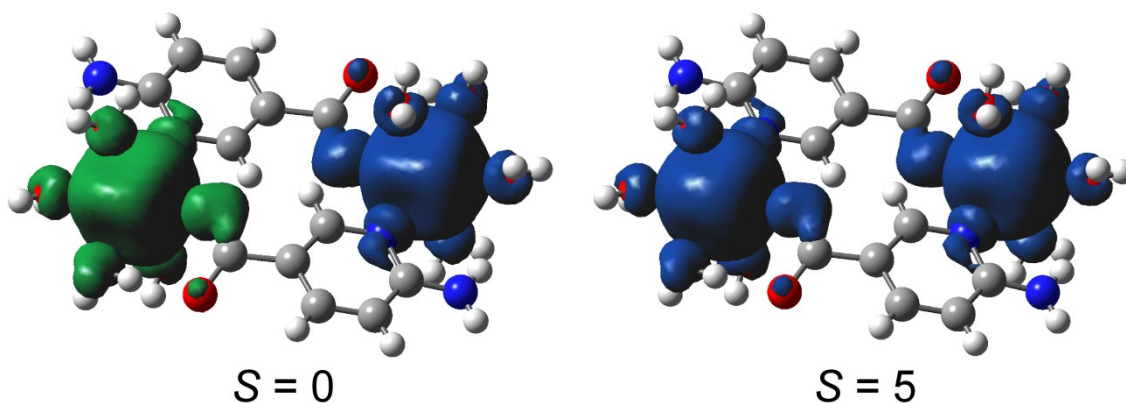

$S = 0$ $S = 5$

Figure S16. Calculated low and high spin density distributions for the simple superexchange pathway for a suitable model of **1**.
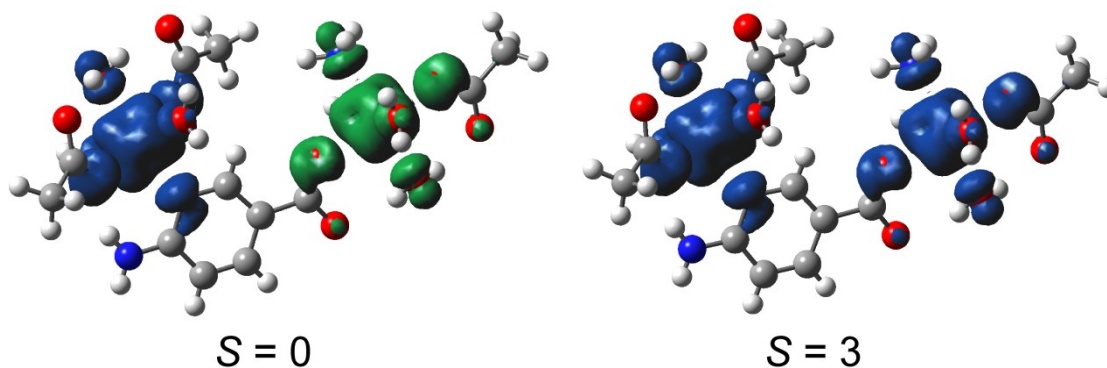

$S = 0$ $S = 3$

Figure S17. Calculated spin density distributions for a suitable model of the 1D chain of **3**.
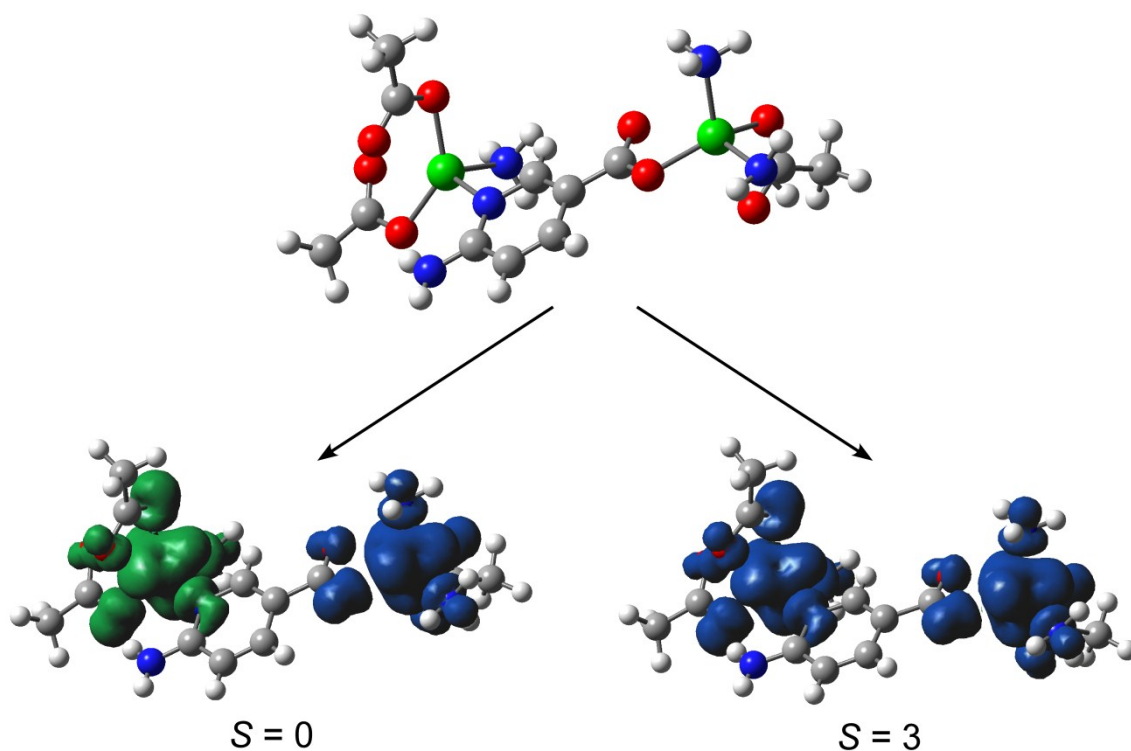
Figure S18. Calculated low- and high-spin density distributions for the dimeric entity for a suitable model of **5**.
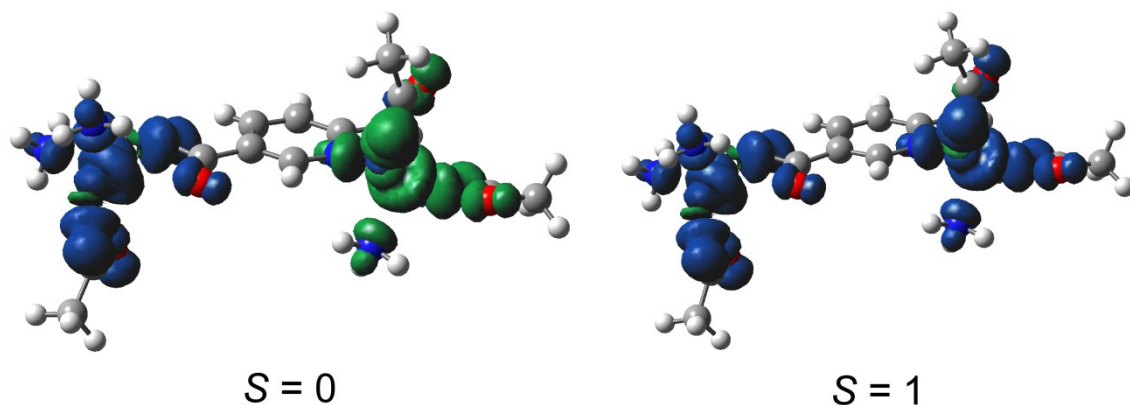

Figure S19. Calculated low- and high-spin density distributions for the dimeric entity for a suitable model of **6**.