

**Electronic supplementary document**

**Crystal Engineering of *p*-sulfocinnamic Acid into Mononuclear Cationic Fe(II), Co(II) and Fe(III) Complexes**

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## Materials and methods

All chemicals were bought from usual chemical companies and used as received without further purification. Solvents were degassed by standard procedures before use. Powder X-ray diffraction (PXRD) measurements were carried out at room temperature on a Bruker D8 ADVANCE X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5148 \text{ \AA}$ ). Thermogravimetric analyses (TGAs) were carried out by Mettler Toledo TGA/SDTA 851e analyzer in N<sub>2(g)</sub> (100 mL min<sup>-1</sup>) at a heating rate of 10 °C min<sup>-1</sup> between 25 °C and 600 °C. Fourier transformed infrared (FT-IR) spectra were recorded by an Equinox 55 (Bruker) equipped with an ATR modulus and an MCT detector. HRMS spectra of compounds **1**, **2** (Figures S1, S2) were recorded in electrospray ionization mode using a ThermoFisher Q-Exactive instrument. HRMS spectrum of compound **4** (Figure S3) was obtained by direct infusion on a Orbitrap Exploris™ 120 mass spectrometer MB11205C (Thermo Fisher Scientific™, from Waltham, Massachusetts, USA) and/or a maXis QTOF-MS (Bruker Daltonics GmbH, Bremen, Germany). The measurement was performed using Orbitrap Exploris 120 Tune Application and Bruker Compass DataAnalysis software. The sum formulas of the detected ions were determined using FreeStyle™ 1.8 SP2 QF1, Modern Data Visualization Software, based on the mass accuracy ( $\Delta m/z \leq 5 \text{ ppm}$ ) and isotopic pattern matching (SmartFormula algorithm).

Single crystal X-ray diffraction data for [Co(H<sub>2</sub>O)<sub>6</sub>](Hpsca)<sub>2</sub>·2H<sub>2</sub>O, [Co(H<sub>2</sub>O)<sub>6</sub>](Hpsca)<sub>2</sub>·4H<sub>2</sub>O and [Co(H<sub>2</sub>O)<sub>6</sub>](Hpsca)<sub>2</sub>·4H<sub>2</sub>O (Irradiated) were collected on a Mar345 image plate detector using MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) generated by a Rigaku Ultra X18S rotating anode with Xenocs Fox3D mirrors. Single crystal X-ray diffraction data for **1**, **2**, [Co(bipy)<sub>3</sub>](Hpsca)<sub>2</sub>·1.26MeOH, **3** and **4** were collected on a Rigaku Oxford Diffraction SuperNova dual-source (Cu at zero operation) diffractometer equipped with an Atlas CCD detector, using  $\omega$  scans with MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Single crystal X-ray diffraction data for **1** and [Co(bipy)<sub>3</sub>](Hpsca)<sub>2</sub>·1.26MeOH were collected at room temperature, whereas **2-4** were collected at 100 K.

Crystallographic data and selected bond lengths and angles are summarized in Tables S1-S6 of the Electronic supplementary information. CCDC 2471352-2471355 and 2517053-2517056 contain the supplementary crystallographic data for the compounds reported in this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via

[www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).  $^{57}\text{Fe}$  Mössbauer spectra of **1** and **4** were recorded at room temperature in transmission geometry using a conventional Wissel Mössbauer spectrometer operated in constant acceleration mode. The spectrometer was equipped with a  $^{57}\text{Co}(\text{Rh})$  radioactive source, a Reuter Stokes proportional counter detector and a CMCA-550 multichannel analyzer. All isomer shifts in Mössbauer spectra are given with respect to  $\alpha\text{-Fe}$ . Magnetic susceptibility measurements were carried out using a Quantum Design MPMS-5s SQUID magnetometer. Photoirradiation experiments were conducted using a 60W Philips lamp.

**Table S1.** Summary of crystallographic data and refinement for [Co(H<sub>2</sub>O)<sub>6</sub>](Hpsca)<sub>2</sub>·nH<sub>2</sub>O.

	[Co(H <sub>2</sub> O) <sub>6</sub> ](Hpsca) <sub>2</sub> ·4H <sub>2</sub> O	[Co(H <sub>2</sub> O) <sub>6</sub> ](Hpsca) <sub>2</sub> ·4H <sub>2</sub> O (Irradiated)	[Co(H <sub>2</sub> O) <sub>6</sub> ](Hpsca) <sub>2</sub> ·2H <sub>2</sub> O
Empirical formula	C <sub>18</sub> H <sub>34</sub> CoO <sub>20</sub> S <sub>2</sub>	C <sub>18</sub> H <sub>34</sub> CoO <sub>20</sub> S <sub>2</sub>	C <sub>18</sub> H <sub>30</sub> CoO <sub>18</sub> S <sub>2</sub>
Formula weight	693.50	693.50	657.47
T [K]	150(2)	297(2)	297(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	6.2135(9)	6.31344(20)	6.512(3)
<i>b</i> [Å]	7.5160(5)	7.5814(3)	6.536(3)
<i>c</i> [Å]	14.987(2)	30.1365(13)	18.147(9)
$\alpha$ [°]	84.066(9)	93.468(4)	81.02(4)
$\beta$ [°]	82.739(11)	95.138(3)	88.71(4)
$\gamma$ [°]	81.653(9)	98.427(3)	64.85(5)
Volume [Å <sup>3</sup> ]	684.35(14)	1417.20(10)	689.7(6)
<i>Z</i>	1	2	1
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.683	1.625	1.583
$\mu$ (mm <sup>-1</sup> )	0.870	0.840	0.853
<i>F</i> (000)	361	722	341
Crystal size (mm <sup>3</sup> )	0.50 x 0.50 x 0.08	0.50x 0.38 x 0.08	0.30x 0.24 x 0.07
Theta range for data collection [°]	3.179 to 26.292	2.722 to 26.646	3.414 to 25.816
Reflections collected	9264	16337	6389
Data / restraints / parameters	2747 / 0 / 264	5664 / 0 / 435	6389 / 252 / 325
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.092	1.059	1.079
Final <i>R</i> indices [ <i>I</i> >2sigma( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0306, <i>wR</i> <sub>2</sub> = 0.0740	<i>R</i> <sub>1</sub> = 0.0409, <i>wR</i> <sub>2</sub> = 0.1154	<i>R</i> <sub>1</sub> = 0.0726, <i>wR</i> <sub>2</sub> = 0.2009
indices (all data) <i>R</i>	<i>R</i> <sub>1</sub> = 0.0316, <i>wR</i> <sub>2</sub> = 0.0745	<i>R</i> <sub>1</sub> = 0.0460, <i>wR</i> <sub>2</sub> = 0.1266	<i>R</i> <sub>1</sub> = 0.0769, <i>wR</i> <sub>2</sub> = 0.2046
CCDC	2471352	2517055	2517053

**Table S2.** Summary of crystallographic data and refinement for **1**.

	[Fe(bipy) <sub>3</sub> ](Hpsca) <sub>2</sub> ·1.8MeOH
Empirical formula	C <sub>49.80</sub> H <sub>45.09</sub> FeN <sub>6</sub> O <sub>11.80</sub> S <sub>2</sub>
Formula weight	1035.58
T [K]	297(2)
Wavelength [Å]	0.71073
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> [Å]	22.629(6)
<i>b</i> [Å]	12.037(2)
<i>c</i> [Å]	18.248(5)
$\alpha$ [°]	90
$\beta$ [°]	101.81(3)
$\gamma$ [°]	90
Volume [Å <sup>3</sup> ]	4865(2)
<i>Z</i>	4
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.415
$\mu$ (mm <sup>-1</sup> )	0.465
<i>F</i> (000)	2154
Crystal size (mm <sup>3</sup> )	0.50 x 0.09 x 0.08
Theta range for data collection [°]	2.838 to 25.243
Reflections collected	10401
Data / restraints / parameters	4338 / 36 / 371
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.082
Final <i>R</i> indices [ <i>I</i> >2sigma( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0685, w <i>R</i> <sub>2</sub> = 0.1699
indices (all data) <i>R</i>	<i>R</i> <sub>1</sub> = 0.0834, w <i>R</i> <sub>2</sub> = 0.1816
CCDC	2471355

**Table S3.** Summary of crystallographic data and refinement for **2**.

	[Co(bipy) <sub>3</sub> ](Hpsca) <sub>2</sub> ·2MeOH	[Co(bipy) <sub>3</sub> ](Hpsca) <sub>2</sub> ·1.26MeOH
Empirical formula	C <sub>50</sub> H <sub>46</sub> CoN <sub>6</sub> O <sub>12</sub> S <sub>2</sub>	C <sub>49.26</sub> H <sub>43.03</sub> CoN <sub>6</sub> O <sub>11.26</sub> S <sub>2</sub>
Formula weight	1045.98	1022.18
T [K]	100(2)	297(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> [Å]	22.1092(9)	22.388(3)
<i>b</i> [Å]	12.0224(4)	12.0378(8)
<i>c</i> [Å]	18.1003(6)	18.003(3)
$\alpha$ [°]	90°	90
$\beta$ [°]	99.191(4)	101.438(15)
$\gamma$ [°]	90°	90
Volume [Å <sup>3</sup> ]	4749.4(3)	4755.6(10)
<i>Z</i>	4	4
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.463	1.428
$\mu$ (mm <sup>-1</sup> )	0.521	0.517
<i>F</i> (000)	2172	2119
Crystal size (mm <sup>3</sup> )	0.50 x 0.25 x 0.18	0.20 x 0.10 x 0.10
Theta range for data collection [°]	2.874 to 26.463	2.341 to 25.423
Reflections collected	16947	9538
Data / restraints / parameters	4828 / 0 / 325	4364 / 133 / 459
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.075	1.098
Final R indices [ <i>I</i> >2sigma( <i>I</i> )]	R <sub>1</sub> = 0.0316, wR <sub>2</sub> = 0.0849	R <sub>1</sub> = 0.0684, wR <sub>2</sub> = 0.1686
indices (all data) <i>R</i>	R <sub>1</sub> = 0.0359, wR <sub>2</sub> = 0.0863	R <sub>1</sub> = 0.0835, wR <sub>2</sub> = 0.1788
CCDC	2517054	2471354

**Table S4.** Summary of crystallographic data and refinement for **3**.

	[Fe(1-bpp)(Hpsca)(H <sub>2</sub> O)(MeOH)]Hpsca·MeOH
Empirical formula	C <sub>31</sub> H <sub>33</sub> FeN <sub>5</sub> O <sub>13</sub> S <sub>2</sub>
Formula weight	803.59
Temperature [K]	100(2)
Wavelength [Å]	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> [Å]	8.10565(14)
<i>b</i> [Å]	8.25059(19)
<i>c</i> [Å]	33.4784(8)
$\alpha$ [°]	90.6588(19)
$\beta$ [°]	90.3372(17)
$\gamma$ [°]	97.2798(17)
Volume [Å <sup>3</sup> ]	2220.66(8)
<i>Z</i>	2
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.202
$\mu$ (mm <sup>-1</sup> )	0.491
<i>F</i> (000)	832
Crystal size (mm <sup>3</sup> )	0.40x 0.28 x 0.20
Theta range for data collection [°]	2.533 to 26.179
Reflections collected	18237
Data / restraints / parameters	8627 / 3 / 488
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.091
Final R indices [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	R <sub>1</sub> = 0.0683, wR <sub>2</sub> = 0.1802
indices (all data) <i>R</i>	R <sub>1</sub> = 0.0715, wR <sub>2</sub> = 0.1820
CCDC	2517056

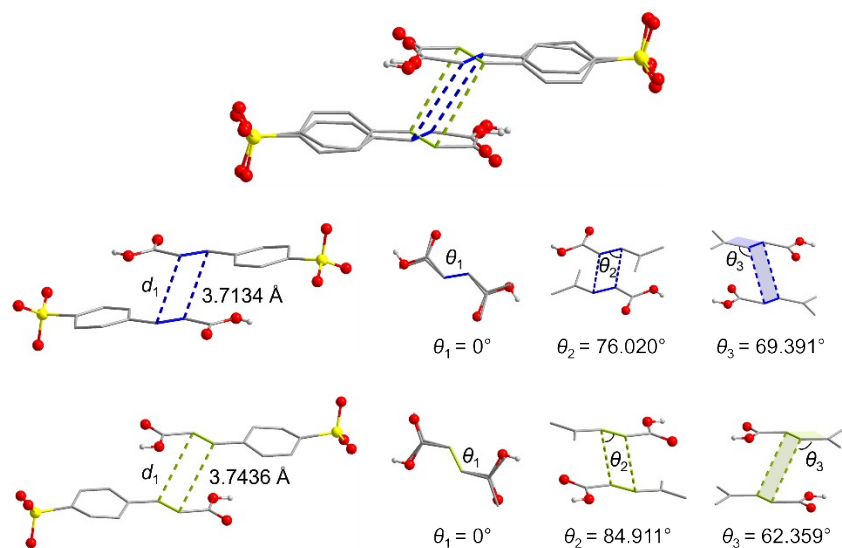
**Table S5.** Summary of crystallographic data and refinement for **4**.

	[Fe(3,2,3-sal <sub>2</sub> tet)]Hpsca·H <sub>2</sub> O
Empirical formula	C <sub>31</sub> H <sub>35</sub> FeN <sub>4</sub> O <sub>7</sub> S
Formula weight	663.54
T [K]	100(2)
Wavelength [Å]	0.81490
Crystal system	Monoclinic
Space group	<i>P2<sub>1</sub>/n</i>
<i>a</i> [Å]	7.77903(18)
<i>b</i> [Å]	19.1459(5)
<i>c</i> [Å]	23.0014(5)
$\alpha$ [°]	90
$\beta$ [°]	94.621(2)
$\gamma$ [°]	90
Volume [Å <sup>3</sup> ]	3414.63(14)
<i>Z</i>	4
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.291
$\mu$ (mm <sup>-1</sup> )	0.551
<i>F</i> (000)	1388
Crystal size (mm <sup>3</sup> )	0.45 x 0.18 x 0.05
Theta range for data collection [°]	2.772 to 26.615
Reflections collected	24187
Data / restraints / parameters	6887/0/402
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.061
Final R indices [ <i>I</i> >2sigma( <i>I</i> )]	R <sub>1</sub> =0.0361, wR <sub>2</sub> = 0.0986
indices (all data) <i>R</i>	R <sub>1</sub> =0.0396, wR <sub>2</sub> = 0.1046
CCDC	2471353

**Table S6.** Selected bond lengths [Å] and angles [°] for [Co(H<sub>2</sub>O)<sub>6</sub>](Hpsca)<sub>2</sub>·nH<sub>2</sub>O and compounds **1-4**.

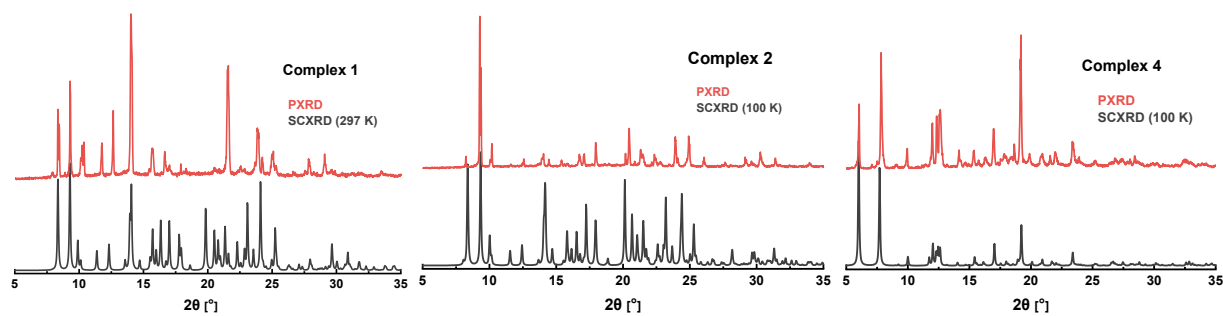
Compound	Bond lengths [Å]		Bond angles [°]	
[Co(H <sub>2</sub> O) <sub>6</sub> ](Hpsca) <sub>2</sub> ·4H <sub>2</sub> O (150 K)	Co1-O3	2.0592(12)	O3-Co1-O3	180.0
	Co1-O4	2.0720(12)	O3-Co1-O4	90.45(5)
	Co1-O2	2.0927(12)	O3-Co1-O4	89.55(5)
	S11-O14	1.4416(12)	O3-Co1-O4	89.55(5)
	S11-O13	1.4458(12)	O3-Co1-O4	90.45(5)
	S11-O12	1.4704(12)	O4-Co1-O4	180.00(6)
[Co(H <sub>2</sub> O) <sub>6</sub> ](Hpsca) <sub>2</sub> ·4H <sub>2</sub> O (Irradiated, 297 K)	Co1-O3	2.0766(17)	O3-Co1-O3	180.0
	Co1-O4	2.1029(15)	O3-Co1-O4	91.26(7)
	Co1-O2	2.0818(15)	O3-Co1-O4	88.74(7)
	S11-O13	1.4503(15)	O3-Co1-O4	88.75(7)
	S11-O14	1.4491(16)	O3-Co1-O4	88.74(7)
	S11-O12	1.4700(15)	O4-Co1-O4	180.0
[Co(H <sub>2</sub> O) <sub>6</sub> ](Hpsca) <sub>2</sub> ·2H <sub>2</sub> O (297 K)	Co1-O3	2.053(5)	O3-Co1-O3	180.0(4)
	Co1-O4	2.084(6)	O3-Co1-O4	91.5(3)
	Co1-O2	2.094(5)	O3-Co1-O4	88.5(3)
	S11-O13	1.450(9)	O3-Co1-O4	88.5(3)
	S11-O14	1.451(9)	O3-Co1-O4	91.5(3)
	S11-O12	1.482(9)	O4-Co1-O4	180.0
<b>1</b> (297 K)	Fe1-N13	1.970(3)	N13-Fe1-N13	173.50(17)
	Fe1-N13	1.970(3)	N13-Fe1-N2	94.07(12)
	Fe1-N2	1.972(3)	N13-Fe1-N2	81.27(13)
	Fe1-N2	1.972(3)	N13-Fe1-N2	81.27(12)
	Fe1-N14	1.973(3)	N2-Fe1-N2	89.21(18)
	Fe1-N14	1.973(3)	N13-Fe1-N14	97.33(12)
<b>2</b> (100 K)	Co1-N2	2.1232(13)	N2-Co1-N2	91.10(7)
	Co1-N2	2.1232(13)	N2-Co1-N14	172.65(5)
	Co1-N14	2.1243(13)	N2-Co1-N14	96.24(5)
	Co1-N14	2.1244(13)	N14-Co1-N14	76.41(7)
	Co1-N9	2.1321(14)	N2-Co1-N9	94.29(5)
	Co1-N9	2.1321(14)	N14-Co1-N9	101.99(5)
[Co(bipy) <sub>3</sub> ](Hpsca) <sub>2</sub> ·1.26MeOH (293 K)	Co1-N15	2.107(3)	N15-Co1-N15	90.82(18)
	Co1-N15	2.107(3)	N15-Co1-N2	172.23(12)
	Co1-N8	2.107(3)	N15-Co1-N8	77.24(12)
	Co1-N8	2.107(3)	N15-Co1-N8	95.25(12)

	Co1-N2	2.118(3)	N15-Co1-N2	172.23(12)
	Co1-N2	2.118(3)	N15-Co1-N2	96.71(12)
3 (100 K)	Fe1-O18	2.053(3)	O18-Fe1-O22	85.20(11)
	Fe1-O22	2.125(3)	O18-Fe1-O19	89.69(12)
	Fe1-O19	2.125(3)	O22-Fe1-O19	169.97(11)
	Fe1-N8	2.153(3)	O18-Fe1-N8	170.22(11)
	Fe1-N2	2.184(3)	O22-Fe1-N8	99.07(11)
	Fe1-N14	2.222(3)	O19-Fe1-N8	87.34(12)
4 (100 K)	Fe1-O2	1.8703(13)	O2-Fe1-O29	174.33(6)
	Fe1-O29	1.8860(13)	O2-Fe1-N21	93.46(6)
	Fe1-N21	1.9423(15)	O29-Fe1-N21	91.01(6)
	Fe1-N10	1.9570(16)	O2-Fe1-N10	89.69(6)
	Fe1-N17	2.0095(15)	O29-Fe1-N10	93.47(6)
	Fe1-N14	2.0221(15)	N21-Fe1-N10	94.20(7)

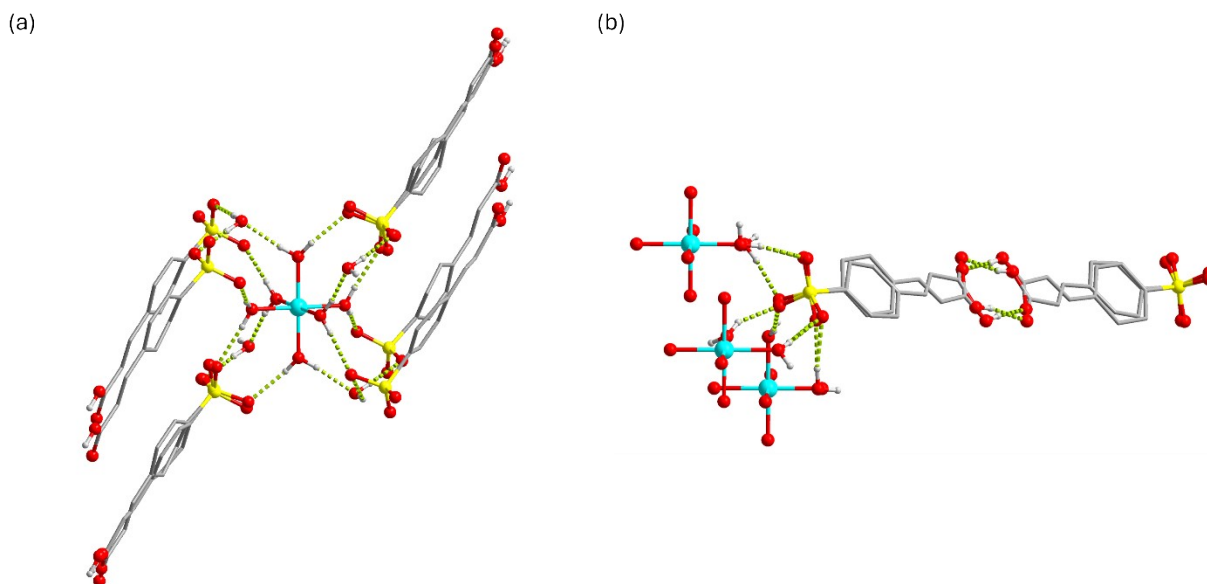


Compounds	$d_1 / \text{Å}$	$\theta_1 / ^\circ$	$\theta_2 / ^\circ$	$\theta_3 / ^\circ$	Disorder
[Co(H <sub>2</sub> O) <sub>6</sub> ](Hpsca) <sub>2</sub> ·2H <sub>2</sub> O	3.7134	0	76.020	69.391	0.38
	3.7436	0	84.911	62.359	0.62
[Co(H <sub>2</sub> O) <sub>6</sub> ](Hpsca) <sub>2</sub> ·4H <sub>2</sub> O	3.8287	0	63.575	53.636	0.50
	4.2696	0	86.608	81.082	0.50
[Co(H <sub>2</sub> O) <sub>6</sub> ](Hpsca) <sub>2</sub> ·4H <sub>2</sub> O (after UV)	3.7780, 4.3924	12.756	86.147, 60.507		No
<b>1</b>	4.1059	0	83.154	41.167	0.11
	4.0155	0	59.085	88.057	0.89
<b>2</b> (100 K)	3.9019	0	59.432	85.429	No
<b>2</b> (r.t.)	4.2614	0	83.191	43.847	0.37
	4.0788	0	57.940	87.891	0.63
<b>3</b> (100 K)	7.0922	0	86.103	81.527	No
<b>4</b>	7.7790	0	55.612	57.153	No

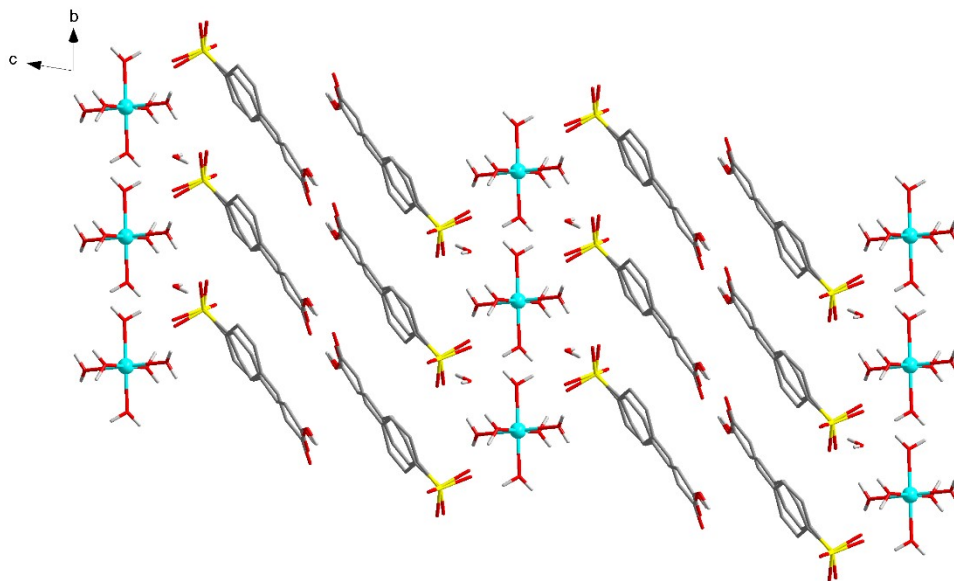
**Table S7.** Alignments of **Hpsca**<sup>-</sup> counter anion in the crystal lattice and related geometric parameters relevant to solid-state photoreactivity across all the complexes ( $d_1$  is defined by the distance between the parallel C=C bonds.  $\theta_1$  denotes the angle formed between two adjacent C=C bonds in the top view.  $\theta_2$  is defined by the angle involving the C=C bond and one of the carbon atoms from the adjacent C=C bond. The blue and green planes for  $\theta_3$  are defined by the two C=C bonds and their related single bond).



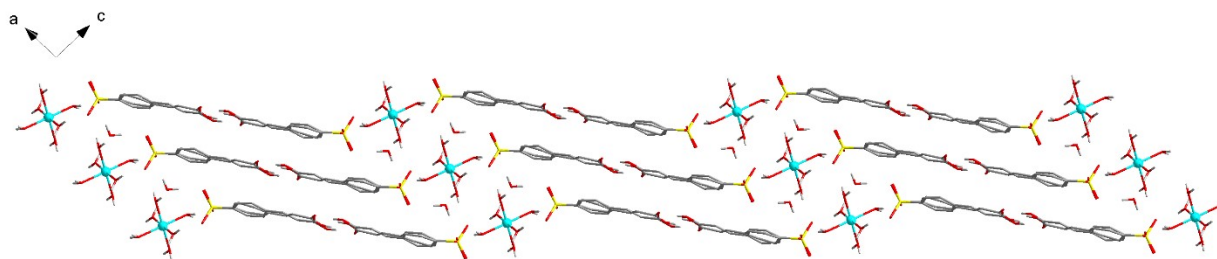
**Figure S1.** PXRD pattern of complexes **1**, **2** and **4** compared with the simulated pattern calculated from single-crystal X-ray diffraction (SCXRD) data (bottom).



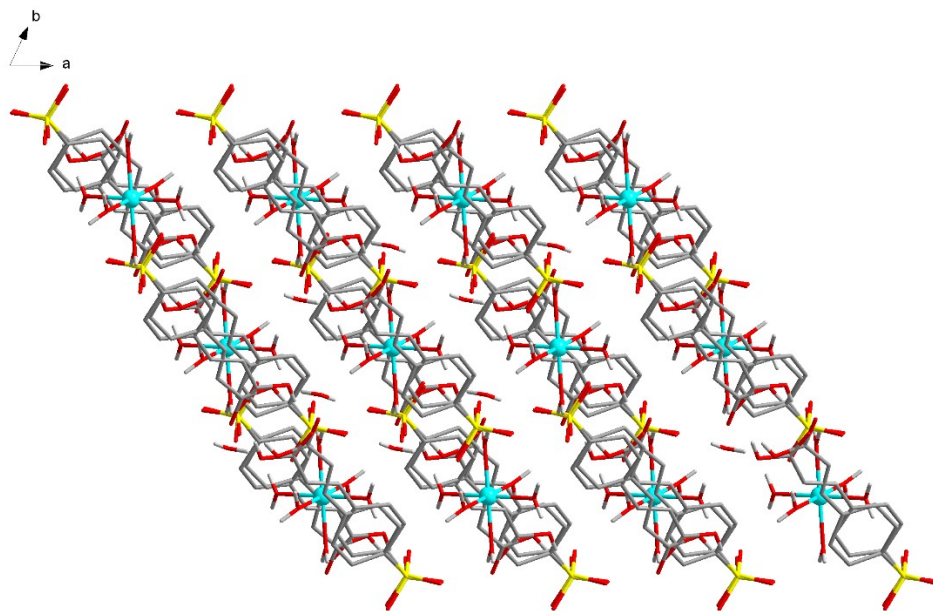
**Figure S2.** Hydrogen bonds around the  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ion (a) and *Hpsca*<sup>-</sup> anion (b) at r.t, in  $[\text{Co}(\text{H}_2\text{O})_6](\text{Hpsca})_2 \cdot 2\text{H}_2\text{O}$



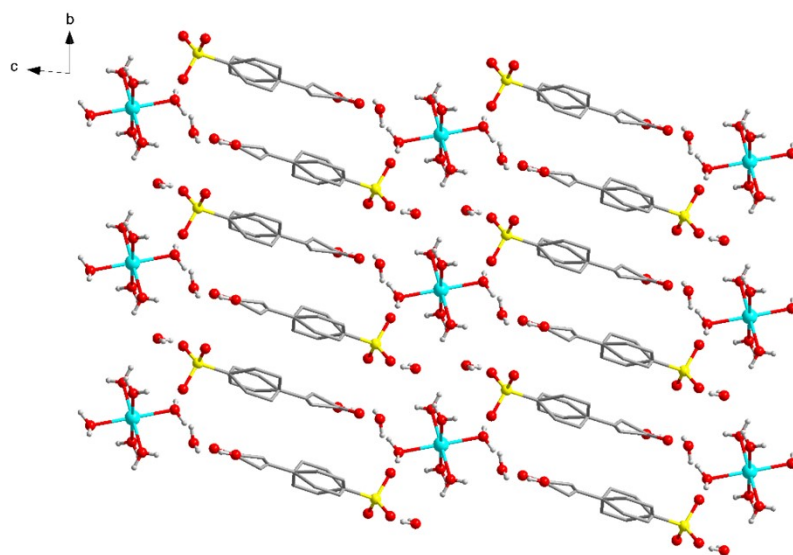
**Figure S3.** Crystal packing of  $[\text{Co}(\text{H}_2\text{O})_6](\text{Hpsca})_2 \cdot 2\text{H}_2\text{O}$  along the  $a$  axis at r.t.



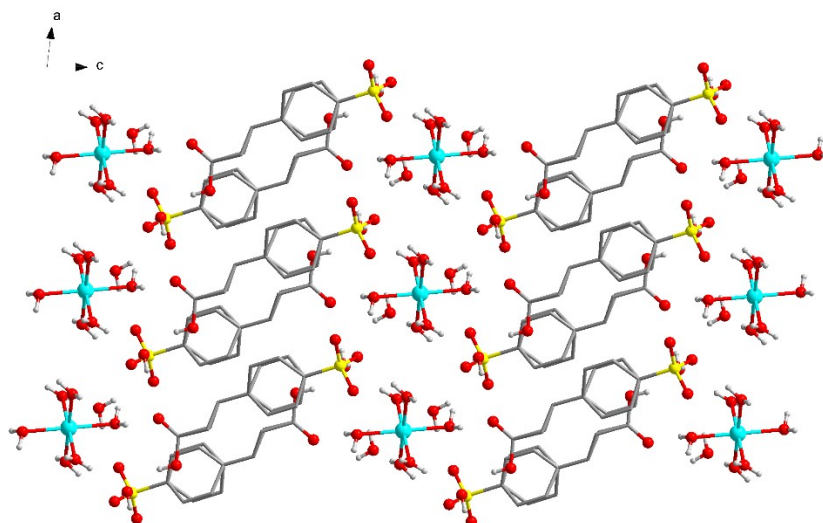
**Figure S4.** Crystal packing of  $[\text{Co}(\text{H}_2\text{O})_6](\text{Hpsca})_2 \cdot 2\text{H}_2\text{O}$  along the  $b$  axis at r.t.



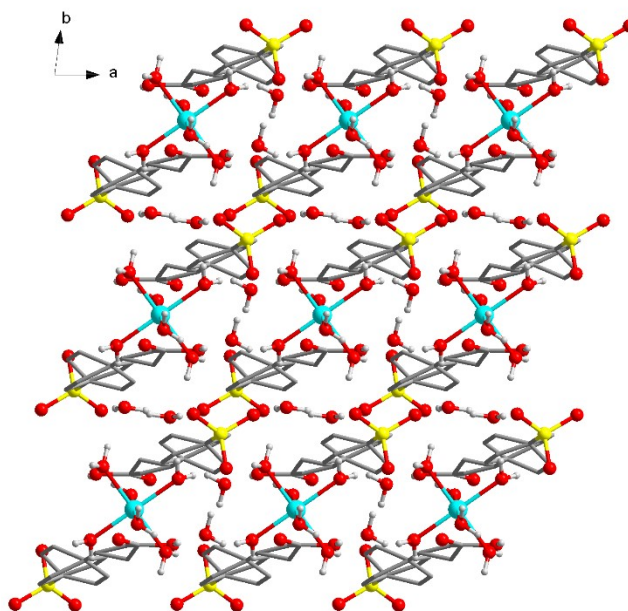
**Figure S5.** Crystal packing of  $[\text{Co}(\text{H}_2\text{O})_6](\text{Hpsca})_2 \cdot 2\text{H}_2\text{O}$  along the *c* axis at r.t.



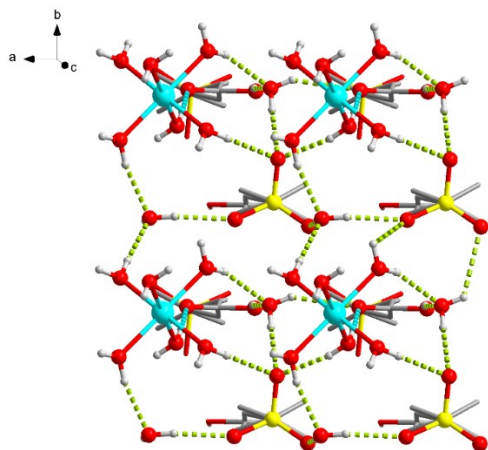
**Figure S6.** Crystal packing of  $[\text{Co}(\text{H}_2\text{O})_6](\text{Hpsca})_2 \cdot 4\text{H}_2\text{O}$  along the *a* axis at 150 K.



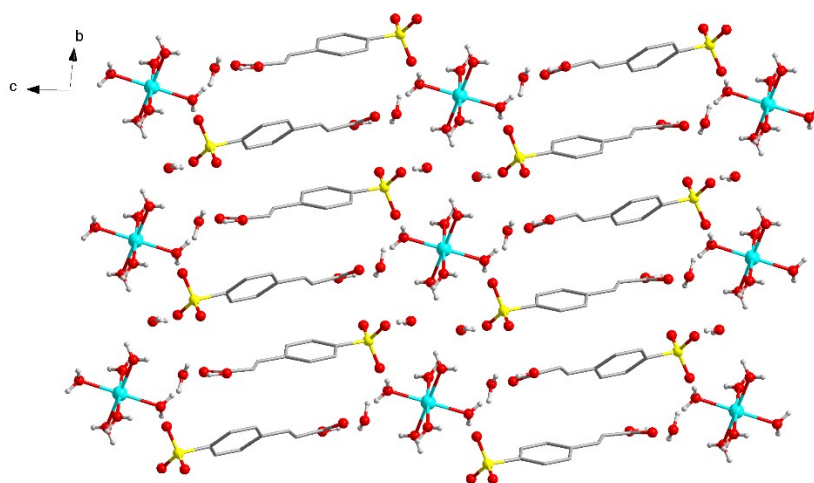
**Figure S7.** Crystal packing of  $[\text{Co}(\text{H}_2\text{O})_6](\text{Hpsca})_2 \cdot 4\text{H}_2\text{O}$  along the *b* axis at 150 K.



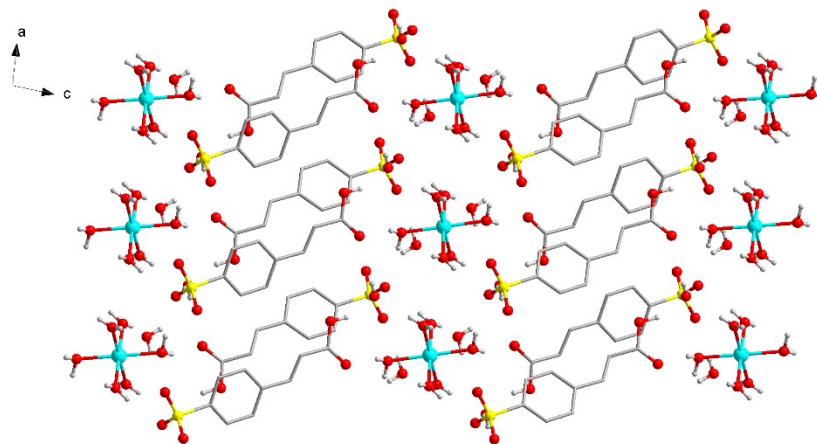
**Figure S8.** Crystal packing of  $[\text{Co}(\text{H}_2\text{O})_6](\text{Hpsca})_2 \cdot 4\text{H}_2\text{O}$  along the *c* axis at 150 K.



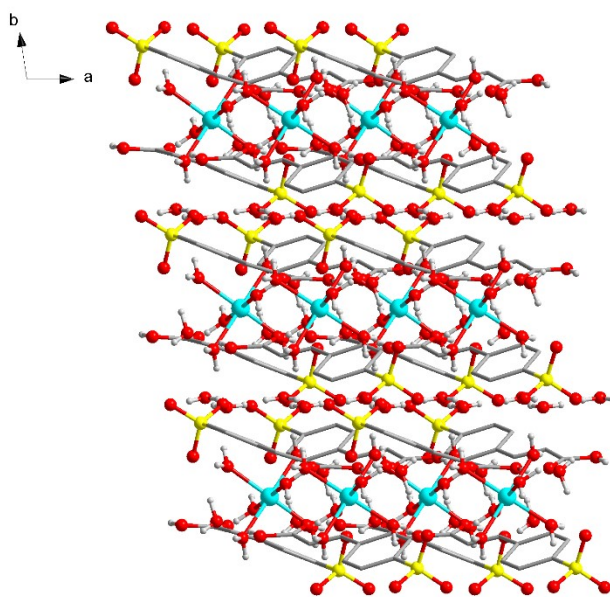
**Figure S9.** Hydrogen bonds around the  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  ion in  $[\text{Co}(\text{H}_2\text{O})_6](\text{Hpsca})_2 \cdot 4\text{H}_2\text{O}$  at 150 K.



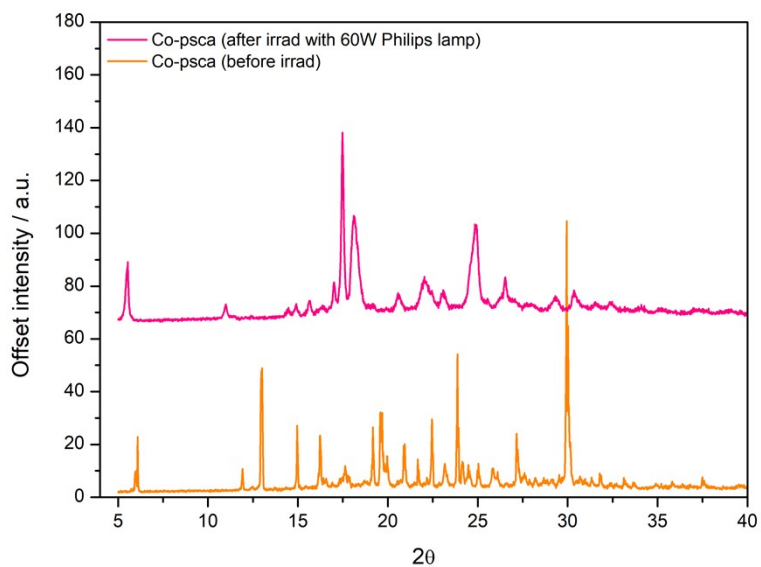
**Figure S10.** Crystal packing of  $[\text{Co}(\text{H}_2\text{O})_6](\text{Hpsca})_2 \cdot 4\text{H}_2\text{O}$  after irradiation along the  $a$  axis at r.t.



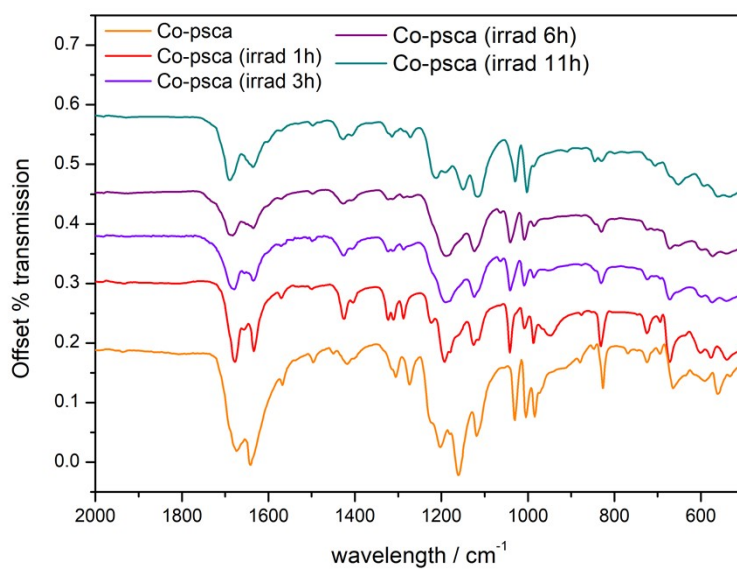
**Figure S11.** Crystal packing of [Co(H<sub>2</sub>O)<sub>6</sub>](Hpsca)<sub>2</sub>·4H<sub>2</sub>O after irradiation along the *b* axis at r.t.



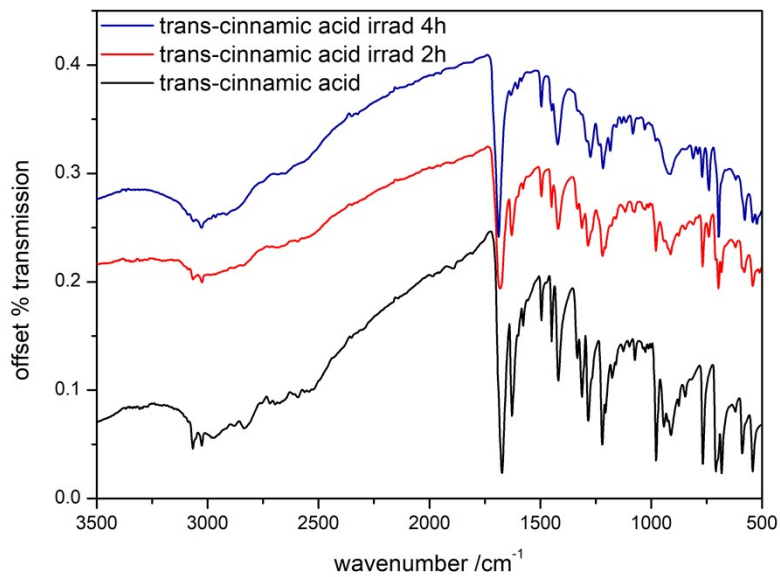
**Figure S12.** Crystal packing of [Co(H<sub>2</sub>O)<sub>6</sub>](Hpsca)<sub>2</sub>·4H<sub>2</sub>O after irradiation along the *c* axis at r.t.



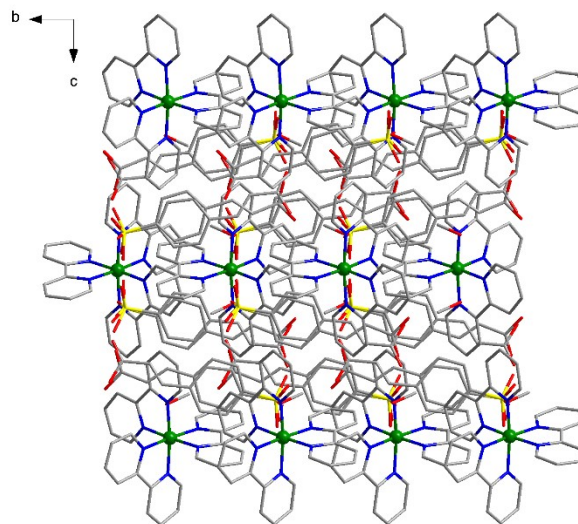
**Figure S13.** PXRD of  $[\text{Co}(\text{H}_2\text{O})_6](\text{Hpsca})_2 \cdot 4\text{H}_2\text{O}$  before and after photoirradiation.



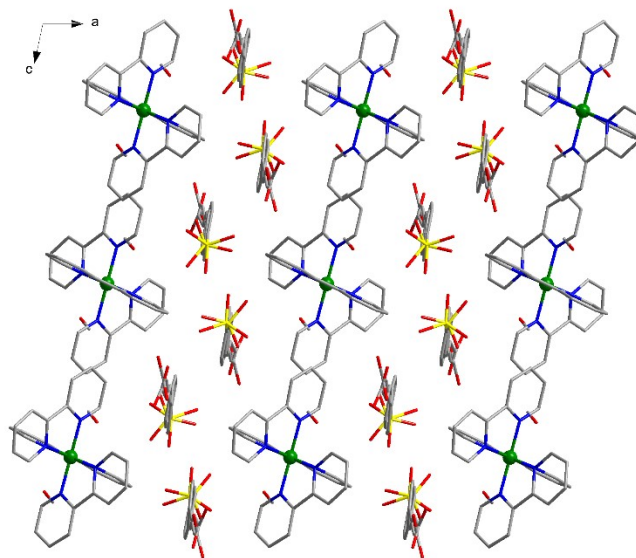
**Figure S14.** FTIR spectra of  $[\text{Co}(\text{H}_2\text{O})_6](\text{Hpsca})_2 \cdot 4\text{H}_2\text{O}$  after various hours of photoirradiation.



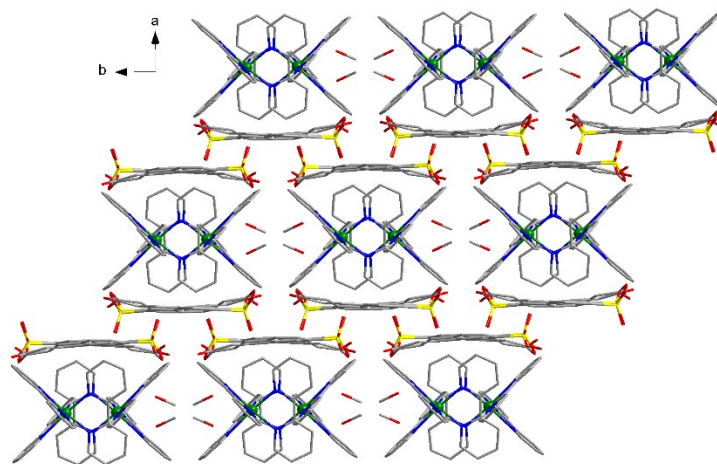
**Figure S15.** FTIR spectra of *trans*-cinnamic acid irradiated with UV light after 2 and 4 h illustrating the disappearance of the olefinic C=C bond at 1630  $\text{cm}^{-1}$ .



**Figure S16.** Crystal packing of  $[\text{Fe}(\text{bipy})_3](\text{Hpsca})_2 \cdot 2\text{MeOH}$  along the  $a$  axis at r.t.

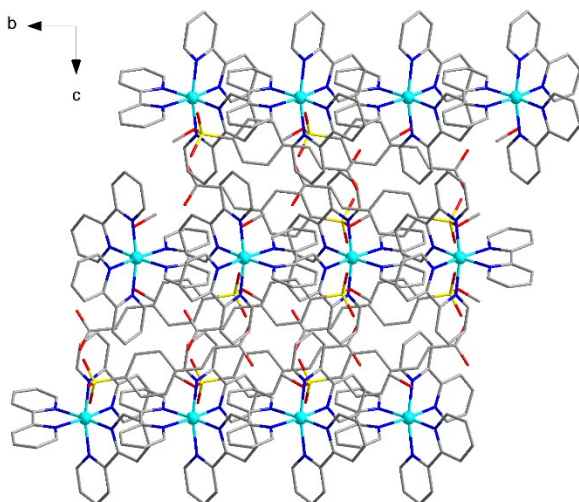


**Figure S17.** Crystal packing of [Fe(bipy)<sub>3</sub>](Hpsca)<sub>2</sub>·2MeOH along the *b* axis at r.t.

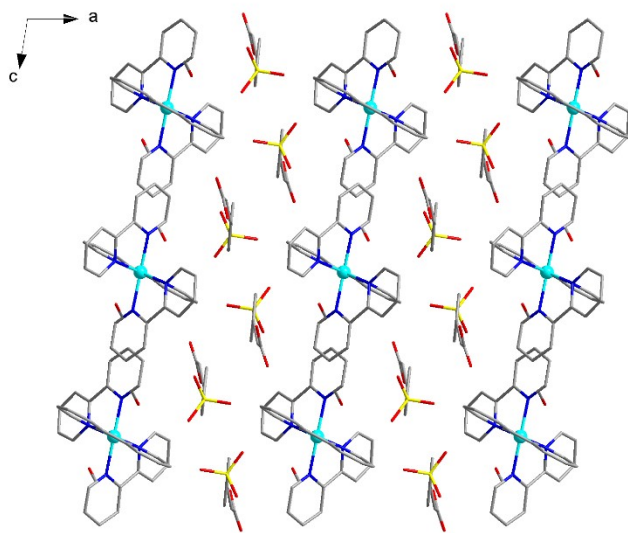


**Figure S18.** Crystal packing of [Fe(bipy)<sub>3</sub>](Hpsca)<sub>2</sub>·2MeOH along the *c* axis at r.t.

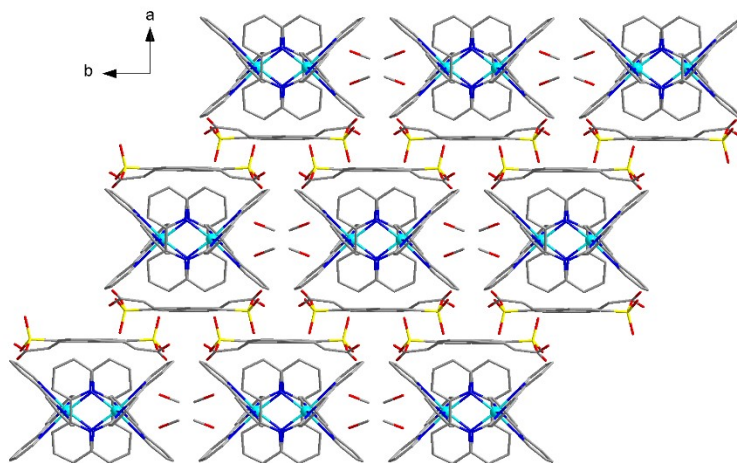




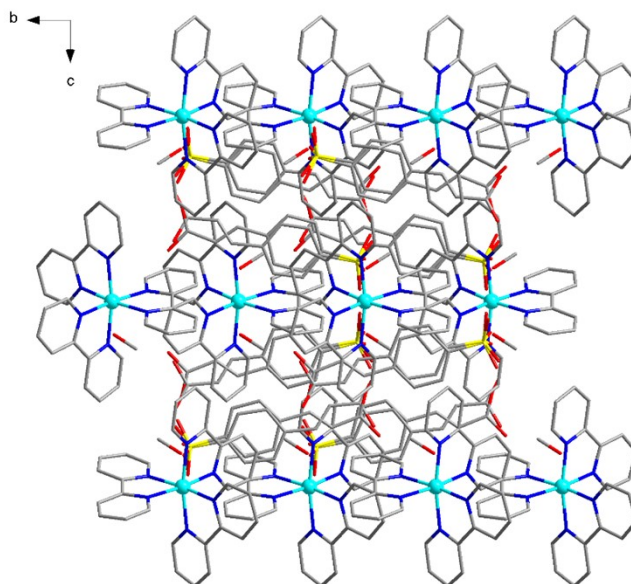
**Figure S20.** Crystal packing of [Co(bipy)<sub>3</sub>](Hpsca)<sub>2</sub>·2MeOH along the *a* axis at 100 K.



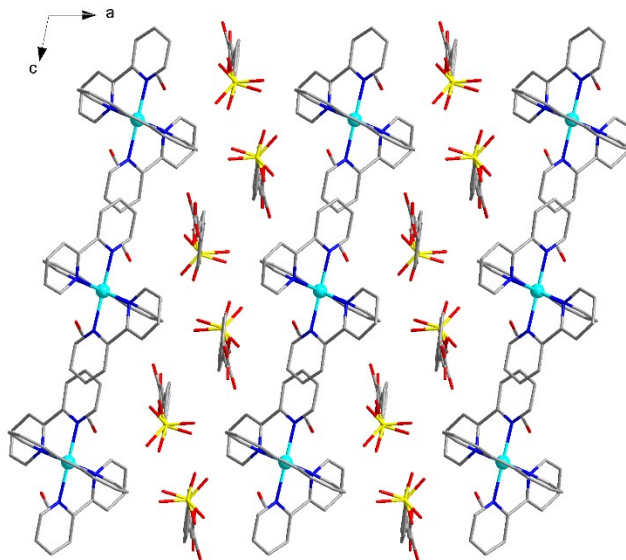
**Figure S21.** Crystal packing of [Co(bipy)<sub>3</sub>](Hpsca)<sub>2</sub>·2MeOH along the *b* axis at 100 K.



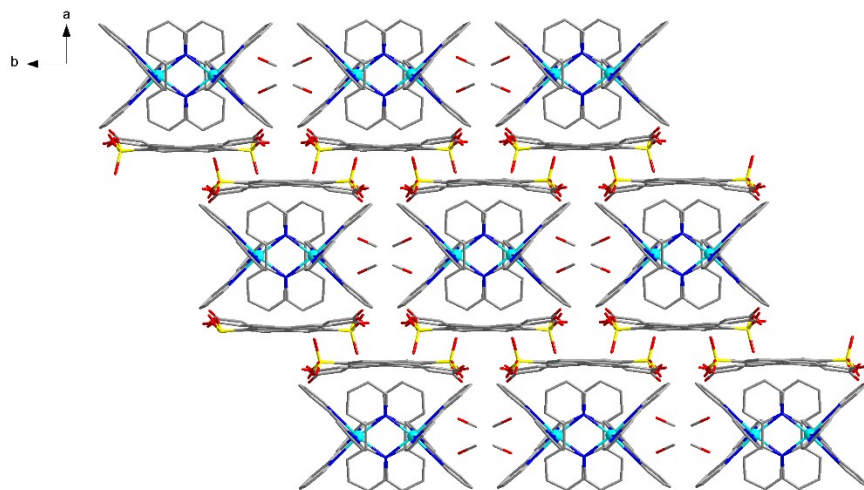
**Figure S22.** Crystal packing of [Co(bipy)<sub>3</sub>](Hpsca)<sub>2</sub>·2MeOH along the *c* axis at 100 K.



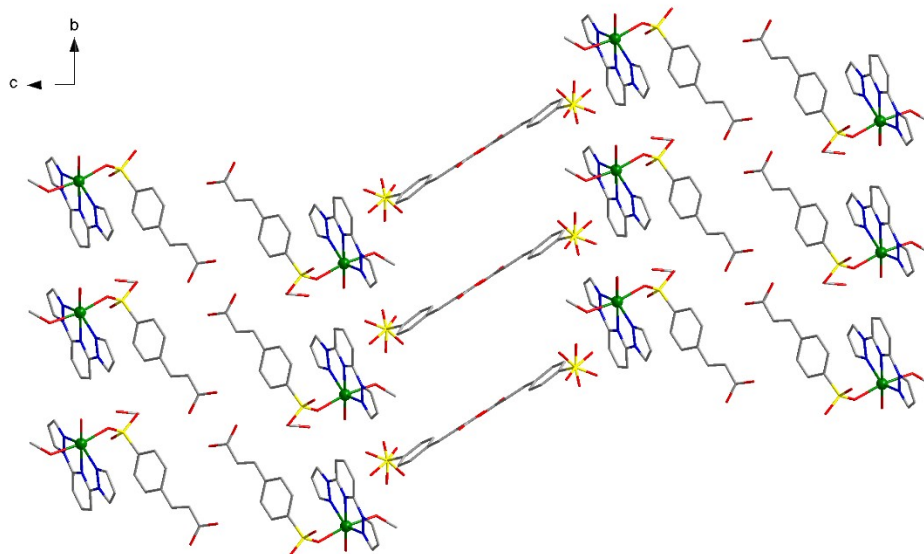
**Figure S23.** Crystal packing of [Co(bipy)<sub>3</sub>](Hpsca)<sub>2</sub>·1.26MeOH along the *a* axis at r.t.



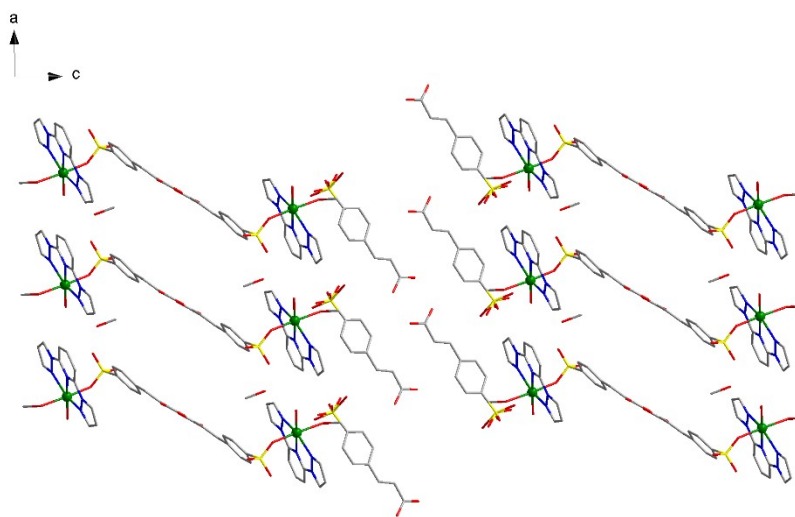
**Figure S24.** Crystal packing of [Co(bipy)<sub>3</sub>](Hpsca)<sub>2</sub>·1.26MeOH along the *b* axis at r.t.



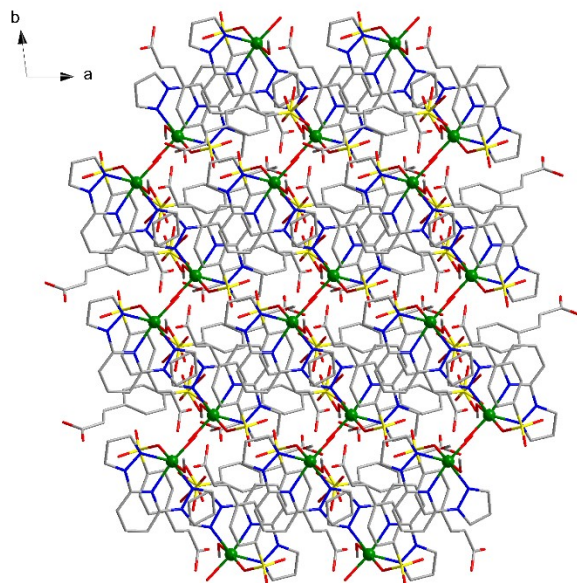
**Figure S25.** Crystal packing of [Co(bipy)<sub>3</sub>](Hpsca)<sub>2</sub>·1.26MeOH along the *c* axis at r.t.



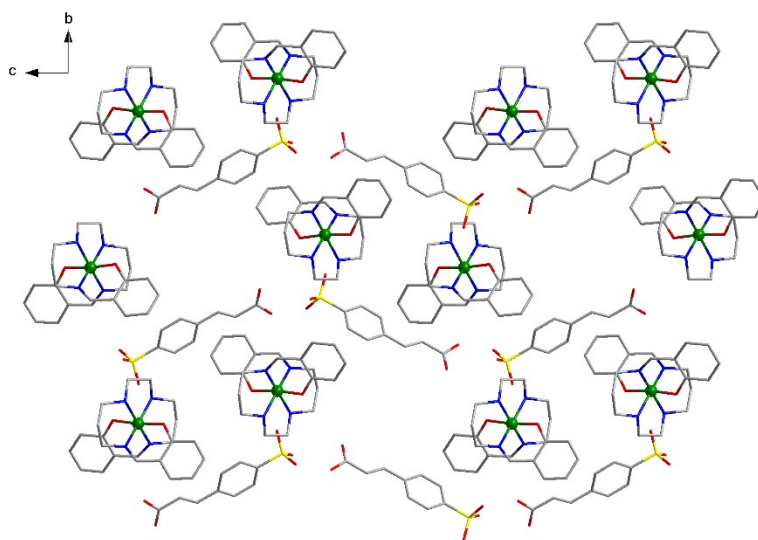
**Figure S26.** Crystal packing of  $[\text{Fe}(1\text{-bpp})(\text{Hpsca})(\text{H}_2\text{O})(\text{MeOH})]\text{Hpsca}\cdot\text{MeOH}$  along the *a* axis at r.t..



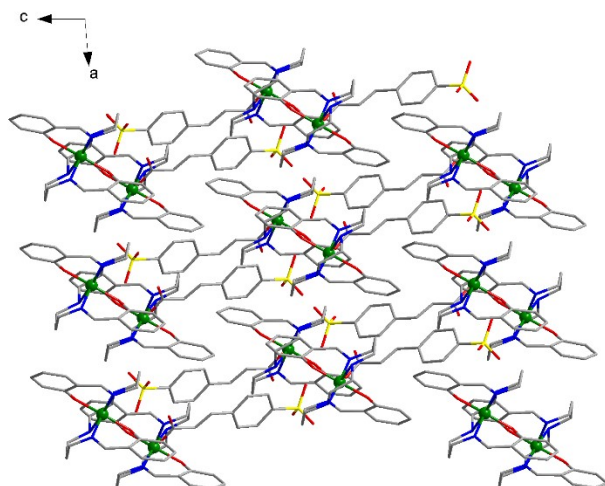
**Figure S27.** Crystal packing of  $[\text{Fe}(1\text{-bpp})(\text{Hpsca})(\text{H}_2\text{O})(\text{MeOH})]\text{Hpsca}\cdot\text{MeOH}$  along the *b* axis at r.t..



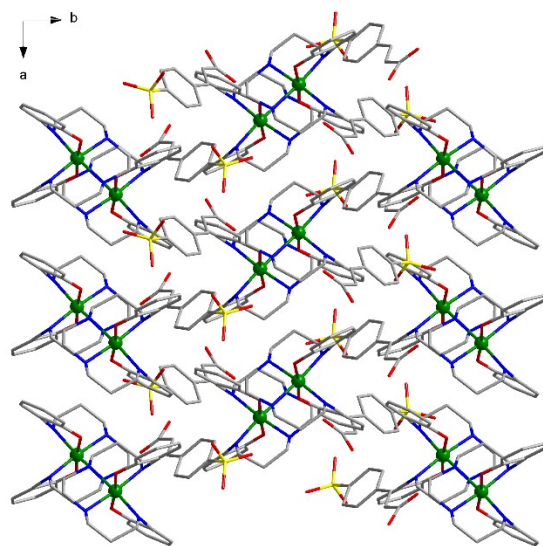
**Figure S28.** Crystal packing of  $[\text{Fe}(1\text{-bpp})(\text{Hpsca})(\text{H}_2\text{O})(\text{MeOH})]\text{Hpsca}\cdot\text{MeOH}$  along the  $c$  axis at r.t..



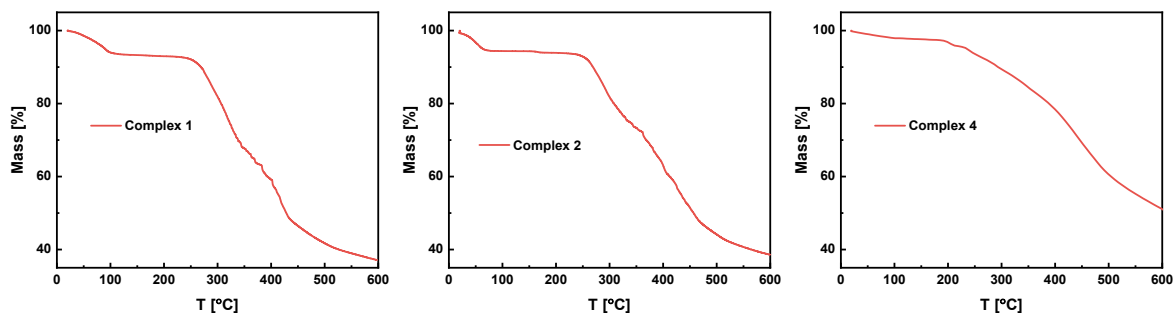
**Figure S29.** Crystal packing of  $[\text{Fe}(3,2,3\text{-sal}_2\text{tet})]\text{Hpsca}\cdot\text{H}_2\text{O}$  along the  $a$  axis at 100 K.



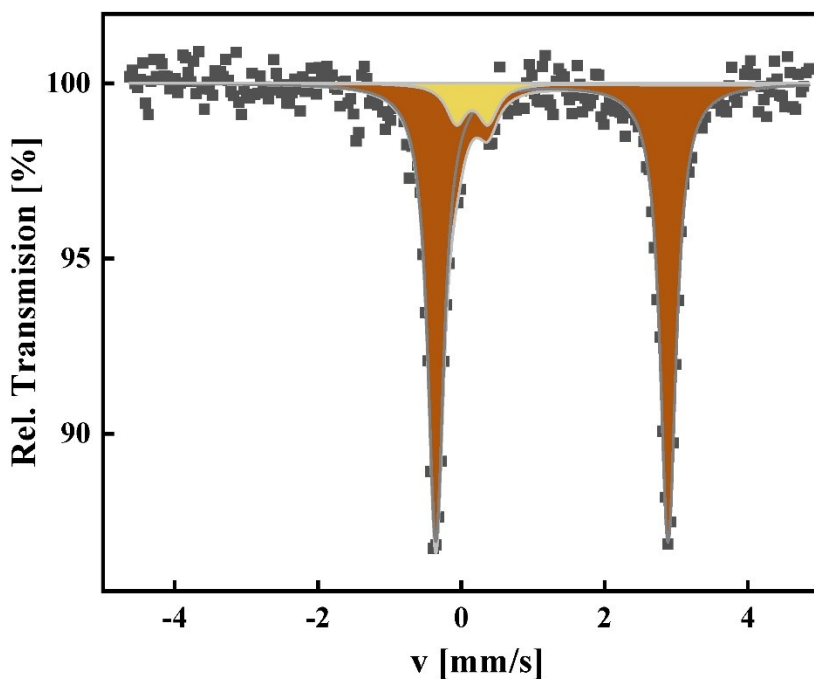
**Figure S30.** Crystal packing of [Fe(3,2,3-sal<sub>2</sub>tet)]Hpsca·H<sub>2</sub>O along the *b* axis at 100 K.



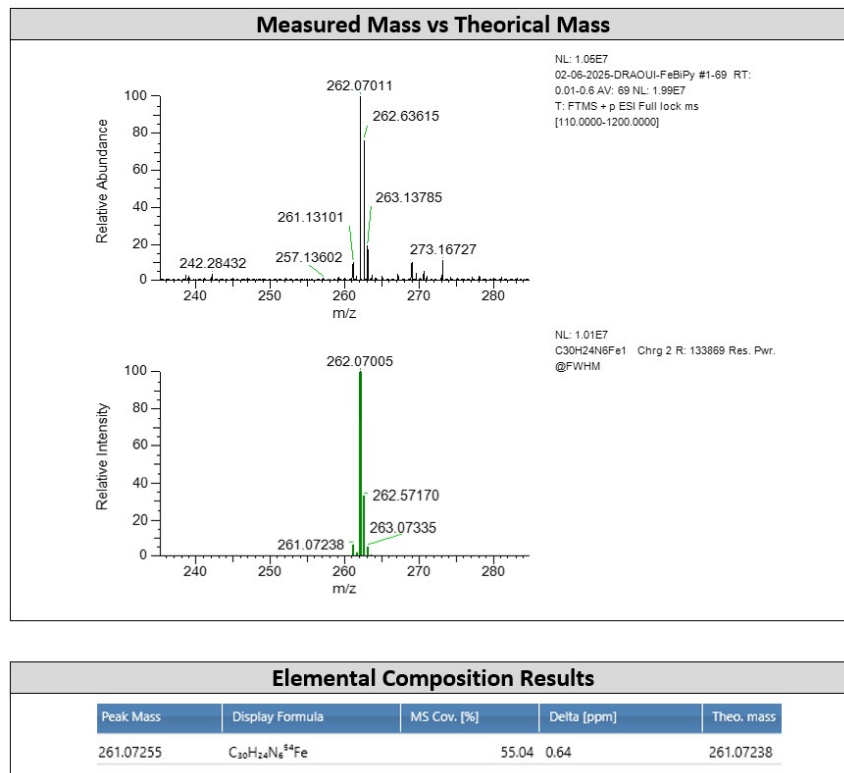
**Figure S31.** Crystal packing of [Fe(3,2,3-sal<sub>2</sub>tet)]Hpsca·H<sub>2</sub>O along the *c* axis at 100 K.



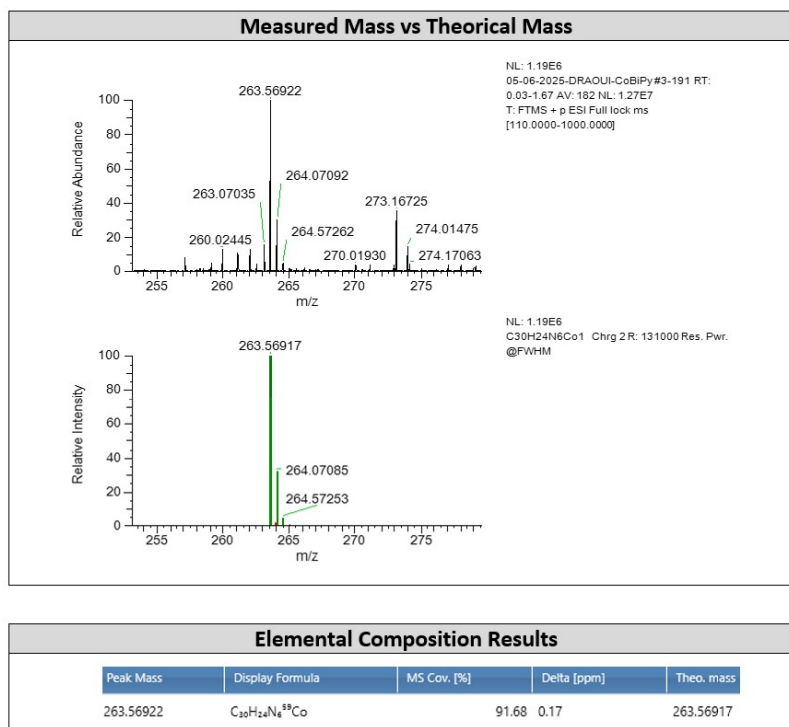
**Figure S32.** TGA curves of complexes **1**, **2** and **4**. **1** shows an initial weight loss of about 6.0% below 100 °C, which corresponds to the release of ca. 2 methanol molecules per formula unit. **2** exhibits a weight loss of ca. 5.5%, consistent with the removal of ca. 1.8 methanol molecule. **4** displays a weight loss of about 2.0%, which can be assigned to the release of ca. one water molecule.



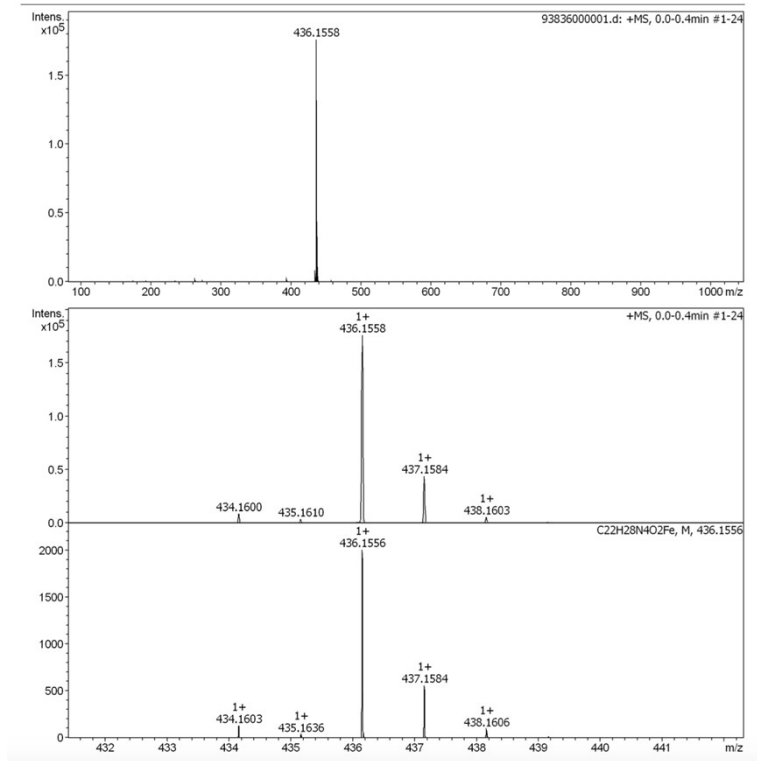
**Figure S33.**  $^{57}\text{Fe}$  Mössbauer spectrum of  $[\text{Fe}(\text{H}_2\text{O})_6](\text{HpscA})_2 \cdot 2\text{H}_2\text{O}$  recorded at 298 K. The signal in red stands for HS Fe(II) ions and in yellow for HS Fe(III) ions.



**Figure S34. HRMS of 1.**



**Figure S35. HRMS of 2.**



**Figure S36.** HRMS of 4.