

## ELECTRONIC SUPPORTING INFORMATION

### Luminescent Er<sup>3+</sup> Based Single Molecule Magnets with Fluorinated Alkoxide or Aryloxy Ligands

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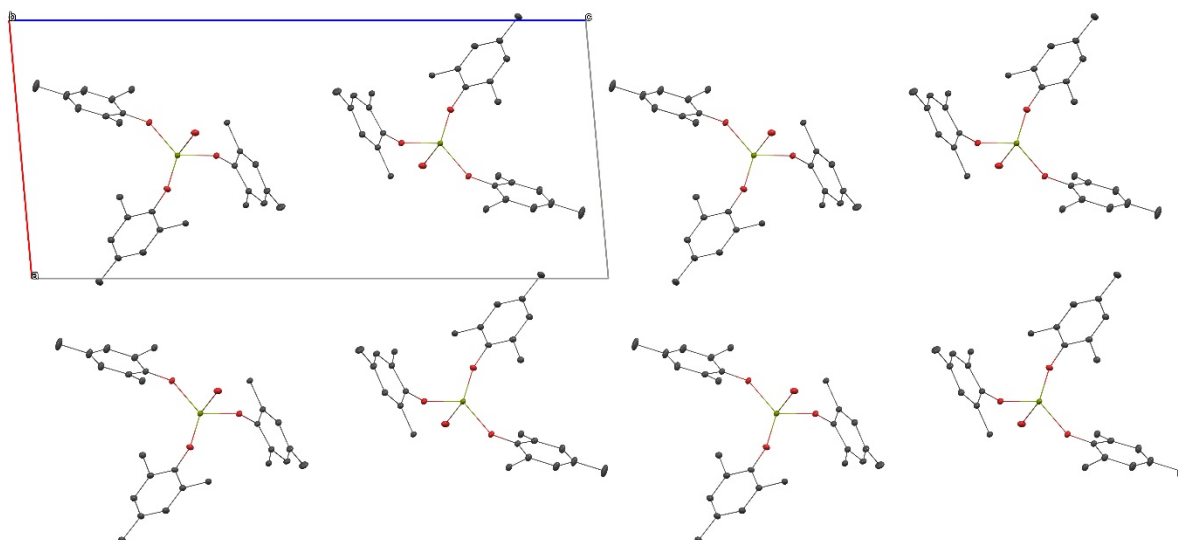
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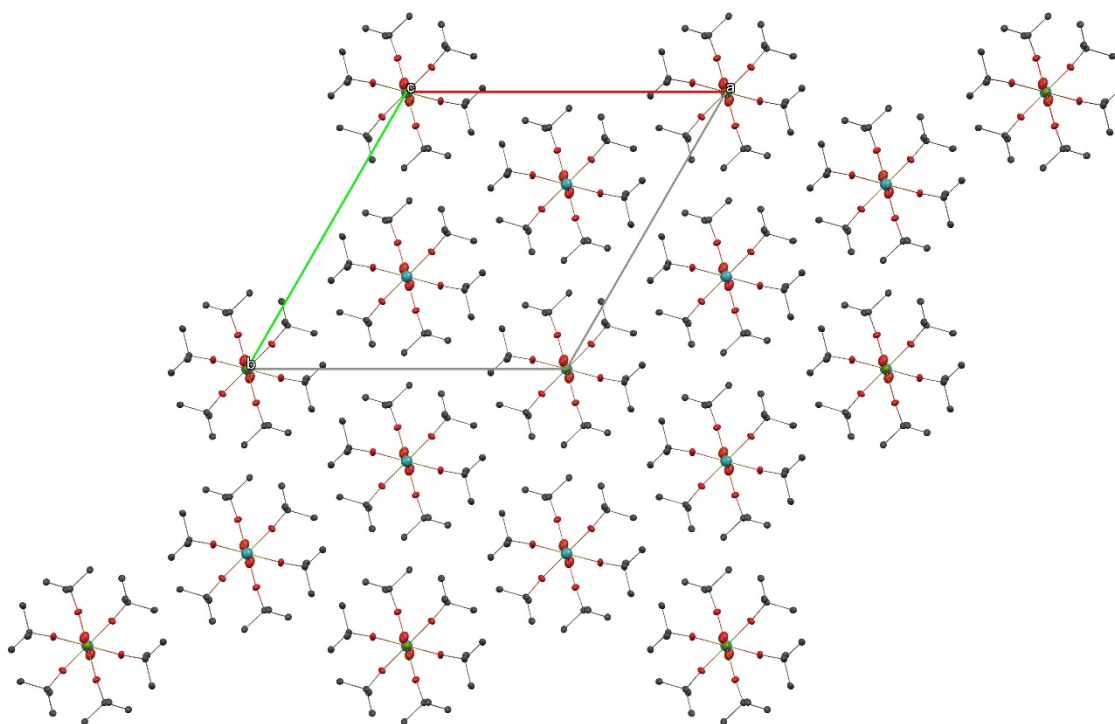
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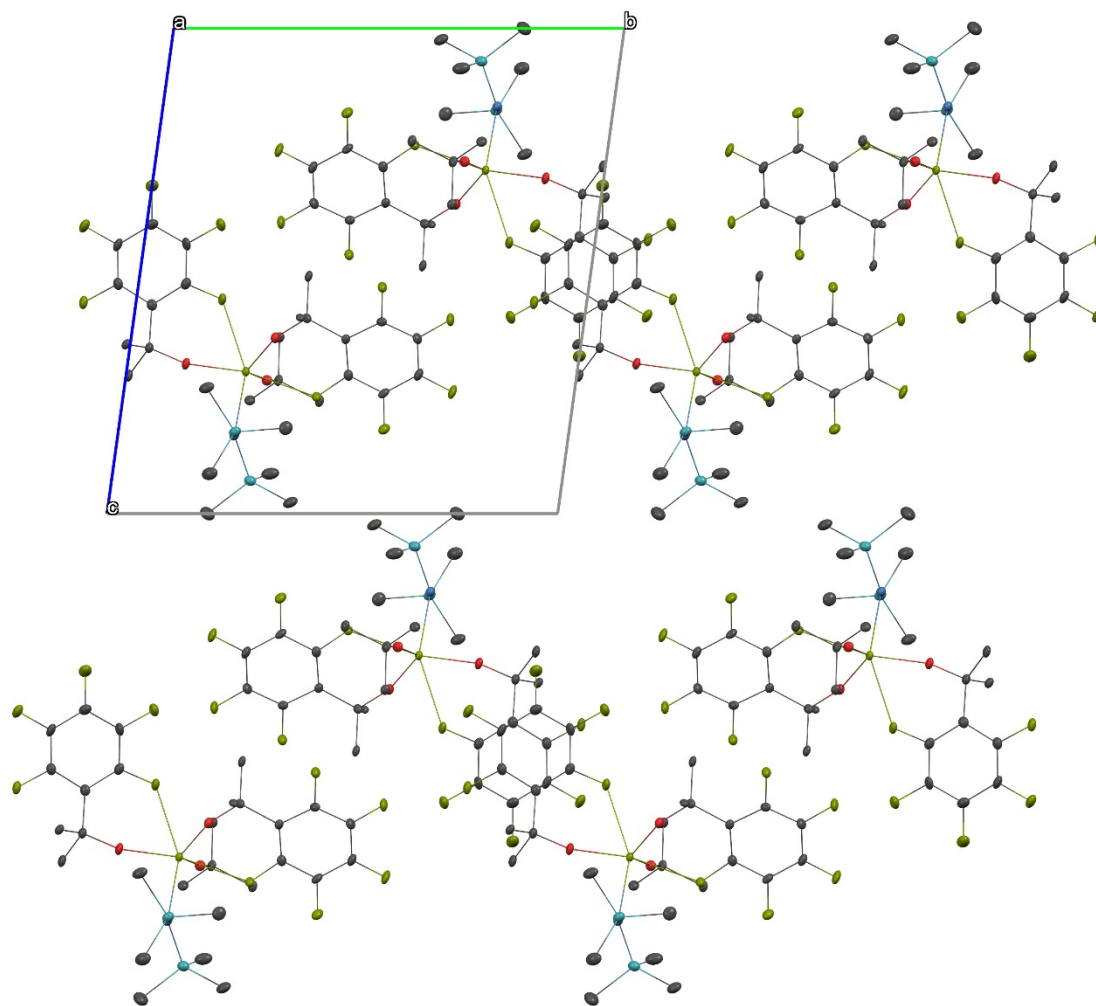
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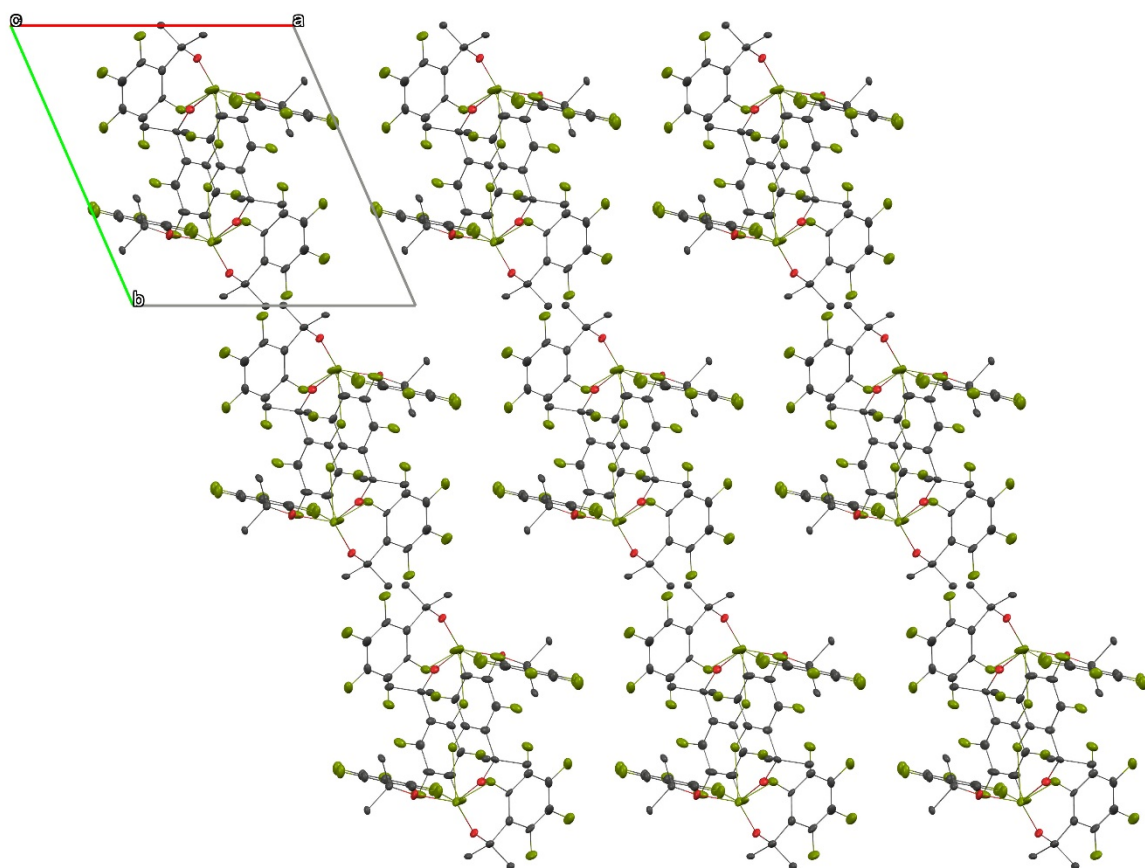
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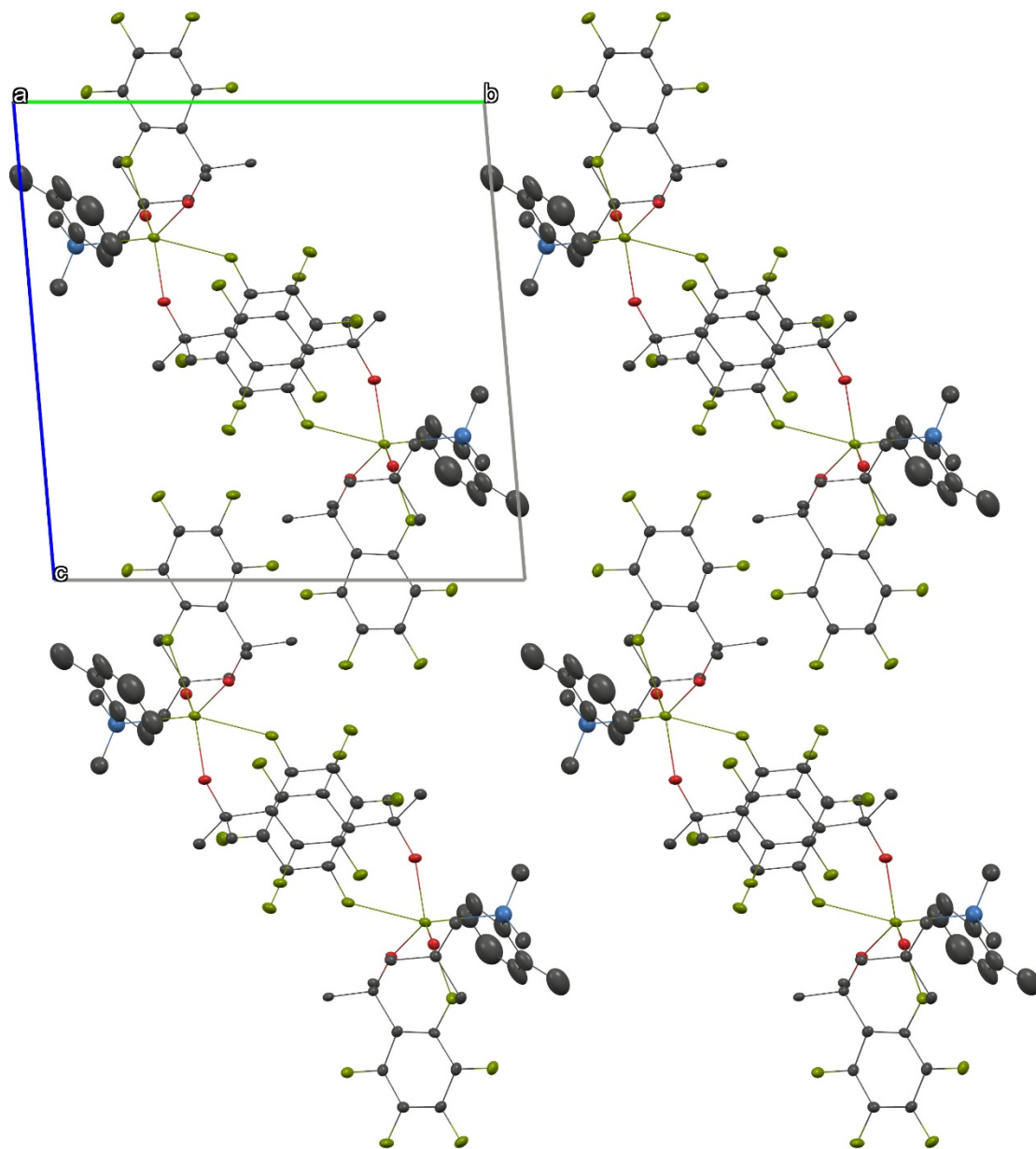
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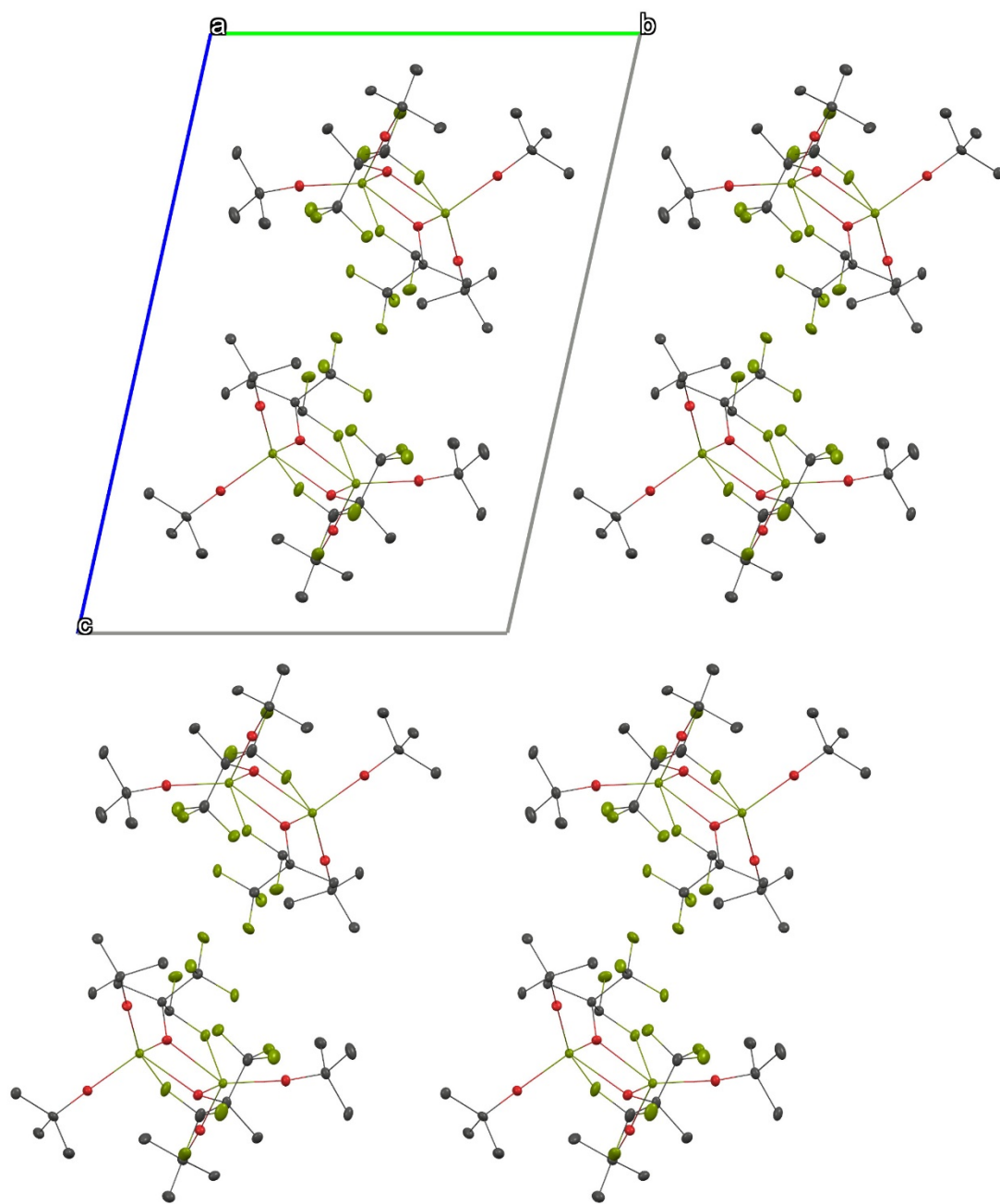


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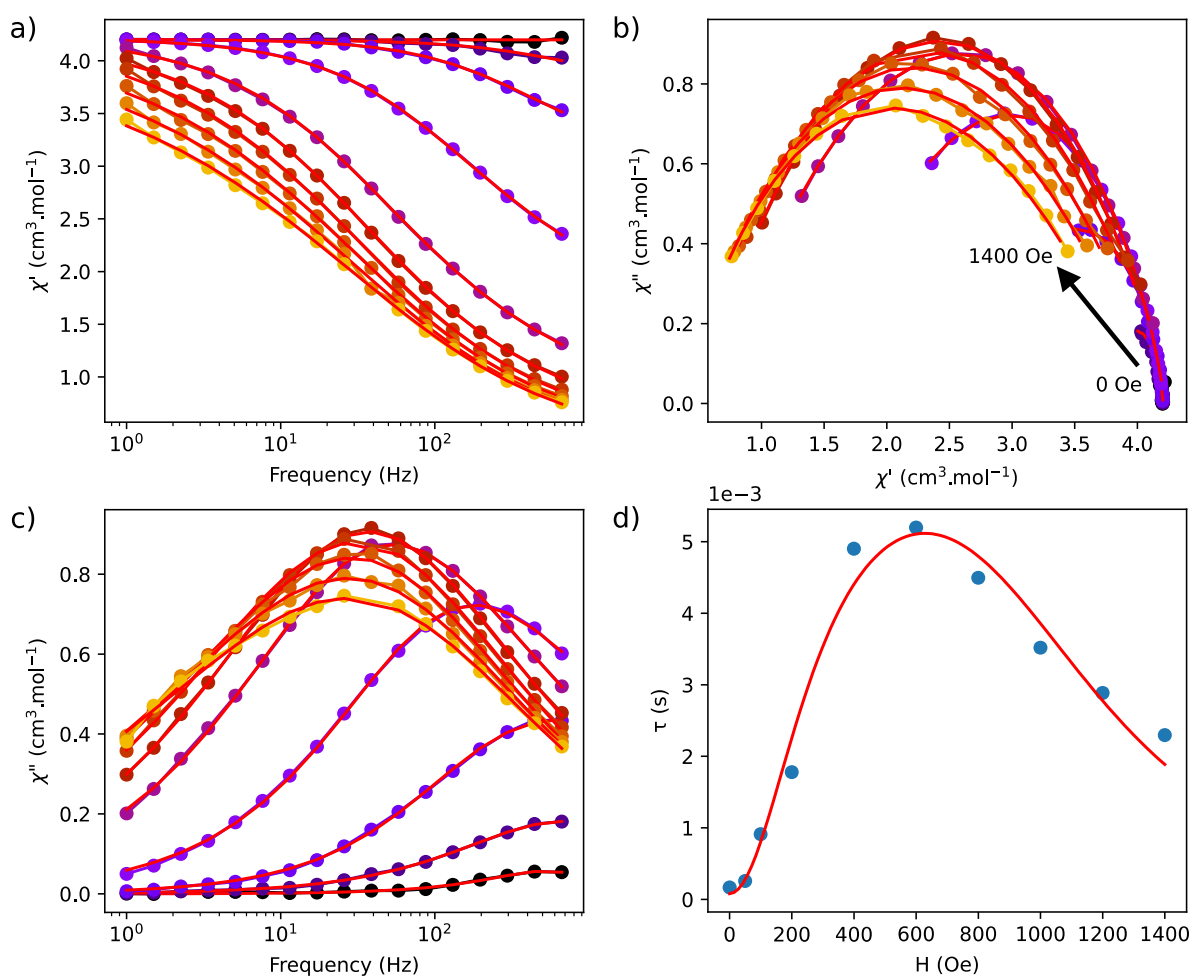


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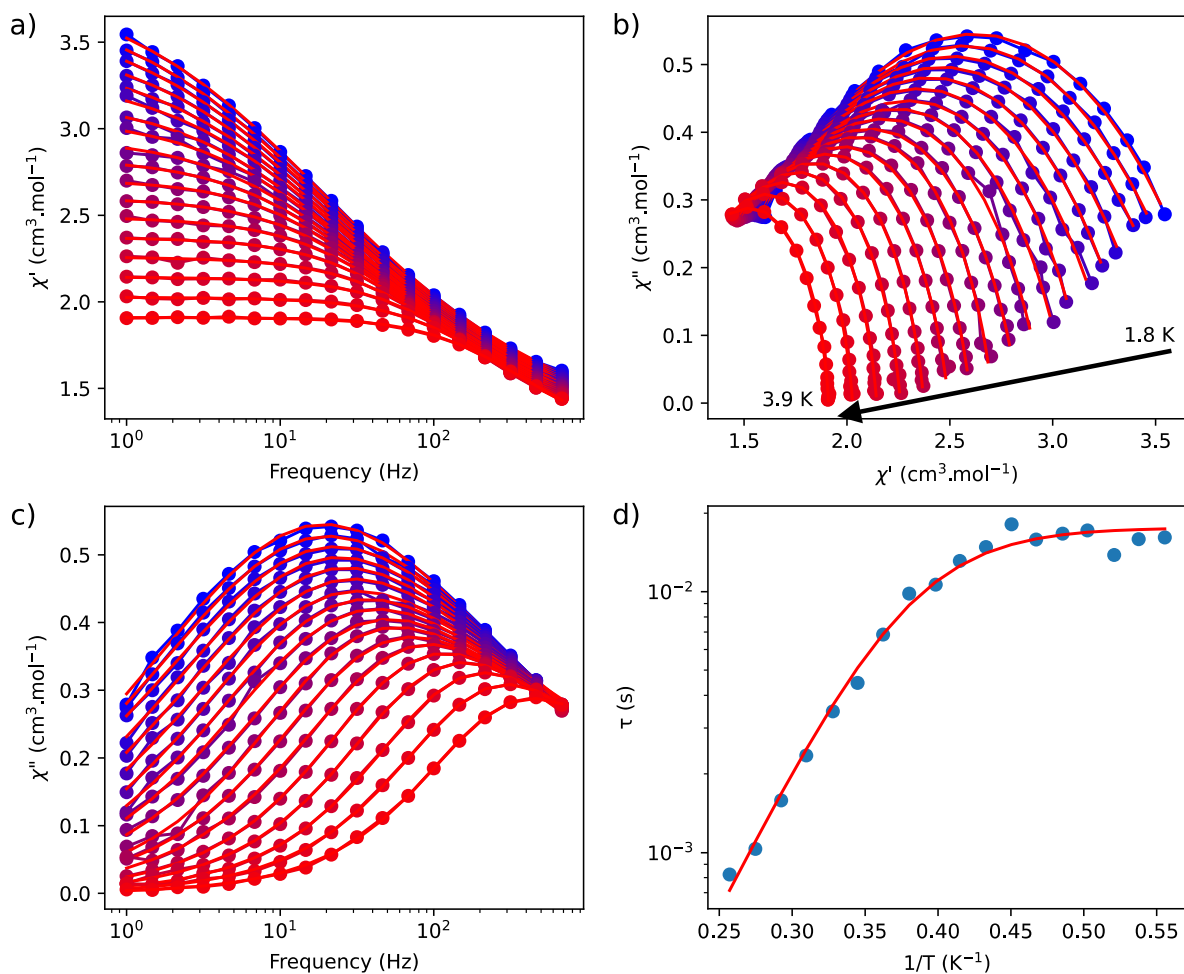




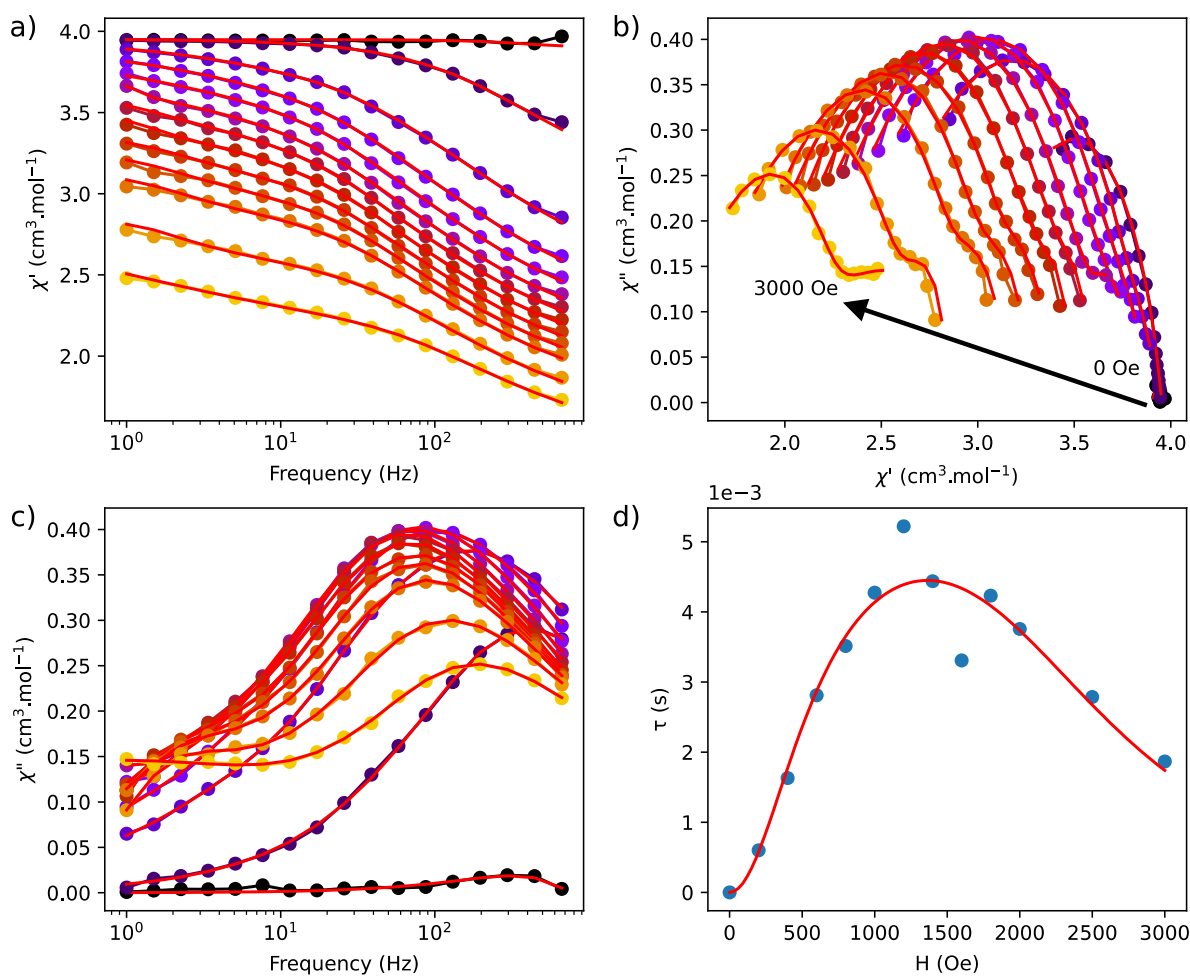
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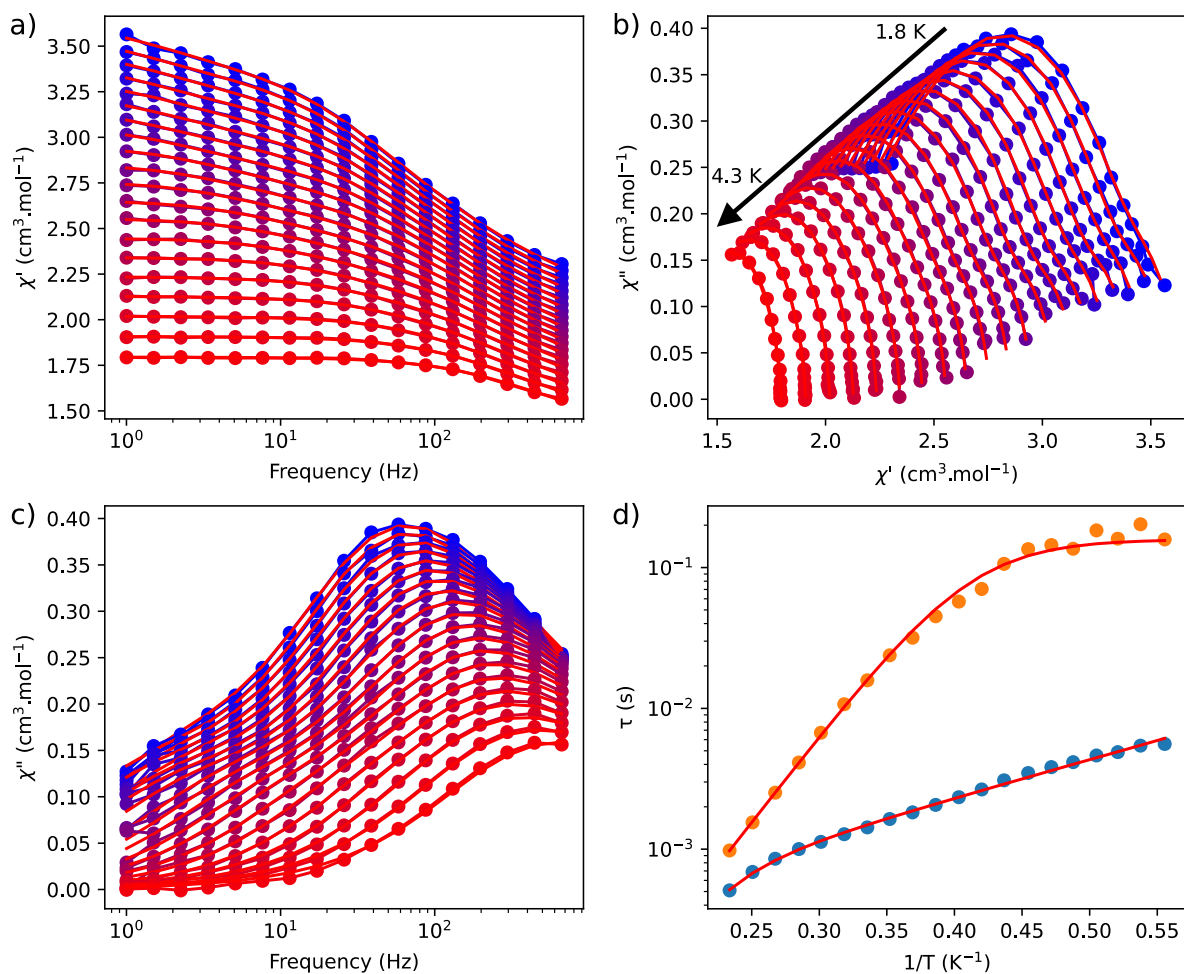
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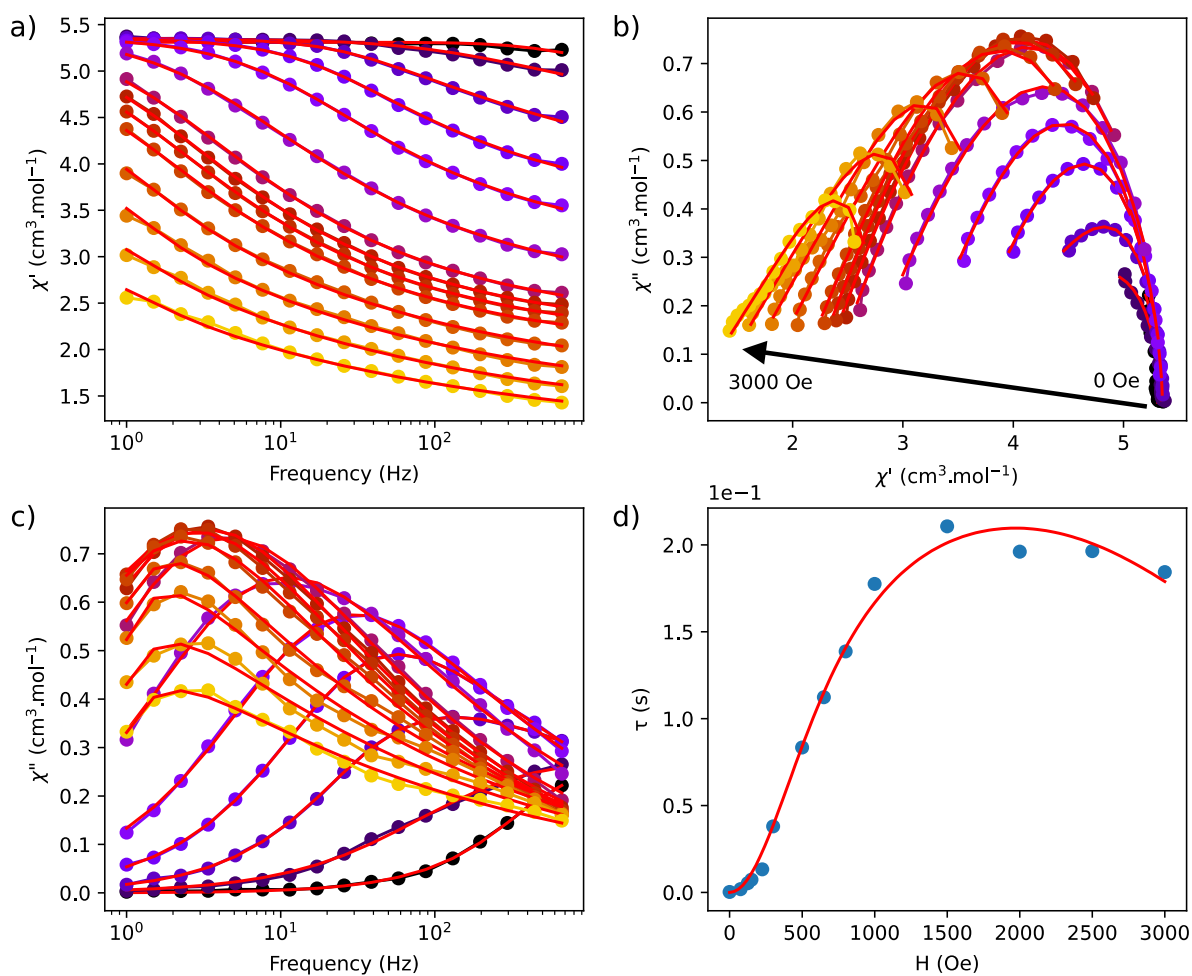
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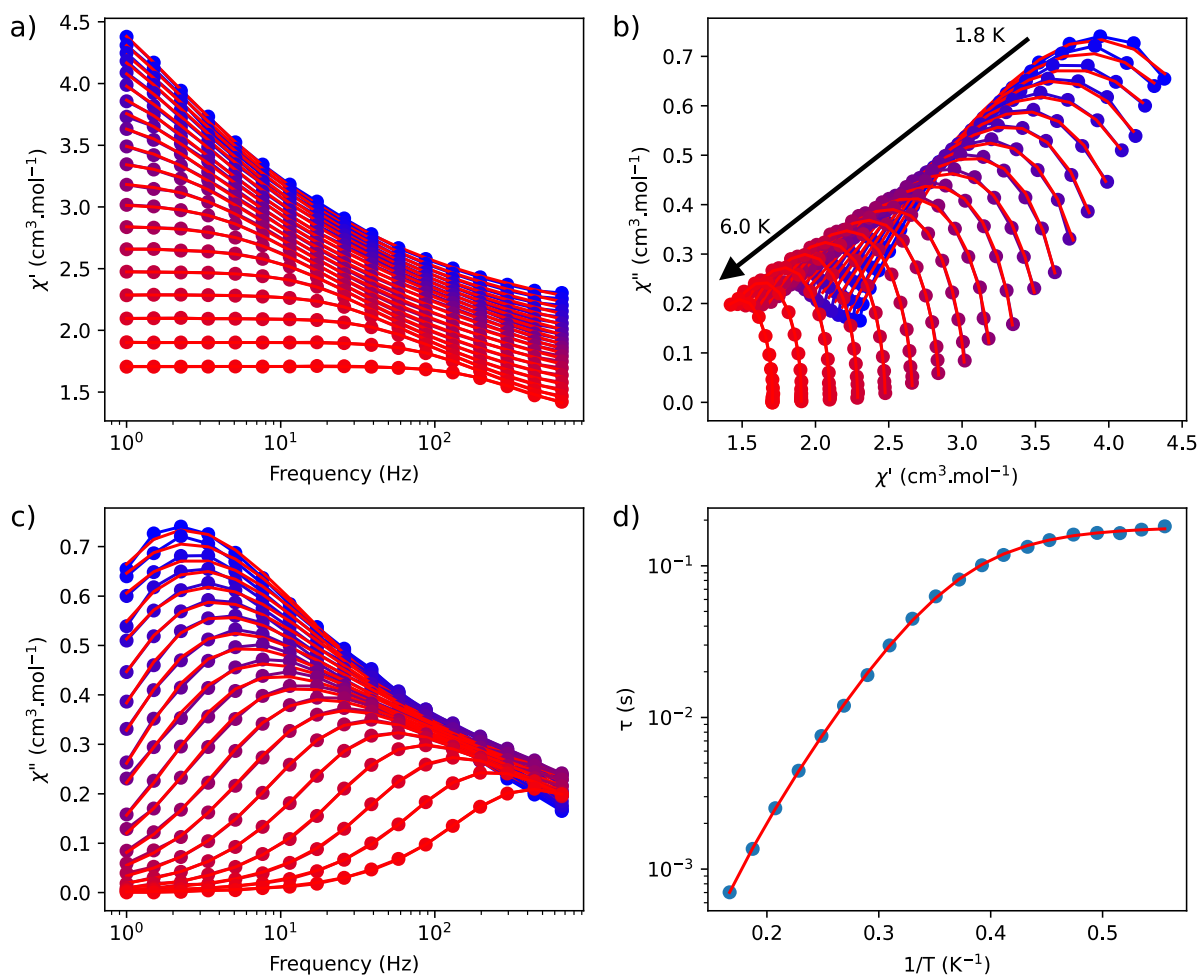
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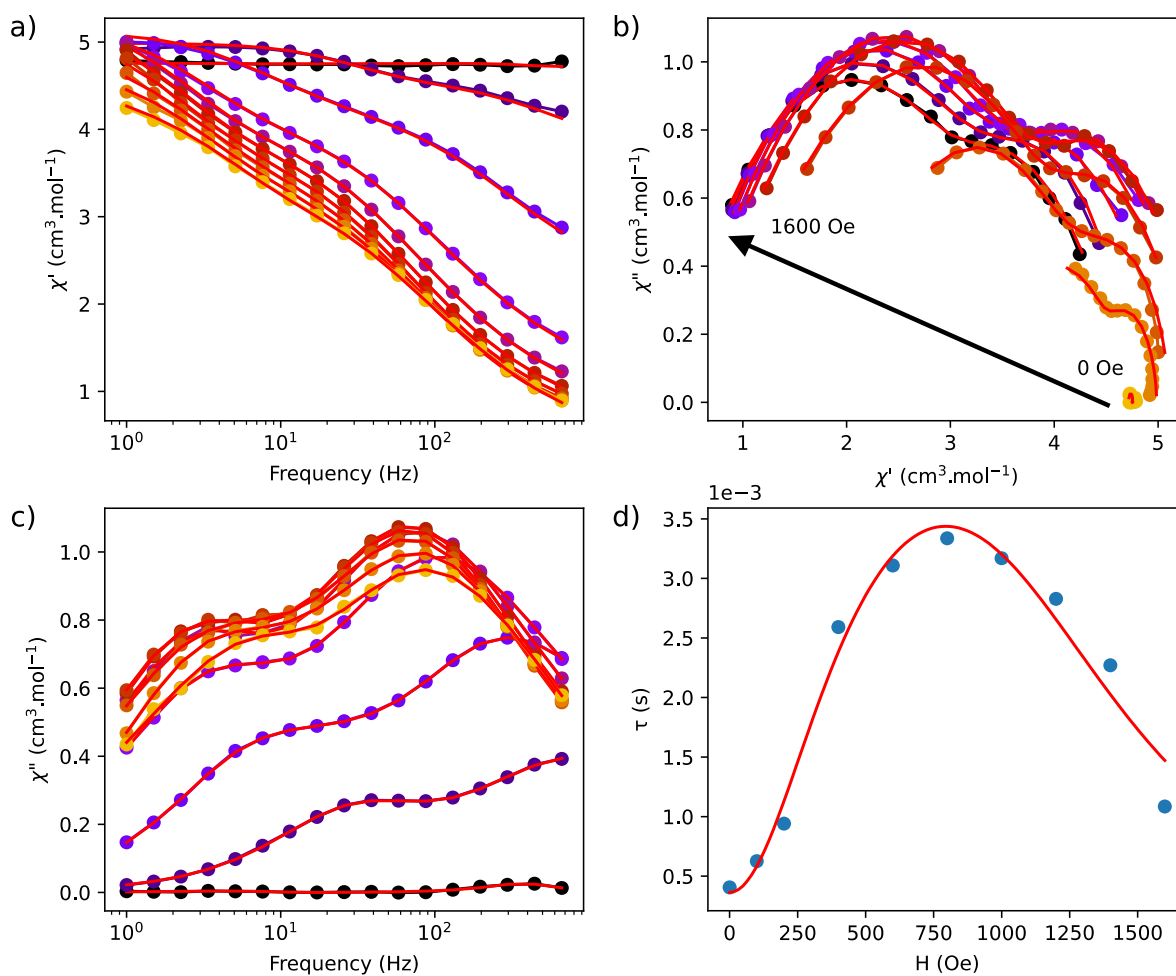
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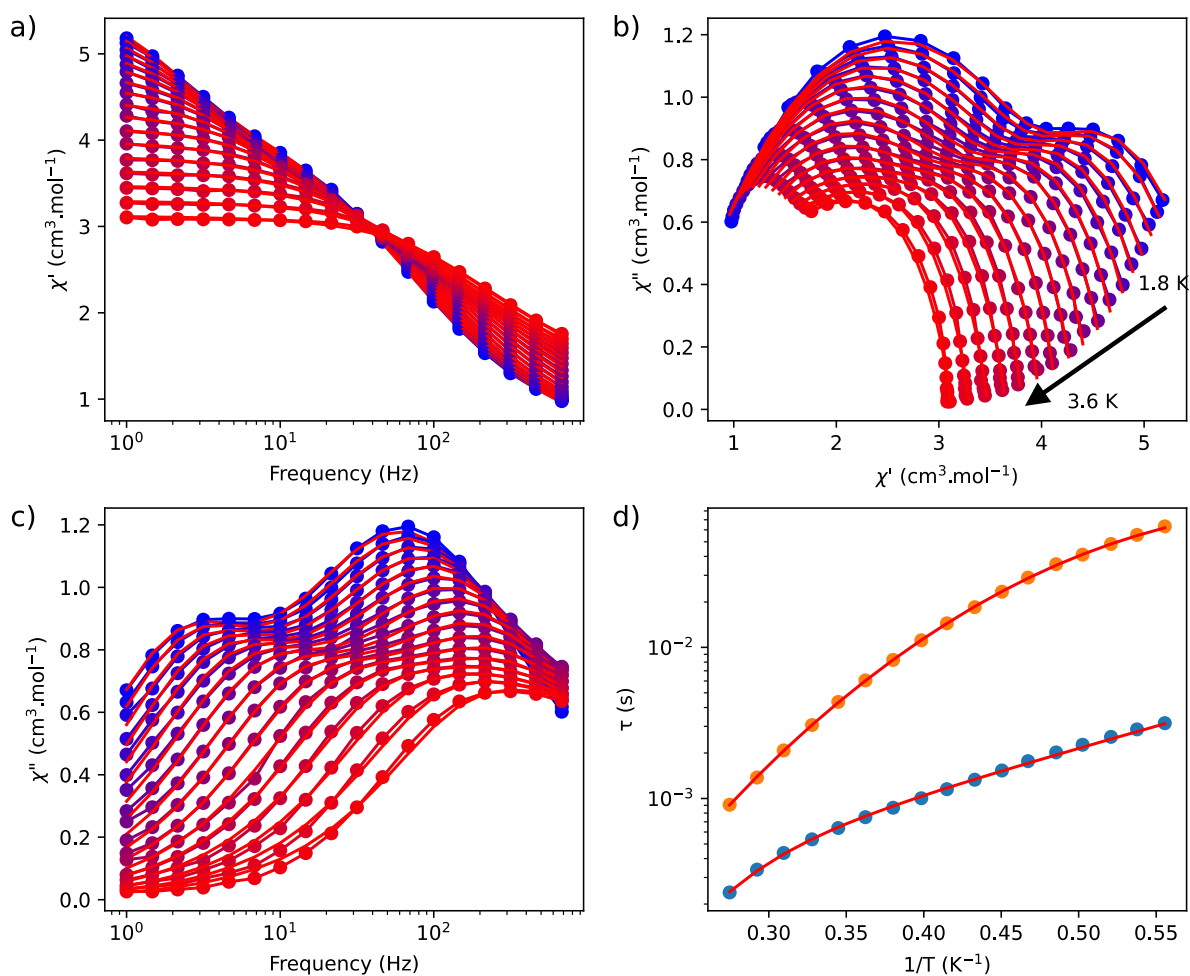


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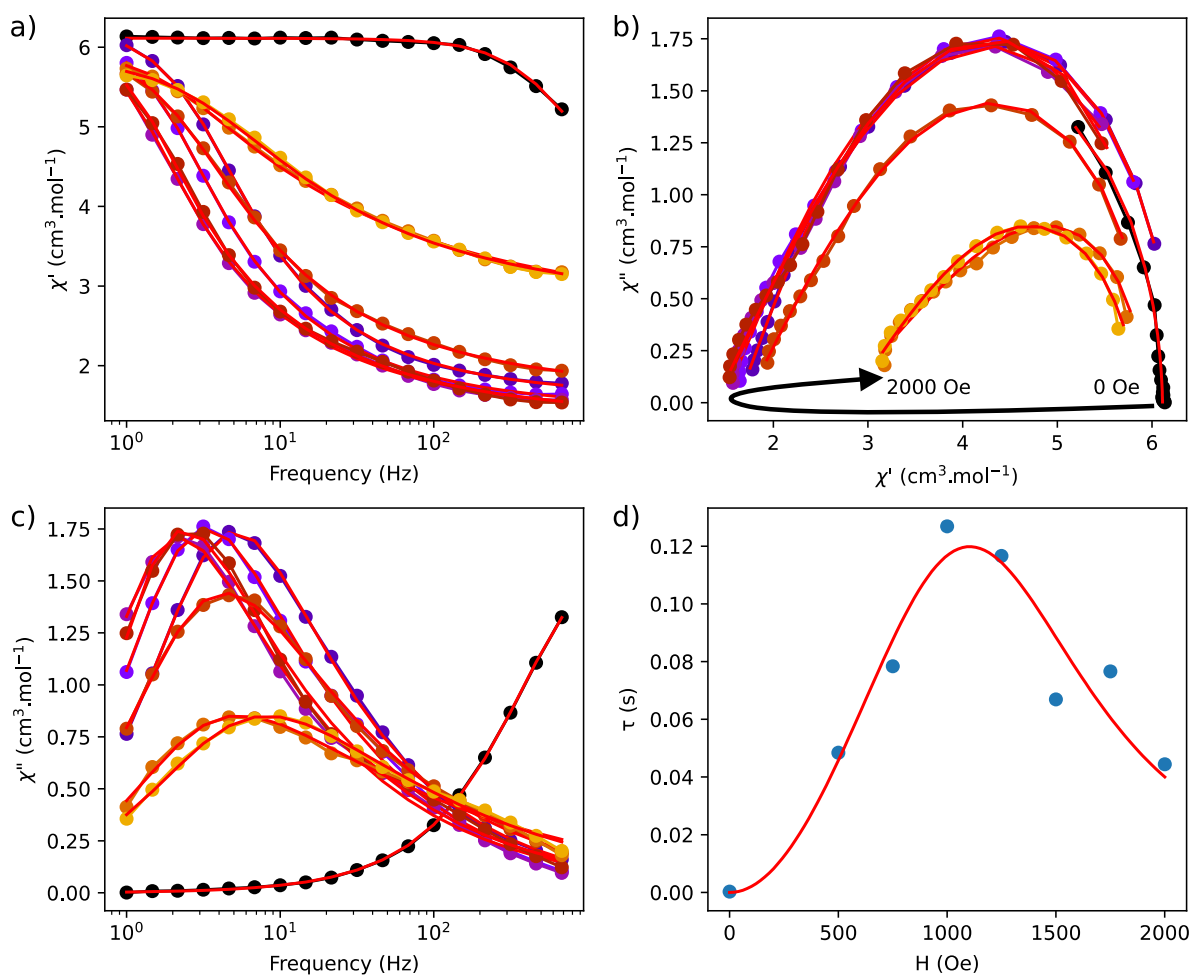


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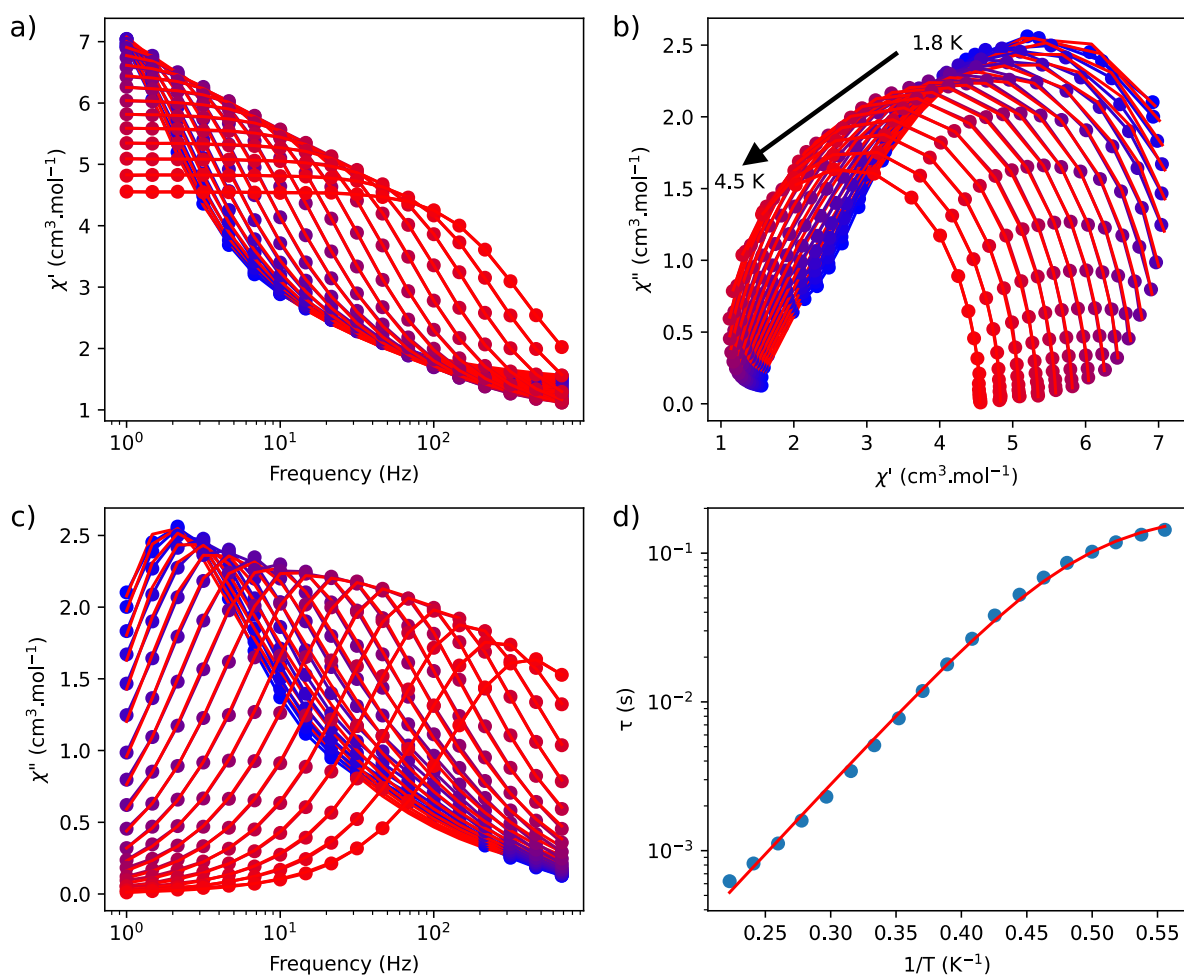




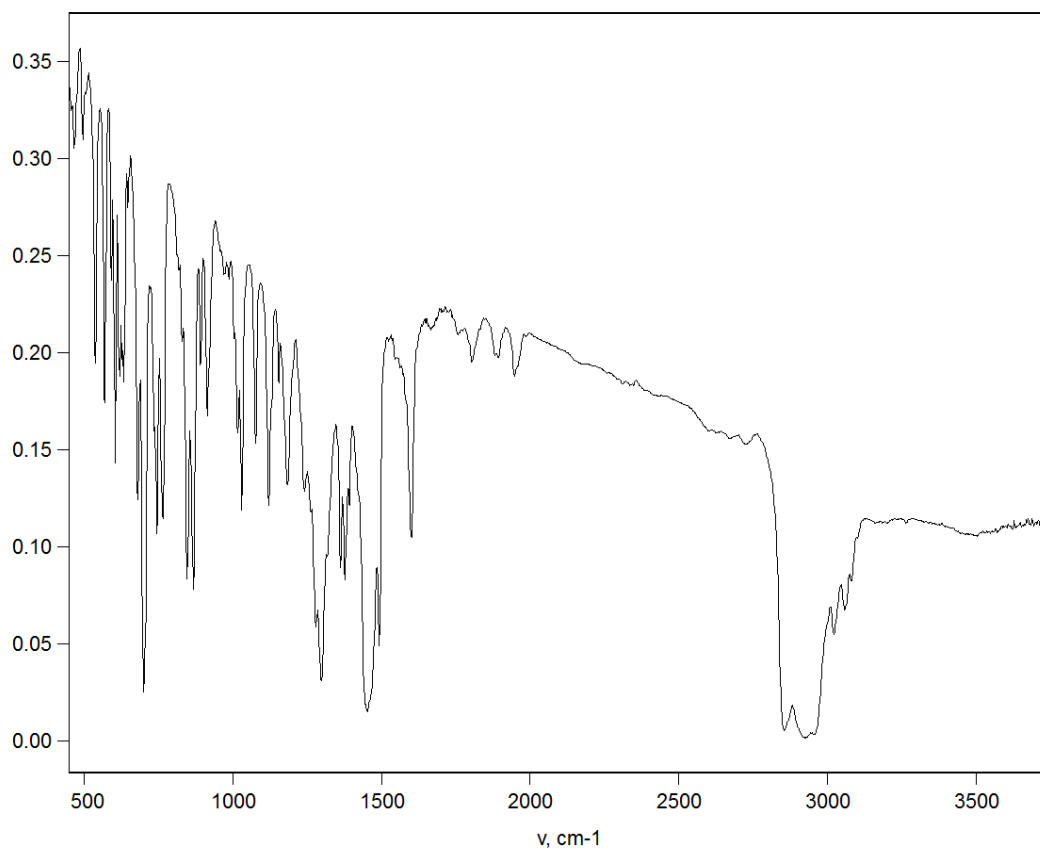
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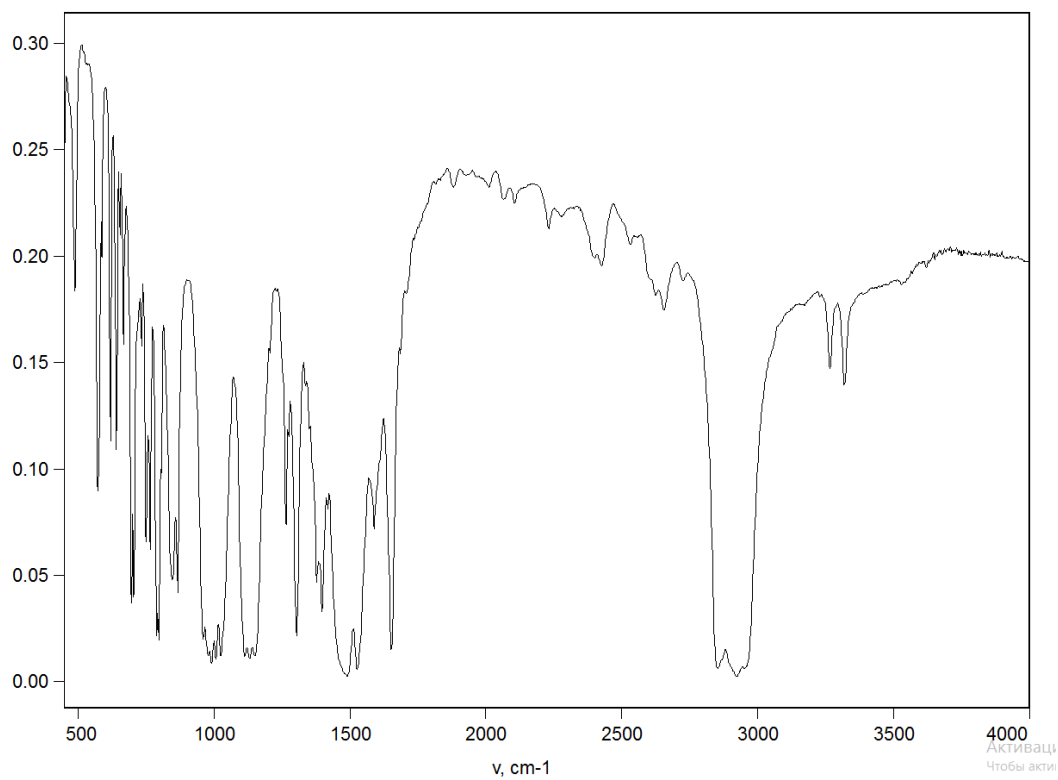
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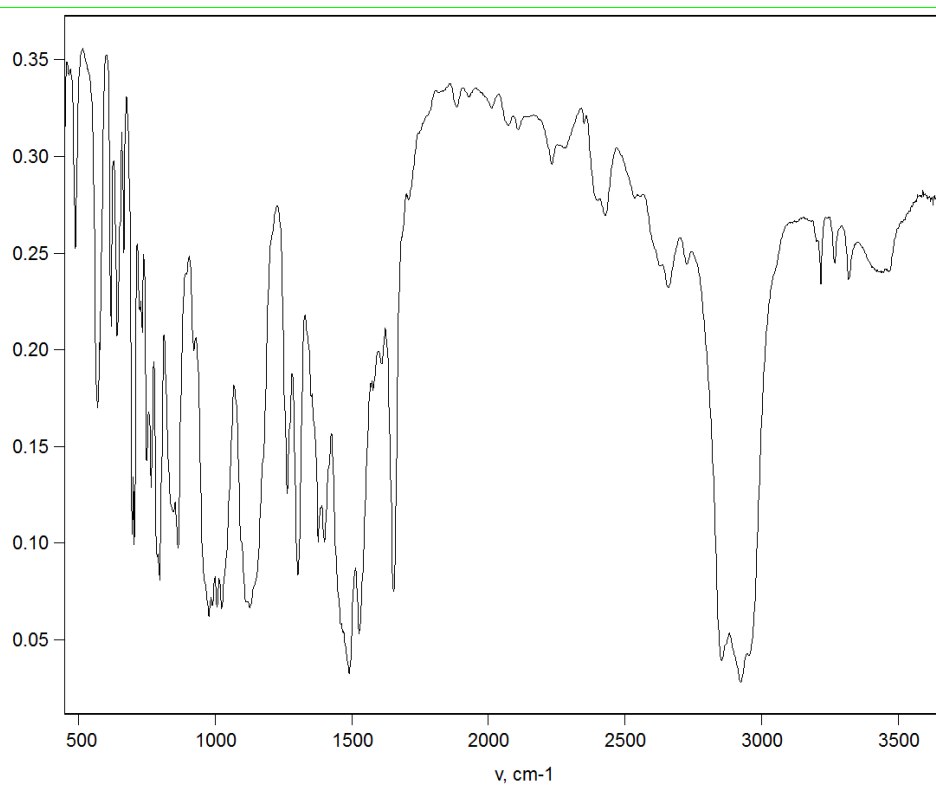
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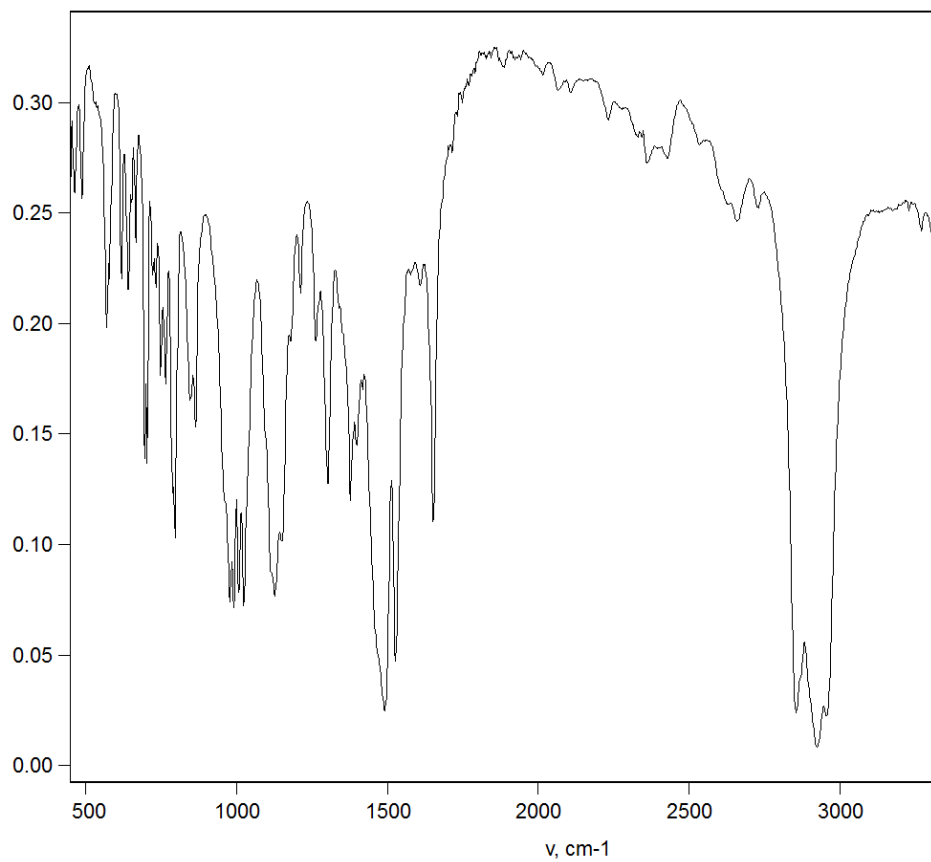
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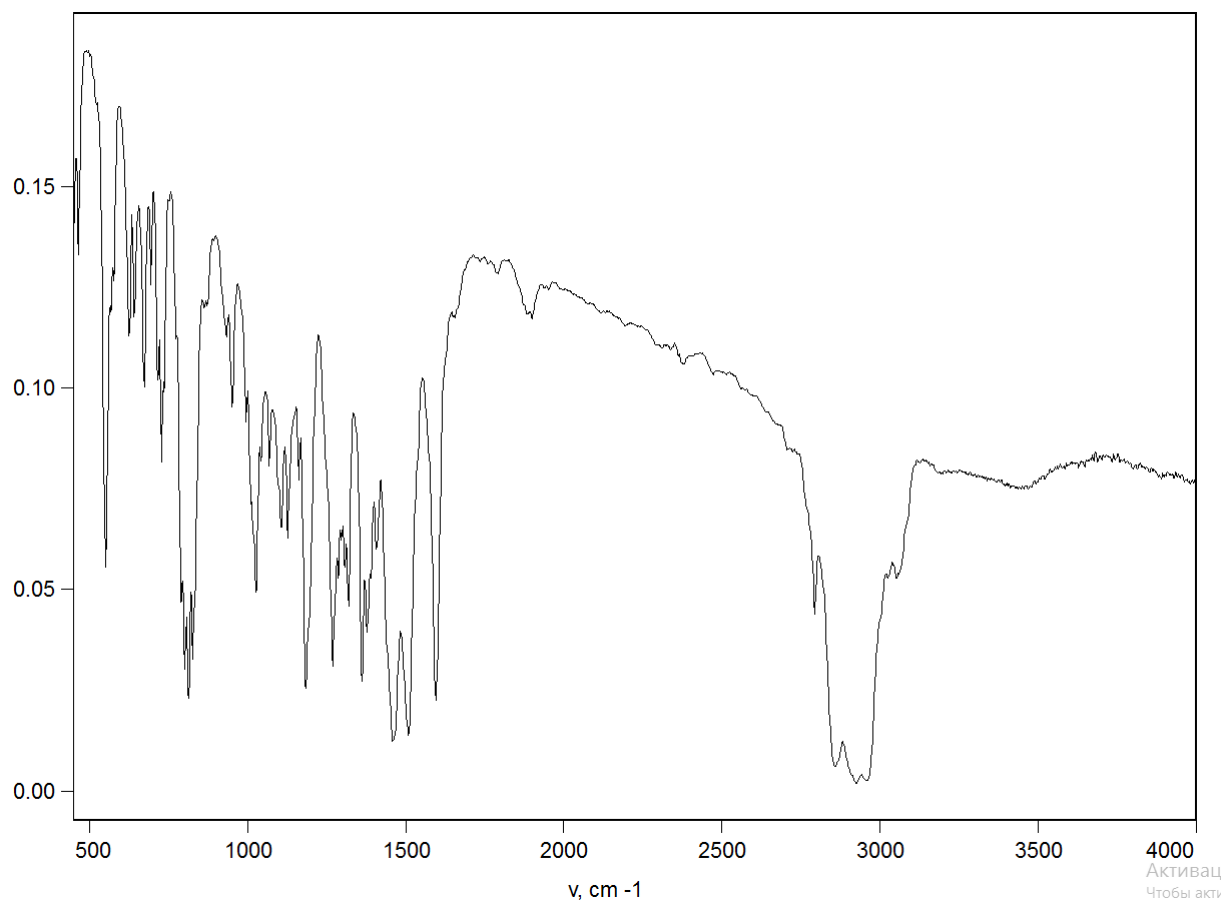
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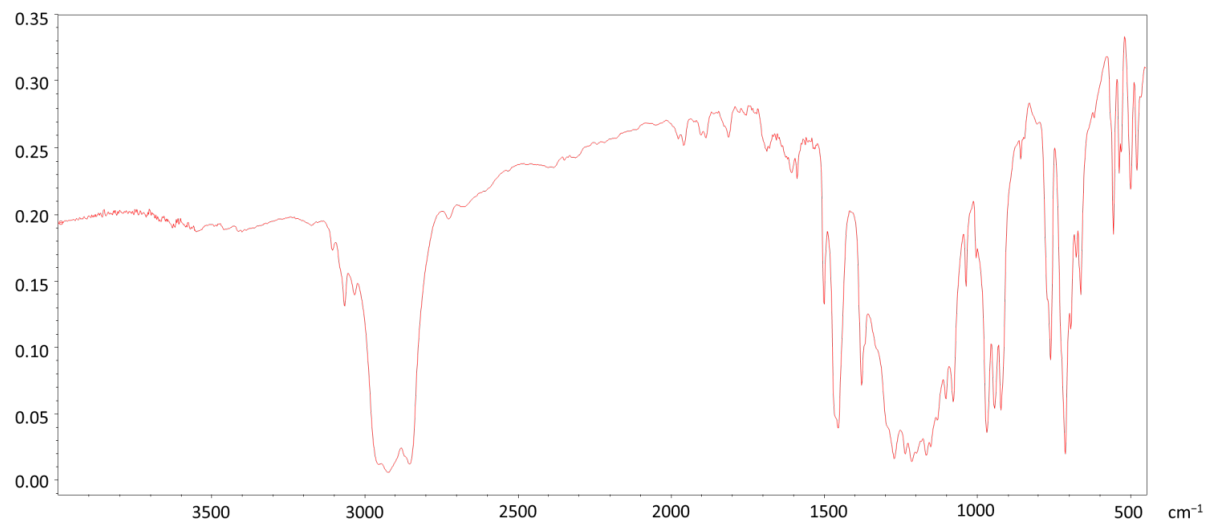
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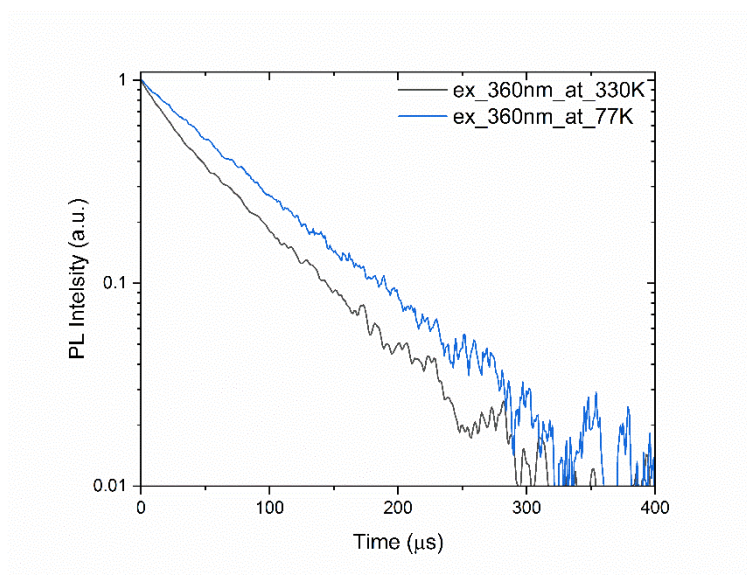
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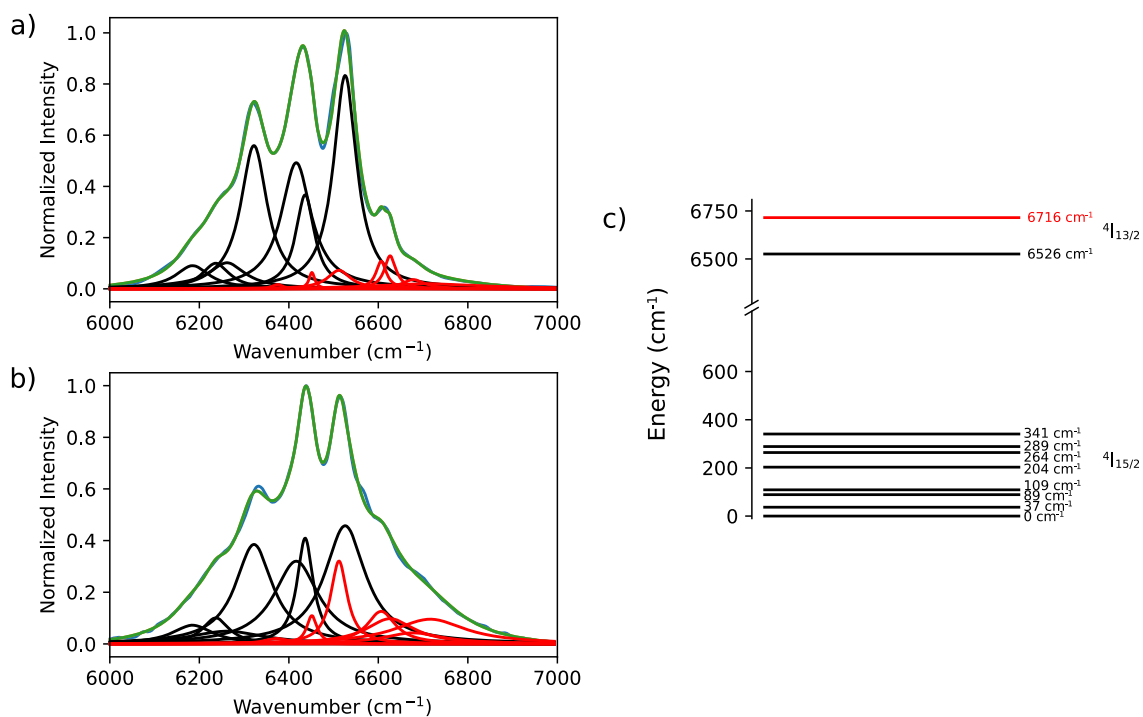
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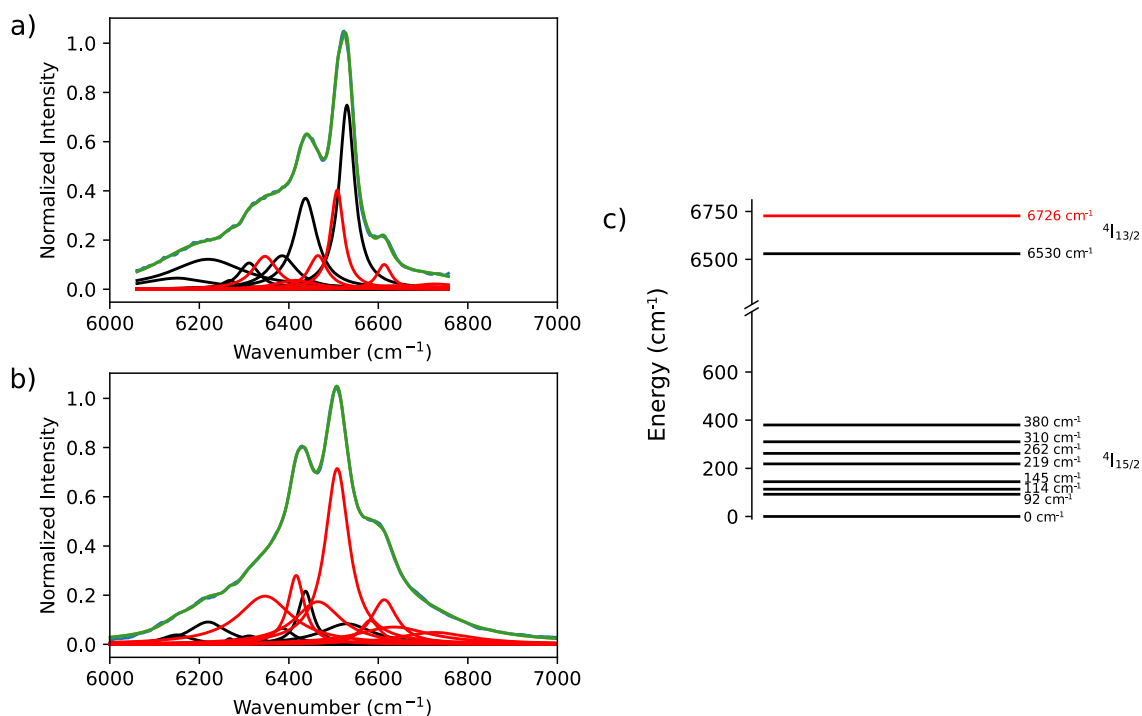
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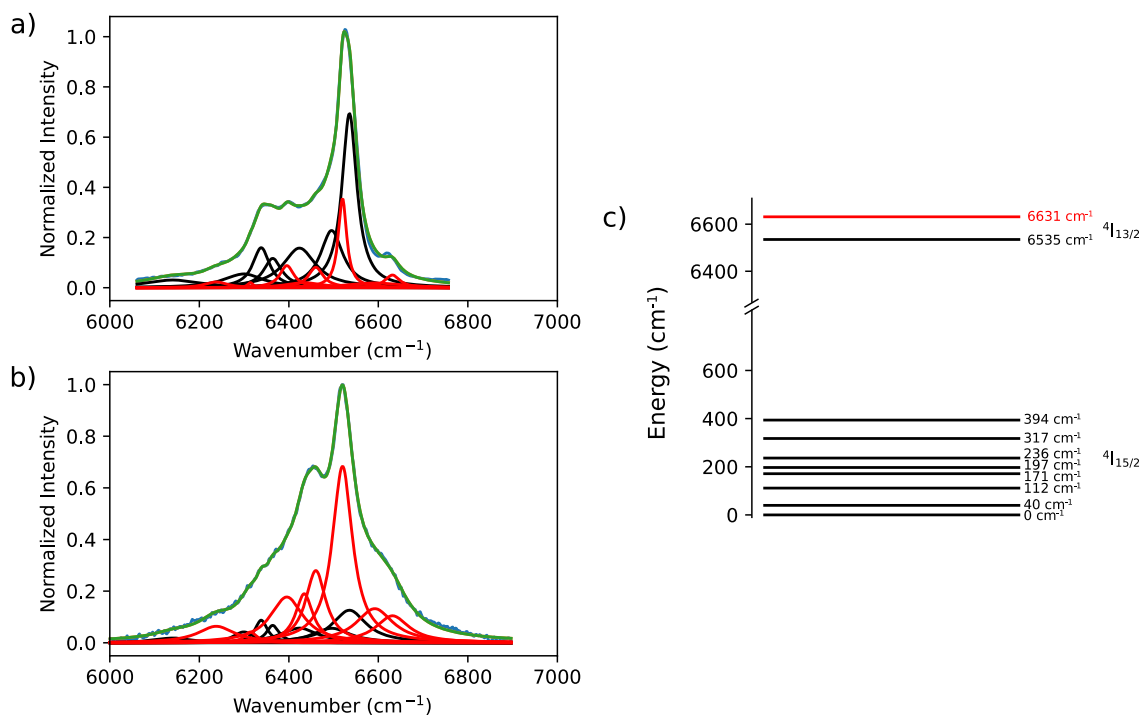
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**Figure S24.** Experimental luminescence emission spectra for crystalline complexes **2** at 77 K (a) and 300 K (b). The blue and green curves represent the experimental data and the optimized fit. The black and red Lorentzian functions represent the radiative relaxation from the first and second <sup>4</sup>I<sub>13/2</sub> states, respectively. c) Schematic representation of the energy levels for sample **2**, extracted from the fitting process.

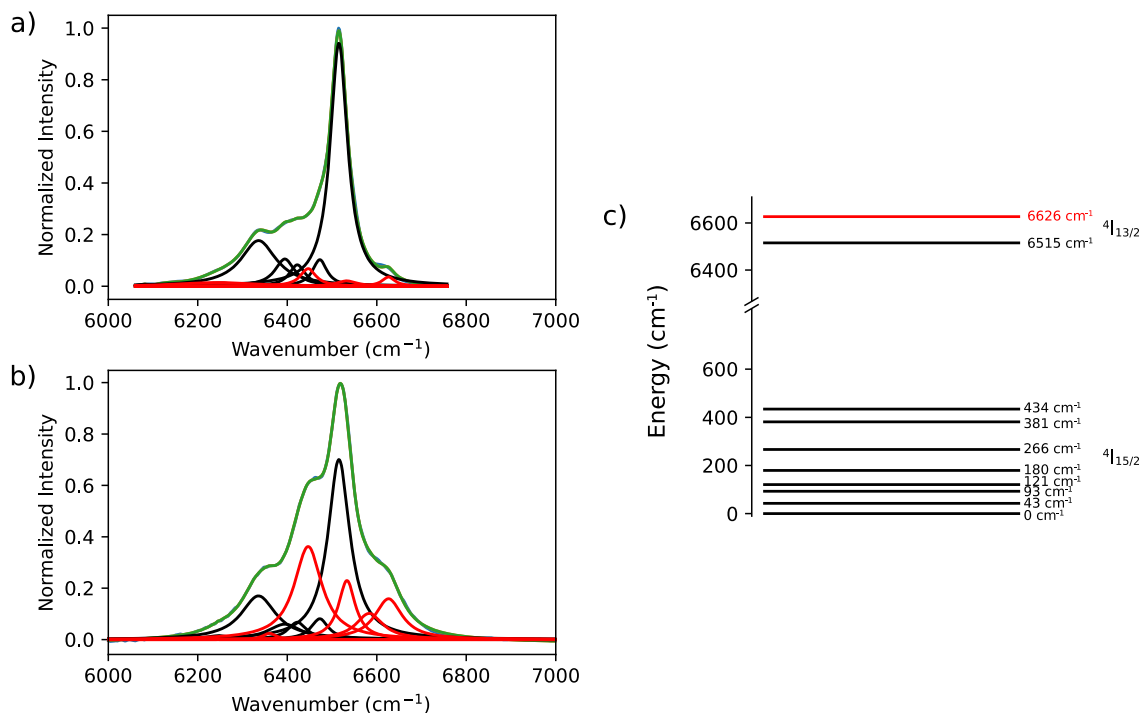


**Figure S25.** Experimental luminescence emission spectra for crystalline complexes **3** at 77 K (a) and 300 K (b). The blue and green curves represent the experimental data and the optimized fit. The black and red Lorentzian functions represent the radiative relaxation from the first and second  ${}^4I_{13/2}$  states, respectively. c) Schematic representation of the energy levels for sample **3**, extracted from the fitting process.

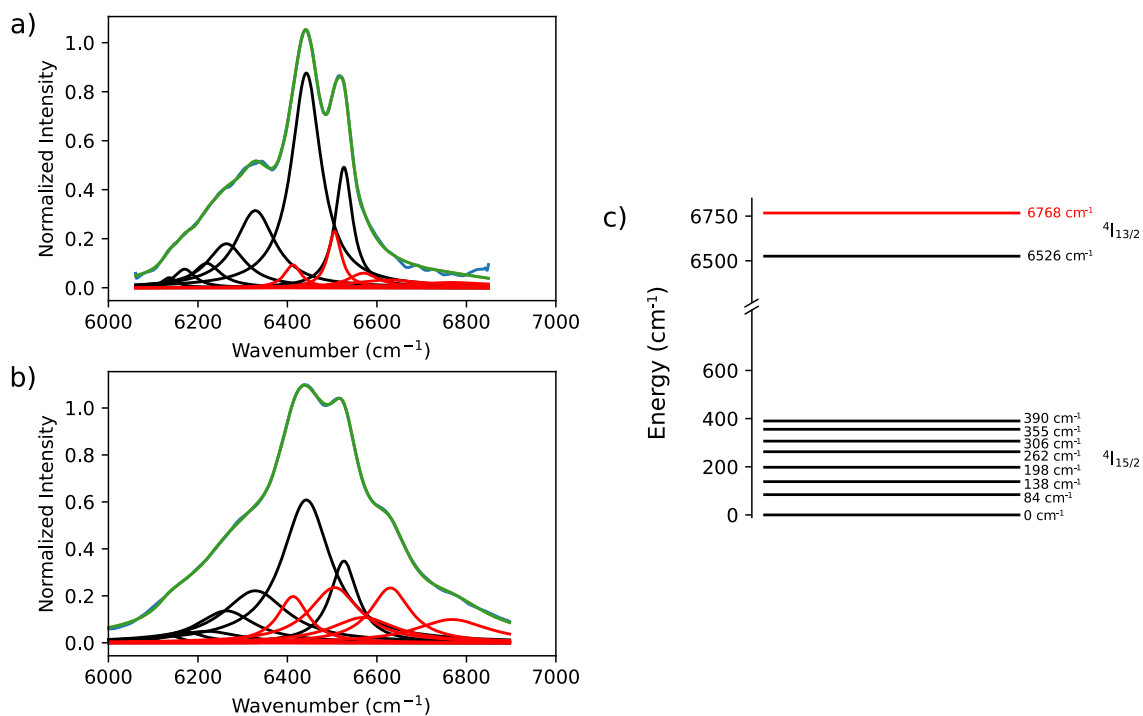


**Figure S26.** Experimental luminescence emission spectra for crystalline complexes **4** at 77 K (a) and 300 K (b). The blue and green curves represent the experimental data and the optimized fit. The black and red Lorentzian functions represent the radiative relaxation from the first and second  ${}^4I_{13/2}$  states, respectively. c) Schematic representation of the energy levels for sample **4**, extracted from the fitting process.





**Figure S27.** Experimental luminescence emission spectra for crystalline complexes **5** at 77 K (a) and 300 K (b). The blue and green curves represent the experimental data and the optimized fit. The black and red Lorentzian functions represent the radiative relaxation from the first and second  ${}^4I_{13/2}$  states, respectively. c) Schematic representation of the energy levels for sample **5**, extracted from the fitting process.



**Figure S28.** Experimental luminescence emission spectra for crystalline complexes **6** at 77 K (a) and 300 K (b). The blue and green curves represent the experimental data and the optimized fit. The black and red Lorentzian functions represent the radiative relaxation from the first and second  ${}^4I_{13/2}$  states, respectively. c) Schematic representation of the energy levels for sample **6**, extracted from the fitting process.

**Table S1:** Representative examples of Er<sup>3+</sup> luminescent SMMs.

Compounds	Magnetism	Luminescence	Ref.
[Er(thd) <sub>3</sub> (bath)] 8-coordinated Er <sup>3+</sup>	Field induced SMM, two relaxations: U <sub>eff</sub> = 15.6 and 22.4 K.	RT NIR emission, λ <sub>ex</sub> =337 nm (antenna effect), λ <sub>em</sub> =1532 nm, associated with the <sup>4</sup> I <sub>13/2</sub> → <sup>4</sup> I <sub>15/2</sub> transition	<sup>1</sup>
8-coordinated Er <sup>3+</sup> [Er(h) <sub>3</sub> (bipy)] [Er(h) <sub>3</sub> (5NO <sub>2</sub> phen)] [Er(h) <sub>3</sub> (bath)]	Field induced SMMs, U <sub>eff</sub> =7.98 K U <sub>eff</sub> =12.97 K U <sub>eff</sub> =22.81 K	RT NIR emission, λ <sub>ex</sub> =405 nm (antenna effect), λ <sub>em</sub> ~1532 nm, associated with the <sup>4</sup> I <sub>13/2</sub> → <sup>4</sup> I <sub>15/2</sub> transition	<sup>2</sup>
[Er(notpH <sub>4</sub> )(H <sub>2</sub> O)]ClO <sub>4</sub> ·3H <sub>2</sub> O 2D layered coordination polymer	Field induced SMM, U <sub>eff</sub> =24 cm <sup>-1</sup> Correlation with luminescence thanks to the presence of hot bands (emission from <sup>4</sup> I <sub>13/2</sub> multiplet) → energy diagram of the Stark-sub- levels	RT NIR emission, λ <sub>ex</sub> = 1064 nm (direct Er <sup>3+</sup> excitation), λ <sub>em</sub> ~1532 nm. The luminescence permitted to establish the energy diagram and determine the energy gap between the ground and first excited state of the <sup>4</sup> I <sub>15/2</sub> CF splitting of 31.2 cm <sup>-1</sup> , close to the U <sub>eff</sub> of 24.2 cm <sup>-1</sup> .	<sup>3</sup>
[Er(dbm) <sub>3</sub> (bipy)] 8-coordinated Er <sup>3+</sup>	Field induced SMM, U <sub>eff</sub> =19.8 K.	RT NIR emission, λ <sub>ex</sub> =380 nm (antenna effect), λ <sub>em</sub> =1532 nm, associated to the <sup>4</sup> I <sub>13/2</sub> → <sup>4</sup> I <sub>15/2</sub> transition; life time 1.1 μs	<sup>4</sup>
[ErL <sup>1</sup> <sub>3</sub> ]·CH <sub>3</sub> OH [ErL <sup>1</sup> <sub>2</sub> (tmh)(CH <sub>3</sub> OH)]·Solv [ErL <sup>1</sup> <sub>2</sub> (tta)(CH <sub>3</sub> OH)]·CH <sub>3</sub> OH 8-coordinated Er <sup>3+</sup>	Field induced SMM, U <sub>eff</sub> =16.0 K U <sub>eff</sub> =30.4 K U <sub>eff</sub> =25.8 K.	RT NIR emission, λ <sub>ex</sub> =355 nm (antenna effect), λ <sub>em</sub> =1530 nm, associated to the <sup>4</sup> I <sub>13/2</sub> → <sup>4</sup> I <sub>15/2</sub> transition; life time 2.37 μs.	<sup>5</sup>
[Er(depma) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ]Cl <sub>3</sub> ]·Solv	Field induced SMM, U <sub>eff</sub> =9.8 K	λ <sub>ex</sub> =330 nm, RT visible emission from anthracene λ <sub>em</sub> =450 nm.	<sup>6</sup>
(nBu <sub>4</sub> N) <sub>2</sub> [Er(NO <sub>3</sub> ) <sub>5</sub> ] 10-coordinated Er <sup>3+</sup>	Field induced SMM, U <sub>eff</sub> =22.3 K	Very low RT NIR emission, at 1550 nm associated to the <sup>4</sup> I <sub>13/2</sub> → <sup>4</sup> I <sub>15/2</sub> transition	<sup>7</sup>
8-coordinated Er <sup>3+</sup> [Er(tpm) <sub>3</sub> (bipy)]  [Er(tfa) <sub>3</sub> (bipy)]	Genuine SMM U <sub>eff</sub> =21 K (zero DC applied field) Field induced SMM U <sub>eff</sub> =15 K	RT NIR emission, λ <sub>ex</sub> =337 or 532 nm (antenna effect), λ <sub>em</sub> =1532 nm, associated to the <sup>4</sup> I <sub>13/2</sub> → <sup>4</sup> I <sub>15/2</sub> transition; life time 1.24 μs	<sup>8</sup>
Coordination polymers [Er{Ir(ppy) <sub>2</sub> (dcbpy)} <sub>2</sub> (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>n</sub> ] [Er <sub>2</sub> (OH){Ir(ppy) <sub>2</sub> (dcbpy)} <sub>4</sub> (NO <sub>3</sub> )(H O) <sub>4</sub> ]	Field induced SMM, U <sub>eff</sub> =13.6 K U <sub>eff</sub> =11.8 K	Emission at 584 nm from Ir unit (λ <sub>ex</sub> =375 nm) and at 1538 nm (λ <sub>ex</sub> = 500 nm); life time 1.4 μs (λ <sub>ex</sub> =500 nm)	<sup>9</sup>
3D neutral polymorphic frameworks [Er <sub>2</sub> (trz <sub>2</sub> An) <sub>3</sub> (H <sub>2</sub> O) <sub>4</sub> ] <sub>n</sub> ·H <sub>2</sub> O	Field induced SMM, U <sub>eff</sub> =42 K	NIR emission at 77K and RT, λ <sub>ex</sub> =355 nm (antenna effect), emission associated to the Er <sup>3+</sup>	<sup>10</sup>

		$^4I_{13/2} \rightarrow ^4I_{15/2}$ transition; life time of 55 ns and 86 ns	
$(Et_3NH)[Er(L^2)_2] \cdot 1.5H_2O$ $[Zn(\mu-L^3)(\mu-NO_3)Er(NO_3)_2]$	Field induced SMM, $U_{eff}=8$ K, $U_{eff}=15$ $cm^{-1}$	NIR emission at RT, $\lambda_{ex}=380-649$ nm (antenna effect), $\lambda_{em}=1550$ nm associated to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition.	<sup>11</sup>
$[Zn(\mu-L^3)(\mu-OAc)Er(NO_3)_2]$	Field induced SMM, $U_{eff}=8$ $cm^{-1}$	NIR emission at RT, $\lambda_{ex}=355$ nm, $\lambda_{em}=1530$ nm associated to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition; life time 2.77 $\mu s$ , 11.82 $\mu s$	<sup>12</sup>
$[Er(hfac)_3(tempo)_2]$	Field induced SMM, $U_{eff}=12$ $cm^{-1}$	NIR emission at 4.2K, $\lambda_{em}$ associated to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition; life time 11.82 $\mu s$ .	<sup>13</sup>

thd = 2,2,6,6-tetramethyl-3,5-heptanedionate, bath = bathophenanthroline; h = 2,4-hexanedionate; bipy = 2,2'-bipyridine; 5NO<sub>2</sub>phen = 5-nitro-1,10-phenanthroline; bath = bathophenanthroline; notpH<sub>4</sub><sup>2-</sup> = 1,4,7-triazacyclononane-1,4,7-triyl-tris(methylenephosphonate); dbm = dibenzoylmethanate; HL<sup>1</sup>=2-(tetrazol-5-yl)-1,10-phenanthroline; tmh = 2,2,6,6-tetramethylheptanoate; tta = thenoyltrifluoroacetate; ppy = 2-phenylpyridine; dcbpy = 2,2'-bipyridine-4,4'-dicarboxylate; depma = 9-diethylphosphono-methylanthracene; Htpm = 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione; Htfa = 4,4,4-trifluoro-1-(2-furyl)-1,3-butanedione); SYML=(N,N0-bis(1-naphthaldiamine)-O-phenylenediamine); H<sub>2</sub>trz<sub>2</sub>An = 3,6-N-ditriazolyl-2,5-dihydroxy-1,4-benzoquinone. L<sup>2</sup> = N,N'-bis(3-nitro-salicylaldehyde)ethylenediamine dianion); H<sub>2</sub>L<sup>3</sup> = N,N',N''-trimethyl-N,N''-bis(2-hydroxy-3-methoxy-5-methylbenzyl)diethylenetriamine ; TEMPO = (2,2,6,6-tetramethylpiperidin-1-oxyl) radical.

**Table S2:** Crystal data, data collection and structure refinement details for **1-6**.

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Formula	C <sub>122.5</sub> H <sub>119</sub> ErO <sub>4</sub>	C <sub>60</sub> H <sub>10</sub> ErF <sub>45</sub> O <sub>4</sub> Si	C <sub>63</sub> H <sub>19</sub> ErF <sub>45</sub> NO <sub>3</sub> Si <sub>2</sub>	C <sub>64</sub> H <sub>8</sub> ErF <sub>45</sub> O <sub>3</sub>	C <sub>66</sub> H <sub>13</sub> ErF <sub>45</sub> NO <sub>3</sub>	C <sub>54</sub> H <sub>30</sub> Er <sub>2</sub> F <sub>36</sub> O <sub>6</sub>
<i>M</i>	1822.43	1845.03	1916.23	1846.96	1890.03	1793.30
<i>T</i> , K	100.0(2)	100.0(2)	100.0(2)	100.0(2)	100.0(2)	100.0(2)
Crystal system	Triclinic	Trigonal	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>R</i> -3	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> , Å	13.02470(10)	17.2887(3)	14.7886(4)	13.5916(6)	15.0250(4)	11.2800(2)
<i>b</i> , Å	14.11930(10)	17.2887(3)	15.4929(4)	15.0450(5)	15.1826(4)	13.6848(3)
<i>c</i> , Å	27.7895(2)	35.2684(5)	18.0735(4)	18.6919(8)	15.5060(4)	20.1615(5)
$\alpha$ , deg	84.4770(10)	90	94.9370(10)	73.966(3)	84.4720(10)	100.9240(10)
$\beta$ , deg	83.5680(10)	90	112.0700(10)	79.560(3)	83.219(2)	104.5260(10)
$\gamma$ , deg	72.6830(10)	120	96.0260(10)	64.614(2)	83.909(2)	94.4460(10)
<i>V</i> , Å <sup>3</sup>	4837.46(7)	9129.4(3)	3780.78(17)	3310.1(2)	3480.03(16)	2932.43(11)
<i>Z</i>	2	6	2	2	2	2
<i>d</i> <sub>calc</sub> , g/cm <sup>3</sup>	1.251	2.014	1.683	1.853	1.804	2.031
$\mu$ , mm <sup>-1</sup>	0.923	1.587	1.296	1.441	1.374	3.007
<i>F</i> <sub>000</sub>	1908	5334	1858	1778	1826	1724
Crystal dimensions, mm	0.62×0.50×0.34	0.15×0.10×0.10	0.15×0.10×0.05	0.25×0.25×0.02	0.25×0.20×0.03	0.25×0.20×0.03
$\theta$ range for data collection, deg	1.74–30.03	2.36–27.00	1.86–27.00	1.82–26.00	1.80–27.00	1.88–27.00
Completeness, %	99.9	99.9	99.7	96.5	99.7	99.8
<i>HKL</i> indices	-18 ≤ <i>h</i> ≤ 18 -19 ≤ <i>k</i> ≤ 19 -39 ≤ <i>l</i> ≤ 39	-22 ≤ <i>h</i> ≤ 22 -18 ≤ <i>k</i> ≤ 22 -45 ≤ <i>l</i> ≤ 45	-18 ≤ <i>h</i> ≤ 18 -17 ≤ <i>k</i> ≤ 19 -23 ≤ <i>l</i> ≤ 23	-10 ≤ <i>h</i> ≤ 16 -18 ≤ <i>k</i> ≤ 18 -22 ≤ <i>l</i> ≤ 23	-19 ≤ <i>h</i> ≤ 19 -19 ≤ <i>k</i> ≤ 19 -18 ≤ <i>l</i> ≤ 19	-14 ≤ <i>h</i> ≤ 14 -17 ≤ <i>k</i> ≤ 17 -25 ≤ <i>l</i> ≤ 22
Reflns. collected	170147	34659	42913	23913	37911	32777
Reflns. unique ( <i>I</i> > 2σ( <i>I</i> ))	26368	4092	12863	6906	12837	11020
<i>R</i> <sub>int</sub>	0.0468	0.0320	0.0597	0.0843	0.0385	0.0355

Data / restraints / parameters	28285 / 1109 / 1199	4433 / 13 / 346	16441 / 0 / 1042	12557 / 30 / 1021	15149 / 56 / 1058	12801 / 0 / 883
$S(F^2)$	1.044	1.079	0.996	0.958	1.020	1.061
$R_1 / wR_2 (I > 2\sigma(I))$	0.0320 / 0.0724	0.0324 / 0.0899	0.0477 / 0.1051	0.0725 / 0.1473	0.0427 / 0.0995	0.0304 / 0.0678
$R_1 / wR_2$ (all data)	0.0360 / 0.0740	0.0363 / 0.0935	0.0663 / 0.1125	0.1312 / 0.1673	0.0528 / 0.1044	0.0382 / 0.0710
Largest diff. peak and hole, e/Å <sup>3</sup>	0.86 / -1.31	0.94 / -1.33	1.49 / -0.86	1.42 / -1.35	1.34 / -0.75	1.40 / -1.10

**Table S3.** Main magnetic parameters utilized in Equation (1) for samples 1–6.

Complex	D (s <sup>-1</sup> .Oe <sup>-4</sup> .K <sup>-1</sup> )	B <sub>1</sub> (s <sup>-1</sup> )	B <sub>2</sub> (Oe <sup>-2</sup> )	C (s <sup>-1</sup> )
		B <sub>0</sub> (s <sup>-1</sup> .Oe <sup>-2</sup> )		
<b>1</b>	(1.6 ± 0.1) 10 <sup>-11</sup>	10 <sup>(4.2 ± 0.9)</sup>	10 <sup>(-2.9 ± 0.9)</sup>	300 ± 7
<b>2</b>	(5.4 ± 1.0) 10 <sup>-11</sup>	10 <sup>(4.1 ± 1.0)</sup>	10 <sup>(-3.0 ± 1.5)</sup>	150 ± 17
<b>3</b>	(2.7 ± 0.7) 10 <sup>-12</sup>	(6.2 ± 1.5) 10 <sup>7</sup>		174 ± 18
<b>4</b>	(9.3 ± 2.0) 10 <sup>-15</sup>	(2.0 ± 0.2) 10 <sup>6</sup>		4.0 ± 0.2
<b>5</b>	(3.9 ± 0.7) 10 <sup>-11</sup>	10 <sup>(3.4 ± 0.2)</sup>	10 <sup>(-4.1 ± 0.3)</sup>	206 ± 28
<b>6</b>	(7.4 ± 2.1) 10 <sup>-13</sup>	(4.8 ± 1.6) 10 <sup>6</sup>		2.4 ± 2.1

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