Supporting Information for:

Phase Transformation Induced Mechanochromism in a Platinum Salt: A Tale of Two Polymorphs

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^eProf. Connick passed away on April 22, 2018. This paper is dedicated to his memory.

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Section S1. Experimental Procedures: General considerations.

K₂PtCl₄ was purchased from Pressure Chemical. COD (1,5-cyclooctadiene) and tpy (2,2':6'2"terpyridine) were obtained from Aldrich. Starting materials, Pt(COD)Cl₂ and [Pt(tpy)Cl]Cl•2H₂O, were prepared according to published procedures.¹ ¹H NMR spectra were recorded at room temperature using a Bruker AC 400 MHz NMR, and chemical shifts are referenced to the solvent. Mass spectra were obtained using a Micromass Q-Tof2 (Waters, Milford, MA, USA). The instrument was 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 agree well with those predicted based on natural isotopic abundances. Emission spectra on powder samples of the red and yellow forms of **1**•NO₃•HNO₃ were measured by exciting the sample at 442 nm using a SPEX Fluorolog-3 fluorimeter equipped with a double emission monochromator and a single excitation monochromator. Single-crystal emission was recorded using a BIACORE 2000 Surface Plasmon Resonance instrument. ATR-IR spectra were obtained using a Nicolet 6700 FTIR with a Smart Orbit diamond crystal ATR attachment from Thermo Fisher Scientific. Live video was recorded on a Keyence Digital Microscope VHX-1000.

Section S2. Experimental Procedures: Synthesis of 1•NO₃•HNO₃

1•NO₃•HNO₃ was prepared by dissolving 10 mg of [Pt(tpy)Cl]Cl into a 1:1 solution of HNO₃:acetone at pH=0. During evaporation, the formation of red crystals was observed. An alternative method to producing single crystals of **1**•NO₃•HNO₃ was by dissolving [Pt(tpy)Cl]Cl into a 1:1 solution of HNO₃:acetonitrile at pH=0. The pH of dissolved crystal solutions was measured to verify the presence of acid incorporation in the crystals. For example, the pH of a solution containing 4.0 mg of complex in 19 mL of water was 3.5.

 ^{1}H NMR (400 MHz, DMSO-d_6, $\delta)$ 8.9 (2H, CH), 8.65 (5H, CH), 8.52 (2H, CH), 7.98 (2H, CH).

MS-ESI (positive ion mode, CH₃CN) (m/z): 464.03 (Pt(tpy)Cl⁺).

MS-ESI (negative ion mode, CH₃CN) (m/z): 587.00 [Pt(tpy)Cl](NO₃)₂⁻.

IR bands were compared with nitric acid. (Table S1, Figs. S3-S4). Emission spectra recorded of the two polymorphs are shown in Figs. S5-S6.

Section S3. Experimental Procedures: Single-Crystal X-ray Diffraction.

{NOTE:(a) APEX2 v2.1-4; SMART v5.631, v5.632 and SAINT v6.45A, v7.34A, v7.46A. Bruker AXS, Inc., Madison, WI; (b) SADABS v2.10, v2004/1, v2007/4, v2008/1.G.M. Sheldrick, University of Göttingen, Germany; (c) SHELXTL v6.14. G.M. Sheldrick, Bruker AXS, Inc., Madison, WI; (d) PLATON v210103. A.L. Spek, Acta Cryst. 1990, A46, C34; (e) Diamond v2.1, v3.0, v3.2. K. Brandenburg, Crystal Impact, Bonn, Germany} Single crystals of the red and yellow polymorphs of $1 \cdot NO_3 \cdot HNO_3$ were obtained from slow evaporation of a CH₃CN solution. The crystallization vial contained the red form as the major product and the yellow form as the minor product.

For X-ray examination and data collection, suitable crystals were mounted in a loop with paratone-N and transferred immediately to the goniostat bathed in a cold N₂ stream. A full sphere of intensity data for the red and the yellow crystals was collected at 150 K using a Bruker SMART6000 CCD diffractometer with graphite-monochromated Cu K α radiation, λ =1.54178Å. The data were collected using the SMART³ program, integrated and corrected for decay, Lorentz

and polarization effects using SAINT³ and absorption corrections applied using the multi-scan technique (SADABS).³ The structures were solved by a combination of direct methods and the difference Fourier technique and refined by full-matrix least squares on F² using the SHELX³ suite of programs. Non-hydrogen atoms were refined with anisotropic displacement parameters. HNO₃ crystallizes in the lattice and hydrogen bonds with the NO₃⁻ anion in both the red and yellow forms of 1•NO₃•HNO₃. H63 bound to O6 of the HNO₃ was located directly from the difference map for the two forms, and in the case of the red form the H63 coordinate was refined. Attempts to refine the H63 coordinate of the yellow form resulted in a long O-H distance (~1.2 Å) so its position was held fixed at an O-H distance of 0.98Å (the refined distance of the red form). This bond lengthening may also be indicative of H-atom delocalization between the two oxygen atoms. The H-atom positions for all cations were calculated and treated with a riding model. The isotropic displacement parameters for all H-atoms were defined as a^*U_{eq} of the adjacent atom, (a=1.5 for HNO₃ and 1.2 for all others). The refinement converged with crystallographic agreement factors summarized in Table S2. Selected bond distances and angles for both polymorphs are listed in Table S3. For convenience, the molecular structures and extended stacking diagrams are included here (Figs. S7-S10) as well as in the manuscript (Figs. 2-3).

After the initial data collection, the yellow crystal was removed from the diffractometer but remained mounted in the loop and left undisturbed for ~1 day at room temperature. During this time the color of the crystal turned red. An additional data collection was performed using the same instrument, temperature, and radiation. The refinement revealed the same structure as the yellow polymorph, however the diffraction quality deteriorates. The results confirm that the transformation is non-reversible and the second color change is only a surface effect. The pertinent crystal data for this second determination is a follows: triclinic, a = 9.0891(4) Å, b = 9.7536(4) Å, c = 10.3973(4) Å, α = 68.648(2)°, β = 84.766(2)°, γ = 89.802(2)°, U = 854.45(6) Å³, space group P-1 (no. 2), T = 150K, Z = 2, ρ_{calcd} = 2.289 Mg/m³, 4006 reflections measured, 2411 independent (Rint = 0.0467) which were used in all calculations, data completeness to 66.76° in θ = 79.5%. The final refinement converged to R₁ = 0.0713 and wR2 = 0.1724 for I>2\sigma(I) and R₁ = 0.0822 and wR2 = 0.1796 for all data, max. and min. residual electron density = 3.414 and -4.023 eA⁻³.

Crystals of the red polymorph undergo single crystal→single crystal transformation to the yellow polymorph; the transformations are verified by unit cell determinations and/or partial data collections on the same crystal before and after a visible color change. It is worth noting that in instances, the considerable deterioration of the diffraction quality makes a complete single crystal determination problematic.



Fig. S1. ¹HNMR of **1**•NO₃•HNO₃ recorded in DMSO-d₆ (*solvent peaks). Numbers indicate integration values. a) ¹HNMR for the red crystals b) ¹HNMR for the yellow crystals

Table S1. Comparison of nitrate band vibrations of nitric acid with **1**•NO₃•HNO₃ using IR spectroscopy

Pure Nitric Acid (cm ⁻¹)	1•NO ₃ •HNO ₃ (cm ⁻¹)
1308-1324	1320
1330-1420	1330; 1420
1708-1646	1650
3550-3060	3400



Fig. S2. Mass spectra (negative ion mode) of 1•NO₃•HNO₃



Fig. S3. Photographs of a representative crystal of the red polymorph of $1 \cdot NO_3 \cdot HNO_3$ subjected to mechanical stimulation (pricked by a needle) to form the yellow polymorph, and the surface effect shown by the yellow polymorph over time, monitored using an optical microscope. Beginning with the top left: A red crystal of $1 \cdot NO_3 \cdot HNO_3$ before pressure was applied. After pressure was applied using a needle, the crystal turned yellow. The yellow crystal was monitored over time (beginning after 3 days and continuing for 45 days), during which the crystal surface turned red. Magnification 50xs.

	Red Form	Yellow Form	
Formula	[C ₁₅ H ₁₁ N ₃ CIPt]NO ₃ •HNO ₃		
Formula wt	588.84		
Temperature, K	150(2)		
Wavelength, Å	1.54	1.54178	
Crystal system	Triclinic	Triclinic	
Space group	P-1	P-1	
a, Å	6.5658(2)	9.0638(1)	
b, Å	10.3732(3)	9.7744(1)	
c, Å	13.0650(4)	10.3917(1)	
α, °	77.632(2)	68.652(1)	
β, °	86.382(2)	84.693(1)	
γ, °	89.238(2)	89.760(1)	
Volume, Å ³	867.45(5)	853.36(2)	
Z	2	2	
$ ho_{calcd}, Mg/m^3$	2.254	2.292	
Crystal size, mm ³	0.37 x 0.05 x 0.01	0.20 x 0.07 x 0.01	
θ range for data collection, °	3.470 to 67.698	4.590 to 67.621	
Refins collected/Indep. Refins	7170 / 2962	7075 / 2905	
R _{int}	0.0311	0.0383	
Max./min. transmission	0.753 and 0.515	0.753 and 0.466	
Absorption correction method		Multi-scan	
Refinement method	Full-matrix least-squares on F ²		
Data/restraints/parameters	2962 / 0 / 256	2905 / 0 / 253	
Goodness-of-fit (S) on F ²	1.04	1.05	
R, wR2 [I>2σ(I)]	0.0333, 0.0871	0.0320, 0.0795	
R, wR2 [all data]	0.0353, 0.0887	0.0349, 0.0811	
Max./min. residual density, eÅ-3	2.572 / -1.610	2.177 / -1.154	

Table S2. Crystal data for red and yellow forms of 1•NO₃•HNO₃

 $\overline{R} = \sum \|F_o\| - |F_c\| / \sum |F_o\|, \ wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table S3. Selected bond distances (Å) and angles (°) in the crystal structures of both polymorphs.

	Red Form	Yellow Form
Pt-N1	2.033(5)	2.034(5)
Pt-N2	1.943(5)	1.953(5)
Pt-N3	2.015(5)	2.033(5)
Pt-Cl1	2.3144(14)	2.3045(13)
N1-Pt-N2	80.2(2)	81.1(2)
N1-Pt-N3	161.9(2)	162.0(2)
N2-Pt-N3	81.1(2)	80.95(19)
N2-Pt-Cl1	179.19(15)	178.70(13)
N4-O1	1.226(8)	1.209(8)
N4-O2	1.233(7)	1.221(8)
N4-O3	1.275(8)	1.332(7)
N5-O4	1.219(9)	1.224(7)
N5-O5	1.209(8)	1.233(7)
N5-O6	1.338(8)	1.313(7)
Intra	amolecular H-bor	ding
O6-H63	0.98(11)	0.98
H63•••O3	1.57(11)	1.58
06•••03	2.540(7)	2.477(7)
O6-H63•••O3	166(10)	150
Intermolecular PtPt Stacking Interactions:		
Pt•••Pt ₁	3.2845(4) ^a	3.3111(4) ^c
Pt•••Pt ₂	3.3705(4) ^b	7.3955(4) ^d
Pt•••Pt ₃		7.9940(4) ^e
Pt ₁ •••Pt•••Pt ₂	161.22(1)	109.68(1)
Pt ₁ •••Pt•••Pt ₃		112.98(1)

a -x, -y+1, -z+1 b -x+1, -y+1, -z+1 c-x, -y, -z+1 d-x+1, -y, -z+1 e-x, -y+1, -z+1



Fig. S4. Molecular structure of the red form of $1 \cdot NO_3 \cdot HNO_3$ (50% probability ellipsoids, H-bonding interaction shown as a dashed line). (Inset) Crystal used in the data collection.



Fig. S5. Extended stacking diagram of the red form of $1 \cdot NO_3 \cdot HNO_3$ (top) viewed down the c-axis showing close intermolecular Pt $\cdot \cdot Pt$ distances (Å) and (bottom) down the a-axis showing the H-bonding interactions of the nitrate counterion with the HNO_3 solvate.



Fig. S6. Molecular structure of the yellow form of $1 \cdot NO_3 \cdot HNO_3$ (50% probability ellipsoids, H-bonding interaction shown as a dashed line). (inset) Crystal used in the data collection.



Fig. S7. Extended stacking diagram of the yellow form viewed down the c-axis showing close intermolecular Pt•••Pt distances (Å).



Fig. S8. Emission spectra of bulk $1 \cdot NO_3 \cdot HNO_3$ excited at 442 nm; red form (-) and yellow form (-).

Section S4. Calculations for the red \rightarrow yellow structure transformation.

In order to understand how the red polymorph of 1•NO₃•HNO₃ is transformed into the yellow polymorph, we converted the yellow form's triclinic unit cell parameters into a non-standard setting that was double in size of the original unit cell with retention of the original c-axis and modified aand b-axes. In the calculations, the converted unit cell parameters were designated with a prime symbol. The b' axis is parallel to what is defined as the stacking axis; in the structure of the red form, the stacking axis is along *a*. The transformed *a*' and *b*' axes lie along the *ab*-face diagonals of the original cell. Thus, the a' and b' cell edges and γ' angle were determined from the law of cosines. Taking the cell origin as the Cartesian origin and placing the a' and b' cell edge vectors in the xy-plane, α' and β were calculated from the dot products, **b'**•**c'** and **a'**•**c'**, respectively. The original fractional coordinates (x,y,z) were converted to fractional coordinates for the new cell (x',y',z') using the relation (x-y)/2(x+y)/2z. The missing fractional coordinates arising from doubling the cell size were generated from inversion symmetry in the original unit cell at $(\frac{1}{2}, 0, 0)$ $\frac{1}{2}$). This gives the fractional coordinates for the new cell (x',y',z') using the relation ((1-x+y)/2,(1-x-y)/2,1-z). Thus, in the converted cell, there are two molecules in the asymmetric unit related by a pseudo-inversion center. This is most easily seen by viewing the structures along the stacking axis and visualizing the reverse process, namely conversion from the yellow form to the red form. It is evident that slippage of adjacent pairs of sheets containing dimers in the yellow form relative to one another by a'/2 (=6.65 Å) produces a packing arrangement somewhat similar to that in the red polymorph. Other slippage directions are possible, but these involve motion of considerably greater distances (>11 Å). The result is that, without any additional adjustment (other than slipping), the Pt(tpy)Cl⁺ complexes stack in a headto-tail arrangement forming a chain of alternating 3.31 and 3.88 Å Pt-Pt distances and a Pt-Pt-Pt angle of 136.3°. Thus, the greatest molecular motion in the red-to-yellow conversion can be viewed as the reverse process, namely slippage of pairs of sheets in the red from by c/2 (6.53 Å).

The atomic positions in each structure were mapped onto one another to determine the minimal rearrangement necessary to convert the red [Pt(tpy)Cl]NO₃.HNO₃ polymorph to the slipped form of the yellow polymorph. The pertinent mapping data are as follows:

δa' (Å)	0.23
%δV (%)	1.62
$\rho(xy)_{max}$	0.05
ρ(z)	0.007

The structures were aligned to have parallel stacking axes, labeled as the Cartesian zaxis. In each structure, the columns of Pt(tpy)Cl⁺ complexes were taken as defining structural elements with the centers of the columns defined as the average x,y coordinates of the Pt atoms. For both structures, the columns formed a two-dimensional oblique lattice unit cell. Thus, the agreement between these two structures was assessed by comparing the two-dimensional oblique lattices, as well as the stacking along z. This was accomplished by overlaying one Pt(tpy)Cl⁺ column in the red crystal form with one column in the slipped yellow structure, thereby defining the Cartesian z-axis for the superposition of the two structures. The alignment of the structures was optimized by rotation of one structure by the angle ω about this axis so as to minimize the sum of the squares of the distances between the nearest neighbor 54 Pt complexes. The value of $|\omega|$ for 1•NO₃•HNO₃ was small (0.31°), indicating that the two-dimensional lattices were already aligned. However, it is important to emphasize that the magnitude of ω is not meaningful in the sense of providing information about the extent of structural rearrangement required to convert the red to the slipped yellow from. Values of ω varied only slightly depending on the selected neighboring columns for optimization.

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