Electronic Supplementary Information (ESI)

Trimercarbazole-based aggregation-induced fluorescence-to-phosphorescence-active gold(I) complexes: Isomeric engineering of auxiliary ligand for high-contrast hypsochromic phosphorescent mechanochromism

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1. Experimental Section

Materials and measurements

To ensure the efficacy of the reaction, all synthesis reactions were performed under anhydrous and anaerobic conditions using standard Schlenk techniques, unless otherwise stated. Dichloromethane (DCM) was purified by CaH_2-drying followed by distillation. Tetrahydrofuran (THF) was treated with sodium metal subsequently distilled. All starting materials were used as received without further purification. Thin-layer chromatography analysis was performed using pre-coated glass plates. Silica gel (200-300 mesh) was used for column chromatography. Analytical-grade reagents were used thoughout the experiments. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Germany Bruker AVANCE NEO 500 MHz. ^{1}H NMR spectra chemical shifts were referenced to TMS (δ = 0.00 ppm) as the internal standard, reporting peak multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet) and coupling constants (J) in hertz. ^{13}C NMR shifts were reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77.00 ppm. High-Resolution Mass Spectrometer (HRMS) data were performed on a Waters Xevo TQ-XS mass spectrometer. Liquid-phase UV-Vis absorption spectra were collected on Thermo Scientific Evolution One UV-Vis spectrophotometer. Absorption spectra of solid samples were recorded on a PerkinElmer Lambda 750 spectrophotometer. Photoluminescence (PL) spectra were conducted on a Hitachi F-4600 spectrophotometer or an Edinburgh FLS1000 spectrophotometer. The aggregate behaviors of three luminogens in THF/H_2O mixture (water content: 90%) were investigated by scanning electron microscopy (SEM, Zeiss, Sigma). Powder X-ray diffraction (PXRD) studies of complexes were recorded on Empyrean XRD diffractometer using Ni-filtered and graphite-monochromated Cu Kα radiation (λ = 1.54 Å, 40 kV, 30 mA). Lifetimes and the absolute fluorescence quantum yields were recorded on the Edinburgh FLS1000 spectrophotometer. We measured the phosphorescent quantum yield (Φ_P) by peak-differentiation-imitating analysis, where the Φ_P and Φ_F from the Φ can be figured out from their integrate area ratios identified from the steady-state PL spectrum using the following equation 1.[1]

$$\Phi_P = \Phi \frac{A'}{A} \quad \text{Equation 1}$$

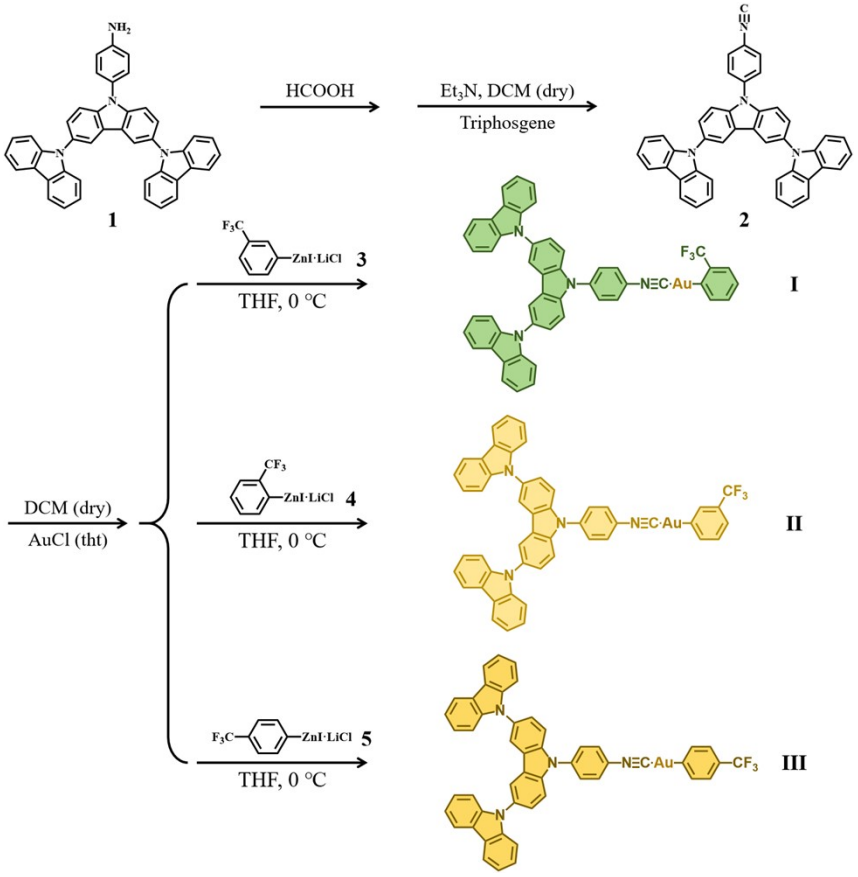
Where A and A' are the integral areas of photoluminescence and phosphorescence from the steady-state PL spectrum, respectively.

General procedure for the synthesis

The compound **1** was synthesized according to the corresponding literature.[2] Synthesis of **2**[3]: A mixture of compound **1** (3.0 g, 5.1 mmol), formic acid (30 mL) were stirred for overnight at 110 ℃. After completion of present reaction, formic acid was removed from reaction system by distillation, the residual mixture was extracted with dichloromethane (3 × 30 mL), the combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residues were purified by column chromatography. Then, the product was dissolved in a CH_2Cl_2 (15 mL), and triethylamine (5 mL) was added. The mixture was cooled to 0℃. To the mixture was added dropwise a CH_2Cl_2 solution (10 mL) of triphosgene (1.16 g, 3.9 mmol). The mixture was refluxed under an argon atmosphere for 3 h, then Na_2CO_3 (50 mL) was added dropwise at room temperature. The mixture was extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residues were purified by column chromatography, affording the expected solid product in a yield of 66%. Compound **2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.28 (s, 2H), 8.17 (d, J = 5.0 Hz, 4H), 7.82 (d, J = 10.0 Hz, 2H), 7.75 (d, J = 5.0 Hz, 2H), 7.65 (s, 4H), 7.39 (t, J = 7.5 Hz, 8H), 7.29 (t, J = 5.0 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm) = 141.6, 140.0, 138.1, 131.0, 128.4, 128.0, 126.5, 125.9, 124.4, 123.2, 120.3, 119.9, 119.8, 111.0, 109.6. HRMS-ESI (m/z): Found: $[M + H]^+$ 599.2230; "molecular formula $C_{43}H_{26}N_4$" requires $[M + H]^+$ 599.2231.

According to the reported procedure, organozinc iodide reagents **3-5** were synthesized.[4] Complexes **I-III** were prepared according to the synthetic procedures presented in the reported references.[5] The synthetic strategies for gold(I) complexes **I-III** are presented in Scheme S1. Synthesis of gold(I) complexes **I-III**: **I-III** were

synthesized in a similar manner.



Scheme S1. Synthetic routes of the gold(I) complexes **I-III**.

The synthetic procedure of complex **I** was used as a representative example: Compound **2** (7.18 g, 12.0 mmol) and chloro(tetrahydrothiophene)gold(I) (3.209 g, 10.0 mmol) were dissolved in CH_2Cl_2 (100 mL) and stirred for 13.5 h at ambient condition. After the reaction completion was monitored by TLC analysis, the solvent was removed with a rotary evaporator under a reduced pressure. The residues were washed with methanol. Then, the product was placed in an oven-dried two-neck flask. The flask was connected to a vacuum/nitrogen manifold through a rubber tube. It was evacuated and then backfilled with nitrogen. This cycle was repeated three times. THF (3.0 mL) was then added in the flask through the rubber septum using a syringe, and stirred at 0 ℃. An organozinc iodide reagent **3** in THF (3.0 mL) was then added to the reaction mixture using a syringe, and stirred at 0 ℃ for 2.5 h. After the reaction completion was monitored by TLC analysis, the reaction mixture was quenched by the addition of a phosphate buffer solution (5.0 mL) and then extracted with CH_2Cl_2 (100 mL) three times and washed with brine (200 mL). The organic layers were

collected and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. Further purification was performed through the repeated washing by using hexane or methanol to give an analytically pure white solid of **I**.

Complex **I** (white solid, yield: 60%): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.29 (s, 2H), 8.17 (d, J = 5.0 Hz, 4H), 7.93-7.87 (m, 4H), 7.70-7.66 (m, 6H), 7.43-7.38 (m, 10H), 7.31-7.28 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 160.8, 141.5, 141.1, 140.0, 139.6, 131.4, 129.9, 128.8, 126.7, 126.0, 126.9, 126.7, 124.7, 124.7, 124.6, 123.6, 123.2, 120.4, 120.3, 120.0, 119.9, 119.7, 111.0, 109.5. ^{13}F NMR ($CDCl_3$): δ (ppm) = -59.6. HRMS-ESI (m/z): Found: $[M + H]^+$ 941.2169; "molecular formula $C_{50}H_{30}AuF_3N_4$" requires $[M + H]^+$ 941.2161.

Complex **II** (white solid, yield: 62 %): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.30 (s, 2H), 8.17 (d, J = 10.0 Hz, 4H), 7.95-7.93 (m, 2H), 7.89 (d, J = 10.0 Hz, 2H), 7.77 (s, 1H), 7.68-7.65 (m, 4H), 7.42-7.35 (m, 11H), 7.31-7.28 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 163.1, 143.4, 141.8, 141.6, 140.1, 139.7, 136.4, 136.4, 131.5, 128.9, 128.8, 128.3, 127.2, 126.7, 126.0, 125.9, 125.9, 124.7, 123.3, 120.4, 120.0, 119.9, 110.9, 109.5. ^{13}F NMR ($CDCl_3$): δ (ppm) = -62.3. HRMS-ESI (m/z): Found: $[M + H]^+$ 941.2162; "molecular formula $C_{50}H_{30}AuF_3N_4$" requires $[M + H]^+$ 941.2161.

Complex **III** (white solid, yield: 70 %): ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 8.30 (s, 2H), 8.17 (d, J = 10.0 Hz, 4H), 7.94 (t, J = 4.3 Hz, 2H), 7.90-7.87 (m, 2H), 7.68 (t, J = 2.3 Hz, 3H), 7.60 (d, J = 10.0 Hz, 2H), 7.50 (d, J = 10.0 Hz, 2H), 7.41-7.37 (m, 9H), 7.31-7.28 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 167.3, 141.6, 139.7, 131.5, 128.8, 128.3, 126.7, 126.0, 125.9, 124. 7, 123.6, 123.5, 123.5, 123.3, 120.4, 120.0, 119.9, 110.9, 109.5. ^{13}F NMR ($CDCl_3$): δ (ppm) = -62.4. HRMS-ESI (m/z): Found: $[M + H]^+$ 941.2170; "molecular formula $C_{50}H_{30}AuF_3N_4$" requires $[M + H]^+$ 941.2161.

2. The UV-Vis absorption spectra and photophysical parameters of complexes I-III in THF-H_2O mixtures (c = 2.0 × 10^{-5} mol·L^{-1}) with different water fractions

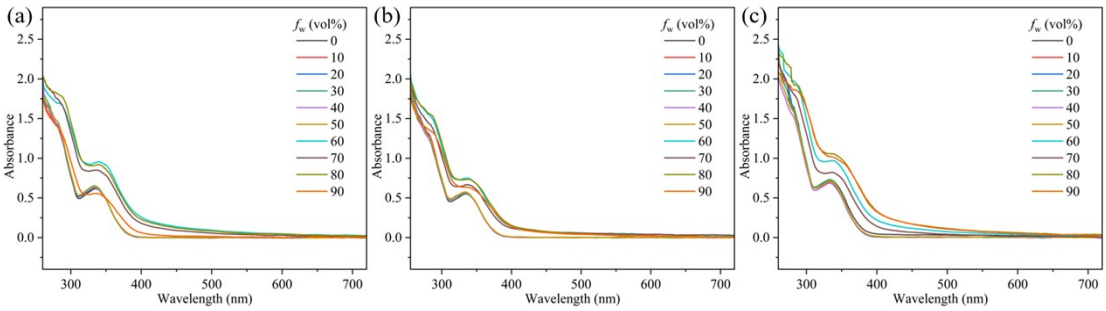


Fig. S1 UV-Vis absorption spectra of complexes **I-III** in THF-H_2O mixtures (c = 2.0 × 10^{-5} mol·L^{-1}) with different water fractions: (a) **I**; (b) **II**; (c) **III**.

Table S1 The maximum emission wavelength (λ_{max}) values, the average lifetime (τ) values, and the absolute photoluminescence quantum yields (Φ) of complexes **I-III** in THF-H_2O mixtures with 0%, 60%, and 90% water fractions.

Complex	$\lambda_{0\%}$ (nm)	$\tau_{0\%}$ (ns)	$\Phi_{0\%}$	$\lambda_{60\%}$ (nm)	$\tau_{60\%}$ (ns)	$\Phi_{60\%}$	$\lambda_{90\%}$ (nm)	$\tau_{90\%}$ (ns)	$\Phi_{90\%}$
I	477	1.10	8.37%	465	1.04	6.10%	445, 541	0.64, 630.20	9.95%
II	479	1.63	7.15%	469	1.65	6.29%	564	882.69	12.19%
III	478	2.09	5.17%	465	1.37	4.23%	569	1059.21	15.72%

Table S2 Bi-exponential fitting parameters for the photoluminescence decay of complex **I** in THF/water mixtures at different water contents (f_w = 0%, 60%, 90%).

I	**λ_{max} (nm)**	**τ_1 (ns)**	**A_1**	**τ_2 (ns)**	**A_2**	**<τ> (ns)**
0%	477	0.9205	91.14%	2.8980	8.86%	1.10
60%	465	0.6309	87.57%	3.9534	12.43%	1.04
90%	445	0.3376	87.71%	2.8103	12.29%	0.64
	541	301.3974	47.47%	927.3350	52.53%	630.20

Table S3 Bi-exponential fitting parameters for the photoluminescence decay of complex **II** in THF/water mixtures at different water contents (f_w = 0%, 60%, 90%).

II	**λ_{max} (nm)**	**τ_1 (ns)**	**A_1**	**τ_2 (ns)**	**A_2**	**<τ> (ns)**
0%	479	0.8580	85.60%	6.2432	14.40%	1.63
60%	469	0.5343	79.35%	5.9252	20.65%	1.65
90%	564	334.4988	28.50%	1101.1980	71.50%	882.69

Table S4 Bi-exponential fitting parameters for the photoluminescence decay of complex **III** in THF/water mixtures at different water contents (f_w = 0%, 60%, 90%).

III	λ_{max} (nm)	τ_1 (ns)	A_1	τ_2 (ns)	A_2	<τ> (ns)
0%	478	0.8563	82.99%	8.1065	17.01%	2.09
60%	465	0.5594	83.01%	5.3474	16.99%	1.37
90%	569	424.7255	28.36%	1310.3794	71.64%	1059.21

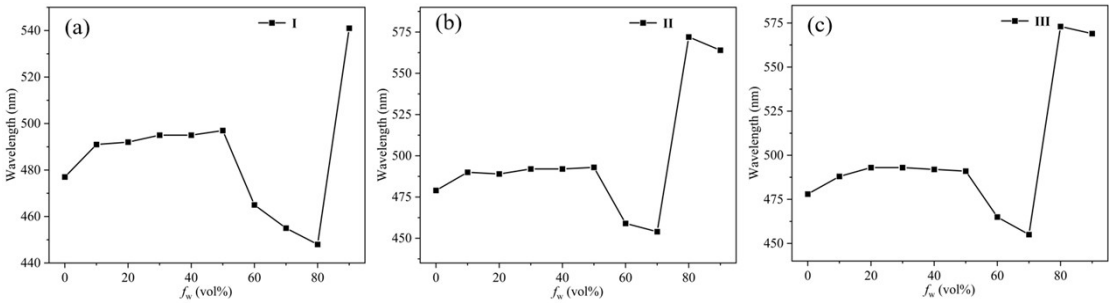


Fig. S2 Plots of the λ_{max} versus f_w values for **I** (a), **II** (b), and **III** (c) in THF-H_2O mixtures.

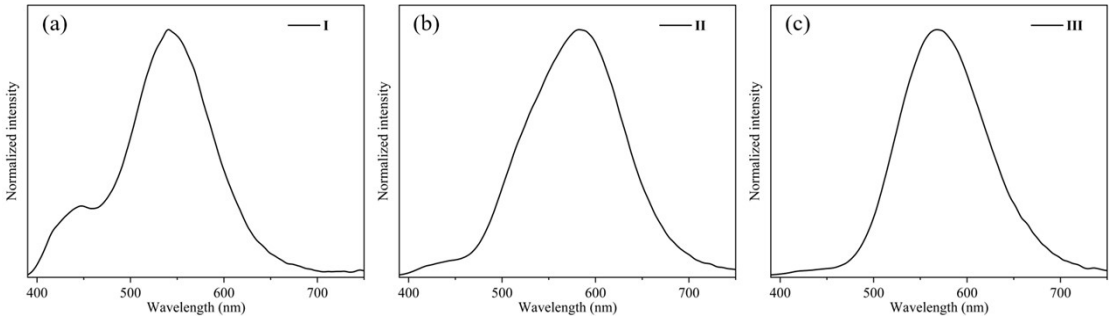


Fig. S3 Normalized phosphorescence spectra of complexes (2.0×10^{-5} mol L^{-1}) in THF-H_2O mixtures with 90% water fraction: (a) **I**; (b) **II**; (c) **III**. Excitation wavelength = 365 nm.

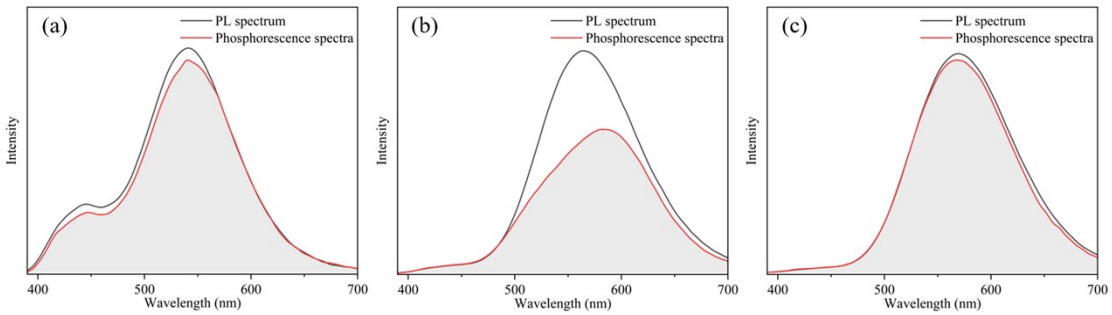


Fig. S4 Spectral integral areas for quantifying fluorescence and phosphorescence contributions. Steady-state PL spectra and corresponding phosphorescence spectra for complexes (a) **I**, (b) **II**, and (c) **III** in THF-H_2O mixtures with 90% water fraction.

Table S5 Quantum yields of complexes **I-III** in THF-H_2O mixtures at f_w = 90%.

	Φ	A	A'	Φ_F	Φ_P
I	9.95%	127.78551	120.05733	0.60%	9.35%
II	12.19%	181.76175	130.57412	3.43%	8.76%
III	15.72%	121.36805	116.91865	0.58%	15.14%

3. SEM images of complexes I-III (c = 2.0 × 10^{-5} mol·L^{-1}) formed from THF-H_2O mixture (f_w = 90%)

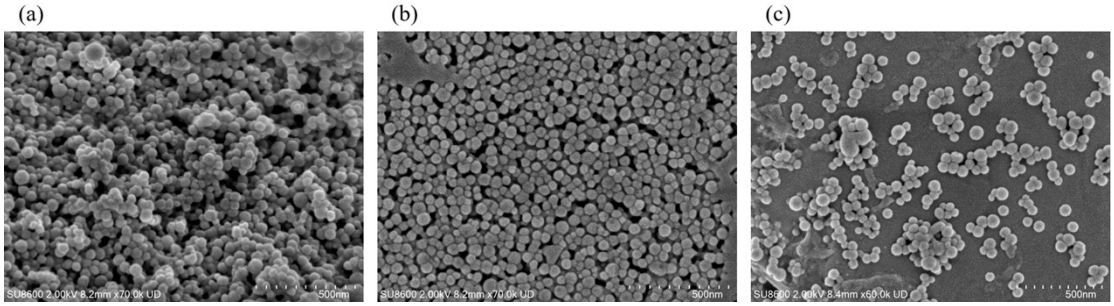


Fig. S5 SEM images of complexes **I-III** (c = 2.0 × 10^{-5} mol·L^{-1}) formed from THF-H_2O mixture (f_w = 90%): (a) **I**; (b) **II**; (c) **III**.

4. Decay curves and photophysical parameters of complexes I-III in various solid states

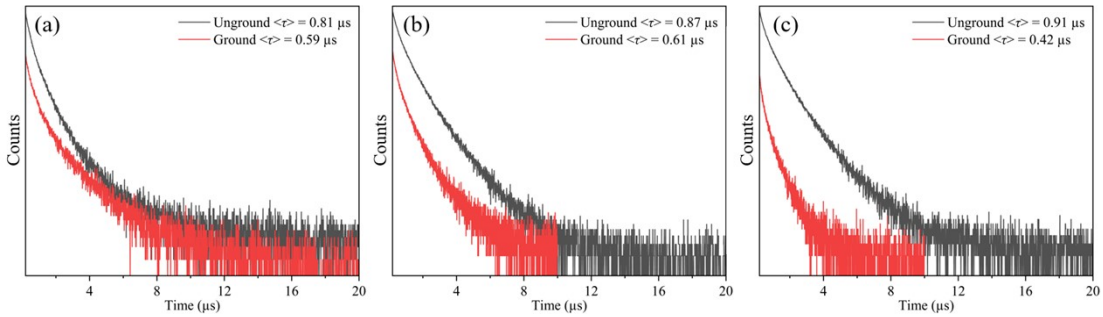


Fig. S6 Decay curves of solids **I** (a), **II** (b), and **III** (c) before and after grinding.

Table S6 The maximum emission wavelength (λ_{max}) values, the average lifetime (τ) values, and the absolute photoluminescence quantum yields (Φ) of complexes **I-III** in various solid states.

Complex	λ_{max} (unground)	τ (unground)	Φ (unground)	λ_{max} (ground)	τ (ground)	Φ (ground)	λ_{max} (treated with DCM)
I	541 nm	805.65 ns	10.09%	491 nm	591.48 ns	4.42%	537 nm
II	566 nm	866.12 ns	13.02%	555 nm	608.63 ns	6.22%	567 nm
III	570 nm	912.55 ns	16.13%	561 nm	419.16 ns	5.71%	573 nm

Table S7 Multi-exponential fitting parameters for the photoluminescence decay of complexes **I-III** before and after grinding.

	λ_{max} (nm)	τ_1 (ns)	A_1	τ_2 (ns)	A_2	τ_3 (ns)	A_3	$<\tau>$ (ns)
I (unground)	541	250.9158	29.38%	792.9191	61.23%	2624.3323	9.39%	805.65
I (ground)	491	2.8741	44.13%	371.9335	27.20%	1705.7750	28.67%	591.48
II (unground)	566	220.1493	14.45%	717.4317	56.47%	1475.8433	29.08%	866.12
II (ground)	555	107.3970	17.89%	451.3384	53.79%	1224.0348	28.32%	608.63
III (unground)	570	188.8743	12.78%	747.3012	58.98%	1585.1702	28.24%	912.55
III (ground)	561	40.6992	12.52%	212.6354	45.30%	753.2962	42.18%	419.16

5. Photophysical properties of complexes I-III in solid states

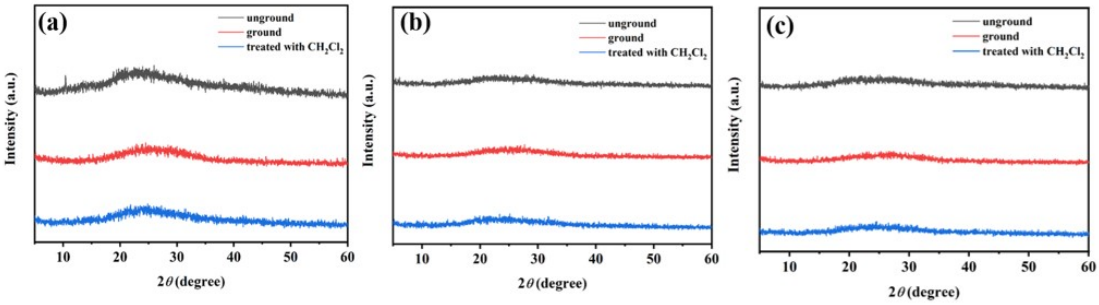


Fig. S7 The powder X-ray diffraction patterns of complexes **I** (a), **II** (b) and **III** (c) in different solid states: unground, ground and treated with DCM.

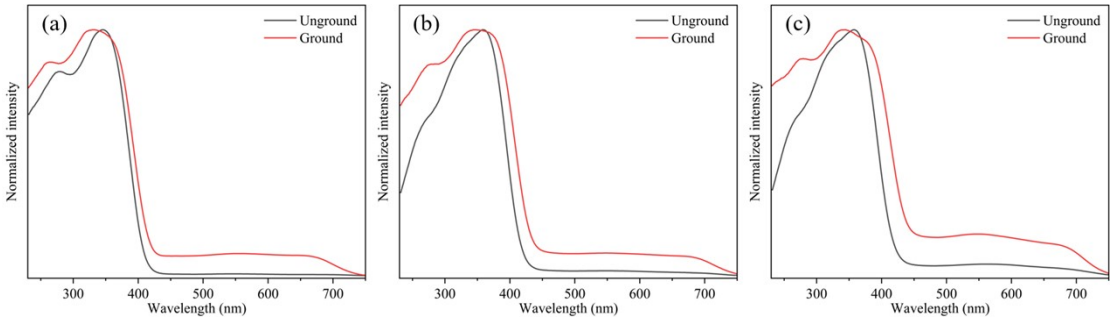


Fig. S8 Solid-state UV-Vis absorbance spectra of solid samples of **I** (a), **II** (b), and **III** (c).

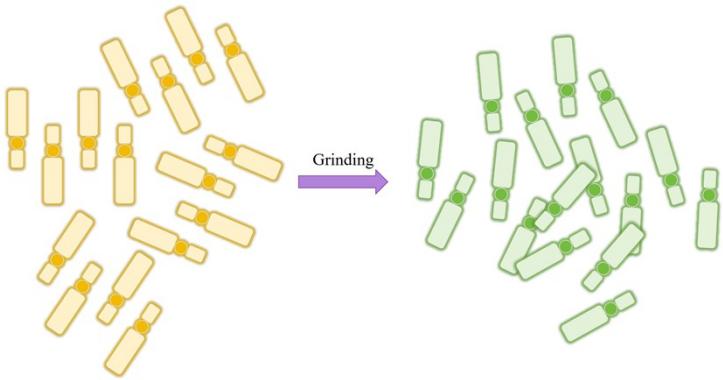


Fig. S9 Schematic diagram of mechanochromic phosphorescence.

6. Decay curves and photophysical parameters of solids I-III at 77 K

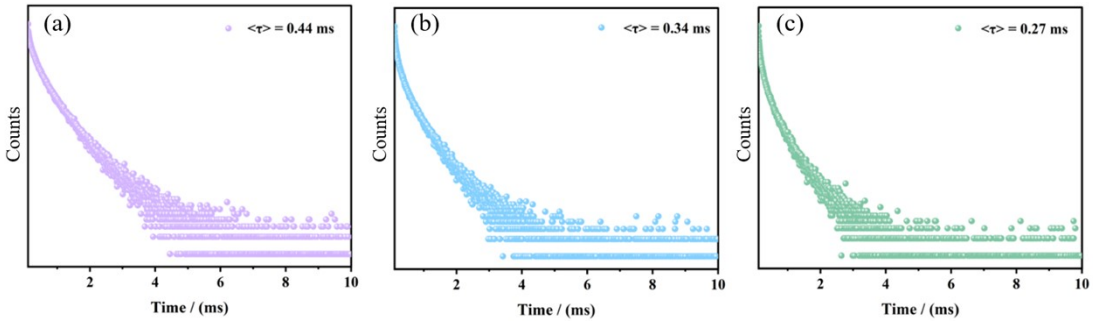


Fig. S10 Decay curves of solids **I** (a), **II** (b), and **III** (c) at 77 K.

Table S8 The maximum emission wavelength (λ_{max}) values and the average lifetime (τ) values of solids **I-III** at 77 K.

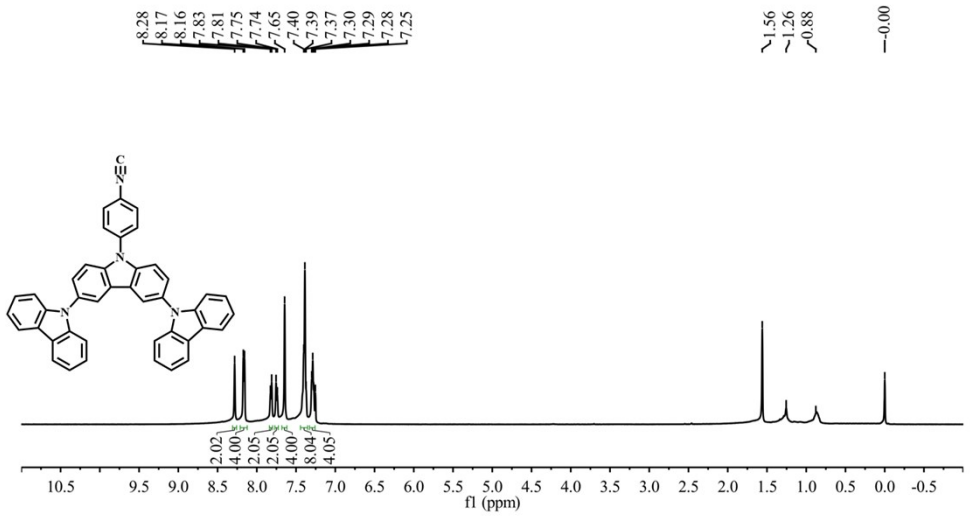
Complex	λ_{max} (77 K)	τ (77 K)
I	456 nm	435.91 μs
II	458 nm	339.85 μs
III	459 nm	268.67 μs

Table S9 Bi-exponential fitting parameters for the photoluminescence decay of complexes **I-III** at 77 K.

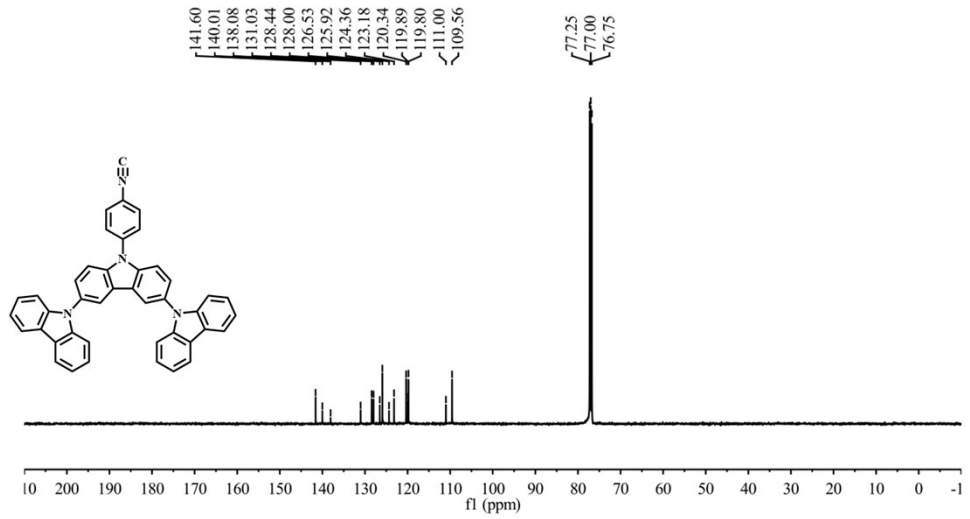
	λ_{max} (nm)	τ_1 (μs)	A_1	τ_2 (μs)	A_2	$\langle\tau\rangle$ (μs)
I (77 K)	456	153.8176	36.36%	597.0774	63.64%	435.91
II (77 K)	458	105.2978	40.75%	501.1650	59.25%	339.85
III (77 K)	459	77.8982	43.48%	415.4314	56.52%	268.67

7. Copies of NMR spectra and HRMS spectra of intermediate

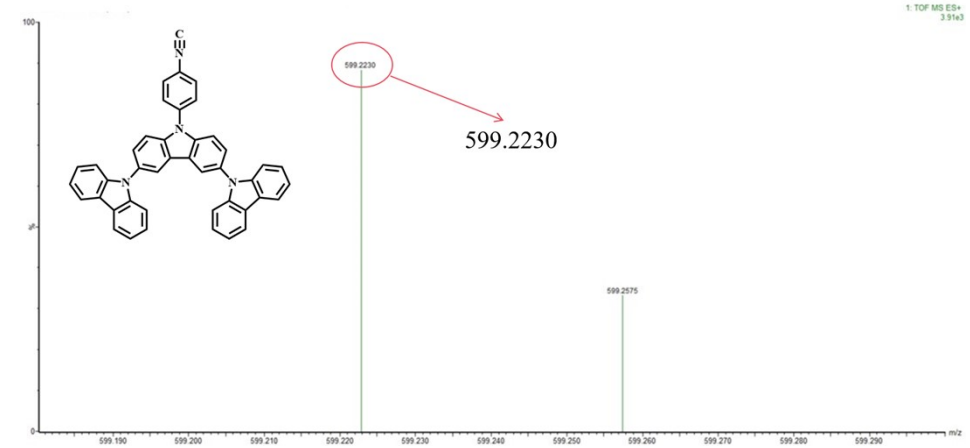
compound 2 and gold(I) complexes I-III



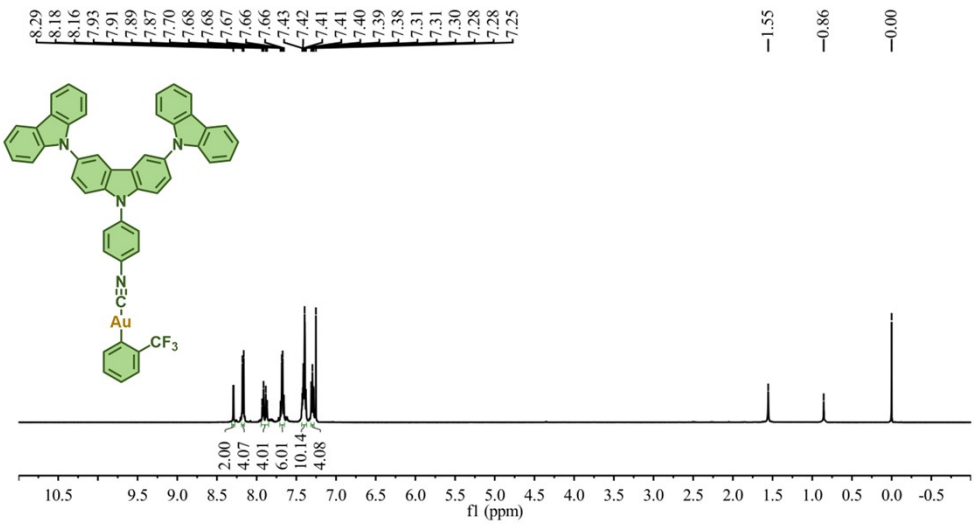
^{1}H NMR spectrum of intermediate compound **2** in $CDCl_3$



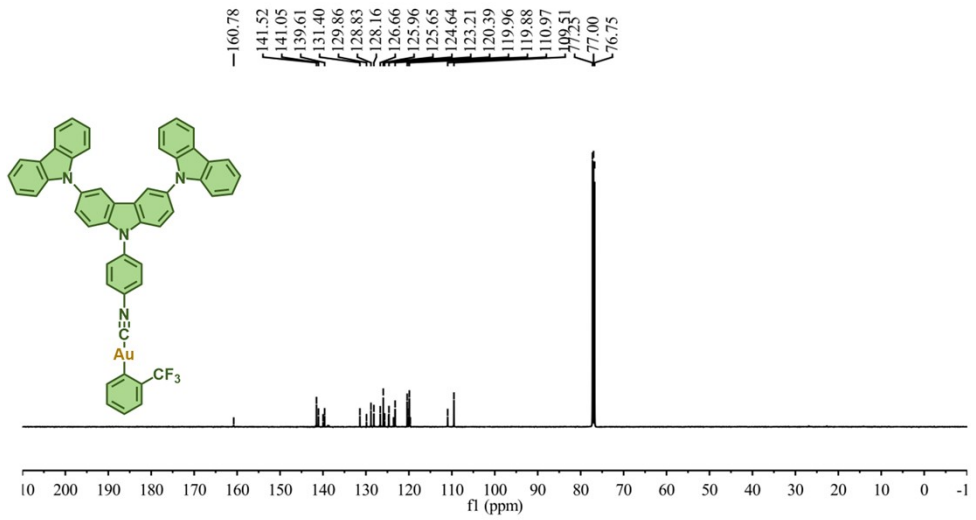
^{13}C NMR spectrum of intermediate compound **2** in $CDCl_3$



HRMS spectrum of intermediate compound **2**



^{1}H NMR spectrum of gold(I) complex **I** in $CDCl_3$



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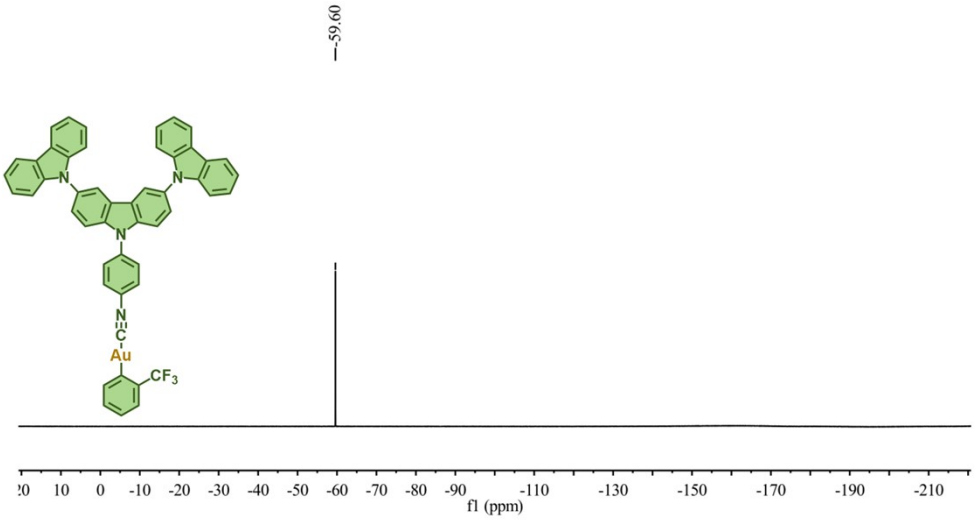
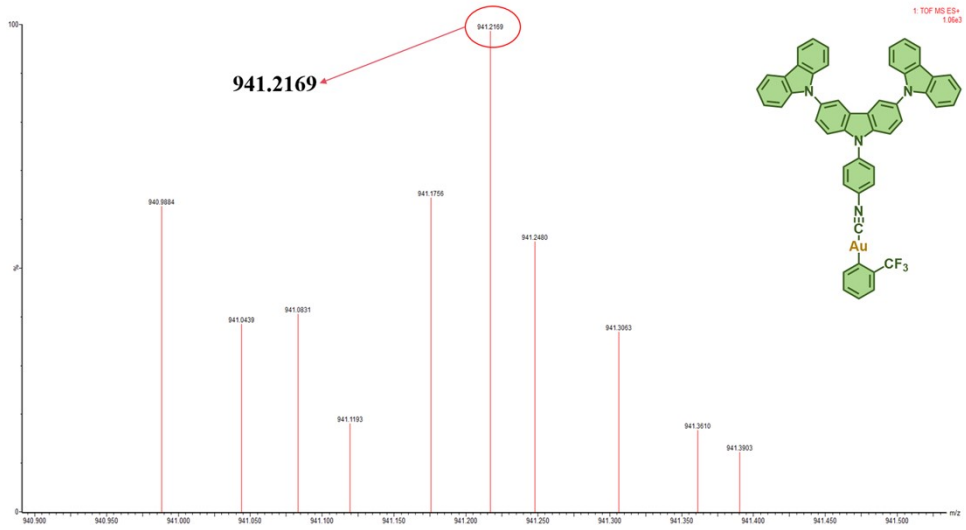
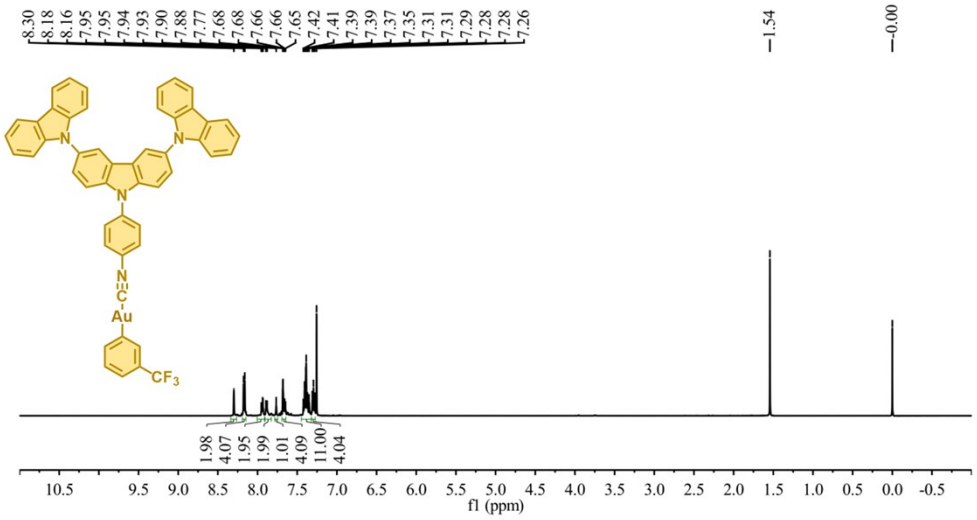


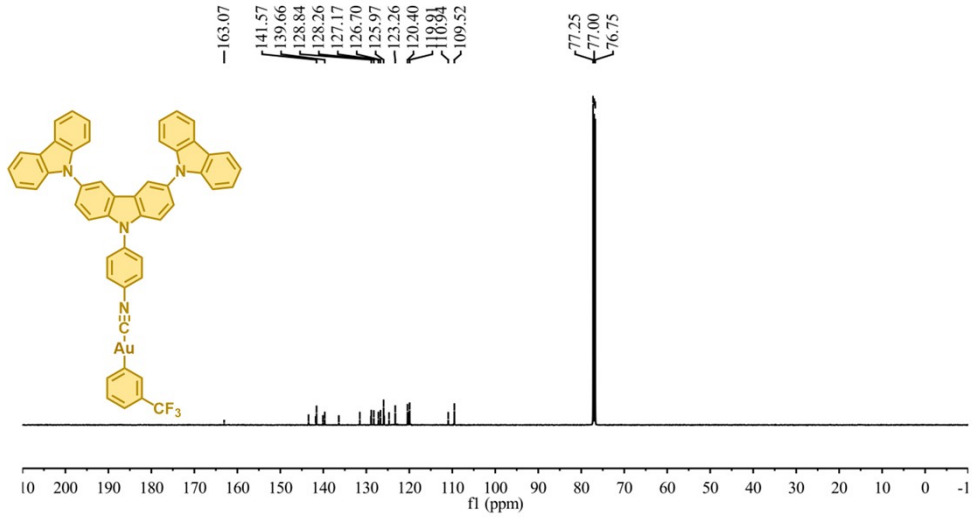
^{19}F NMR spectrum of gold(I) complex **I** in $CDCl_3$



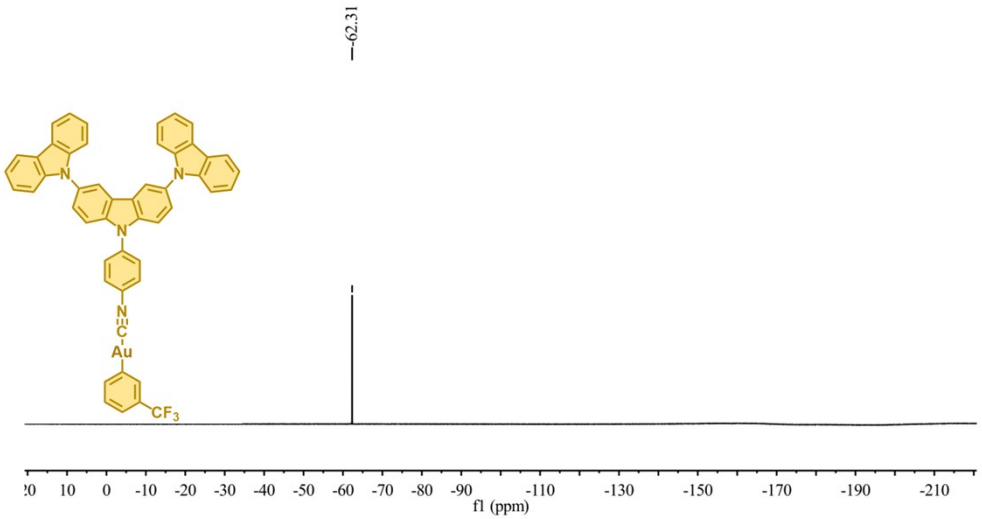
HRMS spectrum of gold(I) complex **I**



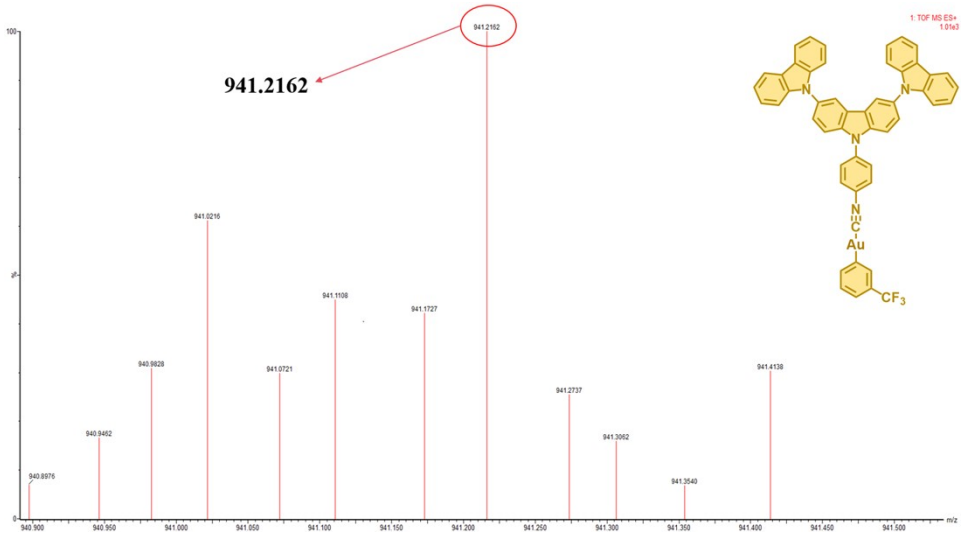
^{1}H NMR spectrum of gold(I) complex **II** in $CDCl_3$



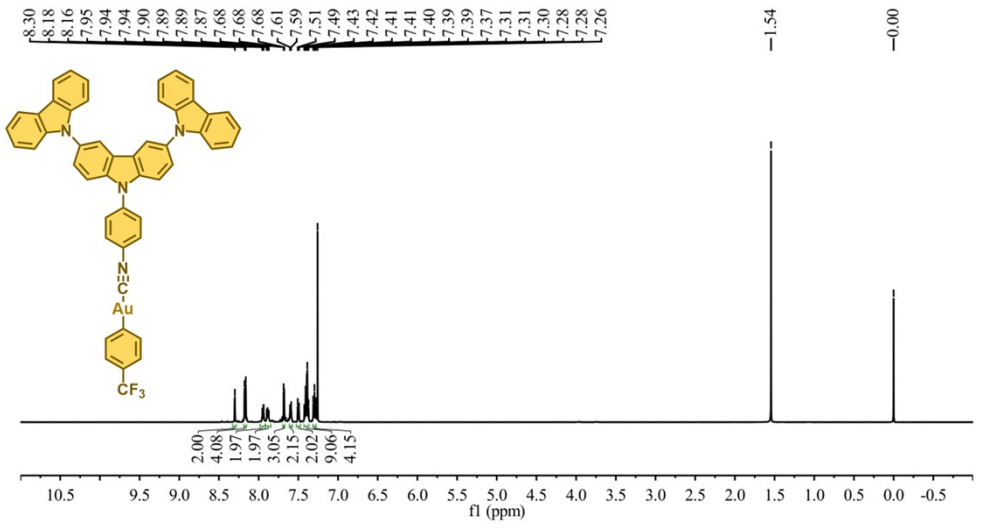
^{13}C NMR spectrum of gold(I) complex **II** in $CDCl_3$



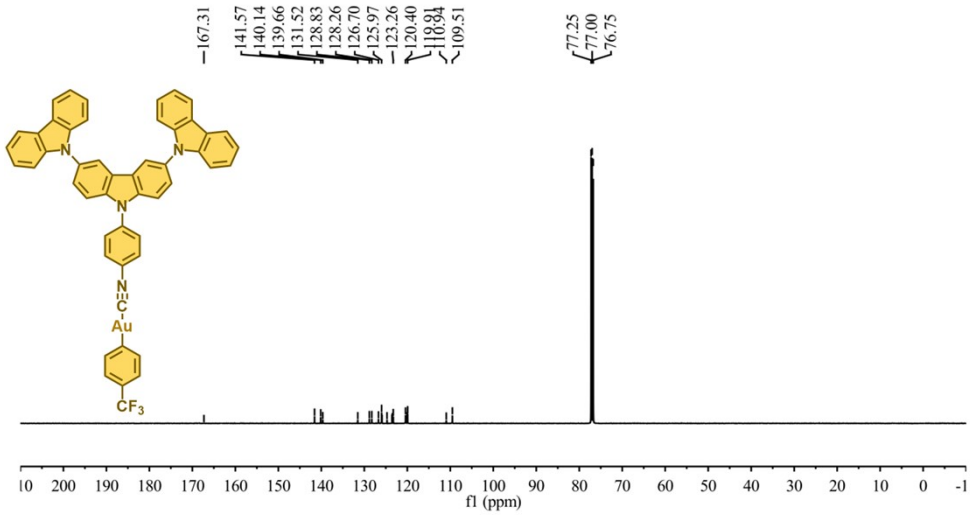
^{19}F NMR spectrum of gold(I) complex **II** in $CDCl_3$



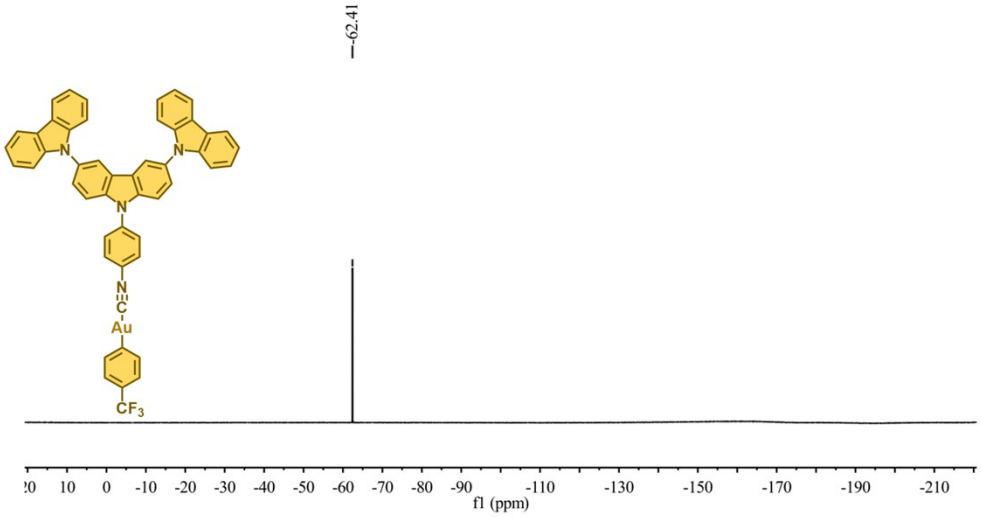
HRMS spectrum of gold(I) complex **II**



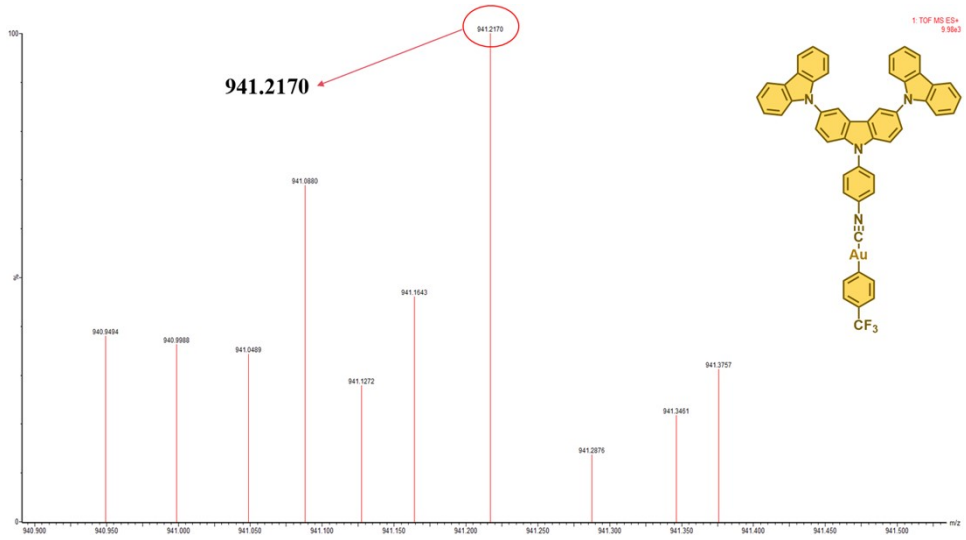
^{1}H NMR spectrum of gold(I) complex **III** in $CDCl_3$



^{13}C NMR spectrum of gold(I) complex **III** in $CDCl_3$



^{19}F NMR spectrum of gold(I) complex **III** in $CDCl_3$



HRMS spectrum of gold(I) complex **III**

8. References

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