Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Deep-red to near-infrared emission of binuclear platinum(II) complexes by breaking hydrogen bonds

Mingying Xie,[ab] Muxin Yu,[ac] Caiping Liu,[a] Yunfang Zhao,[a] Zhijia Li,[a] Shengchang Li,[a] Feilong Jiang,[a] Lian Chen*[a] and Maochun Hong*[a]

a. *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (CAS), Fuzhou, Fujian 350002, China.*

b. *Fujian Normal University, Fuzhou, Fujian, 350007, China.*

c. *Organic Optoelectronics Engineering Research Center of Fujian's Universities, Fujian Jiangxia University, Fuzhou, Fujian, 350108, China.*

Corresponding author:

Email: cl@fjirsm.ac.cn; hmc@fjirsm.ac.cn.

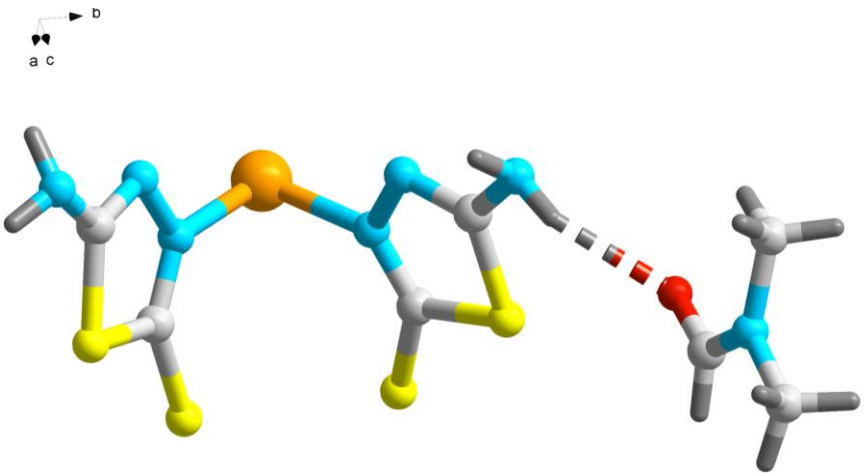

Figure S1. The asymmetric unit of complex **1**.

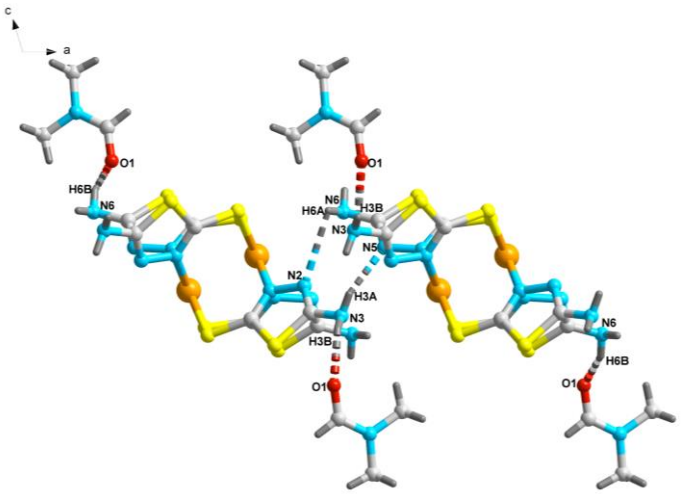

Figure S2. The hydrogen bonds of complex **1**.

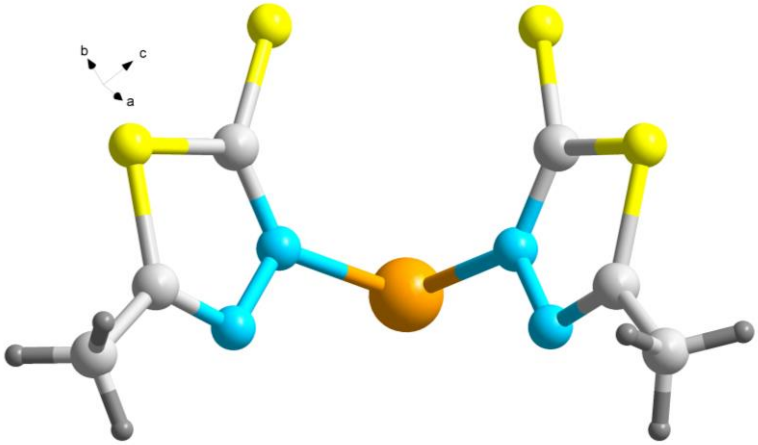

Figure S3. The asymmetric unit of complex **2**.

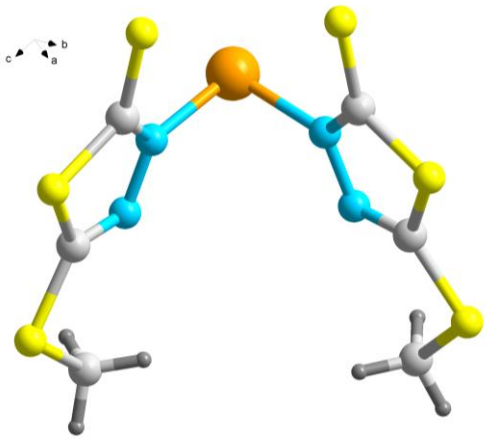

Figure S4. The asymmetric unit of complex **3**.

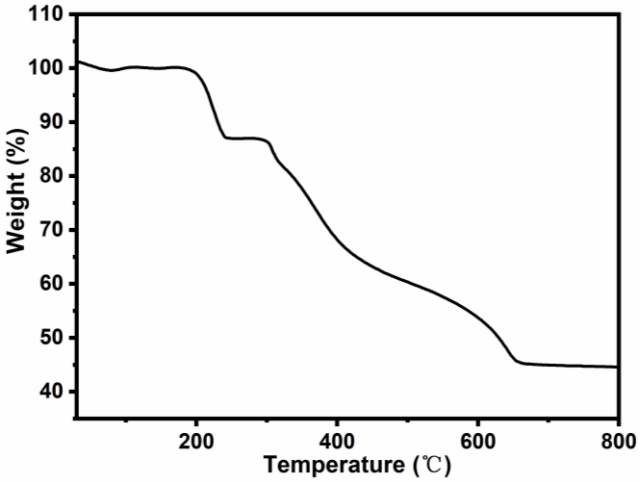

Figure S5. The thermogravimetric curve of complex **1**.

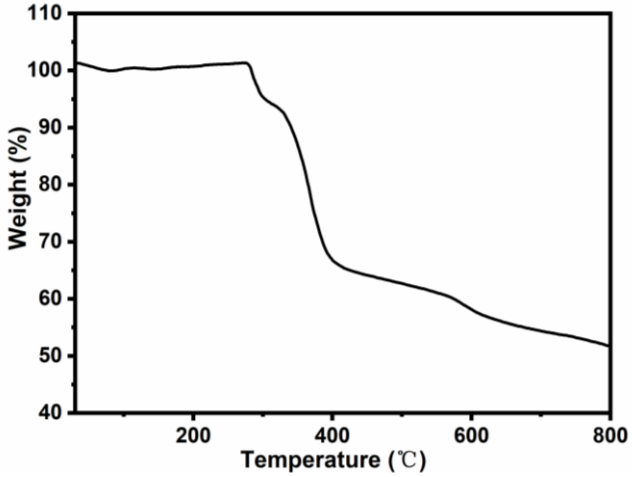

Figure S6. The thermogravimetric curve of complex **2**.

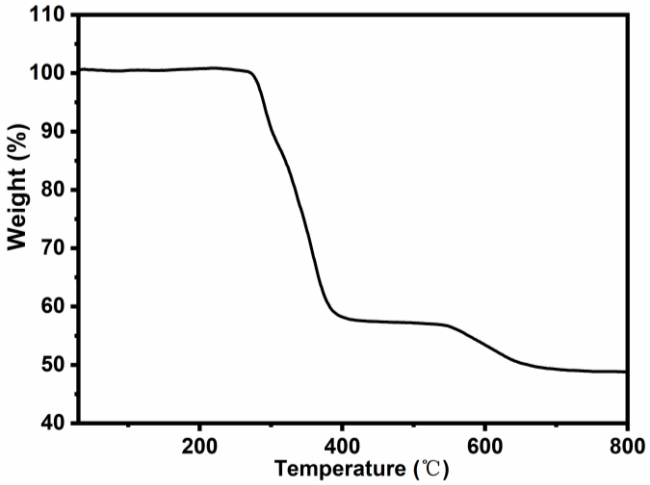

Figure S7. The thermogravimetric curve of complex **3**.

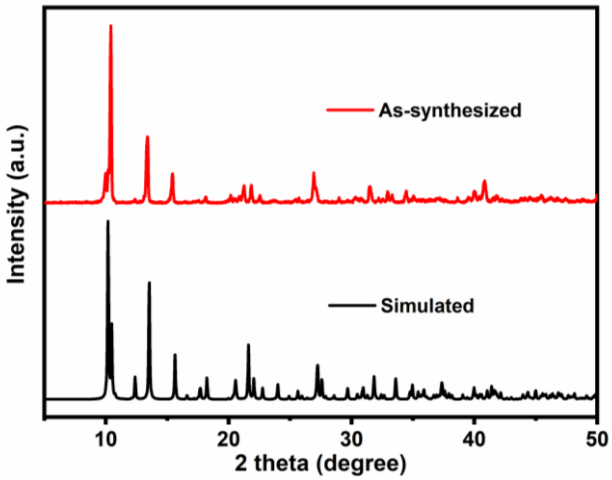

Figure S8. PXRD patterns of complex **1**.

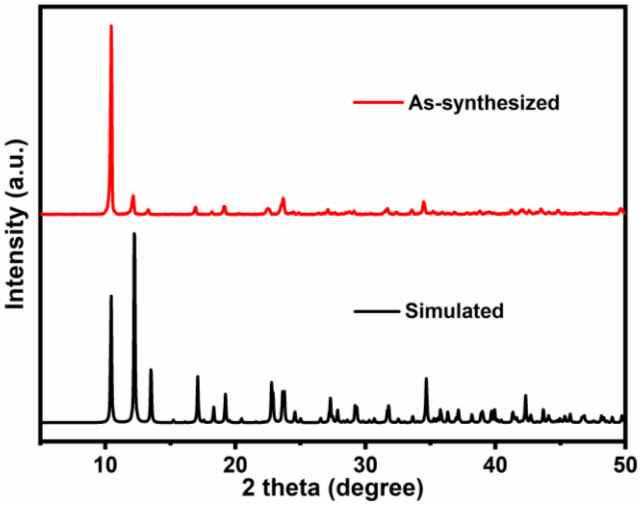

Figure S9. PXRD patterns of complex **2**.

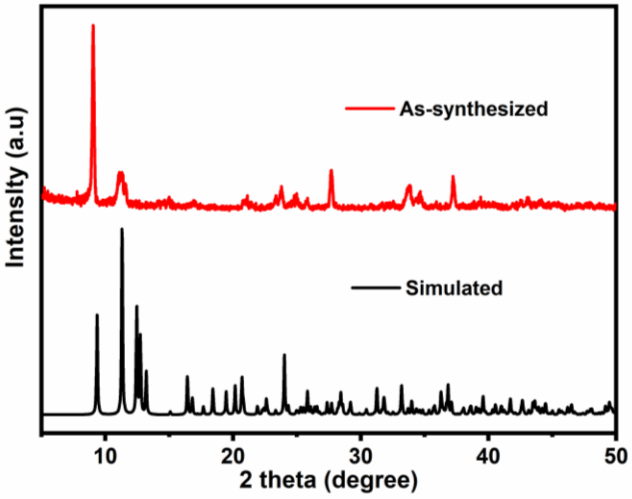

Figure S10. PXRD patterns of complex **3**.

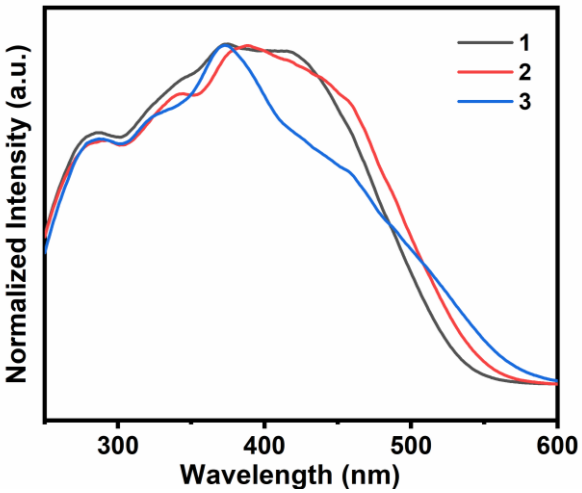

Figure S11. Normalized excitation spectra of complexes **1–3** in the solid state at room temperature.

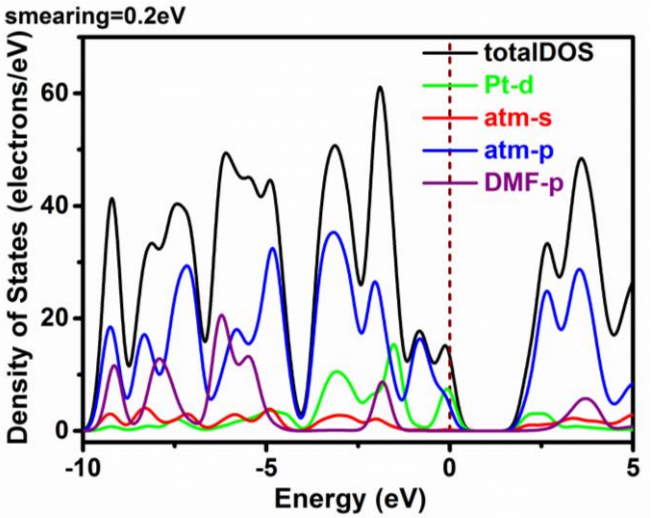

Figure S12. DOS diagram of complex **1**.

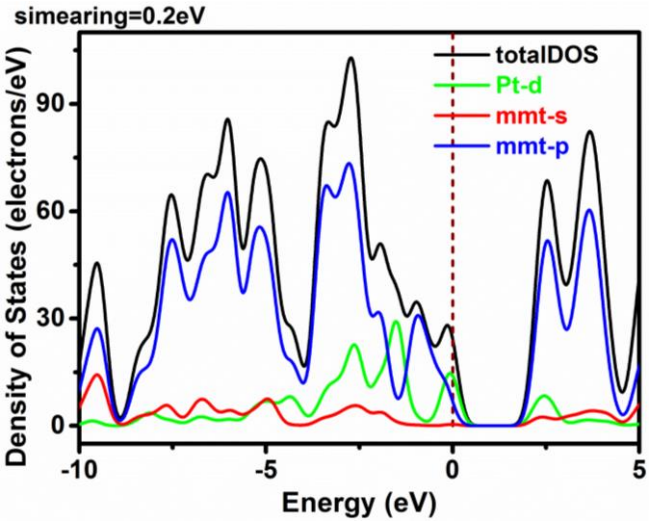

Figure S13. DOS diagram of complex **2**.

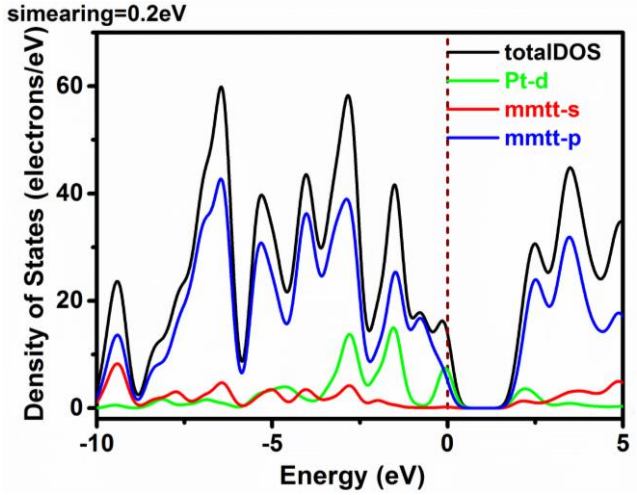

Figure S14. DOS diagram of complex **3**.

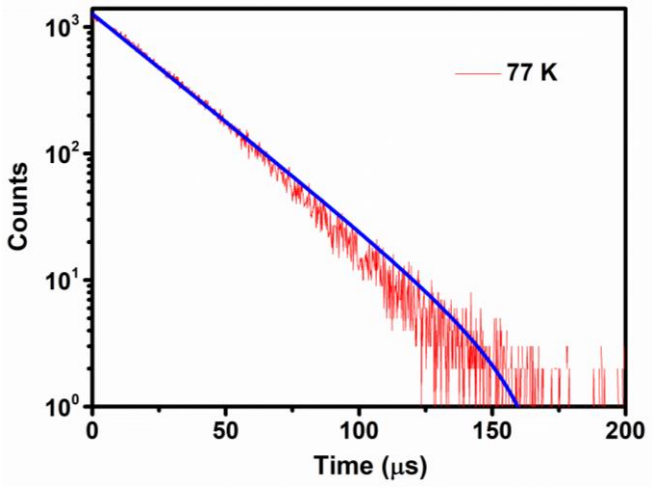

Figure S15. Luminescence lifetime decay curve of complex **1** at 77 K.

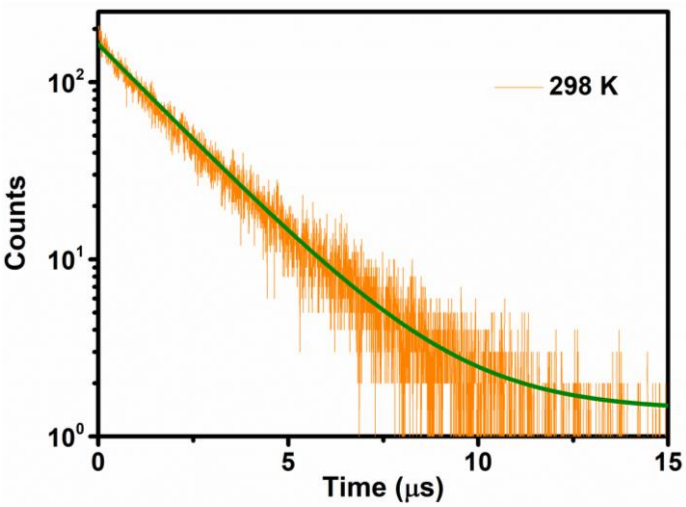

Figure S16. Luminescence lifetime decay curve of complex **1** at 298 K.

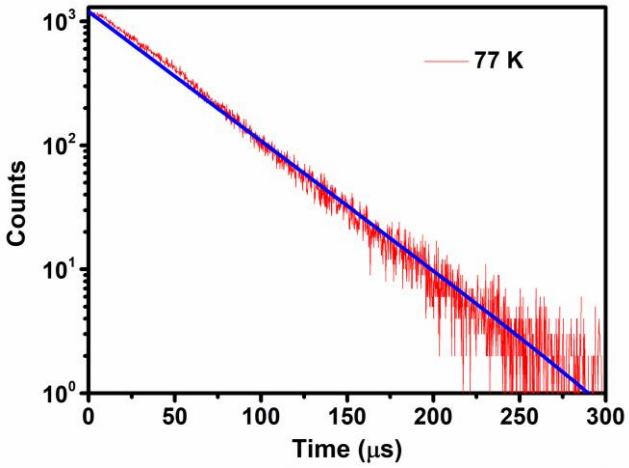

Figure S17. Luminescence lifetime decay curve of complex **2** at 77 K.

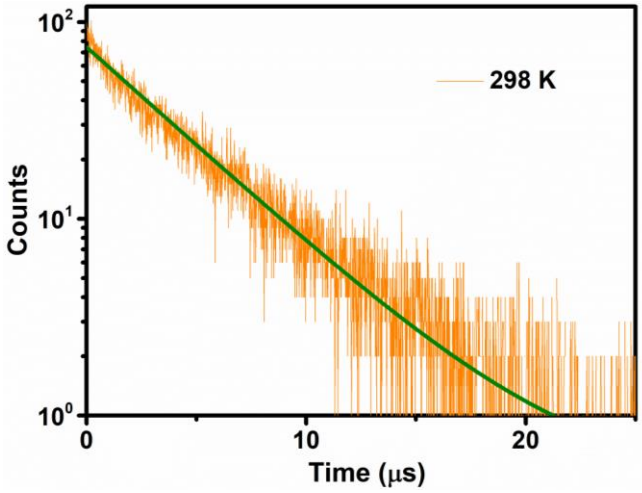

Figure S18. Luminescence lifetime decay curve of complex **2** at 298 K.

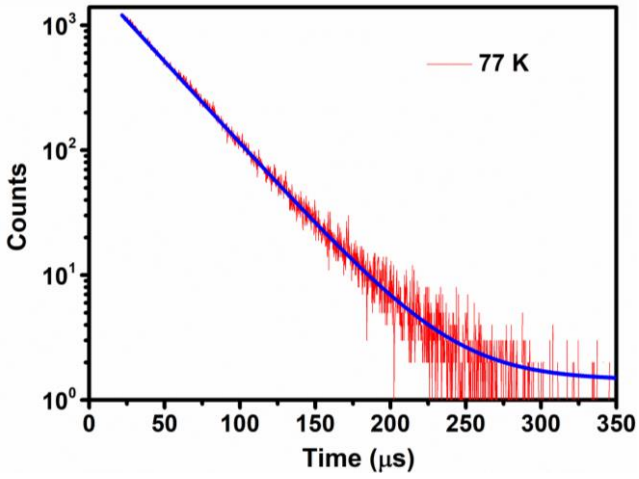

Figure S19. Luminescence lifetime decay curve of complex **3** at 77 K.

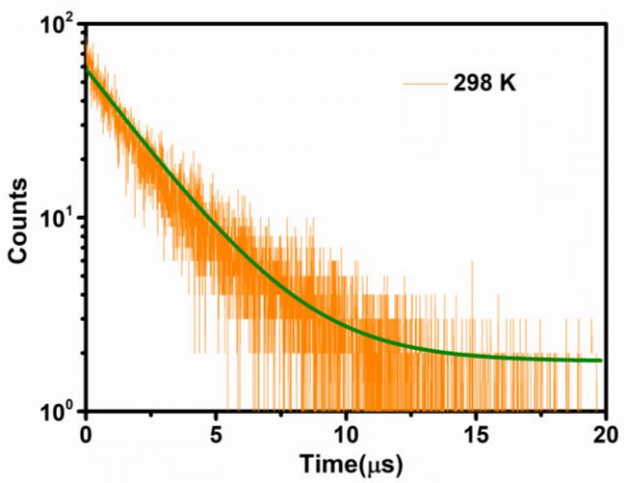

Figure S20. Luminescence lifetime decay curve of complex **3** at 298 K.

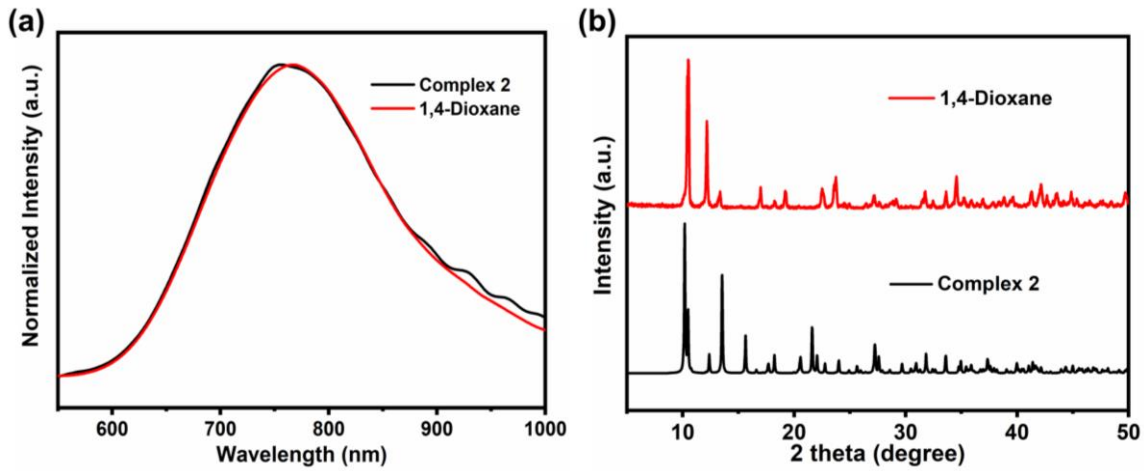

Figure S21. Emission spectra (a) and PXRD patterns (b) of complex **2** soaked in 1,4-dioxane.

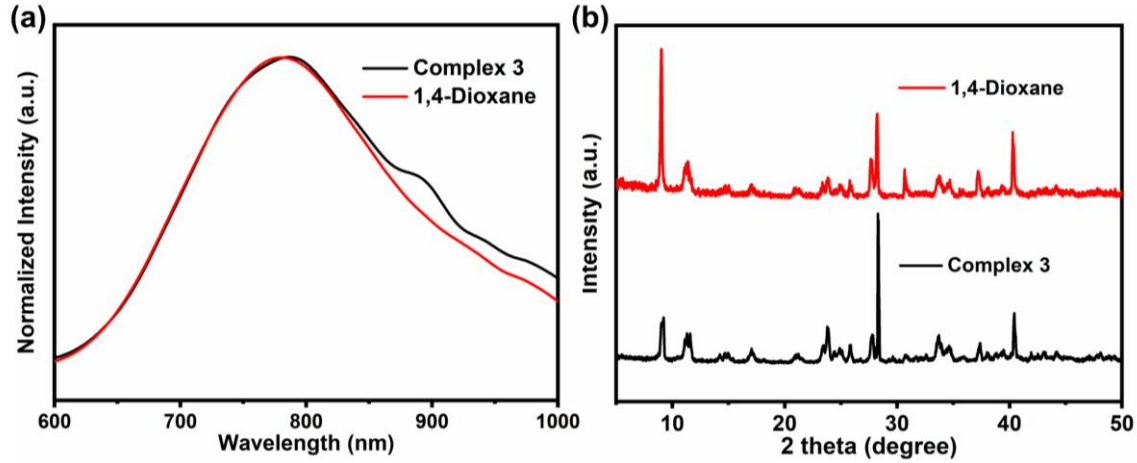

Figure S22. Emission spectra (a) and PXRD patterns (b) of complex **3** soaked in 1,4-dioxane.

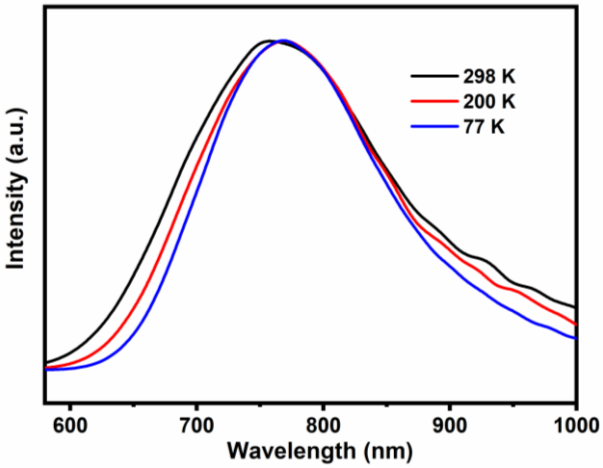

Figure S23. Emission spectra of complex **2** at 298 K, 200 K and 77 K.

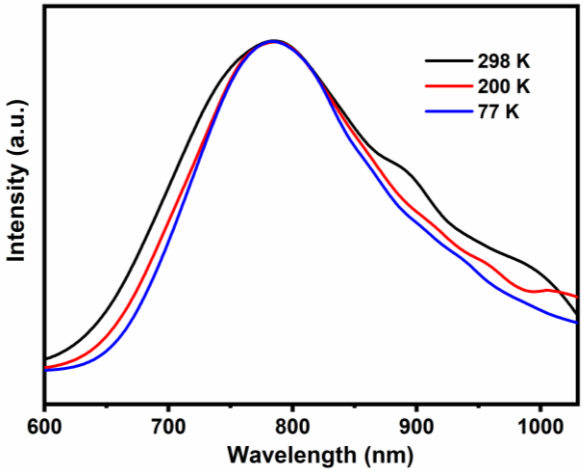

Figure S24. Emission spectra of complex **3** at 298 K, 200 K and 77 K.

Table S1. Crystal data and structure refinements for complexes **1** at 150 K and 298 K.

Complex **1**	**1** (150 K)	**1** (298 K)
CCDC	2177968	2177971
Empirical formula	$C_7H_{11}N_7OPtS_4$	$C_7H_{11}N_7OPtS_4$
Formula weight	532.56	532.56
Crystal system	monoclinic	monoclinic
Space group	*C2/c*	*C2/c*
a [Å]	18.0407(10)	18.0800(4)
b [Å]	10.0804(4)	10.2798(2)
c [Å]	17.6083(10)	17.6880(4)
α [°]	90	90
β [°]	106.473(6)	106.136(2)
γ [°]	90	90
Volume [$Å^3$]	3070.8(3)	3157.96(12)
Z	8	8
ρ_{calc} [g/cm^3]	2.304	2.240
μ [mm^{-1}]	9.688	21.642
F (000)	2016.0	2016.0
GOF	1.116	1.083
Parameters	185	184
R_1	0.0361	0.0323
ωR_2	0.0845	0.0852

Table S2. Crystal data and structure refinements for complexes **2** at 150 K and 298 K.

Complex **2**	**2** (150 K)	**2** (298 K)
CCDC	2177970	2177969
Empirical formula	$C_6H_6N_4PtS_4$	$C_6H_6N_4PtS_4$
Formula weight	457.48	457.48
Crystal system	orthorhombic	orthorhombic
Space group	*Pbca*	*Pbca*
a [Å]	13.1032(5)	13.3396(3)
b [Å]	10.0917(4)	10.1807(3)
c [Å]	16.9410(9)	16.9379(4)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
Volume [$Å^3$]	2240.83(17)	2300.28(10)
Z	8	8
ρ_{calc} [g/cm^3]	2.712	2.642
μ [mm^{-1}]	13.238	29.393
F (000)	1696.0	1696.0
GOF	1.116	1.053
Parameters	138	139
R_1	0.0341	0.0538
ωR_2	0.0923	0.1588

Table S3. Crystal data and structure refinements for complexes **3** at 150 K and 298 K.

Complex **3**	**3** (150 K)	**3** (298 K)
CCDC	2177972	2177973
Empirical formula	$C_6H_6N_4PtS_6$	$C_6H_6N_4PtS_6$
Formula weight	521.60	521.60
Crystal system	monoclinic	monoclinic
Space group	*C2/c*	*C2/c*
a [Å]	19.8187(6)	19.9914(6)
b [Å]	9.6409(3)	9.6803(3)
c [Å]	14.8981(3)	15.0913(5)
α [°]	90	90
β [°]	107.235(3)	107.925(3)
γ [°]	90	90
Volume [$Å^3$]	2718.76(14)	2778.75(16)
Z	8	8
ρ_{calc} [g/cm^3]	2.549	2.494
μ [mm^{-1}]	27.794	27.194
F (000)	1952.0	1696.0
GOF	1.116	1.092
Parameters	156	156
R_1	0.0391	0.0337
ωR_2	0.1341	0.0899

Table S4. Main bond lengths (Å) of complexes **1** at 150 K and 298 K.

Bond	**150 K (Å)**	**298 K (Å)**
Pt1-Pt1[1]	2.7494(5)	2.7594(4)
Pt1-S1[1]	2.2822(18)	2.2993(15)
Pt1-S3[1]	2.3030(19)	2.2847(14)
Pt1-N1	2.046(6)	2.056(4)
Pt1-N4	2.055(5)	2.056(5)
Symmetry codes: [1]1-x, y, 1/2-z.		

Table S5. Main bond lengths (Å) of complexes **2** at 150 K and 298 K.

Bond	**150 K (Å)**	**298 K (Å)**
Pt1-Pt1[1]	2.7610(5)	2.7621(8)
Pt1-S1[1]	2.2935(13)	2.302(3)
Pt1-S3[1]	2.2987(16)	2.287(2)
Pt1-N1	2.069(4)	2.056(7)
Pt1-N3	2.049(5)	2.047(8)
Symmetry codes: [1]1-x, 1-y, 1-z.		

Table S6. Main bond lengths (Å) of complexes **3** at 150 K and 298 K.

Bond	**150 K (Å)**	**298 K (Å)**
Pt1-Pt1[1]	2.7718(6)	2.7713(4)
Pt1-S1[1]	2.294(2)	2.3004(16)
Pt1-S3[1]	2.298(2)	2.2933(16)
Pt1-N1	2.058(8)	2.072(5)
Pt1-N3	2.073(8)	2.073(5)
Symmetry codes: [1]3/2-x, 3/2-y, 1-z.		

Table S7. Bond angles (°) of complexes **1** at 150 K and 298 K.

Atom 1	Atom 2	Atom 3	Angle-150 K (°)	Angle-298 K (°)
$S1^1$	Pt1	$Pt1^1$	92.84(5)	92.33(3)
$S1^1$	Pt1	$S3^1$	90.35(8)	90.35(8)
$S3^1$	Pt1	$Pt1^1$	91.85(5)	90.36(7)
N1	Pt1	$Pt1^1$	86.20(15)	92.82(3)
N1	Pt1	$S1^1$	91.36(17)	86.27(11)
N1	Pt1	$S3^1$	177.47(17)	89.81(14)
N1	Pt1	N4	88.3(2)	179.08(11)
N4	Pt1	$Pt1^1$	86.49(14)	89.20(19)
N4	Pt1	$S1^1$	179.24(16)	85.96(11)
N4	Pt1	$S3^1$	90.02(16)	178.08(11)
C1	S1	$Pt1^1$	103.0(3)	90.61(14)
C3	S3	$Pt1^1$	103.0(2)	103.29(19)
N2	N1	Pt1	118.6(4)	103.59(19)
C1	N1	Pt1	126.9(5)	117.0(3)
N5	N4	Pt1	117.1(4)	127.2(3)
C3	N4	Pt1	126.6(4)	117.6(3)
Symmetry codes: ^{1}1-x, y, 1/2-z.				

Table S8. Bond angles (°) of complexes **2** at 150 K and 298 K.

Atom 1	Atom 2	Atom 3	Angle-150 K (°)	Angle-298 K (°)
$S1^1$	Pt1	$Pt1^1$	91.93(4)	91.61(6)
$S1^1$	Pt1	$S3^1$	90.56(6)	90.79(11)
$S3^1$	Pt1	$Pt1^1$	92.31(4)	92.04(6)
N1	Pt1	$Pt1^1$	87.46(12)	87.4(2)
N1	Pt1	$S1^1$	179.27(13)	179.2(2)
N1	Pt1	$S3^1$	89.88(13)	179.2(3)
N1	Pt1	N3	88.6(2)	88.6(3)
N3	Pt1	$Pt1^1$	87.61(13)	87.6(2)
N3	Pt1	$S3^1$	175.52(16)	178.0(3)
N3	Pt1	$S1^1$	90.92(16)	91.2(3)
C1	S1	$Pt1^1$	104.9(2)	104.4(3)
C4	S3	$Pt1^1$	104.22(19)	105.1(3)
N2	N1	Pt1	118.0(3)	118.1(6)
C1	N1	Pt1	126.8(4)	126.5(6)
N4	N3	Pt1	119.0(3)	119.3(6)
C4	N3	Pt1	124.8(4)	125.8(6)
Symmetry codes: ^{1}1-x, 1-y, 1-z.				

Table S9. Bond angles (°) of complexes **3** at 150 K and 298 K.

Atom 1	Atom 2	Atom 3	Angle-150 K (°)	Angle-298 K (°)
S1[1]	Pt1	Pt1[1]	90.80(6)	91.30(4)
S1[1]	Pt1	S4[1]	91.41(9)	91.16(6)
S4[1]	Pt1	Pt1[1]	91.44(6)	90.71(4)
N1	Pt1	Pt1[1]	88.3(2)	87.84(15)
N1	Pt1	S4[1]	91.7(2)	89.44(14)
N1	Pt1	S1[1]	176.8(2)	178.96(14)
N1	Pt1	N3	87.8(3)	87.93(19)
N3	Pt1	Pt1[1]	87.6(2)	88.64(13)
N3	Pt1	S4[1]	178.9(2)	177.32(14)
N3	Pt1	S1[1]	89.1(2)	91.46(14)
C1	S1	Pt1[1]	105.7(4)	104.8(2)
C4	S4	Pt1[1]	105.1(3)	105.8(2)
N2	N1	Pt1	117.0(6)	117.6(4)
C1	N1	Pt1	125.0(6)	124.6(4)
N4	N3	Pt1	119.2(6)	119.5(4)
C4	N3	Pt1	126.0(6)	123.5(4)
Symmetry codes: [1]3/2-x, 3/2-y, 1-z.				

Table S10. Photoluminescence properties of complexes **1–3**.

Complex	λ_{em} [nm][a)]		PLQY [%][b)]	τ_{obs}[μs][c)]	
	77 K	298 K		77 K	298 K
1	750	737	0.21	25.56	1.92
2	765	764	0.12	41.64	4.32
3	789	789	< 0.01	33.06	2.44

[a)] Wavelength of emission peak max; [b)]PL quantum yield; [c)]Observed lifetimes of emission.