Electronic Supporting Information for

Heteroleptic Platinum(II) Isocyanide Complexes: Convenient Synthetic Access, Polymorphs, and Vapoluminescence

Daron E. Janzen[a] and Kent R. Mann[b]

[a] St. Catherine University, Department of Chemistry and Biochemistry, 2004 Randolph Avenue, St. Paul, MN, USA.
[b] University of Minnesota, Twin Cities, Department of Chemistry, 207 Pleasant St. SE, Minneapolis, MN, USA.

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Table S1. X-ray Crystallographic Data Collection and Refinement for (TBA)[$Pt(CN)_3(CNCH_3)$] (**1**), colorless (TBA)[$Pt(CN)_3(CN$-*c*-$C_6H_{11})$] (**2-c**), orange (TBA)[$Pt(CN)_3(CN$-*c*-$C_6H_{11})$] (**2-o**), (TBA)[$Pt(CN)_3(CN$-*p*-(C_2H_5)-$C_6H_4)$] (**3**)

Compound	**1**	**2-c**	**2-o**	**3**
formula	$C_{21}H_{39}N_5Pt$	$C_{26}H_{47}N_5Pt$	$C_{26}H_{47}N_5Pt$	$C_{28}H_{45}N_5Pt$
habit, color	block, colorless	block, colorless	block, orange	rod, yellow
size, mm	0.36 x 0.23 x 0.17	0.25 x 0.24 x 0.12	0.28 x 0.12 x 0.08	0.50 x 0.10 x 0.10
lattice type	tetragonal	monoclinic	triclinic	monoclinic
space group	$P4_12_12$	$P2_1/c$	P1-	$P2_1/n$
a, Å	14.0744(6)	13.8830(11)	9.737(7)	9.1124(6)
b, Å	14.0744(6)	12.4658(10)	12.790(10)	18.6090(13)
c, Å	12.4525(11)	17.7056(15)	13.612(10)	18.2156(14)
α, deg	90	90	105.497(12)	90
β, deg	90	108.6250(10)	105.990(12)	104.4760(10)
γ, deg	90	90	109.101(12)	90
V, $Å^3$	2466.7(3)	2903.7(4)	1415.7(18)	2990.8(4)
Z	4	4	2	4
formula wt, g mol^{-1}	556.66	624.78	624.78	646.78
D_c, g cm^{-3}	1.499	1.429	1.466	1.436
Temperature	173(2)	223(2)	173(2)	173(2)
μ, mm^{-1}	5.702	4.853	4.976	4.714
F (000)	1112	1264	632	1304
θ range, deg	2.05 to 25.03	1.55 to 27.53	1.69 to 25.17	1.59 to 25.05
index ranges	$-16 \le h \le 16$, $-16 \le k \le 16$, $-9 \le l \le 14$	$-18 \le h \le 15$, $-15 \le k \le 16$, $-21 \le l \le 23$	$-11 \le h \le 10$, $-15 \le k \le 14$, $0 \le l \le 16$	$-10 \le h \le 10$, $-22 \le k \le 22$, $-20 \le l \le 21$
reflns collected	13264	23652	25251	25310
unique reflns	2183	6647	5037	5290
weighting factors,[a] a,b	0.0133, 0.0000	0.0177, 0.0000	0.1425, 0.0000	0.0409, 6.2765
max, min transmission	1.000, 0.695	1.000, 0.804	0.67, 0.216	1.000, 0.680
data/restraints/parameters	2183 / 0 / 127	6647 / 0 / 289	5037 / 3 / 260	5290 / 5 / 314
R_1, wR_2 ($I > 2\sigma(I)$)	0.0190, 0.0412	0.0284, 0.0609	0.0873, 0.2000	0.0391, 0.0843
R_1, wR_2 (all data)	0.0220, 0.0420	0.0435, 0.0641	0.1111, 0.2108	0.0524, 0.0888
goodness-of-fit	1.033	0.916	1.017	1.075
largest diff peak, hole, e $Å^{-3}$	0.269, -0.592	0.586, -1.636	5.855, -5.654	0.640, -2.190

[a] $w = [\sigma^2(F_o^2) + (aP)^2 + (bP)]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$.

Table S2. Bond Lengths (Å) and Angles (Deg) Summary for (TBA)[$Pt(CN)_3(CNCH_3)$] (**1**), (TBA)[$Pt(CN)_3$(CN-*c*-C_6H_{11})] (**2-c**), (TBA)[$Pt(CN)_3$(CN-*c*-C_6H_{11})] (**2-o**), (TBA)[$Pt(CN)_3$(CN-*p*-(C_2H_5)-C_6H_4)] (**3**)

Compound	**1**	**2-c**	**2-o**	**3**
Pt(1)-C(1)	1.974(5)	1.946(4)	1.945(16)	1.947(6)
Pt(1)-C(2)	1.994(4)	1.998(4)	1.972(17)	1.995(7)
Pt(1)-C(3)	1.979(5)	1.976(4)	1.983(17)	1.988(6)
Pt(1)-C(4)	na	1.998(4)	1.975(17)	2.005(7)
C(1)-N(1)	1.144(6)	1.143(5)	1.153(19)	1.147(7)
C(2)-N(2)	1.153(5)	1.131(4)	1.131(19)	1.141(8)
C(3)-N(3)	1.147(5)	1.153(5)	1.113(19)	1.140(8)
C(4)-N(4)	na	1.150(4)	1.141(19)	1.128(8)
N(1)-C(5)	na	1.454(5)	1.443(19)	1.412(7)
N(1)-C(4)	1.437(6)	na	na	na
C(1)-Pt(1)-C(2)	92.28(11)	89.65(15)	89.9(6)	91.1(2)
C(1)-Pt(1)-C(3)	180.0	175.81(4)	177.6(6)	179.2(2)
C(1)-Pt(1)-C(4)	na	92.28(15)	91.8(6)	90.5(2)
C(2)-Pt(1)-C(3)	87.72(11)	87.39(16)	91.5(6)	89.6(2)
C(2)-Pt(1)-C(4)	na	177.50(14)	177.7(6)	178.3(2)
C(3)-Pt(1)-C(4)	na	90.60(16)	86.9(6)	88.8(2)
Pt(1)-C(1)-N(1)	180.0(4)	174.9(3)	176.1(13)	178.4(5)
Pt(1)-C(2)-N(2)	176.1(4)	178.0(4)	177.1(13)	179.7(7)
Pt(1)-C(3)-N(3)	180.0(4)	175.3(4)	176.2(14)	179.6(6)
Pt(1)-C(4)-N(4)	na	177.9(3)	177.8(15)	178.1(7)
C(1)-N(1)-C(5)	na	170.9(4)	175.5(14)	178.1(6)
C(1)-N(1)-C(4)	180.0(4)	na	na	na

na = not applicable

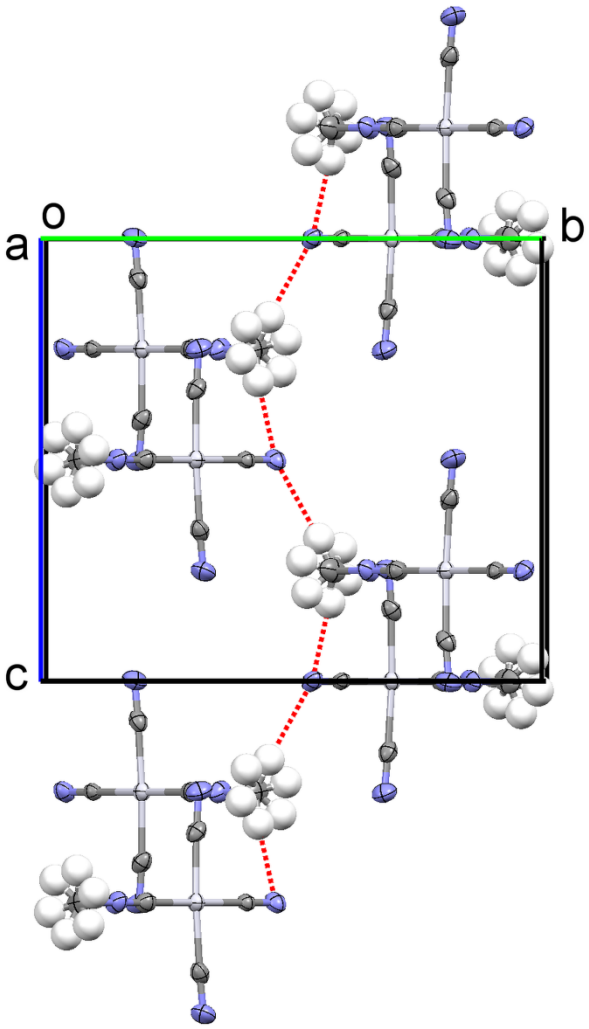

Fig. S1. Intermolecular Interactions in the Structure of **1**. Two positions of the methyl hydrogens are shown as a 2-fold axis is coincident with the C2-N1-C1-Pt1-C4-N3 vector.

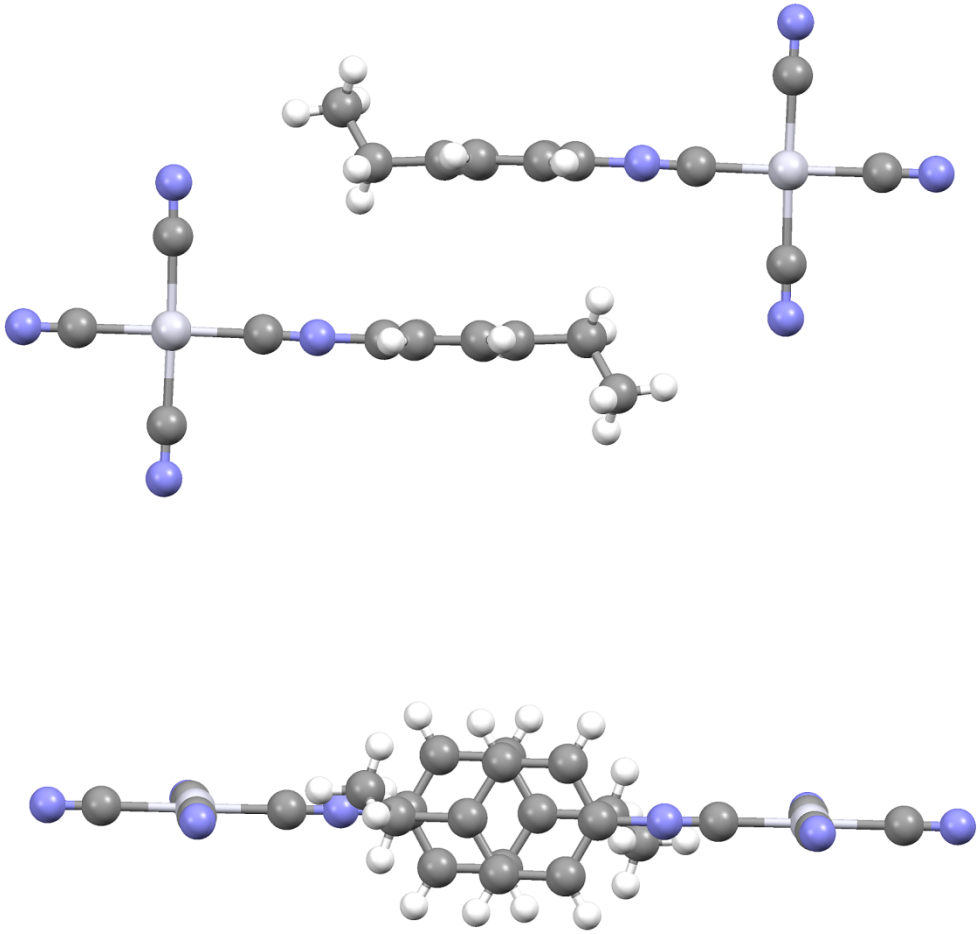

Fig. S2. Intermolecular Interactions in the Structure of **3**. π-π stacking view perpendicular to dimer stacking interaction vector (above) and parallel view to dimer stacking interaction vector (below).

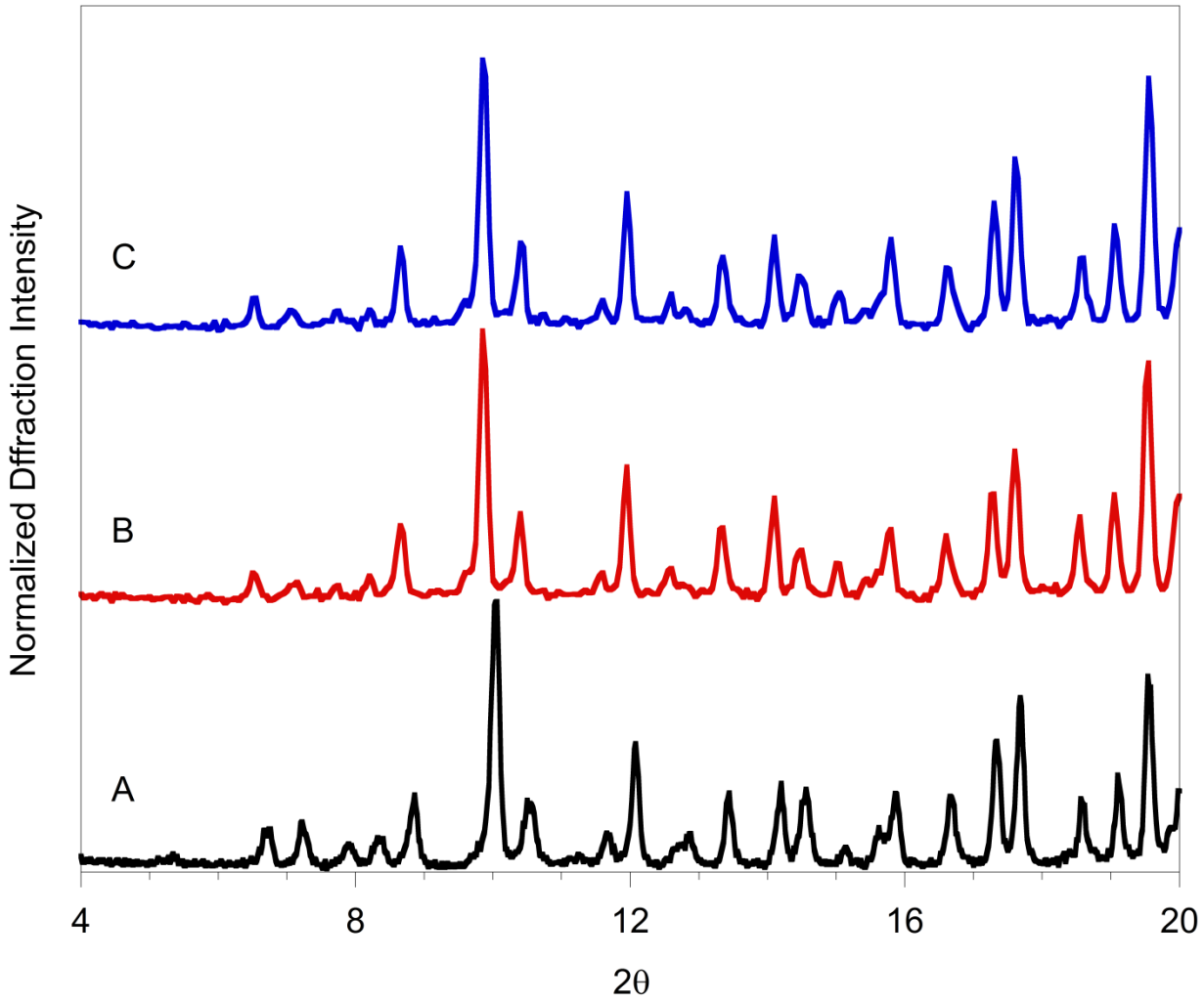

Fig. S3. Powder X-ray Diffraction of **2** at room temperature (20°C) (A, black), -150°C (B, red), and -190°C (C, blue)

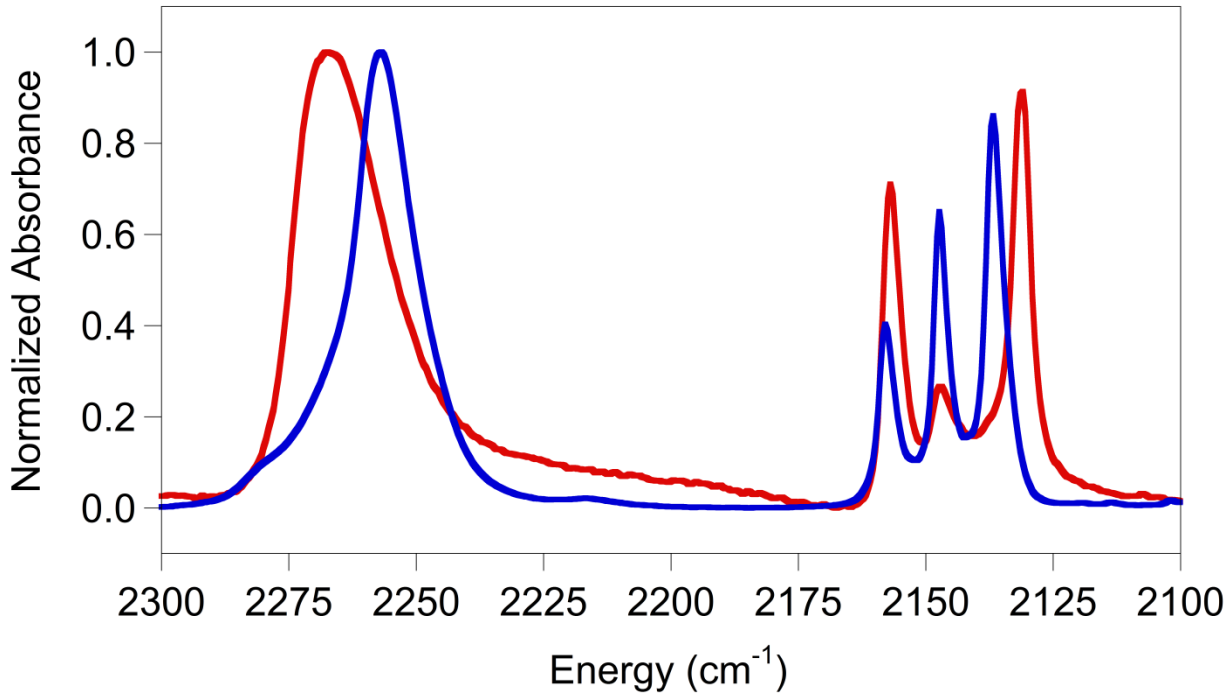

Fig. S4. Normalized ATR-IR Spectra of **1** (blue) and **4** (red).

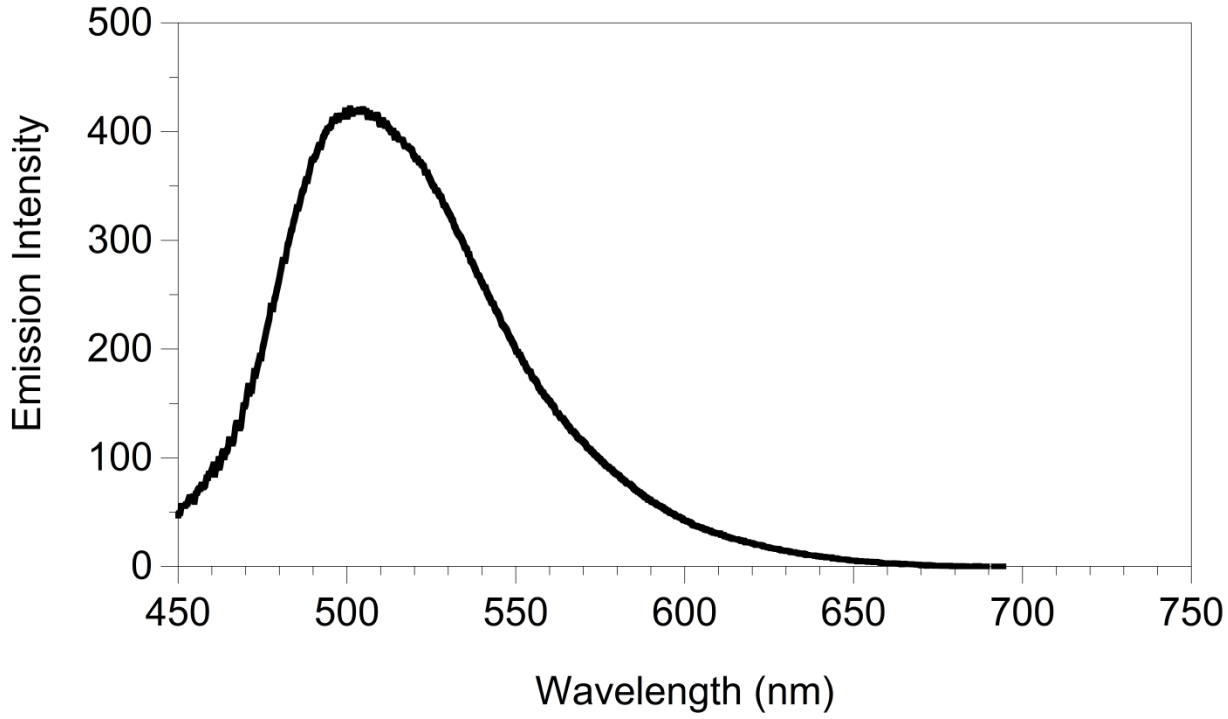

Fig. S5. Uncorrected Solid-state Emission Spectrum of a Film of **1**.

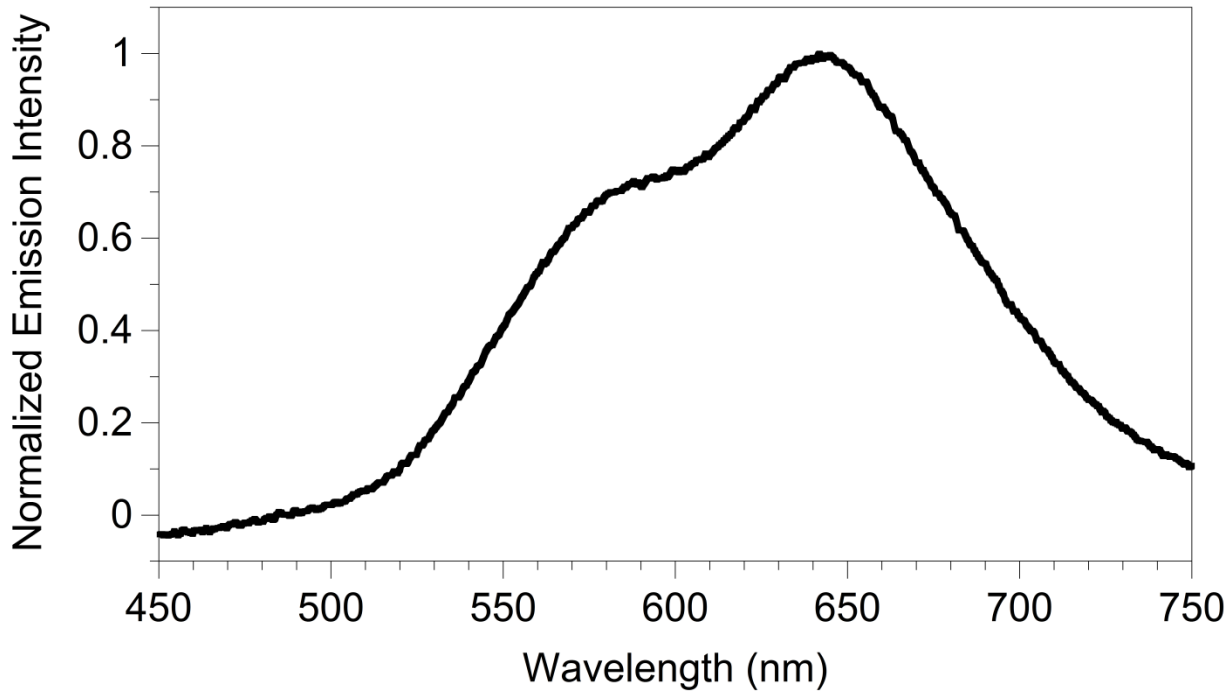

Fig. S6. Uncorrected Normalized Solid-state Emission Spectrum of Crystalline **3**

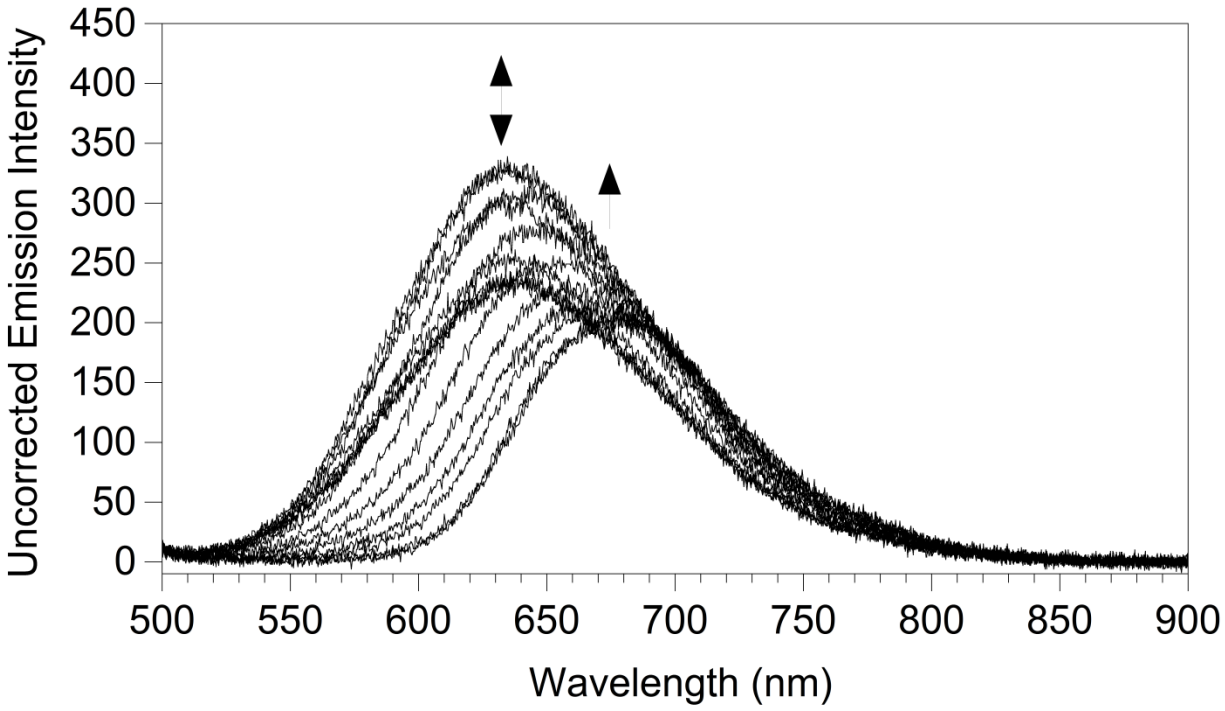

Fig. S7. Uncorrected Solid-state Emission Spectra of 4 Exposed to Water Vapor.

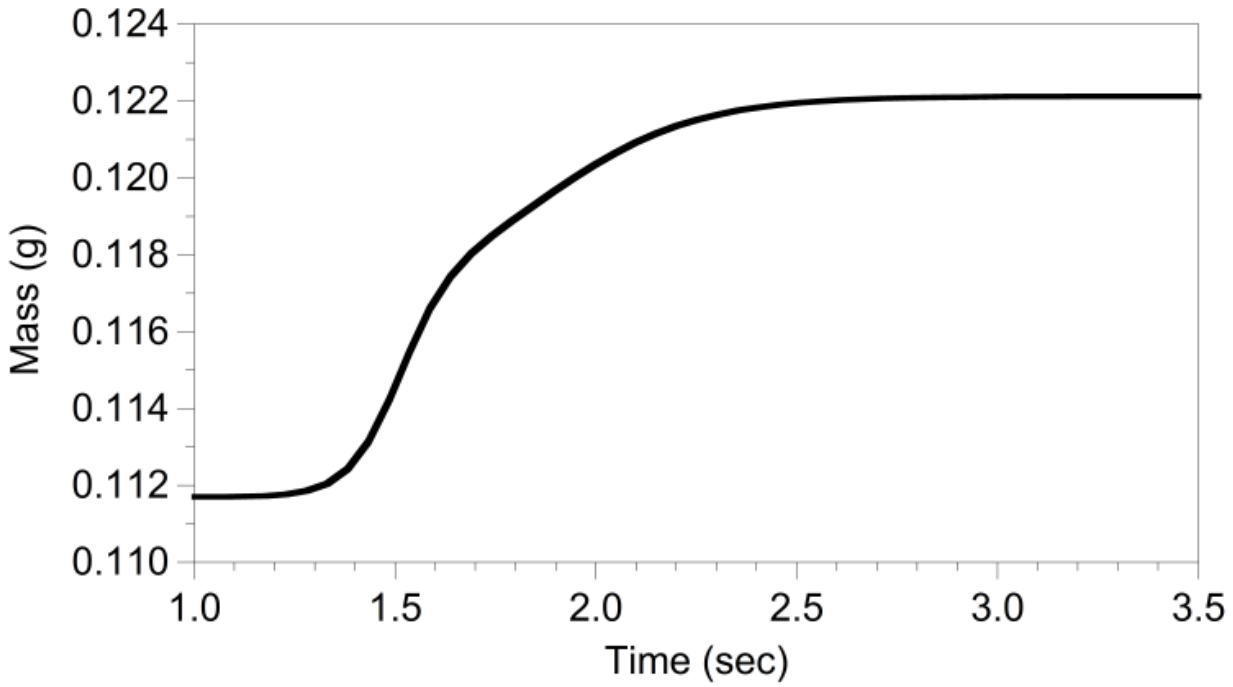

Fig. S8 Simulated mass pickup of **4** by water based on the concentration profiles calculated from PCA analysis.