Electronic Supplementary Material (ESI) for Dalton Transactions.

Contents:

1. NMR spectra

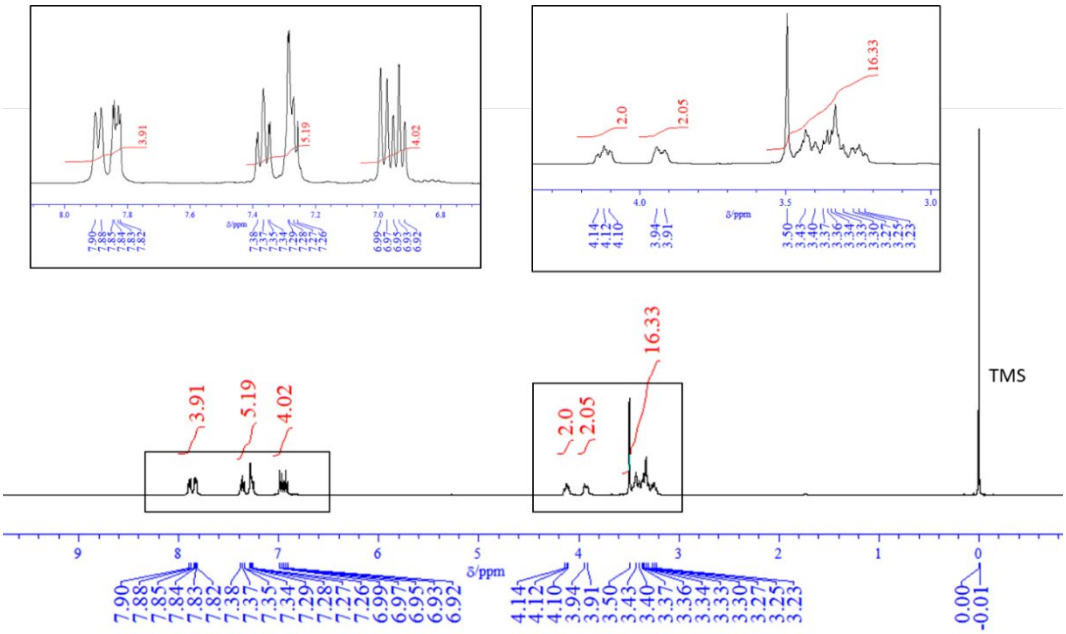


Figure S1. ^{1}H-NMR (400 MHz) spectrum of $[PtCl_2(\mathbf{1})_2]$ in $CDCl_3$.

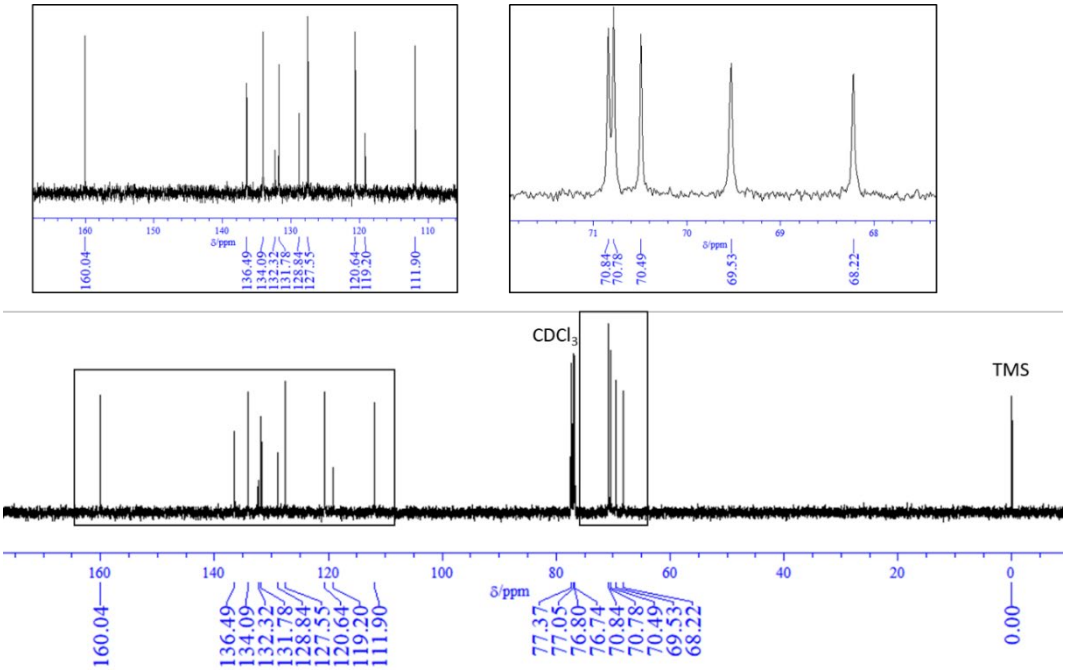


Figure S2. ^{13}C-NMR (100 MHz) spectrum of $[PtCl_2(\mathbf{1})_2]$ in $CDCl_3$.

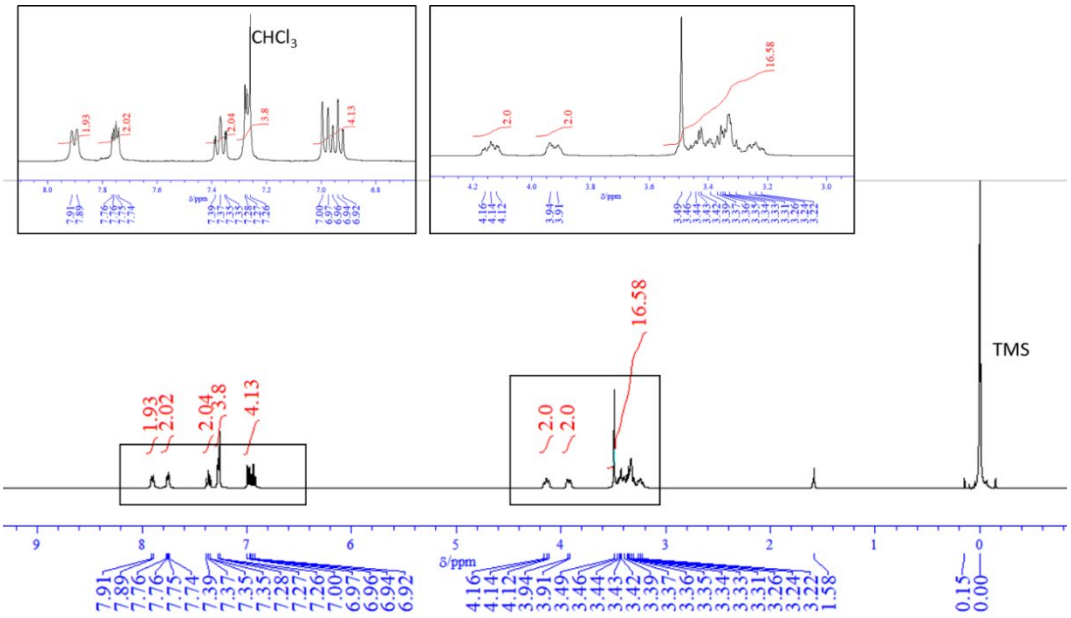


Figure S3. ^{1}H-NMR (400 MHz) spectrum of [$PtBr_2$(**1**)$_2$] in $CDCl_3$.

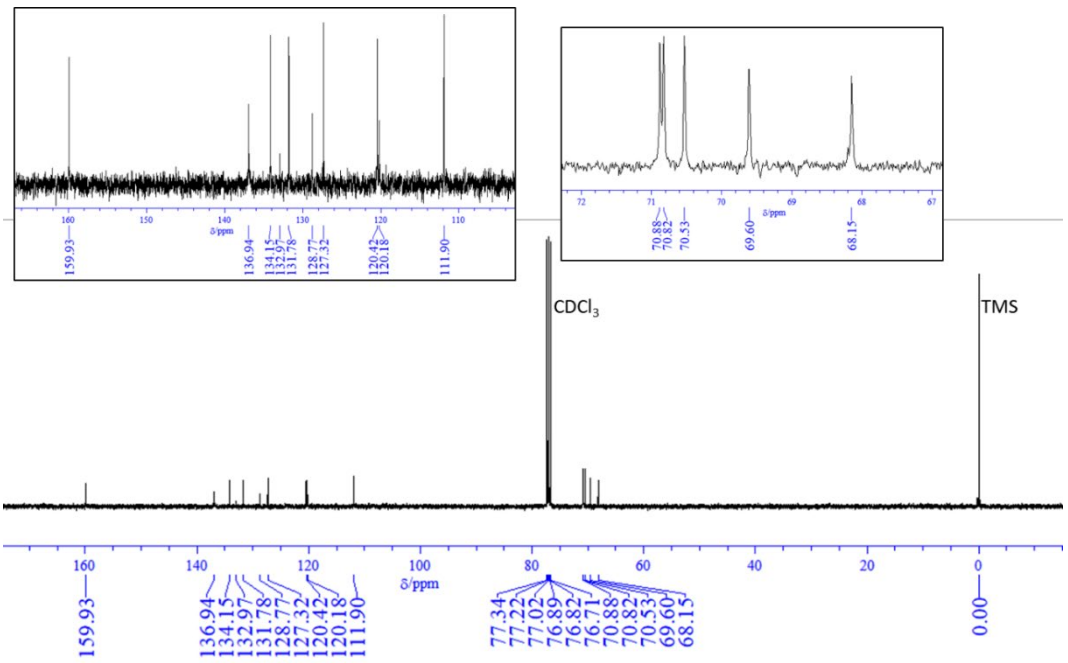


Figure S4. ^{13}C-NMR (100 MHz) spectrum of [$PtBr_2$(**1**)$_2$] in $CDCl_3$.

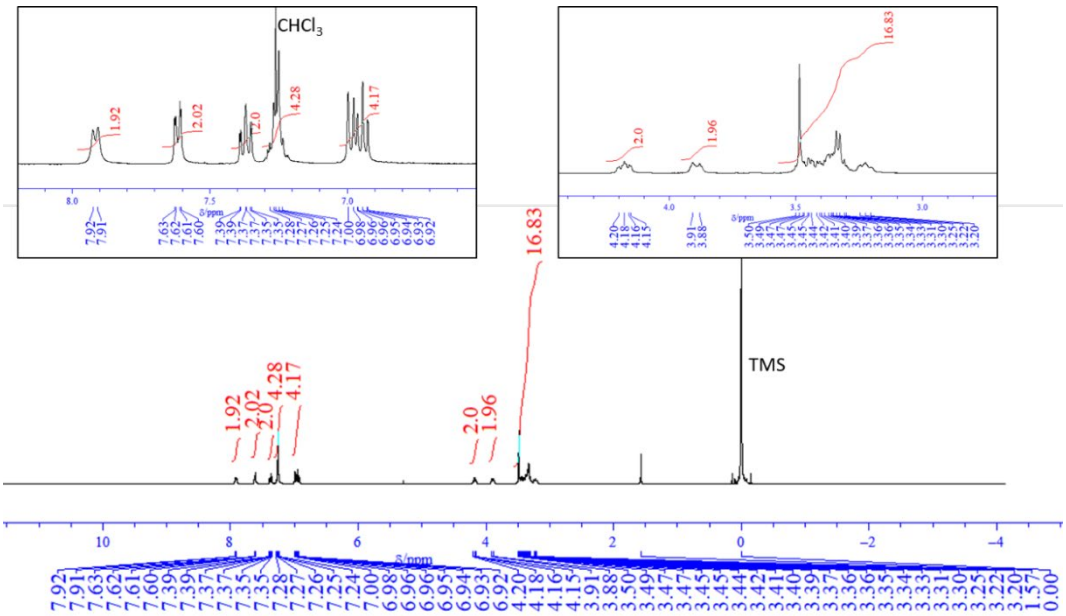


Figure S5. ^{1}H-NMR (400 MHz) spectrum of [PtI_2(**1**)$_2$] in $CDCl_3$.

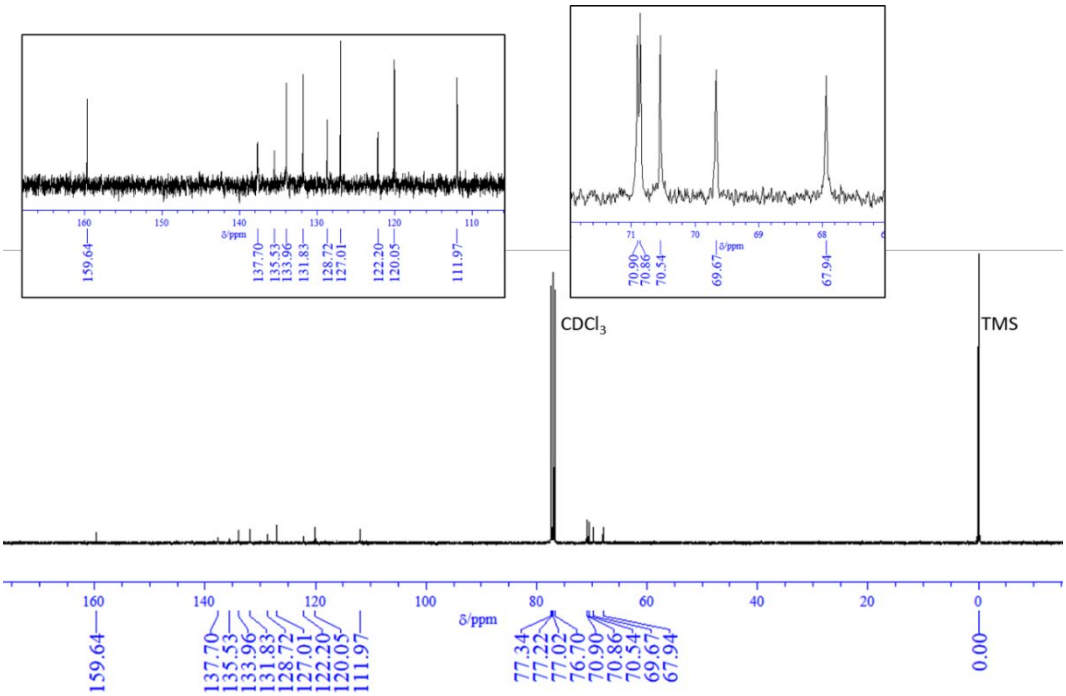


Figure S6. ^{13}C-NMR (100 MHz) spectrum of [PtI_2(**1**)$_2$] in $CDCl_3$.

2. Crystallographic data

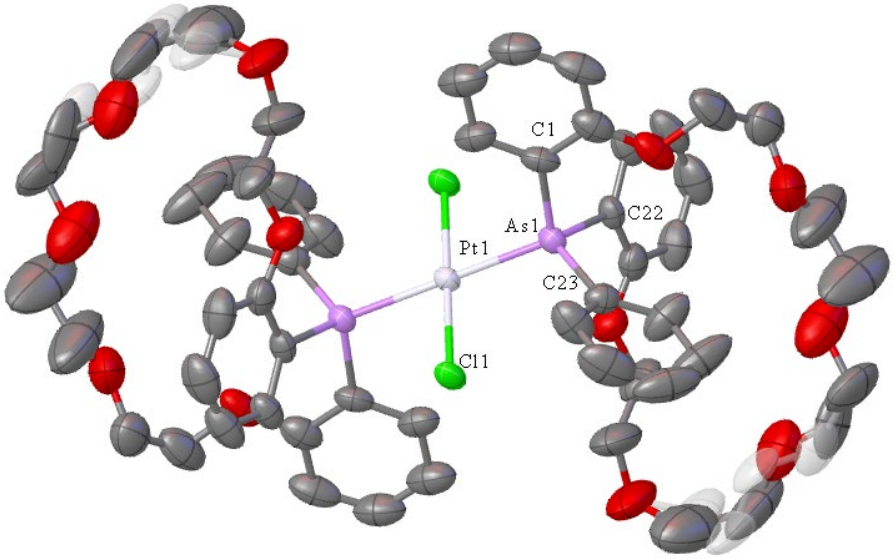
Table S1. Crystallographic data of $[PtCl_2(\mathbf{1})_2]$ and $[PtCl_2(\mathbf{1})_2]\cdot MeOH$.

	$[PtCl_2(\mathbf{1})_2]$	$[PtCl_2(\mathbf{1})_2]\cdot MeOH$
Crystal data		
Empirical Formula	$C_{56}H_{66}As_2Cl_2O_{12}Pt$	$C_{58}H_{74}As_2Cl_2O_{14}Pt$
Formula Weight	1346.91	1411.05
Crystal Dimension, mm^3	0.36 × 0.23 × 0.18	0.280 × 0.220 × 0.180
Crystal System	Orthorhombic	Orthorhombic
Space Group	*Pbca*	*Pbca*
a, Å	15.4501(4)	16.027(11)
b, Å	15.5883(6)	16.087(10)
c, Å	22.6136(6)	22.522(15)
α, deg	-	-
β, deg	-	-
γ, deg	-	-
Volume, $Å^3$	5446.3(3)	5807(7)
D_{calcd}, g cm^{-3}	1.643	1.614
Z	4	4
F(000)	2704.0	2848.0
Data Collection		
Temperature, deg	-180	-180
2θmax, deg.	52.7	55.0
Tmin/Tmax	0.376 / 0.492	0.444 / 0.600
Refinement		
No. of Observed Data	5573	6501
No. of Parameters	368	351
$R1^a$, $wR2^b$	0.0389, 0.1028	0.0608, 0.1498
Goodness of Fit Indictor	1.076	1.120

$^aR1 = \Sigma \, | \, |Fo| - |Fc| \, | \, / \, \Sigma \, |Fo|$ $^bwR^2 = [\Sigma \, w((Fo^2-Fc^2)^2 \, / \, \Sigma \, w(Fo^2)^2 \,]^{1/2}$ $w = [\sigma^2(Fo^2)]^{-1}$

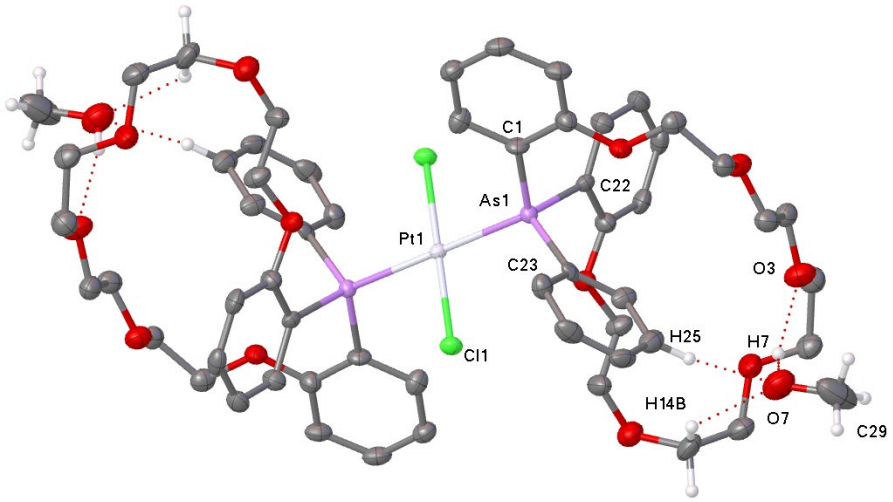
CCDC # 2063097 ($[PtCl_2(\mathbf{1})_2]$), 2063098 ($[PtCl_2(\mathbf{1})_2]\cdot MeOH$)

Table S2. ORTEP (ellipsoids at 50% probability), selected distances and angles of $[PtCl_2(\mathbf{1})_2]$. All hydrogens of the ligands were omitted for clarity.



Distances (Å)		Angles (°)	
As1-C1	1.941(7)	C1-As1-C22	104.1(2)
As1-C22	1.933(5)	C1-As1-C23	104.2(3)
As1-C23	1.931(7)	C22-As1-C23	107.2(2)
As1-Pt1	2.4002(5)	Pt1-As1-C1	110.7(2)
Pt1-Cl1	2.305(1)	Pt1-As1-C22	112.3(2)
		Pt1-As1-C23	117.3(2)
		Cl1-Pt1-As1	93.89(3

Table S3. ORTEP (ellipsoids at 50% probability), selected distances and angles of $[PtCl_2(\mathbf{1})_2]$·MeOH. All hydrogens of the ligands were omitted for clarity.



Distances (Å)		Angles (°)	
As1-C1	1.942(7)	C1-As1-C22	102.8(3)
As1-C22	1.952(7)	C1-As1-C23	103.2(3)
As1-C23	1.950(7)	C22-As1-C23	108.7(3)
As1-Pt1	2.412(1)	Pt1-As1-C1	114.6(2)
Pt1-Cl1	2.319(2)	Pt1-As1-C22	111.9(2)
O7-H7	0.840(7)	Pt1-As1-C23	114.7(2)
O3-H7	2.089(6)	Cl1-Pt1-As1	92.26(5)
O7-H25	2.560(7)	O7-H7-O3	165.2(5)
O7-H14b	2.592(8)	C29-O7-H25	123.0(8)
		C29-O7-C14B	147.0(8)

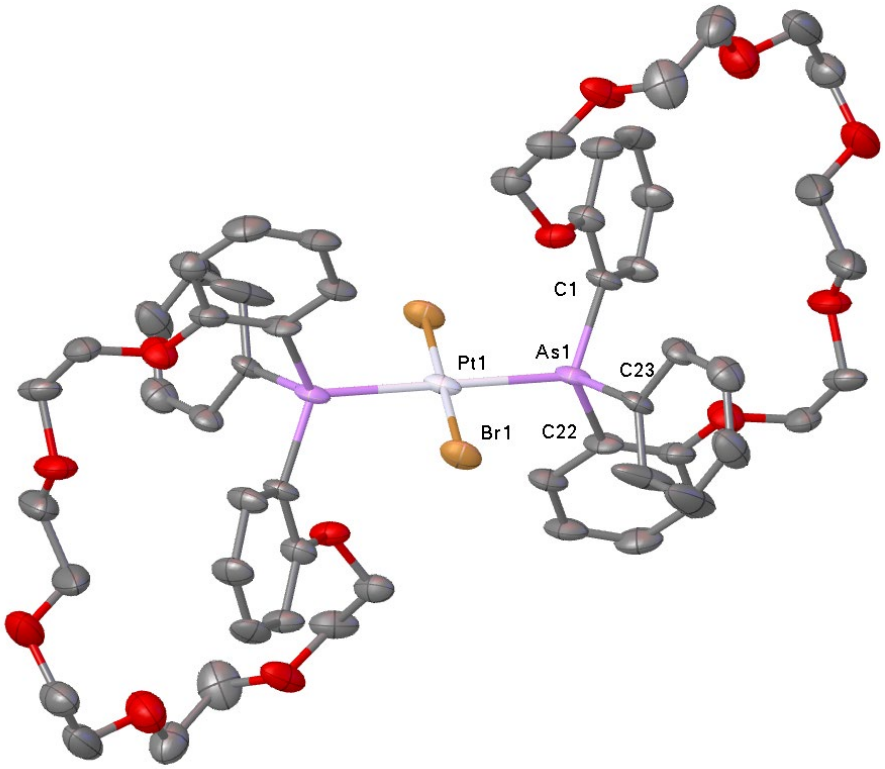
Table S4. Crystallographic data of $[PtBr_2(\mathbf{1})_2]$, $[PtI_2(\mathbf{1})_2]$, and $[PtCl_2(\mathbf{1})_2]$+KPF_6.

	$[PtBr_2(\mathbf{1})_2]$	$[PtI_2(\mathbf{1})_2]$	$[PtCl_2(\mathbf{1})_2]$+KPF_6
Crystal data			
Empirical Formula	$C_{56}H_{66}As_2Br_2O_{12}Pt$	$C_{56}H_{66}As_2I_2O_{12}Pt$	$C_{58}H_{70}As_2Cl_6F_{12}K_2O_{12}P_2Pt$
Formula Weight	1435.83	1529.81	1884.96
Crystal Dimension, mm^3	0.272 × 0.136 × 0.079	0.424 × 0.119 × 0.100	0.200 × 0.070 × 0.060
Crystal System	Triclinic	Monoclinic	Monoclinic
Space Group	*P*-1	$P2_1/c$	$C2/c$
a, Å	9.4839(7)	15.5612(5)	27.946(17)
b, Å	11.2922(7)	9.5156(3)	15.065(9)
c, Å	13.6685(10)	19.2931(7)	18.145(11)
α, deg	92.689(5)	-	-
β, deg	96.897(6)	105.920(4)	107.168(6)
γ, deg	108.594(6)	-	-
Volume, $Å^3$	1371.71(17)	2747.24(17)	7299(8)
D_{calcd}, g cm^{-3}	1.738	1.849	1.715
Z	2	2	4
F(000)	712.0	1496.0	3744.0
Data Collection			
Temperature, deg	-180	-180	-180
2θmax, deg	54.966	65.296	55.0
Tmin/Tmax	0.382 / 0.763	0.684 / 0.826	0.614 / 0.852
Refinement			
No. of Observed Data	6259	8998	7913
No. of Parameters	319	350	439
R1[a], wR2[b]	0.0794, 0.2245	0.0306, 0.0669	0.0541, 0.1170
Goodness of Fit Indictor	1.053	1.000	1.153

[a]$R1 = \Sigma \mid |Fo| - |Fc| \mid / \Sigma |Fo|$ [b]$wR^2 = [\Sigma w((Fo^2-Fc^2)^2 / \Sigma w(Fo^2)^2]^{1/2}$ $w = [\sigma^2(Fo^2)]^{-1}$

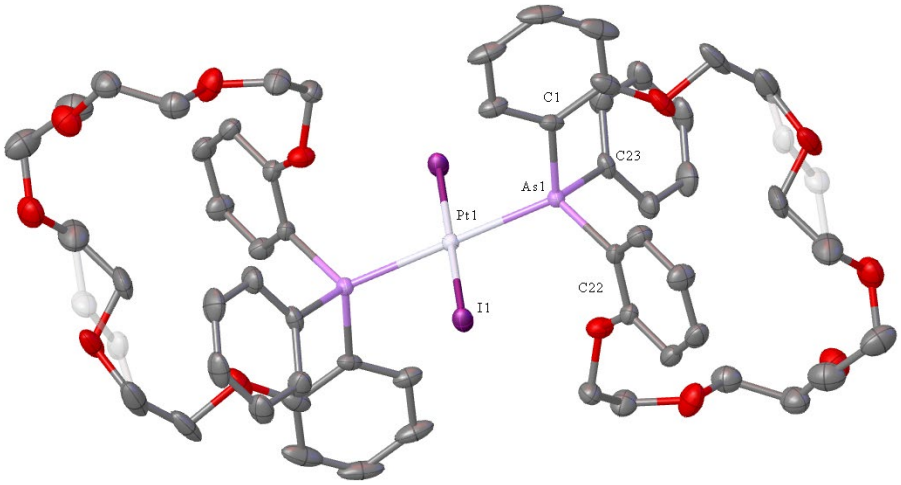
CCDC # 2063096 ($[PtBr_2(\mathbf{1})_2]$), 2063095 ($[PtI_2(\mathbf{1})_2]$), 2063099 ($[PtCl_2(\mathbf{1})_2]$ + KPF_6)

Table S5. ORTEP (ellipsoids at 50% probability), selected distances and angles of [$PtBr_2$(**1**)$_2$]. All hydrogens of the ligands were omitted for clarity.



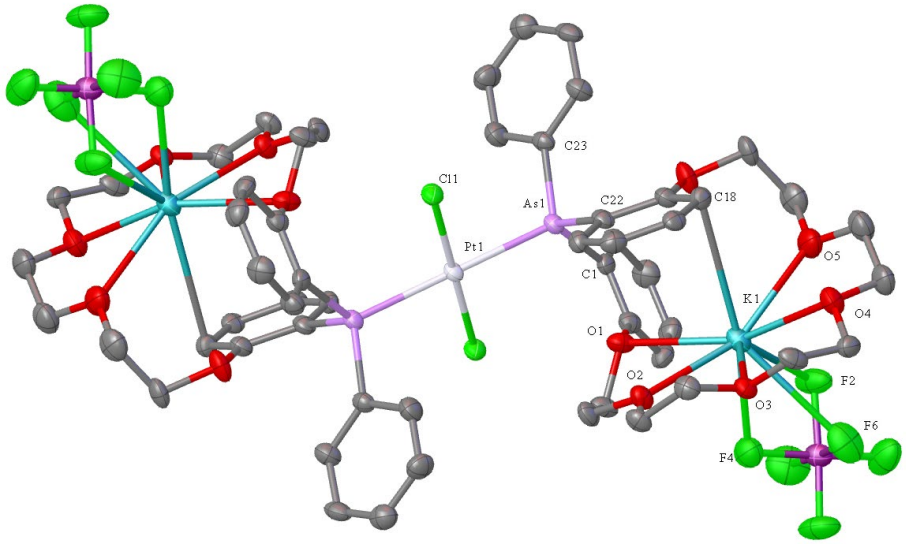
Distances (Å)		Angles (°)	
As1-C1	1.93(1)	C1-As1-C22	105.4(5)
As1-C22	1.95(1)	C1-As1-C23	106.3(4)
As1-C23	1.923(7)	C22-As1-C23	101.6(4)
As1-Pt1	2.410(1)	Pt1-As1-C1	113.8(2)
Pt1-Br1	2.430(1)	Pt1-As1-C22	111.2(4)
		Pt1-As1-C23	117.23(4)
		Br1-Pt1-As1	92.57(4)

Table S6. ORTEP (ellipsoids at 50% probability), selected distances and angles of $[PtI_2(\mathbf{1})_2]$. All hydrogens of the ligands were omitted for clarity.



Distances (Å)		Angles (°)	
As1-C1	1.949(3)	C1-As1-C22	102.5(1)
As1-C22	1.943(3)	C1-As1-C23	101.9(1)
As1-C23	1.957(3)	C22-As1-C23	104.4(1)
As1-Pt1	2.4153(3)	Pt1-As1-C1	111.36(1)
Pt1-I1	2.6076(2)	Pt1-As1-C22	115.70(9)
		Pt1-As1-C23	118.87(9)
		I1-Pt1-As1	90.537(9)

Table S7. ORTEP (ellipsoids at 50% probability), selected distances and angles of $[PtCl_2(\mathbf{1})_2]+KPF_6$. All hydrogens of the ligands and solvents were omitted for clarity.



Distances (Å)		Angles (°)	
As1-C1	1.939(6)	C1-As1-C22	106.4(2)
As1-C22	1.933(6)	C1-As1-C23	102.7(2)
As1-C23	1.928(6)	C22-As1-C23	109.2(2)
As1-Pt1	2.405(1)	Pt1-As1-C1	114.0(2)
Pt1-Cl1	2.314(2)	Pt1-As1-C22	114.3(2)
O1-K1	2.850(5)	Pt1-As1-C23	109.6(2)
O2-K1	2.669(4)	Cl1-Pt1-As1	87.01(6)
O3-K1	2.821(5)	O1-K1-O2	59.5(1)
O4-K1	2.677(6)	O2-K1-O3	58.6(1)
O5-K1	2.723(5)	O3-K1-O4	62.2(1)
C18-K1	3.365(6)	O4-K1-O5	61.7(2)
F2-K1	2.876(5)	O5-K1-C18	63.7(2)
F4-K1	2.766(6)		
F6-K1	3.219(6)		

3. Optical measurement

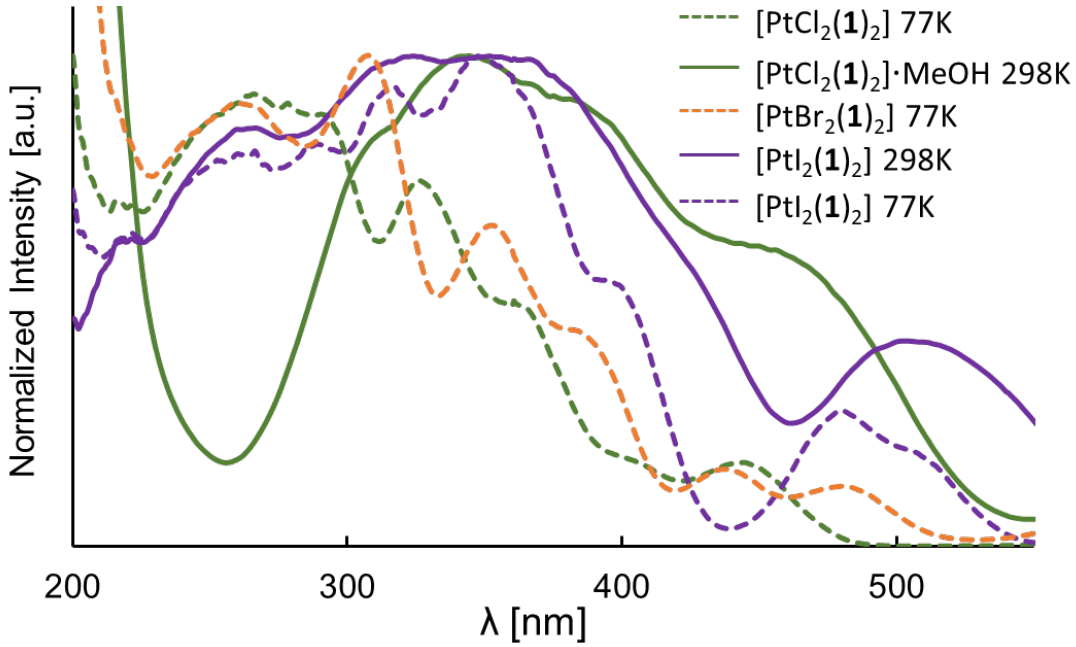


Figure S7. Excitation spectra of $[PtX_2(\mathbf{1})_2]$ (X = Cl, Br, I) in the solid state.

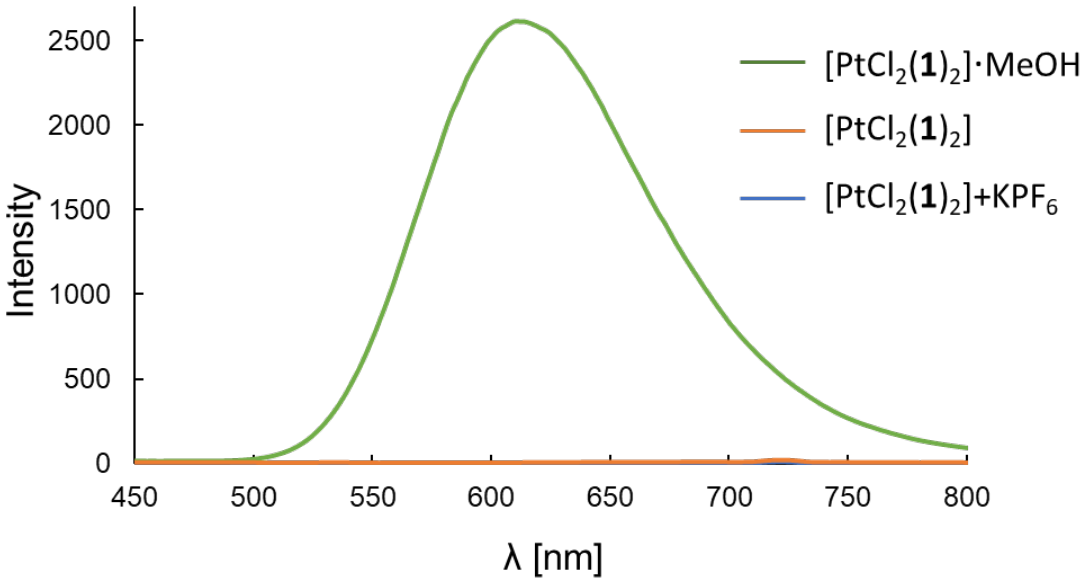


Figure S8. PL spectra of $[PtCl_2(\mathbf{1})_2]\cdot MeOH$, $[PtCl_2(\mathbf{1})_2]$, and $[PtCl_2(\mathbf{1})_2]+KPF_6$ in the solid state at 298 K.

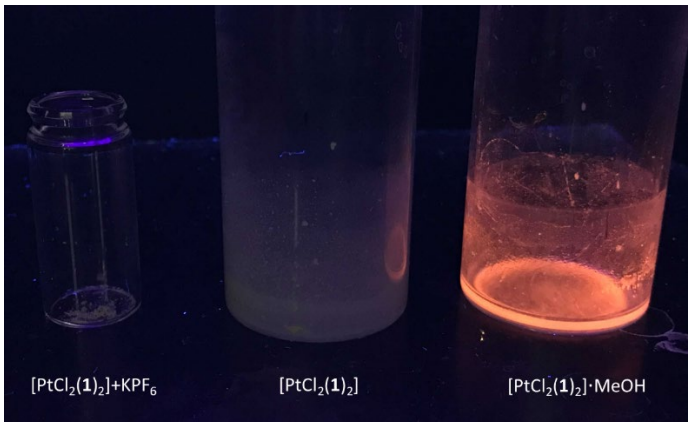


Figure S9. Photographs of $[PtCl_2(\mathbf{1})_2]+KPF_6$, $[PtCl_2(\mathbf{1})_2]$, and $[PtCl_2(\mathbf{1})_2]\cdot MeOH$ crystals under UV irradiation (365 nm).

4. Crystal structure analysis

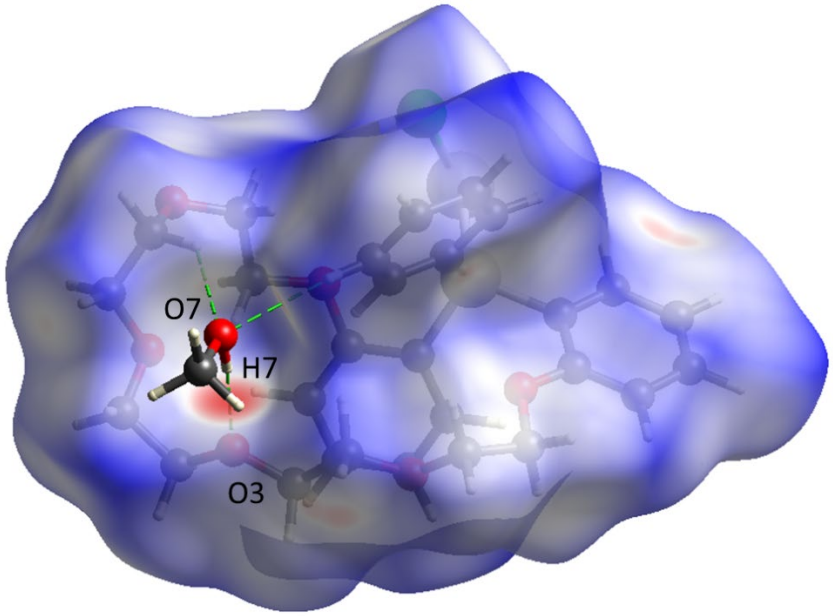


Figure S10. The three-dimensional Hirshfeld surface showing the intermolecular interaction of $[PtCl_2(\mathbf{1})_2]$·MeOH plotted over d_{norm} calculated by Crystal explorer 3.0 software.[1] The green dotted lines signify the O-H…O or C-H…O hydrogen bonds. The hydrogen bonding between acceptor and donor atoms showing O-H···O intermolecular interaction (for O7-H7···O3) are indicated as red regions on the Hirshfeld surface.

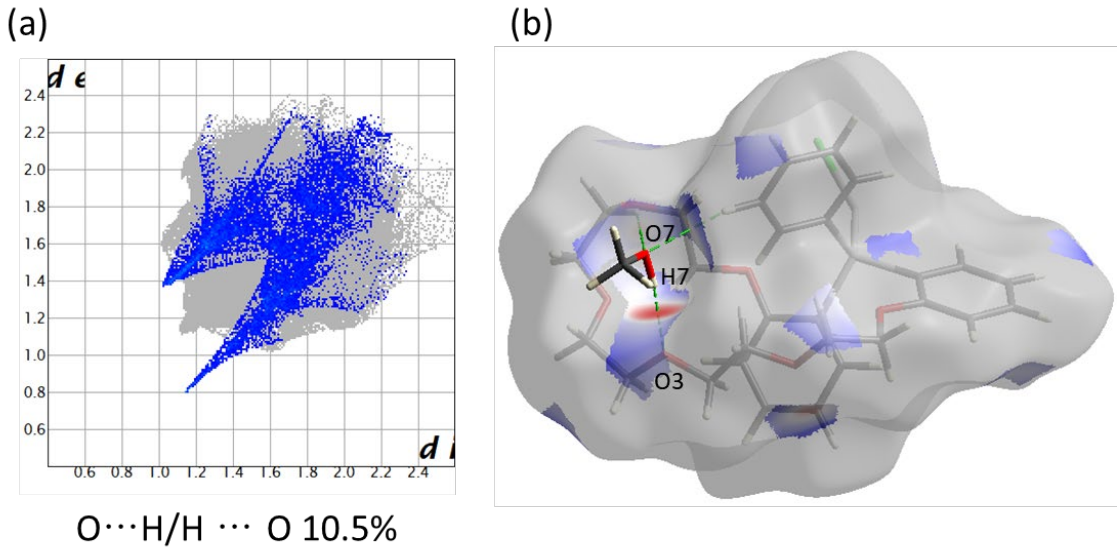


Figure S11. (a) Fingerprint plots of $[PtCl_2(\mathbf{1})_2]$·MeOH representing the contribution of H ···O interactions. (b) The surface map of $[PtCl_2(\mathbf{1})_2]$·MeOH indicates the applicable areas (indicated in blue) that are associated with the H···O interactions.

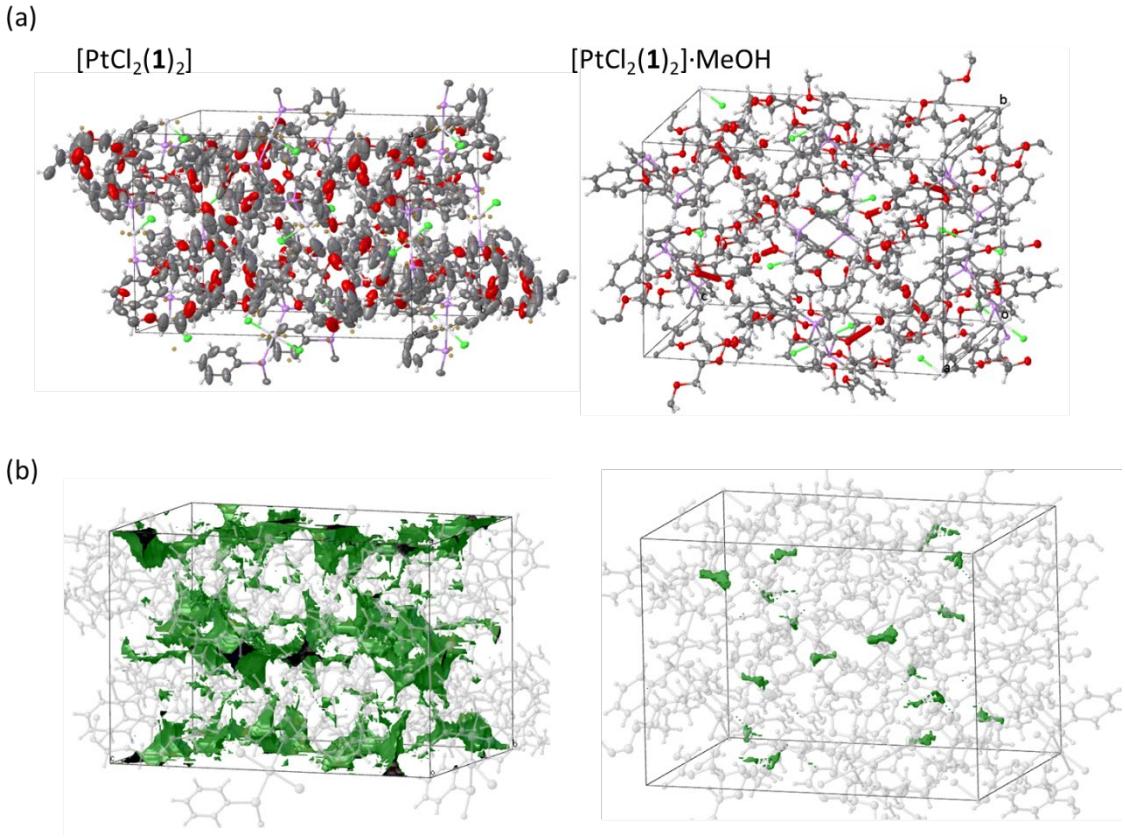


Figure S12. (a) Packing structures of $[PtCl_2(\mathbf{1})_2]$ (left) and $[PtCl_2(\mathbf{1})_2]$·MeOH (right). (b) Void maps in the unit cell of $[PtCl_2(\mathbf{1})_2]$ (left) and $[PtCl_2(\mathbf{1})_2]$·MeOH (right) calculated by Olex2.[9] The resolution of the maps is 0.2 Å and 0.0 Å away from the surface of the molecule.

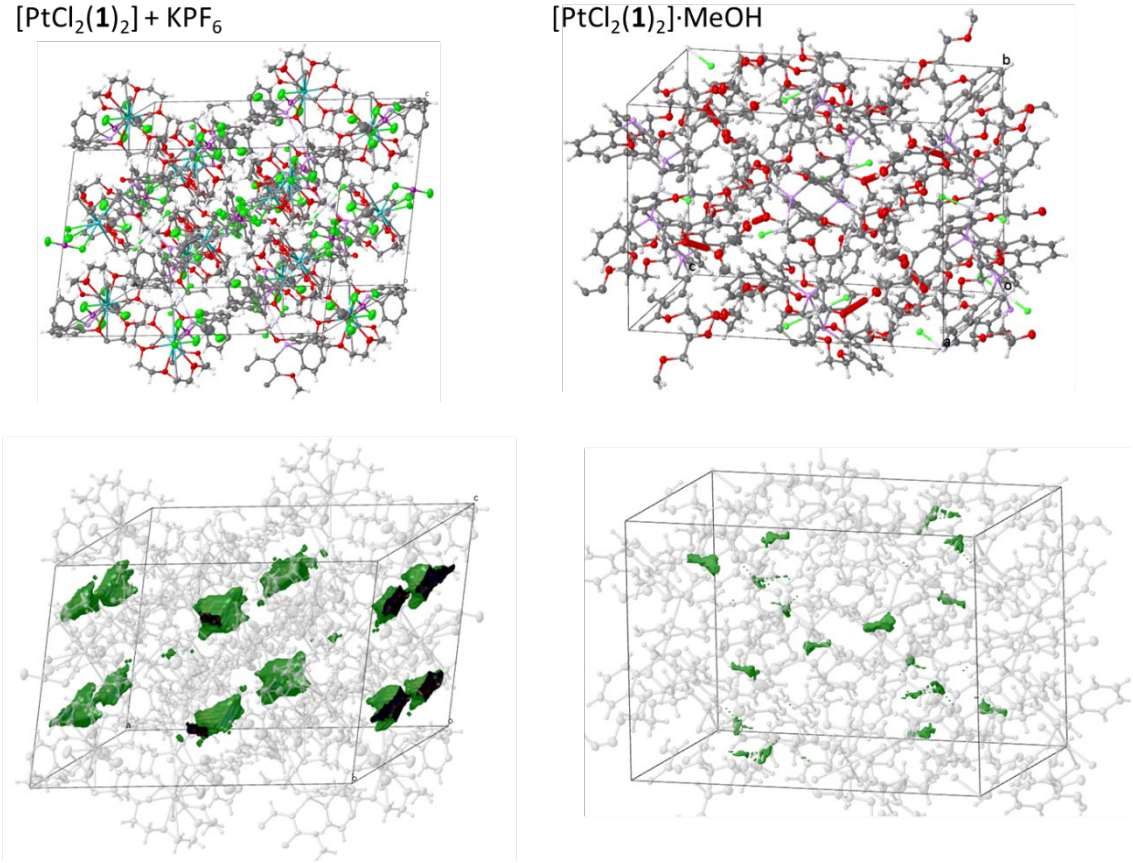


Figure S13. (a) Packing structures of $[PtCl_2(\mathbf{1})_2]$ + KPF_6 (left) and $[PtCl_2(\mathbf{1})_2]$·MeOH (right). (b) Void maps in the unit cell of $[PtCl_2(\mathbf{1})_2]$ + KPF_6 (left) and $[PtCl_2(\mathbf{1})_2]$·MeOH (right) calculated by Olex2.[9] The resolution of the maps is 0.2 Å and 0.0 Å away from the surface of the molecule.

5. Methanol sensing tests

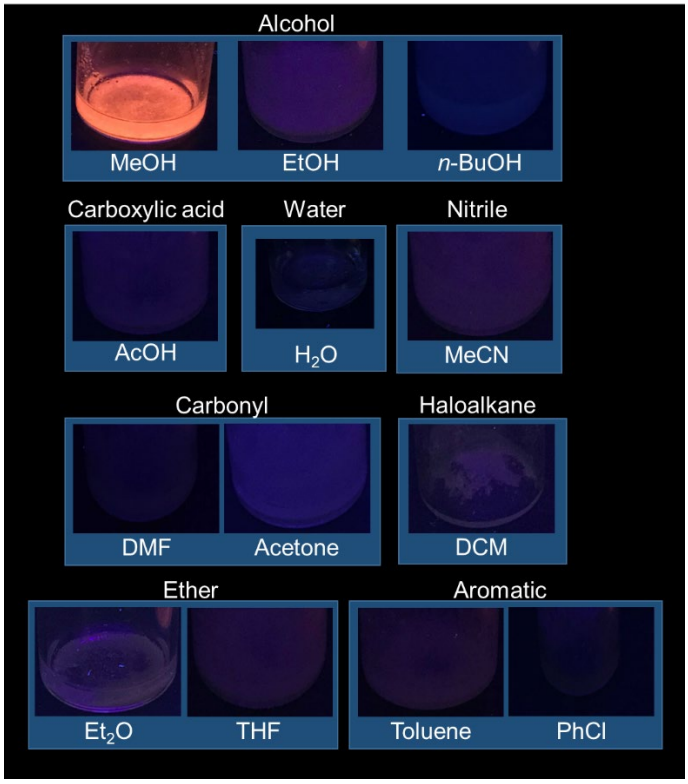
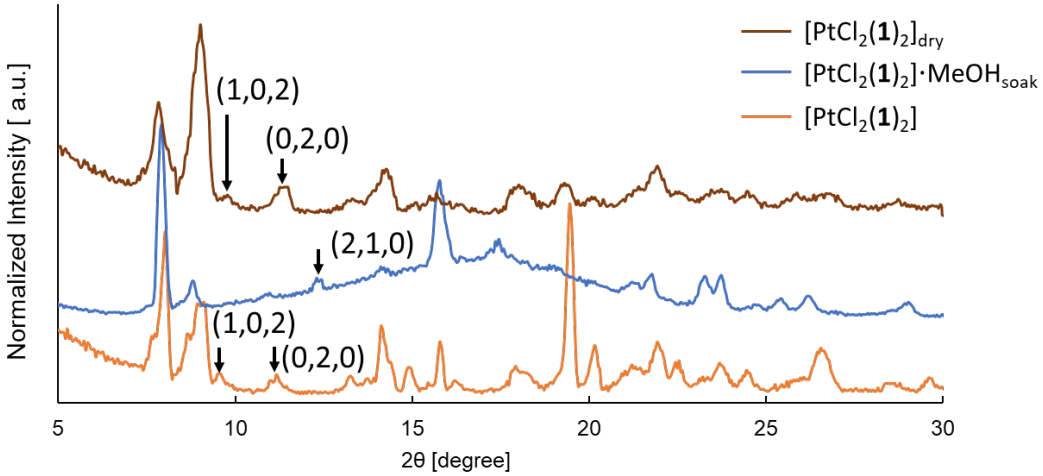


Figure S14. Photographs of $[PtCl_2(\mathbf{1})_2]$ crystals soaked into various solvents under UV irradiation (365 nm). Abbreviation: MeOH (methanol), EtOH (ethenol), *n*-BuOH (*n*-butanol), AcOH (acetic acid), MeCN (acetonitrile), DMF (*N*,*N*-dimethylformamide), DCM (dichloromethane), Et_2O (diethyl ether), THF (tetrahydrofuran), and PhCl (chlorobenzene).

6. Powder XRD measurement

(a) Experimental patterns



(b) Simulated patterns

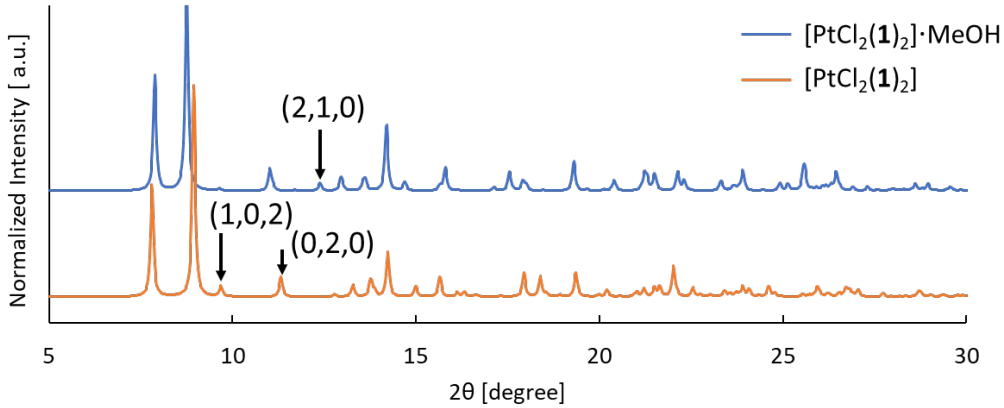


Figure S15. (a) Powder XRD patterns of $[PtCl_2(\mathbf{1})_2]$ (orange) and $[PtCl_2(\mathbf{1})_2]$ soaked with methanol (blue). (b) Simulated powder XRD patterns of $[PtCl_2(\mathbf{1})_2]$ soaked with methanol (blue) calculated by single -crystal XRD data.

7. Reference

[1] S. K. Wolff, D. J. Grimwood, J. J. McKinnon, M. J. Turner, D. Jayatilaka and M. A. Spackman, CrystalExplorer (Version 3.0), University of Western Australia, 2012.