

Cracking Down on Vapochromic Salts: Unveiling Vapomechanical Stress in Gas-Sorbing Platinum Complexes

Amie E. Norton^{b,c*} Stephen D. Taylor^{c, d*} Caroline Williams,^a Ann Zoller,^a Watts Dietrich,^a
William B. Connick,^{a, e} and Sayandev Chatterjee^{e*}

^aDepartment of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, United States

^bDepartment of Entomology, Kansas State University, Manhattan, KS 66506, United States

^cAuthors contributed equally to the work

^dThe Laboratory Safety Institute, Natick, MA 01760, United States

^eTerraPower LLC, Bellevue, WA 98008

[€]This work is dedicated to the memory of Prof. William B Connick who passed away on April 22, 2018.

*Corresponding authors' email: amien@ksu.edu; stephen@labsafetyinstitution.org;
schatterjee@terrapower.com

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Figure SI 1. Microscope slide of microcrystals (left) Luminescence of crystals before exposure to acetonitrile (right) Luminescence of crystals after exposure to acetonitrile and desolvated



Figure SI 2. Pictures of crystals after 5 cycles of solvated and desolvated. The same crystals that were used in the emission experiment

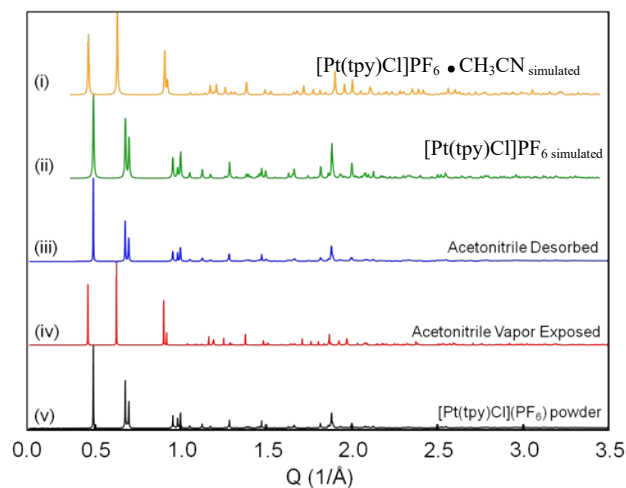


Figure SI 3. X-ray powder diffractograms of $[\text{Pt}(\text{tpy})\text{Cl}](\text{PF}_6)$ under different conditions. Simulated powder diffraction patterns for and $[\text{Pt}(\text{tpy})\text{Cl}](\text{PF}_6)\cdot\text{CH}_3\text{CN}$ (i, orange) and $[\text{Pt}(\text{tpy})\text{Cl}](\text{PF}_6)$ at 298K (ii, green).

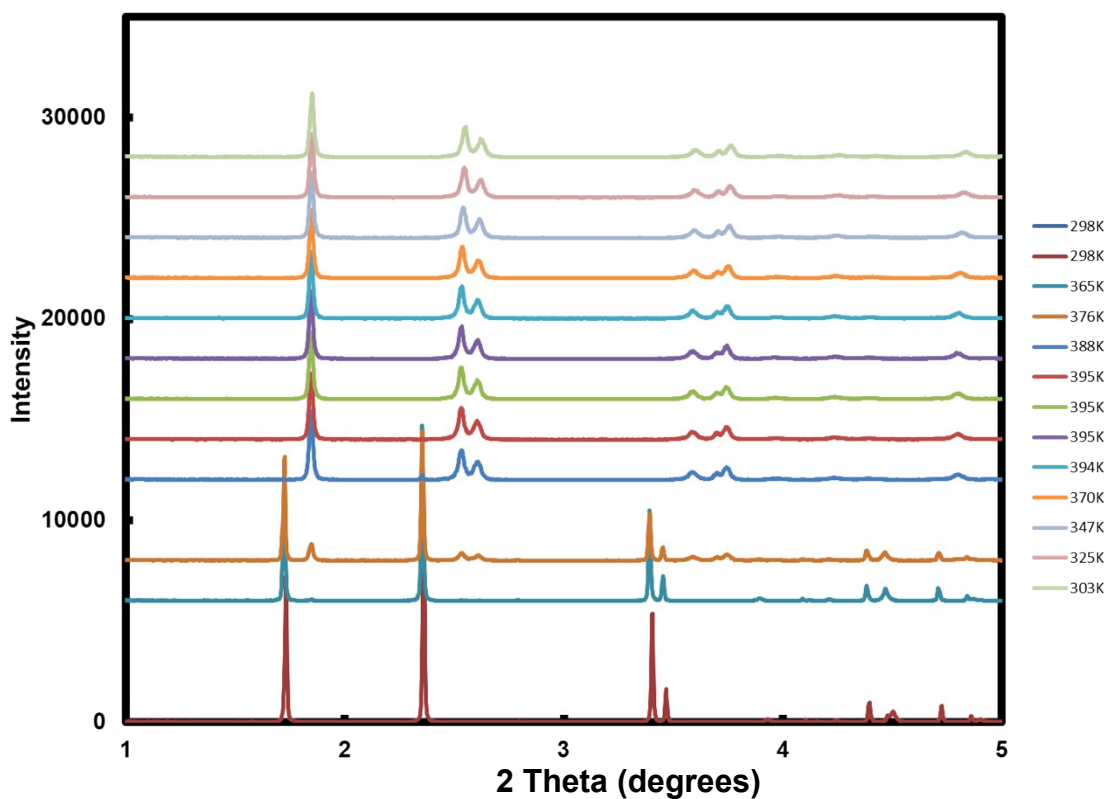
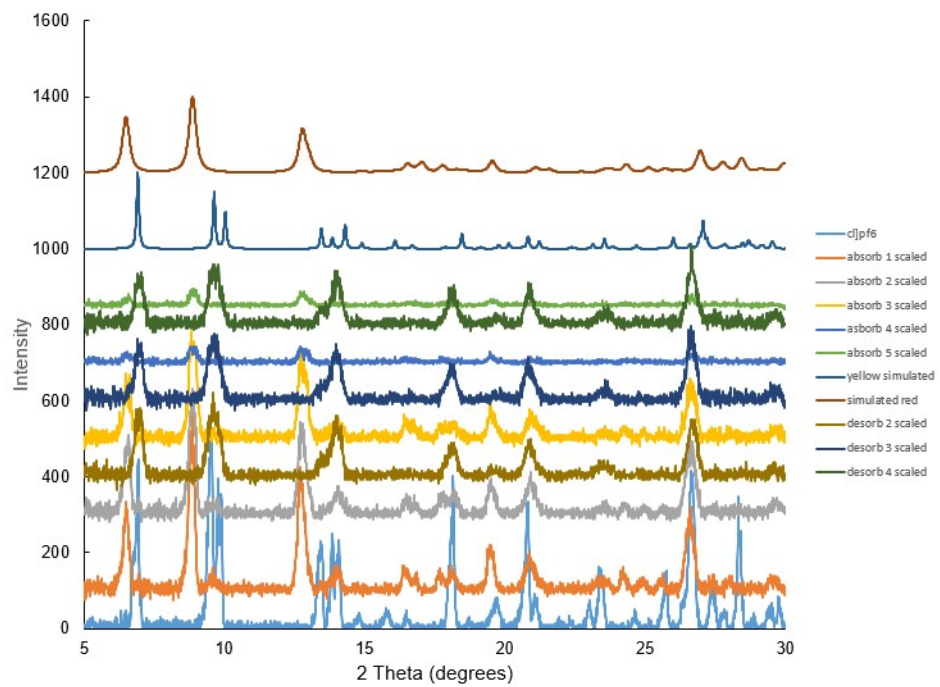
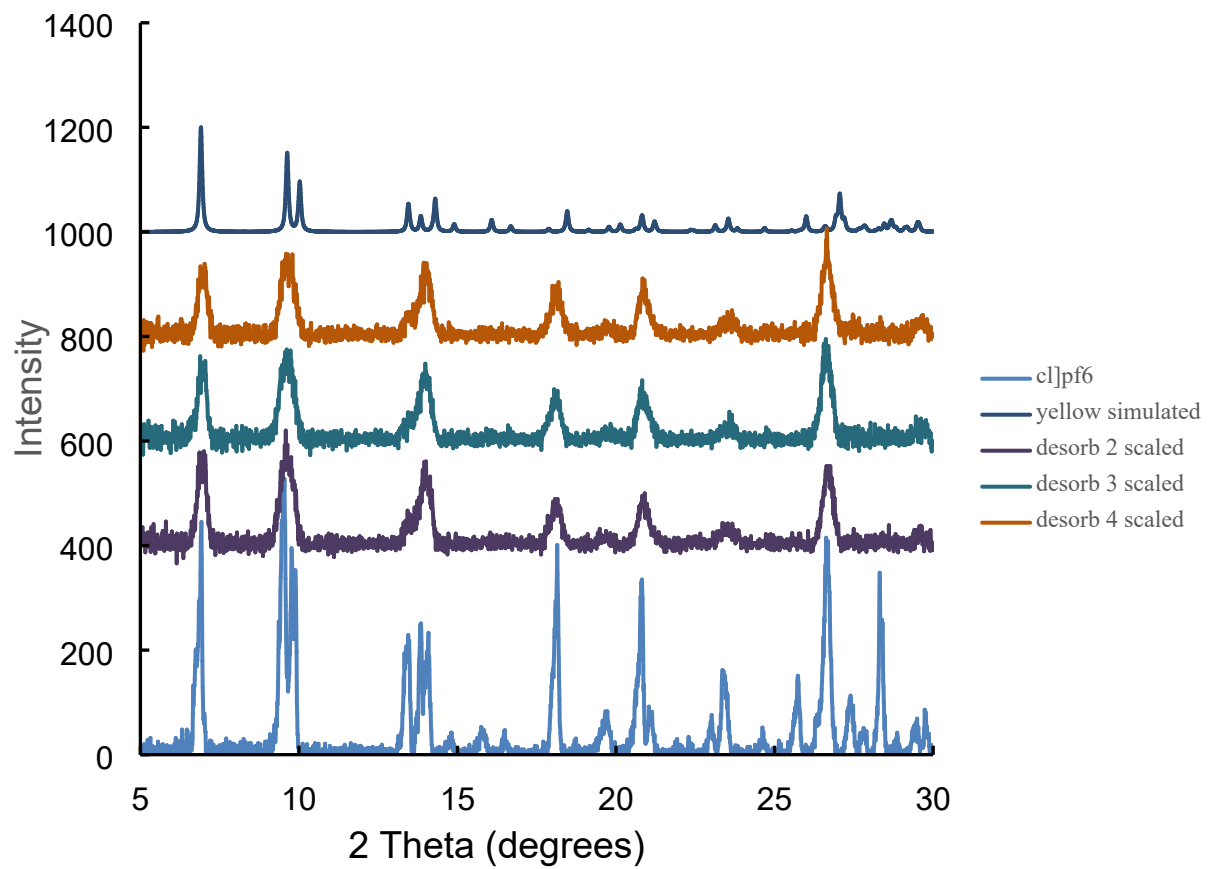


Figure SI 4: XRPD pattern of $[\text{Pt}(\text{tpy})\text{Cl}]\text{PF}_6\cdot\text{CH}_3\text{CN}$ as it is being heated.

a)



b)



c)

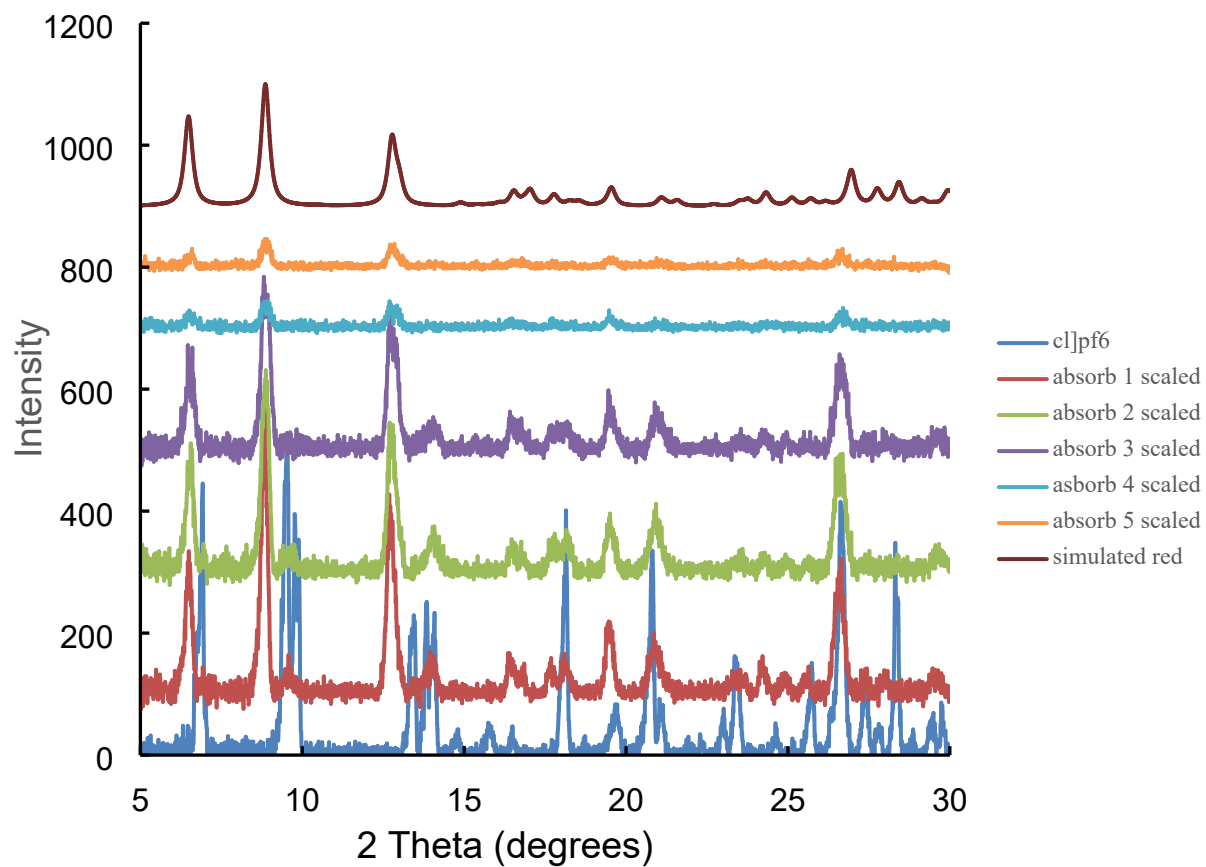


Figure SI 5. XRPD diffractograms of $[\text{Pt}(\text{tpy})\text{Cl}](\text{PF}_6)$ cycled a) all the cycles together b) only the desorbed “yellow” forms together c) the absorbed “red” forms together

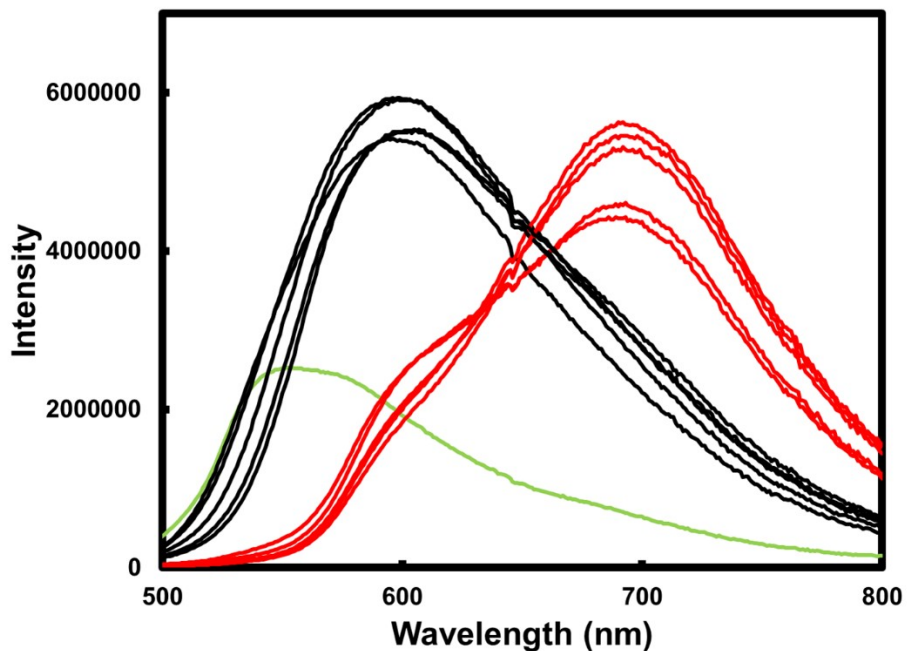


Figure SI 6. Emission spectra of crystals of $[\text{Pt}(\text{tpy})\text{Cl}](\text{PF}_6)$ before (—, (green)) and during vapor absorption (—, (red)) / vapor desorption (—, (black)) cycling.

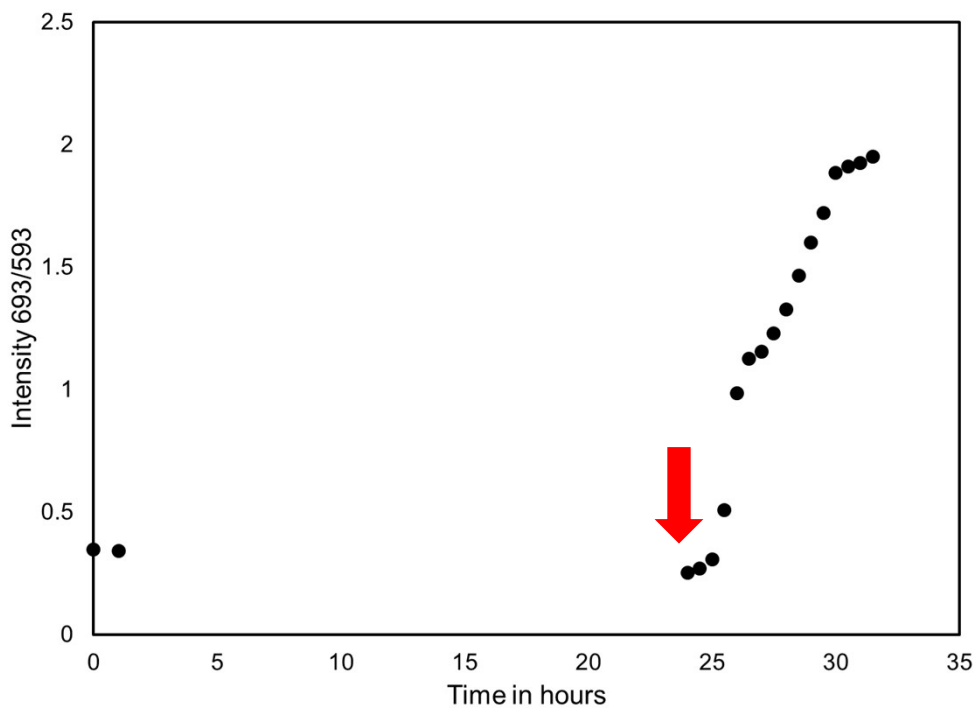


Figure SI 7. Intensity at 693nm divided by intensity at 593 nm. The red arrow depicts the point at which the sample was heated during desorption.

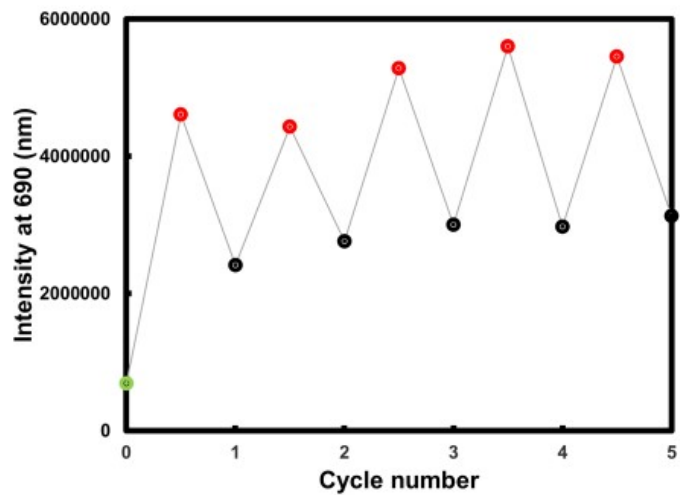


Figure SI 8. Intensity at 690 nm vs cycle number for crystals of [Pt(tpy)Cl](PF₆) (●, green), as well as the acetonitrile vapor-desorbed (●, black) and vapor-absorbed (●, red) forms vs. cycle number.

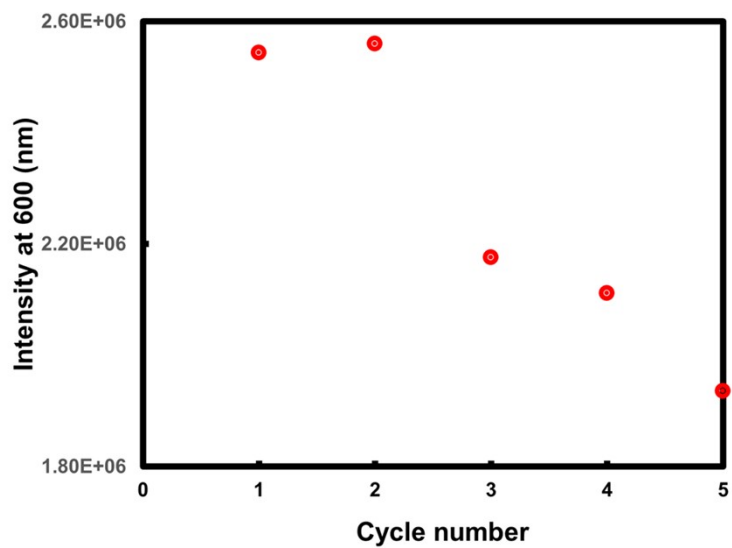


Figure SI 9. Solvated intensity at 600 nm vs cycle number

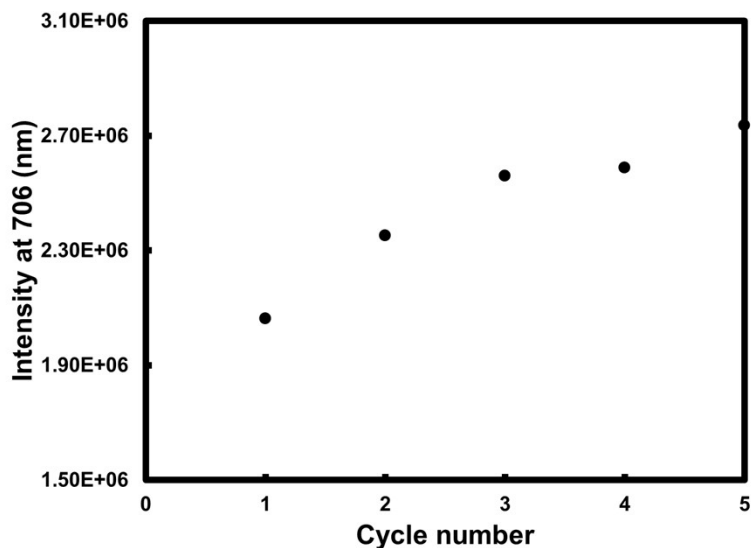


Figure SI 10. Intensity at 706 nm vs cycle number

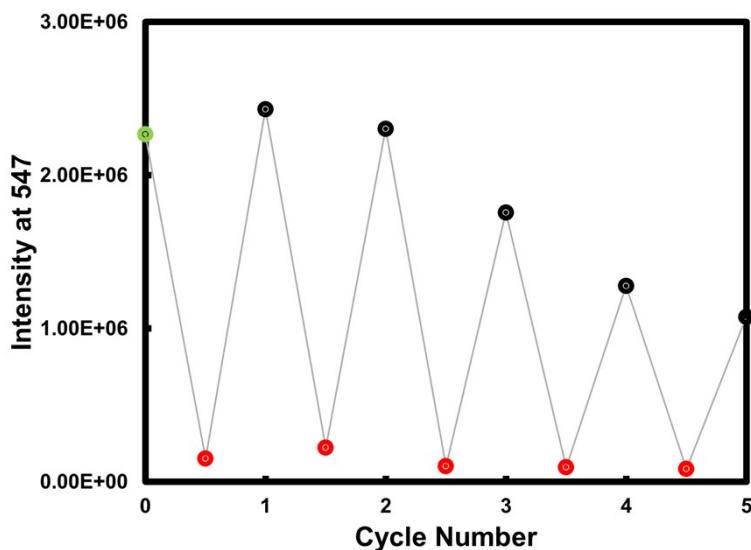


Figure SI 11. Intensity at 690 nm, Intensity at 600 nm for solvated form, Intensity at 706 nm for non-solvated form and Intensity at 547 nm required to complete vapor absorption vs. cycle number for crystals of [Pt(tpy)Cl](PF₆) (●, green), as well as the acetonitrile vapor-desorbed (●, black) and vapor-absorbed (●, red) forms vs. cycle number.

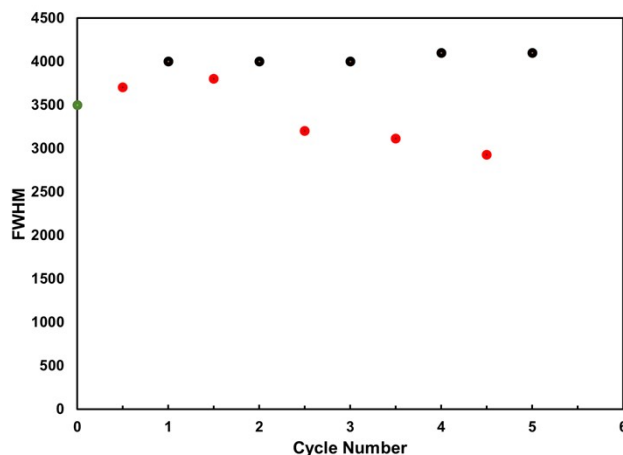


Figure SI 12. FWHM of desorption (black) and absorption (red). The original spectrum FWHM is in green.

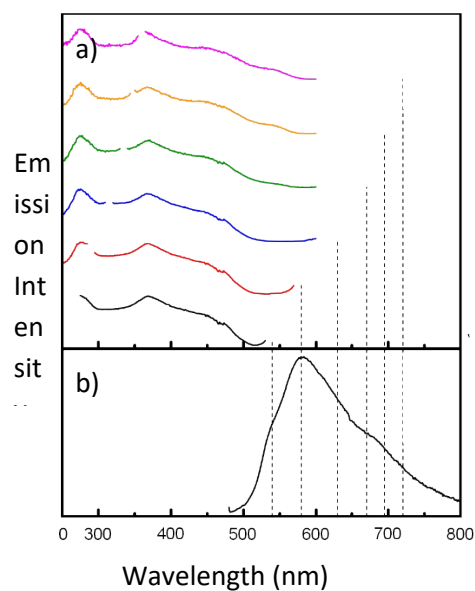


Figure SI 13. a) Excitation spectra of $[\text{Pt}(\text{tpy})\text{Cl}](\text{PF}_6)$ crystals at different monitored emission wavelengths (—, $\lambda_{\text{em}} = 540$ nm; — (red), 580 nm; —, (blue) 630 nm; —, (green) 670 nm; —, (orange) 695 nm; —, (pink) 720 nm. b) Emission spectrum of **1** crystal (—, $\lambda_{\text{ex}} = 436$ nm). Dashed lines indicate monitored emission wavelengths for each excitation spectra in a). The emission intensities were arbitrarily scaled.

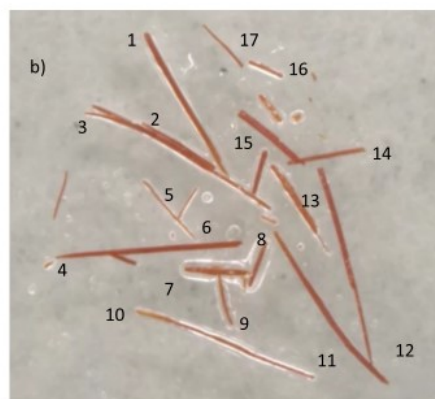
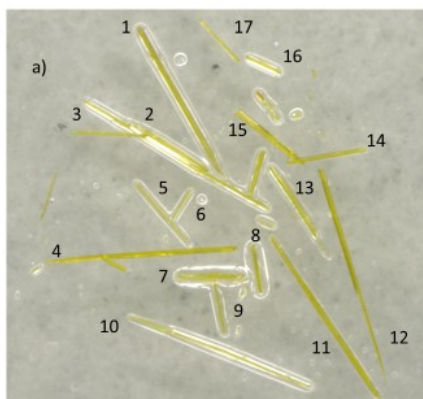


Figure SI 14. Picture of 17 crystals that were absorbed with acetonitrile. A) before absorption. B) after absorption

SI Table 1. The motions of seventeen crystals of [Pt(tpy)Cl](PF)₆ in paratone oil when exposed to acetonitrile vapor.

Crystal Number	size l x w (mm)	First Appearance of color	Movement
1	1.5x0.2	Needle tip	none
2	0.5x.1	edge	spins and splits at top
3	0.45x.05	edge	rotates 15° and translates by ~0.125 mm
4	1x0.05	edge	none
5	0.375 x0.1	Needle tip	curls
7	0.375x.1	Needle tip	rotates 3° clockwise
8	0.3x0.1	Needle tip	rotates about needle axis
9	0.1x0.001	Needle edge	bends 5°
10	0.55x0.15	Needle edge	curls
11	1.125x0.15	Needle edge	bends 25°
12	1.125x0.15	Needle edge	Crystal bends 25°
13	0.25x0.1	Needle edge	none
14	0.75x0.05	Needle edge	none
15	1x0.1	middle	Rotated 17.6°
16	0.15x0.01	Needle edge	none
17	0.25x0.01	Needle edge	none

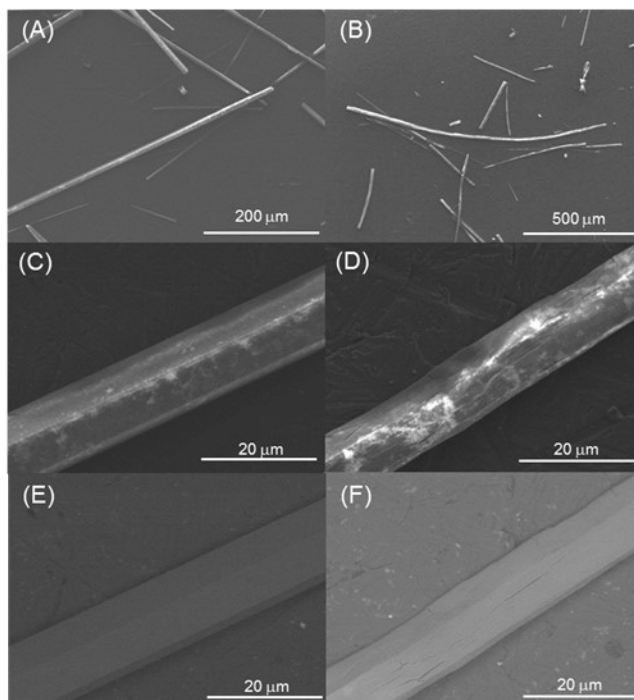


Figure SI 15. SEM images (A, B, C and D) and BSE images (E and F) of $[\text{Pt}(\text{tpy})\text{Cl}](\text{PF}_6)$ before (Left column) and after (Right column) exposure to acetonitrile.

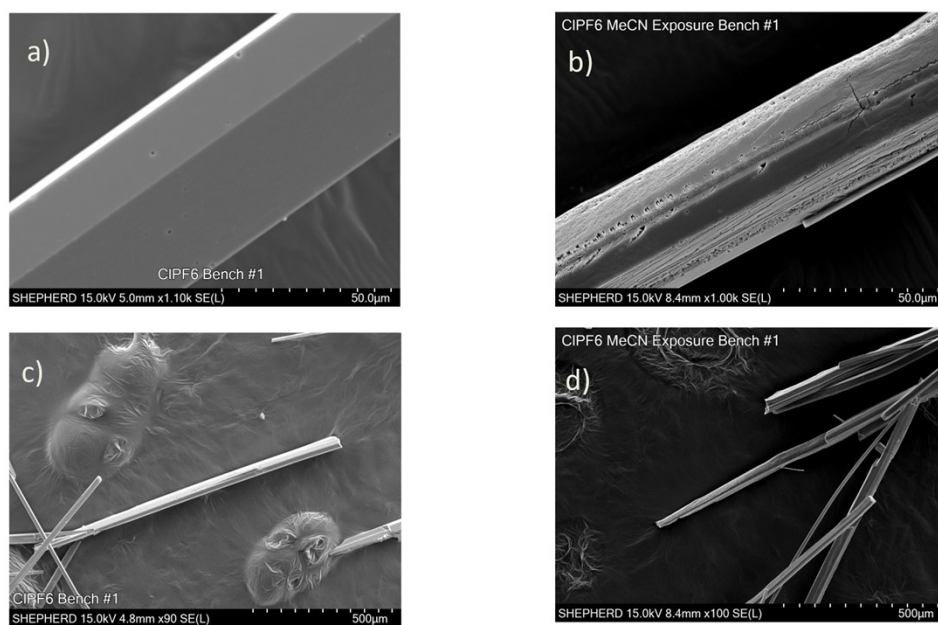


Figure SI 16. SEM images of crystals grown at 20°C before (a,c) acetonitrile and after acetonitrile.