

**Supplementary Information for:**

**Between Red and Yellow: Evidence of Intermediates in a Vapochromic Pt(II) Salt.**

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**Experimental:** K<sub>2</sub>PtCl<sub>4</sub> was purchased from Pressure Chemical. COD (1,5-cyclooctadiene) and tpy (2,2':6',2''-terpyridine) were obtained from Aldrich. NH<sub>4</sub>ClO<sub>4</sub> was purchased from Fisher Scientific. Starting materials, Pt(COD)Cl<sub>2</sub> and [Pt(tpy)Cl]Cl·2H<sub>2</sub>O, were prepared according to published procedures.<sup>1,2</sup> Pre-cleaned gold seal micro slides (Portsmouth, NH) were used for solid-state absorption spectroscopy. [Pt(tpy)Cl]ClO<sub>4</sub>·H<sub>2</sub>O (1·H<sub>2</sub>O) was prepared as previously described; red needles of [Pt(tpy)Cl]ClO<sub>4</sub>·H<sub>2</sub>O were grown from acetone/water.<sup>3</sup> Anal Calcd for C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>Cl<sub>2</sub>O<sub>4</sub>Pt·H<sub>2</sub>O (FW:581.27): C, 30.99; H, 2.25; N, 7.23. Found: C, 31.23; H, 1.92; N, 7.12. MS-ESI (+, MeCN) (m/z): 464.0463. MS-ESI (-, MeCN) (m/z): 98.9727. <sup>1</sup>H NMR: (*d*<sub>6</sub>-DMSO, δ): 8.92 (2H, d), 8.66-8.63 (5H, m), 8.54 (2H, dd), 7.98 (2H, dd). MS-ESI (positive ion mode, MeCN) (m/z): 464.0. MS-ESI (negative ion mode, MeCN) (m/z): 100.9. Elemental analyses were performed by Atlantic Microlab (Norcross, GA). Mass spectra were obtained using a Micromass Q-TOF 2 (Waters, Milford, MA, USA). The instrument conditions were optimized and calibrated in positive ion mode using poly-alanine (Sigma, St. Louis, MO, USA) and in negative ion mode using sodium iodide (Fisher Scientific). The observed isotope patterns agreed well with those predicted based on natural isotopic abundances. <sup>1</sup>H NMR spectra were recorded at room temperature using a Bruker AC

400 MHz instrument. Deuterated solvents were purchased from Cambridge Isotope Laboratories.

To characterize interconversion between the red and yellow forms, an acetone solution of  $[\text{Pt}(\text{tpy})\text{Cl}]\text{ClO}_4 \cdot \text{H}_2\text{O}$  was evaporated to give a “thin film” of needle-like crystallites dispersed on a glass slide, the majority measuring 1-2  $\mu\text{m}$  thick and 5 - 20  $\mu\text{m}$  in length. UV-visible absorption spectra were obtained using a HP8453 diode array spectrometer, while exposing the sample to a dry or water-saturated argon atmosphere under very low argon flow. Room-temperature steady-state emission spectra were collected in the front face configuration using a SPEX Fluorolog-3 fluorimeter equipped with a double emission monochromator and a single excitation monochromator. Solid samples were placed into a quartz EPR tube, and then exposed to water-saturated air overnight in a sealed chamber. 77K emission were obtained by placing the quartz EPR tube into a quartz dewar with liquid nitrogen.

**Structure Determination:**<sup>4</sup> Red needles of  $[\text{Pt}(\text{tpy})\text{Cl}]\text{ClO}_4 \cdot \text{H}_2\text{O}$  (**1.H<sub>2</sub>O**) were grown from acetone-water, whereas orange needles of  $[\text{Pt}(\text{tpy})\text{Cl}]\text{ClO}_4$  (**1**) needles were grown from acetone. For X-ray examination and data collection, suitable crystals, approximate dimensions 0.18 x 0.03 x 0.02 mm for  $[\text{Pt}(\text{tpy})\text{Cl}]\text{ClO}_4 \cdot \text{H}_2\text{O}$  and 0.04 x 0.005 x 0.005 mm for  $[\text{Pt}(\text{tpy})\text{Cl}]\text{ClO}_4$ , were each mounted in loops with paratone-N and were transferred immediately to a goniostat bathed in a cold stream. Intensity data for  $[\text{Pt}(\text{tpy})\text{Cl}]\text{ClO}_4 \cdot \text{H}_2\text{O}$  were collected at T=230K using a Bruker SMART6000 CCD diffractometer with a graphite-monochromated Cu  $K\alpha$  radiation,  $\lambda=1.54178\text{\AA}$ . Crystal data are summarized in Table S1 and select bond distances and angles are listed in Table S2. Unit cells also were determined on the same crystal from 160-240K (10K increments, Table S3).

We also reproduced the twinned  $[\text{Pt}(\text{tpy})\text{Cl}]\text{ClO}_4$  (42% pseudo-merohedral twinning) structure reported by Bailey *et al.*<sup>9</sup> as well as an untwinned structure reported here and determined that the structure remains essentially unchanged at 150 K. The latter observation establishes that the Bailey polymorph does not undergo a phase transition and convert to the structure of the dehydrated form over this temperature range. Intensity data for  $[\text{Pt}(\text{tpy})\text{Cl}]\text{ClO}_4$  were collected at 150K on a Bruker APEXII CCD detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to  $\lambda=0.88560\text{\AA}$ . A series of 1-s data frames measured at  $0.2^\circ$  increments of  $\omega$  were collected to calculate a unit cell. For data collection, frames were measured for a duration of 1-s for low angle and 4-s for high angle data at  $0.3^\circ$  intervals of  $\omega$  with a maximum  $2\theta$  value of  $\sim 65^\circ$ . The data frames were collected using the program APEX2 and processed using the program SAINT routine within APEX2. The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS.

Both structures were solved by a combination of direct methods SHELXTL v6.14 and the difference Fourier technique and refined by full-matrix least squares on  $F^2$ . Non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the hydrogen atoms on the cation were calculated and treated with a riding model. For  $[\text{Pt}(\text{tpy})\text{Cl}]\text{ClO}_4\cdot\text{H}_2\text{O}$ , the water hydrogen atoms were located from the difference map at distances of approximately  $1.05\text{\AA}$ . The O-H distance was adjusted closer to the accepted value of  $0.90\text{\AA}$  and held fixed in subsequent refinements. The isotropic displacement parameters for the H-atoms were defined as  $a^*U_{\text{eq}}$  of the adjacent atom, ( $a=1.5$  for O-H and  $1.2$  for all others). The oxygen atoms of the anion (O1-O4) are disordered. The refined occupancies for O1 and O4 are 78 and 77% for the major component; the major component for O2 and O3 refines to 51 and 50%, respectively. Although

O5 of the water molecule also shows disorder, a suitable multi-component disorder model was not realized. Crystal data are summarized in Table S1 and select bond distances and angles are listed in Table S2.

**X-ray Powder Diffraction:** Data for [Pt(tpy)Cl]ClO<sub>4</sub>.H<sub>2</sub>O were collected at the Advanced Photon Source Station 11-BM, Argonne National Laboratory using 0.413620 Å photons in transmission geometry as the sample was rotated. [Pt(tpy)Cl]ClO<sub>4</sub>.H<sub>2</sub>O was exposed to water-vapor prior to data collection. The incident photons were selected with platinum striped mirrors and a double Si(111) monochromator with adjustable sagittal focus. The scattered beams were selected with (12) perfect Si(111) analyzer crystals. Discrete detectors covering an angular range from -6 to 16° 2θ were scanned over a 34° 2θ range, with data points collected every 0.001° 2θ at a scan speed of 0.01°/s. For variable temperature scans, 10 consecutive three minute scans were recorded as the sample temperature increased from 255 to 400 K at a ramp rate of ~ 0.1°C/s. Temperatures of the first seven scans were recorded at the beginning of the scan; the last three temperatures were estimated by linear extrapolation of the temperature with respect to time for the first seven scans. We determined the temperatures at the start of the scans to be: 255, 270, 287, 301, 321, 338, 356, 371, 388, and 400 K. Complete descriptions of the instrument and data collection system have been reported previously.<sup>5-7</sup> Simulated powder diffraction patterns of [Pt(tpy)Cl]ClO<sub>4</sub>.H<sub>2</sub>O<sup>8</sup> and Bailey's [Pt(tpy)Cl]ClO<sub>4</sub><sup>9</sup> were calculated from the corresponding single-crystal structures using the program Mercury.

Rietveld analysis of data for dehydrated [Pt(tpy)Cl]ClO<sub>4</sub> was attempted using GSAS-EXPGUI rev. 1225.<sup>10,11</sup> We constructed a model of the dehydrate structure in the P-1 space group using a unit cell of  $a = 14 \text{ \AA}$ ,  $b = 7 \text{ \AA}$ ,  $c = 13 \text{ \AA}$ ,  $\alpha = 78^\circ$ ,  $\beta = 127^\circ$ ,  $\gamma = 70^\circ$ , a cell volume of 813 Å<sup>3</sup> and Z=2. The Pt(tpy)Cl<sup>+</sup> and perchlorate ions were modeled as rigid bodies and

placed heuristically. The unit cell parameters were refined and converged to  $a = 13.86 \text{ \AA}$ ,  $b = 6.98 \text{ \AA}$ ,  $c = 13.35 \text{ \AA}$ ,  $\alpha = 77.89^\circ$ ,  $\beta = 126.89^\circ$ ,  $\gamma = 70.26^\circ$ . Attempts to refine other structural parameters diverged. Significant peak broadening, especially at temperatures of 300 K and above, was observed and is due to some combination of crystallite size reduction, increased mosaic spread, strain and preferred orientation. Without constraining information on any of these parameters, it is impossible to know the magnitude or type of contribution of any of them so deconvolution of the broadening was not attempted. This model reasonably recreates the diffraction pattern from 0 to  $1.3 \text{ \AA}^{-1}$  in Q-space. However, it is not a solved structure, and the model shows some unreasonably short contacts.

**Thermogravimetric Analysis:** Simultaneous thermogravimetric and differential thermal analyses (TGA-DTA) were carried out on a TA Instruments SDT Q600.  $[\text{Pt}(\text{tpy})\text{Cl}]\text{ClO}_4 \cdot \text{H}_2\text{O}$  was stored under a water-saturated air atmosphere prior to data collection to minimize water loss prior to the experiment. Typically, a sample of  $[\text{Pt}(\text{tpy})\text{Cl}]\text{ClO}_4 \cdot \text{H}_2\text{O}$  crystals ( $\sim 5 \text{ mg}$ ) was loaded in a  $300 \text{ \mu L}$  platinum pan, and an identical pan was used as a reference. Data were collected in  $0.5 \text{ s}$  increments up to  $150^\circ\text{C}$  at a furnace ramp rate of  $1^\circ\text{C}/\text{min}$ . Measurements were performed using compressed air as a purge gas at  $100 \text{ mL}/\text{min}$ . For isothermal experiments, approximately  $5 \text{ mg}$  of sample was allowed to equilibrate at  $22^\circ\text{C}$  for 2 hours. After 2 hours the sample was heated to  $150^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$  to complete the dehydration. Differential scanning calorimetry (DSC) measurements were carried out on a NETZSCH DSC 200F3 instrument. Two different pan assemblies were used in this experiment: an open Al-pan and a clamped Al-pan with a pierced lid. The lid was pierced using a small pin. Both samples (with and without lid) were stored under a water-saturated air atmosphere for an hour before starting the experiment.

The instrument was cooled to  $-20^{\circ}\text{C}$ , and samples were quickly loaded in the instrument. Data collection was done at a furnace ramp rate of  $5^{\circ}\text{C}/\text{min}$  starting from  $\sim -10^{\circ}\text{C}$  to  $115^{\circ}\text{C}$ .

**Figures and Tables:**

Table S1: Crystallographic Data for [Pt(tpy)Cl]ClO<sub>4</sub>.H<sub>2</sub>O (230 K) and [Pt(tpy)Cl]ClO<sub>4</sub>.

	[Pt(tpy)Cl]ClO <sub>4</sub> .H <sub>2</sub> O	[Pt(tpy)Cl]ClO <sub>4</sub>
Formula	[C <sub>15</sub> H <sub>11</sub> N <sub>3</sub> ClPt]ClO <sub>4</sub> .H <sub>2</sub> O	[C <sub>15</sub> H <sub>11</sub> N <sub>3</sub> ClPt]ClO <sub>4</sub>
CDCC No.	948313	948314
Formula Weight	581.27	563.26
Temperature (K)	230(2)	150(2)
Wavelength (Å)	1.54178	0.88560
Crystal System	Triclinic	Monoclinic
Space Group	P-1	P2 <sub>1</sub> /c
<i>a</i> , Å	6.6710(6)	7.0189(3)
<i>b</i> , Å	10.2403(9)	16.8805(8)
<i>c</i> , Å	13.3874(14)	26.8979(13)
$\alpha$ , °	103.816(5)	90
$\beta$ , °	102.813(5)	90.336(3)
$\gamma$ , °	90.485(5)	90
<i>V</i> , Å <sup>3</sup>	864.14(14)	3186.9(3)
<i>Z</i>	2	8
$\rho_{\text{calc}}$ , mg m <sup>-3</sup>	2.234	2.348
$\mu$ , mm <sup>-1</sup>	18.348	15.972
No. reflns colld	6655	41902
No. ind reflns/ <i>R</i> <sub>int</sub>	2879/0.0464	6536 / 0.0945
GOF on <i>F</i> <sup>2</sup>	1.052	1.009
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> [ <i>I</i> >2σ( <i>I</i> )] <sup>a</sup>	0.0534/0.1212	0.0332/0.0600
<i>wR</i> <sub>2</sub> (all data) <sup>a</sup>	0.0658/0.1264	0.0633/0.0690

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

Table S2: Select Distances (Å) and Angles (°) for [Pt(tpy)Cl]ClO<sub>4</sub>.H<sub>2</sub>O (230 K) and [Pt(tpy)Cl]ClO<sub>4</sub>.

	[Pt(tpy)Cl]ClO <sub>4</sub> .H <sub>2</sub> O	[Pt(tpy)Cl]ClO <sub>4</sub>	
		Molecule A	Molecule B
Pt-N1	2.020(10)	2.015(5)	2.022(5)
Pt-N2	1.933(9)	1.937(5)	1.928(5)
Pt-N3	2.048(9)	2.020(5)	2.029(5)
Pt-Cl1	2.314(3)	2.301(1)	2.3071(15)
N1-Pt-N3	161.3(4)	162.9(2)	162.0(2)
N1-Pt-N2	81.3(4)	81.5(2)	81.9(2)
N2-Pt-N3	80.0(4)	81.4(2)	81.1(2)
N2-Pt-Cl1	179.4(3)	177.56(14)	178.56(14)
Pt...Pt	3.3305(10)/3.3808(10)	3.2455(4)/ 4.1667(4)	
Pt...Pt...Pt	167.45(3)	142.2(1)	



Table S3: Unit cell parameters for a single crystal of [Pt(tpy)Cl]ClO<sub>4</sub>.H<sub>2</sub>O with increasing temperatures from 150 to 240 K.

Temperature (K)	<i>a</i>	<i>b</i>	<i>c</i>	$\alpha$	$\beta$	$\gamma$	<i>V</i>
150	6.6339(17)	10.2189(11)	13.3573(31)	104.384(17)	103.610(12)	90.519(16)	850.3(3)
160	6.6316(13)	10.2191(11)	13.3524(30)	104.335(17)	103.555(12)	90.517(15)	850.1(3)
170	6.6406(11)	10.2237(11)	13.3670(31)	104.277(17)	103.511(11)	90.537(13)	853.0(3)
180	6.6412(10)	10.2207(10)	13.3642(27)	104.243(15)	103.436(10)	90.528(12)	853.1(2)
190	6.6431(10)	10.2196(9)	13.3614(27)	104.185(14)	103.354(10)	90.542(11)	853.6(2)
200	6.6498(9)	10.2220(9)	13.669(26)	104.099(14)	103.243(9)	90.507(11)	855.8(2)
210	6.6560(7)	10.2217(7)	13.3663(20)	103.967(10)	103.103(7)	90.502(8)	857.6(2)
220	6.6596(8)	10.2242(8)	13.3636(21)	103.856(11)	102.953(8)	90.451(9)	859.1(2)
230	6.6636(9)	10.2240(9)	13.3581(23)	103.768(12)	102.792(9)	90.402(10)	860.3(2)
235	6.6564(42)	10.2647(50)	13.2771(147)	103.190(85)	102.619(107)	90.538(53)	860.2(2)
240	6.6565(76)	10.2307(85)	13.2983(179)	104.284(165)	102.548(197)	90.267(83)	855.0(9)

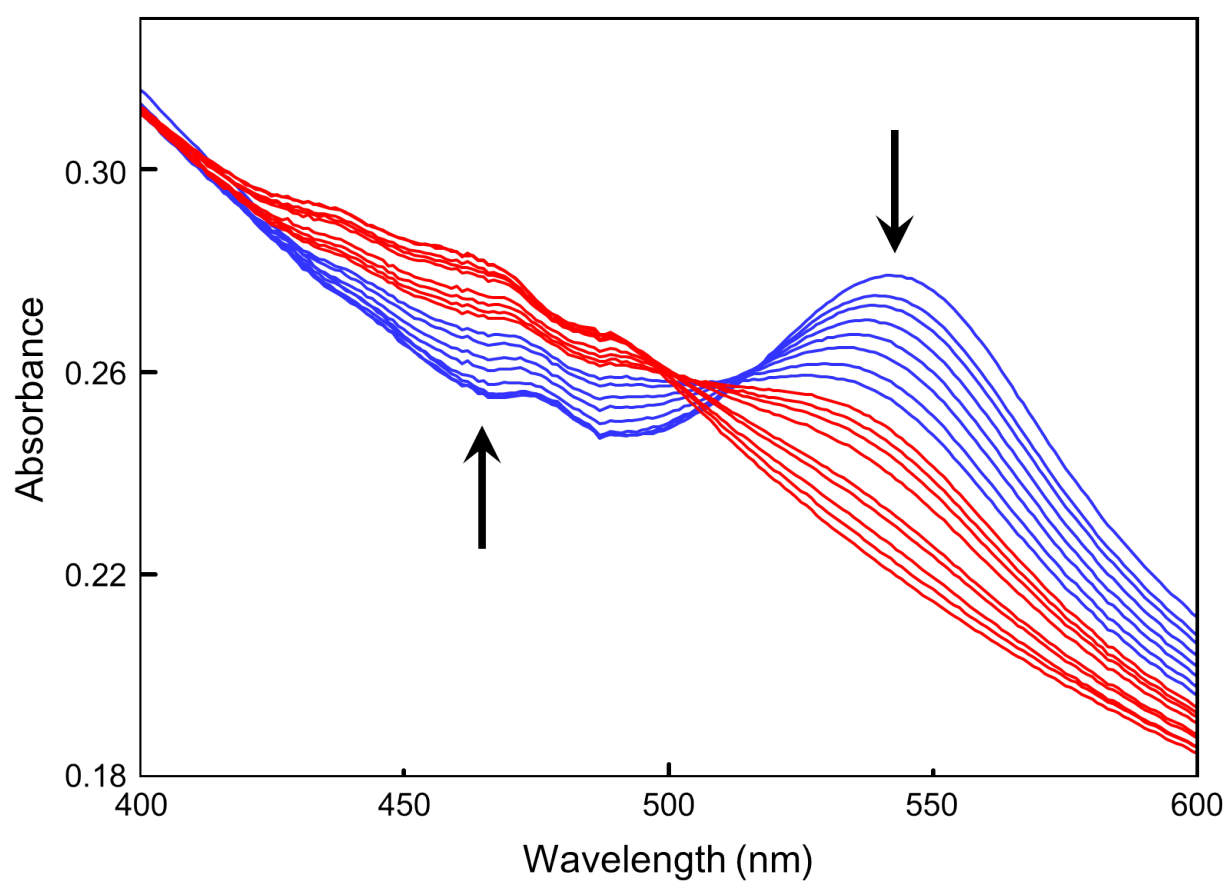


Figure S1: UV-visible absorption spectra of thinly dispersed crystallites of [Pt(tpy)Cl]ClO<sub>4</sub> recorded during exposure to water vapour. The red and blue colours draw attention to the fact that the earliest spectra have an approximate isosbestic point shifted slightly from that of the later spectra.

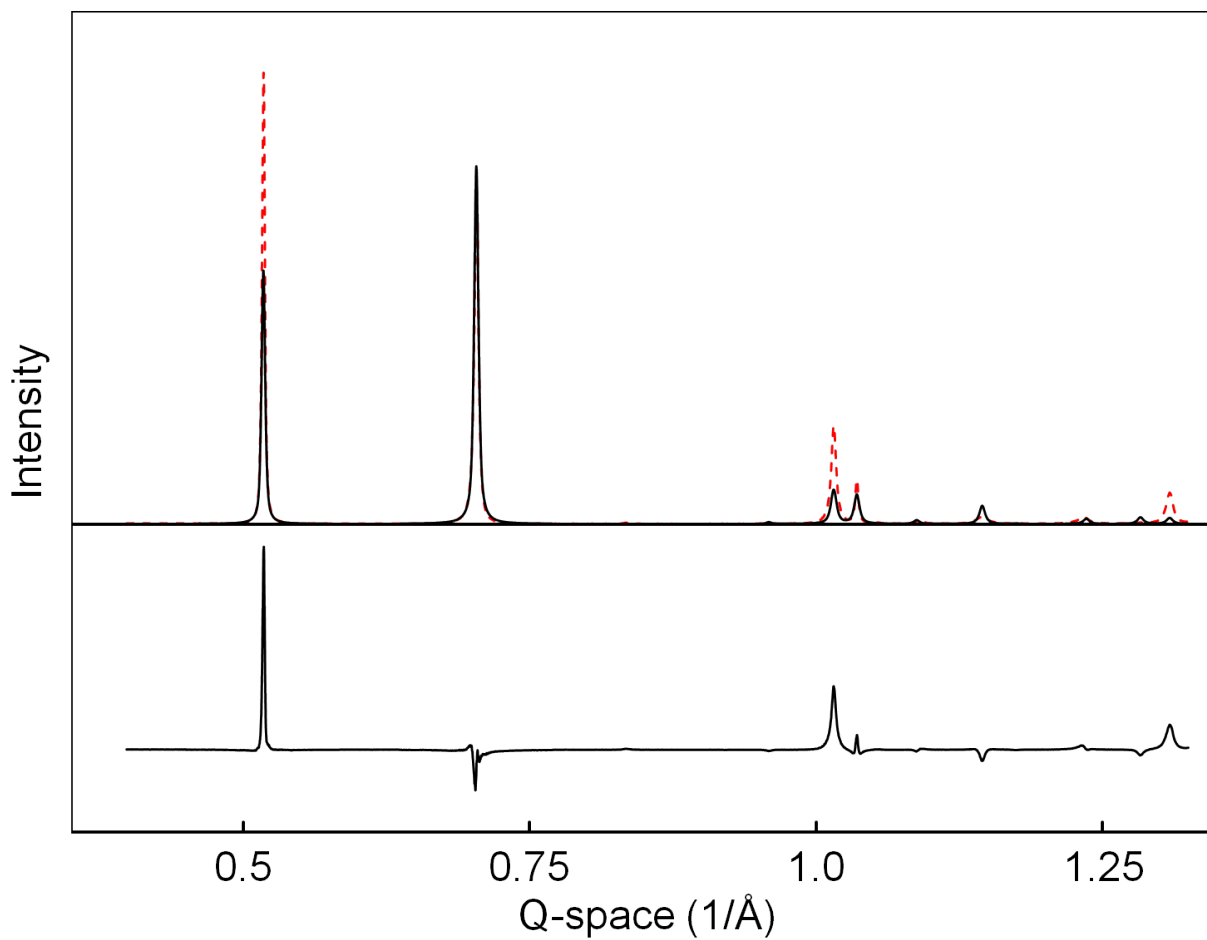


Figure S2: XRPD pattern of dehydrated [Pt(tpy)Cl]ClO<sub>4</sub> (- - -), the simulated powder diffraction pattern for model structure of dehydrated [Pt(tpy)Cl]ClO<sub>4</sub> (—), and the difference spectrum (bottom).

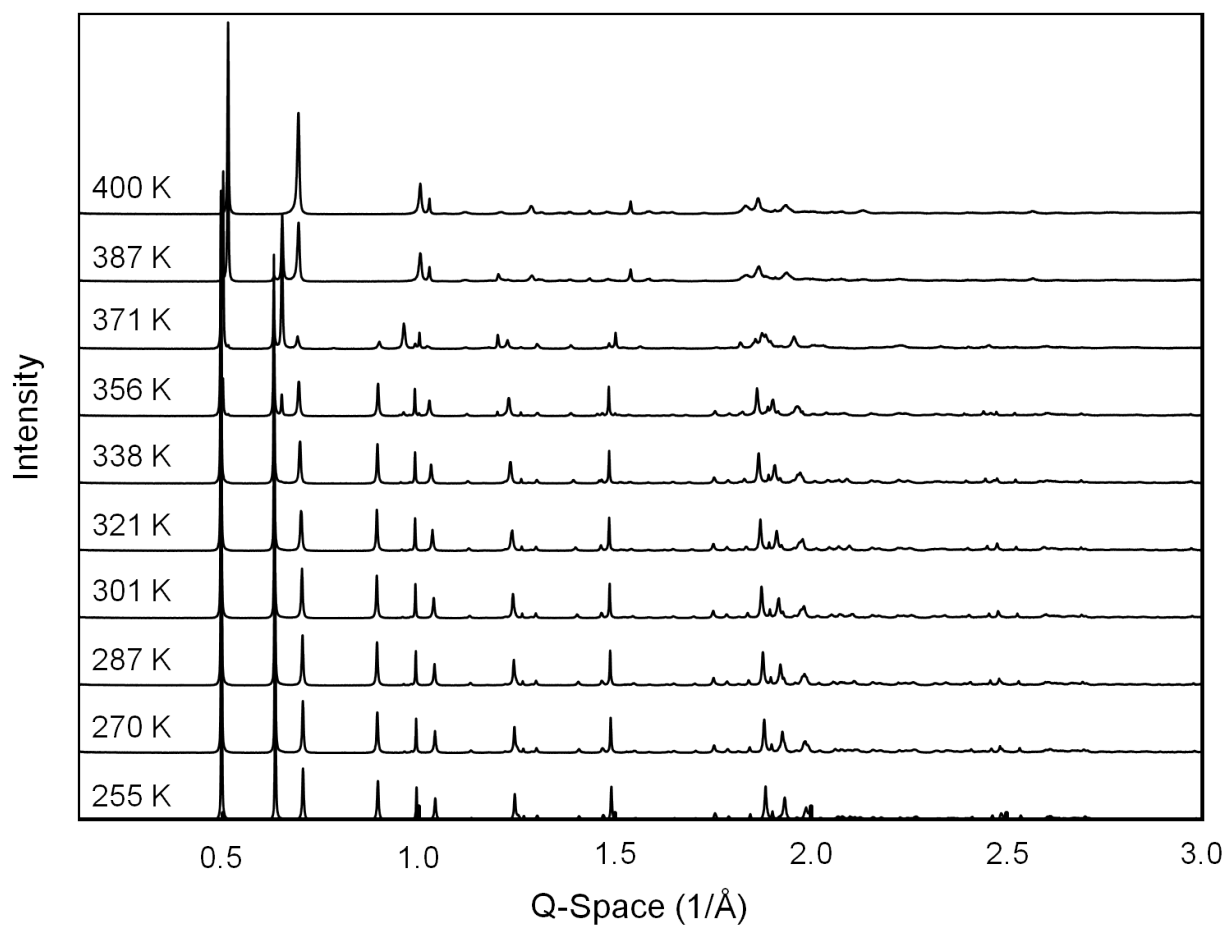


Figure S3: X-ray powder diffractograms of [Pt(tpy)Cl]ClO<sub>4</sub>.H<sub>2</sub>O (Q = 0.13-3.0) recorded at 255, 270, 287, 301, 321, 338, 356, 371, 387 and 400 K.

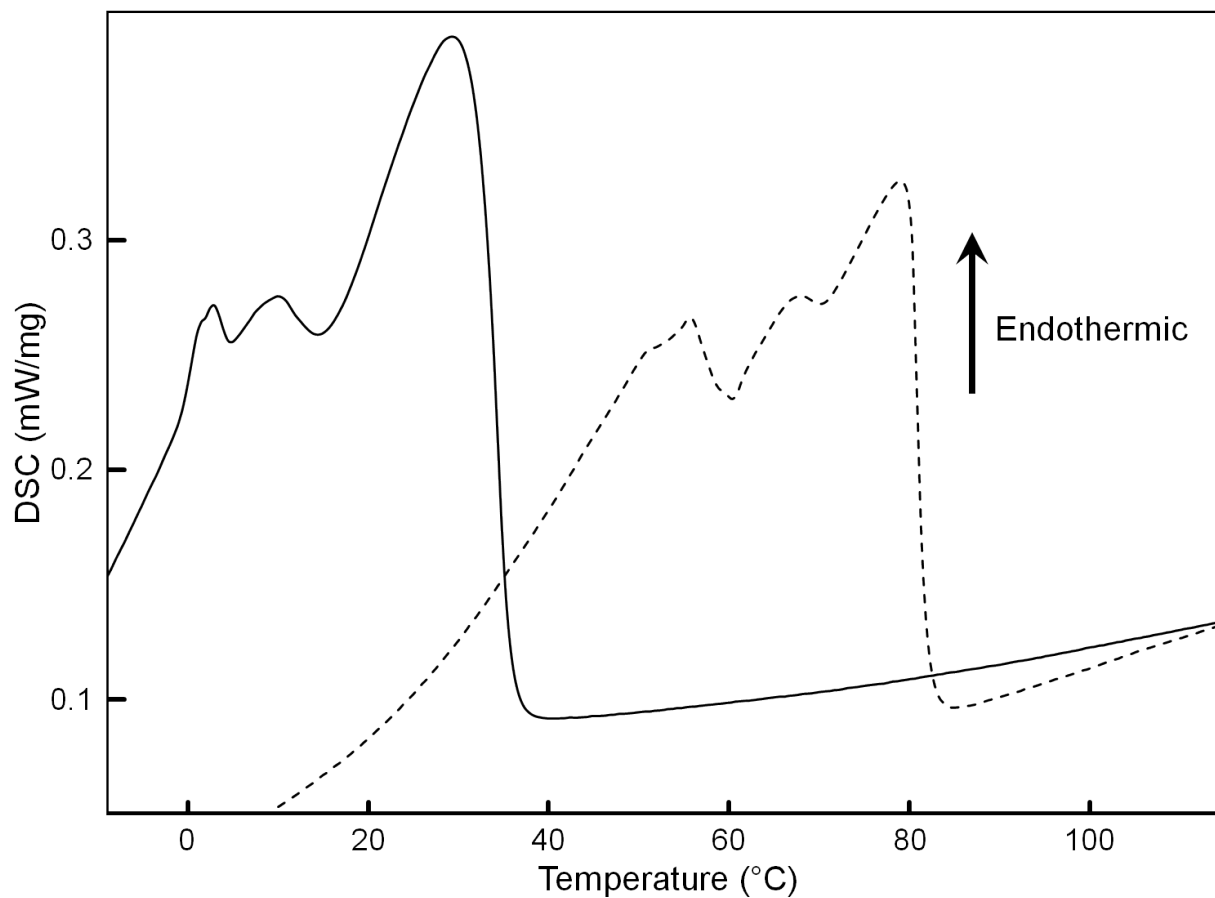


Figure S4: DSC analysis of  $[\text{Pt}(\text{tpy})\text{Cl}]\text{ClO}_4 \cdot \text{H}_2\text{O}$  at  $5^\circ\text{C}/\text{min}$  without a lid (—) and with a pierced lid (- - -).

## References

- (1) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.
- (2) Annibale, G.; Brandolisio, M.; Pitteri, B. *Polyhedron* **1995**, *14*, 451.
- (3) Taylor, S. D.; Howard, W.; Kaval, N.; Hart, R.; Krause, J. A.; Connick, W. B. *Chem. Commun. (Cambridge, U. K.)* **2010**, *46*, 1070.
- (4) (a) APEX2 v2010.3.0; SMART v5.632 and SAINT v6.45A, v7.60A. Bruker AXS, Inc., Madison, WI; (b) SADABS v2.10, v2008/1. G.M. Sheldrick, University of Göttingen, Germany; (c) SHELXTL v6.14. G.M. Sheldrick, Bruker AXS, Inc., Madison, WI; (d) Diamond v2.1, v3.0, v3.2. K. Brandenburg, Crystal Impact, Bonn, Germany
- (5) Dalesio, L. R.; Hill, J. O.; Kraimer, M.; Lewis, S.; Murray, D.; Hunt, S.; Watson, W.; Clausen, M.; Dalesio, J. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1994**, *352*, 179.
- (6) Wang, J.; Toby, B. H.; Lee, P. L.; Ribaud, L.; Antao, S. M.; Kurtz, C.; Ramanathan, M.; Von, D. R. B.; Beno, M. A. *Rev Sci Instrum* **2008**, *79*, 085105.
- (7) Lee, P. L.; Shu, D.; Ramanathan, M.; Preissner, C.; Wang, J.; Beno, M. A.; Von, D. R. B.; Ribaud, L.; Kurtz, C.; Antao, S. M.; Jiao, X.; Toby, B. H. *J Synchrotron Radiat* **2008**, *15*, 427.
- (8) Taylor, S. D.; Howard, W.; Kaval, N.; Hart, R.; Krause, J. A.; Connick, W. B. *Chem. Commun. (Cambridge, U. K.)* **2010**, *46*, 1070.
- (9) Bailey, J. A. H., G. M.; Marsh, R. E.; Miskowski, V. M.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 4591.
- (10) Toby, B. H. *J. Appl. Crystallogr.* **2001**, *34*, 210.
- (11) Larson, A. C.; Dreele, R. B. V. *Los Alamos National Laboratory Report LAUR* **2004**, 86.