Electronic Supplementary Information

for

Dual emissive ionic liquid based on an anionic platinum(II) complex

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References

Experimental details

Physical measurements

^{1}H NMR spectroscopy was performed using a JEOL EX-270 NMR spectrophotometer. Elemental analyses were carried out at the analysis center in Hokkaido University. Thermogravimetry-differential thermal analysis (TG-DTA) measurements were recorded using a Rigaku Thermoplus EVO TG-DTA 8120 with Al sample pans under a N_2 flow. Differential scanning calorimetry (DSC) measurements were performed using a METTLER DSC 1 under a N_2 flow. Variable-temperature powder X-ray diffraction measurements (VT-PXRD) were measured with Cu Kα using a Bruker D8 Advance diffractometer equipped with a graphite monochrometer, a one dimensional LinxEye detector and Anton Paar TTK 450 low-temperature chamber. Absorption spectra were measured using a Shimadzu UV-2500PC Spectrophotometer under N_2 atmosphere using quartz cells with a thickness of either 1 cm or 1 mm.

Luminescence measurements

All luminescence measurements of neat **1** were performed under N_2 atmosphere. Luminescence spectra were measured using a JASCO FR-6600 spectrofluorometer at room temperature and 77 K. Slit widths of the excitation and emission light were 5 or 6 nm. Variable Temperature luminescence spectra were measured by single photon counting using a Hamamatsu Absolute PL Quantum Yield Measurement System C9920-02. Luminescence quantum yields were recorded on a Hamamatsu Photonics C9920-02 absolute photoluminescence quantum yield measurement system equipped with an integrating sphere apparatus and 150 W CW Xenon light source. Hamamatsu Photonics A10095-03 non-luminescent quartz sample holder was used for absolute photoluminescence quantum yield measurements. The accuracy of the instrument was confirmed by the measurement of quantum yield of anthracene in ethanol solution (Φ = 0.27).[1] Emission life time measurements were recorded using a Hamamatsu Photonics, C4334 system equipped with a streak camera as a Photo detector and a nitrogen laser for the 337 nm excitation. Liquid N_2 cryostat (Optistat-DN optical Dewar and ITC-503 temperature controller, Oxford Instruments) was used for the temperature control.

Single crystal X-ray diffraction measurements

All single crystal X-ray diffraction measurements were performed using a Rigaku AFC-7R diffractometer with a Mercury CCD area detector and graphite monochromatized Mo Kα

radiation (λ = 0.71069 Å) at 200 K (complex **2**) and 150 K (complex **3**), respectively. Each single-crystal was mounted on a MicroMount using liquid paraffin. These crystals were cooled using a N_2-flow type temperature controller. Diffraction data were collected and processed using the Crystal-Clear software.[2] The structures were solved by direct methods (SIR2004[3] for **2**, SIR2011[4] for **3**). Structural refinements were conducted by the full-matrix least-squares method using SHELXL-97.[5] Non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were refined using the rigid model. All calculations were performed using the CrystalStructure crystallographic software package[6] except for refinement. The crystallographic data of **2** and **3** are summarized in Table S2.

Synthesis

Materials

2-(*p*-tolyl)pyridine (Hptpy), $AgClO_4$, KCN, *n*-Bu_4NClO_4, *N*-methylimidazole, bromoethane and 2-ethoxyethanol were purchased from Wako Pure Chemical Industries. Potassium tetrachloroplatinate(II) ($K_2[PtCl_4]$) was purchased from Tanaka Holdings Co., Inc. All solvents were purchased from Kanto Chemical Co., Inc. All of solvents for the measurements were distilled by standard methods under a N_2 atmosphere.

1-methyl-3-ethylimidazolium Bromide ([C_2mim][Br]) was synthesized by the literature method.[7]

[Pt(ptpy)(μ-Cl)]$_2$ was synthesized according to the synthetic method reported previously.[8] All of the solvents for syntheses were used without further purification. All measurements were performed under a N_2 atmosphere.

K[Pt(CN)$_2$(ptpy)] (3)

K[Pt(CN)$_2$(ptpy)] was synthesized according to the literature method[9] with slight modifications as follows. To the suspension of [Pt(ptpy)(μ-Cl)]$_2$ (163 mg, 0.41 mmol) in acetonitrile (45 mL) was added $AgClO_4$ (85 mg, 0.82 mmol). After stirred for 7 h in the dark condition, the mixture was filtered through celite. The resulting yellow solution was evaporated to dryness. The yellow solid was suspended in methanol (45 mL), and KCN (53 mg, 0.82 mmol) was added. After stirring for 2h, the reaction mixture was filtered through celite and evaporated to dryness. Luminescent yellow powder was produced. By the recrystallization from acetone/Et$_2$O, yellow crystals suitable for the single X-ray crystallography were obtained as **3**·$2H_2O$·CH_3COCH_3, although the included acetone and water molecules were easily released in the air.

Yield, 140 mg (0.31 mmol, 74%). ^{1}H NMR (Acetone-*d$_6$*, 270 MHz): δ = 9.42 (td, *J* = 15.1,

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1.6 Hz, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.98 (t, J = 25.1 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.24 (td, J = 5.4, 1.3 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 2.27 (s, 3H). Anal: Calc. for $C_{14}H_{10}N_3PtK \cdot 1.5H_2O$: C, 34.93; H, 2.72; N, 8.73%. Found: C, 35.09; H, 2.72; N, 8.45%

[C$_2$mim][Pt(CN)$_2$(ptpy)] (1)

K[Pt(CN)$_2$(ptpy)] (181 mg, 0.40 mmol) and [C$_2$mim][Br] (76 mg, 0.40 mmol) were dissolved in dichloromethane (50 mL) and stirred for 1h at room temperature. The yellow suspension was filtrated using celite, and then the yellow solution was washed with water until no bromine ions were detected in AgNO$_3$ test. The organic layer was evaporated and dried under reduced pressure at 100°C for 12h. The yellow viscous liquid was yielded. Yield, 134 mg (0.152 mmol, 38%). ^{1}H NMR (CDCl$_3$, 270 MHz): δ = 9.65 (s, 1H), 9.28 (td, J = 16.7, 7.8 Hz, 1H), 7.90 (t, J = 24.9 Hz, 1H), 7.72 (t, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.18 (m, 2H), 7.00 (t, J = 7.2 Hz, 2H), 6.86 (d, J = 7.6 Hz, 1H), 4.41 (q, J = 7.2 Hz, 2H), 4.06 (s, 3H), 2.26 (s, 3H), 1.55 (s, 3H). Anal: Calc. for $C_{20}H_{22}N_5Pt \cdot 0.5H_2O$: C, 44.86; H, 4.14; N, 13.08%. Found: C, 44.94; H, 3.89; N, 12.90%. Included water molecules were checked by thermogravimetry-differential thermal analysis.

n-Bu$_4$N[Pt(CN)$_2$(ptpy)] (2)

n-Bu$_4$N[Pt(CN)$_2$(ptpy)] was synthesized according to the literature method with slight modifications as follows. To the suspension of [Pt(ptpy)(μ-Cl)]$_2$ (144 mg, 0.18 mmol) in acetonitrile (35 mL) was added AgClO$_4$ (75 mg, 0.36 mmol). After stirred for 7 h in the dark condition, the mixture was filtered through celite. The resulting yellow solution was evaporated to dryness. The yellow solid was suspended in methanol (35 mL), and KCN (45 mg, 0.70 mmol) was added. After stirring for 2h, the reaction mixture was filtered through celite and evaporated to dryness. The resulting yellow solid was suspended in acetone (35 mL) and *n*-Bu$_4$NClO$_4$ (119 mg, 0.35 mmol) was added. Then, the suspension was filtered through celite and evaporated under reduced pressure. By the recrystallization from MeCN/Et$_2$O, pale yellow crystals were obtained as the acetonitrile solvated form.

Yield, 205 mg (0.31 mmol, 90%). ^{1}H NMR (Acetone-d_6, 270 MHz): δ = 9.46 (td, J = 15.1, 1.6 Hz, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.96 (t, J = 25.1 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.23 (td, J = 5.4, 1.3 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 3.46 (m, 8H), 2.27 (s, 3H), 1.83(m, 8H), 1.45 (m, 8H), 0.97 (t, J = 7.3 Hz, 12H). Anal.: Calc. for $C_{30}H_{46}N_4Pt \cdot 0.5CH_3CN$: C, 54.89; H, 7.06; N, 9.29%. Found: C, 54.71; H, 7.06; N, 9.26%.

Table S1. Luminescence data of neat **1** at 298 K and 77 K.

Temperature	$\lambda_{em}{}^a$ (nm)	Φ^b	τ^c [μs (A^d)]	$\chi^{2\,e}$	$\tau_{av}{}^f$ (μs)	$k_r{}^g$ (s^{-1})	$k_{nr}{}^h$ (s^{-1})
298 K	493, 532, 564	0.06	0.91 (0.86), 3.57 (0.362)	1.185	2.57	2.3×10^4	3.6×10^5
77 K	494, 532, 561	0.47	9.72 (0.646), 22.09 (0.449)	1.023	17.2	2.7×10^4	3.1×10^4

^{a} Emission maxima. ^{b} Photoluminescence quantum yield. ^{c} Emission lifetimes; Emission decays were analyzed with two components: $I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$. ^{d} Pre-exponential factors. ^{e} Fitting parameter. ^{f} Average emission lifetimes were determined by using the equation 1.[10] ^{g} Radiative rate constants k_r were estimated by Φ/τ_{av}. ^{h} Nonradiative rate constants k_{nr} were estimated by $k_{nr.} = -k_r + 1/\tau_{av}$.

$$\tau_{av} = \frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2} \qquad (1)$$

Table S2. Emission lifetime data of neat **1** at 298 K recorded by different wavelength.

$\lambda_{det}{}^a$ (nm)		486 - 500	501 - 550	551 - 629
τ^b [μs (A^c)]	$\tau_1(A_1)$	0.192 (0.760)	1.035 (0.285)	1.330 (0.401)
	$\tau_2(A_2)$	0.849 (0.243)	3.565 (0.467)	4.164 (0.485)
	$\tau_3(A_3)$	3.240 (0.154)		
$\tau_{av}{}^d$ (μs)		2.14	3.18	3.57
$\chi^{2\,e}$		1.009	1.172	1.149
k^f (s^{-1})		5×10^6, 1.2×10^6, 3.1×10^5	9.6×10^5, 2.8×10^5	7.5×10^5, 2.4×10^5

^{a} Emission detection regions. ^{b} Emission lifetimes; Emission decays were analyzed with two or three components: $I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$ or $I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) + A_3\exp(-t/\tau_3)$. ^{c} Pre-exponential factors. ^{d} Average emission lifetimes determined using equation 1 or 2.[10] ^{e} Fitting parameter. ^{f} Rate constants of each lifetime components estimated by ($k = 1/\tau$).

$$\tau_{av} = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3} \qquad (2)$$

Table S3. Luminescence data of **1** at 298 K in MeOH (1.0×10^{-4}).

$\lambda_{em}{}^{a}$ (nm)	Φ^{b}	τ^{c} [µs (A^{d})]	$\chi^{2\,e}$	$\tau_{av}{}^{f}$ (µs)	$k_r{}^{g}$ (s^{-1})	$k_{nr}{}^{h}$ (s^{-1})
486, 518, 560(sh)	0.03	1.335 (0.636)	1.198	2.53	1.2×10^{4}	3.8×10^{5}
		3.196 (0.486)				

[a] Emission maxima. [b] Photoluminescence quantum yield. [c] Emission lifetimes; Emission decays were analyzed with two components: $I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2)$. [d] Pre-exponential factors. [e] Fitting parameter. [f] Average emission lifetimes were determined by using the equation 1. [g] Radiative rate constants k_r were estimated by Φ/τ_{av}. [h] Nonradiative rate constants k_{nr} were estimated by $k_{nr.} = -k_r + 1/\tau_{av}$.

Table S4. Emission spectral data of **2**

	n-Bu$_4$N[Pt(CN)$_2$(ptpy)] (**2**)	
Temperature	77 K	298 K
λ_{max} / nm	486, 520, 550(sh)	487, 521, 560(sh)
Φ_{em}	0.95	0.72

Table S5. Emission spectral data of **3**

	K[Pt(CN)$_2$(ptpy)] (**3**)	
Temperature	77 K	298 K
λ_{max} / nm	561	558
Φ_{em}	0.32	0.09

Table S6. Crystallographic data of **2**·CH_3CN and **3**·$2H_2O$·CH_3COCH_3

	n-Bu$_4$N[Pt(CN)$_2$(ptpy)]·CH$_3$CN (**2**·CH$_3$CN)	K[Pt(CN)$_2$(ptpy)]·2H$_2$O·CH$_3$COCH$_3$ (**3**·2H$_2$O·CH$_3$COCH$_3$)
Formula	$C_{32}H_{48}N_5Pt$	$C_{31}H_{30}K_2N_6O_3Pt_2$
Formula Weight	697.85	1002.99
Crystal system	monoclinic	monoclinic
Space group	P2$_1$/c	P2$_1$/c
a (Å)	22.614(8)	19.743(5)
b (Å)	8.529(3)	12.197(3)
c (Å)	17.808(6)	14.509(4)
α (°)	90	90
β (°)	107.887(5)	108.445(3)
γ (°)	90	90
V (Å^3)	3269(2)	3314(2)
T (K)	200	150
Z	4	4
D_{calc} (g cm^{-3})	1.418	2.010
$F(000)$	1412.00	1904.00
measured reflns	21244	25015
unique refns	7163	7536
GOF on F^2	1.074	1.068
R_{int}	0.0393	0.0524
R_1[a]	0.0365	0.0458
wR_2[b](all data)	0.0961	0.1278

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o)^2]^{1/2}$, $w = [\sigma_c^2(F_o^2) + (xP)^2 + yP]^{-1}$, $P = (F_o^2 - 2F_c^2)/3$.

Table S7. Selected bond lengths of **2**·CH$_3$CN

Atom1	Atom2	Length
Pt1	N1	2.066(4)
Pt1	C11	2.023(5)
Pt1	C13	1.942(5)
Pt1	C14	2.028(5)
N1	C1	1.340(7)
N1	C5	1.358(6)
N2	C13	1.145(7)
N3	C14	1.138(7)
C1	C2	1.39(1)
C2	C3	1.38(1)
C3	C4	1.360(8)
C4	C5	1.398(9)
C5	C6	1.463(6)
C6	C7	1.411(7)
C6	C11	1.413(8)
C7	C8	1.371(9)
C8	C9	1.394(9)
C9	C10	1.396(7)
C9	C12	1.534(9)
C10	C11	1.393(6)

Table S8. Selected bond angles of **2**·CH₃CN

Atom1	Atom2	Atom3	Angle
N1	Pt1	C11	80.5(2)
N1	Pt1	C13	175.1(2)
N1	Pt1	C14	95.3(2)
C11	Pt1	C13	94.7(2)
C11	Pt1	C14	175.8(2)
C13	Pt1	C14	89.5(2)
Pt1	N1	C1	125.4(3)
Pt1	N1	C5	115.4(3)
C1	N1	C5	119.1(4)
N1	C1	C2	122.5(5)
C1	C2	C3	118.1(6)
C2	C3	C4	120.2(6)
C3	C4	C5	119.7(5)
N1	C5	C4	120.2(4)
N1	C5	C6	114.1(4)
C4	C5	C6	125.7(4)
C5	C6	C7	122.5(4)
C5	C6	C11	116.2(4)
C7	C6	C11	121.3(4)
C6	C7	C8	119.2(5)
C7	C8	C9	121.5(5)
C8	C9	C10	118.3(5)
C8	C9	C12	121.3(5)
C10	C9	C12	120.5(5)
C9	C10	C11	122.9(5)
Pt1	C11	C6	113.6(3)
Pt1	C11	C10	129.7(4)
C6	C11	C10	116.7(4)
Pt1	C13	N2	178.6(4)
Pt1	C14	N3	177.3(5)

Table S9. Selected bond lengths of **3**·2H$_2$O·CH$_3$COCH$_3$

Atom1	Atom2	Length
Pt1	N1	2.055(8)
Pt1	C11	2.018(7)
Pt1	C13	1.926(9)
Pt1	C14	2.022(7)
N1	C1	1.35(1)
N1	C5	1.360(9)
N2	C13	1.16(1)
N3	C14	1.16(1)
C1	C2	1.39(1)
C2	C3	1.37(1)
C3	C4	1.37(1)
C4	C5	1.40(1)
C5	C6	1.46(1)
C6	C7	1.394(9)
C6	C11	1.42(1)
C7	C8	1.39(1)
C8	C9	1.42(1)
C9	C10	1.39(1)
C9	C12	1.49(1)
C10	C11	1.40(1)
Pt2	N4	2.055(8)
Pt2	C25	2.018(7)
Pt2	C27	1.926(9)
Pt2	C28	2.022(7)
N4	C15	1.35(1)
N4	C19	1.360(9)
N5	C27	1.16(1)
N6	C28	1.16(1)
C15	C16	1.38(1)
C16	C17	1.38(1)
C17	C18	1.37(1)

C18	C19	1.39(1)
C19	C20	1.47(1)
C20	C21	1.39(1)
C20	C25	1.36(1)
C21	C22	1.36(1)
C22	C23	1.43(1)
C23	C24	1.39(1)
C23	C26	1.50(1)
C24	C25	1.41(1)

Table S10. Selected bond angles of **3**·2H$_2$O·CH$_3$COCH$_3$

Atom1	Atom2	Atom3	Angle
N1	Pt1	C11	81.0(3)
N1	Pt1	C13	174.9(3)
N1	Pt1	C14	95.6(3)
C11	Pt1	C13	94.0(3)
C11	Pt1	C14	176.3(3)
C13	Pt1	C14	89.3(3)
Pt1	N1	C1	124.7(6)
Pt1	N1	C5	115.4(5)
C1	N1	C5	119.9(7)
N1	C1	C2	121.4(8)
C1	C2	C3	117.9(8)
C2	C3	C4	121.9(9)
C3	C4	C5	118.3(8)
N1	C5	C4	120.5(7)
N1	C5	C6	114.3(7)
C4	C5	C6	125.2(7)
C5	C6	C7	123.3(7)
C5	C6	C11	116.0(7)
C7	C6	C11	120.7(7)
C6	C7	C8	121.3(7)
C7	C8	C9	118.6(7)
C8	C9	C10	119.6(7)
C8	C9	C12	121.4(7)
C10	C9	C12	122.6(7)
C9	C10	C11	122.9(5)
Pt1	C11	C6	113.3(6)
Pt1	C11	C10	129.4(6)
C6	C11	C10	117.3(7)
Pt1	C13	N2	178.0(8)
Pt1	C14	N3	178.9(8)
N4	Pt2	C25	80.2(3)

N4	Pt2	C27	175.3(3)
N4	Pt2	C28	95.8(3)
C25	Pt2	C27	95.5(3)
C25	Pt2	C28	174.7(3)
C27	Pt2	C28	88.4(4)
Pt2	N4	C15	123.7(5)
Pt2	N4	C19	115.3(5)
C15	N4	C19	120.9(6)
N4	C15	C16	121.3(7)
C15	C16	C17	119.4(8)
C16	C17	C18	118.5(8)
C17	C18	C19	121.1(7)
N4	C19	C18	118.8(7)
N4	C19	C20	114.2(6)
C18	C19	C20	127.0(7)
C19	C20	C21	122.5(7)
C19	C20	C25	115.9(7)
C21	C20	C25	121.6(7)
C20	C21	C22	121.2(8)
C21	C22	C23	119.7(8)
C22	C23	C24	118.1(7)
C22	C23	C26	120.7(7)
C24	C23	C26	121.2(7)
C23	C24	C25	122.6(7)
Pt2	C25	C20	114.0(5)
Pt2	C25	C24	129.1(5)
C20	C25	C24	116.8(7)
Pt2	C27	N5	175.8(8)
Pt2	C28	N6	176.4(8)
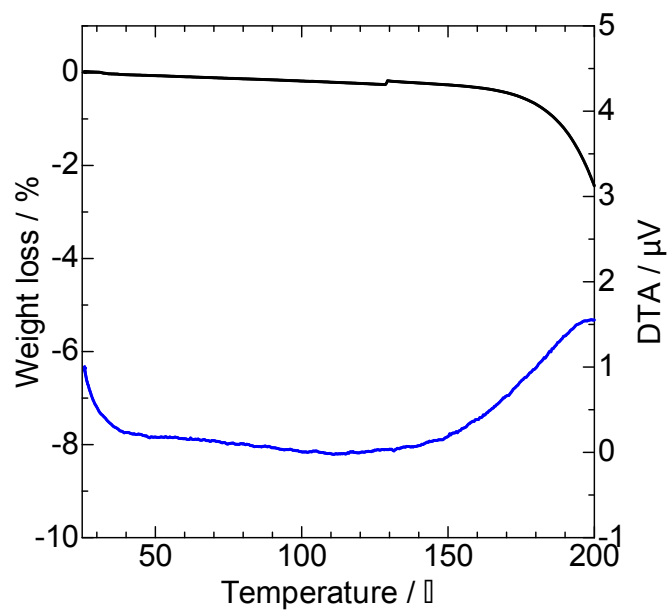
Fig. S1 Thermogravimetry-differential thermal analyses of **1** at scan rate of 5 K min^{-1} (TG (black), DTA (blue)).
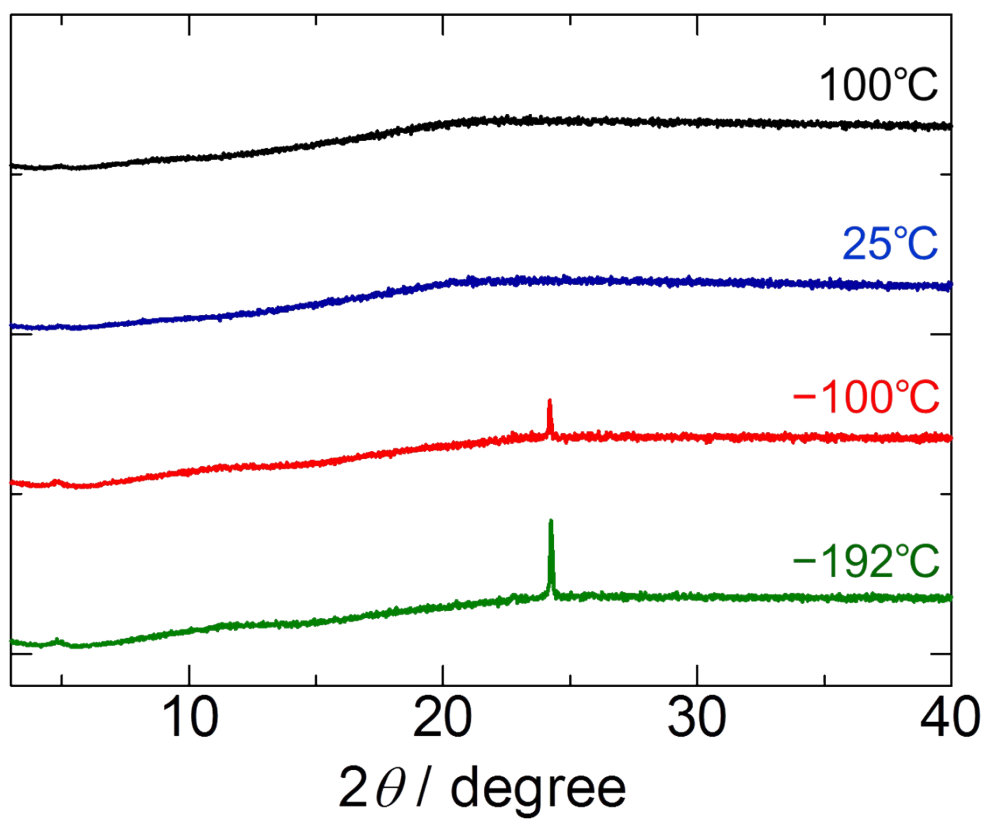
Fig. S2 VT-PXRD patterns of **1** at 100°C (black), 25°C (blue), −100°C (red) and −192°C (green).
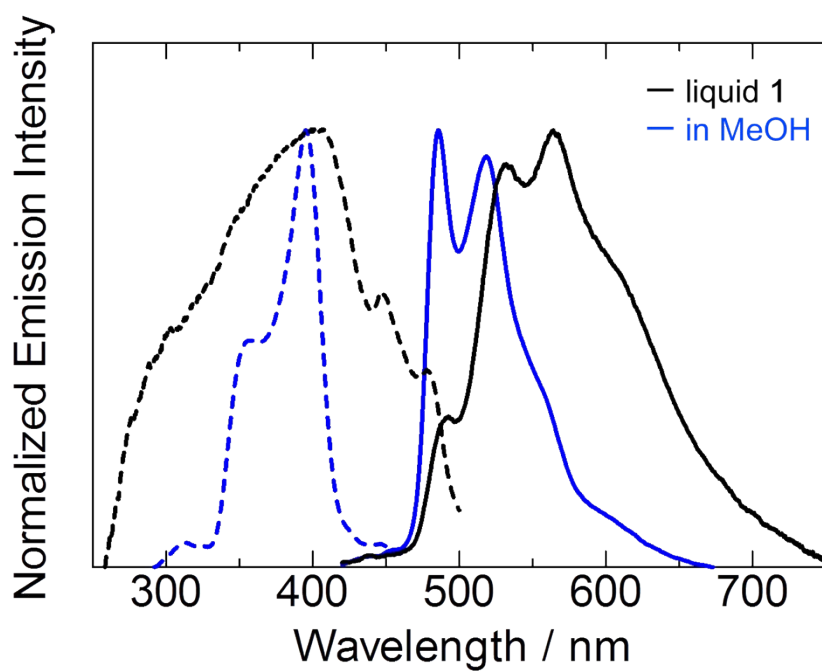
Fig. S3 Emission (solid lines) and excitation (dotted lines) spectra of **1** in liquid state (black, λ_{ex} = 400 nm, λ_{em} = 560 nm) and a MeOH solution (1.0×10^{-3} mol L^{-1}) (blue, λ_{ex} = 400 nm, λ_{em} = 480 nm) at 298 K under N_2 atmosphere.
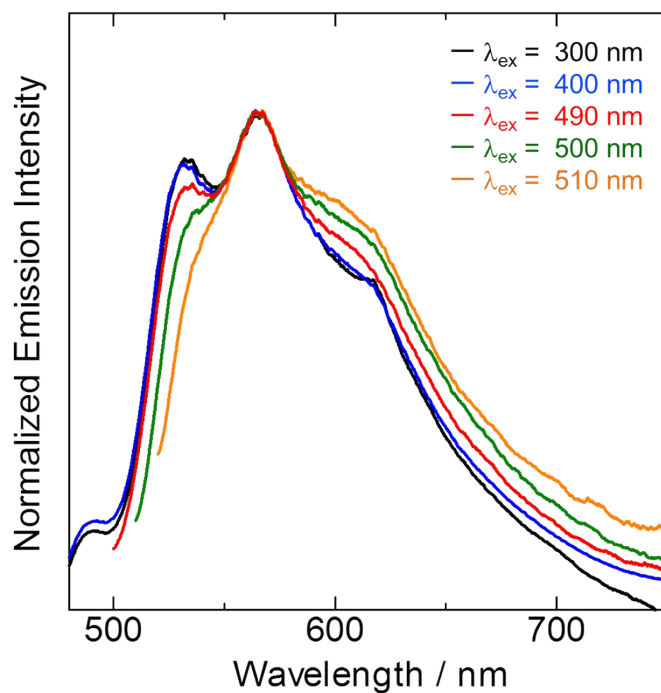
Fig. S4 Excitation wavelength dependency for emission spectra of **1**. Thin liquid membrane condition of neat **1** sandwiched in two quartz plates were measured under N_2 atmosphere at 298 K.
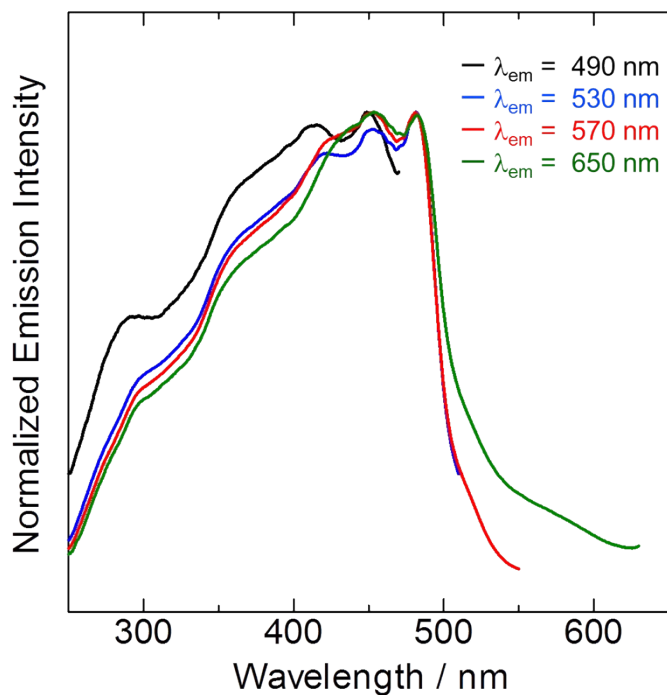
Fig. S5 Excitation spectra of **1** detected at different emission wavelengths at 298 K. Neat liquid state of **1** were measured with quartz tube under N_2 atmosphere.
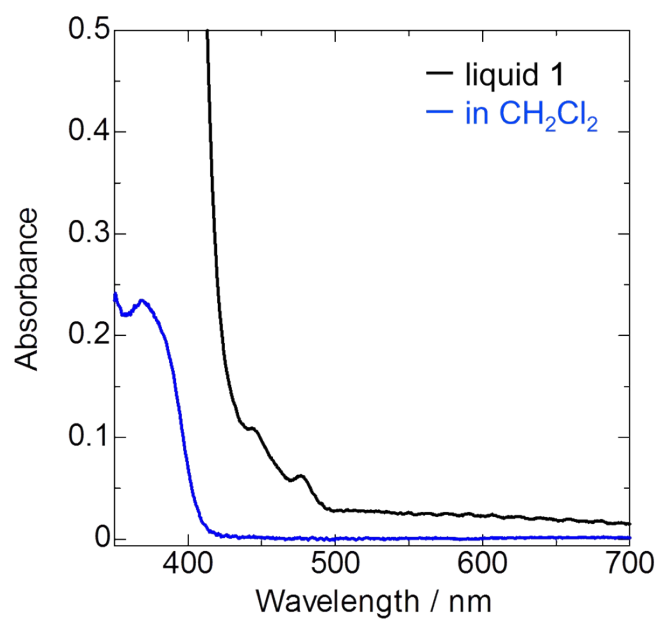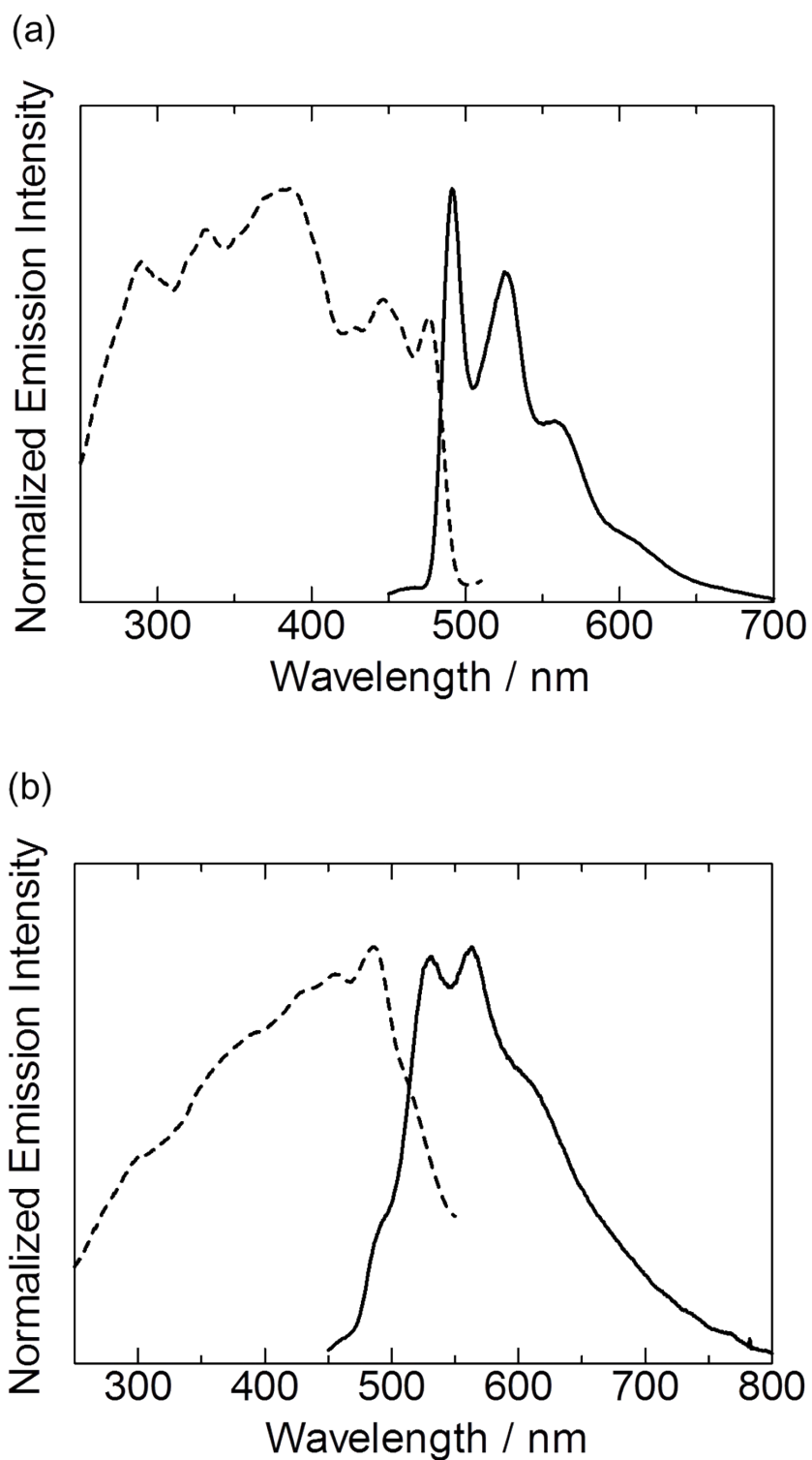
Fig. S6 Absorption spectra of neat liquid **1** (black line) and **1** in CH_2Cl_2 (blue line, 1.0×10^{-4} M)
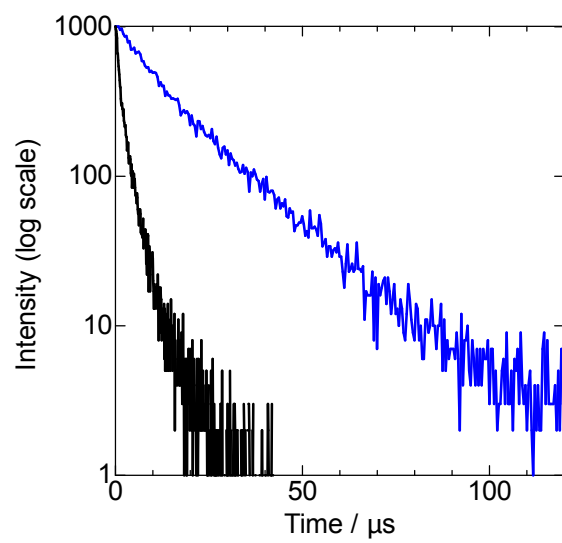
Fig. S7 Emission decay curves of ionic liquid **1** at 298 K (black line) and 77 K (blue line).
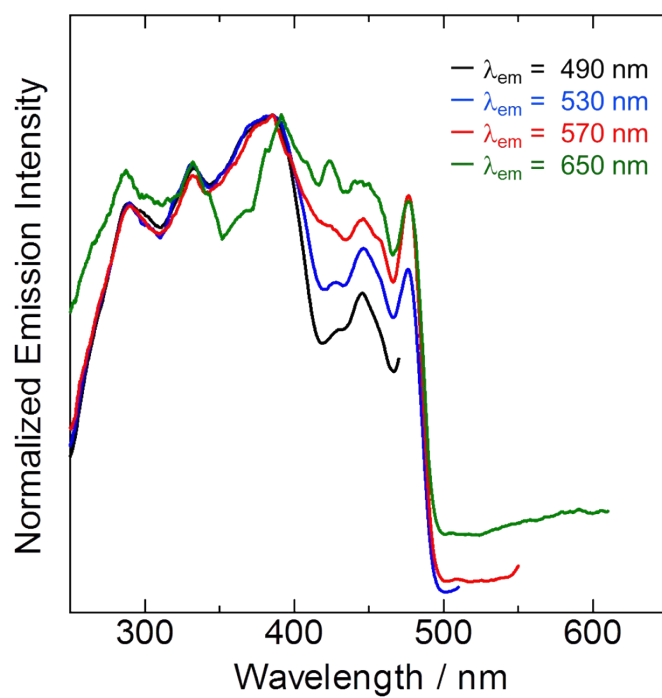
Fig. S8 Excitation spectra of **1** detected at different emission wavelengths at 77 K. Neat of **1** was measured with a quartz tube under N$_2$ atmosphere.

(a)

(b)

Fig. S9 Emission (solid lines) and excitation (dotted lines) spectra of neat **1** at (a) 77 K (λ_{ex} = 400 nm, λ_{em} = 560 nm) and (b) 333 K (λ_{ex} = 400 nm, λ_{em} = 570 nm) under N_2 atmosphere.
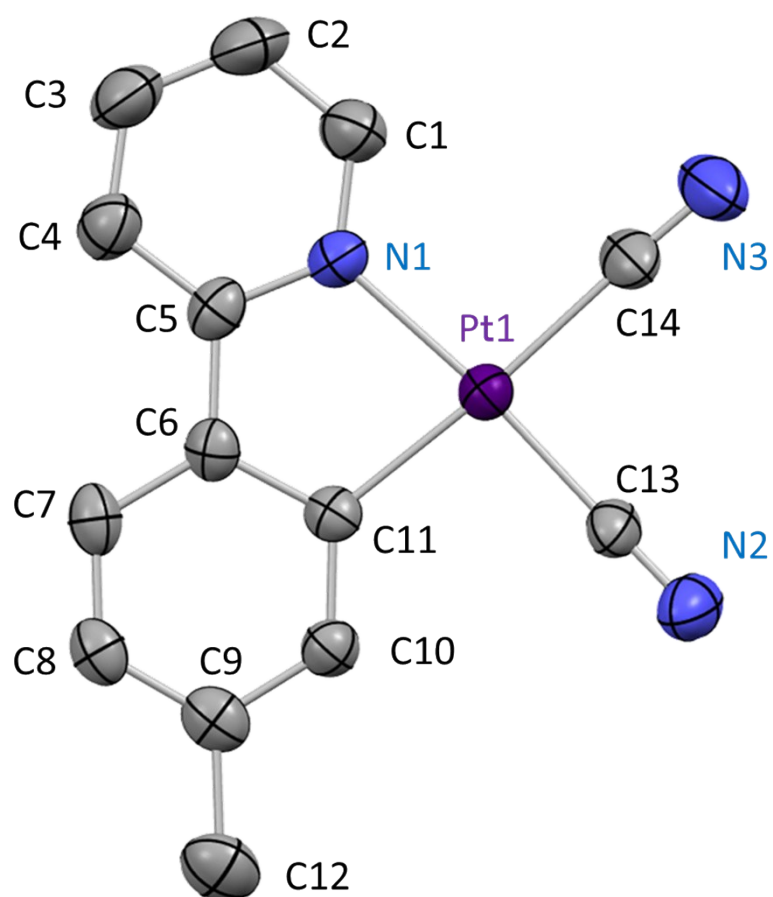
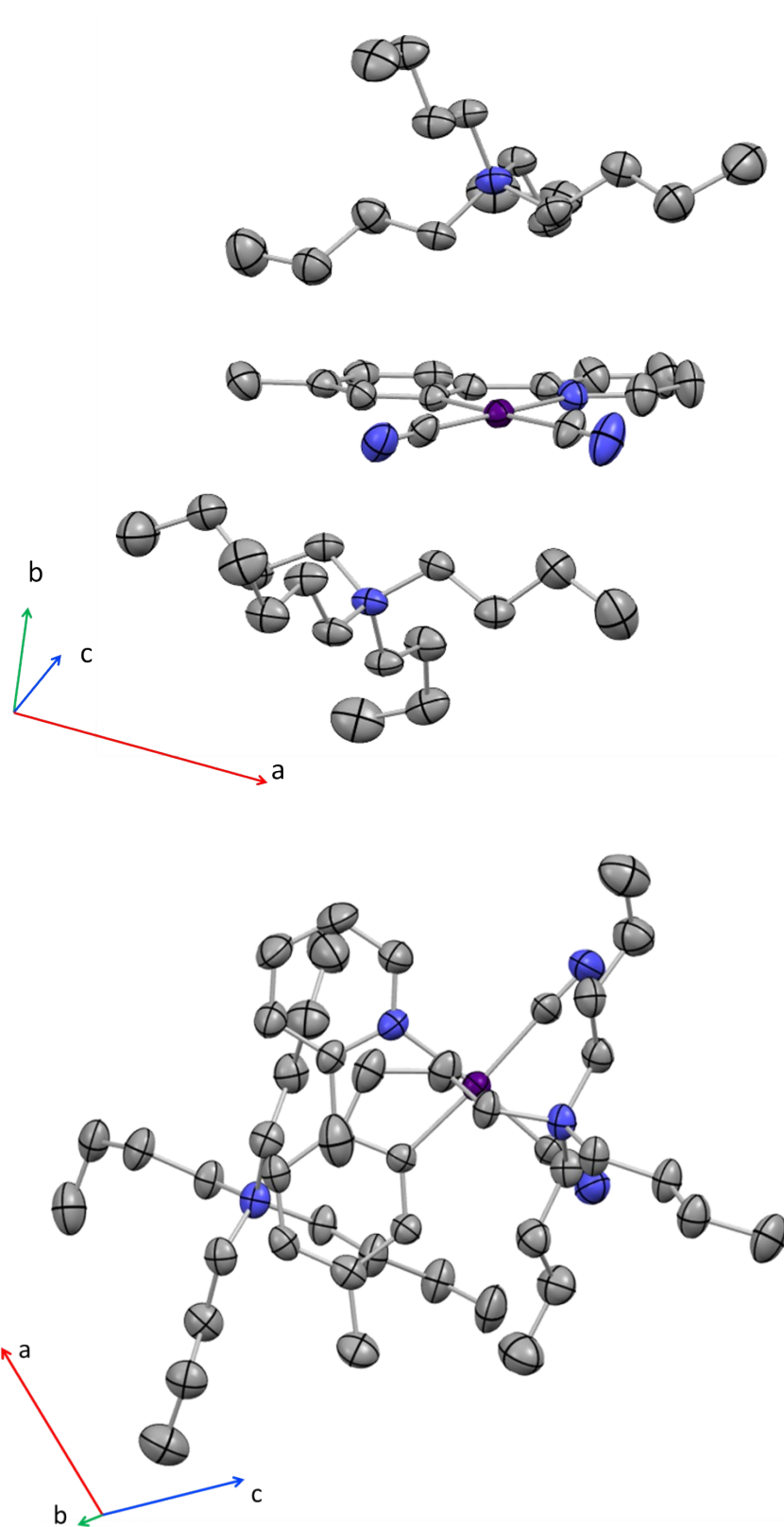**Fig. S10** Molecular structure of $[Pt(CN)_2(ptpy)]^-$ in complex **2**·CH_3CN. H atoms are omitted for clarity.

Fig. S11 Perspective views of the complex anion and adjacent *n*-Bu$_4$N$^+$ cations in **2**·CH$_3$CN. H atoms are omitted for clarity.
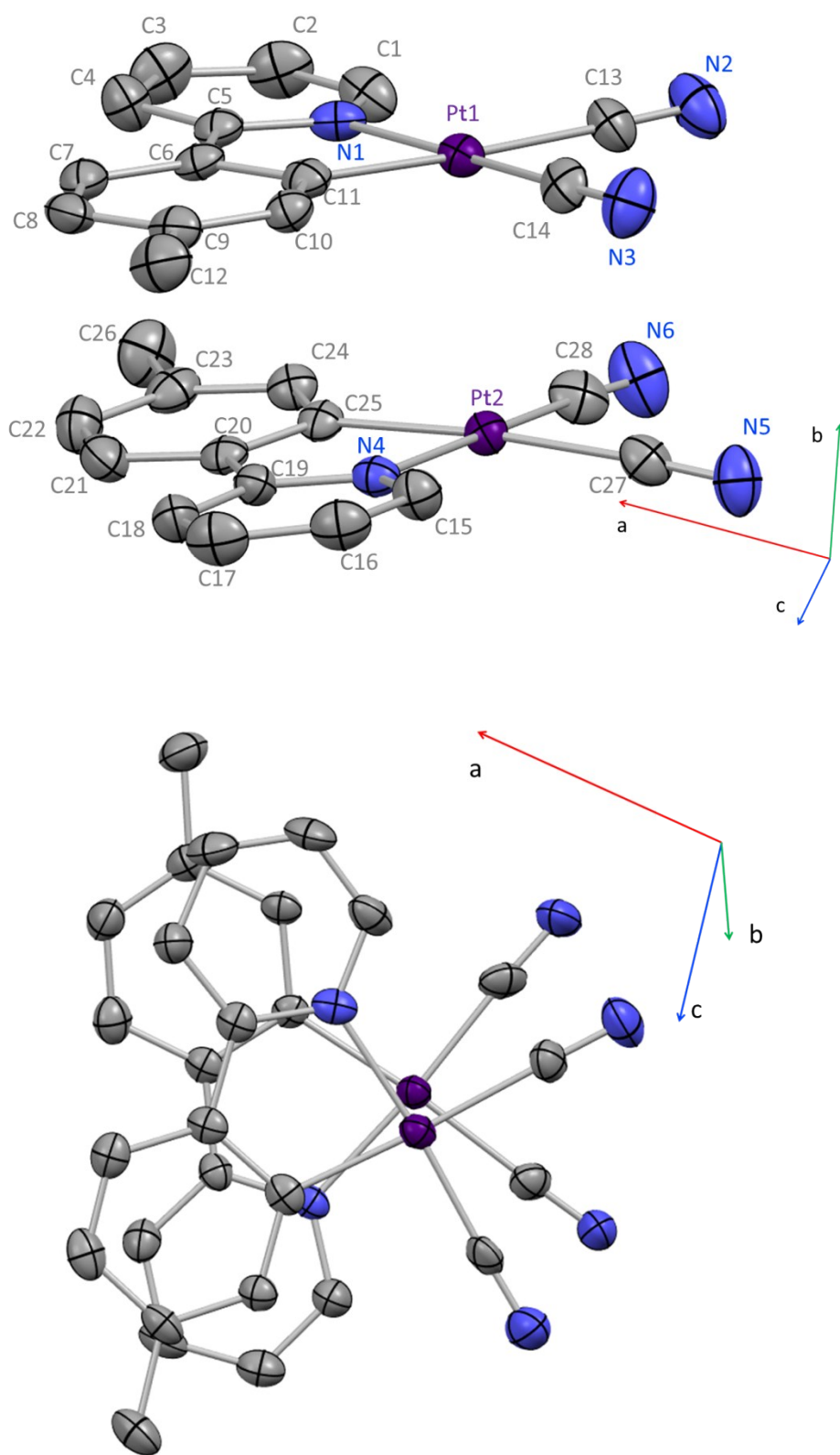
Fig. S12 Perspective views illustrating the dimeric complex anions in **3**·2H$_2$O·CH$_3$COCH$_3$. H atoms are omitted for clarity.
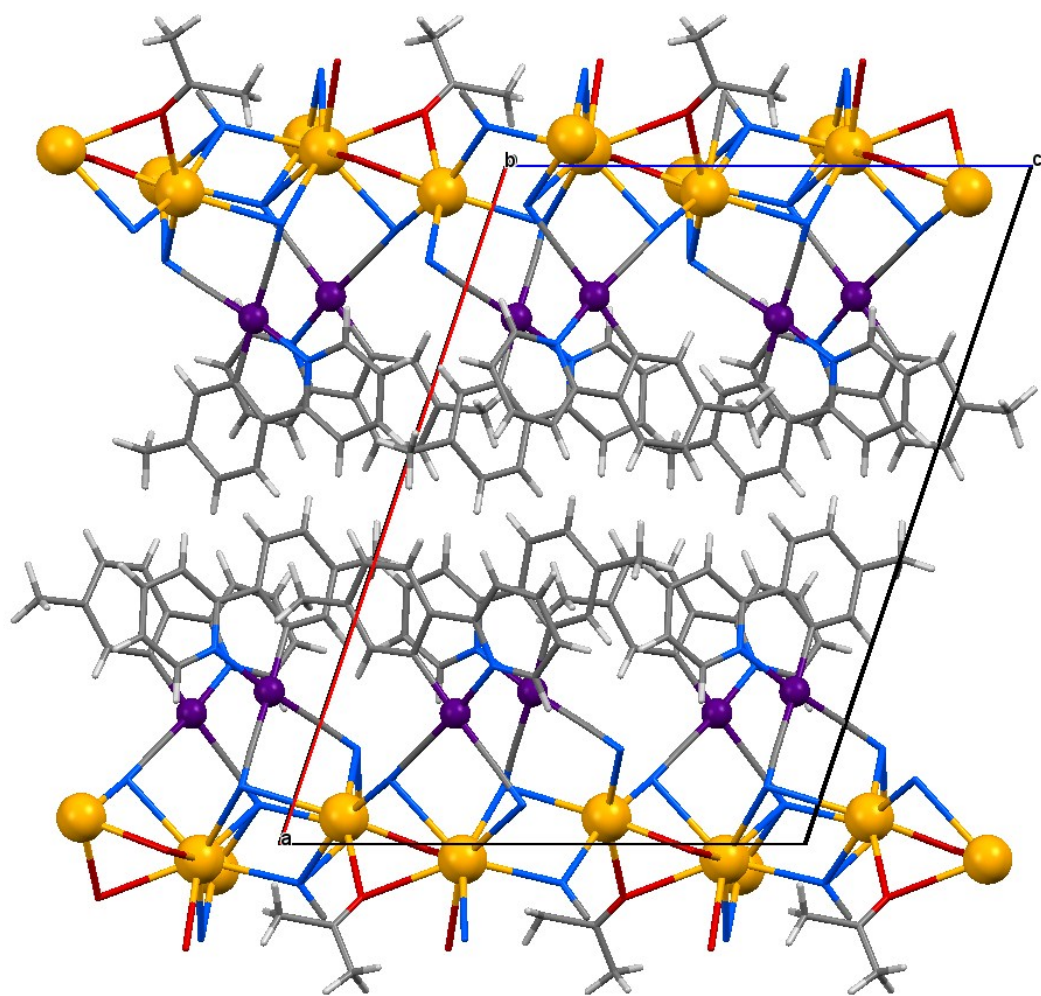
Fig. S13 Packing diagram of **3**·2H$_2$O·CH$_3$COCH$_3$. Colour code: Pt, purple; C grey; N, blue;

O, red; K, orange.

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