Electronic Supplementary Information

Highly emissive polymorphs of anhydrous cadmium tetracyanoplatinate and their solvated coordination networks

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Table S1: Bond Distances in **1**.

	Distance (Å)
Pt(1)-C(1)	1.983(4)
Pt(1)-C(2)	1.978(4)
Pt(1)-Pt(1)	3.3324(4)
C(1)-N(1)	1.132(5)
C(2)-N(2)	1.142(5)
Cd(1)-N(1)	2.271(3)
Cd(1)-N(2)	2.240(4)
Cd(1)-O(1)	2.459(2)
O(1)-H(1)	0.82(4)
O(2)-H(2)	0.94(2)

Table S2: Bond Angles in **1**.

	Angle (°)
C(1)-Pt(1)-C(1)	176.5(2)
C(2)-Pt(1)-C(2)	177.7(2)
C(1)-Pt(1)-C(2)	89.966(4)
Pt(1)-C(1)-N(1)	178.1(4)
Pt(1)-C(2)-N(2)	178.5(4)
C(1)-N(1)-Cd(1)	148.1(3)
C(2)-N(2)-Cd(1)	178.2(4)
N(2)-Cd(1)-N(1)	92.58(6)
N(2)-Cd(1)-N(2)	171.10(19)
N(2)-Cd(1)-O(1)	86.51(8)
N(1)-Cd(1)-N(1)	109.08(19)
N(1)-Cd(1)-O(1)	87.22(11)
N(1)-Cd(1)-O(1)	163.70(12)
Cd(1)-O(1)-Cd(1)	103.52(14)
O(1)-Cd(1)-O(1)	76.48(14)

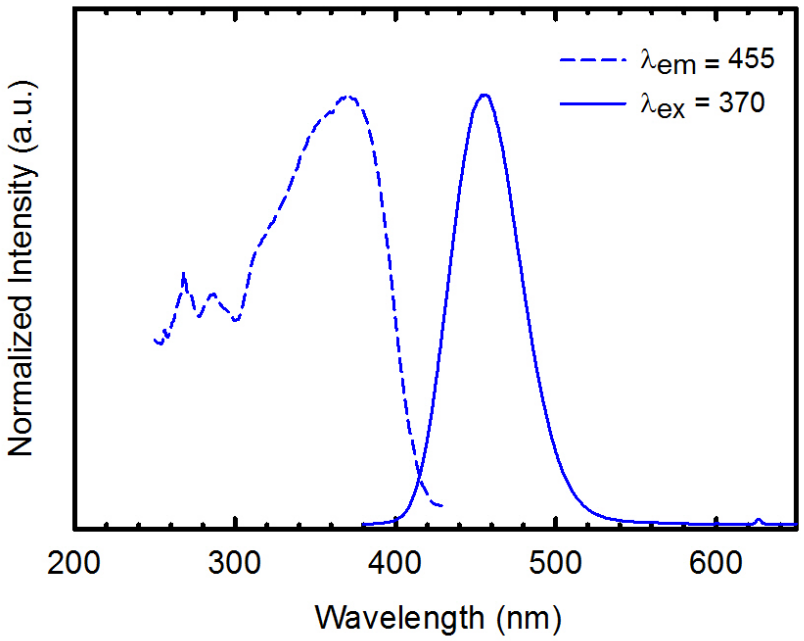

Figure S1: Emission and excitation of a solid sample of **1**.

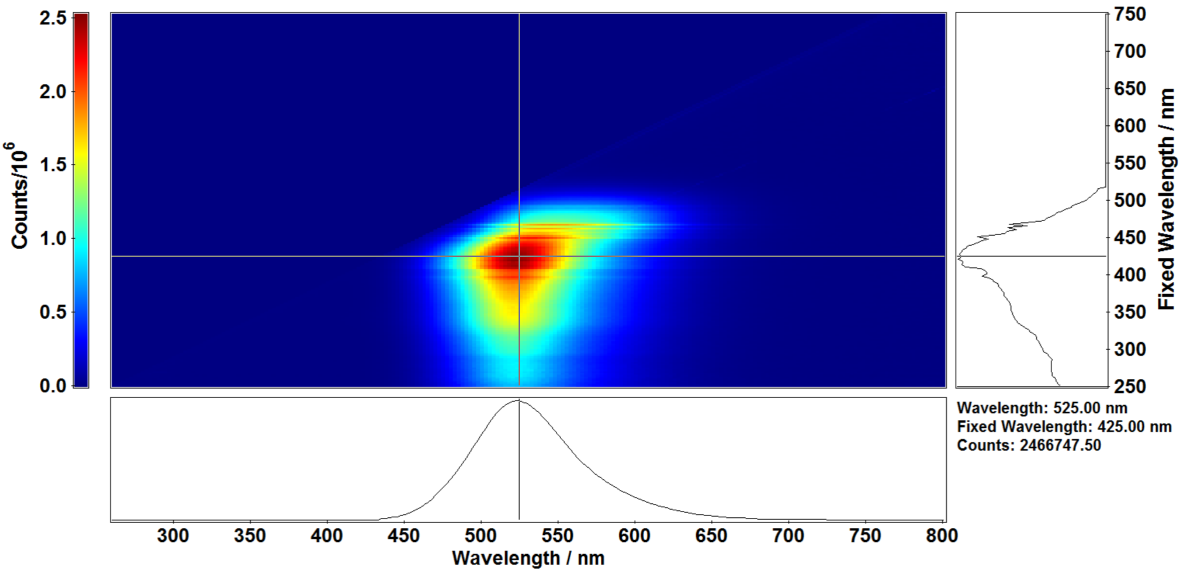

Figure S2: 2D excitation/emission map of a solid sample of **2**.

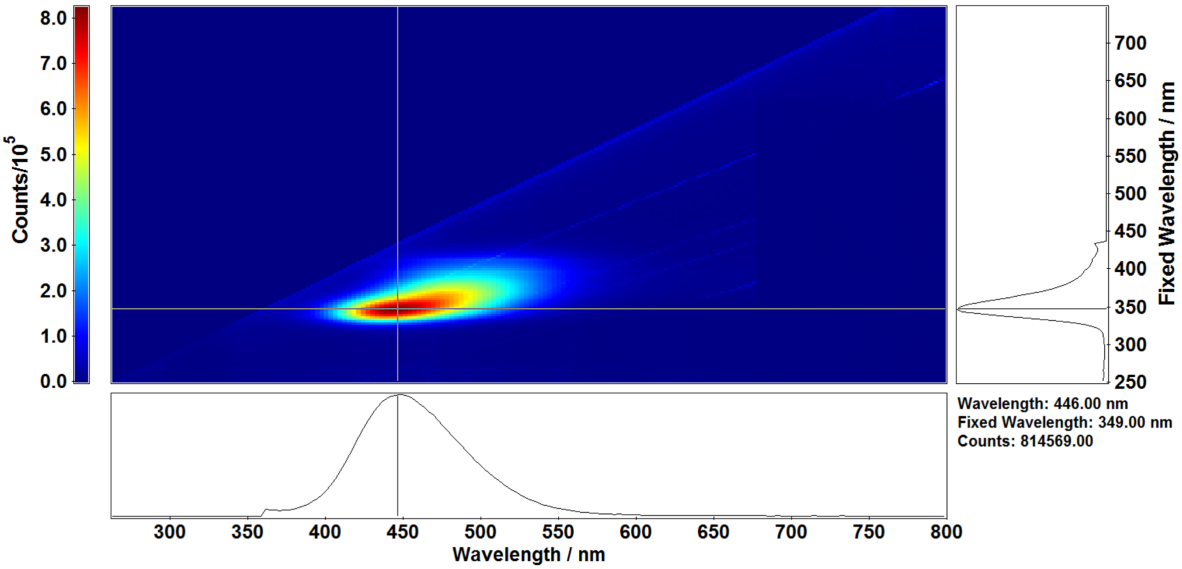

Figure S3: 2D excitation/emission map of a solid sample of **3**.

Table S3: Selected Interatomic Distances in **4**.

Bond	**Distance (Å)**
Pt(1)-C(1)	1.9808(13)
Pt(1)-C(2)	2.0024(15)
C(1)-N(1)	1.1498(18)
C(2)-N(2)	1.153(2)
Cd(1)-N(1)	2.2692(12)
Cd(1)-O(1)	2.3101(10)
Cd(1)-O(2)	2.2896(11)
S(1)-O(1)	1.5177(11)
S(2)-O(2)	1.5246(11)
S(1)-C(3)	1.777(2)
S(1)-C(4)	1.7796(19)
S(2)-C(6)	1.7818(16)
S(2)-C(5)	1.7836(17)

Table S4: Selected Bond Angles in **4**.

	Angle (°)
C(1)-Pt(1)-C(2)	89.55(6)
C(1)-Pt(1)-C(2)	90.45(6)
Pt(1)-C(1)-N(1)	179.55(14)
Pt(1)-C(2)-N(2)	178.84(14)
C(1)-N(1)-Cd(1)	158.44(12)
N(1)-Cd(1)-O(1)	85.95(5)
N(1)-Cd(1)-O(1)	94.05(5)
N(1)-Cd(1)-O(2)	89.97(4)
N(1)-Cd(1)-O(2)	90.03(4)
N(1)-Cd(1)-O(2)	89.14(5)
N(1)-Cd(1)-O(2)	90.86(5)
Cd(1)-O(1)-S(1)	120.26(6
Cd(1)-O(2)-S(2)	123.62(6)
O(1)-S(1)-C(3)	104.44(9)
O(1)-S(1)-C(4)	105.19(9)
C(3)-S(1)-C(4)	98.25(12)
O(2)-S(2)-C(5)	105.52(8)
O(2)-S(2)-C(6)	104.28(8)
C(5)-S(2)-C(6)	98.80(8)

Table S5: Crystallographic Information (PXRD) and xyz coordinates for **2** and **3**.

	2 (**α**)	**3** (**β**)
empirical formula	C_4CdN_4Pt	C_4CdN_4Pt
formula weight (g mol^{-1})	411.56	411.56
crystal system	triclinic	orthorhombic
space group	P-1	P222
a (Å)	5.9873(11)	7.1032(2)
b (Å)	7.3251(9)	6.7328(3)
c (Å)	7.4190(7)	3.87885(15)
α (deg)	99.240(9)	90
β (deg)	105.605(9)	90
γ (deg)	77.29(2)	90
V (Å^3)	303.92(8)	185.502(12)
Z	2	1
T (K)	299(2)	299(2)
ρ_{calcd} (g cm^{-3})	4.4973(11)	3.6841(2)
$2\theta_{min}/2\theta_{max}$ (deg.)	11.5/47	10/84
R_{exp}	0.947	1.134
R_p, wR_p	11.389/17.614	5.284/7.734
GOF	18.595	6.818

xyz coordinates for α-$Cd[Pt(CN)_4]$ (**2**)

Label	X	Y	Z	Symm. op.
Pt11	0.24	0.0132	-0.0158	x,y,z
Cd11	0	0.5	0.5	-x,1-y,1-z
Cd	0.5	0.5	0.5	1-x,1-y,1-z
C11	0.2534	0.2298	0.1863	x,y,z
C12	0.2866	-0.1627	0.1769	x,y,z
C13	0.2265	-0.2033	-0.2180	x,y,z
C14	0.1934	0.1892	-0.2084	x,y,z
N11	0.2611	0.3532	0.3016	x,y,z
N12	0.3131	-0.2630	0.2867	x,y,z
N13	0.2189	-0.3267	-0.3333	x,y,z
N14	0.1669	0.2895	-0.3187	x,y,z

xyz coordinates for β-$Cd[Pt(CN)_4]$ (**3**)

Label	X	Y	Z	Symm. op.
Cd11	0.5	0.5	0.5	1-x,1-y,z
Pt51	0	0	0	-x,-y,z
C11	0.2059	0.2026	0	x,y,z
N11	0.3233	0.3180	0	x,y,z

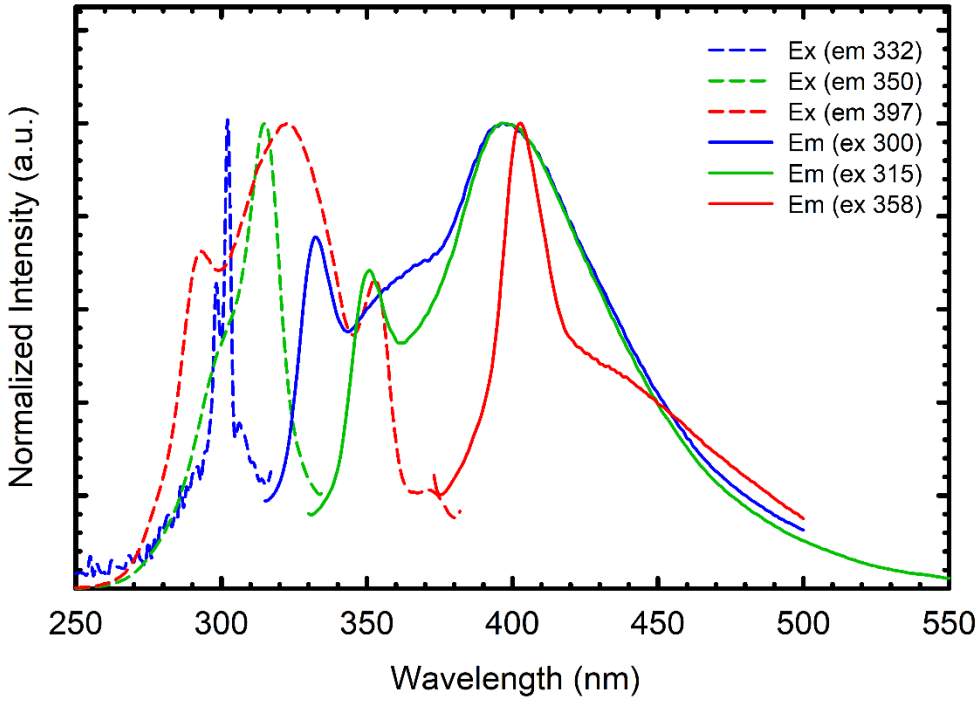

Figure S4: Emission and excitation of crystals of **4** suspended in DMSO solvent.

Table S6: Crystallographic Information (PXRD) and xyz coordinates for **5** and **6**.

	$Cd(H_2O)_2[Pt(CN)_4]\cdot 2DMSO$ (5)	**$Cd(C_5H_5N)_2[Pt(CN)_4]$ (6)**
empirical formula	C8H16N4CdO4PtS2	C14H10N6CdPt
formula weight (g mol^{-1})	603.86	569.76
crystal system	tetragonal	monoclinic
space group	P4/m	P2/m
a (Å)	7.6768(8)	8.5940(5)
b (Å)	7.6768(8)	7.7142(7)
c (Å)	7.8682(7)	7.7061(4)
α (deg)	90	90
β (deg)	90	63.348(5)
γ (deg)	90	90
V ($Å^3$)	463.70(7)	456.60(6)
Z	1	1
T (K)	299(2)	299(2)
ρ_{calcd} (g cm^{-3})	3.2057(5)	2.4139(3)
$2\theta_{min}/2\theta_{max}$ (deg.)	9.8/56.6	10/84
R_{exp}	1.091	1.394
R_p, wR_p	10.008, 13.630	7.452, 9.942
GOF	12.494	7.132

xyz coordinates for $Cd(DMSO)_2[Pt(CN)_4]\bullet 2H_2O$ (**5**)

Label	X	Y	Z	Symm. op.
Pt11	0.5	0.5	0.5	1-x,1-y,1-z
C11	0.6842	0.3158	0.5	x,y,1-z
N11	0.7892	0.2108	0.5	x,y,1-z
Cd11	1	0	0.5	2-x,-y,1-z
O11	1	0	0.2420	2-x,-y,z
S11	-0.0040	0.4016	0.0817	x,y,z

xyz coordinates for $Cd(pyridine)_2[Pt(CN)_4]$ (**6**)

Label	X	Y	Z	Symm. op.
Pt31	0	0.5	0.5	-x,1-y,1-z
C31	0.0022	0.3469	0.7067	x,y,z
N31	0.0034	0.2591	0.8251	x,y,z
Cd11	0	0	0	-x,-y,-z
N11	0.2734	0	-0.1368	x,-y,z
C11	0.3613	0.1497	-0.2045	x,y,z
C12	0.5371	0.1497	-0.2924	x,y,z
C13	0.6249	0	-0.3126	x,-y,z

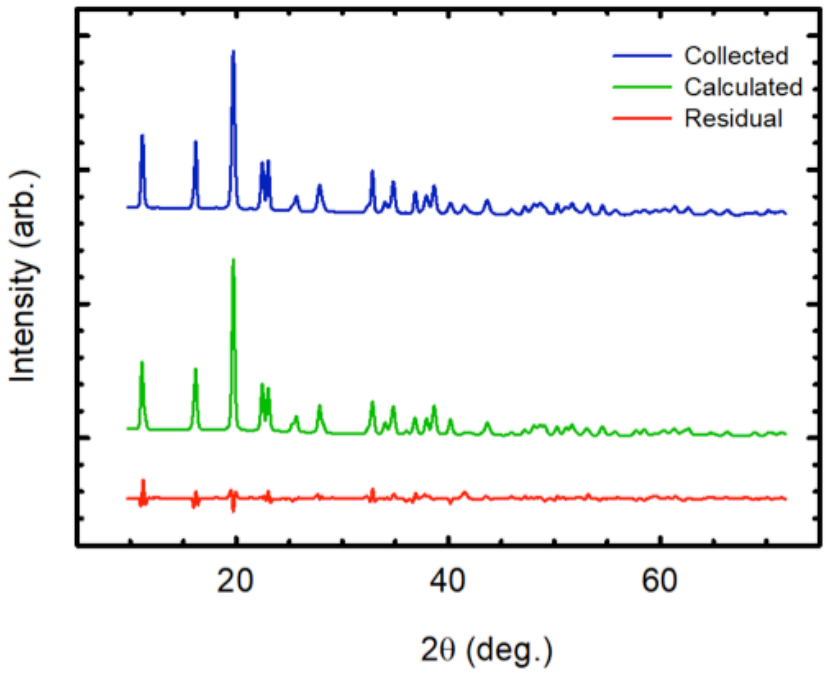

Figure S5: Collected, calculated and residual data for the PXRD solution of **5**.

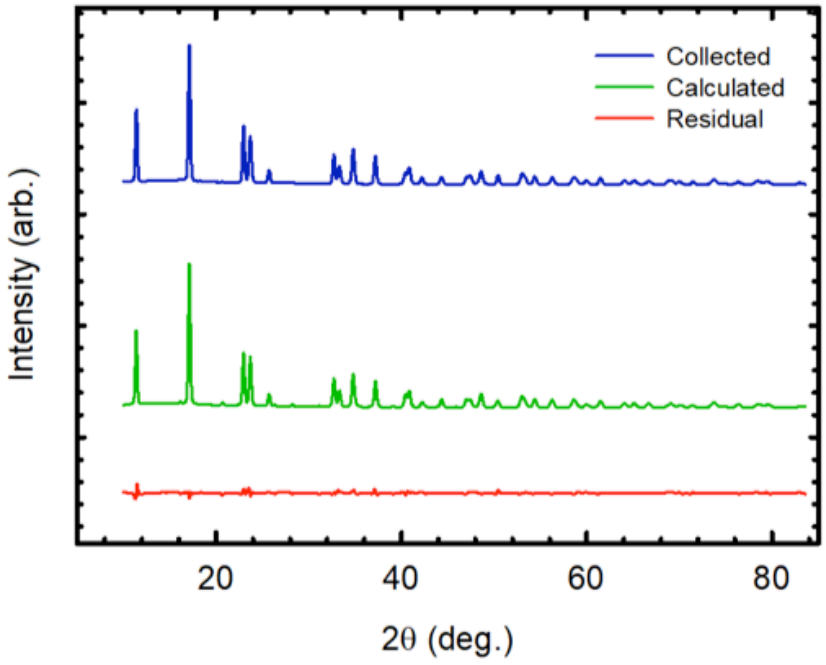

Figure S6: Collected, calculated and residual data for the PXRD solution of **6**.

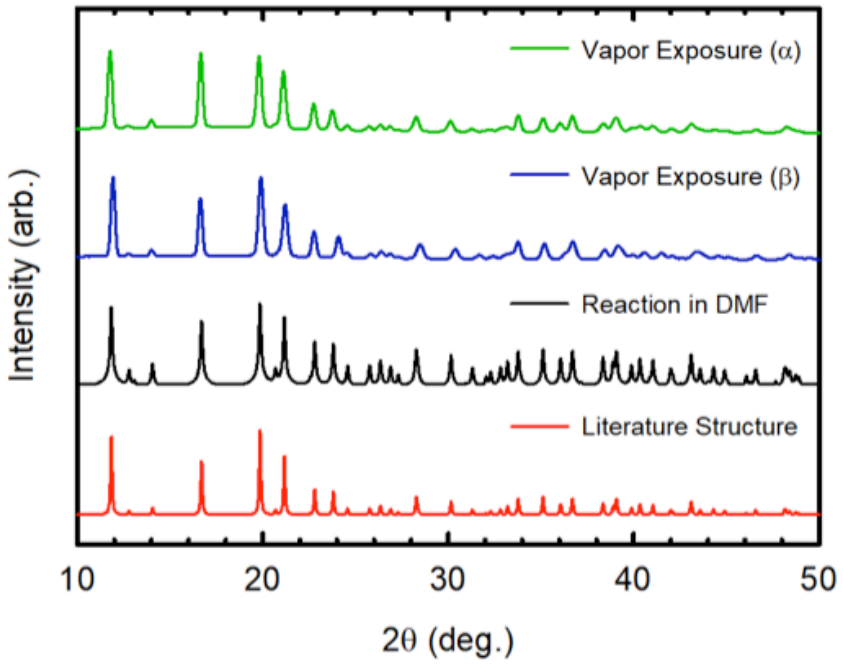

Figure S7: Powder X-ray Diffraction Patterns of **7**; vapor exposure of α (green) and β-$Cd[Pt(CN)_4]$ (blue) to DMF compared to the product isolated from reaction in DMF solution (black) and the literature crystal structure of $Cd(DMF)_2[Pt(CN)_4]$.[1]

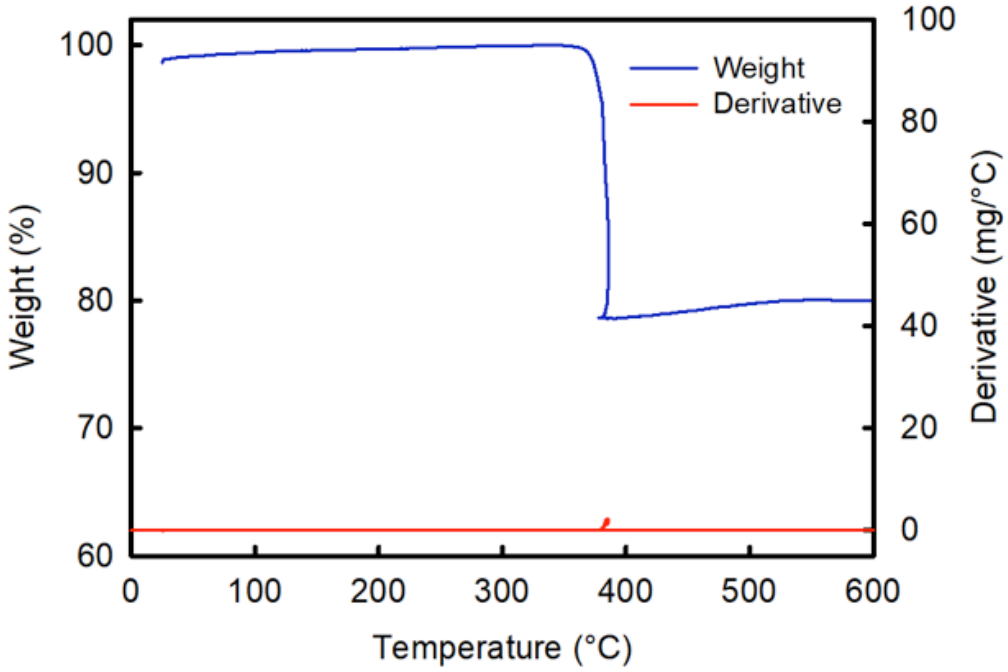

Figure S8: Thermogravimetric analysis of α-$Cd[Pt(CN)_4]$ (**2**).

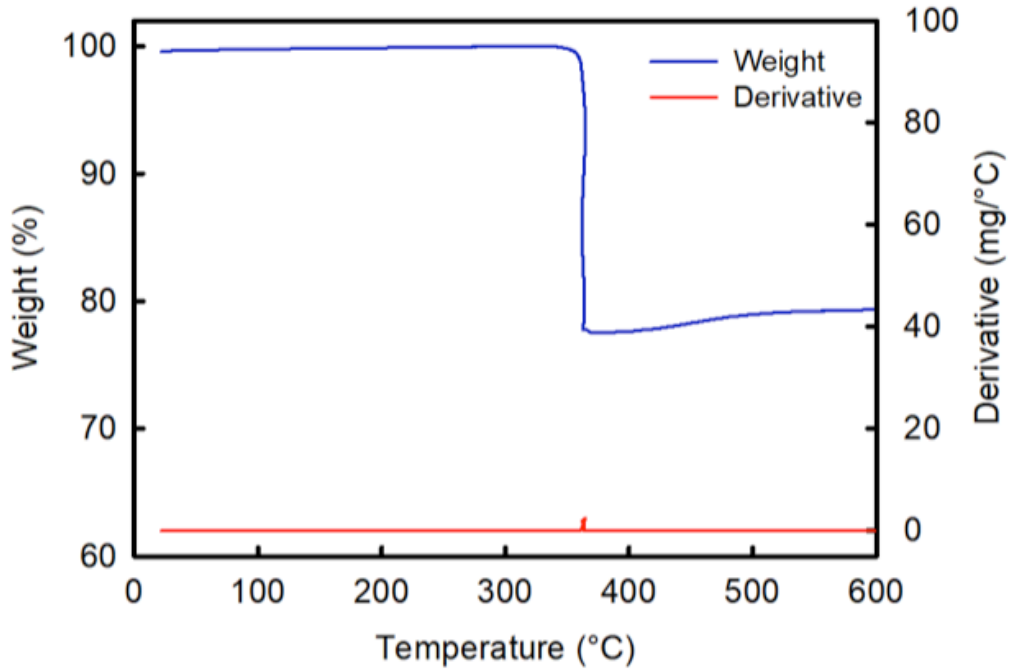

Figure S9: Thermogravimetric analysis of β-Cd[Pt(CN)$_4$] (**3**).

Table S7. Observed Raman frequencies for α-CdPt(CN)$_4$ and β-CdPt(CN)$_4$, determined from the spectra in Figure 5. Experimental values reported here are compared to results for $K_2Pt(CN)_4$ and theoretical frequencies, with assignments (D_{4h} point group labels). All values are given in wavenumber (cm^{-1}) units. Only frequencies above 100 cm^{-1} are given in the Table.

α-CdPt(CN)$_4$	β-CdPt(CN)$_4$	Calculated frequency[a]	Assignment[a]	KPt(CN)$_4$[b]
2220s	2221s	2168s	a_{1g}, υ_{CN}	2165s
2160s	2192s	2149s	b_{1g}, υ_{CN}	2143s
-	468vw	488vw	b_{2g}, π_{PtCN} in-plane	467m
		408vw	a_{1g}, υ_{PtC}	
		405vw	b_{1g}, υ_{PtC}	
330m, 340sh	333m	345m	e_g, π_{PtCN} out-of-plane	323m
196m	189m			173m
137m	145m	119m	b_{2g}, δ_{CPtC} in-plane	

a From Table 1 of ref 80, uncorrected frequencies given in this Table, correction does not change energy order
b ref 80, Figure S1 and Table S1
Intensities: s: strong, m: medium, vw: very weak, sh: shoulder

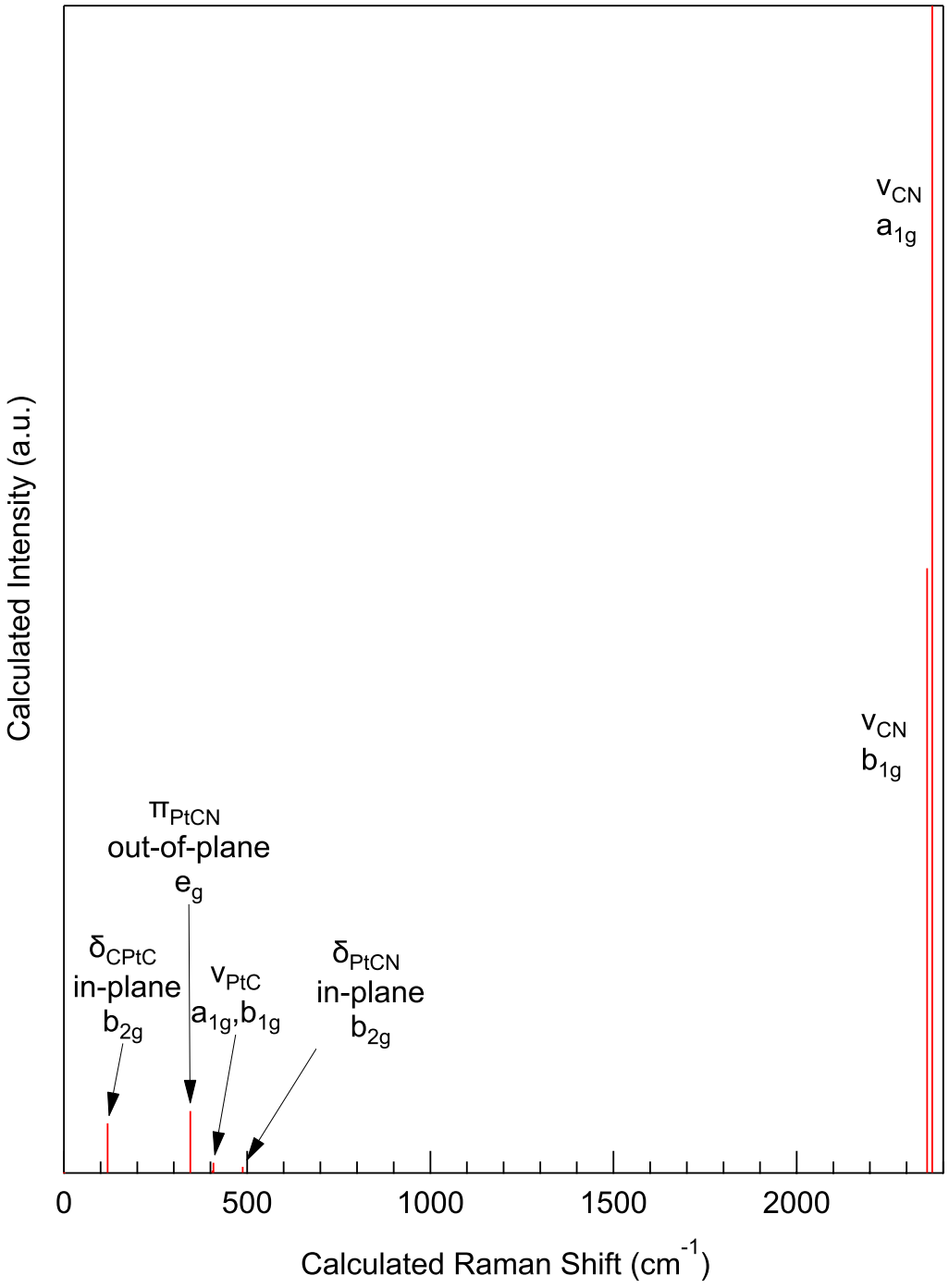

Figure S10. Calculated Raman shifts and intensities, values and assignments from Table 1 of ref. 80, as listed in Table S12.

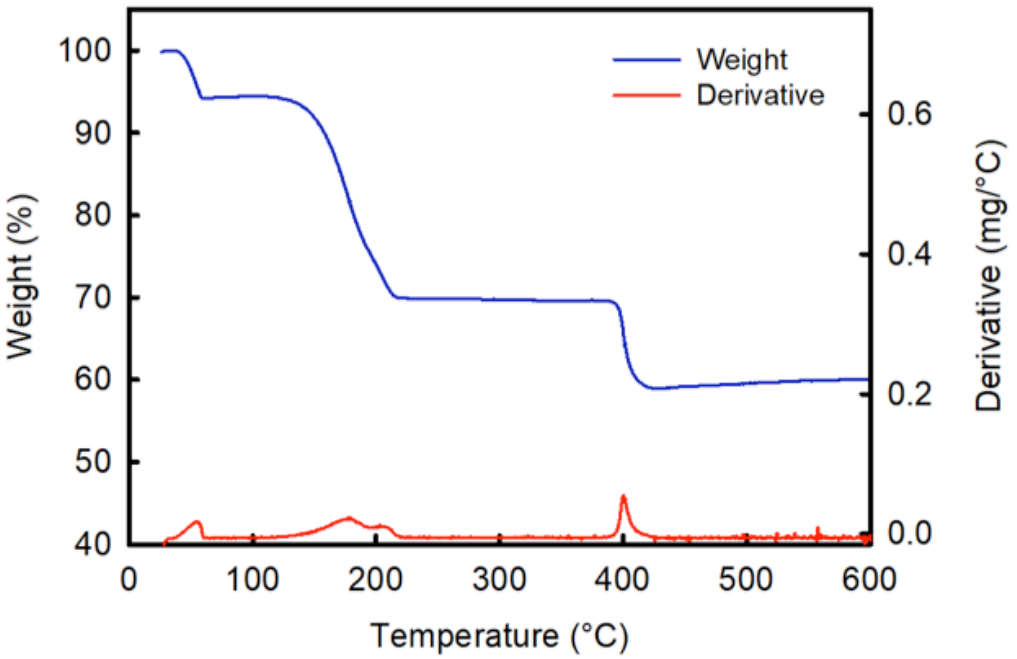

Figure S11: Thermogravimetric analysis of $Cd(DMSO)_2[Pt(CN)_4]\cdot 2H_2O$ (**5**).

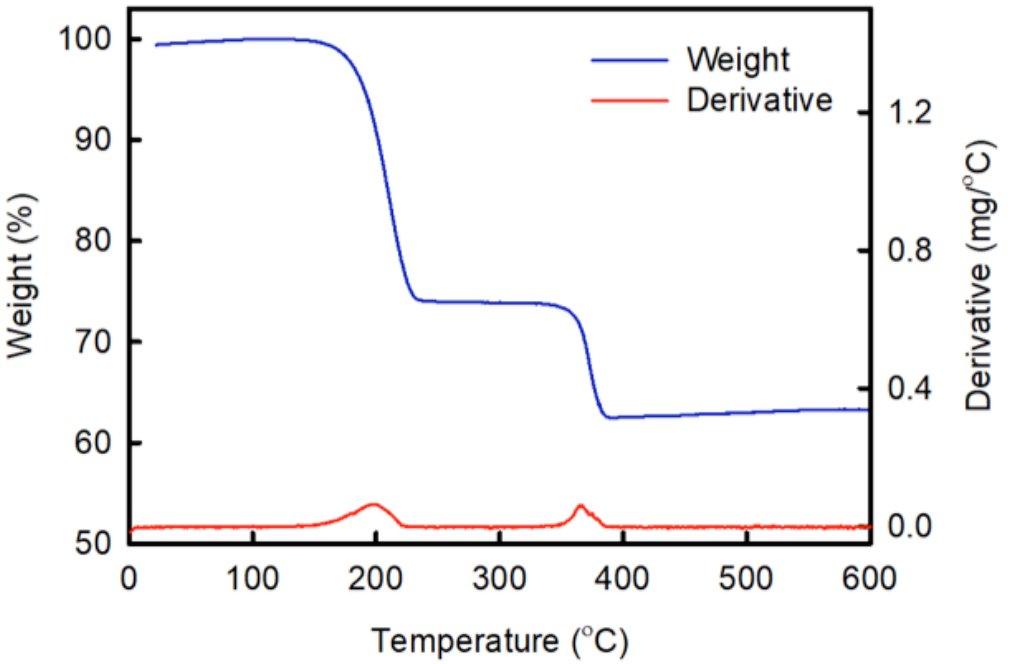

Figure S12: Thermogravimetric analysis of $Cd(pyridine)_2[Pt(CN)_4]$ (**6**).

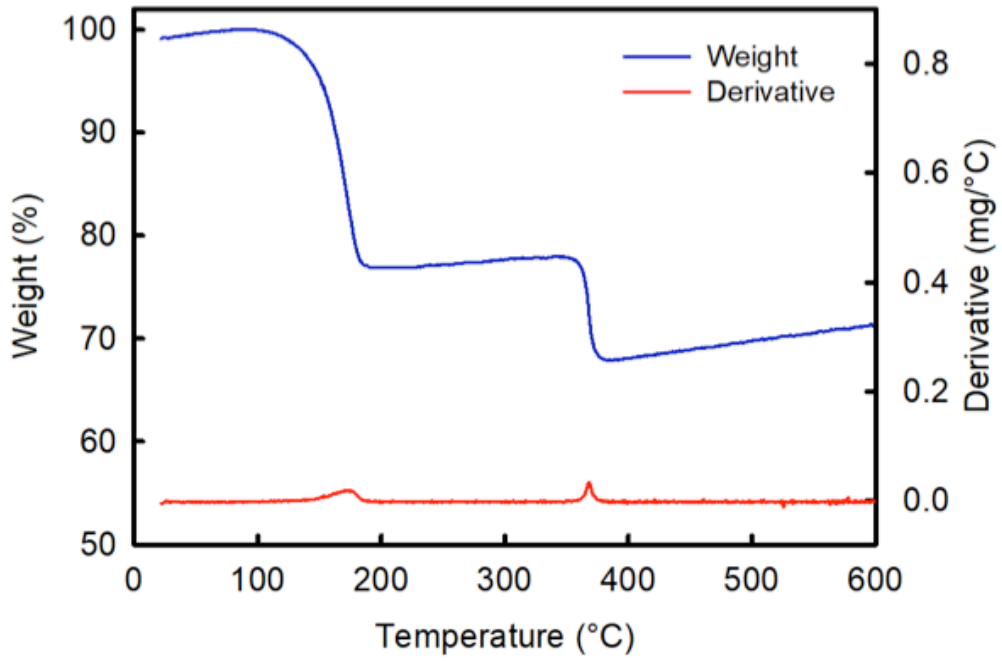

Figure S13: Thermogravimetric analysis of $Cd(DMF)_2[Pt(CN)_4]$ (**7**).

Table S8. TGA decomposition mass fragments and temperature ranges for **5-7**

Compound	**Group**	**Loss (%)**	**Temperature Range (°C)**
5	2 x H_2O	6	35-63
	2 x DMSO	24	140-215
	2 x C_2N_2	12	390-420
6	2 x Pyridine	24	170-220
	2 x C_2N_2	15	360-390
7	2 x DMF	23	145-194
	2 x C_2N_2	10	365-385

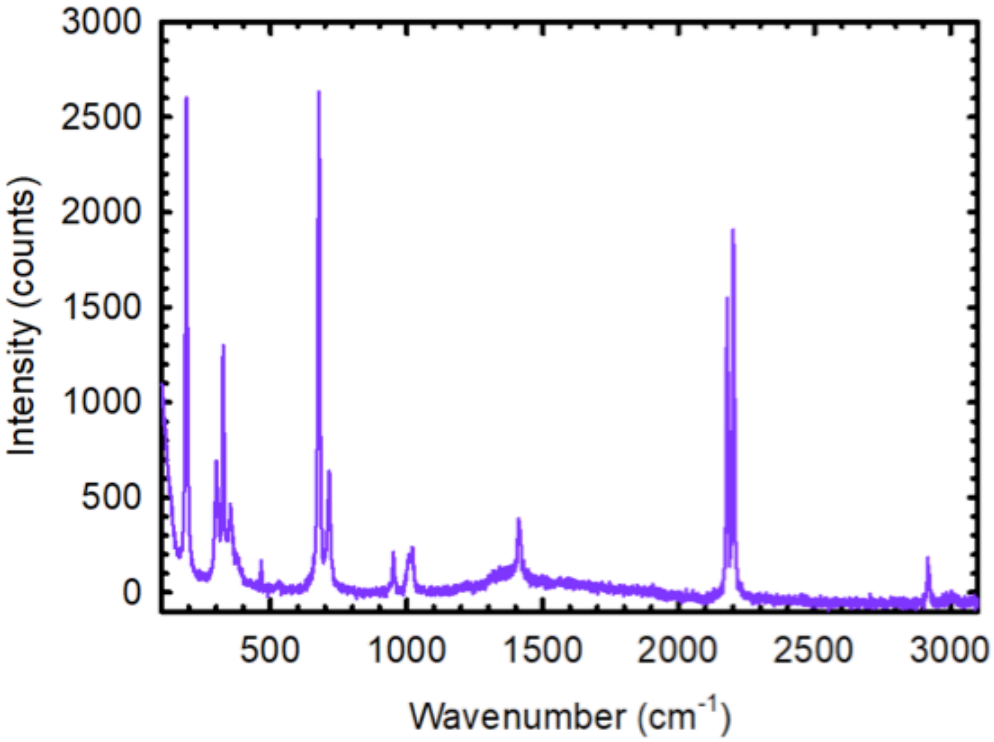

Figure S14: Raman spectrum of $Cd(DMSO)_2[Pt(CN)_4]\cdot 2H_2O$ (**5**).

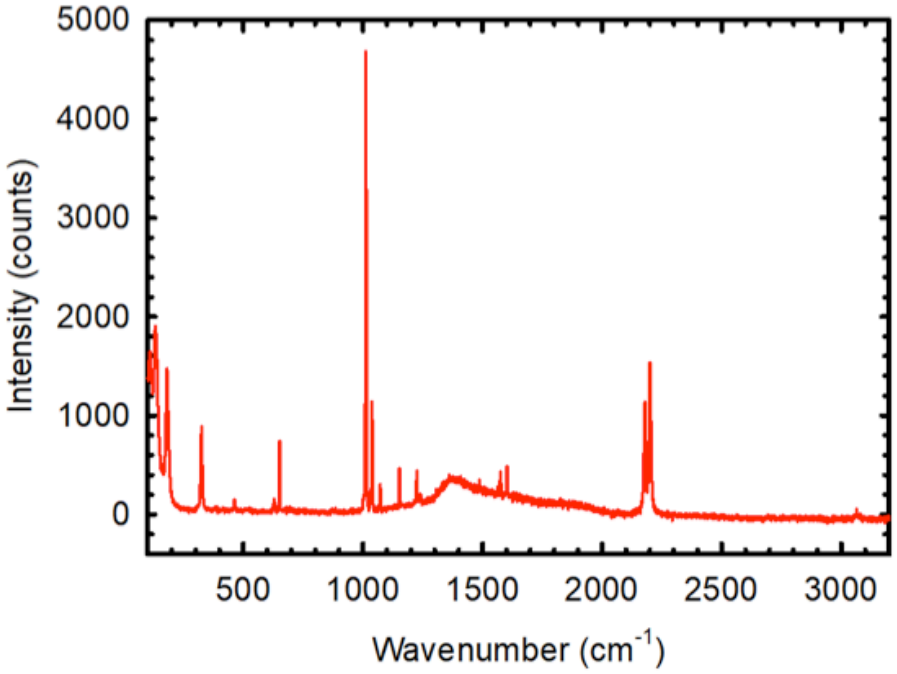

Figure S15: Raman spectrum of $Cd(pyridine)_2[Pt(CN)_4]$ (**6**).

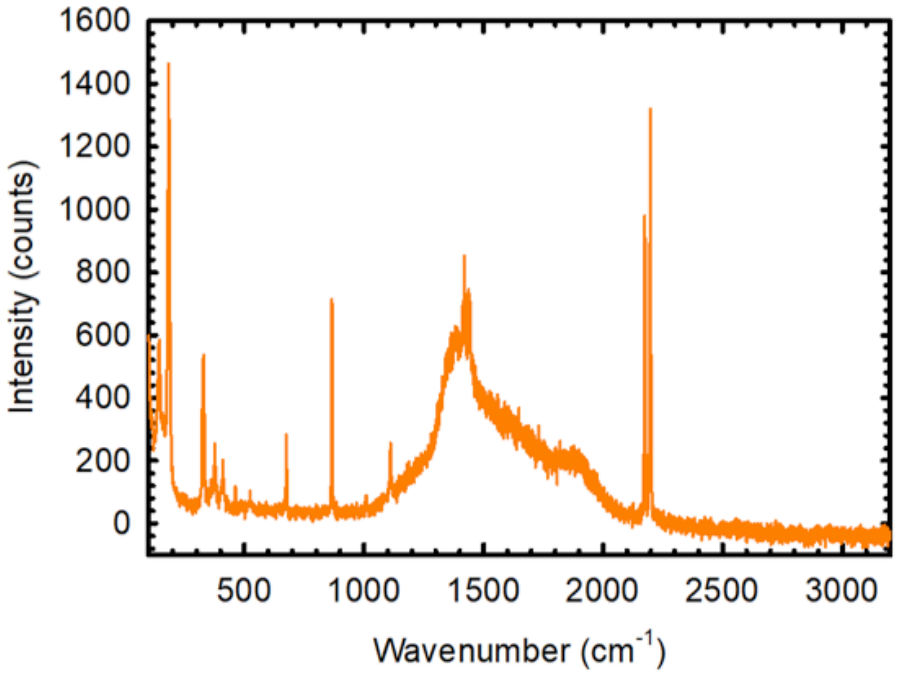

Figure S16: Raman spectrum of $Cd(DMF)_2[Pt(CN)_4]$ (**7**).

(1) Zhang, M.; Li, B. Bin; Sun, J.; Kong, X. P.; Gu, P. P.; Chen, Y. Y.; Yuan, A. H. *Zeitschrift für Anorg. und Allg. Chemie* **2014**, *640* (5), 1007–1011.