

# Light and Thermally Activated Spin Crossover Coupled to an Order-Disorder Transition of a Propyl Chain in an Iron(III) Complex

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**Table S1.** Key FT-IR peaks and UV-Vis absorption band of [Fe(naphPren)<sub>2</sub>]I·solv complexes where solv = CH<sub>2</sub>Cl<sub>2</sub>, **1**, CHCl<sub>3</sub>, **2** and acetone, **3**

**Figure S1.** FT-IR (KBr disc) curves for **1-3**

**Figure S2.** UV-Visible absorption of **1** (CH<sub>2</sub>Cl<sub>2</sub>, 0.125 mM)

**Figure S3.** TGA curves for **1-3**, with the assigned mass losses

**Figure S4.** Mass spectrum of **1** (ESI+)

**Figure S5.** Mass spectrum of **1** (ESI-)

**Figure S6.** Asymmetric Unit of **2** (A) and **3** (B) at 150 K

**Table S2.** Crystallographic data and refinement parameters for [Fe(naphPren)<sub>2</sub>]I·solv complexes where solv = CH<sub>2</sub>Cl<sub>2</sub>, **1**, CHCl<sub>3</sub>, **2** and acetone, **3**

**Table S3.** Solid state intermolecular interaction of [Fe(naphPren)<sub>2</sub>]I·solv complexes where solv = CH<sub>2</sub>Cl<sub>2</sub>, **1**, CHCl<sub>3</sub>, **2** and acetone, **3** (Å or °)

**Figure S7.** Experimental PXRD diffractograms (orange) and the corresponding simulated patterns (blue) for **1-3**

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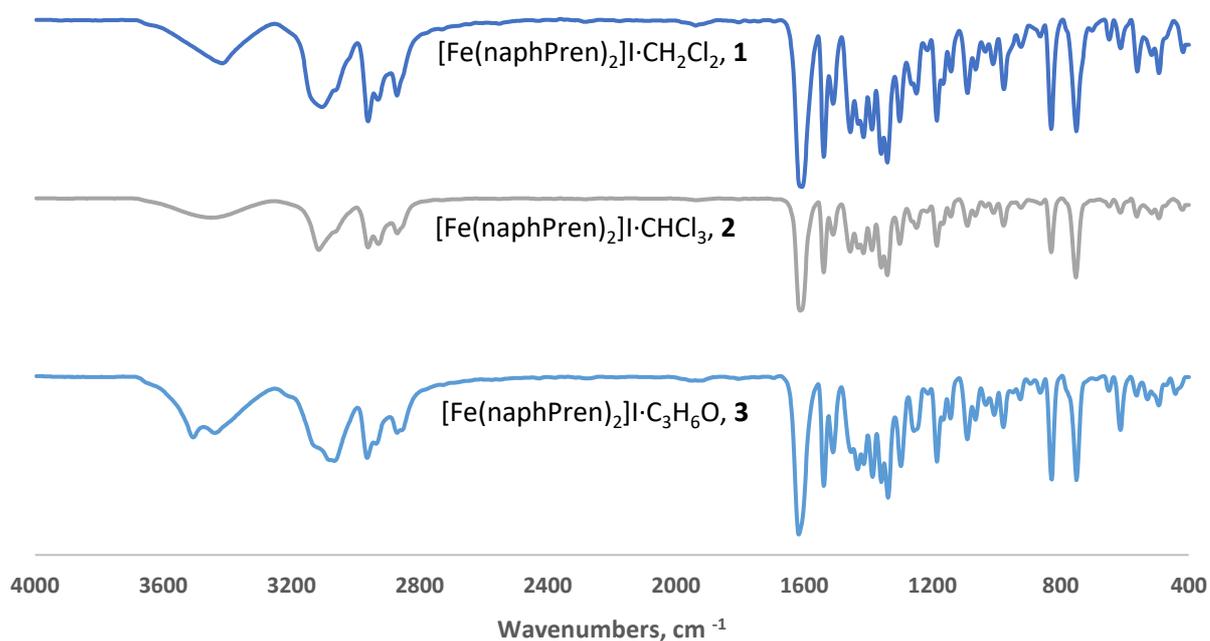
**Figure S9.** 1-D chain in **1**, **2**, and **3** at different temperatures.

**Figure S10.** 2-D plane viewed down the 001 axis of **1**, **2**, and **3** in different spin-state. The distance between each Fe center is illustrated by the yellow arrow, with the distances shown on the side.

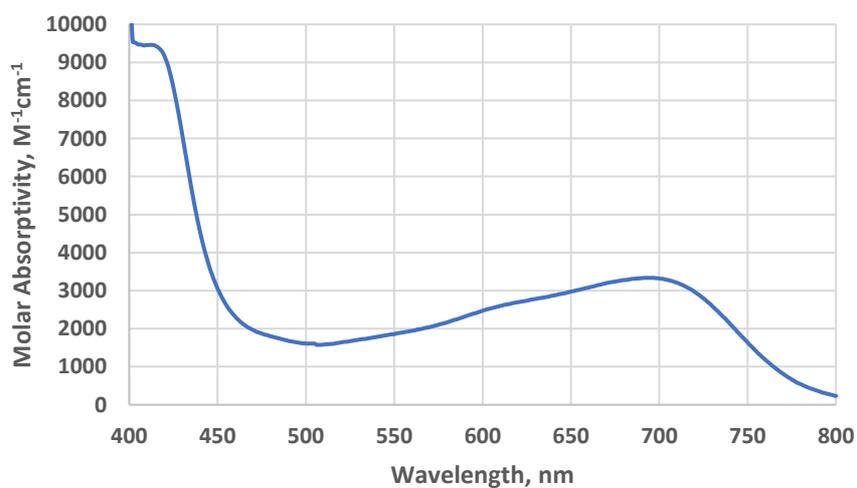
## FT-IR spectroscopy and UV-Vis Absorption

**Table S1:** Key FT-IR peaks and UV-Vis absorption band of  $[\text{Fe}(\text{naphPren})_2]\text{I}$ -solv complexes where solv =  $\text{CH}_2\text{Cl}_2$ , **1**,  $\text{CHCl}_3$ , **2** and acetone, **3**.

	FT-IR			UV-Visible absorption ( $\text{CH}_2\text{Cl}_2$ )
	$\nu$ (N-H)	$\nu$ (C-H)	$\nu$ (C=N)	
$[\text{Fe}(\text{naphPren})_2]\text{I}\cdot\text{CH}_2\text{Cl}_2$ , <b>1</b>	3105	2961, 2930, 2871	1608	415 nm ( $9430 \text{ M}^{-1}\text{cm}^{-1}$ ), 634 nm
$[\text{Fe}(\text{naphPren})_2]\text{I}\cdot\text{CHCl}_3$ , <b>2</b>	3115	2961, 2929, 2870	1612	(shoulder, $2815 \text{ M}^{-1}\text{cm}^{-1}$ ), 697 nm ( $3335 \text{ M}^{-1}\text{cm}^{-1}$ )
$[\text{Fe}(\text{naphPren})_2]\text{I}\cdot\text{C}_3\text{H}_6\text{O}$ , <b>3</b>	3066	2964, 2933, 2871	1616	

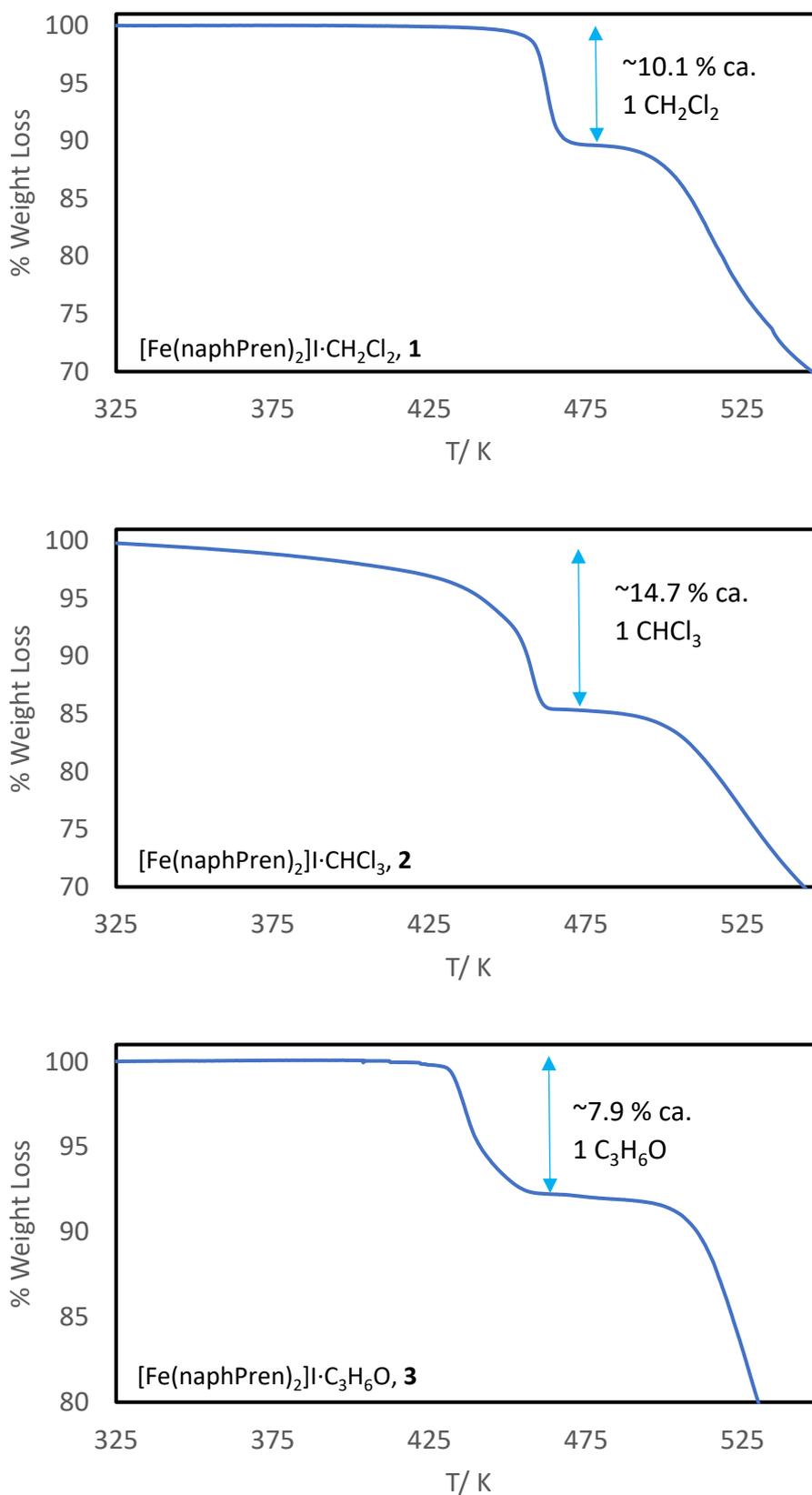


**Figure S1.** FT-IR (KBr disc) curves for **1-3**



**Figure S2.** UV-Visible absorption spectrum of **1** ( $\text{CH}_2\text{Cl}_2$ , 0.125 mM).

## Thermogravimetric Analysis



**Figure S3.** TGA curves for **1-3**, with the assigned mass losses.

## Mass Spectrometry

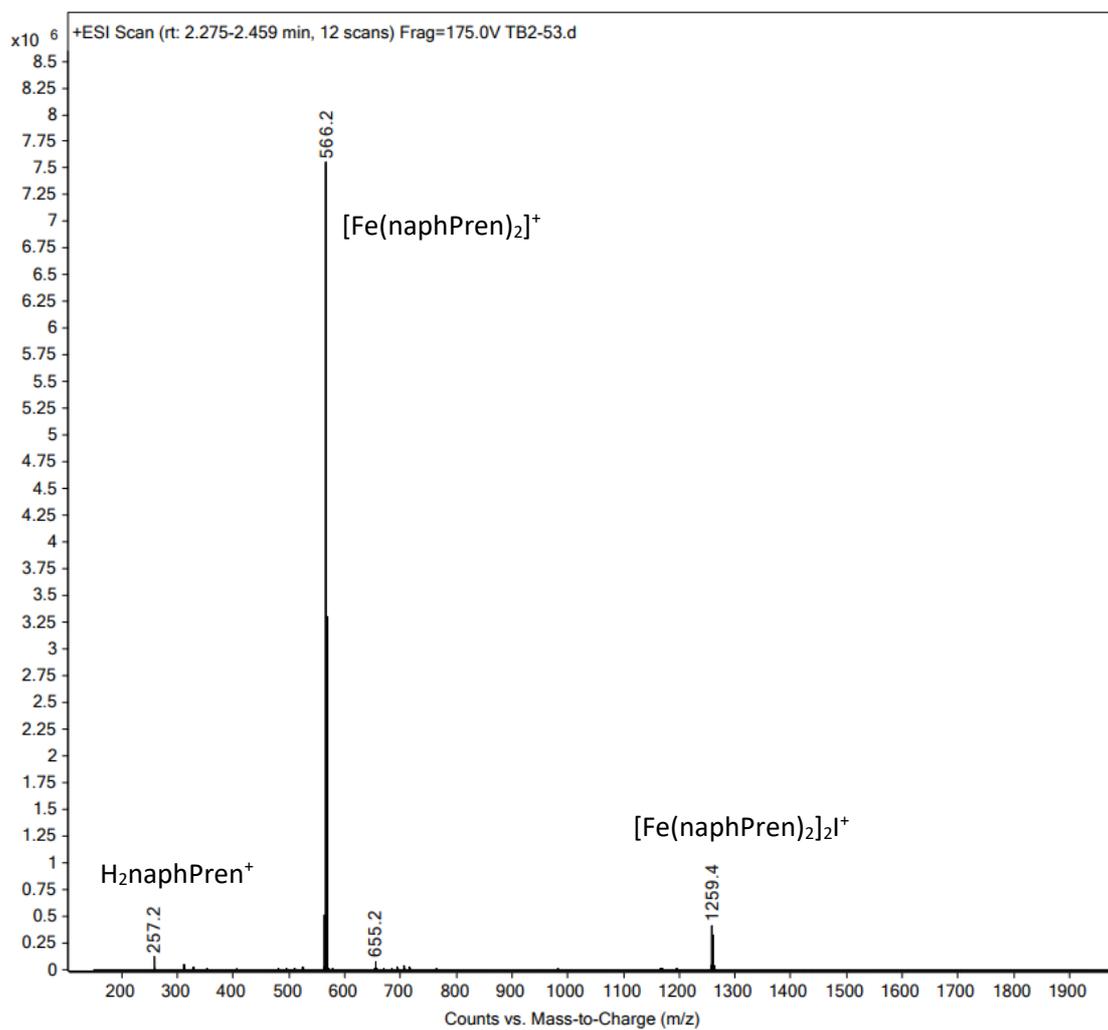


Figure S4. Mass spectrum of **1** (ESI+)

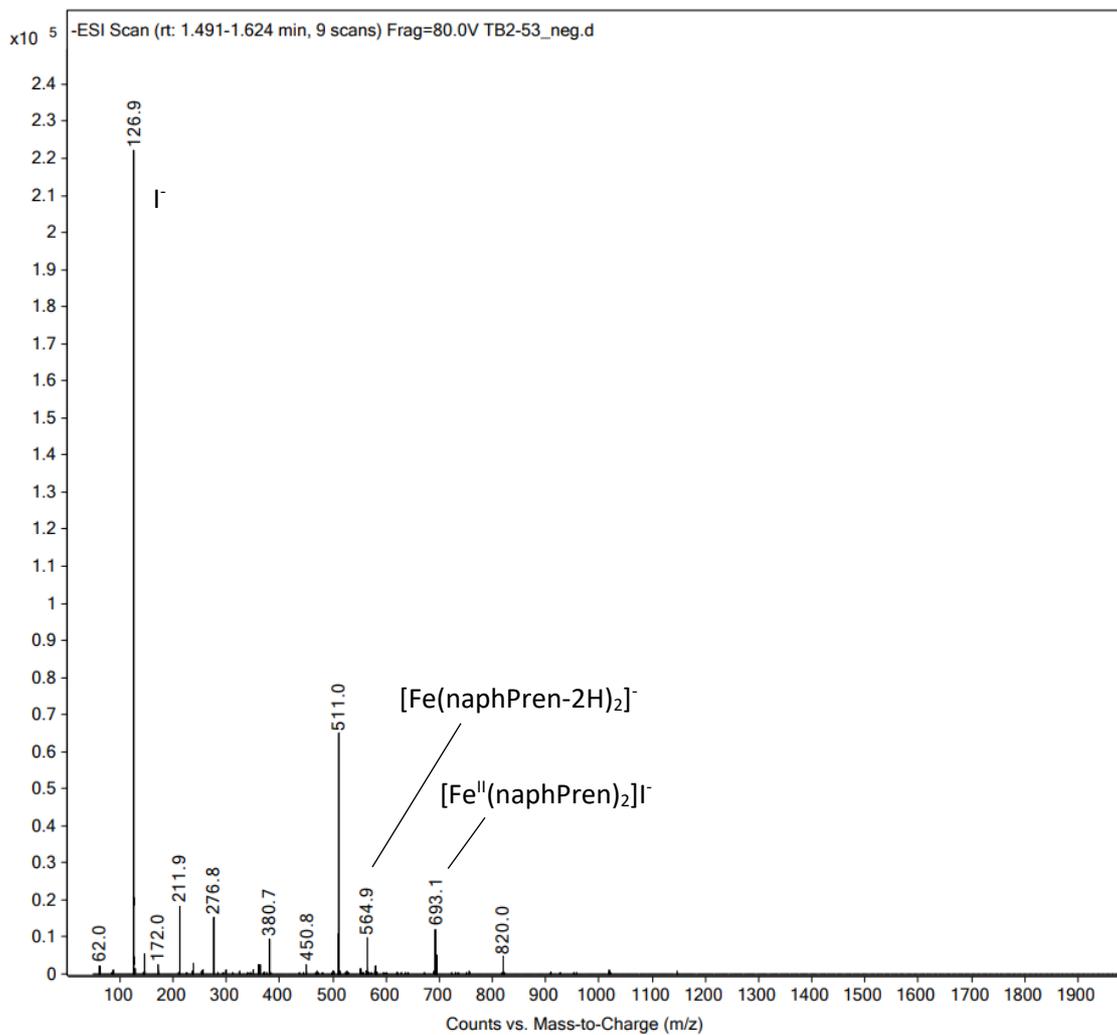
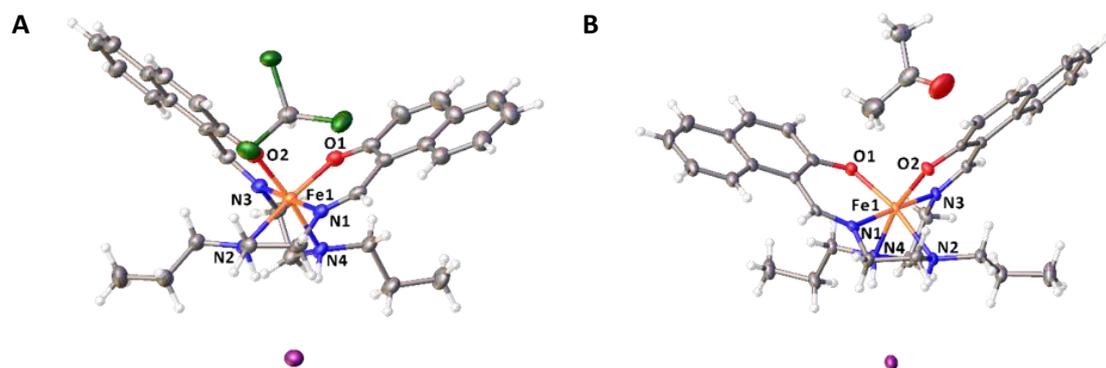


Figure S5. Mass spectrum of **1** (ESI-)



**Figure S6.** Asymmetric Unit of **2** (A) and **3** (B) at 150 K.

**Table S2** Crystallographic data and refinement parameters for [Fe(naphPren)<sub>2</sub>]I·solv complexes where solv = CH<sub>2</sub>Cl<sub>2</sub>, **1**, CHCl<sub>3</sub>, **2** and acetone, **3**.

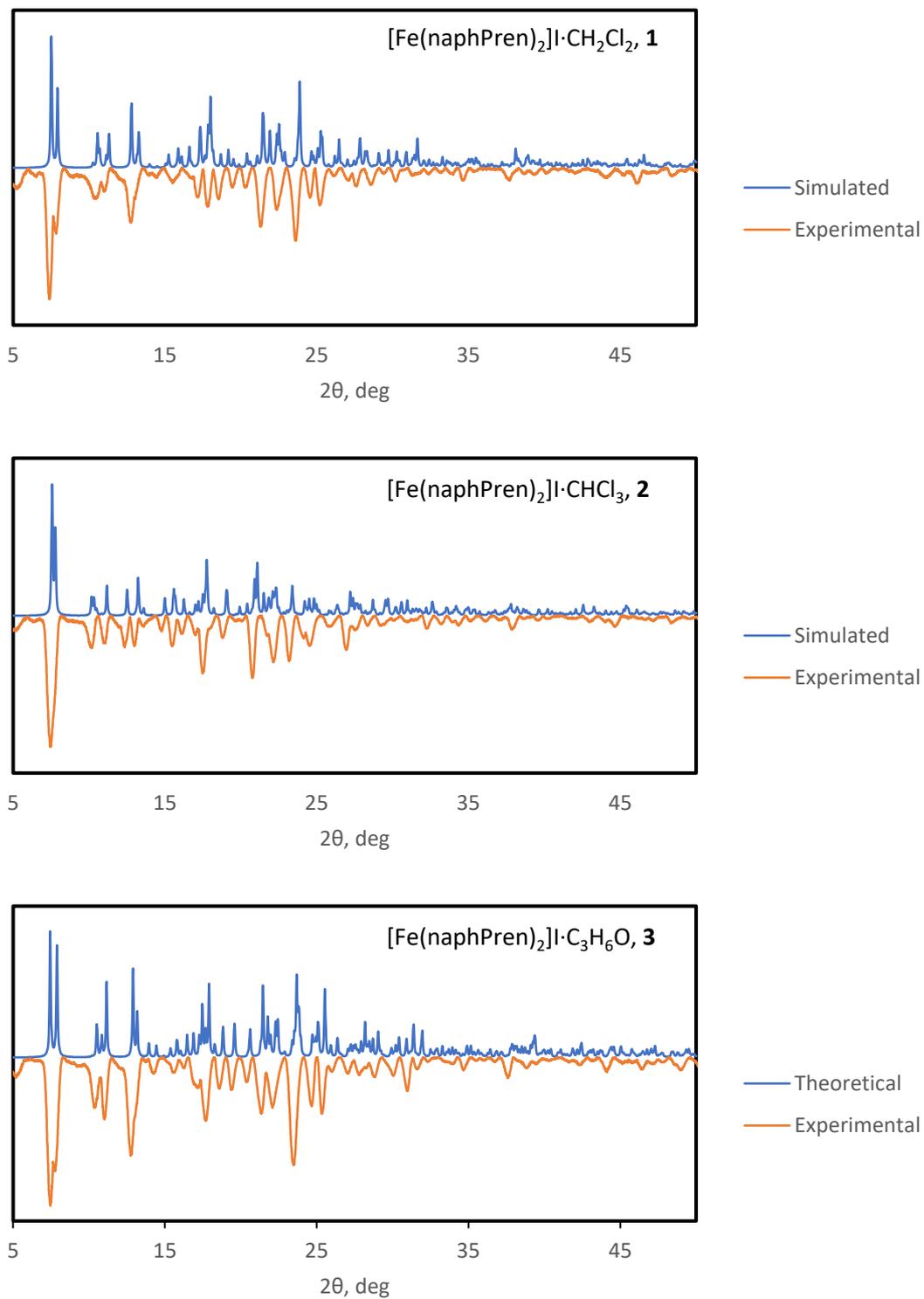
	<b>1</b>		<b>2</b>				<b>3</b>
Formula	C <sub>32</sub> H <sub>38</sub> FeIN <sub>4</sub> O <sub>2</sub> ·CH <sub>2</sub> Cl <sub>2</sub>			C <sub>32</sub> H <sub>38</sub> FeIN <sub>4</sub> O <sub>2</sub> ·CHCl <sub>3</sub>			C <sub>32</sub> H <sub>38</sub> FeIN <sub>4</sub> O <sub>2</sub> ·C <sub>3</sub> H <sub>6</sub> O
T (K)	150	200	130	150	200	298	150
MW (g/mol)	778.34	778.37		812.78		812.81	751.49
Radiation	CuKα			CuKα			CuKα
λ (Å)	1.54184			1.54184			1.54184
Crystal system	Monoclinic			Monoclinic			Monoclinic
Space group	P2 <sub>1</sub> /c			P2 <sub>1</sub> /c			P2 <sub>1</sub> /c
a (Å)	11.17020 (10)	11.3870 (1)	11.37248 (11)	11.38862 (17)	11.47081 (14)	11.54644 (13)	11.22140 (10)
b (Å)	12.64770 (10)	12.6060 (1)	13.01255 (13)	13.0145 (2)	12.93413 (16)	13.04848 (16)	12.68900 (10)
c (Å)	23.5283 (3)	23.8251 (2)	23.3736 (2)	23.4046 (4)	23.8498 (3)	23.9438 (3)	23.7424 (2)
α (°)	90	90	90	90	90	90	90
β (°)	92.2150 (10)	90.177 (1)	93.9098 (8)	93.6869 (14)	92.8489 (11)	93.0092 (10)	90.0330 (10)
γ (°)	90	90	90	90	90	90	90
Cell volume (Å <sup>3</sup> )	3321.53 (6)	3419.95 (5)	3450.89 (6)	3461.78 (10)	3534.10 (7)	3602.48 (7)	3380.64 (5)
Z	4	4	4	4	4	4	4
μ (mm <sup>-1</sup> )	12.702	12.337	12.949	12.908	12.644	12.405	11.061
Reflections collected	23172	25119	27351	26930	27434	29102	34357
Independent reflections,	6065,	6259,	6314,	6334,	6473,	6587,	6186,
R <sub>int</sub> (%)	7.28	7.08	12.82	10.66	9.19	8.04	9.32
R-Factor (%), wR <sub>2</sub> (%) [I ≥ 2σ]	5.52, 15.16	5.26, 14.12	5.40, 14.29	6.63, 18.49	5.28, 14.53	5.52, 15.51	4.47, 12.03
CCDC No.	2259253	2259254	2259255	2259257	2259258	2259256	2259259

**Table S3** Solid state intermolecular interaction of [Fe(naphPren)<sub>2</sub>]<sup>+</sup>I<sup>-</sup> solv complexes where solv = CH<sub>2</sub>Cl<sub>2</sub>, **1**, CHCl<sub>3</sub>, **2** and acetone, **3** (Å or °)<sup>1</sup>

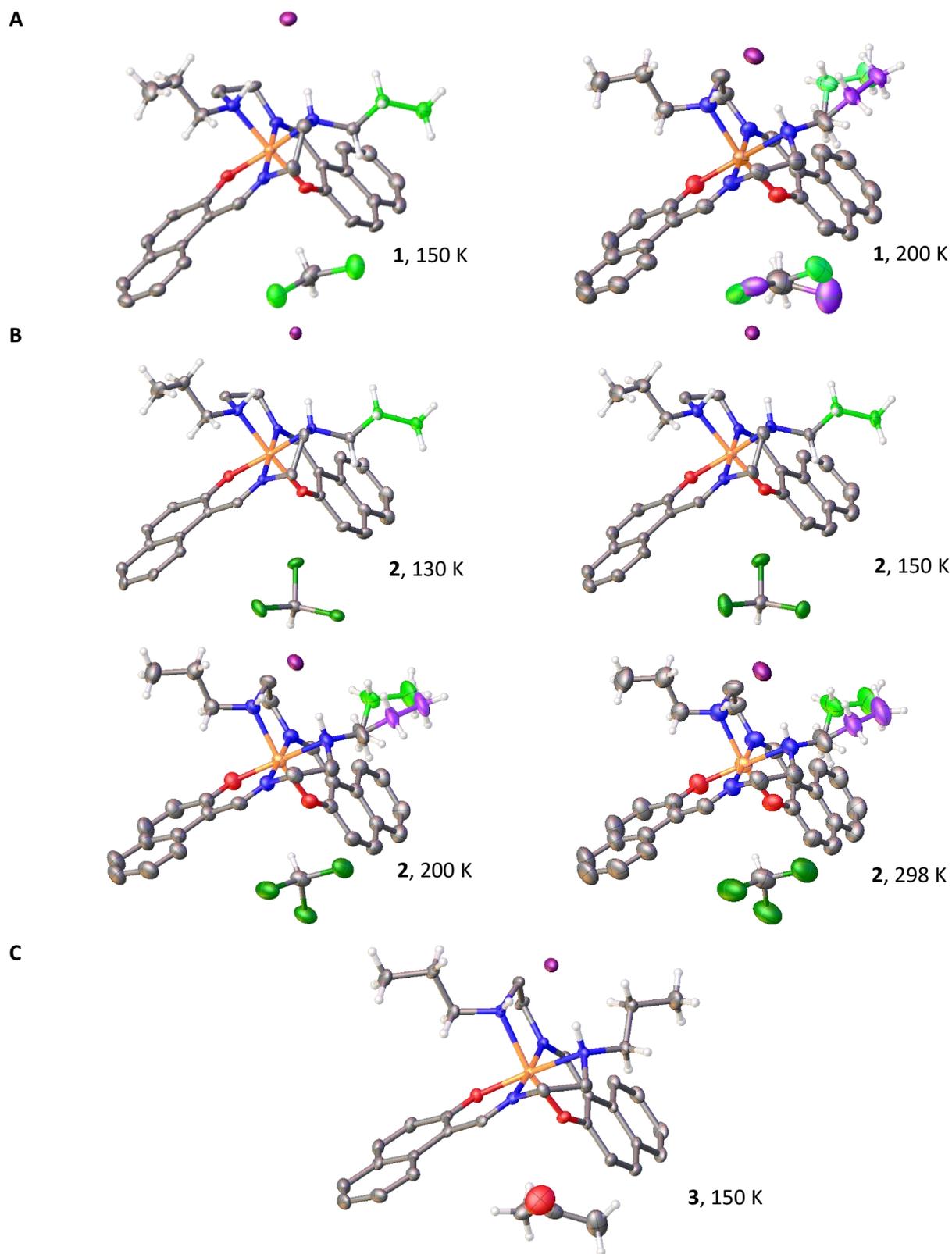
	<b>1</b>		<b>2</b>				<b>3</b>
T (K)	150	200	130	150	200	298	150
<i>Torsion angle of the propyl chain</i>							
<b>Fe-N2-C14-C15</b>	179.4	91.7, 166.2	179.7	179.0	102.2, 174.6	99.2, 170.6	85.1
<b>Fe-N4-C30-C31</b>	170.8	171.9	170.0	170.1	168.5	169.2	174.2
<b>N2-C14-C15-C16</b>	166.8	159.7, 169.8	167.7	168.1	167.0, 169.1	111.4, 164.3	173.7
<b>N4-C30-C31-C32</b>	175.7	175.3	178.3	178.2	176.5	177.8	174.2
<i>1-D chain of cationic complex and solvent along b-axis</i>							
<b>N-H2...I or N-H4...I</b>	2.67, 2.88	2.71, 2.84	2.63, 2.69	2.62, 2.69	2.65, 2.68	2.75, 2.78	2.70, 2.75
<b>C-H33...I</b>	-	3.08/3.24 (ds)	-	-	-	-	-
<b>C-H34...I</b>	-	-	-	-	-	-	3.19
<b>C-Cl<sub>solv</sub>(1/2/3)...I</b>	4.10	-	3.54	3.54	3.54	3.55	-
<b>C-H34...O1/2</b>	2.58, 2.63	2.56/2.59 (ds)	2.45	2.46	2.56	2.60	2.74
<b>C-Cl<sub>solv</sub>(1/2/3)...O1/2</b>	-	3.28/3.89 (ds)	3.10	3.11	3.11	3.18	-
<b>C-H33...O1</b>	-	-	-	-	-	-	2.83
<b>C-H24...π or C-H27...π</b>	3.34, 3.38	3.14, 3.42	-	-	-	-	-
<b>C-H8...π or C-H11...π</b>	-	-	3.28, 3.32	3.28, 3.31	3.22, 3.36	3.28, 3.42	3.27, 3.40
<b>C-H19...π</b>	3.43	3.60	-	-	-	-	-
<b>C-H3...π</b>	-	-	3.75	3.77	3.82	3.90	3.54
<b>C-H32...π</b>	2.92, 3.10	3.12/3.26, 2.87/none (ds)	-	-	-	-	-

<b>C-H16<math>\cdots\pi</math></b>	-	-	3.19, 3.44	3.20, 3.47	3.35/3.87, 3.16/ <i>none</i> ( <i>ds</i> )	3.21/3.73, 3.20/ <i>none</i> ( <i>ds</i> )	2.96, 3.12
<b>Fe-Fe (Å)</b>	7.73	7.55	7.98	7.97	7.84	7.86	7.52
<i>Interaction between 1-D chains</i>							
<b>C-H24<math>\cdots I</math> or C-H27<math>\cdots I</math></b>	3.13, 3.14	3.14, 3.21	3.08, 3.14	3.07, 3.15	3.04, 3.15	3.09, 3.19	3.15, 3.18
<b>C-H3<math>\cdots\pi</math></b>	3.06	2.93	-	-	-	-	-
<b>C-H19<math>\cdots\pi</math></b>	-	-	2.93	2.94	2.87	2.92	2.94
<b>CH16<math>\cdots\pi</math></b>	2.90	2.95	-	-	-	-	-
<b>CH32<math>\cdots\pi</math></b>	-	-	2.94	3.00	3.01	3.12	2.87
<b>Tilting of staggered <i>ab</i> plane, <math>\beta</math> (°)</b>	92.2	90.2	93.9	93.7	92.9	93.0	90.0

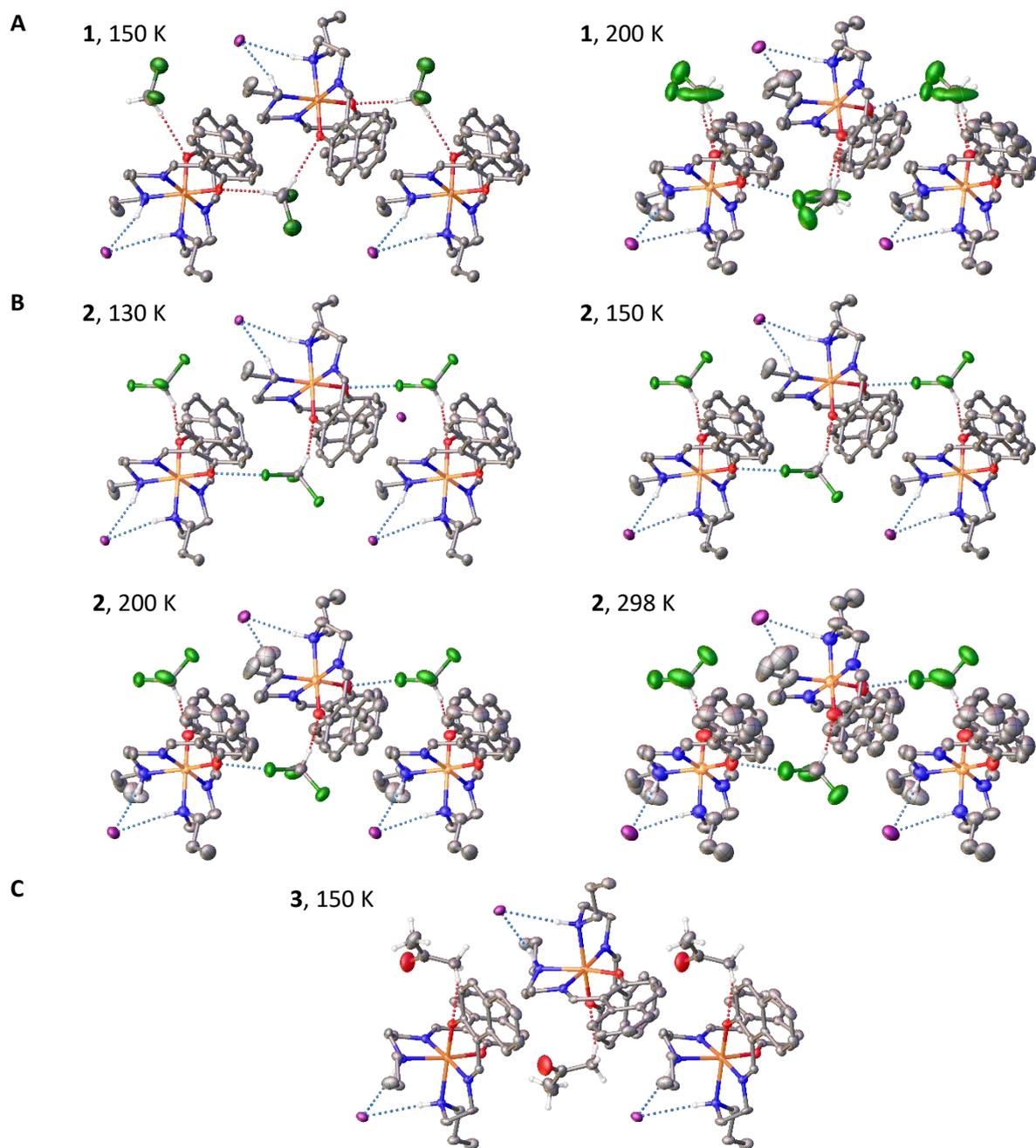
<sup>1</sup>(*ds*) represents the values from the disordered motifs



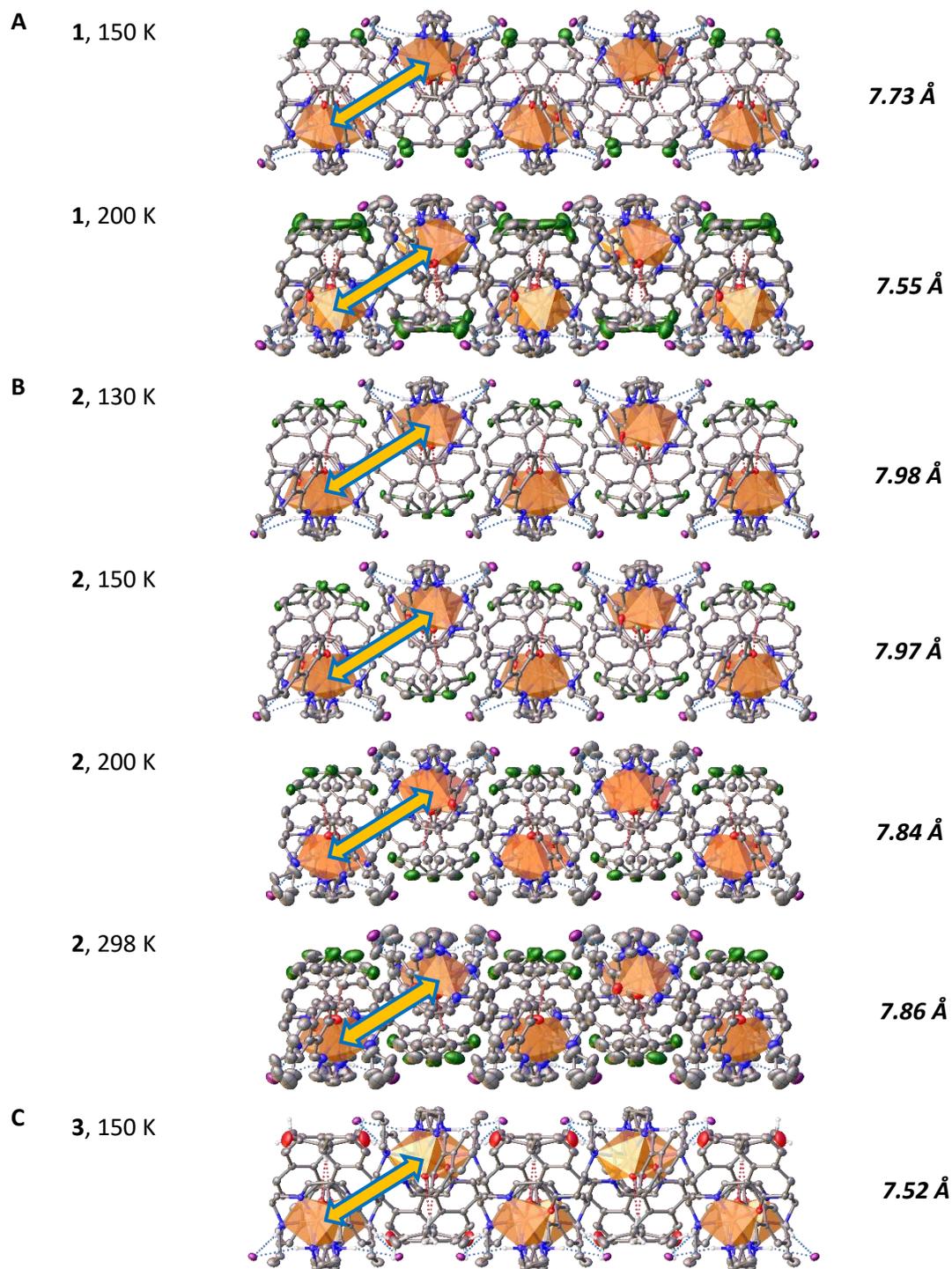
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