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AIPE-Active Pt(II) Complexes with Tunable Triplet Excited State: Design, Mechanochromism and Application in Anti-Counterfeiting

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CONTENTS

1. General information

Materials and Instruments

All solvents and reagents were purchased from Energy Chemical. and used as is unless otherwise stated. The synthetic routes for ligands **L1–L5** and complexes **Pt-1–Pt-5** are illustrated in Scheme **1**. The synthesis of **1a**（2-bromo-9,9-dibutyl-9*H*-fluorene），**2a, 3a**, **4a**, **5a**, **6** have been reported previously.[1-5] The synthetic procedures and characterization data for the key precursors **7**, ligands **L1–L5** and complexes **Pt-1–Pt-5** are provided below. **L1–L5** were obtained by suzuki coupling reactions between **1a–5a** and **7**, respectively. The ligands **L1–L5** reacted respectively with $Pt(DMSO)_2Cl_2$ in refluxing acetic acid under nitrogen for 24 hours to afford complexes **Pt-1–Pt-5.** All intermediates, ligands and the Pt(II) complexes were characterized by ^{1}H NMR and ^{13}C NMR. Ligands **L1–L5** and complexes **Pt-1–Pt-5** were also characterized by ESI-HRMS and elemental analyses. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer using $CHCl_3$-d_6 as the solvent, with tetramethylsilane as internal standard. The elemental analyses were performed with a Vario El III elemental analyzer. ESI-HRMS analyses were performed on a Bruker BioTOF III mass spectrometer. Powder X-ray diffraction (XRD) patterns of the samples were collected on a Bruker D8 Advance powder diffractometer. DSC experiments were recorded on a NETZSCH DSC 204 instrument at a scanning rate of 10 K min^{-1}.

Photophysical measurements

The spectroscopic grade solvents were used for the photophysical experiments. Optical absorption spectra were obtained by using a Cary-5000 UV-vis spectrophotometer in different solvents. Photoluminescence spectra were carried out on a Hitachi F-7000 fluorescence spectrophotometer. The emission quantum yields of **L1–L5** and **Pt-1–Pt-5** were determined by the relative actinometry method (**Pt-1–Pt-5** were measured in degassed solutions). A 1 N sulfuric acid solution of quinine bisulfate (Φ_{em} = 0.546, λ_{ex} = 347.5 nm) was used as the reference for ligands **L1–L5** and a degassed aqueous solution of $[Ru(bpy)_3]Cl_2$ (Φ_{em} = 0.042, λ_{ex} = 436 nm) was used as the reference for complexes **Pt-1–Pt-5**. Fluorescence Lifetime were performed using time-correlated single-photon counting (TCSPC) method and collected on an LP980 laser flash photolysis spectrometer and FS5 spectrometer.

X-ray diffraction crystallography.

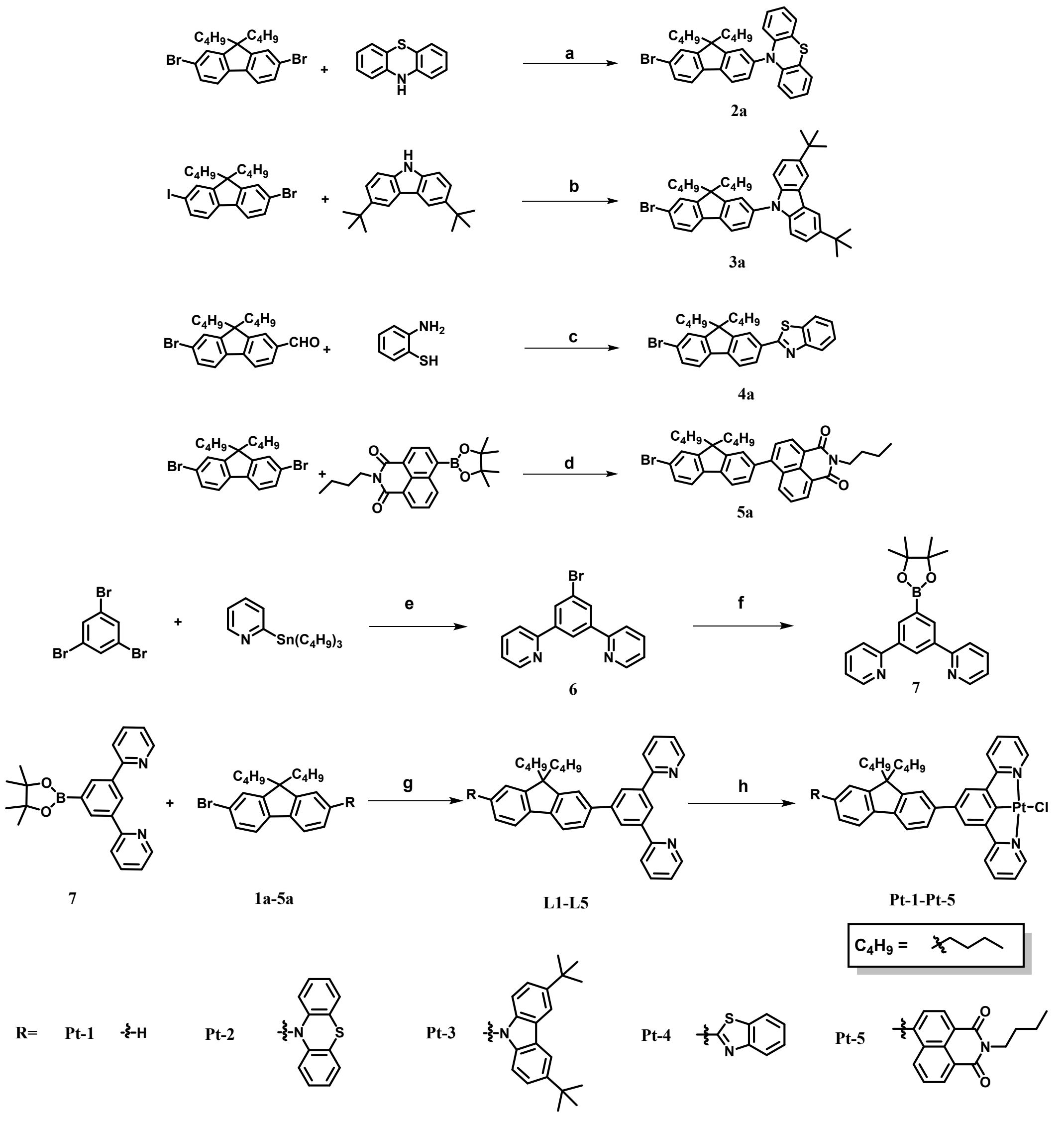
The single crystal **Pt-2** was grown by the slow evaporation of its solution in the mixture solvent of CH_2Cl_2 and n-hexane at room temperature. The diffraction data were collected on a Nonius CAD4 Single Crystal Diffractometer equipped with a graphite-monochromated MoKα radiation (λ = 0.71073 Å) by using an $\omega/2\theta$ scan mode at 296 K. The crystal structures were solved by the direct method and refined by the full-matrix leastsquares procedure on F2 using SHELXL-97 program. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced at calculated positions. CCDC 1558700 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambrige Crystallographic Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT Calculations.

The ground electronic state frontier molecular orbitals (FMOs) of complexes **Pt-1**-**Pt-5** were simulated by density functional theory (DFT), and their excited electronic states were calculated using the time-dependent density function theory (TDDFT) method. All calculations were performed using the Gaussian 09 software package. The specific DFT method used was PBE1PBE for calculating excited electronic states. The basis sets used in all calculations were the 6-31G* set for all light atoms and the LANL2DZ set for the Pt atom. Full equilibrium geometry optimizations were performed for the ground electronic states of all complexes. Excited-state calculations for 10 excited states were performed at the fully optimized ground-state molecular geometry of the complexes. For consistency with experiments, dichloromethane (CH_2Cl_2) which was used as the solvent for experimental measurements was selected as the solvent in theoretical calculations as well.

2. Synthesis of Pt-1-Pt-5.

Synthesis of ligands and complexes



Scheme S1 Synthetic route for **L1–L5** and **Pt-1–Pt-5**. (a) $Pd_2(dba)_3$/ether/sodium ter-butoxide, toluene, 60^{o}C,12h ; (b) mesitylene, CuI, 18-crown-6, K_2CO_3, reflux, 48 h; (c) DMSO, reflux,3h; (d) $Pd(PPh_3)_4$, K_2CO_3 a.q., toluene, reflux, 12 h; (e) $Pd(PPh_3)_4$, toluene, reflux, 24 h; (f) bis(pinacolato)diboron, $Pd(dppf)_2Cl_2$, AcOK, 1,4-dioxane, 80℃ ,4h; (g) $Pd(PPh_3)_4$, Na_2CO_3 a.q., toluene, EtOH, reflux, 12 h; (h) $Pt(DMSO)_2Cl_2$, CH_3COOH, reflux, 48h.

Synthesis of 7

A mixture of dpyb-Br (310 mg, 1 mmol), potassium acetate (294 mg, 3 mmol), bis(pinacolato)diboron (508 mg, 2 mmol) and 1,1-[bis(diphenylphosphino)]ferrocene palladium(II) dichloride (82 mg, 0.1 mmol) in anhydrous 1,4-dioxane(25 mL) was degassed by three freeze–

pump–thaw cycles and back-filled with nitrogen. The mixture was heated at 80 °C for 4 h under nitrogen. After cooling to ambient temperature, the solution washed with water (3×20 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and the solvent removed under reduced pressure. Purification was carried out by column chromatography (silica gel) eluted with mixed solvent of hexane–ethyl acetate 3: 1. 0.24 g light yellow was collected as the product (yield: 83%).^{1}H NMR (400MHz, $CDCl_3$): δ 8.78 (t, *J*= 2 Hz,1H), 8.71-8.73 (m,2H), 8.465 (d, J= 2, 2H), 7.89 (d, J =4, 2H),7.74-7.78(m, 2H), 7.22-7.25 (m, 2H), 1.38 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 157.3, 149.5, 139.3, 136.8, 133.82, 128.7, 122.8, 122.2, 121.1, 83.5, 24.9. MS(FAB+): m/z 358. Anal. calcd (%) for $C_{22}H_{23}BN_2O_2$: C, 73.76; H, 6.47; N, 7.82; Found: C, 73.71; H, 6.51; N, 7.85.

General synthetic procedure for L1–L5

The mixture of **7** (0.358g, 1 mmol), **1a–5a** (1 mmol), Na_2CO_3 (0.4238g, 4mmol), $Pd(PPh_3)_4$ (0.1155g, 0.1mmol), toluene (20 mL),ethanol (20 mL) and water (5 mL) was heated to reflux under nitrogen for 12 hours. After cooling to ambient temperature, the solution washed with water (3×20 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and the solvent removed under reduced pressure. Purification was carried out by column chromatography (silica gel) eluted with mixed solvent of hexane–ethyl acetate 4 : 1 (v/v).

L1. 0.32 g white solid was collected as the product (yield:63%). ^{1}H NMR ($CDCl_3$, 400 MHz): 8.77 (d, *J* = 2 Hz, 2H,), 8.55 (s, 1H), 8.35 (s, 2H), 7.93 (d, *J*=4 Hz, 2H), 7.79-7.84 (m, 3H), 7.71-7.75 (m, 3H),7.28-7.37 (m, 5H), 2.03-2.06 (m, 4H), 1.07-1.12 (m, 4H), 0.67-0.70 (m,10H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 157.4, 151.4, 151, 149.7, 143.1, 140.7, 140.5, 139.8, 136.8, 127.1,126.7, 126.5,126.3, 124.7, 122.9, 122.4, 121.7, 121.1, 119.9, 119.7, 55.2, 40.2, 26, 23.1, 13.8. ESI-HRMS: m/z calc. for $[C_{37}H_{36}N_2 + H]^+$: 509.29513, found 509.29514 .Elemental analysis calculated for $C_{37}H_{36}N_2$: C, 87.36; H, 7.13; N, 5.51. Found: C, 81.27; H, 8.07; N, 5.80.

L2: 0.289 g light yellow solid was collected as the product (yield:41%).^{1}H NMR ($CDCl_3$, 400 MHz): 8.77 (d, *J* = 2 Hz, 2H,), 8.57 (s, 1H), 8.39 (s, 2H), 7.95 (t, *J* = 8 Hz, 3H), 7.80-7.86 (m, 4H),7.76 (s, 1H), 7.38 (t, *J* = 8 Hz,, 2H), 7.30 (t, *J* = 8 Hz, 2H), 7.02 (t, *J* = 4 Hz, 2H), 6.78-6.84 (m, 4H), 6.23 (d, *J* = 4 Hz, 2H), 2.01-2.11 (m, 4H), 1.07-1.14 (m, 4H), 0.68-0.78 (m,10 H). ^{13}C NMR (100 MHz, $CDCl_3$):157.3, 154.5, 151.9, 149.7, 144.6, 142.8, 141.0, 140.6, 139.7,136.8, 129.6, 126.8, 126.7, 126.5, 126.0,124.6,122.4,122.3,121.9,121.8,119.5,115.6, 55.6, 40, 26.2, 22.9, 13.9. ESI-HRMS: m/z calc. for [$C_{49}H_{43}N_3S$+H]+: 706.32505, found 706.32397.Elemental analysis calculated for $C_{49}H_{43}N_3S$: C, 83.37; H, 6.14; N, 5.95. Found: C, 83.27; H, 6.09; N, 5.90.

L3: 0.463 g white solid was collected as the product (yield:59%).^{1}H NMR ($CDCl_3$, 400 MHz): 8.77 (d, *J* = 2 Hz, 2H,), 8.58 (s, 1H), 8.39 (s, 2H), 8.18 (s, 2H), 7.93 (t, *J* = 8 Hz, 3H), 7.77-7.87 (m, 5H), 7.56 (d, *J* = 4 Hz, 2H), 7.49 (d, *J*=4 Hz, 2H), 7.41 (d, *J*=4 Hz, 2H), 7.30 (t, *J* = 4 Hz, 2H), 2.05-2.11 (m, 4H), 1.49 (s, 18H),1.13-1.18 (m, 4H), 0.74-0.79 (m,10 H). ^{13}C NMR (100 MHz, $CDCl_3$): 157.4, 152.8, 151.7, 149.8, 142.9, 142.8, 140.8, 140.6, 139.6,139.4, 136.8, 126.6, 125.0, 124.5, 123.8, 123.4, 122.4, 121.3, 121.0, 120.8, 120.4, 120.1, 116.3, 109.2, 55.6, 40.2, 34.8, 32.1, 26.2, 23.1, 13.9. ESI-HRMS: m/z calc. for [$C_{57}H_{59}N_3$+H]+: 786.47818, found 786.47736. Elemental analysis calculated for $C_{57}H_{59}N_3$: C, 87.09; H, 7.57; N, 5.35. Found: C, 87.07; H, 7.51; N, 5.43.

L4: 0.339 g light yellow solid was collected as the product (yield:53%).^{1}H NMR ($CDCl_3$, 400 MHz): 8.77 (d, *J* = 2 Hz, 2H,), 8.57 (s, 1H), 8.37 (s, 2H), 8.15 (s, 1H), 8.06-8.12 (m, 2H), 7.94 (d, *J* = 2 Hz, 3H), 7.85 (d, *J* = 4 Hz, 3H),7.79 (d, *J* = 4 Hz, 2H), 7.75 (s, 1H), 7.51 (t, *J* = 8 Hz, 1H), 7.39 (t, *J* = 8 Hz, 1H), 7.31 (t, *J* = 8 Hz, 2H), 2.12-2.16 (m, 4H), 1.09-1.13 (m, 4H), 0.67-0.70 (m,10 H). ^{13}C NMR (100 MHz, $CDCl_3$):168.8, 157.3, 154.2, 152.2, 151.9, 149.8, 143.9, 142.8, 140.8, 140.6, 139.7,136.8, 135.0, 133.7, 132.3, 127.1, 126.6, 126.4, 125.0,124.6, 122.9, 122.3, 121.8 ,121.6, 121.5,121, 120.8, 120.2, 55.6,40.23, 26.1, 23.1, 13.8. ESI-HRMS: m/z calc. for [$C_{44}H_{39}N_3S$+H]+: 642.29375, found 642.29376.Elemental analysis calculated for $C_{44}H_{39}N_3S$: C, 82.33; H, 6.12; N, 6.55. Found: C, 82.27; H, 6.07; N, 6.57.

L5. 0.34 g yellow-green solid was collected as the product (yield: 45%). ^{1}H NMR ($CDCl_3$, 400 MHz): 8.78 (d, J = 2 Hz, 2H,), 8.67 (q, 2H), 8.56 (s, 1H), 8.34-8.39 (m, 3H), 7.90-7.96 (m, 4H), 7.78-7.88 (m, 5H),7.70 (t, J = 8 Hz, 1H), 7.52 (d, J = 4 Hz, 2H), 7.32 (t, J = 4 Hz, 2H), 4.24 (t, J = 8 Hz, 2H),2.09-2.13 (m, 4H), 1.75-1.78(m, 2H), 1.46-1.51 (m, 2H), 1.10-1.16 (m, 4H), 1.01 (t, J = 8 Hz ,3H), 0.67-0.79 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 164.2, 157.3, 151.7, 149.7, 147.5, 142.8, 141.3, 140.5 ,139.87, 137.4, 136.9, 132.7, 131.1, 130.9, 130.2, 128.9, 128.8, 127.8, 126.7, 124.6, 122.4, 121.1, 120.4, 55.49, 40.31, 40.12, 30.27, 26.2, 23, 20.4, 13.89, 13.85. ESI-HRMS: m/z calc. for [$C_{53}H_{49}N_3O_2$ + H]+: 760.38975, found 760.38898. Elemental analysis calculated for $C_{53}H_{49}N_3O_2$: C, 83.76; H, 6.50; N, 5.53; .Found: C, 83.67; H,6.52; N, 5.59.

General synthetic procedure for Pt-1–Pt-5

The mixture of **L1–L5** (0.2 mmol), $Pt(DMSO)_2Cl_2$ (0.2 mmol), and acetic acid (10 mL) was refluxed under nitrogen for 24 hours. After cooling to room temperature, the reaction mixture was filtered. The precipitate was washed with water, ethanol, and ether. The crude product was further purified by recrystallization in DCM/ hexane.

Pt-1: 51 mg yellow powder was collected as the product (yield:35%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.28 (dd, J_1 =16 Hz, J_2 = 2 Hz, 2H), 7.93 (t, J =8 Hz, 2H), 7.77 (t, J =8 Hz, 4H), 7.60 (d, J =4 Hz, 4H). 7.36(m, d, J =4 Hz, 3H), 7.22(s, 2H), 2.00-2.06 (m, 4H), 1.10-1.15 (m, 4H), 0.69-0.73 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1,152.2, 151.6, 150.8, 141.1, 140.7, 140.6, 140.3, 138.8, 137.1, 127.1, 126.8, 125.8, 123.3, 123.1, 122.9, 121.1,120.1, 119.7, 119.3, 55.2, 40.2, 26, 23.1, 13.8. HRMS (MALDI-TOF), m/z calcd for $[C_{37}H_{35}ClN_2Pt+H]^+$: 738.2209, found 738.2169. Anal. Calcd. for $C_{37}H_{35}ClN_2Pt$: C, 60.20; H, 4.78; N, 3.79. Found: C, 60.26; H, 4.81; N, 3.78.

Pt-2: 59 mg yellow powder was collected as the product (yield:32%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.38 (dd, J_1 =16 Hz, J_2 = 2 Hz, 2H), 7.97-8.02 (m, 3H), 7.84 (t, J = 8 Hz, 3H), 7.67-7.72 (m, 3H),7.63 (s, 1H), 7.39 (t, J = 8 Hz,, 2H), 7.32 (t, J = 4 Hz, 2H), 7.03 (t, J = 4 Hz, 2H), 6.81-6.83 (m, 4H), 6.24-6.27 (m, 2H), 2.06-2.11 (m, 4H), 1.10-1.17 (m, 4H), 0.70-0.76 (m,10 H). HRMS (MALDI-TOF), m/z calcd for $[C_{49}H_{42}ClN_3PtS+H]^+$ 935.2509, found 935.2507. Anal. Calcd. for $C_{49}H_{42}ClN_3PtS$: C, 62.91; H, 4.53; N, 4.49. Found: C, 62.99; H, 4.58; N, 4.54.

Pt-3: 38 mg yellow powder was collected as the product (yield:19%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.38 (dd, J_1 =16 Hz, J_2 = 2 Hz, 2H), 8.18 (s, 2H), 8.00 (t, J = 8 Hz, 2H), 7.94 (d, J = 4 Hz, 1H), 7.84 (t, J = 8 Hz, 3H), 7.72 (s, 2H), 7.68 (d, J = 4 Hz, 1H), 7.63 (s, 1H), 7.58 (s, 2H), 7.50 (d, J=4 Hz, 2H), 7.42 (d, J = 8 Hz, 2H), 7.32 (d, J = 4 Hz, 2H),2.07-2.14 (m, 4H), 1.49 (s, 18H),1.15-1.19 (m, 4H), 0.75-0.81 (m,10 H). HRMS (MALDI-TOF), m/z calcd for $[C_{57}H_{58}ClN_3Pt+H]^+$: 1015.4040, found 1015.4023. Anal. Calcd. for $C_{57}H_{58}ClN_3Pt$: C, 67.41; H, 5.76; N, 4.14. Found: C, 67.52; H, 5.81; N,4.19.

Pt-4: 50 mg yellow powder was collected as the product (yield:29%).^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.34 (dd, J_1 =16 Hz, J_2 = 2 Hz, 2H), 8.17 (s, 1H), 8.08-8.13 (m, 2H), 7.94-7.99 (m, 3H), 7.85 (d, J =4 Hz, 2H), 7.80 (d, J = 4 Hz, 2H), 7.67 (d, J = 4 Hz, 3H), 7.63 (s, 1H), 7.52 (t, J = 8 Hz, 1H), 7.40 (t, J = 4 Hz, 1H), 7.29 (d, J = 4 Hz, 2H), 2.13-2.19 (m, 4H), 1.12-1.17 (m, 4H), 0.69-0.73 (m,10H). HRMS (MALDI-TOF), m/z calcd for $[C_{44}H_{38}ClN_3PtS+H]^+$: 871.2196, found 871.2191.

Anal. Calcd. for $C_{44}H_{38}ClN_3PtS$: C, 60.65; H, 4.40; N, 4.82. Found: C, 60.60; H, 4.33; N,4.78.

Pt-5: 82 mg yellow powder was collected as the product (yield:41%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.39 (dd, J_1 =16 Hz, J_2 = 2 Hz, 2H), 8.65-8.71 (m, 2H), 8.35 (d, J = 4 Hz,1H), 8.0(t, J = 4 Hz, 2H), 7.88-7.94 (m, 2H), 7.82 (t, J = 8 Hz, 3H),7.64-7.73 (m, 5H), 7.53 (d, J = 4 Hz, 2H), 7.33 (t, J = 4 Hz, 2H), 4.24 (t, J = 8 Hz, 2H),2.10-2.14 (m, 4H), 1.75-1.78(m, 2H), 1.48-1.52 (m, 2H), 1.15-1.19 (m, 4H), 1.01 (t, J = 8 Hz ,3H), 0.75-0.82 (m, 10H). HRMS (MALDI-TOF), m/z calcd for $[C_{53}H_{48}ClN_3O_2Pt+H]^+$: 989.3156, found 989.3186. Anal. Calcd. for $C_{53}H_{48}ClN_3O_2Pt$: C, 64.33; H, 4.89; N, 4.25;. Found: C, 64.30; H, 4.85; N, 4.29.

3. Photophysical properties of Pt-1-Pt-5

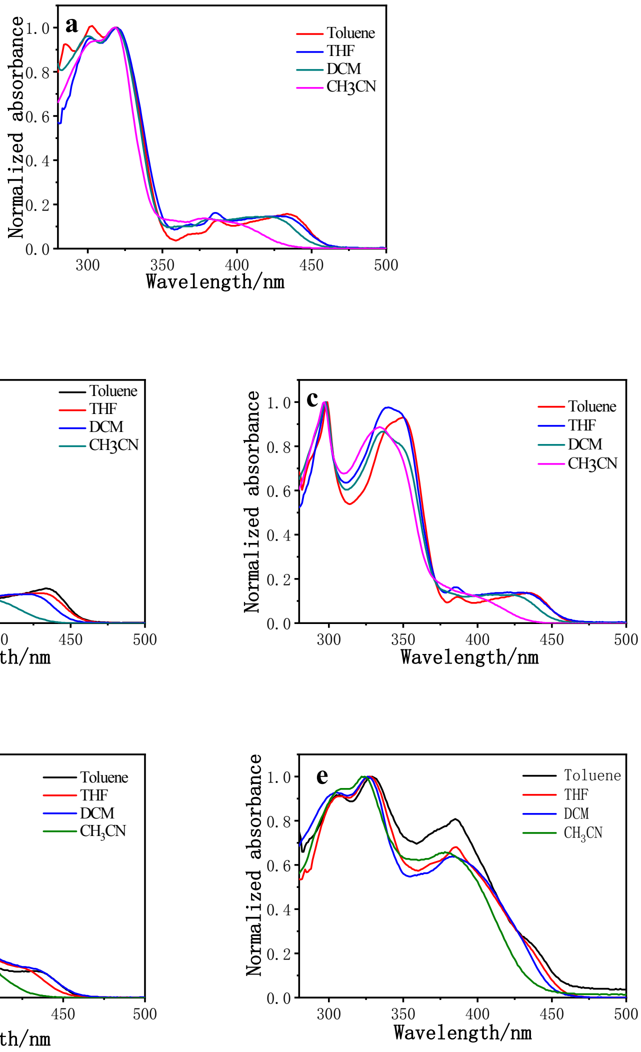


Fig. S1 Normalized absorption spectra of **Pt-1**(a), **Pt-2**(b), **Pt-3**(c), **Pt-4**(d) and **Pt-5**(e) in different solvents.

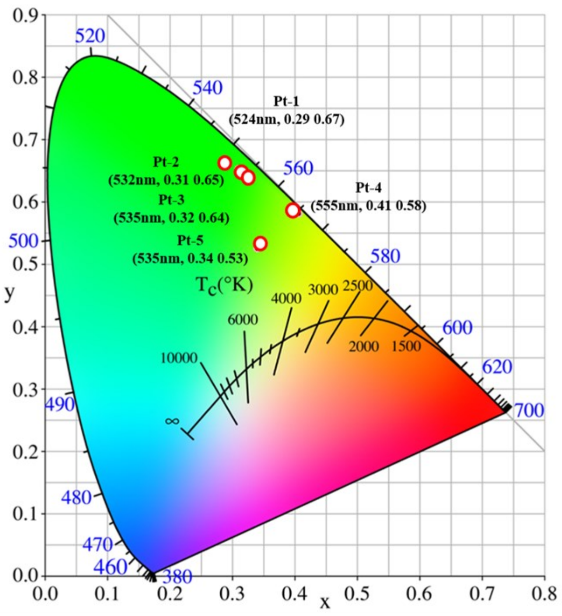


Fig. S2 The corresponding CIE chromaticity coordinate of **Pt-1−Pt-5** in CH_2Cl_2 ($c = 1.0 \times 10^{-5}$ M).

Table S1. Contour plots of the other highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) for **Pt-1 -Pt-5** in CH_2Cl_2.

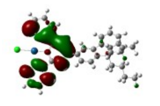
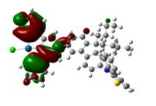
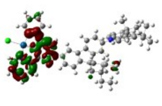
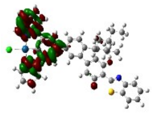
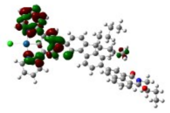
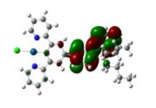
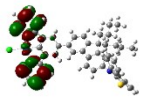
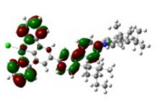
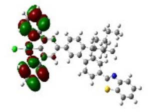
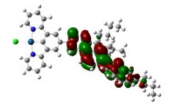
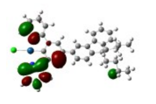
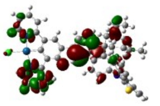
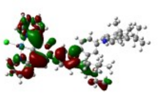
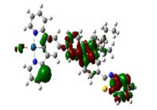
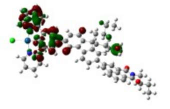
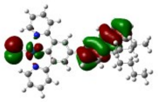
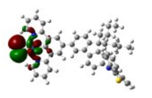
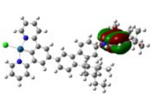
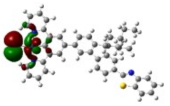
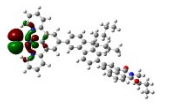
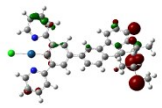
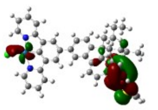
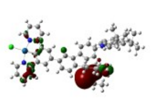
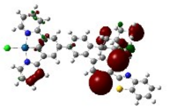
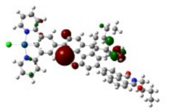
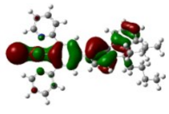
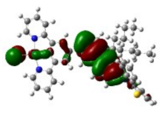
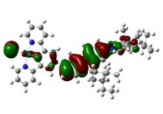
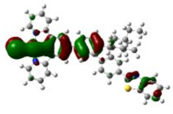
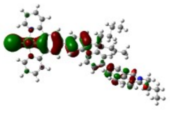
	Pt-1	**Pt-2**	**Pt-3**	**Pt-4**	**Pt-5**
LUMO+4					
LUMO+3					
LUMO+2					
HOMO-2					
HOMO-3					
HOMO-4					

Table S2 Excitation Energies (eV), Wavelengths (nm), Oscillator Strengths, Dominant Contributing Configurations, and the Associated Configuration Coeffcients of 10 Low-Lying Electronic States of

Complexes **Pt-1-Pt-5** Obtained at the PBE1PBE Level of Theory.

	Sn	excitation energy		f	active orbital pair of dominant configuration	configuration coefficient
		eV	nm			
Pt-1	1	3.1811	388.75	0.1267	HOMO-LUMO	0.68
	2	3.2044	386.92	0.0215	HOMO-LUMO+1	0.67
	3	3.6461	340.05	0.0109	HOMO-3-LUMO+1	0.68
	4	3.7547	330.21	0.0051	HOMO-2-LUMO+1	0.59
	5	3.7835	327.70	0.0018	HOMO-3-LUMO	0.65
	6	3.8210	324.48	0.0018	HOMO-1-LUMO+1	0.60
	7	3.9082	317.24	0.0148	HOMO-1-LUMO+1	0.65
	8	3.9336	315.19	0.0001	HOMO-4-LUMO+1	0.68
	9	4.0612	305.29	0.0644	HOMO-LUMO	0.60
	10	4.0870	303.37	0.0019	HOMO-LUMO	0.65
Pt-2	1	3.2014	387.28	0.1266	HOMO-1-LUMO	0.67
	2	3.2069	386.62	0.0067	HOMO-LUMO	0.68
	3	3.2275	384.14	0.0198	HOMO-1-LUMO+1	0.68
	4	3.2509	381.38	0.0000	HOMO-LUMO+2	0.68
	5	3.4858	355.69	0.0005	HOMO-LUMO+2	0.68
	6	3.6626	338.52	0.0108	HOMO-LUMO+6	0.58
	7	3.7669	329.14	0.0042	HOMO-LUMO+6	0.58
	8	3.7736	328.56	0.0119	HOMO-4-LUMO+1	0.66
	9	3.7941	326.78	0.0002	HOMO-5-LUMO	0.68
	10	3.9367	314.95	0.0006	HOMO-6-LUMO+1	0.67
Pt-3	1	3.1776	390.18	0.1108	HOMO-1-LUMO	0.60
	2	3.2068	386.62	0.0218	HOMO-1-LUMO+1	0.63
	3	3.3354	371.72	0.0223	HOMO-LUMO	0.61
	4	3.3834	366.45	0.0004	HOMO-LUMO+1	0.64
	5	3.6550	339.22	0.0104	HOMO-5-LUMO+1	0.69
	6	3.7332	332.11	0.6227	HOMO-LUMO+2	0.69
	7	3.7725	328.65	0.0154	HOMO-4-LUMO+1	0.67
	8	3.7907	327.08	0.0000	HOMO-5-LUMO	0.69
	9	3.9087	317.20	0.0001	HOMO-2-LUMO	0.69
	10	3.9351	315.07	0.0000	HOMO-6-LUMO+1	0.69
Pt-4	1	3.1921	388.41	0.1251	HOMO-LUMO	0.65
	2	3.2154	385.60	0.0293	HOMO-LUMO+1	0.64
	3	3.5248	351.75	1.1151	HOMO-LUMO+2	0.63
	4	3.6538	339.33	0.0114	HOMO-3-LUMO+1	0.69
	5	3.7340	332.04	0.0006	HOMO-1-LUMO	0.54
	6	3.7767	328.29	0.4204	HOMO-1-LUMO+2	0.51
	7	3.7806	327.95	0.1244	HOMO-2-LUMO+1	0.46
	8	3.7934	326.85	0.0039	HOMO-3-LUMO	0.64
	9	3.8345	323.34	0.0260	HOMO-1-LUMO+1	0.62
	10	3.9301	315.47	0.0000	HOMO-5-LUMO+1	0.69

Pt-5	1	3.0774	402.89	0.1031	HOMO-LUMO	0.61
	2	3.1883	388.87	0.1302	HOMO-LUMO+1	0.66
	3	3.2144	385.71	0.0225	HOMO-LUMO+2	0.65
	4	3.3554	369.50	0.0283	HOMO-1-LUMO	0.60
	5	3.6609	338.67	0.0107	HOMO-3-LUMO+2	0.69
	6	3.7301	332.39	0.0019	HOMO-1-LUMO+1	0.58
	7	3.7838	327.67	0.0174	HOMO-2-LUMO+2	0.58
	8	3.8006	326.23	0.0054	HOMO-3-LUMO+1	0.63
	9	3.8141	325.07	0.3257	HOMO-4-LUMO	0.67
	10	3.8351	323.28	0.0144	HOMO-1-LUMO+2	0.63

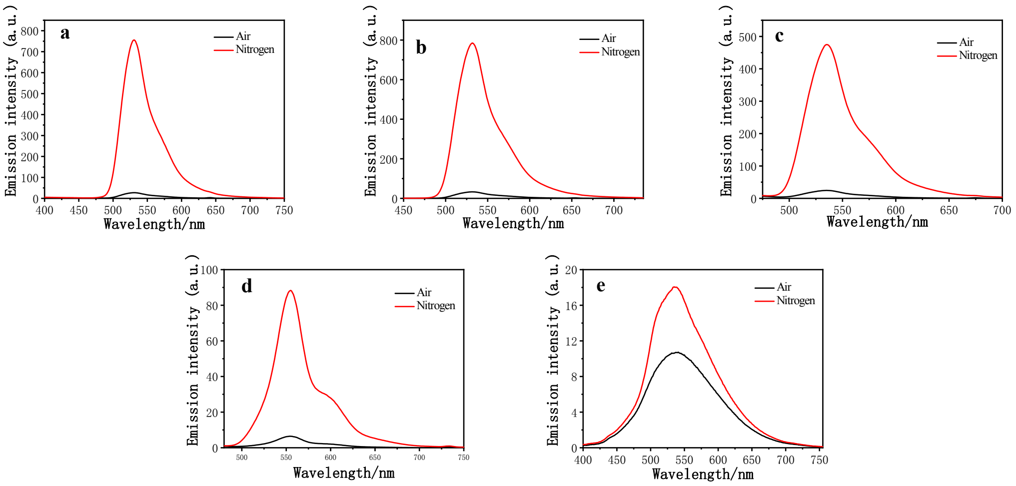
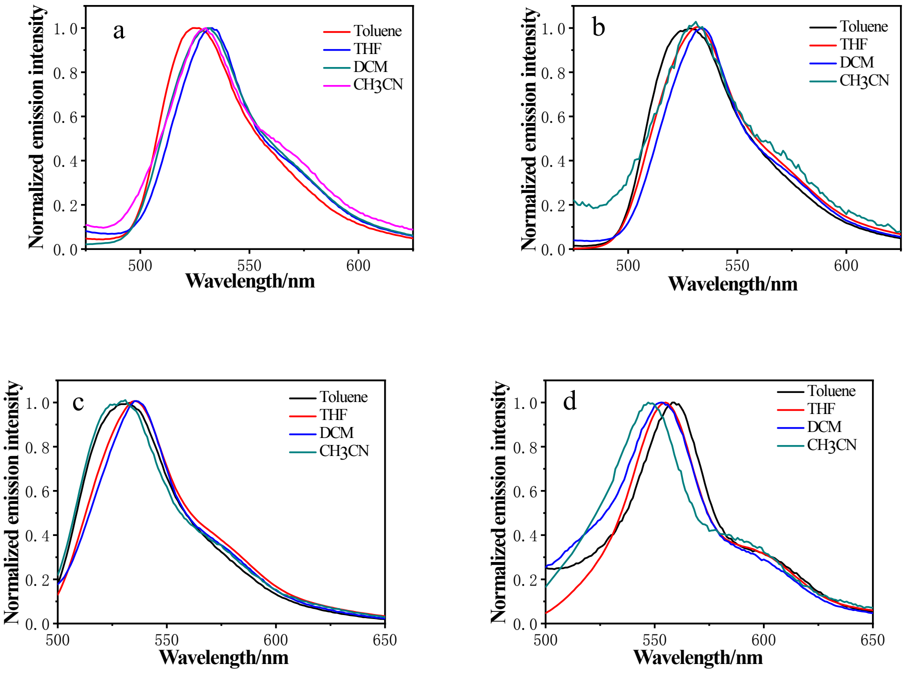


Fig. S3 Emission spectra of complexes **Pt-1**(a), **Pt-2**(b), **Pt-3**(c), **Pt-4**(d) and **Pt-5**(e) in air-saturated and degassed CH_2Cl_2 solution.



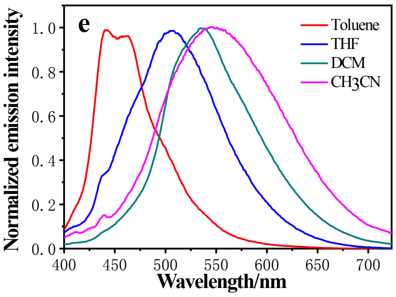


Fig. S4 Normalized emission spectra of **Pt-1**(a), **Pt-2**(b), **Pt-3**(c), **Pt-4**(d) and **Pt-5**(e) in different solvents.

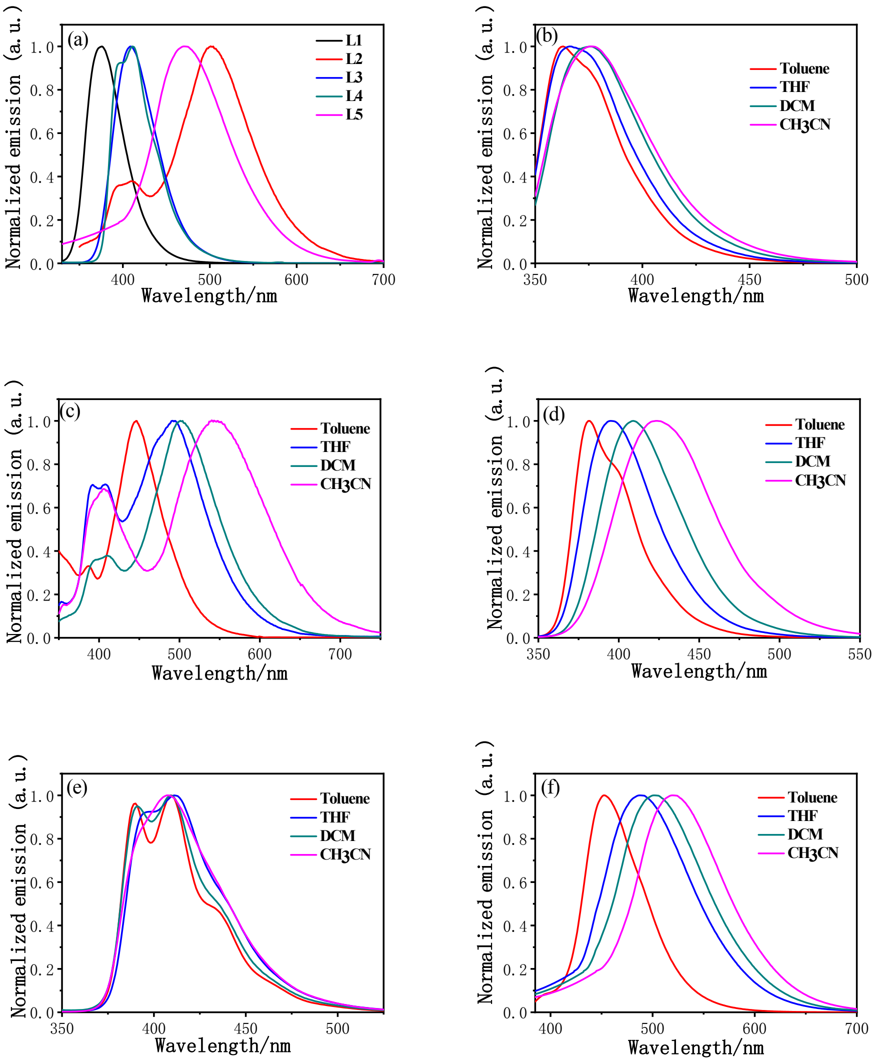


Fig. S5 (a) Normalized emission spectra of (a) ligands **L1** (λ_{ex} = 316nm), **L2** (λ_{ex} = 318 nm), **L3** (λ_{ex} = 340 nm), **L4** (λ_{ex} = 355 nm) and **L5** (λ_{ex} = 381 nm) in CH_2Cl_2 (c = 1 ×10^{-5} mol/L); (b-f) Normalized emission spectra of **L1− L5** in different solvents.

4. AIPE property

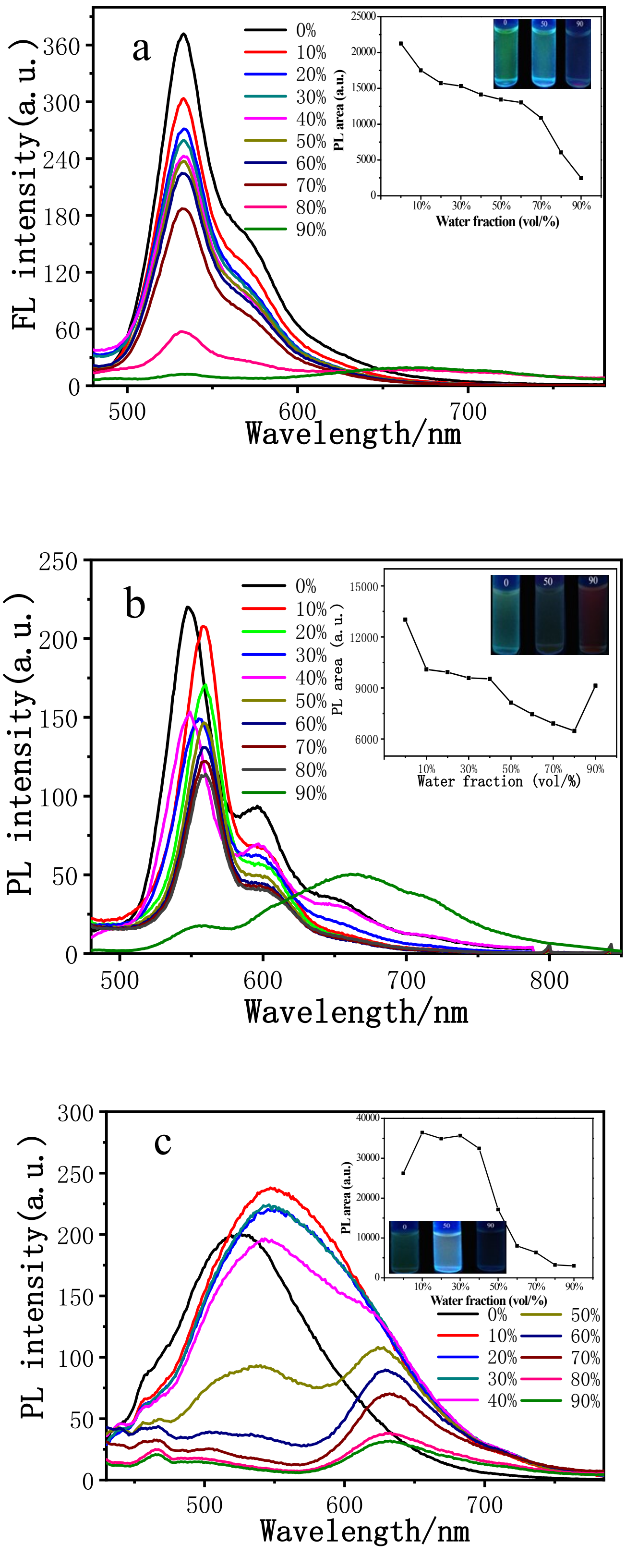


Fig. S6 Emission spectra of complexes **Pt-1**(a), **Pt-4**(b), **Pt-5**(c) (c = 1.0×10^{-5} M) in THF-water mixtures with different water fractions (0-90%). Plots of fluorescent areas versus water fractions in THF-H_2O. The insets and the photographs show the complexes in different water fraction mixtures under 365 nm UV illumination.

5. Piezochromism

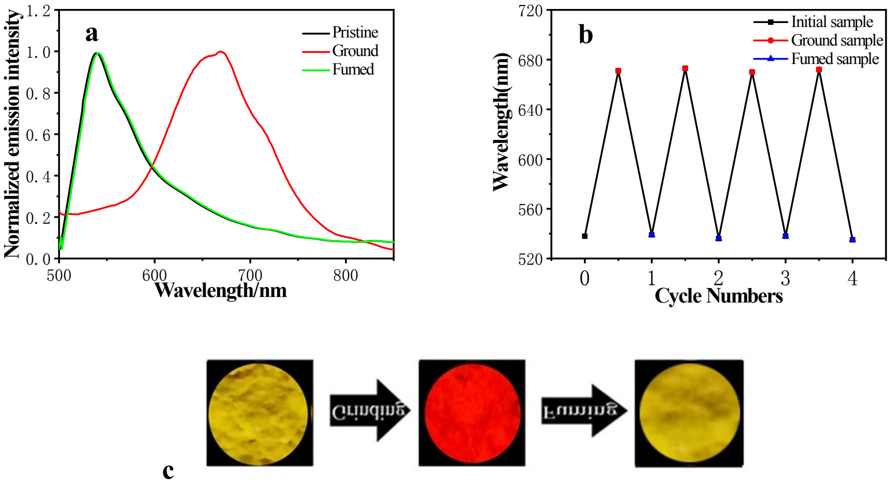


Fig. S7 Pt-1(a) Emission spectra of initial, ground and fumed samples. (b) Cycle numbers for reversible grinding–fuming. (c) Reversible grinding–fuming photographs of complex based on piezochromic and vapochromic properties obtained under UV light at 365 nm.

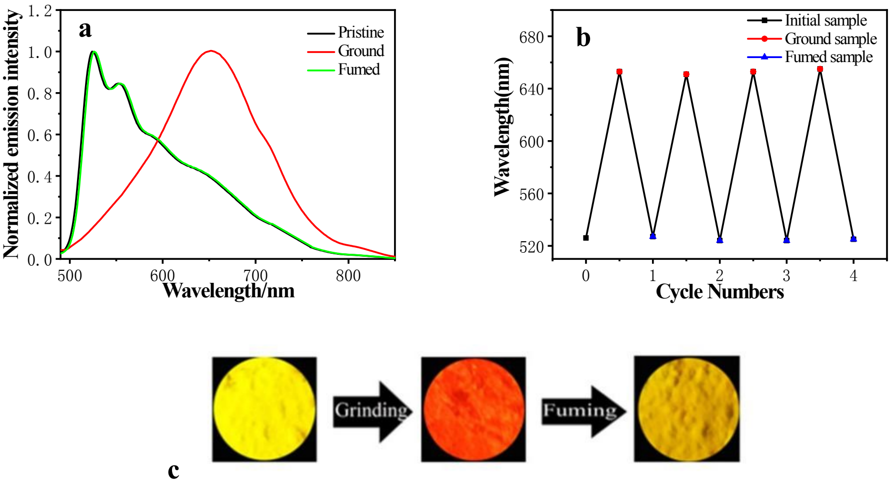


Fig. S8 Pt-3 (a) Emission spectra of initial, ground and fumed samples. (b) Cycle numbers for reversible grinding–fuming. (c) Reversible grinding–fuming photographs of complex based on piezochromic and vapochromic properties obtained under UV light at 365 nm.

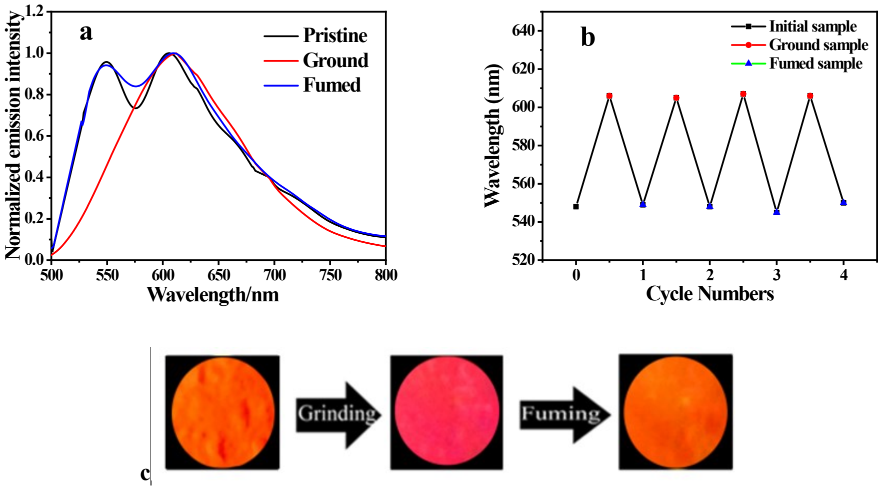


Fig. S9 Pt-4 (a) Emission spectra of initial, ground and fumed samples. (b) Cycle numbers for reversible grinding–fuming. (c) Reversible grinding–fuming photographs of complex based on piezochromic and vapochromic properties obtained under UV light at 365 nm.

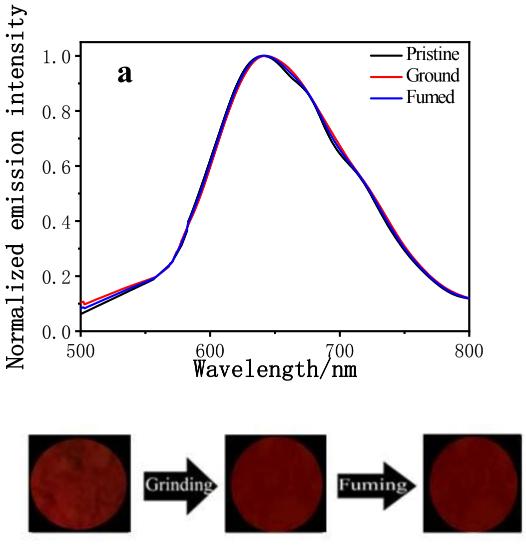


Fig. S10 Pt-5 (a) Emission spectra of initial, ground and fumed samples. (b).Reversible grinding–fuming photographs of complex based on piezochromic and vapochromic properties obtained under UV light at 365 nm.

6. XRD and DSC

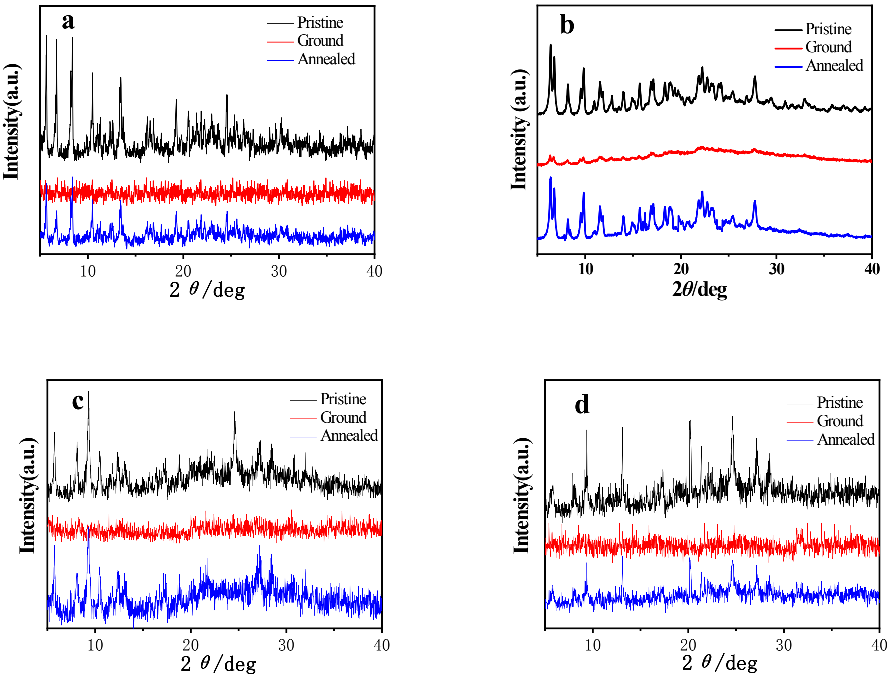


Fig. S11 Changes in XRD patterns by mechanical grinding and solvent treatment for **Pt-1**(a), **Pt-3**(b), **Pt-4**(c), **Pt-5**(d).

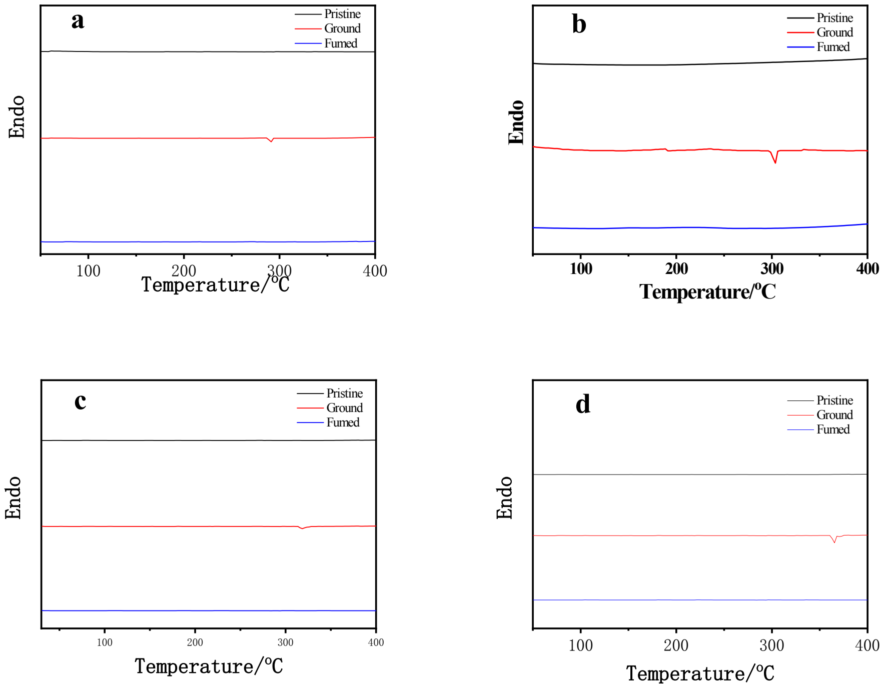


Fig. S12 DSC curves of **Pt-1**(a), **Pt-3**(b), **Pt-4**(c), **Pt-5**(d) in pristine, ground, and annealed states.

7. Crystallographic data

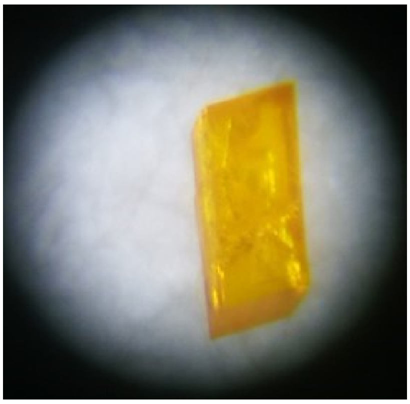


Fig. S13 The picture of crystal **Pt-2**.

Table S3 Crystallographic data of **Pt-2**

	Pt-2 (1558700)
formula	C_{50} C_{l3} N_3 Pt S
fw	976.074
crystal system	Triclinic
space group	*P*-1 (2)
a, Å	9.1509(4)
b, Å	9.7957(4)
c, Å	24.3327(11)
a, deg	86.999(2)
β, deg	82.305(2)
γ, deg	75.544(2)
V, $Å^3$	2092.69(16)
Z	2
ρ_{calcd},g cm^{-3}	1.54893
T / K	296(2)
μ, mm−1	3.634
θ, deg	2.32 to 27.58
F(000)	1020
index ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 11$, $-28 \leq 1 \leq 28$
data/restraints/parameters	7342/ 0 /525
GOF (F^2)	1.041
$R_1{}^a$,$wR_2{}^b$ (I>2σ(I))	0.0312, 0.0632

R_1^a, wR_2^b (all data)	0.0388, 0.0659

$R_1^a = \Sigma||F_o| - |F_c||/\Sigma F_o|$. $wR_2^b = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^1$

Table S4 Selected bond distances and angles in the crystal

Bond distances (Å)			
Pt(1)-N(2)	2.04(28)	Pt(1)-Cl(1)	2.42(12)
Pt(1)-N(3)	2.02(36)	C(12)-N(1)	1.43(53)
Pt(1)- C(37)	1.90(54)	S(1)-C(7)	1.76 (55)

Bond angles (˚)			
N(2)-Pt(1)-N(3)	161.0(136)	C(1)-N(1)-C(12)	121.5(366)
C(37)-Pt(1)-N(3)	80.5(154)	C(7)-S(1)-C(6)	99.9(221)
Cl(1)-Pt(1)-N(3)	99.8(108)	N(1)-C(13)-C(14)	120.3(402)

Table S4 Summary of the molecular interactions in the crystal

Entry	Orientation of Interaction	d (Å)
1	C-H…Pt	2.84(4)
2	C-H…Cl	2.84(11)

References

1. J. Khunchalee, R. Tarsaeng, S. Jungsuttiwong, T. Keawin, T. Sudyoadsuk and V. Promarak, *Tetrahedron Lett.*, 2012, **53**, 5939-5943.
2. L. Wang, H. Yin, M. A. Jabed, M. Hetu, C. Wang, S. Monro, X. Zhu, S. Kilina, S. A. McFarland and W. Sun, *Inorg. Chem.*, 2017, **56**, 3245-3259.
3. C. J. Yao, R. H. Zheng, Q. Shi, Y. W. Zhong and J. Yao, *Chem. Commun.*, 2012, **48**, 5680-5682.
4. Y. Li, N. Dandu, R. Liu, S. Kilina and W. Sun, *Dalton Trans*, 2014, **43**, 1724-1735.
5. A. Saini, K. R. J. Thomas, C.-T. Li and K.-C. Ho, *J. Mater. Sci. Mater. Electron.*, 2016, **27**, 12392-12404.