

Electronic Supplementary Information for

Smallest Optical Gap for Quasi-One-Dimensional Iodo-bridged Platinum Compounds via Chemical Pressure

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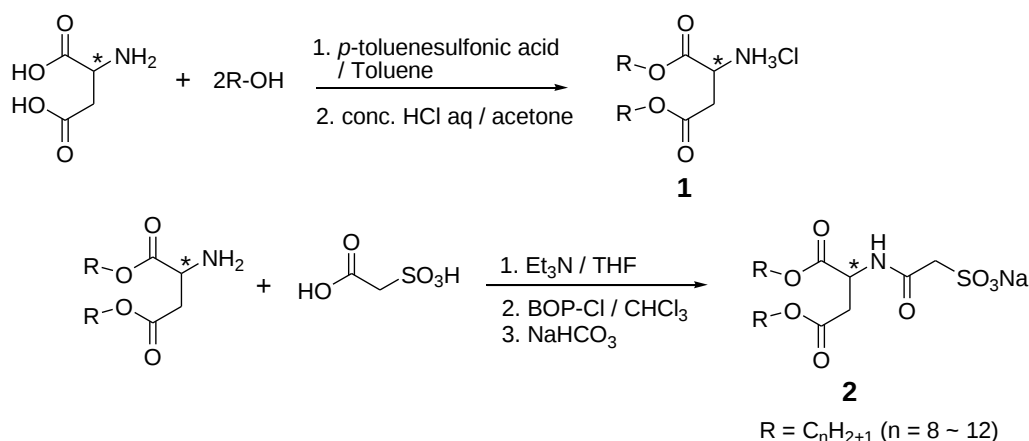
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Experimental



Scheme S1 Synthetic route of Na(L-Asp-C_n).

Compound 1

The synthesis of compound **1** was performed as described previously.¹⁴ 4.00g (30.1 mmol) of *L*-Aspartic acid (Wako Chemical Co.), 2.4 equivalent (72.2 mmol) of alkylalcohol (Wako Chemical Co.) and 5.95 g (31.3 mmol) of *p*-toluenesulfonic acid (Wako Chemical Co.) were dissolved in toluene, and water was removed as an azeotropic mixture with a Dean-Stark trap. The reaction was continued until the stoichiometric amount of water was recovered. After removing toluene under the reduced pressure, pale yellow solution was obtained. It was dissolved in 100 ml chloroform and washed with sodium carbonate solution and diluted water. Dry the organic layer with sodium sulfate. The filtrate was condensed and dissolved in acetone. White precipitation was obtained by adding hydrochloric acid solution and collected by suction filtration to give white solid. Yield: 80.14%. The product was identified by NMR spectra.

n = 8: ¹H-NMR (500 MHz, chloroform-*d*). δ (ppm) 0.88 (6.0H*, t, CH₃-), 1.26-1.30 (20.6 H, m, -(CH₂)₅-), 1.60 (4.0H, m, -(CH₂)₅-CH₂-CH₂-O), 3.16-3.34 (1.8H, dd, -C(=O)-CH₂-CH(-OCO)-), 4.08-4.24 (4.13H, m, -(CH₂)₆-CH₂-O-), 4.52 (1.0H, m, -CH₂-CH(-OCO)-NH₂-), 8.02 (2.0H, d, -C(=O)-CH-NH₂-).

n = 9: ¹H-NMR (500 MHz, chloroform-*d*). δ (ppm) 0.88 (6.0H*, t, CH₃-), 1.26-1.30 (24.3 H, m, -(CH₂)₆-), 1.60 (4.0H, m, -(CH₂)₆-CH₂-CH₂-O), 3.16-3.34 (1.8H, dd, -C(=O)-CH₂-CH(-OCO)-), 4.08-4.24 (4.13H, m, -(CH₂)₇-CH₂-O-), 4.52 (1.0H, m, -CH₂-CH(-OCO)-NH₂-), 8.02 (2.0H, d, -C(=O)-CH-NH₂-).

n = 10: ¹H-NMR (500 MHz, chloroform-*d*). δ (ppm) 0.88 (6.0H*, t, CH₃-), 1.26-1.30 (28.2 H, m, -(CH₂)₇-), 1.60 (4.0H, m, -(CH₂)₇-CH₂-CH₂-O), 3.16-3.34 (1.8H, dd, -C(=O)-CH₂-CH(-OCO)-), 4.08-4.24 (4.13H, m, -(CH₂)₈-CH₂-O-), 4.52 (1.0H, m, -CH₂-CH(-OCO)-NH₂-), 8.02 (2.0H, d, -C(=O)-CH-NH₂-).

n = 11: ¹H-NMR (500 MHz, chloroform-*d*). δ (ppm) 0.88 (6.0H*, t, CH₃-), 1.26-1.30 (32.4 H, m, -(CH₂)₈-), 1.60 (4.0H, m,

$-(\text{CH}_2)_8-\text{CH}_2-\text{CH}_2-\text{O}$), 3.16-3.34 (1.8H, dd, $-\text{C}(=\text{O})-\text{CH}_2-\text{CH}(-\text{OCO})-$), 4.08-4.24 (4.13H, m, $-(\text{CH}_2)_9-\text{CH}_2-\text{O}-$), 4.52 (1.0H, m, $-\text{CH}_2-\text{CH}(-\text{OCO})-\text{NH}_2-$), 8.02 (2.0H, d, $-\text{C}(=\text{O})-\text{CH}-\text{NH}_2-$).

n = 12: ^1H -NMR (500 MHz, chloroform-*d*). δ (ppm) 0.88 (6.0H*, t, CH_3-), 1.26-1.30 (36.6 H, m, $-(\text{CH}_2)_9-$), 1.60 (4.0H, m, $-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{O}$), 3.16-3.34 (1.8H, dd, $-\text{C}(=\text{O})-\text{CH}_2-\text{CH}(-\text{OCO})-$), 4.08-4.24 (4.13H, m, $-(\text{CH}_2)_{10}-\text{CH}_2-\text{O}-$), 4.52 (1.0H, m, $-\text{CH}_2-\text{CH}(-\text{OCO})-\text{NH}_2-$), 8.02 (2.0H, d, $-\text{C}(=\text{O})-\text{CH}-\text{NH}_2-$).

Compound 2

The synthesis of compound **2** was performed as described previously.¹⁵ 4.00 g (ca. 8.37 mmol) of Compound **1** was dissolved in THF and add 3 ml of triethylamine, and filter white precipitation to obtain colorless solution. Colorless solution, 1.24 g (8.58 mmol) of sulfoacetic acid, 2.28 g (8.96 mmol) of Bis(2-oxo-3-oxazolidinyl)phosphinic Chloride (BOP-Cl, TCI Co.) and 3 ml of triethylamine were dissolved in 50 ml of chloroform and the mixture was cooled in ice bath, and was stirred for 18 h. After removing chloroform under the reduced pressure, colorless residue was obtained. It was dissolved in 50ml of chloroform and washed with saturated sodium chloride solution, and then with 5% sodium bicarbonate solution. Dry the organic layer with sodium sulfate. After separating sodium sulfate by filtration, the filtrate was condensed (pale yellow oil) and added to ethyl acetate. Precipitate obtained was collected by suction filtration to give white solid. It was recrystallized from methanol. Yield: 27.10 %. The product was identified by NMR spectra.

n = 8: ^1H -NMR (500 MHz, chloroform-*d*). δ (ppm) 0.88 (6.0H*, t, CH_3-), 1.26-1.30 (20.7 H, m, $-(\text{CH}_2)_5-$), 1.60 (4.0H, m, $-(\text{CH}_2)_5-\text{CH}_2-\text{CH}_2-\text{O}$), 3.17-3.35 (1.8H, dd, $-\text{C}(=\text{O})-\text{CH}_2-\text{CH}(-\text{OCO})-$), 4.10-4.26 (4.0H, m, $-(\text{CH}_2)_6-\text{CH}_2-\text{O}-$), 4.42 (2.0H, m, $-\text{C}(=\text{O})-\text{CH}_2-\text{SO}_3-$), 4.89 (1.0H, m, $-\text{CH}_2-\text{CH}(-\text{OCO})-\text{NH}-$), 8.02 (0.9H, d, $-\text{CH}-\text{NH}-\text{C}(=\text{O})-$).

n = 9: ^1H -NMR (500 MHz, chloroform-*d*). δ (ppm) 0.88 (6.0H*, t, CH_3-), 1.26-1.30 (24.5 H, m, $-(\text{CH}_2)_6-$), 1.60 (4.0H, m, $-(\text{CH}_2)_6-\text{CH}_2-\text{CH}_2-\text{O}$), 3.17-3.35 (1.8H, dd, $-\text{C}(=\text{O})-\text{CH}_2-\text{CH}(-\text{OCO})-$), 4.10-4.26 (4.0H, m, $-(\text{CH}_2)_7-\text{CH}_2-\text{O}-$), 4.42 (2.0H, m, $-\text{C}(=\text{O})-\text{CH}_2-\text{SO}_3-$), 4.89 (1.0H, m, $-\text{CH}_2-\text{CH}(-\text{OCO})-\text{NH}-$), 8.02 (0.9H, d, $-\text{CH}-\text{NH}-\text{C}(=\text{O})-$).

n = 10: ^1H -NMR (500 MHz, chloroform-*d*). δ (ppm) 0.88 (6.0H*, t, CH_3-), 1.26-1.30 (28.4 H, m, $-(\text{CH}_2)_7-$), 1.60 (4.0H, m, $-(\text{CH}_2)_7-\text{CH}_2-\text{CH}_2-\text{O}$), 3.17-3.35 (1.8H, dd, $-\text{C}(=\text{O})-\text{CH}_2-\text{CH}(-\text{OCO})-$), 4.10-4.26 (4.0H, m, $-(\text{CH}_2)_8-\text{CH}_2-\text{O}-$), 4.42 (2.0H, m, $-\text{C}(=\text{O})-\text{CH}_2-\text{SO}_3-$), 4.89 (1.0H, m, $-\text{CH}_2-\text{CH}(-\text{OCO})-\text{NH}-$), 8.02 (0.9H, d, $-\text{CH}-\text{NH}-\text{C}(=\text{O})-$).

n = 11: ^1H -NMR (500 MHz, chloroform-*d*). δ (ppm) 0.88 (6.0H*, t, CH_3-), 1.26-1.30 (32.4 H, m, $-(\text{CH}_2)_8-$), 1.60 (4.0H, m, $-(\text{CH}_2)_8-\text{CH}_2-\text{CH}_2-\text{O}$), 3.17-3.35 (1.8H, dd, $-\text{C}(=\text{O})-\text{CH}_2-\text{CH}(-\text{OCO})-$), 4.10-4.26 (4.0H, m, $-(\text{CH}_2)_9-\text{CH}_2-\text{O}-$), 4.42 (2.0H, m, $-\text{C}(=\text{O})-\text{CH}_2-\text{SO}_3-$), 4.89 (1.0H, m, $-\text{CH}_2-\text{CH}(-\text{OCO})-\text{NH}-$), 8.02 (0.9H, d, $-\text{CH}-\text{NH}-\text{C}(=\text{O})-$).

n = 12: ^1H -NMR (500 MHz, chloroform-*d*). δ (ppm) 0.88 (6.0H*, t, CH_3-), 1.26-1.30 (36.8 H, m, $-(\text{CH}_2)_9-$), 1.60 (4.0H, m, $-(\text{CH}_2)_9-\text{CH}_2-\text{CH}_2-\text{O}$), 3.17-3.35 (1.8H, dd, $-\text{C}(=\text{O})-\text{CH}_2-\text{CH}(-\text{OCO})-$), 4.10-4.26 (4.0H, m, $-(\text{CH}_2)_{10}-\text{CH}_2-\text{O}-$), 4.42 (2.0H, m, $-\text{C}(=\text{O})-\text{CH}_2-\text{SO}_3-$), 4.89 (1.0H, m, $-\text{CH}_2-\text{CH}(-\text{OCO})-\text{NH}-$), 8.02 (0.9H, d, $-\text{CH}-\text{NH}-\text{C}(=\text{O})-$).

General procedure of syntheses of [Pt(en)₂I](L-Asp-C_n)₂·H₂O

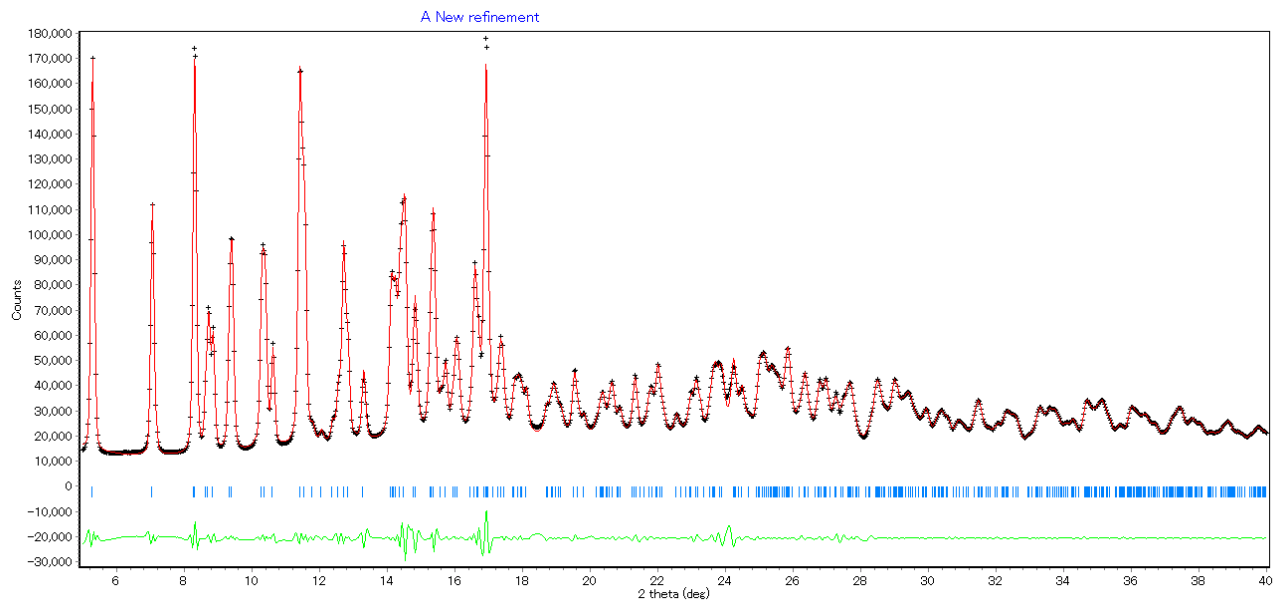
Crystals of [Pt(en)₂I](L-Asp-C_n)₂·H₂O (*n* = 8, 9, 10, 11 and 12) were synthesized by slow diffusion of aqueous solution (2 ml) of [Pt(en)₂I](ClO₄)₂ (6 mg, 10 μmol) and THF solution (1 ml) of sodium salt of L-Asp-C_n (20 μmol) in the 8mmϕ straight glass tube. Thin single crystals were formed at an interface of two solutions in several weeks.

Crystal structure determination and physical properties measurements

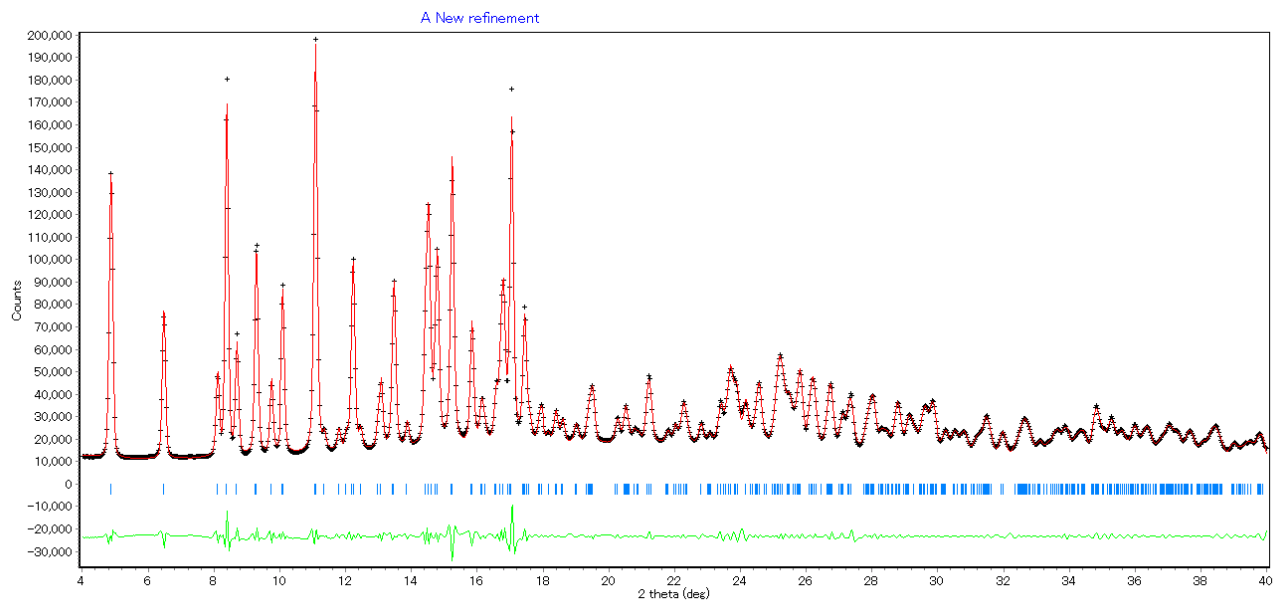
X-ray crystal structure determination of [Pt(en)₂I](L-Asp-C_n)₂·H₂O (*n* = 8, 10, 12) was made using a Rigaku CCD diffractometer (Saturn 70) with graphite monochromated Mo K α radiation (λ = 0.7107 Å). The unit cell parameters for [Pt(en)₂I](L-Asp-C_n)₂·H₂O (*n* = 8, 9, 10, 11, 12, and 14) were determined by LeBail fitting with Rietica software of the powder X-ray diffraction (PXRD) patterns taken with the synchrotron generated X-ray source (beam line 8A) at photon-factory of High Energy Accelerator Research Organization. An observation of superlattice (diffuse) scatterings are made with the Huber four-axes diffractometer on the beam line 4A combined with the synchrotron generated X-ray source installed in the photon-factory of High Energy Accelerator Research Organization.

LeBail fitting of PXRD patterns of $[\text{Pt}(\text{en})_2\text{I}](\text{L-Asp-C}_n)_2 \cdot \text{H}_2\text{O}$ ($n = 8, 9, 10, 11, 12$, and 14)

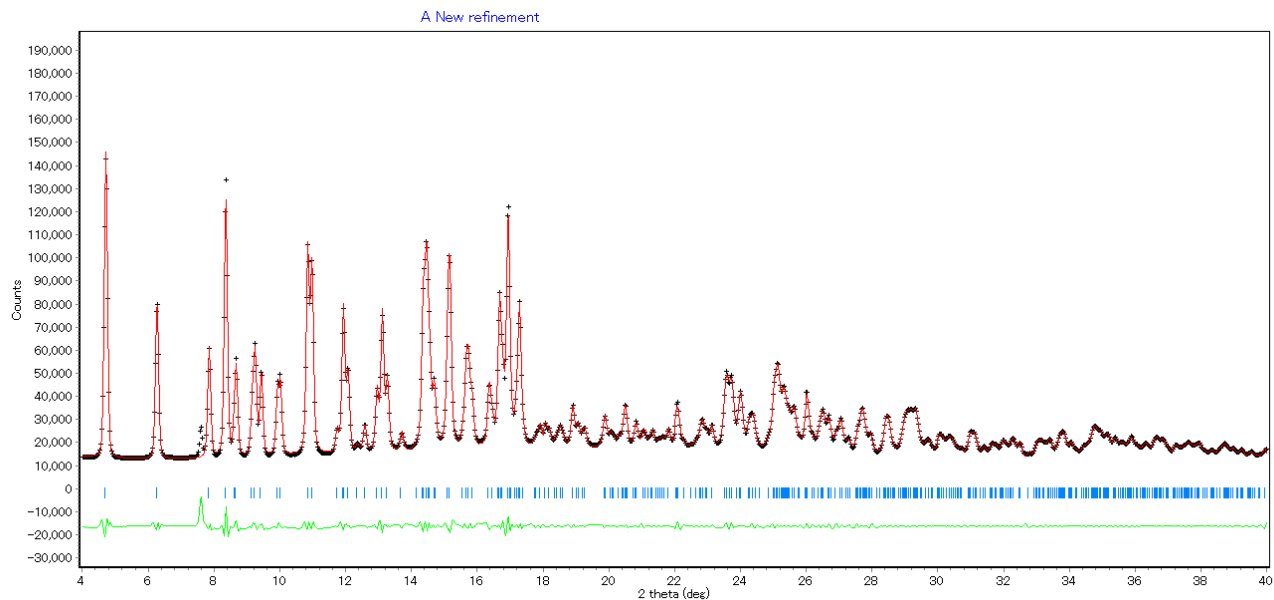
$[\text{Pt}(\text{en})_2\text{I}](\text{L-Asp-C}_8)_2 \cdot \text{H}_2\text{O}$ (300 K)



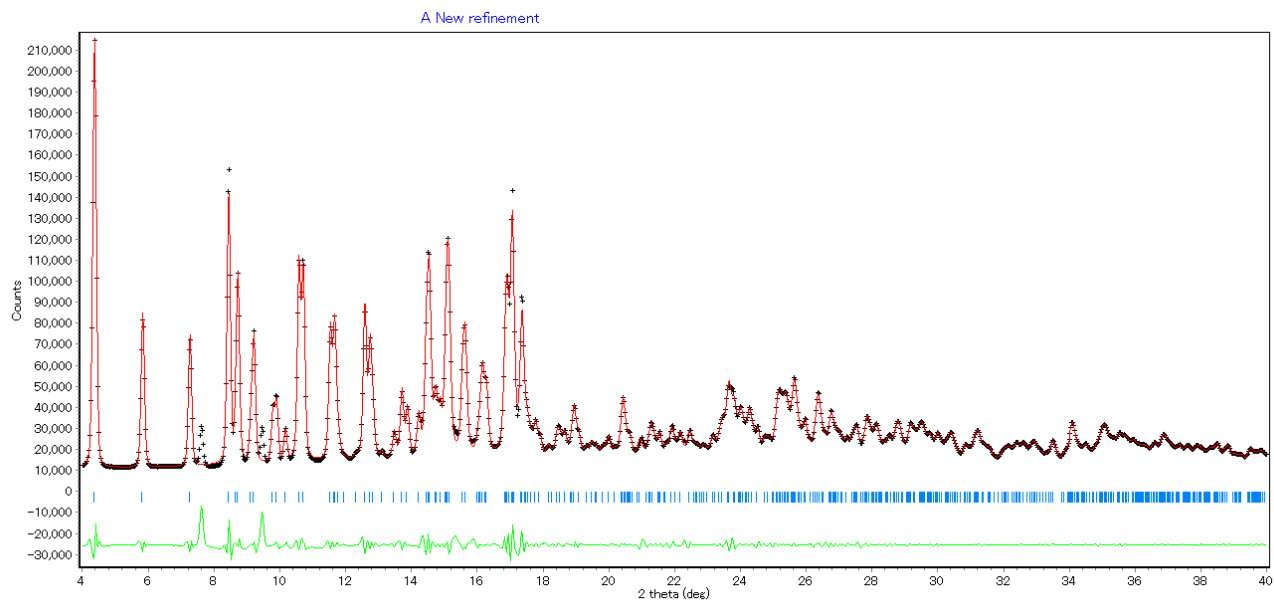
$[\text{Pt}(\text{en})_2\text{I}](\text{L-Asp-C}_9)_2 \cdot \text{H}_2\text{O}$ (300 K)



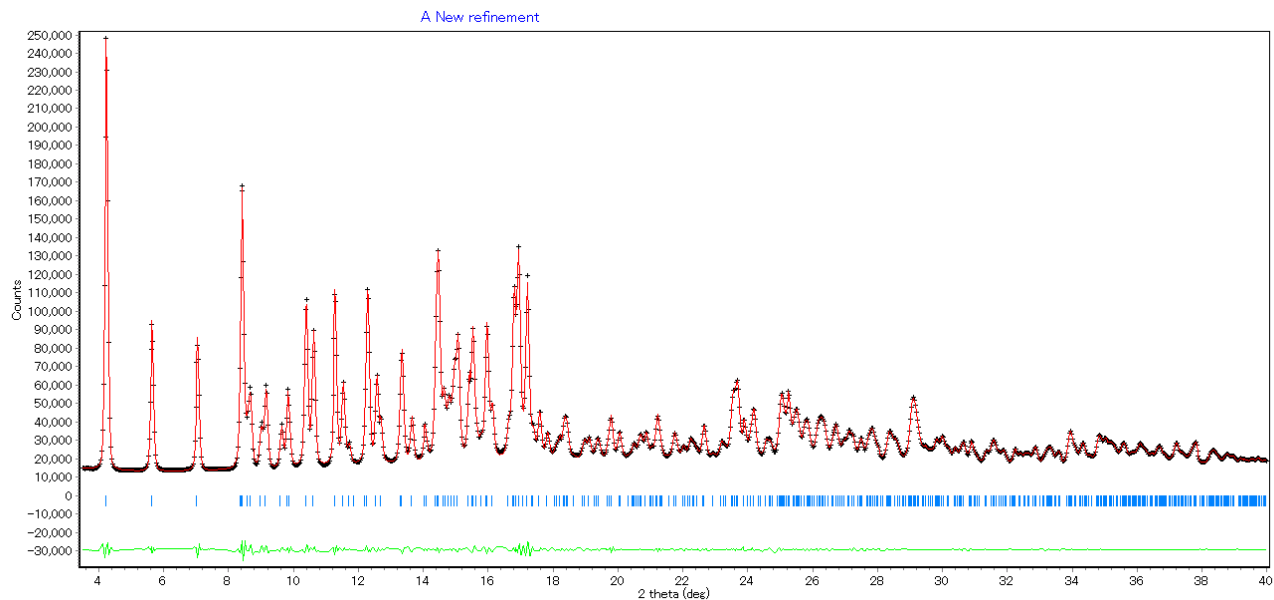
[Pt(en)₂](L-Asp-C₁₀)₂·H₂O (300 K)



[Pt(en)₂](L-Asp-C₁₁)₂·H₂O (300 K)



[Pt(en)₂](L-Asp-C₁₂)₂·H₂O (300 K)



[Pt(en)₂](L-Asp-C₁₄)₂·H₂O (300 K)

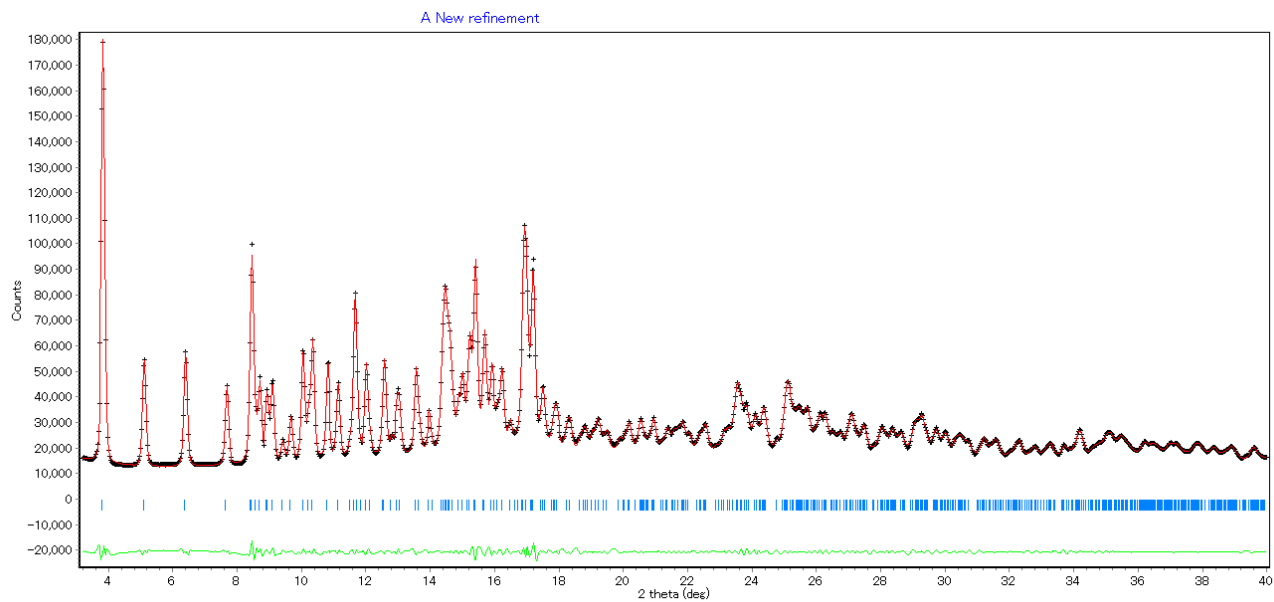


Table S1 Crystallographic parameters of [Pt(en)₂I](L-Asp-C_n)₂·H₂O (n = 8, 9, 10, 11, 12, and 14)

n	8	9	10	11	12	14
Empirical formula	C ₄₈ H ₉₈ IN ₆ O ₁₇ PtS ₂	C ₅₂ H ₁₀₆ IN ₆ O ₁₇ PtS ₂	C ₅₆ H ₁₁₄ IN ₆ O ₁₇ PtS ₂	C ₆₀ H ₁₂₂ IN ₆ O ₁₇ PtS ₂	C ₆₄ H ₁₃₀ IN ₆ O ₁₇ PtS ₂	C ₇₂ H ₁₄₆ IN ₆ O ₁₇ PtS ₂
Formula weight	1417.43	1473.54	1529.65	1585.75	1641.86	1754.07
Temperature / K	300(2)	300(2)	300(2)	300(2)	300(2)	300(2)
λ(Mo-Kα) / Å	1.1267	1.1267	1.1267	1.1267	1.1267	1.1267
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2	C2	C2	C2	C2	C2
a / Å	73.405(5)	80.233(4)	82.658(6)	89.388(9)	91.942(3)	101.270(6)
b / Å	5.5008(4)	5.5051(3)	5.5260(3)	5.5118(5)	5.5312(2)	5.5274(3)
c / Å	7.8131(6)	7.7682(4)	7.7794(5)	7.7106(8)	7.7291(3)	7.6803(5)
β	95.542(2)	95.347(3)	94.721(2)	94.226(3)	93.546	92.574(2)
Rp, Rwp	0.0168, 0.0275	0.0234, 0.0327	0.0172, 0.0322	0.0236, 0.0510	0.0130, 0.0198	0.0138, 0.0198

Oscillation photograph of $[\text{Pt}(\text{en})_2\text{I}](\text{L-Asp-C}_8)_2 \cdot \text{H}_2\text{O}$ at 300 K and 50 K

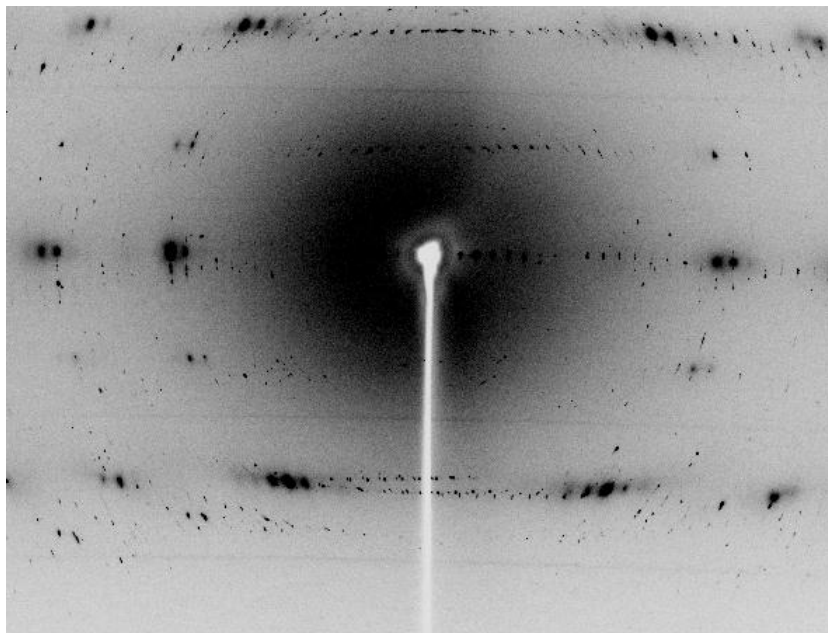


Figure S1 X-ray oscillation photograph of $[\text{Pt}(\text{en})_2\text{I}](\text{L-Asp-C}_8)_2 \cdot \text{H}_2\text{O}$ at 300 K.

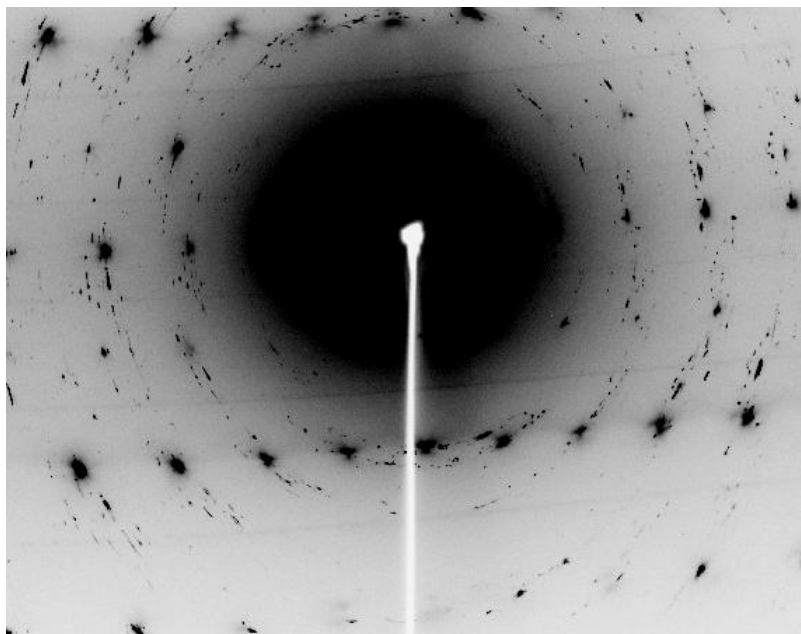


Figure S2 X-ray oscillation photograph of $[\text{Pt}(\text{en})_2\text{I}](\text{L-Asp-C}_8)_2 \cdot \text{H}_2\text{O}$ at 50 K.