ELECRONIC SUPPLEMENTAR INFORMATION (ESI)

Slow magnetic relaxation in penta-coordinate cobalt(II) field-induced single-ion magnets (SIMs) with easy-axis magnetic anisotropy†

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† Electronic supplementary information (ESI) available: Crystallographic data for selected bond parameters for compounds **1** and **2** are summarized in Tables S1 and S2 as well as the corresponding non-covalent interactions are shown in Tables S3 and S4, respectively. The computational details are given in tables S5–S8. X-ray powder diffractions of the two compounds and packing views are given in Figs S1-S4. The magnetic properties of the complexes are represented in Figs S5-S8. Selected spectral data for Ligands and their complexes are illustrated in Figs. S9-S11, and S12-S13, respectively. The solid state UV/Vis spectra are shown in Figs. S14 and S15. Also, the CCDC deposition numbers are CCDC-1994620 for **1** and CCDC-1994621 for **2**. For ESI and crystallographic data in CIF or other electronic format see DOI:

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Table S1 Selected bond distances (Å) and bond angles (°) of **1**.

Co1-N7	2.029(5)	Co1-N1	2.052(5)
Co1-N6	2.060(5)	Co1-N4	2.077(5)
Co1-N3	2.217(4)	S1-C23	1.636(6)
N7-C23	1.146(7)	N7-Co1-N1	106.94(19)
N7-Co1-N6	92.96(19)	N1-Co1-N6	104.26(19)
N7-Co1-N4	90.14(19)	N1-Co1-N4	100.74(19)
N6-Co1-N4	152.69(19)	N7-Co1-N3	158.76(19)
N1-Co1-N3	93.08(18)	N6-Co1-N3	88.80(17)
N4-Co1-N3	78.97(19)	C23-N7-Co1	170.2(5)
N7-C23-S1	179.0(6)		

Table S2 Selected bond distances (Å) and bond angles (°) of **2**.

Co1-N6	2.022(4)	Co1-N7	2.037(4)
Co1-N4	2.044(4)	Co1-N1	2.060(4)
Co1-N2	2.311(3)	Co2-N12	2.012(4)
Co2-N13	2.026(3)	Co2-N10	2.040(4)
Co2-N9	2.061(3)	Co2-N8	2.289(4)
S1-C24	1.630(4)	C24-N7	1.163(5)
S2-C25	1.633(7)	C25-N12	1.175(8)
N6-Co1-N7	99.57(14)	N6-Co1-N4	111.16(14)
N7-Co1-N4	94.34(14)	N6-Co1-N1	127.74(14)
N7-Co1-N1	95.94(14)	N4-Co1-N1	117.01(14)
N6-Co1-N2	87.43(13)	N7-Co1-N2	172.49(13)
N4-Co1-N2	85.57(13)	N1-Co1-N2	77.50(13)
N12-Co2-N13	98.92(15)	N12-Co2-N10	94.74(16)
N13-Co2-N10	113.34(14)	N12-Co2-N9	95.23(16)
N13-Co2-N9	128.07(14)	N10-Co2-N9	114.89(14)
N12-Co2-N8	172.14(14)	N13-Co2-N8	87.53(13)
N10-Co2-N8	86.74(13)	N9-Co2-N8	77.18(13)
C24-N7-Co1	168.6(3)	C25-N12-Co2	161.1(5)
N12-C25-S2	175.7(6)	N7-C24-S1	179.3(4)

Table S3: Non-covalent interactions in **1**.

5-Membered Ring (1) N1 --> N2 --> C1 --> C2 --> C5
5-Membered Ring (2) N5 --> N6 --> C12 --> C11 --> C10
6-Membered Ring (3) N4 --> C16 --> C17 --> C18 --> C19 --> C20

Analysis of Ring…Ring Interactions (Cg-Cg < 6 Å, Alpha < 20 °,Beta < 60 °)

- Cg(I),Cg(J) = Center of gravity of ring with plane number I (resp. J) (= ring number in () above)
- Alpha = Dihedral angle between planes I and J (°)
- Beta = Angle Cg(I) --> Cg(J) or Cg(I) --> Me vector and normal to plane I (°)
- Gamma = Angle Cg(I) --> Cg(J) vector and normal to plane J (°)
- Cg-Cg = Distance between ring centroids (Å)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Å)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Å)

Cg(I)	Cg(J)[ARU(J)]	Cg-Cg	Alpha	Beta	Gamma	CgI_Perp	CgJ_Perp
Cg1	Cg2 [1555]	4.739(3)	67.7(3)	35.7	56.7	2.598(2)	3.847(2)
Cg2	Cg1 [1555]	4.739(3)	67.7(3)	56.7	35.7	3.847(2)	2.598(2)
Cg3	Cg1 [1555]	5.297(3)	62.9(3)	49.5	68.3	1.955(2)	3.443(2)
Cg3	Cg3 [4564]	5.669(3)	23.0(3)	45.4	36.2	4.573(2)	3.981(2)
Cg3	Cg3 [4565]	5.670(3)	23.0(3)	36.2	45.4	3.982(2)	4.574(2)

Translation of ARU-Code to CIF and Equivalent Position Code
[1555] = X,Y,Z
[4564] = X,3/2-Y,-1/2+Z
[4565] = X,3/2-Y,1/2+Z

Analysis of X-H...Cg(π-Ring) Interactions (H..Cg < 3 Å Gamma < 40 °)

- Cg(J) = Center of gravity of ring J (Plane number above)
- H-Perp = Perpendicular distance of H to ring plane J
- Gamma = Angle between Cg-H vector and ring J normal
- X-H..Cg = X-H-Cg angle (degrees)
- X..Cg = Distance of X to Cg (Angstrom)
- X-H, Pi = Angle of the X-H bond with the Pi-plane (Perp. = 90 °,Par. = 0 °)

X--H(I)	Cg(J) [ARU(J)]	H..Cg	H-Perp	Gamma	X-H..Cg	X..Cg	X-H,Pi
C14-H14A	Cg1 [1555]	2.87	2.67	21.25	159	3.797(7)	66

Translation of ARU-Code to CIF and Equivalent Position Code
[1555] = X,Y,Z

Analysis of Y-X...Cg(π-Ring) Interactions (X..Cg < 4 Å Gamma < 30 °)

Y--X(I)	Cg(J)[ARU(J)]	X..Cg	X-Perp	Gamma	Y-X Cg	Y..Cg	Y-X,Pi
C23-S1	Cg2 [1655]	3.511(3)	-3.410	13.76	144.6(2)	4.937(6)	52.28
Cl1-O1	Cg1 [3565]	3.512(12)	-3.096	28.16	148.2(7)	4.779(3)	34.98
Cl1-O9	Cg3 [2645]	3.76(3)	3.380	25.88	125.5(14)	4.667(3)	22.33
Cl1-O10	Cg1 [3565]	3.69(3)	-3.220	29.00	138.9(18)	4.779(3)	30.82

Translation of ARU-Code to CIF and Equivalent Position Code
[1655] = 1+X,Y,Z
[3565] = -X,1-Y,-Z

[2645] = 1-X,-1/2+Y,1/2-Z

The Cg(I) refer to the ring Centre-of-Gravity numbers given in ()

Cg(I)	x	y	z
Cg1	0.2287(3)	0.58066(8)	-0.0173(2)
Cg2	0.2398(3)	0.56339(8)	0.4134(2)
Cg3	0.5267(2)	0.72563(8)	0.1123(2)

Analysis of Potential Hydrogen Bonds and Schemes

(d(D...A) < R(D) + R(A) + 0.50 Å, d(H...A) < R(H) + R(A) - 0.12 Å, D-H...A > 100.0 °)

Nr	D--H	Accept	[ARU]	D--H	D-H..A	A..H..A*
1	O7--H7	O2	[1555]	2.963(14)	154	
2	O7--H7	O8	[1555]	3.15(3)	149	43'
3	O7--H7	O11	[1555]	3.12(2)	134"	21"
4	C7--H7A	S1	[1455]	3.689(6)	159	
5	C7--H7B	O11	[3565]	3.37(2)	161	
6	C8--H8A	O5	[4565]	3.143(7)	123	
7	C8--H8B	O8	[3566]	3.47(2)	160	
8	C13--H13A	O1	[3566]	3.337(12)	134	
9	C14--H14B	O7	[1555]	3.385(8)	162	
10	C15--H15B	O5	[1555]	2.872(7)	102	
11	C15--H15B	O4	[2555]	3.533(10)	166'	85'
12	C19--H19	O3	[3665]	3.441(10)	174	
13	C19--H19	O11	[3665]	3.17(2)	123'	53'
14	C21--H21A	O4	[2655]	3.311(11)	157	
15	C21--H21A	O8	[2655]	3.05(2)	130'	34'
16	C21--H21C	O9	[3665]	3.25(3)	131	
17	C22--H22C	O2	[2655]	3.388(12)	163	

Translation of ARU-Code to CIF and Equivalent Position Code

[3565] = -X,1-Y,-Z
[4565] = X,3/2-Y,1/2+Z
[1455] = -1+X,Y,Z
[3566] = -X,1-Y,1-Z
[2655] = 1-X,1/2+Y,1/2-Z
[3665] = 1-X,1-Y,-Z
[2555] = -X,1/2+Y,1/2-Z

Table S4: Non-covalent interactions in **2**.

5-Membered Ring (1) N10 --> N11 --> C37 --> C36 --> C39
5-Membered Ring (2) N13 --> N14 --> C43 --> C45 --> C46
6-Membered Ring (3) N9 --> C28 --> C26 --> C29 --> C31 --> C33
5-Membered Ring (4) N3 --> N4 --> C15 --> C13 --> C12
5-Membered Ring (5) N5 --> N6 --> C20 --> C22 --> C19
6-Membered Ring (6) N1 --> C1 --> C4 --> C3 --> C8 --> C9

Analysis of Ring-Ring Interactions (Cg-Cg < 6 Å, Alpha < 20 °, Beta < 60 °)

- Cg(I), Cg(J) = Center of gravity of ring with plane number I (resp. J) (= ring number in () above)
- Alpha = Dihedral Angle between Planes I and J (°)
- Beta = Angle Cg(I) --> Cg(J) or Cg(I)-->Me vector and normal to plane I (°)
- Gamma = Angle Cg(I) --> Cg(J) vector and normal to plane J (°)
- Cg-Cg = Distance between ring Centroids (Å)
- CgI_Perp = Perpendicular distance of Cg(I) on ring J (Å)
- CgJ_Perp = Perpendicular distance of Cg(J) on ring I (Å)

Cg(I)	Cg(J) [ARU(J)]	Cg-Cg	Alpha	Beta	Gamma	CgI_Perp	CgJ_Perp
Cg1	Cg5 [2665]	5.429(3)	55.5(3)	13.8	65.5	2.2518(19)	5.2730(19)
Cg3	Cg1 [1555]	5.436(3)	86.7(2)	53.3	65.6	2.2445(18)	3.2456(18)
Cg3	Cg6 [1655]	5.456(3)	26.4(2)	33.9	53.0	3.2814(18)	4.5266(18)
Cg4	Cg2 [2666]	5.380(3)	54.4(3)	12.0	65.2	2.2561(19)	5.2620(19)
Cg6	Cg3 [1455]	5.456(3)	26.4(2)	53.0	33.9	4.5266(18)	3.2815(18)
Cg6	Cg4 [1555]	5.522(3)	89.0(2)	55.3	66.8	2.1792(18)	3.1413(18)

Translation of ARU-Code to CIF and Equivalent Position Code
[2665] = 1-X,1-Y,-Z
[1555] = X,Y,Z
[1655] = 1+X,Y,Z
[2666] = 1-X,1-Y,1-Z
[1455] = -1+X,Y,Z
[1555] = X,Y,Z

Analysis of X-H...Cg(π-Ring) Interactions (H..Cg < 3.0 Å, Gamma < 40 °)

- Cg(J) = Center of gravity of ring J (Plane number above)
- H-Perp = Perpendicular distance of H to ring plane J
- Gamma = Angle between Cg-H vector and ring J normal
- X-H..Cg = X-H-Cg angle (°)
- X..Cg = Distance of X to Cg (Å)
- X-H, π = Angle of the X-H bond with theπ-plane (Perp. = 90 °, Par. = 0 °)

X--H(I)	Cg(J) [ARU(J)]	H..Cg	H-Perp	Gamma	X-H..Cg	X..Cg	X-H,Pi
C23-H23A	Cg1 [2665]	2.75	-2.65	15.33	133	3.495(5)	53
C35-H35B	Cg3 [1555]	2.98	-2.47	33.86	152	3.880(5)	30
C44-H44A	Cg4 [2666]	2.80	2.60	21.61	131	3.520(5)	53

Translation of ARU-Code to CIF and Equivalent Position Code
[2665] = 1-X,1-Y,-Z
[1555] = X,Y,Z

[2666] = 1-X,1-Y,1-Z

Analysis of Y-X...Cg(π-Ring) Interactions (X..Cg < 4.0 Å - Gamma < 30.0 °)

Y--X(I)	Cg(J) [ARU(J)]	X..Cg	X-Perp	Gamma	Y-X..Cg	Y..Cg	Y-X,Pi
C24-S1	Cg2 [2666]	3.744(2)	3.669	11.47	80.06(18)	3.816(5)	0.88
C25-S2	Cg5 [2665]	3.574(3)	-3.546	7.11	91.1(3)	3.958(7)	5.24
C49-S3	Cg6 [1655]	3.712(5)	-3.595	14.41	103.3(5)	4.385(16)	24.13
Cl1-O2	Cg6 [1655]	3.913(5)	3.541	25.16	118.2(2)	4.757(2)	51.17
Cl1-O3	Cg1 [1565]	3.526(5)	3.249	22.85	139.3(2)	4.699(2)	66.26
Cl2-O5	Cg3 [1555]	3.922(5)	-3.450	28.41	120.3(2)	4.809(2)	57.05
Cl2-O8	Cg4 [1545]	3.463(4)	-3.256	19.89	145.9(2)	4.716(2)	70.09

[2666] = 1-X,1-Y,1-Z
[2665] = 1-X,1-Y,-Z
[1655] = 1+X,Y,Z
[1565] = X,1+Y,Z
[1555] = X,Y,Z
[1545] = X,-1+Y,Z

The Cg(I) refer to the Ring Centre-of-Gravity numbers given in ()

Cg(I)	x	y	z
Cg1	0.71278(16)	0.08252(12)	0.18014(12)
Cg2	0.94498(16)	0.29634(12)	0.42166(12)
Cg3	0.49043(16)	0.34185(12)	0.26430(12)
Cg4	0.16866(16)	0.92528(12)	0.32348(12)
Cg5	0.26404(16)	0.70668(12)	0.08822(12)
Cg6	-0.21543(16)	0.66370(12)	0.23740(12)

Analysis of Potential Hydrogen Bonds and Schemes
(d(D...A) < R(D) + R(A) + 0.50 Å, d(H...A) < R(H) + R(A)-0.12 Å, D-H...A > 100.0 °)

Donor--H	Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
C5--H5A	O10		0.98	2.41	2.862(6)	107
C6--H6A	O2	[1455]	0.98	2.59	3.415(8)	142
C9--H9	N7		0.95	2.56	3.144(6)	120
C11--H11B	N1		0.99	2.58	3.323(6)	132
C14--H14C	O1	[1455]	0.98	2.53	3.478(6)	162
C28--H28	N12		0.95	2.53	3.105(6)	119
C30--H30A	O5	[1555]	0.98	2.53	3.442(7)	155
C32--H32B	O9		0.98	2.56	2.889(6)	100
C35--H35B	N9		0.99	2.54	3.279(6)	131
C38--H38C	O7	[1555]	0.98	2.44	3.382(6)	162

No standard hydrogen bonds found
Translation of ARU-Code to CIF and Equivalent Position Code Translation of ARU-Code
[1455] = -1+X,Y,Z

PLATON Reference: Spek, A.L. (2015) Acta Cryst. C71, 9-18

Table S5 Cartesian coordinates of 1 used for theoretical calculations.

Co	3.31100000	19.09500000	2.33000000
S	7.45500000	16.85700000	3.22500000
O	3.06900000	24.34600000	1.73400000
O	5.19500000	24.52800000	0.10400000
N	2.59000000	18.44800000	0.52100000
N	1.24100000	18.30700000	0.34100000
N	1.62800000	20.50700000	2.63100000
N	4.19500000	20.89100000	1.77500000
N	1.67400000	18.23800000	4.75800000
N	2.43900000	17.83200000	3.70500000
N	5.14500000	18.26000000	2.56900000
C	0.95100000	17.33100000	-0.54200000
C	2.16800000	16.82500000	-0.95900000
H	2.30300000	16.11400000	-1.57500000
C	-0.43600000	16.95300000	-0.91400000
H	-0.96300000	16.80600000	-0.10100000
H	-0.42000000	16.13200000	-1.44700000
H	-0.84000000	17.67600000	-1.43900000
C	4.63700000	17.41300000	-0.44800000
H	5.07600000	18.20200000	-0.06600000
H	4.86900000	17.33900000	-1.39700000
H	4.93900000	16.61000000	0.02600000
C	3.15400000	17.55000000	-0.30500000
C	0.85100000	20.56400000	1.36000000
H	1.44000000	20.90500000	0.64200000
H	0.10800000	21.20700000	1.47100000
C	0.27800000	19.23800000	0.92000000
H	-0.14600000	18.80400000	1.70300000
H	-0.43300000	19.40900000	0.25400000
C	1.41900000	19.64800000	4.96600000
H	2.27800000	20.11900000	5.11100000
H	0.86700000	19.76500000	5.78000000
C	0.70200000	20.26400000	3.77900000
H	-0.02600000	19.65900000	3.48800000
H	0.29200000	21.12200000	4.05500000
C	1.21800000	17.19200000	5.47000000
C	1.72700000	16.07400000	4.88200000
H	1.60000000	15.17800000	5.16900000
C	2.46700000	16.49300000	3.77900000
C	0.32200000	17.34600000	6.64800000
H	0.74500000	17.93700000	7.30500000
H	0.16100000	16.46800000	7.05300000
H	-0.53100000	17.73400000	6.36100000
C	3.18000000	15.64000000	2.78700000
H	3.00600000	15.97500000	1.88300000
H	2.85800000	14.71700000	2.86100000
H	4.14200000	15.66500000	2.96700000

C	2.26100000	21.83000000	2.86000000
H	2.51700000	21.91100000	3.81200000
H	1.60900000	22.54600000	2.65600000
C	3.48500000	22.01100000	1.99800000
C	3.83200000	23.24200000	1.48600000
C	4.95800000	23.32400000	0.64200000
C	5.70600000	22.17800000	0.44200000
H	6.49300000	22.20200000	-0.09000000
C	5.29600000	21.00800000	1.02100000
H	5.82500000	20.23300000	0.88000000
C	6.37700000	24.63400000	-0.72900000
H	7.16700000	24.38300000	-0.20700000
H	6.47200000	25.55600000	-1.04500000
H	6.28800000	24.03100000	-1.49700000
C	3.41500000	25.04600000	2.93100000
H	3.19900000	24.49000000	3.70800000
H	2.90900000	25.88400000	2.97700000
H	4.37500000	25.24400000	2.92700000
C	6.09200000	17.67300000	2.83400000

Table S6 Cartesian coordinates of **2** used for theoretical calculations.

Co	-1.60800000	11.25500000	3.62000000
C	-4.40800000	10.82700000	2.77400000
C	-3.84700000	11.56400000	1.60600000
H	-3.51400000	10.91400000	0.93700000
H	-4.56500000	12.09800000	1.18000000
C	-6.13700000	9.64600000	3.91300000
C	-5.74500000	10.40200000	2.82300000
C	-6.71000000	10.76000000	1.71700000
H	-7.55000000	10.27200000	1.84300000
H	-6.31800000	10.51900000	0.85100000
H	-6.88700000	11.72400000	1.73700000
C	-8.35600000	10.09500000	4.57700000
H	-8.04200000	10.34900000	5.47000000
H	-9.23600000	9.67100000	4.64900000
H	-8.42400000	10.89600000	4.01600000
C	-5.64300000	8.39600000	6.06800000
H	-4.85800000	8.18100000	6.61400000
H	-6.04300000	7.56800000	5.73100000
H	-6.30000000	8.87600000	6.61700000
C	-5.22700000	9.26600000	4.90500000
C	-3.93500000	9.72600000	4.76000000
H	-3.30000000	9.48700000	5.42600000
C	-3.26700000	13.76500000	2.52900000
H	-4.10900000	13.97400000	2.05100000
H	-2.61800000	14.48100000	2.31100000
C	-3.54000000	13.80200000	4.02200000
H	-4.14200000	14.56000000	4.23300000
H	-3.98900000	12.96500000	4.30000000
C	-1.88800000	14.93700000	5.58900000
C	-0.57200000	14.66900000	5.92500000
H	-0.02100000	15.17400000	6.51200000
C	-2.75400000	16.07500000	5.97700000
H	-2.88100000	16.66600000	5.20600000
H	-2.32900000	16.57600000	6.70500000
H	-3.62300000	15.73700000	6.27700000
C	-0.21500000	13.50900000	5.23300000
C	1.10400000	12.79700000	5.17500000
H	1.08800000	12.02900000	5.78600000
H	1.82000000	13.41100000	5.44400000
H	1.26800000	12.48400000	4.26200000
C	-1.90600000	12.78700000	0.80900000
H	-2.28300000	13.58000000	0.35300000
H	-1.94200000	12.02600000	0.17700000
C	-0.45900000	13.06400000	1.17300000
H	-0.03500000	13.60000000	0.45800000
H	-0.42400000	13.58700000	2.01300000
C	1.26200000	11.30400000	0.56600000

C	0.51200000	9.74700000	1.98700000
C	0.24800000	8.46100000	2.70300000
H	0.81900000	8.40700000	3.49800000
H	0.44500000	7.70900000	2.10700000
H	-0.69300000	8.42500000	2.97500000
C	1.44000000	9.99900000	0.98100000
H	2.08000000	9.38500000	0.64100000
C	1.91500000	12.06100000	-0.52400000
H	1.34700000	12.04000000	-1.32300000
H	2.78300000	11.65500000	-0.73100000
H	2.04900000	12.99100000	-0.24400000
C	-0.21500000	9.64700000	5.99300000
N	-3.51700000	10.49200000	3.74000000
N	-2.73500000	12.46800000	2.00800000
N	-2.27700000	13.95400000	4.75600000
N	-1.27100000	13.06000000	4.51700000
N	0.27500000	11.81300000	1.34700000
N	-0.20600000	10.86500000	2.21500000
N	-0.84900000	10.16800000	5.16700000
O	-7.43500000	9.18300000	3.99100000
S	0.68100000	8.90600000	7.13300000

Table S7 Energy levels (cm^{-1}) of ligand field multiplets for **1** and **2** calculated using CASSCF/NEVTP2 in zero magnetic field.

	1	**2**
0	0.0000	0.0000
1	0.0000	0.0000
2	85.6	14.5
3	85.6	14.5
4	1446.9	3519.1
5	1446.9	3519.1
6	1656.2	3667.5
7	1656.2	3667.5
8	2068.0	5019.7
9	2068.0	5019.7
10	2175.9	5146.6
11	2175.9	5146.6
12	5061.0	6143.3
13	5061.0	6143.3
14	5158.5	6288.6
15	5158.5	6288.6
16	9183.2	7083.0
17	9183.2	7083.0
18	9205.3	7187.9
19	9205.3	7187.9
20	9567.6	13136.3
21	9567.6	13136.3
22	10575.4	13204.7
23	10575.4	13204.7
24	10694.5	13413.3
25	10694.5	13413.3
26	14925.4	15215.1
27	14925.4	15215.1
28	16022.3	15475.8
29	16022.3	15475.8
30	16386.1	15507.8
31	16386.1	15507.8
32	16577.0	18521.9
33	16577.0	18521.9
34	16655.8	19261.5
35	16655.8	19261.5
36	19146.0	20369.6
37	19146.0	20369.6
38	19656.4	20441.8
39	19656.4	20441.8
40	20506.2	20650.8
41	20506.2	20650.8
42	20722.0	21561.2
43	20722.0	21561.2
44	20777.8	21904.2

45	20777.8	21904.2
46	20860.6	22380.3
47	20860.6	22380.3
48	21070.5	22872.6
49	21070.5	22872.6
50	21248.6	23021.8
51	21248.6	23021.8
52	22252.2	23163.5
53	22252.2	23163.5
54	23167.0	23363.5
55	23167.0	23363.5
56	23419.4	24201.8
57	23419.4	24201.8
58	24015.5	24258.3
59	24015.5	24258.3
60	25765.3	24442.4
61	25765.3	24442.4
62	25836.5	25526.1
63	25836.5	25526.1
64	27332.3	27331.0
65	27332.3	27331.0
66	28123.5	27822.1
67	28123.5	27822.1
68	28632.9	29385.0
69	28632.9	29385.0
70	29383.7	30577.9
71	29383.7	30577.9
72	30551.3	30939.5
73	30551.3	30939.5
74	31157.3	31957.0
75	31157.3	31957.0
76	32047.2	32429.4
77	32047.2	32429.4
78	32749.8	32641.8
79	32749.8	32641.8
80	33102.7	32987.0
81	33102.7	32987.0
82	33657.1	33142.6
83	33657.1	33142.6
84	34351.9	33601.6
85	34351.9	33601.6
86	34758.2	34565.1
87	34758.2	34565.1
88	35150.6	35153.8
89	35150.6	35153.8
90	36221.6	35527.3
91	36221.6	35527.3
92	36640.1	37447.1
93	36640.1	37447.1

94	37309.1	38121.7
95	37309.1	38121.7
96	41535.3	42422.2
97	41535.3	42422.2
98	43019.5	42733.0
99	43019.5	42733.0
100	43198.8	43123.1
101	43198.8	43123.1
102	44862.0	44360.0
103	44862.0	44360.0
104	45114.3	44983.0
105	45114.3	44983.0
106	45575.7	45210.7
107	45575.7	45210.7
108	45657.8	45553.3
109	45657.8	45553.3
110	62233.7	63746.5
111	62233.7	63746.5
112	63671.2	64102.9
113	63671.2	64102.9
114	66522.7	65137.5
115	66522.7	65137.5
116	66747.9	66378.1
117	66747.9	66378.1
118	68065.9	67141.0
119	68065.9	67141.0

Table S8. Individual contributions to *D*-tensor for **1** and **2** calculated using CASSCF/NEVTP2.

1				**2**			
Multiplicity	Root	*D*	*E*	Multiplicity	Root	*D*	*E*
4	0	0.000	0.000	4	0	0.000	0.000
4	1	-20.124	-6.991	4	1	5.940	-7.511
4	2	-12.000	-7.987	4	2	-8.983	-0.382
4	3	-10.689	1.566	4	3	-10.466	-0.451
4	4	5.504	2.057	4	4	8.477	5.777
4	5	-0.424	-0.132	4	5	-0.602	-0.094
4	6	0.034	0.079	4	6	0.156	0.057
4	7	0.118	-0.038	4	7	-0.002	0.000
4	8	-0.034	0.001	4	8	0.073	-0.001
4	9	-0.096	-0.009	4	9	-0.097	0.002
2	0	-1.463	1.568	2	0	-0.629	0.194
2	1	-0.157	0.015	2	1	0.560	-0.002
2	2	-0.942	0.166	2	2	-0.686	0.373
2	3	-0.204	-0.379	2	3	0.005	0.001
2	4	0.552	0.050	2	4	0.092	0.041
2	5	1.957	-0.009	2	5	-0.532	0.644
2	6	0.499	-0.074	2	6	-1.430	1.620
2	7	-1.300	1.396	2	7	3.052	0.134
2	8	-1.929	-1.701	2	8	-2.557	-2.267
2	9	0.169	-0.055	2	9	-0.085	0.065
2	10	0.010	-0.008	2	10	0.138	0.007
2	11	0.156	0.007	2	11	0.026	0.000
2	12	0.188	-0.004	2	12	-0.141	0.149
2	13	-0.037	0.078	2	13	0.028	0.002
2	14	0.213	-0.001	2	14	0.487	0.021
2	15	0.107	-0.046	2	15	-0.174	-0.002
2	16	-0.158	0.143	2	16	-0.032	-0.044
2	17	-0.292	-0.169	2	17	0.368	0.006
2	18	0.200	-0.004	2	18	-0.067	0.076
2	19	-0.085	0.070	2	19	0.041	-0.003
2	20	-0.577	0.118	2	20	-0.227	-0.137
2	21	0.054	0.054	2	21	-0.092	-0.079
2	22	0.098	0.001	2	22	-0.034	-0.162
2	23	-0.492	-0.208	2	23	-0.220	0.051
2	24	0.148	-0.035	2	24	-0.067	0.085
2	25	-0.059	-0.033	2	25	0.316	0.031
2	26	-0.029	0.077	2	26	0.033	0.007
2	27	0.103	0.018	2	27	-0.011	-0.015
2	28	0.271	-0.048	2	28	0.245	0.001
2	29	-0.051	0.043	2	29	-0.114	-0.037
2	30	-0.098	0.086	2	30	0.089	0.004
2	31	-0.023	-0.028	2	31	-0.080	0.006
2	32	-0.001	-0.001	2	32	0.006	-0.005
2	33	0.126	0.008	2	33	-0.001	-0.000

2	34	-0.024	0.008	2	34	0.001	-0.000
2	35	-0.015	-0.023	2	35	-0.036	0.011
2	36	-0.000	0.000	2	36	-0.002	0.002
2	37	-0.000	-0.002	2	37	-0.004	-0.003
2	38	-0.019	0.019	2	38	0.003	-0.001
2	39	-0.015	0.009	2	39	-0.000	0.007

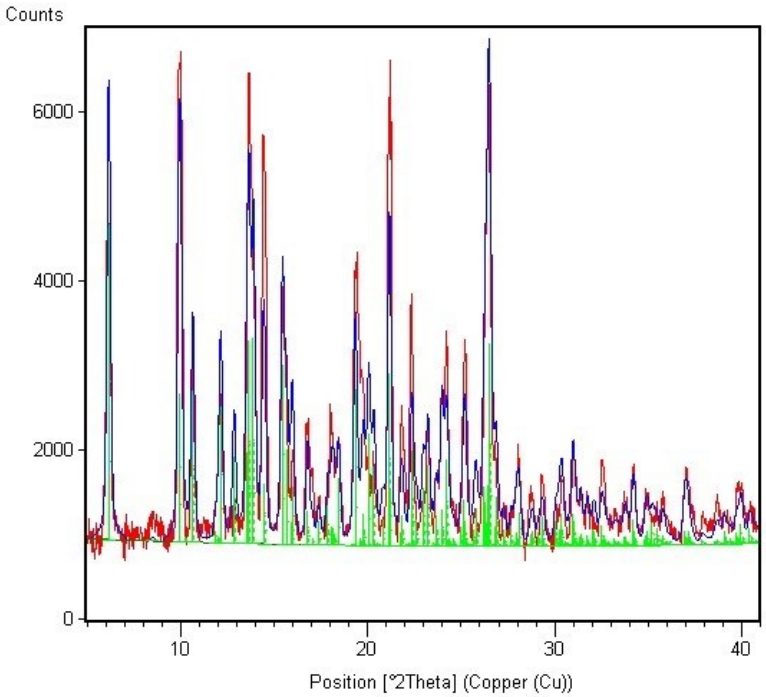

Fig. S1 Comparison of experimental and simulated XRPD spectra of **1**.

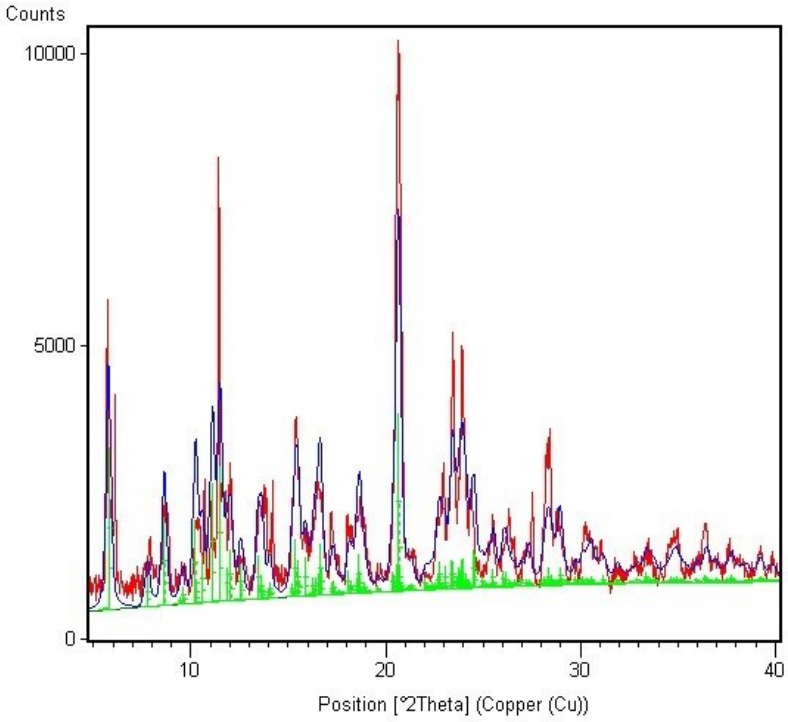

Fig. S2 Comparison of experimental and simulated XRPD spectra of **2**.

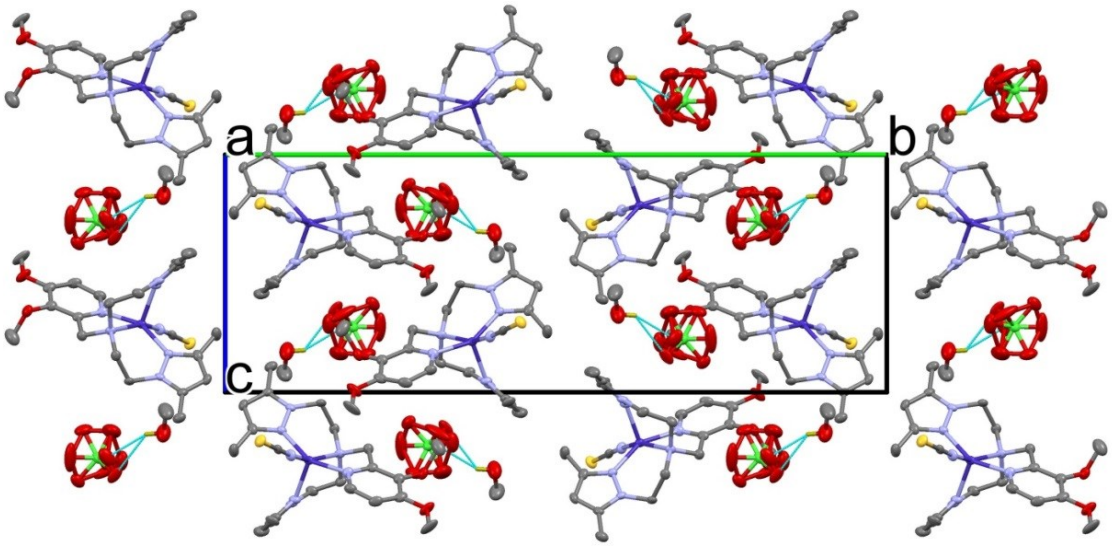

Fig. S3 Packing view of **1.**

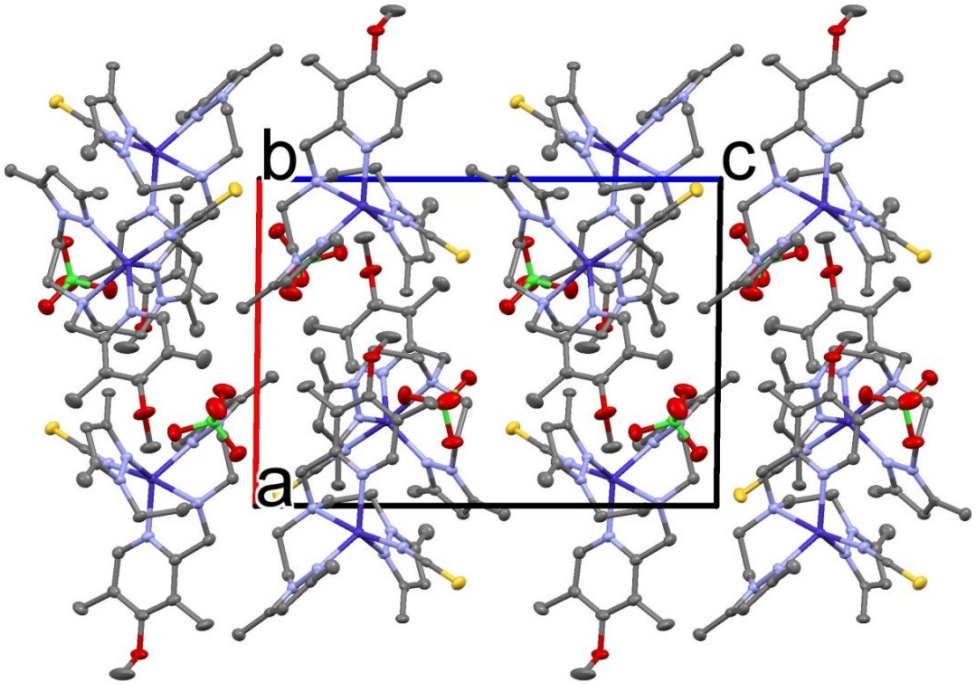

Fig. S4 Packing view of **2.**

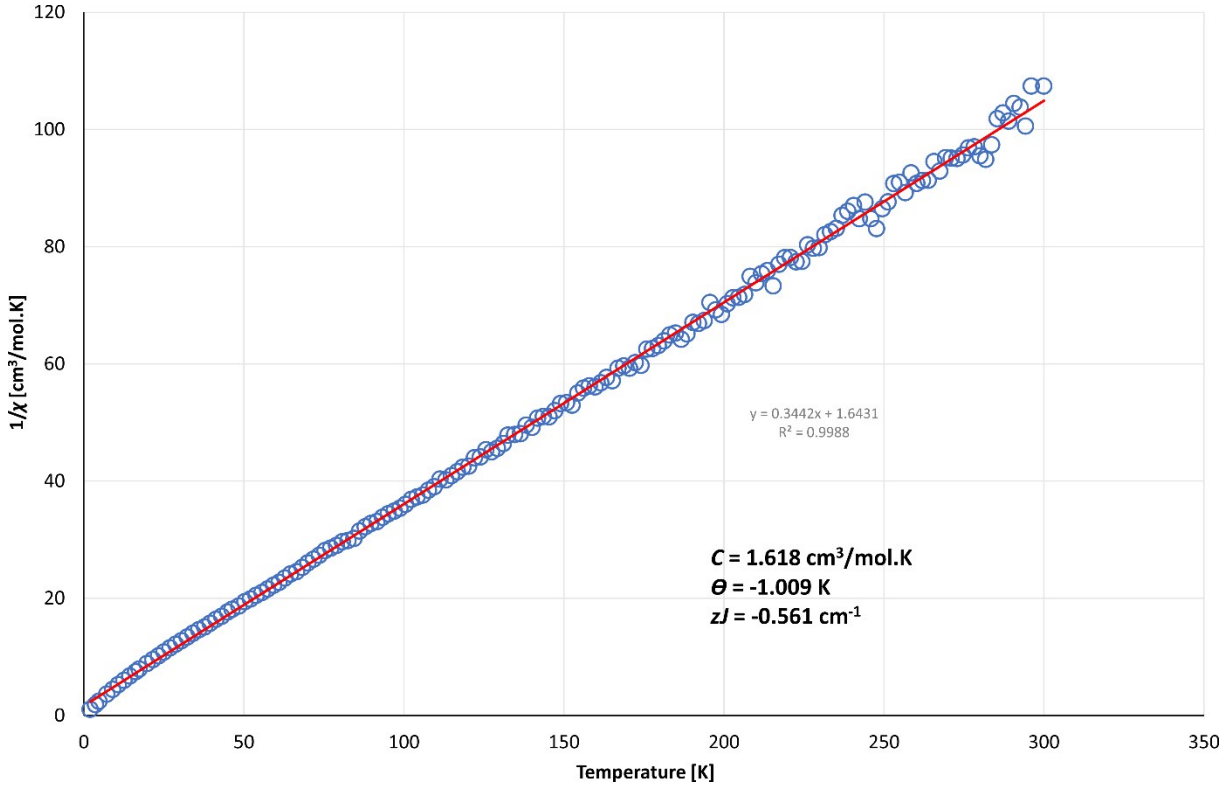

Fig. S5 The Curie-Weiss fitting (red line) of the magnetic data (blue circles) for **1** ($1/\chi$ vs. T plot) together with the calculated values of the C, θ and zJ parameters.

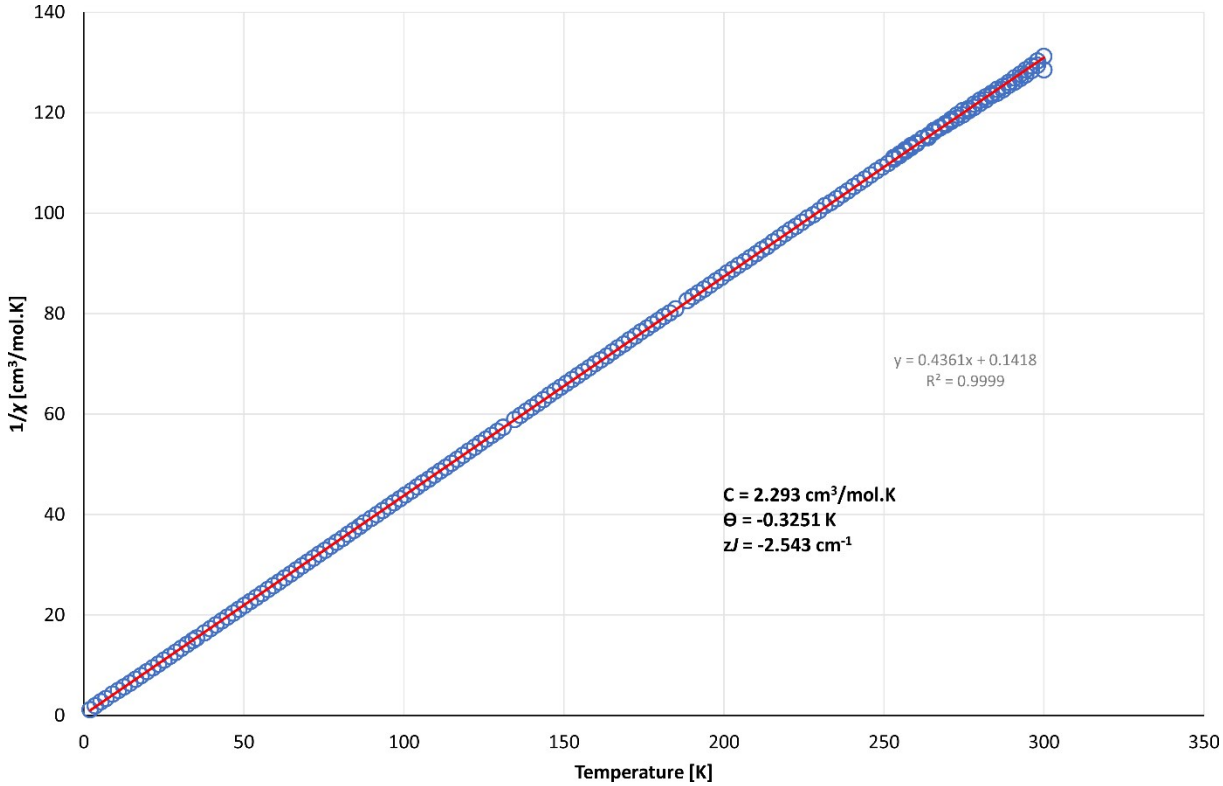

Fig. S6 The Curie-Weiss fitting (red line) of the magnetic data (blue circles) for **2** ($1/\chi$ vs. T plot) together with the calculated values of the C, θ and zJ parameters.

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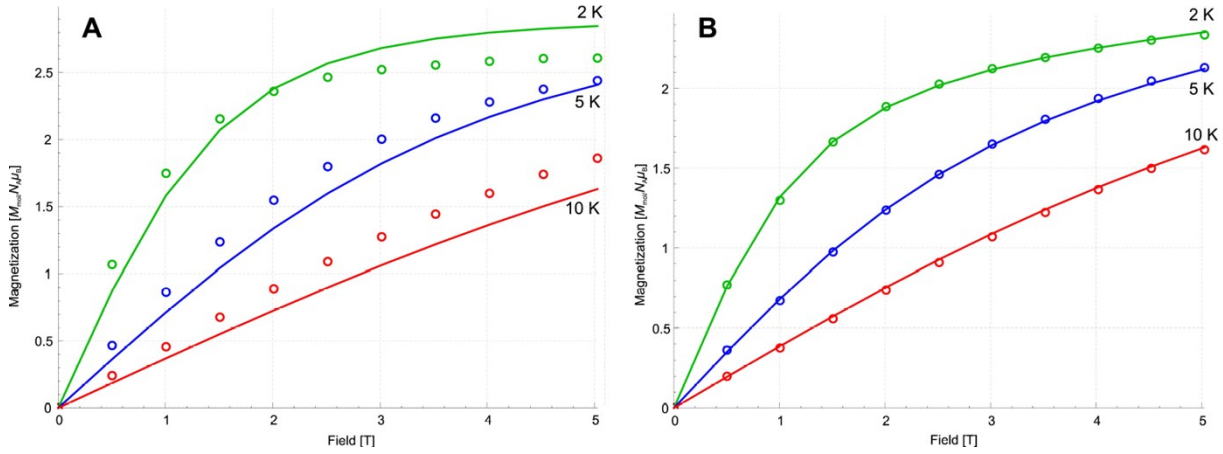

Fig. S7 Dot charts showing dependences of magnetization [$M_{mol}/N_A\mu_B$] vs. magnetic field [T] for **1** (**A**) and **2** (**B**) at different temperatures, including the corresponding fits (full lines).

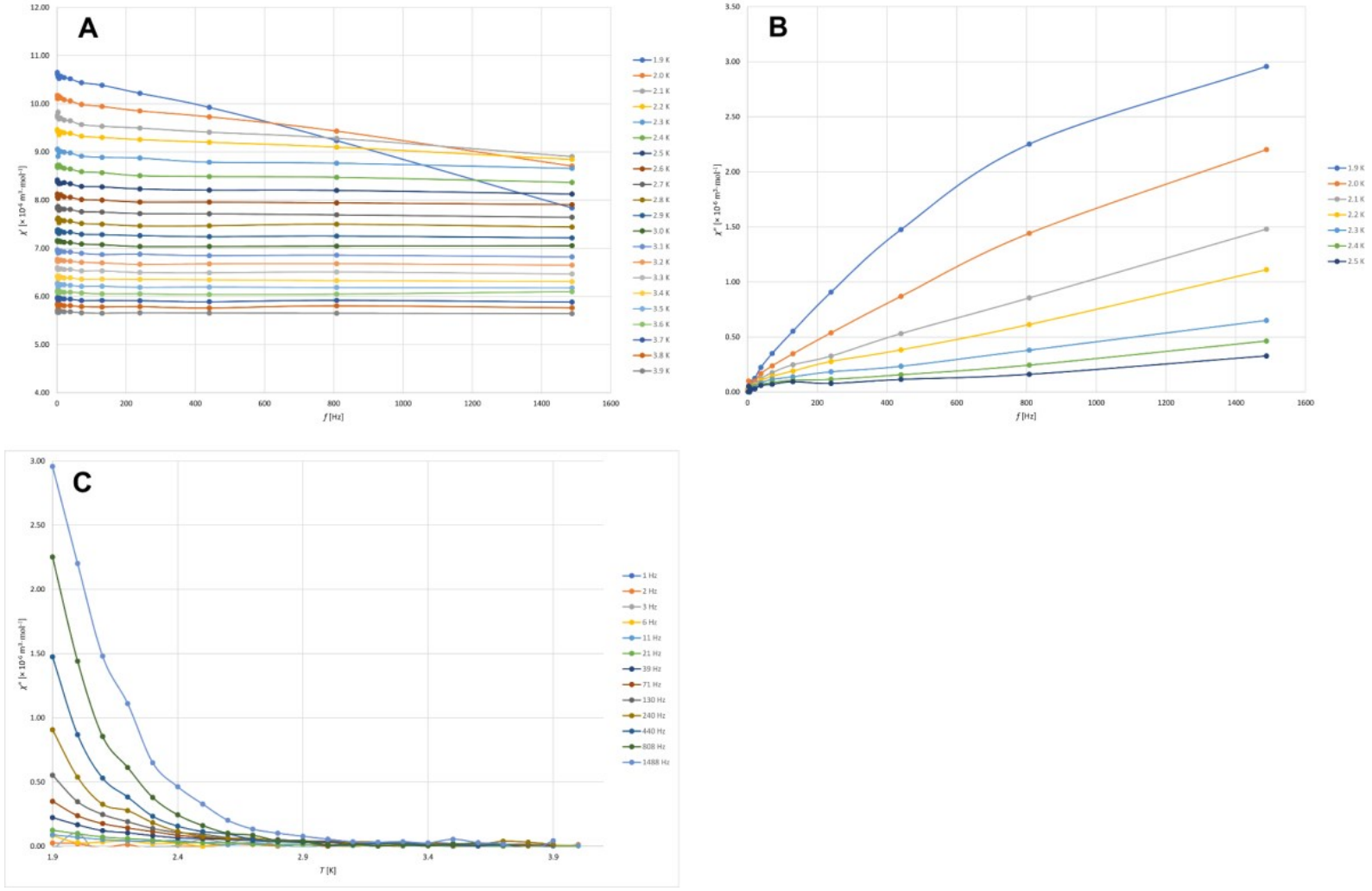

Fig. S8 The results of ac measurements for complex **2**, χ' vs. f plot (**A**), χ'' vs. f plot (**B**), χ'' vs. T plot (**C**) showing no distinct maxima.

ESI

#2553

18381

Sample Name	Unavailable	**Position**	Unavailable	**Instrument Name**	Unavailable	**User Name**	Unavailable
Inj Vol	Unavailable	**InjPosition**	Unavailable	**SampleType**	Unavailable	**IRM Calibration Status**	Some Ions Missed
Data Filename	18381_150v_0.1ul.d	**ACQ Method**		**Comment**	Sample information is unavailable	**Acquired Time**	Unavailable

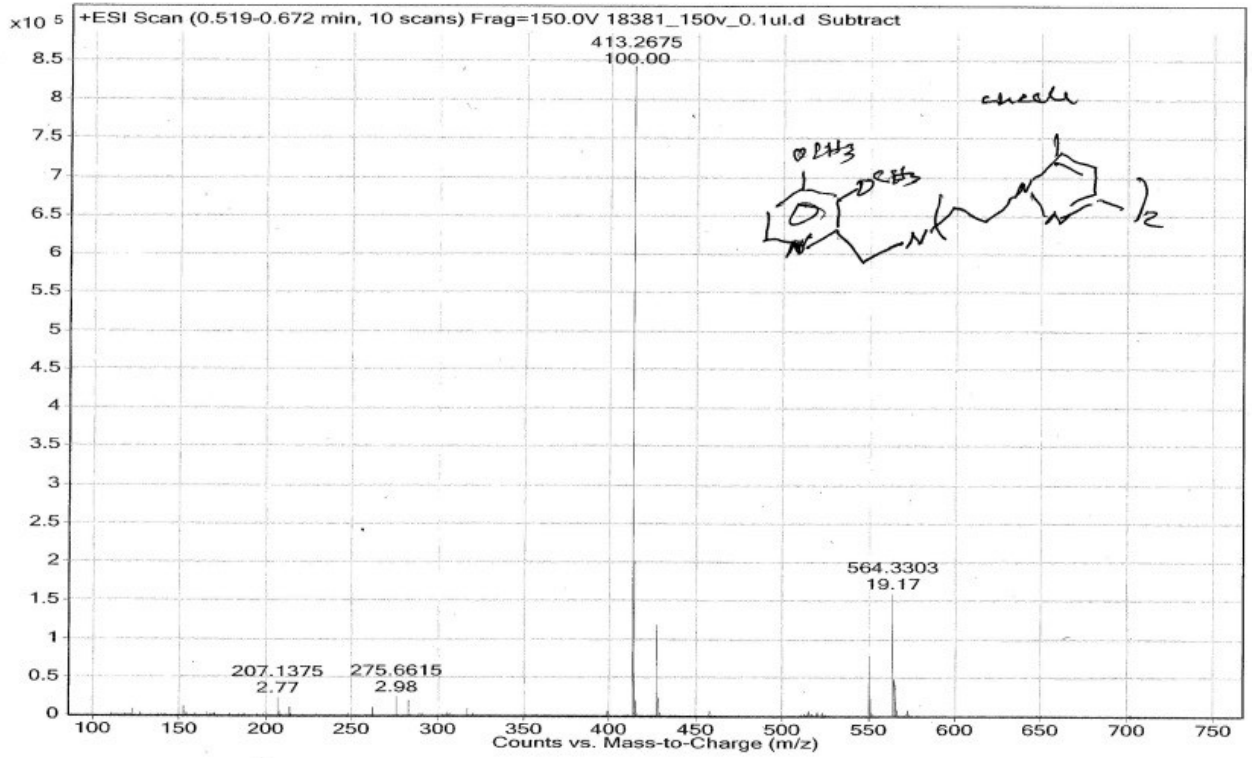

Fig. S9 ESI-MS of L^1 ligand in MeOH

F (

#2518 (

ESI
#K3384

Sample Name	18384_150v_0.1ul	**Position**	P1-A6	**Instrument Name**	Instrument 1	**User Name**	
Inj Vol	0.1	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Some Ions Missed
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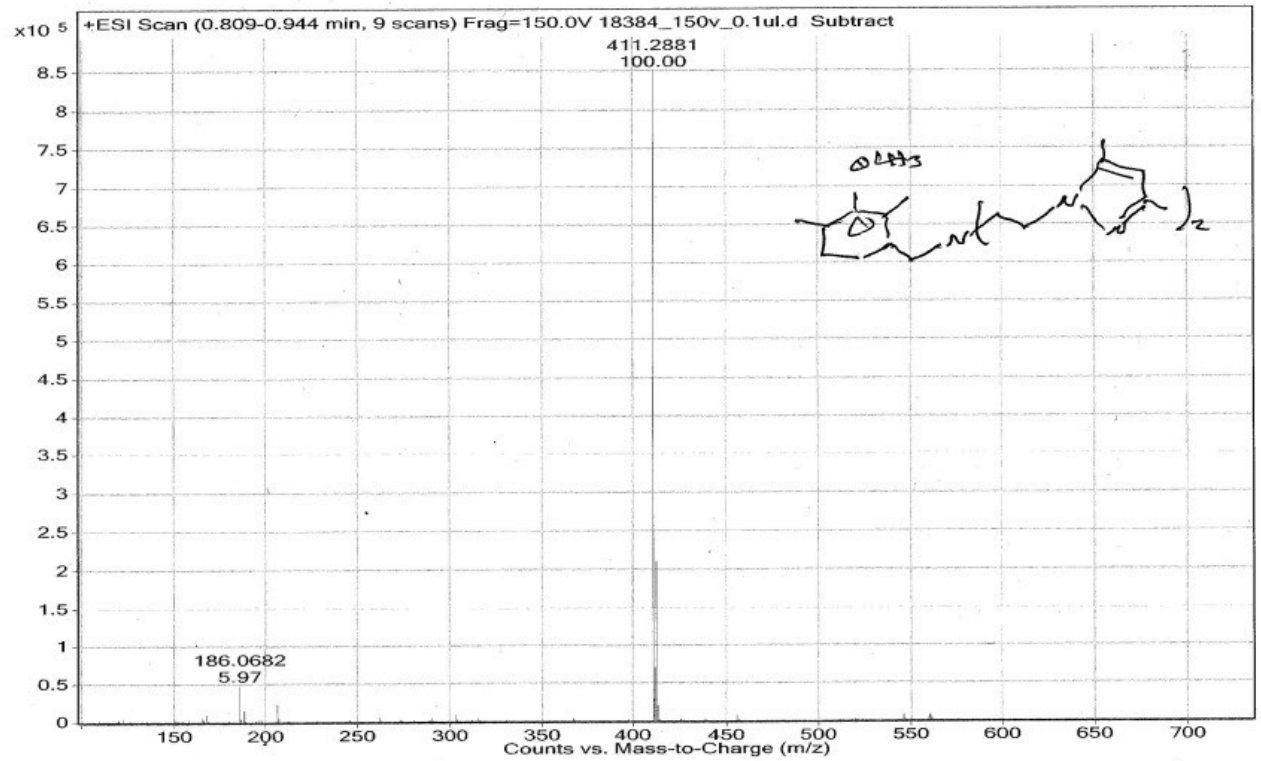
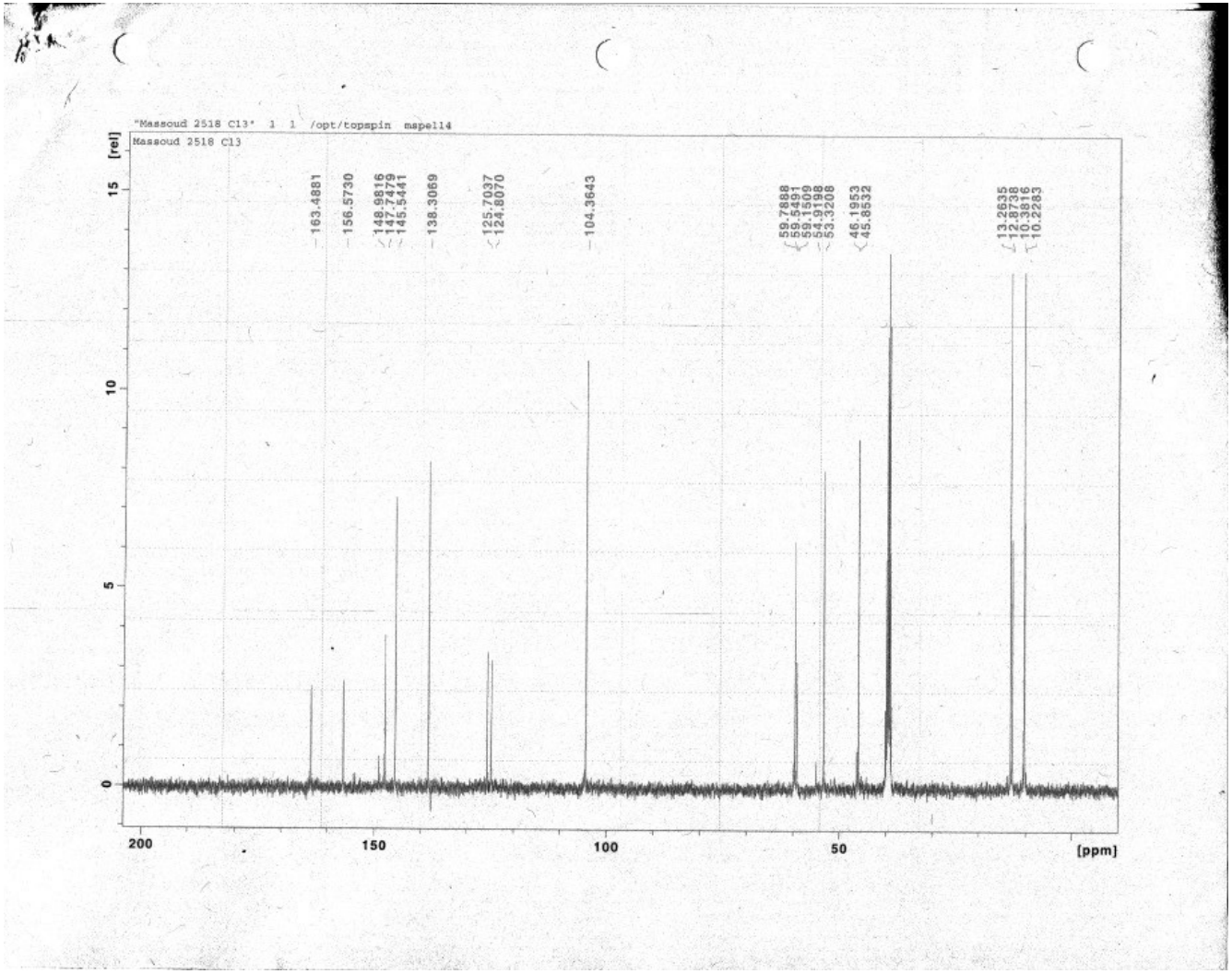


Fig. S10 ESI-MS of L^2 ligand in MeOH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Massoud 2518 C13
[rel]
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10
5
0
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156.5730
148.9816
147.7479
145.5441
138.3069
125.7037
124.8070
104.3643
59.7888
59.1451
58.5013
54.9198
53.3208
46.1953
45.8532
13.2635
12.6738
11.3816
10.2283
200
150
100
50
[ppm]

Fig. S11 ^{13}C NMR spectrum of L^2 ligand in DMSO-d_6

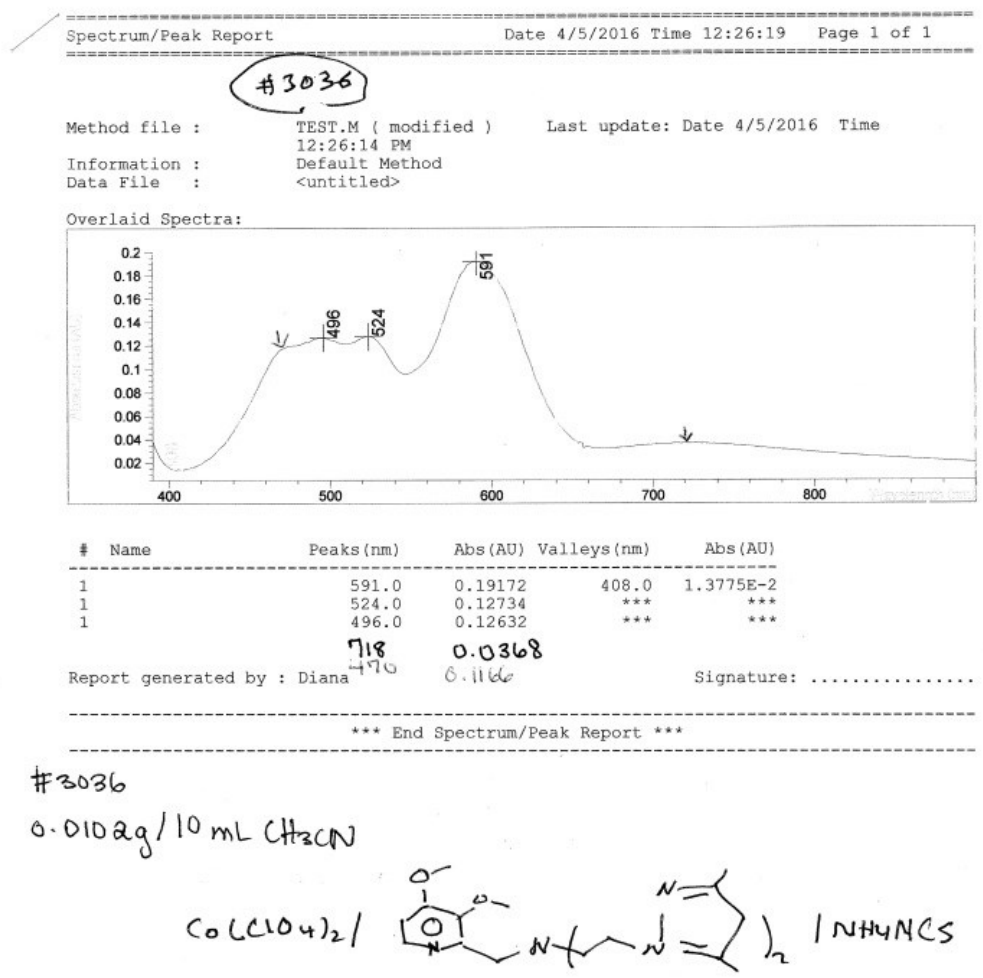

Fig. S12 UV-Vis. spectrum of complex **1** in CH_3CN.

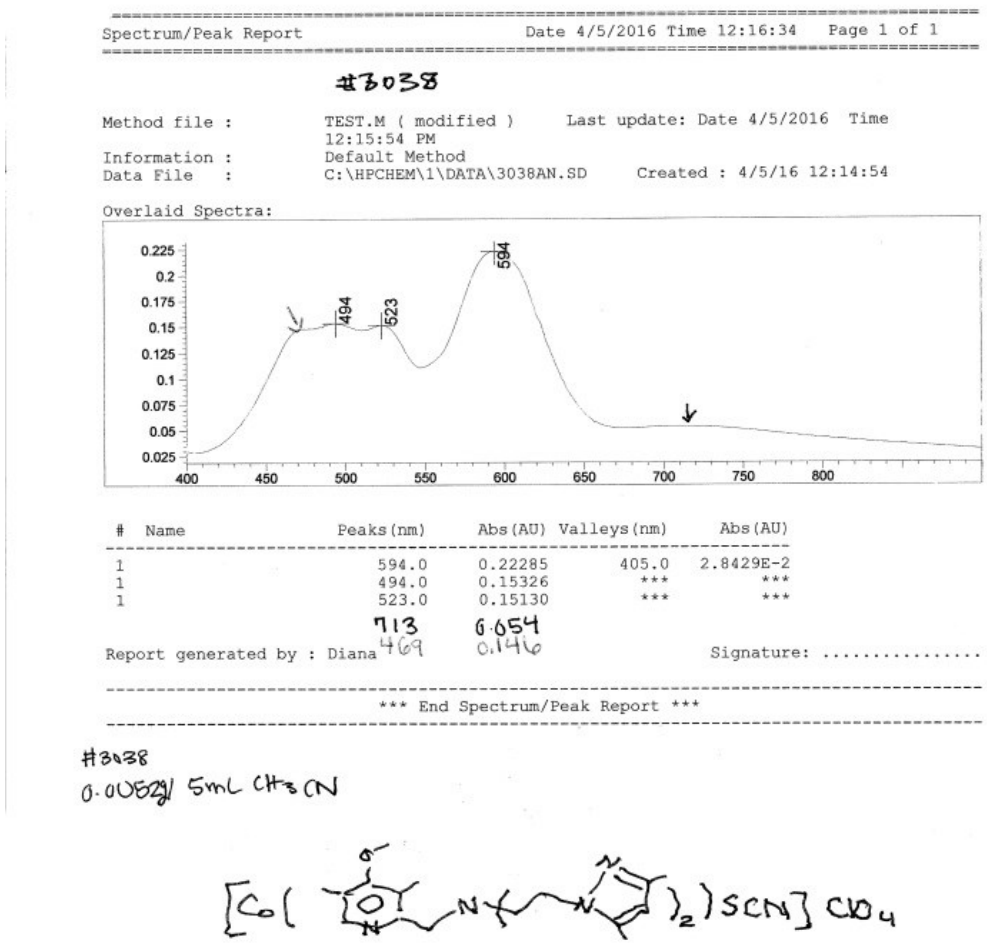

Fig. S13 UV-Vis. spectrum of complex **2** in CH_3CN.

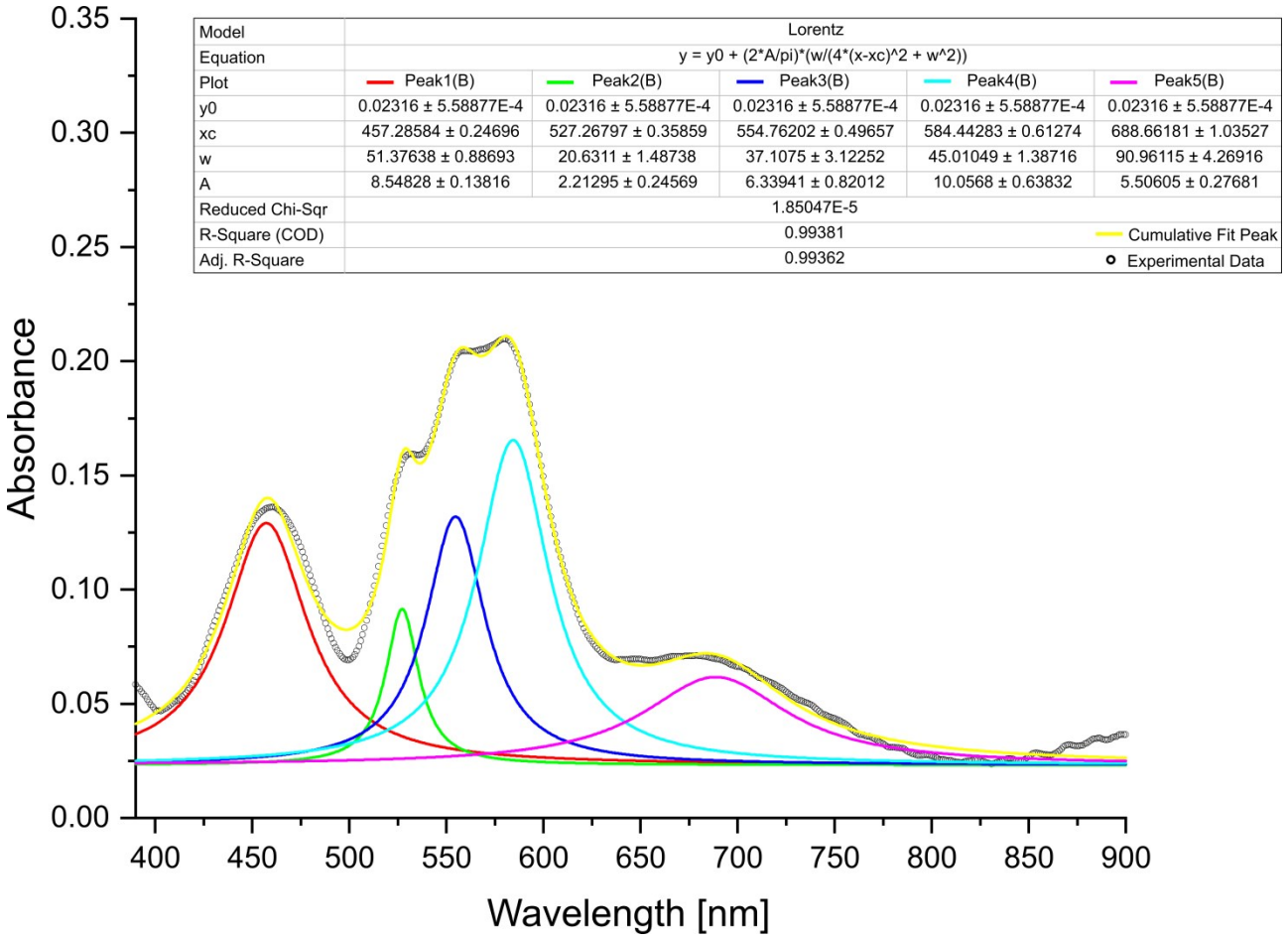

Fig. S14 Solid state spectrum of **1** and its deconvolution analysis.

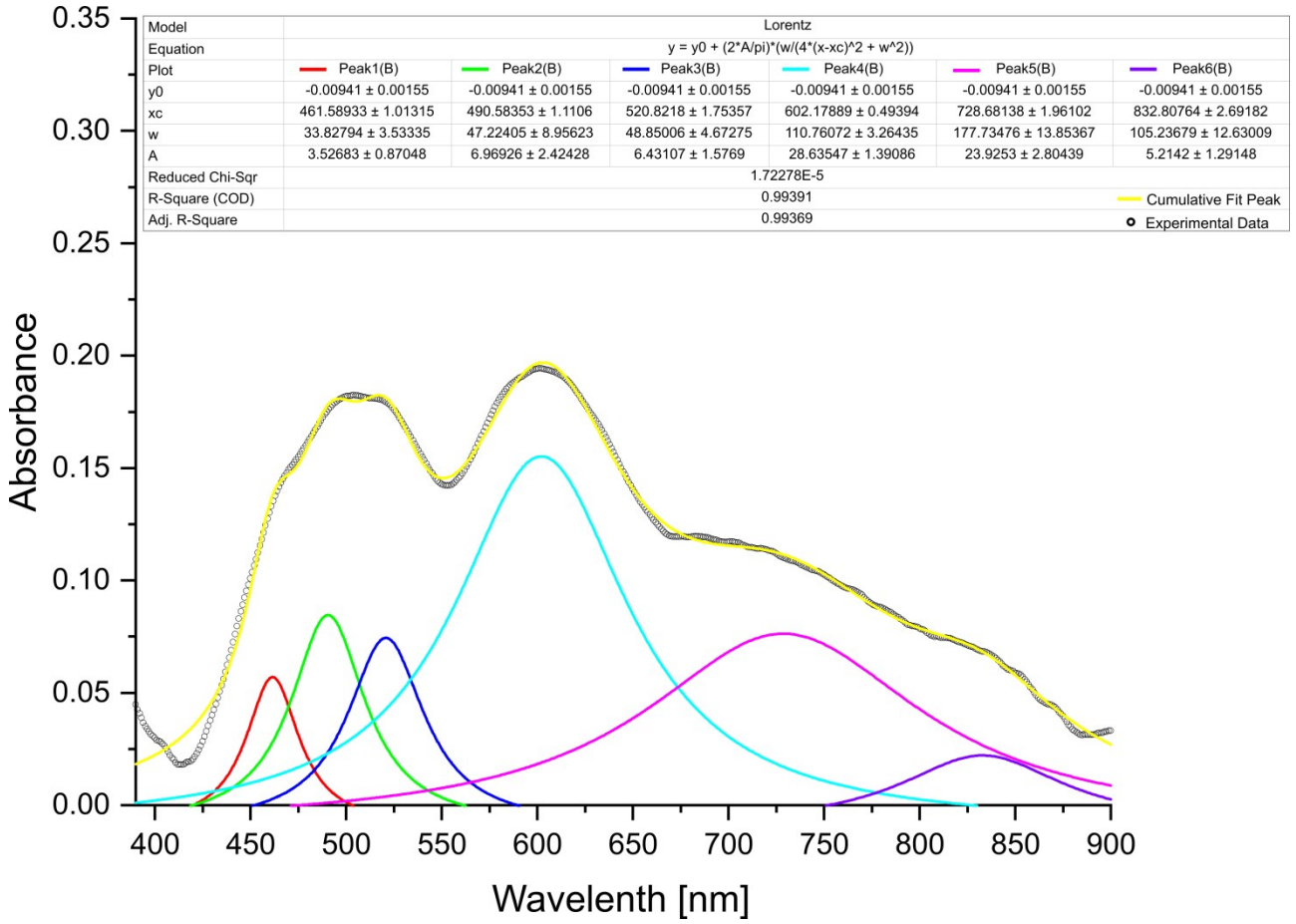

Fig. S15 Solid state spectrum of **2** and its deconvolution analysis.