Supplementary Information for

AIPE-active platinum(II) complexes with tunable photophysical properties and the application in constructing thermosensitive probes used for intracellular temperature imaging

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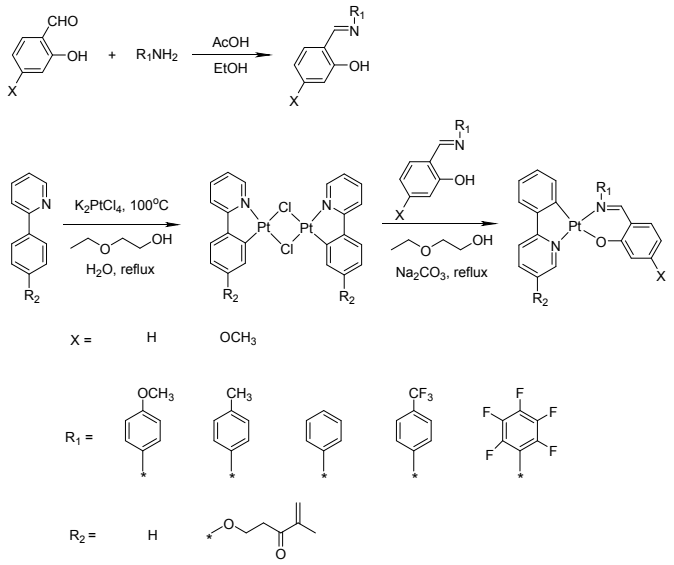
Experimental Section

Synthetic route to AIPE-active platinum(II) complexes



General syntheses of Schiff base ligands.

Salicylaldehyde (22.0 mmol) was added to an EtOH solution (40 mL) of aniline (22.0 mmol). A drop of acetic acid as a catalyst was added to the reaction solution, and then the reaction mixture was stirred at room temperature for 3 hr. Finally, concentration and subsequent silica gel column purification gave yellow solid (19.8 mmol, 94% yield). All the other ligands were synthesized by the same method to give yellow powder or liquid. The yields of these Schiff base ligands were quantitative (> 90%).

General syntheses of Pt(II) μ-dichloro-bridged dimers

Pt(II)μ-dichloro-bridged dimers were synthesized from the starting materials of K_2PtCl_4 and C^N ligands, K_2PtCl_4(415 mg, 1 mmol) and ppy (2.5 mmol) were dissolved in a mixed solvent of 2-ethoxyethanol and water(v/v = 3/1), the reaction mixture was heated at 80°C for 20 - 24 hours. The reaction solution was poured into an appropriate amount of water and filtered to obtain a green powder.

General syntheses of Pt(II) complexes

All Pt(II) complexes were prepared by the same procedure according to the literature. A solution of Pt(II)-dichloro-bridged dimers, 3 equiv of the Schiff base ligand and 5 equiv of Na_2CO_3 in 2-ethoxyethanol was heated to 100°C for 16 hr. Then the reaction mixture was filtered and subsequently concentrated under reduced pressure. The obtained crude product was purified by silica gel column chromatography using dichloromethane and PE as the eluent to give pure products with moderate yield (30% to 57%).

^{1}H NMR and MALDI-TOF-MS Characterization of Pt(II) Complexes

1a. Yield: 57%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.55 (d, J = 5.02 Hz, 1H), 8.21 (s, 1H), 7.8 (t, J = 6.30 Hz, 1H), 7.62 (d, J = 6.02 Hz, 1H), 7.52 (m, 2H),7.45 (t, J = 6.80 Hz, 1H), 7.38 (M, 1H), 7.31 (m, 2H), 7.23 (m, 1H), 7.08 (d, J = 8.55 Hz, 1H), 6.91 (m, J = 6.20 Hz, 2H) 6.86 (t, J = 6.88 Hz, 1H), 6.56 (m, 2H), 5.68 (d, J = 7.08 Hz, 1H), 3.85 (s, 3H). MS (MALDI-TOF/TOF): m/z 575.69.

1b. Yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.55 (d, J = 5.02 Hz, 1H), 8.21 (s, 1H), 7.8 (t, J = 6.30 Hz, 1H), 7.62 (d, J = 6.02 Hz, 1H), 7.52 (m, 2H),7.43 (d, J = 6.80 Hz, 1H), 7.38 (d, 1H), 7.30 (d, 1H), 7.23 (m, 3H), 7.08 (d, J = 8.55 Hz, 1H), 6.86 (t, J = 6.88 Hz, 1H), 6.56 (m, 2H), 5.76 (d, J = 7.08 Hz, 1H), 2.42 (s, 3H). MS (MALDI-TOF/TOF): m/z 558.96.

1c. Yield: 44%.^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.55 (d, J = 5.02 Hz, 1H), 8.25 (s, 1H), 7.8 (t, J = 6.30 Hz, 1H), 7.6 (m, 3H), 7.47 (t, J = 6.80 Hz, 1H), 7.39 (m, 3H), 7.31 (m, 2H),7.23 (m, 1H), 7.08 (d, J = 8.55 Hz, 1H), 6.86 (t, J = 6.88 Hz, 1H), 6.56 (m, 2H), 5.68 (d, J = 7.08Hz, 1H). MS (MALDI-TOF/TOF): m/z 546.17.

1d. Yield: 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.52 (d, J = 4.50Hz, 1H), 8.24 (s, 1H), 7.83 (t, J = 5.40 Hz, 1H), 7.73 (d, J = 6.30 Hz, 2H), 7.65 (m, 3H), 7.5 (m, 1H),7.37(d, J = 6.00 Hz, 1H), 7.31 (m, 1H), 7.25 (d, J = 6.60 Hz, 1H), 7.09 (d, J = 6.30 Hz, 1H), 6.87 (t, J = 5.4 Hz, 1H), 6.59 (m, 2H), 5.63 (d, J = 5.40 Hz, 1H). MS (MALDI-TOF/TOF): m/z 613.07.

1e. Yield: 55%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.47 (d, J = 4.75 Hz, 1H), 8.11 (s, 1H), 7.8 (t, J = 6.30 Hz, 1H), 7.63 (d, J = 6.02 Hz, 1H), 7.57 (t, J = 5.12 Hz, 1H),7.42 (d, J = 5.70 Hz, 1H), 7.28 (M, 1H), 7.23 (t, J = 5.72 Hz, 1H), 7.07 (d, J = 6.22 Hz, 1H), 6.96 (t, J = 5.70 Hz, 1H) 6.77 (t, J = 5.70 Hz, 1H), 6.594 (t, J = 6.02 Hz, 1H), 5.67 (d, J = 6.02 Hz, 1H). MS (MALDI-TOF/TOF): m/z 634.99.

2a. Yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.55 (d, J = 5.02 Hz, 1H), 8.06 (s, 1H), 7.8 (t, J = 6.30 Hz, 1H), 7.63 (d, J = 6.02 Hz, 1H), 7.47 (m, 2H), 7.37 (d, J = 4.8 Hz, 1H), 7.24 (m, 1H), 7.18 (d, J = 4.8 Hz, 1H), 6.90 (m, 3H), 6.63 (m, 1H), 6.55 (d, J = 2.1 Hz, 1H), 6.25 (m, 1H). 5.82 (d, J = 6.02 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H). MS (MALDI-TOF/TOF): m/z 605.18.

2b. Yield: 45%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.55 (d, J = 4.20Hz, 1H), 8.06 (s, 1H), 7.8 (t, J = 5.70 Hz, 1H), 7.63 (d, J = 6.00 Hz, 1H), 7.43 (d, J = 6.00 Hz, 2H), 7.36 (d, J = 6.00 Hz, 1H), 7.23 (m, 1H), 7.17 (m, 3H), 6.87 (t, J = 5.70 Hz, 1H), 6.54 (m, 2H), 6.25 (m, 1H), 5.78 (d, J = 6.00 Hz, 1H), 3.87 (s, 3H), 2.41 (s, 3H). MS (MALDI-TOF/TOF): m/z 589.06.

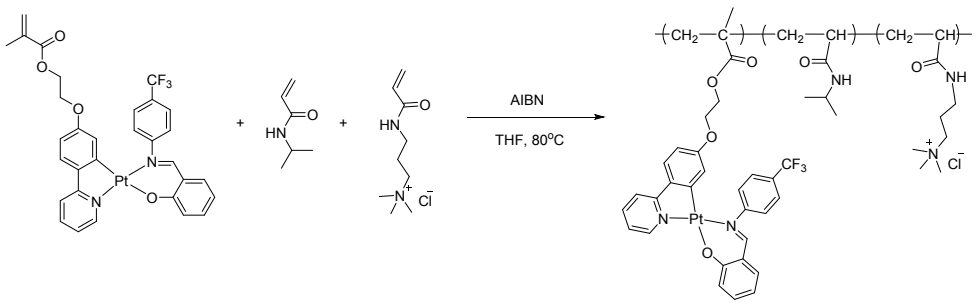
2c. Yield: 37%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.55 (d, J = 4.20Hz, 1H), 8.09 (s, 1H), 7.80 (t, J = 5.10 Hz, 1H), 7.63 (d, J = 6.00 Hz, 1H), 7.56 (d, J = 5.40 Hz, 2H), 7.38 (t, J = 5.40 Hz, 3H), 7.29 (d, J = 6.00 Hz, 1H), 7.24 (m, 1H), 7.17 (d, J = 6.6 Hz, 1H), 6.86 (t, J = 6.00 Hz, 1H), 6.55 (m, 2H), 6.26 (m, 1H), 5.70 (d, J = 6.00 Hz, 1H), 3.87 (s, 3H). MS (MALDI-TOF/TOF): m/z 574.79.

2d. Yield: 29%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)= 9.55 (d, J = 4.20Hz, 1H), 8.09 (s, 1H), 7.84 (t, J = 5.10 Hz, 1H), 7.69 (d, J = 6.00 Hz, 2H), 7.65 (m, 3H), 7.37 (d, J = 6.00 Hz, 1H), 7.24 (m, 1H), 7.17 (d, J = 6.60 Hz, 1H), 6.87 (t, J = 5.7 Hz, 1H), 6.54 (m, 2H), 6.27 (d, J = 6.60 Hz, 1H), 5.65 (d, J = 6.00 Hz, 1H), 3.87 (s, 3H). MS (MALDI-TOF/TOF): m/z 642.86.

2e. Yield: 41%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.50 (d, J = 4.20Hz, 1H), 7.88 (s, 1H), 7.81 (t, J = 5.70 Hz, 1H), 7.64 (d, J = 6.00 Hz, 1H), 7.43 (d, J = 6.00 Hz, ,1H), 7.23 (m, 1H), 7.12 (d, J = 6.60 Hz, 1H), 6.97 (t, J = 5.7 Hz, 1H), 6.77 (t, J = 5.10 Hz, 1H). 6.49 (d, J = 1.8Hz, 1H). 6.27 (m, 1H), 5.67 (d, J = 6.00 Hz, 1H), 3.88 (s, 3H). MS (MALDI-TOF/TOF): m/z 664.89.

AIPE-active Monomer: Yield: 30% ^{1}H NMR (400 MHz, DMSO-d6): δ (ppm) = 9.36 (d, 1H), 8.61 (s, 1H), 8.02 (d, 1H), 7.96 (d, 2H), 7.87 (d, 3H), 7.61 (d, 1H), 7.52 (m, 2H), 7.42 (t, 1H), 7.03 (d, 1H), 6.64 (t, 1H), 6.48 (d, 1H), 6.04 (s, 1H), 5.73 (m, 1H), 5.24 (d, 1H), 4.26 (m, 2H), 3.55 (m, 2H), δ = 1.91 (s, 3H). MS (MALDI-TOF/TOF): m/z 741.52.

Synthetic route to phosphorescent temperature sensitive probes



P1: N-isopropylacrylamide (135mg, 1.2 mmol), APTMA chloride (30 µL, 106.5 µmol), AIPE-active Monomer (20 mg, 27 µmol) and 2,2-azobisisobutyronitrile (2 mg, 12.2 µmol) were dissolved in THF (5 mL). The solution was bubbled with dry nitrogen for 45 min to remove dissolved oxygen, and the solution was heated to 80°C for 12 h. After cooling to room temperature, the reaction mixture was poured into diethyl ether (200 mL), and the obtained **P1** was purified by reprecipitation using methanol/diethyl ether (5 mL/250 mL) and dialysis. GPC (THF, polystyrene standard): Mn = 3539, Mw = 4428, Mw/Mn = 1.25.

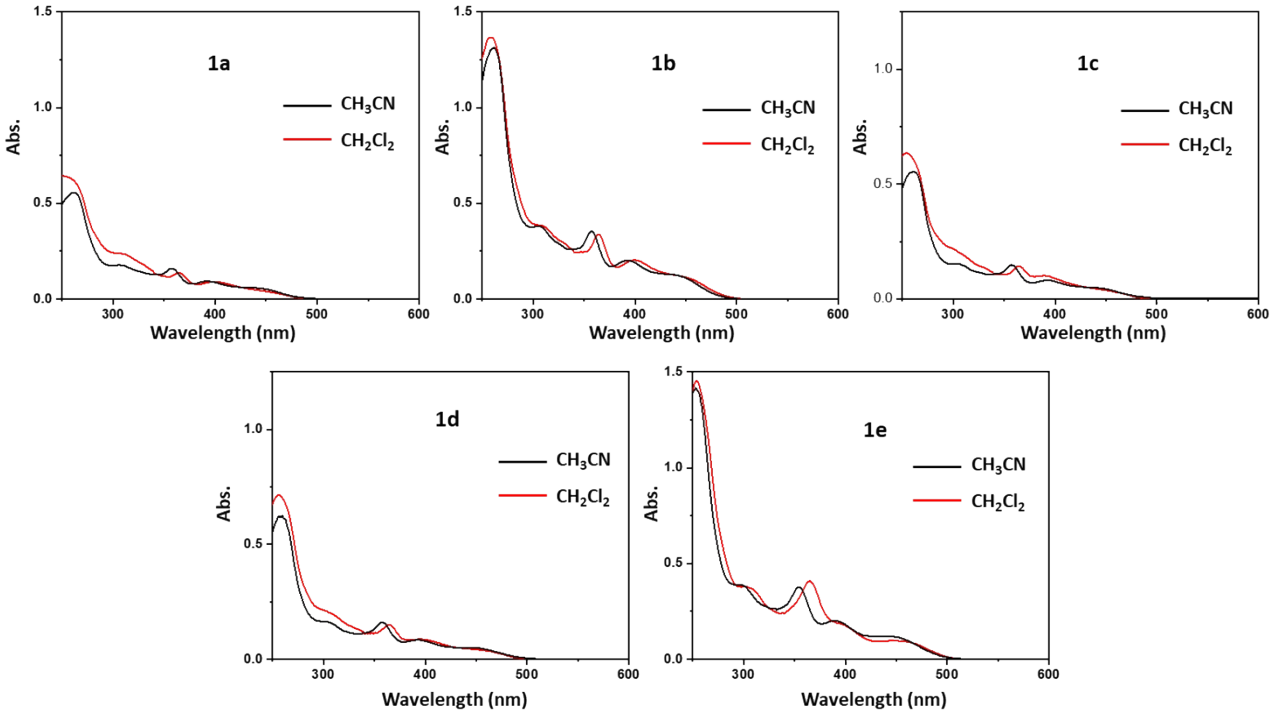


Fig. S1. UV-vis absorption spectra of complexes **1** in CH_3CN and CH_2Cl_2.

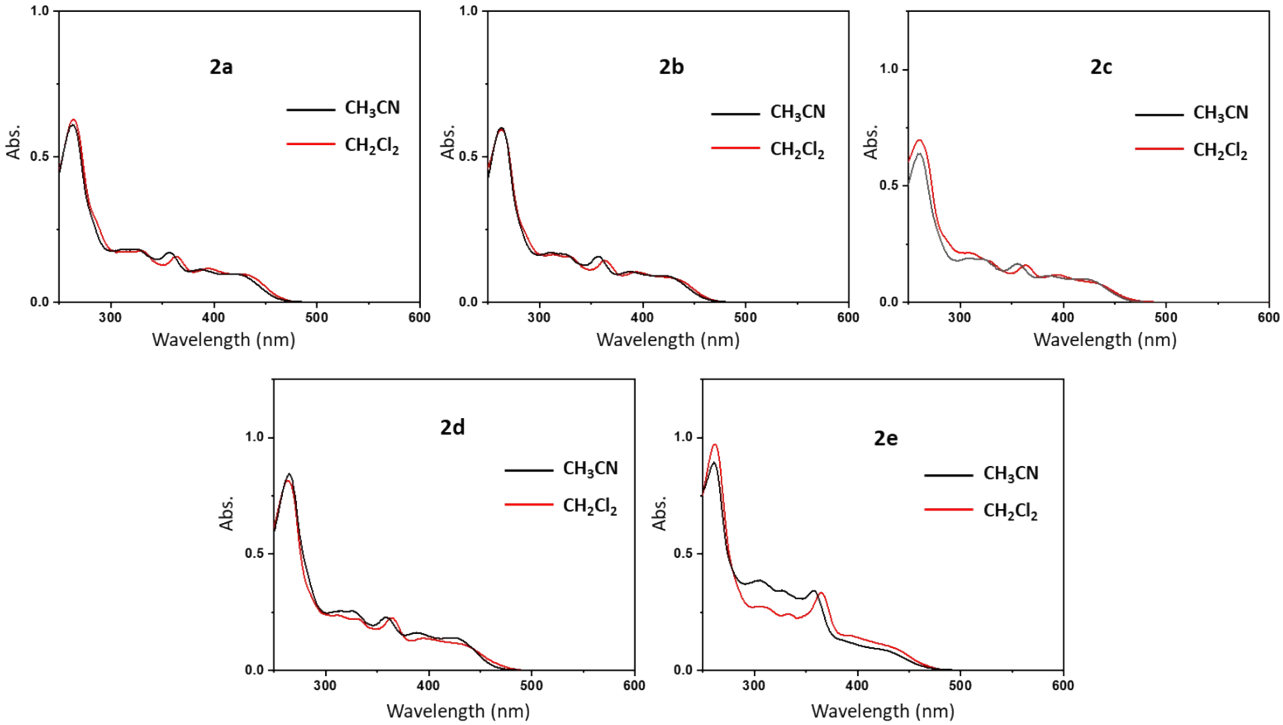


Fig. S2. UV-vis absorption spectra of complexes **2** in CH_3CN and CH_2Cl_2.

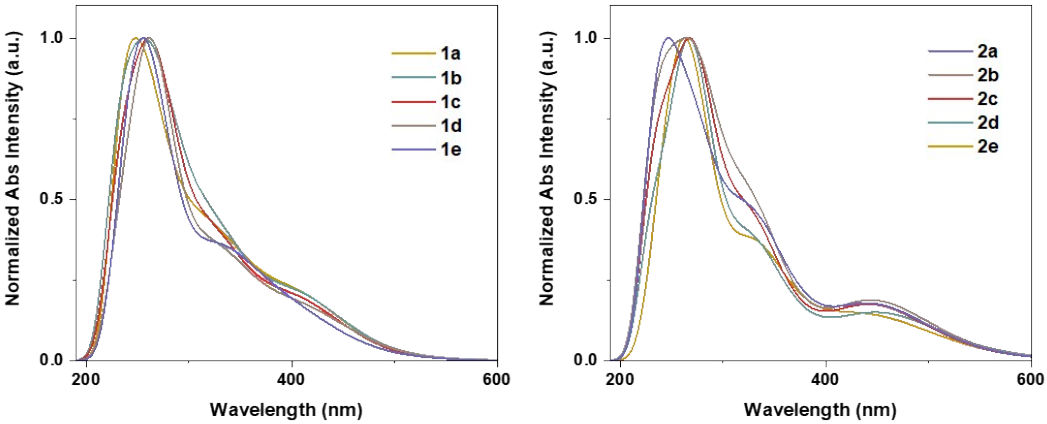


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Fig. S3. Calculated absorption spectra of all complexes at room temperature in CH_2Cl_2 solution.

Table S1 HOMOs and LUMOs distributions of complexes **1** at the lowest singlet state.

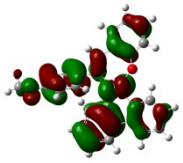
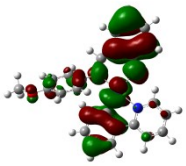
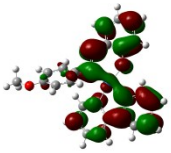
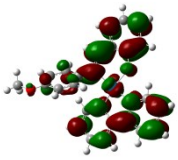
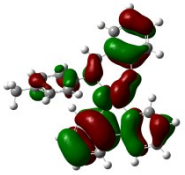
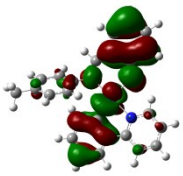
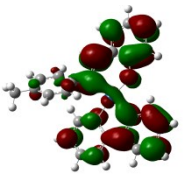
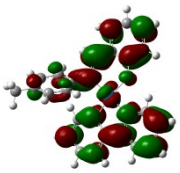
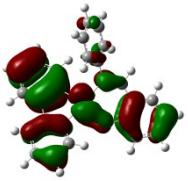
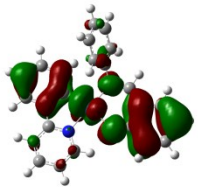
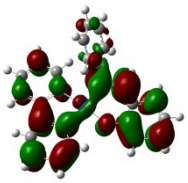
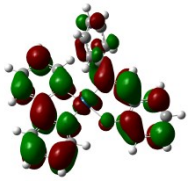
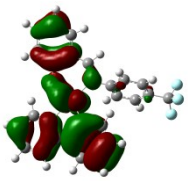
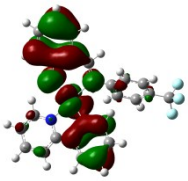
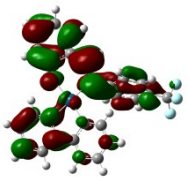
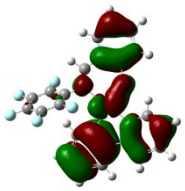
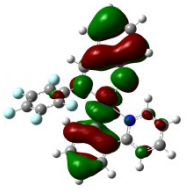
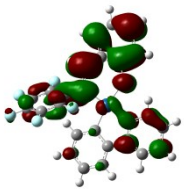
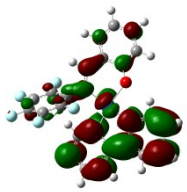
Complexes	HOMO-1	HOMO	LUMO	LUMO+1
1a				
1b				
1c				
1d				
1e				

Table S2 HOMOs and LUMOs distributions of complexes **2** at the lowest singlet state.

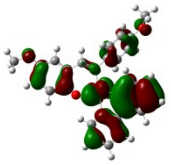
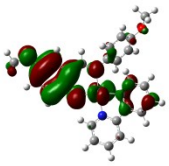
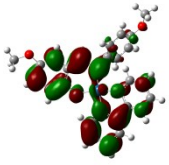
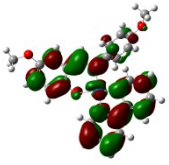
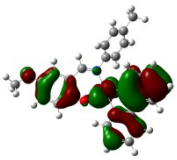
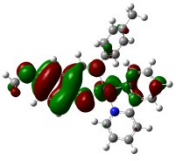
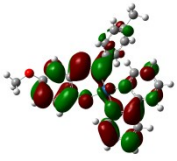
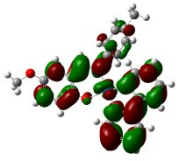
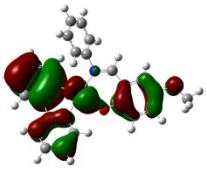
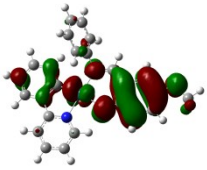
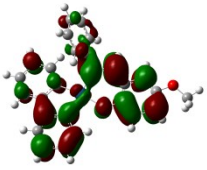
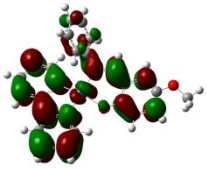
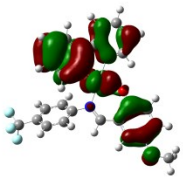
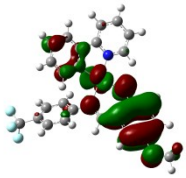
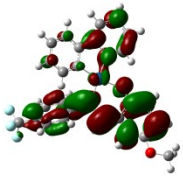
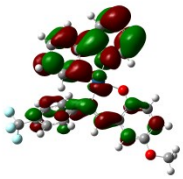
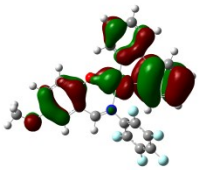
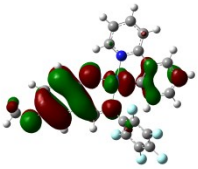
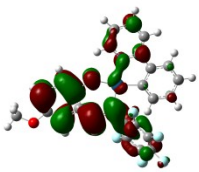
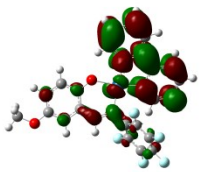
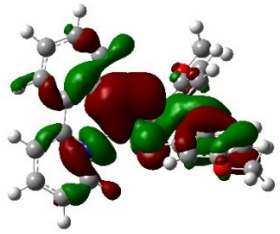
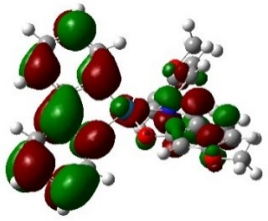
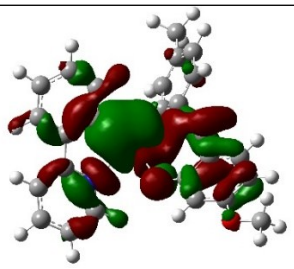
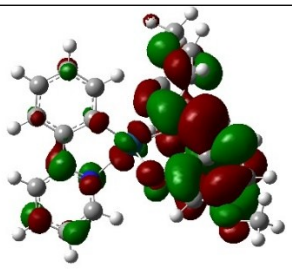
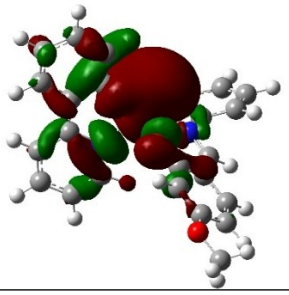
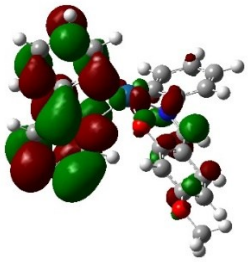
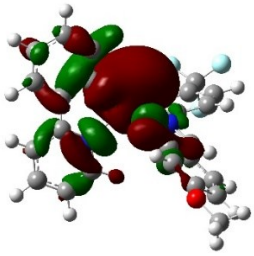
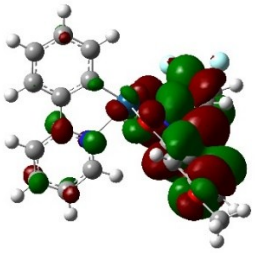
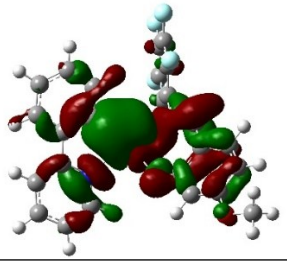
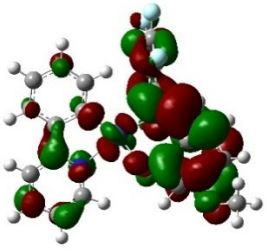
Complexes	HOMO-1	HOMO	LUMO	LUMO+1
2a				
2b				
2c				
2d				
2e				

Table S3 Absorption of all complexes in CH_2Cl_2 solution from TDDFT Calculations.

Complex	states	λ (nm)	E (eV)	oscillator	main configurations (CI coeff)	assignment
1a	S1	430	2.88	0.0628	HOMO→LUMO (0.69)	LC/MLCT
	S2	404	3.07	0.1177	HOMO→LUMO+1 (0.68)	LLCT/ILCT
	S3	357	3.47	0.1154	HOMO-1→LUMO (0.64)	MLCT/LLCT
1b	S1	430	2.88	0.0562	HOMO→LUMO (0.69)	LC/MLCT
	S2	404	3.07	0.1079	HOMO→LUMO+1 (0.68)	LLCT/ILCT
	S3	355	3.49	0.1067	HOMO-1→LUMO (0.65)	MLCT/LLCT
1c	S1	429	2.89	0.0510	HOMO→LUMO (0.70)	LC/MLCT
	S2	403	3.08	0.1034	HOMO→LUMO+1 (0.68)	LLCT/ILCT
	S3	354	3.50	0.1078	HOMO-1→LUMO (0.65)	MLCT/LLCT
1d	S1	436	2.84	0.0567	HOMO→LUMO (0.70)	LC/MLCT
	S2	405	3.06	0.1004	HOMO→LUMO+1 (0.68)	LLCT/ILCT
	S3	355	3.49	0.1168	HOMO-1→LUMO (0.62)	MLCT/LLCT
1e	S1	434	2.85	0.0412	HOMO→LUMO (0.70)	LC/MLCT
	S2	398	3.12	0.0952	HOMO→LUMO+1 (0.68)	LLCT/ILCT
	S4	353	3.51	0.1646	HOMO-1→LUMO (0.62)	MLCT/LLCT
2a	S1	469	2.64	0.0762	HOMO→LUMO (0.70)	LC/MLCT
	S2	435	3.85	0.1002	HOMO→LUMO+1 (0.69)	LLCT/ILCT
	S3	366	3.39	0.0595	HOMO-1→LUMO (0.65)	MLCT/LLCT
2b	S1	470	2.64	0.0723	HOMO→LUMO (0.70)	LC/MLCT
	S2	435	3.85	0.0928	HOMO→LUMO+1 (0.69)	LLCT/ILCT
	S3	367	3.38	0.0540	HOMO-1→LUMO (0.66)	MLCT/LLCT
2c	S1	469	2.65	0.0681	HOMO→LUMO (0.70)	LC/MLCT
	S2	434	3.86	0.0923	HOMO→LUMO+1 (0.69)	LLCT/ILCT
	S3	365	3.39	0.0543	HOMO-1→LUMO (0.65)	MLCT/LLCT
2d	S1	478	2.60	0.0785	HOMO→LUMO (0.70)	LC/MLCT
	S2	436	3.84	0.0850	HOMO→LUMO+1 (0.69)	LLCT/ILCT
	S3	369	3.36	0.0629	HOMO-1→LUMO (0.67)	MLCT/LLCT
2e	S1	478	2.59	0.0652	HOMO→LUMO (0.70)	LC/MLCT
	S2	426	2.90	0.0835	HOMO→LUMO+1 (0.69)	LLCT/ILCT
	S3	372	3.34	0.0723	HOMO-1→LUMO (0.68)	MLCT/LLCT

Table S4 HOMO and LUMO distributions of **2a**-**2e** at the triplet states.

Complex	HOMO	LUMO
2a		
2b		
2c		
2d		
2e		

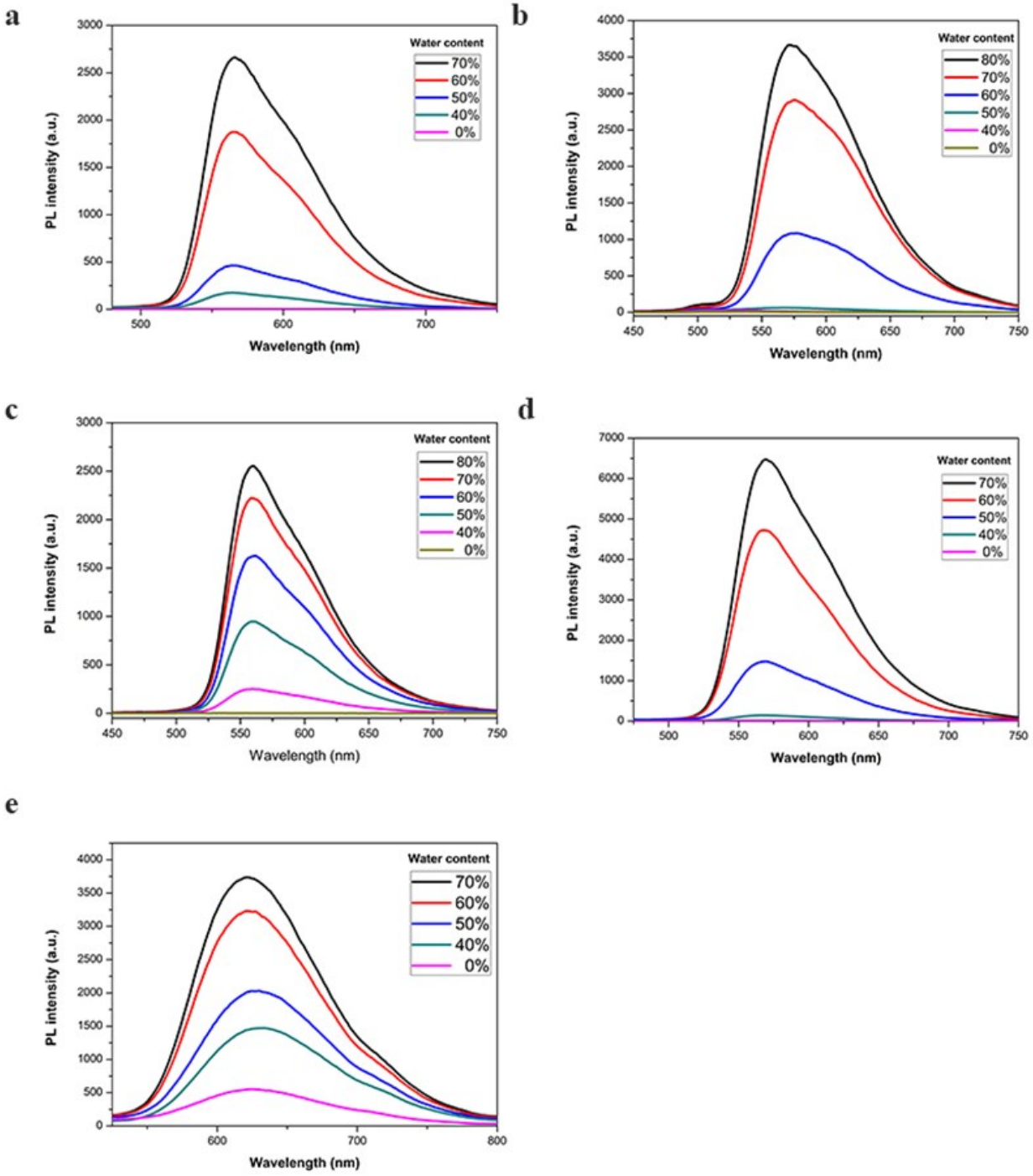


Fig. S4. Photoluminescence spectra of platinum complexes of **1a** (a), **1b** (b), **1c** (c), **1d** (d), **1e** (e) in THF–water mixtures.

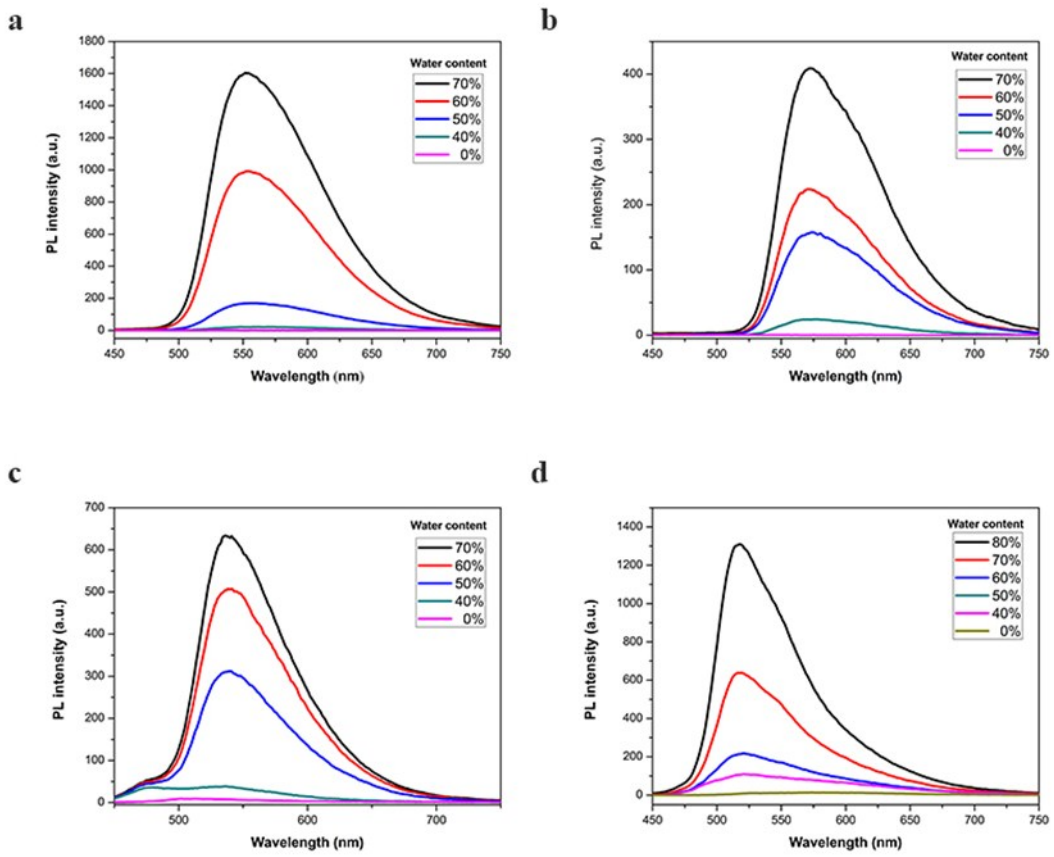


Fig. S5. Photoluminescence spectra of platinum complexes of **2a** (a), **2b** (b), **2d** (c), **2e** (d) in THF–water mixtures.

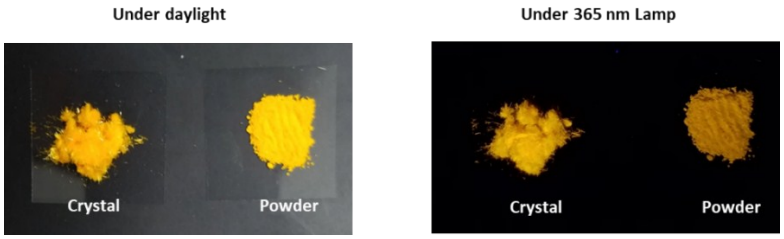


Fig. S6. Photoluminescence images of complex **1c** before and after grinding under daylight and 365 nm lamp, respectively.

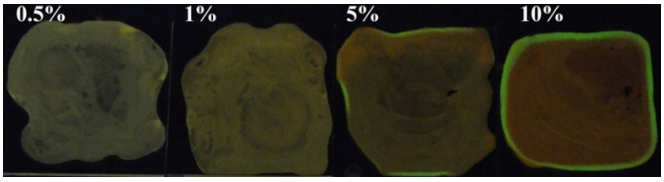


Fig. S7. Luminescence photographs of the solid poly(methyl methacrylate) (PMMA) film doped with different contents of **2c**.

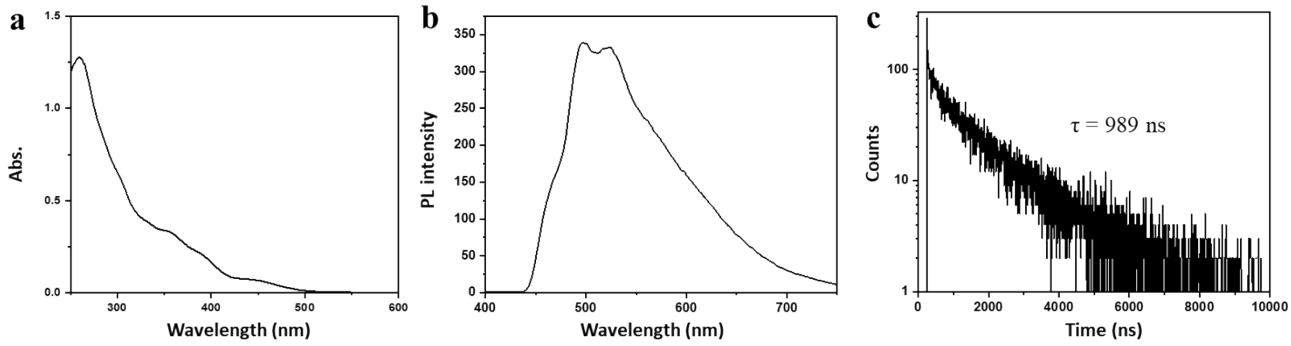


Fig. S8. UV-Vis absorption spectrum (a), emission spectrum (b) and experimental luminescence decay curves (c) of **P1** in PBS (pH = 7.4).

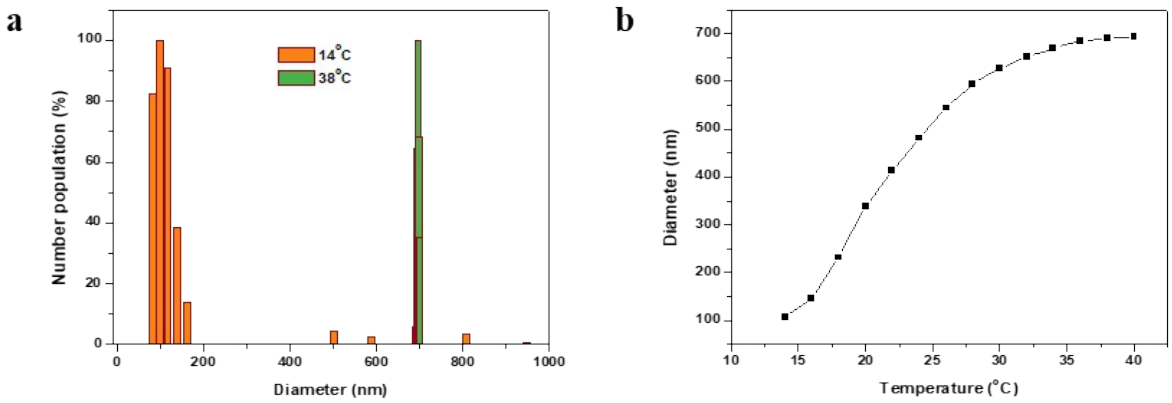


Fig. S9. The hydrodynamic diameters of **P1** (0.01 w/v%, pH = 7.4) at different temperatures (a); A correlation between the temperatures and the micelles sizes of the **P1** as examined by DLS measurements (b).

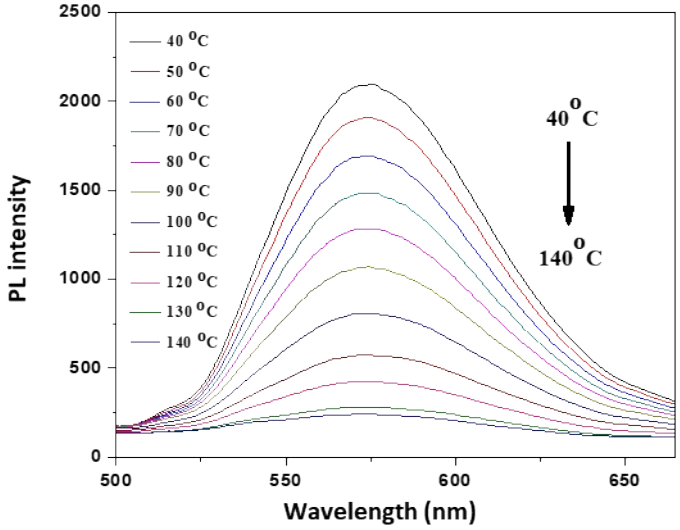


Fig. S10. Emission spectra of **1d** in solid-state at various temperatures.

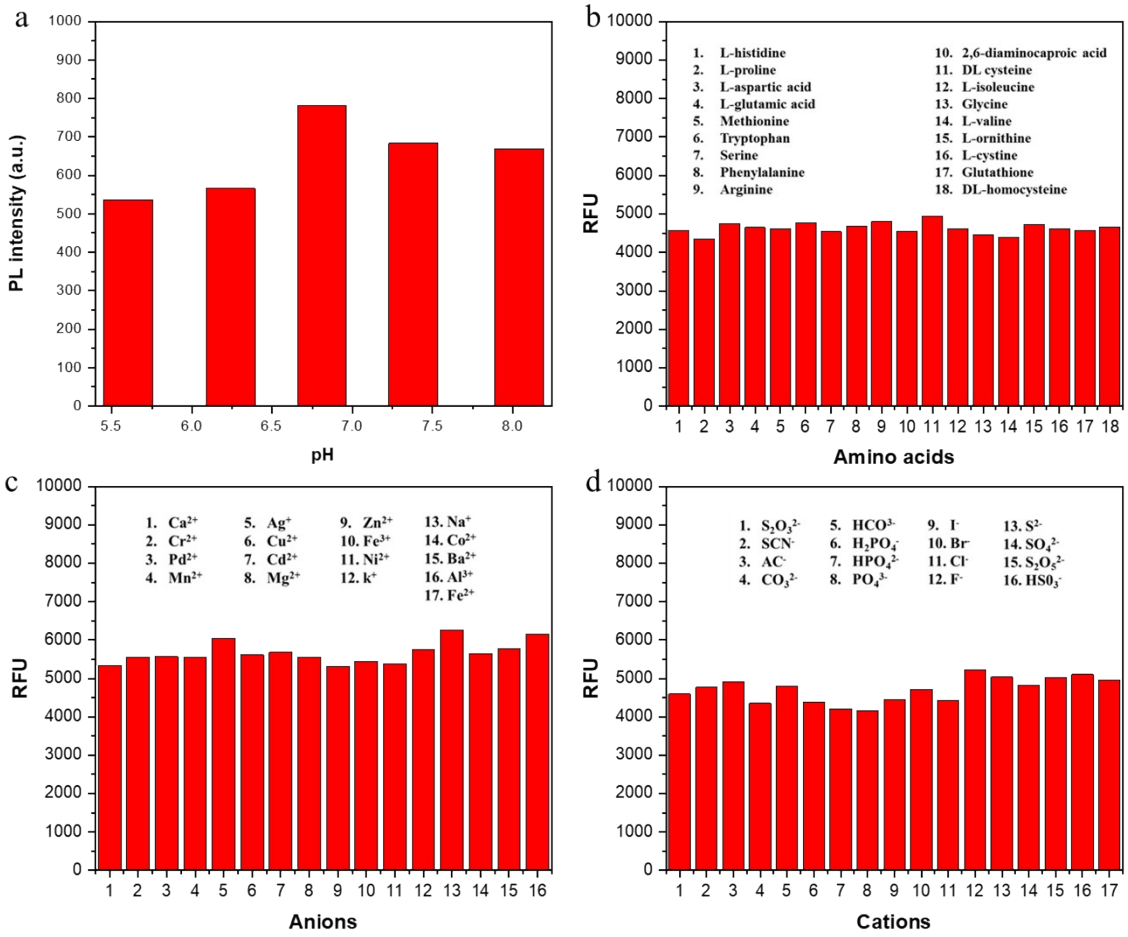


Fig. S11. Stability of **P1** (0.01 w/v%) in PBS with different pH (a), amino acids (b), anions (c) and cations (d).

Table S5. Crystal data and structure refinement for **1e**-cif.

Structural parameters	1e
Empirical formula	$C_{24}\ H_{13}\ F_5\ N_2\ O\ Pt$
F_w	635.45
crystal system	orthorhombic
space	P b c a (61)
crystal size (mm^3)	0.12×0.11 × 0.10
a, Å	15.764(3)
b, Å	11.846(2)
c, Å	22.623(4)
α, deg	90
β, deg	90
γ, deg	90
V, $Å^3$	4224.63(130)
Z	8
calculated density, g/cm^{-3}	1.99805 g/cm^3
μ, mm^{-1}	6.706
F (000)	2416.0
final R1 [I>2σ(I)]	0.0282
wR2 [I>2σ(I)]	0.0649
R1 (all data)	0.0519
wR2 (all data)	0.0760
GOF on F^2	0.975