

# Supporting Information

## **Mononuclear Fe(III) complexes with 2,4-dichloro-6-((quinoline-8-ylimino)methyl)phenolate: synthesis, structure, and magnetic behavior**

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**Table S1** Summary of crystallographic data for **1a–3b**

	<b>1a</b>	<b>1b</b>	<b>2a</b>	<b>2b</b>	<b>3a</b>	<b>3b</b>
formula	C <sub>32</sub> H <sub>20</sub> Cl <sub>4</sub> Fe N <sub>5</sub> O <sub>6</sub>	C <sub>32</sub> H <sub>20</sub> Cl <sub>4</sub> Fe N <sub>5</sub> O <sub>6</sub>	C <sub>38</sub> H <sub>30</sub> BCl <sub>4</sub> F 4FeN <sub>4</sub> O <sub>4</sub>	C <sub>32</sub> H <sub>18</sub> BCl <sub>4</sub> F 4FeN <sub>4</sub> O <sub>2</sub>	C <sub>32</sub> H <sub>18</sub> Cl <sub>5</sub> Fe N <sub>4</sub> O <sub>6</sub>	C <sub>32</sub> H <sub>18</sub> Cl <sub>5</sub> Fe N <sub>4</sub> O <sub>6</sub>
$M_r$	768.18	768.18	891.12	774.96	787.60	787.60
crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
$a$ (Å)	9.4930(19)	9.5590(19)	9.4580(19)	9.5750(19)	14.227(3)	14.289(3)
$b$ (Å)	11.327(2)	11.905(2)	12.391(3)	12.544(3)	17.461(4)	17.702(4)
$c$ (Å)	15.069(3)	15.101(3)	16.320(3)	16.518(3)	15.213(3)	15.399(3)
$\alpha$ (deg)	105.08(3)	108.20(3)	95.32(3)	94.12(3)	90	90
$\beta$ (deg)	100.34(3)	98.16(3)	103.38(3)	103.45(3)	107.55(3)	107.82(3)
$\gamma$ (deg)	94.92(3)	96.48(3)	97.00(3)	97.39(3)	90	90
$V$ (Å <sup>3</sup> )	1524.1(6)	1593.2(6)	1832.3(7)	1902.8(7)	3603.2(14)	3708.1(14)
$Z$	2	2	2	2	4	4
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.674	1.601	1.615	1.353	1.485	1.443
$T$ (K)	100(2)	298(2)	100(2)	298(2)	100(2)	293(2)
$\lambda$ (Å)	0.70000	0.70000	0.63000	0.63000	0.63000	0.63000
$\mu$ (mm <sup>-1</sup> )	0.868	0.831	0.552	0.520	0.595	0.579
Reflections collected	14642	12123	28979	15631	37245	37942
Independent reflections	7484	6283	14908	9786	9566	9877
Reflections with $> 2\sigma(I)$	5520	4194	8986	6035	8284	7465
$R_{\text{int}}$	0.0184	0.0238	0.0347	0.0478	0.0267	0.0435
Goodness-of-fit on $F^2$	1.041	0.983	1.083	1.500	1.031	1.047
$R_1^a$ ( $4\sigma$ data)	0.0711	0.0611	0.0732	0.0967	0.0607	0.0748
$wR_2^b$ ( $4\sigma$ data)	0.1912	0.1566	0.2274	0.2870	0.1557	0.2342
CCDC no.	2002656	2002657	2002658	2002659	2002660	2002661

<sup>a</sup>  $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ . <sup>b</sup>  $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ .

**Table S2** Temperature-dependent  $\mu_{\text{eff}}$  of **1** obtained by NMR spectra of Fig. S1

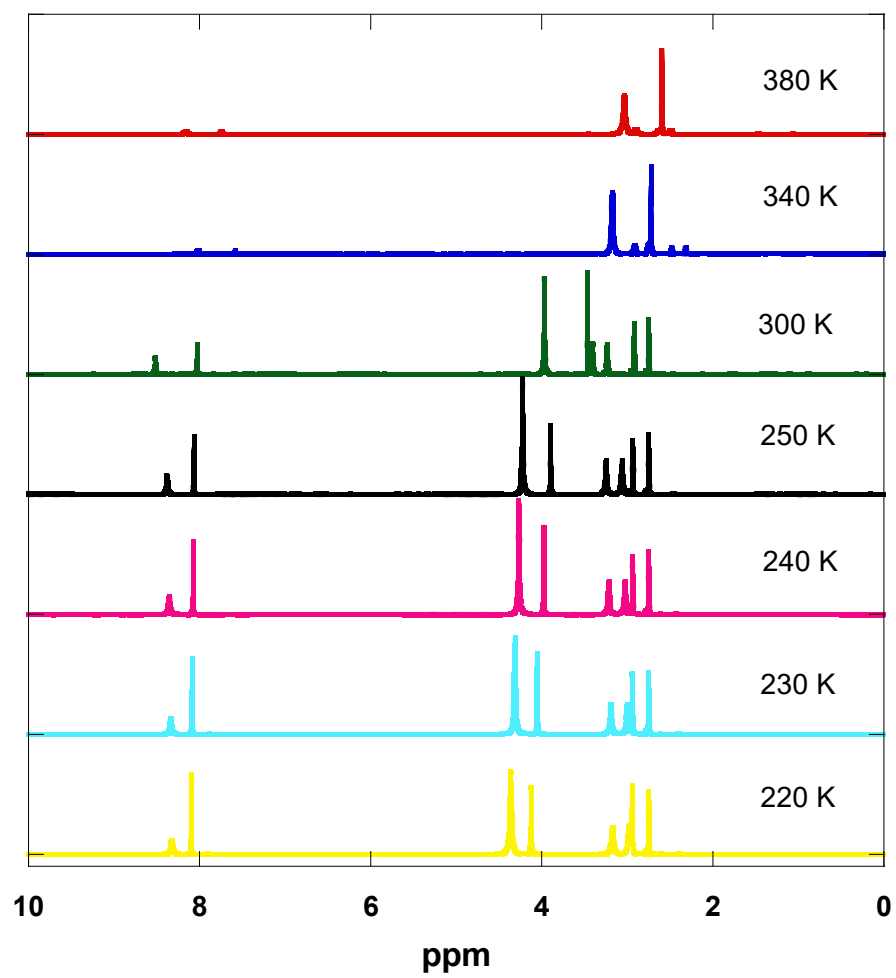
Molarity (M)	A (ppm)	B (ppm)	$\Delta\delta$ (ppm)	$\chi_M$	$T$ (K)	$\mu_{\text{eff}}$
$1.68 \times 10^{-2}$	8.324	8.096	0.228	$3.23 \times 10^{-3}$	220	2.38
$1.68 \times 10^{-2}$	8.337	8.087	0.250	$3.55 \times 10^{-3}$	230	2.56
$1.68 \times 10^{-2}$	8.355	8.077	0.278	$3.96 \times 10^{-3}$	240	2.76
$1.68 \times 10^{-2}$	8.381	8.067	0.314	$4.46 \times 10^{-3}$	250	2.99
$1.68 \times 10^{-2}$	8.514	8.031	0.483	$6.88 \times 10^{-3}$	300	4.04
$1.68 \times 10^{-2}$	8.016	7.582	0.434	$6.29 \times 10^{-3}$	340	4.14
$1.68 \times 10^{-2}$	8.160	7.744	0.416	$6.03 \times 10^{-3}$	380	4.28

**Table S3** Temperature-dependent  $\mu_{\text{eff}}$  of **2** obtained by NMR spectra of Fig. S2

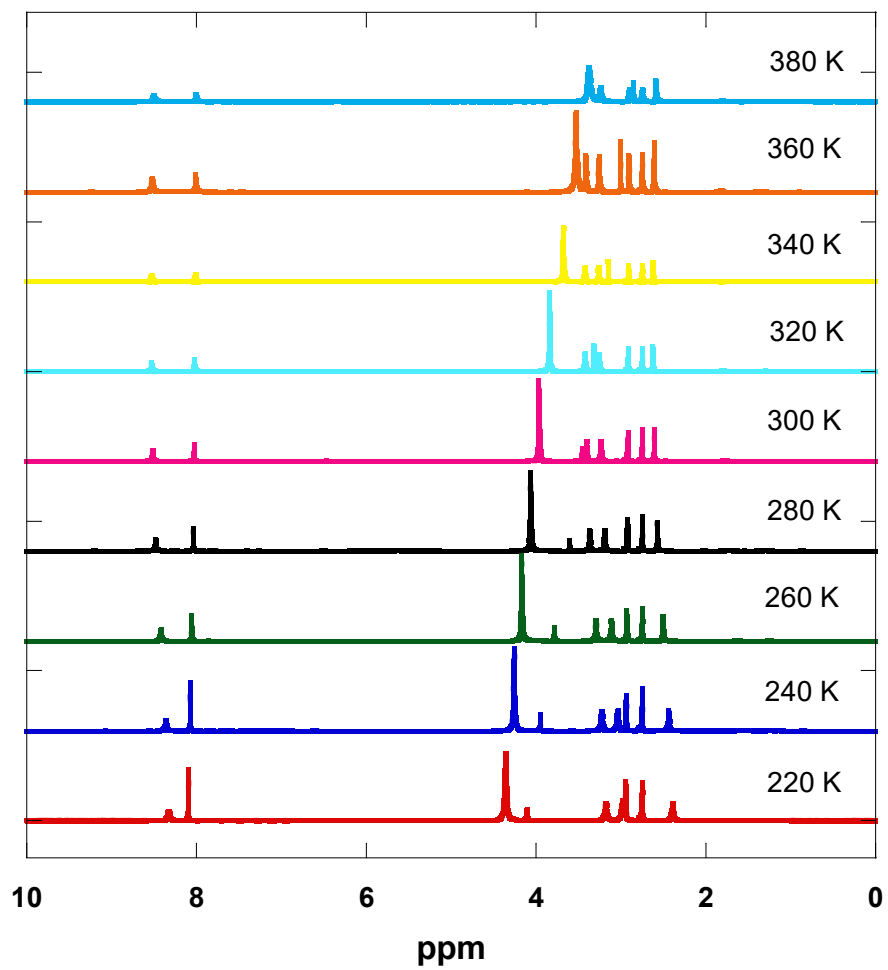
Molarity (M)	A (ppm)	B (ppm)	$\Delta\delta$ (ppm)	$\chi_M$	$T$ (K)	$\mu_{\text{eff}}$
$1.26 \times 10^{-2}$	8.326	8.095	0.231	$4.36 \times 10^{-3}$	220	2.77
$1.26 \times 10^{-2}$	8.361	8.074	0.287	$5.41 \times 10^{-3}$	240	3.22
$1.26 \times 10^{-2}$	8.420	8.056	0.364	$6.87 \times 10^{-3}$	260	3.78
$1.26 \times 10^{-2}$	8.483	8.040	0.443	$8.36 \times 10^{-3}$	280	4.33
$1.26 \times 10^{-2}$	8.517	8.030	0.487	$9.18 \times 10^{-3}$	300	4.70
$1.26 \times 10^{-2}$	8.530	8.021	0.508	$9.58 \times 10^{-3}$	320	4.95
$1.26 \times 10^{-2}$	8.528	8.014	0.514	$9.70 \times 10^{-3}$	340	5.14
$1.26 \times 10^{-2}$	8.523	8.008	0.515	$9.71 \times 10^{-3}$	360	5.29
$1.26 \times 10^{-2}$	8.504	8.004	0.500	$9.43 \times 10^{-3}$	380	5.35

**Table S4** Temperature-dependent  $\mu_{\text{eff}}$  of **3** obtained by NMR spectra of Fig. S3

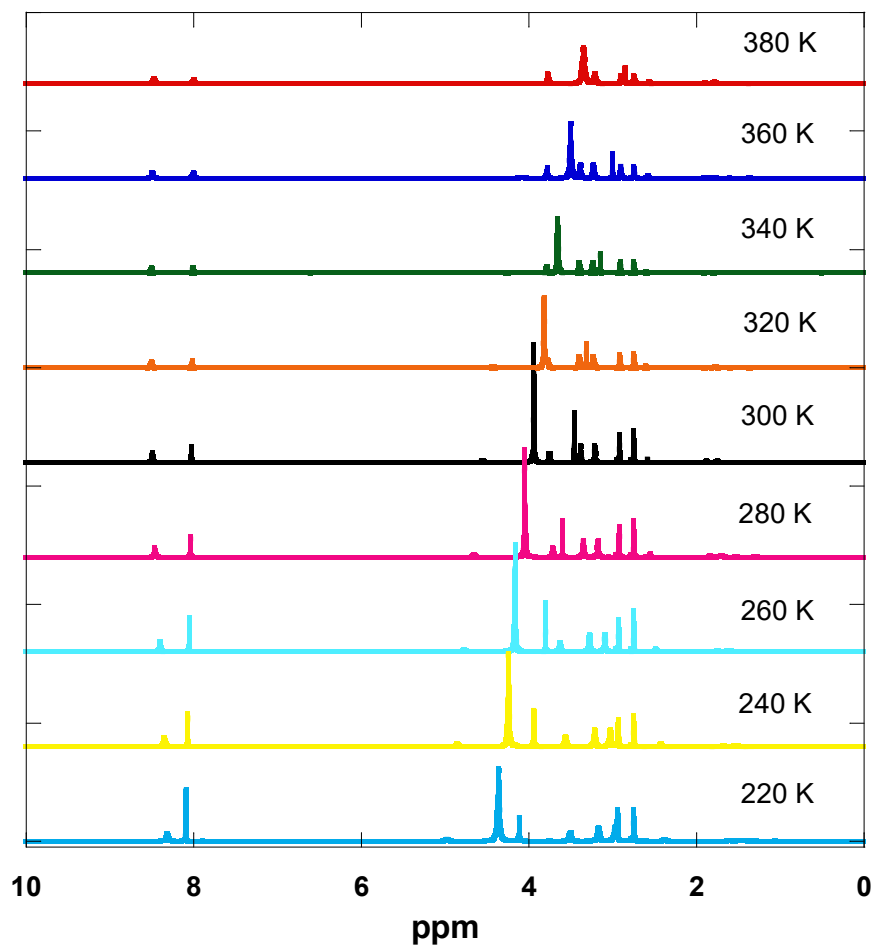
Molarity (M)	A (ppm)	B (ppm)	$\Delta\delta$ (ppm)	$\chi_M$	$T$ (K)	$\mu_{\text{eff}}$
$1.32 \times 10^{-2}$	8.319	8.096	0.223	$4.03 \times 10^{-3}$	220	2.66
$1.32 \times 10^{-2}$	8.352	8.072	0.280	$5.05 \times 10^{-3}$	240	3.11
$1.32 \times 10^{-2}$	8.402	8.057	0.345	$6.23 \times 10^{-3}$	260	3.60
$1.32 \times 10^{-2}$	8.466	8.039	0.427	$7.71 \times 10^{-3}$	280	4.16
$1.32 \times 10^{-2}$	8.495	8.030	0.465	$8.40 \times 10^{-3}$	300	4.49
$1.32 \times 10^{-2}$	8.507	8.022	0.485	$8.76 \times 10^{-3}$	320	4.74
$1.32 \times 10^{-2}$	8.505	8.014	0.491	$8.88 \times 10^{-3}$	340	4.91
$1.32 \times 10^{-2}$	8.495	8.008	0.487	$8.80 \times 10^{-3}$	360	5.03
$1.32 \times 10^{-2}$	8.479	8.005	0.474	$8.56 \times 10^{-3}$	380	5.10



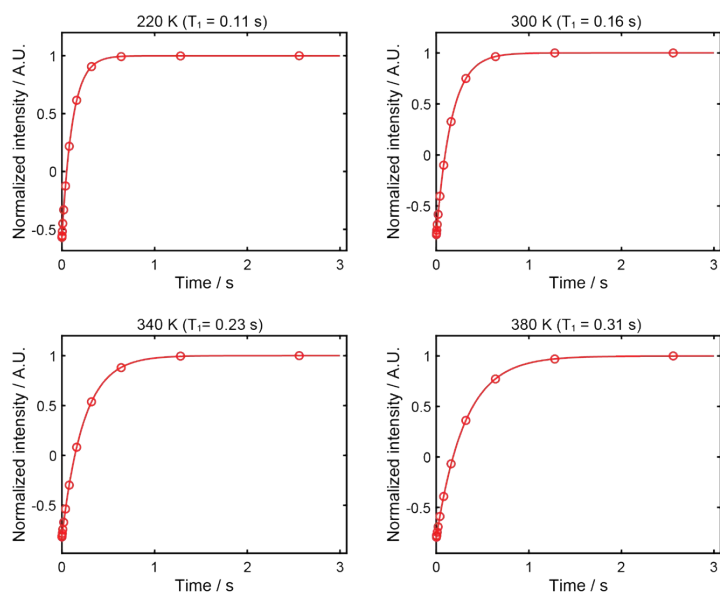
**Fig. S1** Temperature-dependent NMR spectra of **1** measured by Evans method in DMF-d<sub>7</sub>.



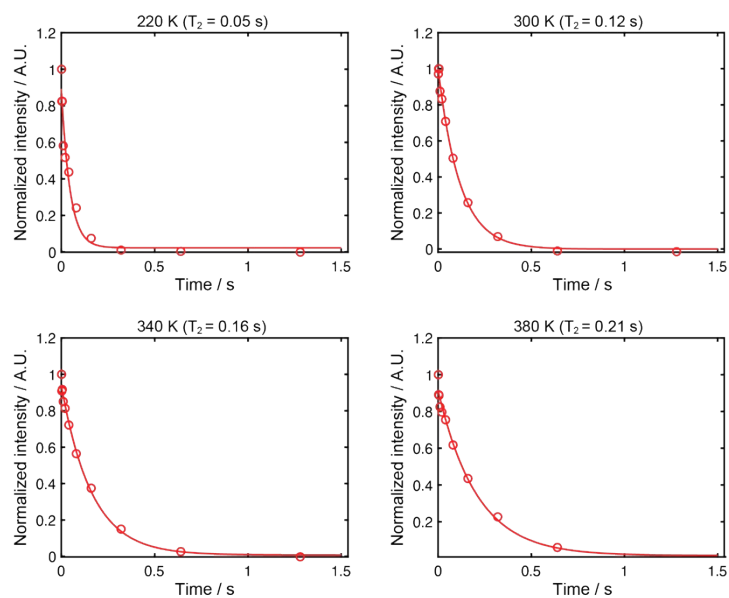
**Fig. S2** Temperature-dependent NMR spectra of **2** measured by Evans method in DMF-d<sub>7</sub>.



**Fig. S3** Temperature-dependent NMR spectra of **3** measured by Evans method in DMF-d<sub>7</sub>.

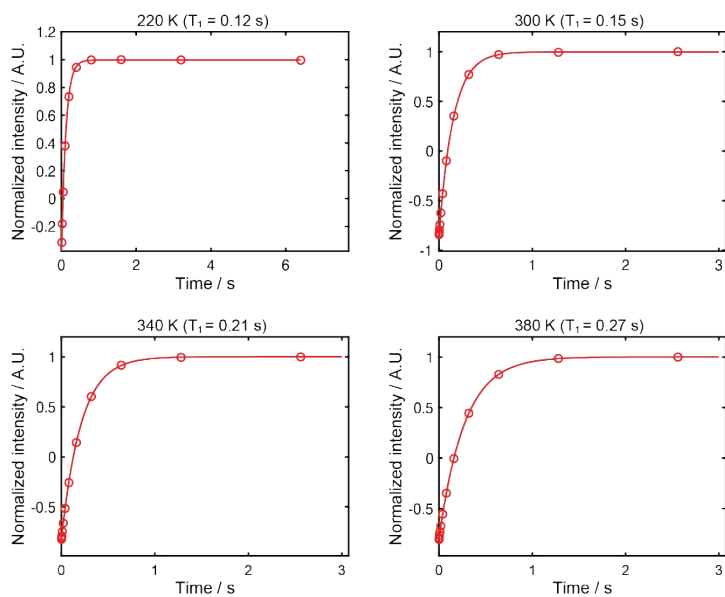


**Fig. S4**  $^1\text{H}$   $T_1$  relaxation curve fitting of DMF with **1** at 220, 300, 340, and 380 K.

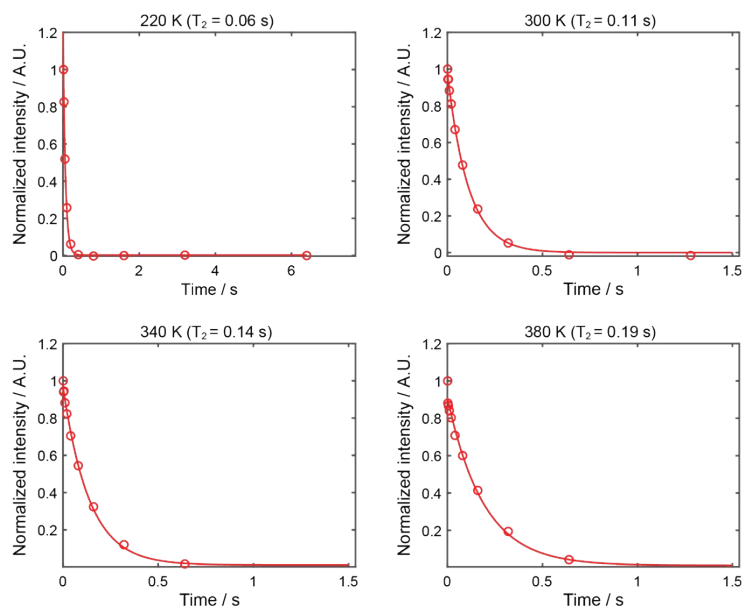


**Fig. S5**  $^1\text{H}$   $T_2$  relaxation curve fitting of DMF with **1** at 220, 300, 340, and 380 K.





**Fig. S6**  $^1\text{H}$   $T_1$  relaxation curve fitting of DMF with **2** at 220, 300, 340, and 380 K.

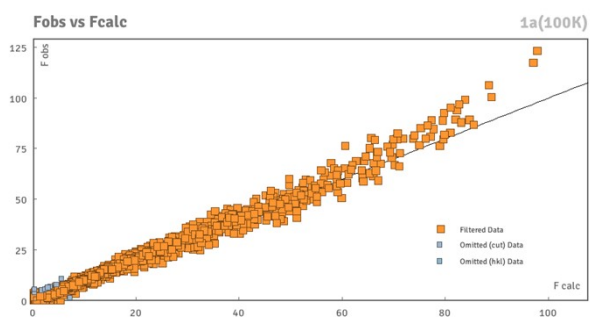
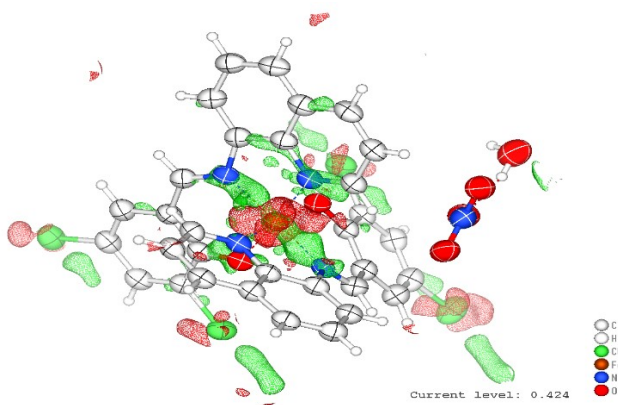


**Fig. S7**  $^1\text{H}$   $T_2$  relaxation curve fitting of DMF with **2** at 220, 300, 340, and 380 K.

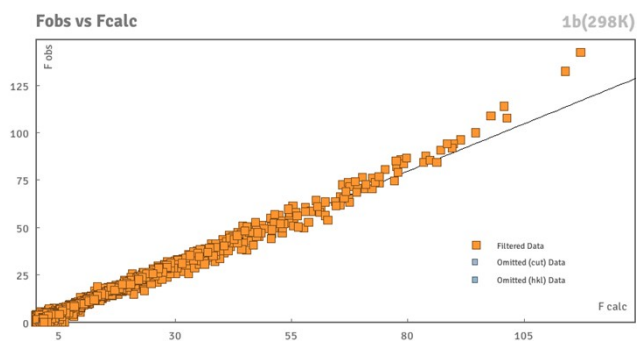
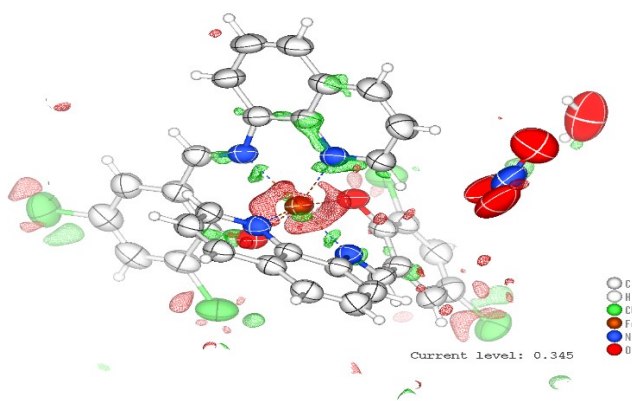
### **Analyses of electron density map and $F_{\text{obs}}$ vs $F_{\text{calc}}$ plot of complexes 1a, 1b, 2a, 2b, 3a, and 3b.**

Although the quality of the crystallographic data obtained may not be ideal (Figs S8~S13), but we are confident that the structural information derived is sufficient to support the conclusions presented in our manuscript. In particular, it is important to emphasize that the crystals available for complexes **1a**, **1b**, **2a**, **2b**, **3a**, and **3b** were not sufficient size, quality, or scattering strength for the laboratory diffractometer, so that satisfactory structures could only be collected using synchrotron radiation.

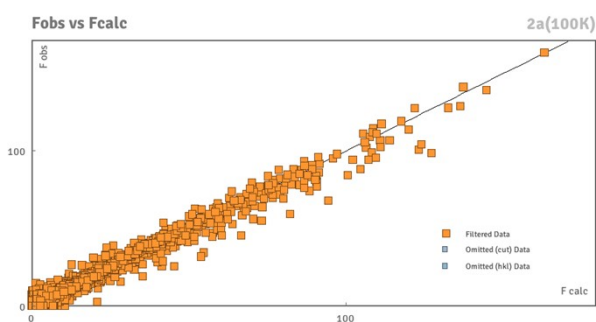
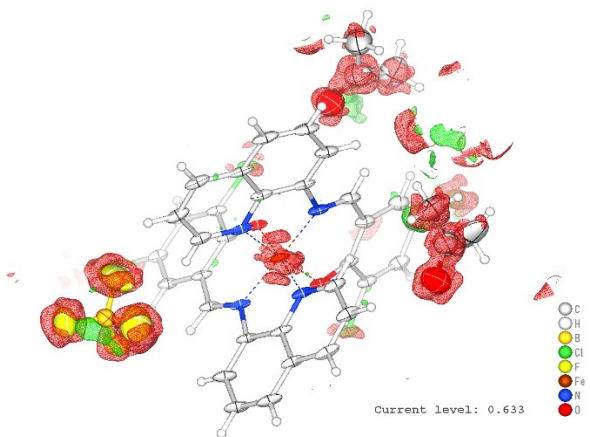
Specifically, the electron density maps of **1a**, **1b**, **2a**, **2b**, **3a**, and **3b** (Figs S8~S13) indicate some disorders in the anions, solvent areas, and high electron density of Cl atoms in the qsal-type ligand. Additionally, the  $F_{\text{obs}}$  vs.  $F_{\text{calc}}$  plots do not show narrow lines with numerous strong reflections, indicative of relatively poor agreements with the structural models (Figs S8~S13). This may also, in part, be attributed to the fact that single crystal data were acquired at a synchrotron beamline dedicated to small-molecule crystallography, which only permits a high-accuracy omega scan. This limitation could contribute to observed features in the  $F_{\text{obs}}$  vs.  $F_{\text{calc}}$  plots and completeness, particularly, for structures with low symmetry, tri-/monoclinic space group as here.



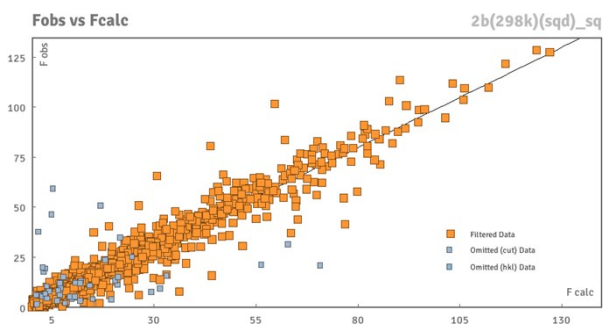
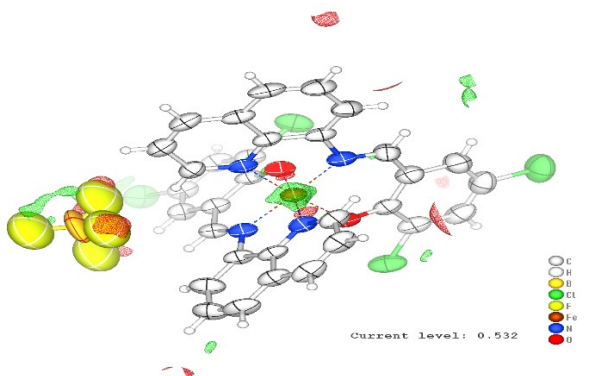
**Fig. S8** Electron density map(up) and  $F_{\text{obs}}$  vs  $F_{\text{calc}}$  plot(down) of complex **1a**.



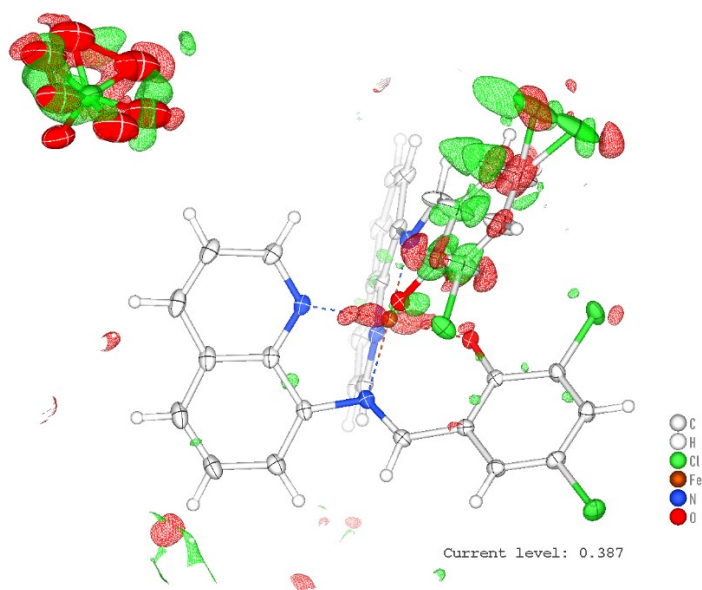
**Fig. S9** Electron density map(up) and  $F_{\text{obs}}$  vs  $F_{\text{calc}}$  plot(down) of complex **1b**.



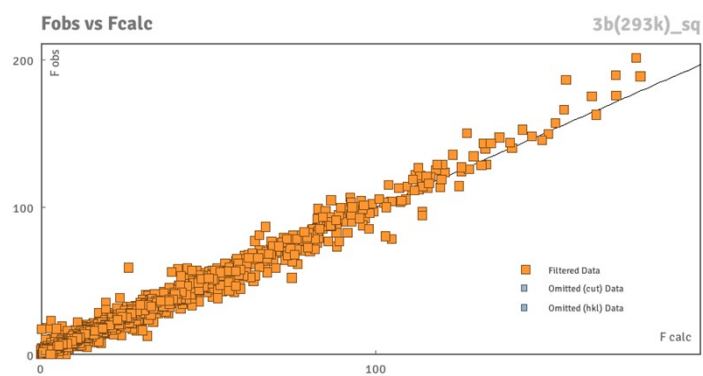
**Fig. S10** Electron density map(up) and  $F_{\text{obs}}$  vs  $F_{\text{calc}}$  plot(down) of complex **2a**.



**Fig. S11** Electron density map(up) and  $F_{\text{obs}}$  vs  $F_{\text{calc}}$  plot(down) of complex **2b**.



**Fig. S12** Electron density map of **3a**.



**Fig. S13**  $F_{obs}$  vs  $F_{calc}$  plot of complex **3b**.