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Electronic Supplementary Information

Persistent room-temperature phosphorescence or high-contrast phosphorescent mechanochromism: Polymorphism-dependent different emission characteristics from a single gold(I) complex

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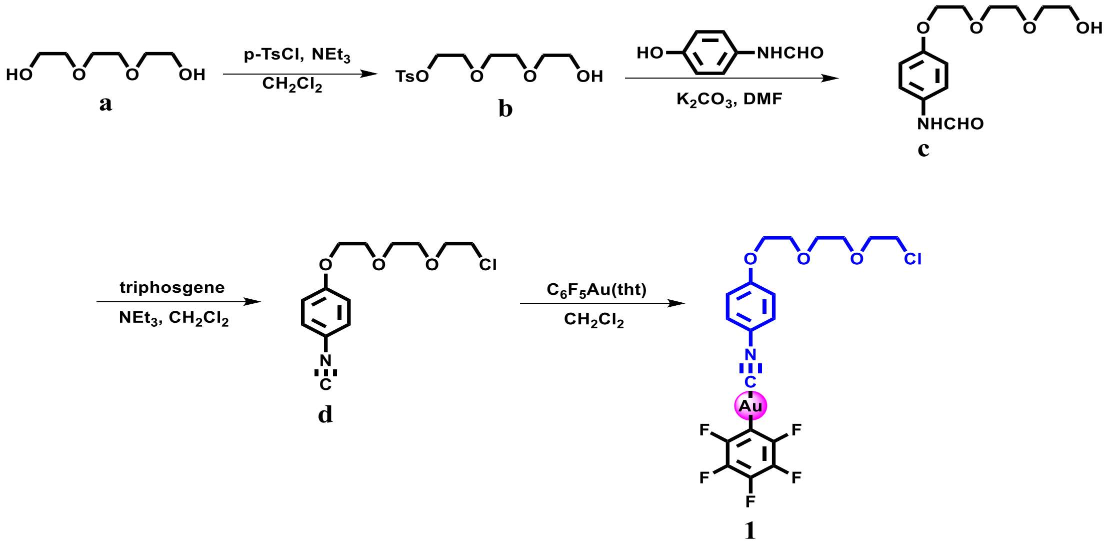
Contents

1. Measurements and Materials

NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz) or Varian Mercury Plus 600 MHz instrument. The ^{13}C NMR spectrum of compound **b** was collected by American Varian Mercury Plus 400 spectrometer (400 MHz), with the frequency of 101 MHz. The ^{13}C NMR spectra of compounds **c**, **d** and **1** were obtained on Varian Mercury Plus 600 MHz instrument, with the frequency of 151 MHz. ^{1}H and ^{13}C NMR chemical shifts were relative to TMS. ^{19}F NMR chemical shifts were relative to C_6F_6 (δ = -163.00). Mass spectra were recorded on a Bruker ultrafleXtreme MALDI-TOF-TOF mass spectrometer and 6224 TOF LC/MS spectrometer. Steady-state PL spectra were obtained by Edinburgh FLS1000 spectrometer with Xe lamp as excitation light source. Delayed emission spectra, time-resolved emission spectra and decay curves were measured by Edinburgh FLS1000 spectrometer with μF2 lamp as excitation light source. The X-ray crystal-structure data were obtained by the Bruker APEX DUO CCD system. All manipulations were carried out in argon atmosphere by using standard Schlenk techniques, unless otherwise stated. All starting meterials and reagents were purchased from Shen Shi Hua Gong Company (China) and used without further purification.

2. Synthesis



Scheme S1 Synthetic route to the gold(I) complex **1** (tht = tetrahydrothiophene).

Synthesis of **b**: Tetraethylene glycol (15.0 g, 0.1 mol) was added to 100 mL CH_2Cl_2. Then triethylamine (5.05 g, 50 mmol) was added later. After stirring at room temperature for a while, *p*-TsCl (4.77 g, 25 mmol) was slowly added to the reaction system in batches. The mixture was stirred at room temperature for 1.5 hours to end the reaction. The reaction was washed with 5% $NaHCO_3$, dried over anhydrous sodium sulfate, and purified by column chromatography to obtain colorless oily liquid with the yield of 56% (4.30 g). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.22-4.17 (m, 2H), 3.74 (q, *J* = 4.4 Hz, 4H), 3.64 (s, 4H), 3.62 - 3.59 (m, 2H), 2.48 (s, 3H), 2.41 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.9, 132.6, 129.8, 127.7, 72.4, 70.4, 70.0, 69.4, 68.4, 61.2, 21.4. EI-MS: m/z = 304.4 $[M]^+$; Found: m/z = 304.0 $[M]^+$.

Synthesis of **c**: N-(4-hydroxyphenyl)formamide (2.47 g, 18.0 mmol) and potassium carbonate (4.97 g, 36.0 mmol) were dissolved in 50 mL DMF and stirred for several minutes. Then **b** (5.47 g, 18.0 mmol) was added. The mixture were reacted overnight at 60 °C. After that, most solvents were removed by vacuum distillation. The residual mixture were extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were combined and concentrated. The residues were purified by column chromatography, and the brown-black oily liquid (3.1 g) was obtained in the yields of 65%. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 12.0 Hz, 0.5H), 8.28 (s, 0.5H), 8.22 (d, *J* = 12.0 Hz, 0.5H), 7.94 (s, 0.5H), 7.43 (d, *J* = 6.0 Hz, 1H), 7.01 (d, *J* = 6.0 Hz, 1H), 6.89-6.84 (m, 2H), 4.10 (d, *J* = 6.0 Hz, 1H), 3.86-3.83 (m, 2H), 3.71 (t, *J* = 9.0 Hz, 6H), 3.62-3.60 (m, 2H), 2.27 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 163.0, 159.2, 156.5, 155.5, 130.4, 129.9, 121.7, 121.4, 115.6, 114.9, 72.5, 70.7, 70.2, 69.6, 67.6, 61.6. EI-MS: m/z = 269.3 $[M]^+$; Found: m/z = 269.3 $[M]^+$.

Synthesis of **d**: Under an argon atmosphere, the intermediate **c** (269.3 mg, 1.0 mmol) and triethylamine (3 mL) was dissolved in dry CH_2Cl_2. The CH_2Cl_2 solution of triphosgene (326.4 mg, 1.1 mmol) was dropped slowly into the reaction system at 0 °C. Afterwards, the reaction was refluxed for 3 hours. It was returned to room temperature after the reaction was completed. The reaction bottle was placed in an ice bath, 10% Na_2CO_3 solution (50 mL) was added to the system for neutralization. And then the solution was extracted three times with CH_2Cl_2. The organic phases were combined, washed with water (3 × 30 mL) and dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography. Yellow oily liquid was obtained in a yield with 58% (214.0 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.23 (s, 2H), 6.82 (s, 2H), 4.07 (s, 2H), 3.80 (s, 2H), 3.67 (d, *J* = 14.9 Hz, 6H), 3.56 (s, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.3, 158.6, 127.2, 118.9, 114.8, 70.8, 70.3, 70.1, 69.0, 67.3, 42.4. EI-MS: *m/z* = 269.7 $[M]^+$; Found: *m/z* = 269.7 $[M]^+$.

Synthesis of **1**: A mixture of C_6F_5Au(tht) (237.4 mg, 0.525 mmol) and **c** (0.5 mmol) was stirred in CH_2Cl_2 (20 mL) overnight at room temperature. After completion of present reaction, the solvent was evaporated. A small amount of CH_2Cl_2 was added, and then a lot of *n*-hexane was added. Collecting the white solid product by suction filtration. Yield: 62% (392.9 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 8.9 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 4.23 - 4.16 (m, 2H), 3.94 - 3.87 (m, 2H), 3.79 - 3.68 (m, 6H), 3.64 (t, *J* = 5.8 Hz, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.96, -157.61, -162.44. ^{13}C NMR (151 MHz, Chloroform-*d*) δ 161.0, 156.8, 150.3, 148.6, 140.2, 138.5, 137.7, 136.2, 128.4, 116.8, 115.9, 71.4, 70.9, 70.7, 69.4, 68.1, 42.8. Mass spectrum (Maldi-TOF-MS) (*m/z*): $[M+Na]^+$, calcd. for $C_{19}H_{16}AuF_5ClNO_3$, 656.0297; found, 656.3512.

3. Figures S1-S10

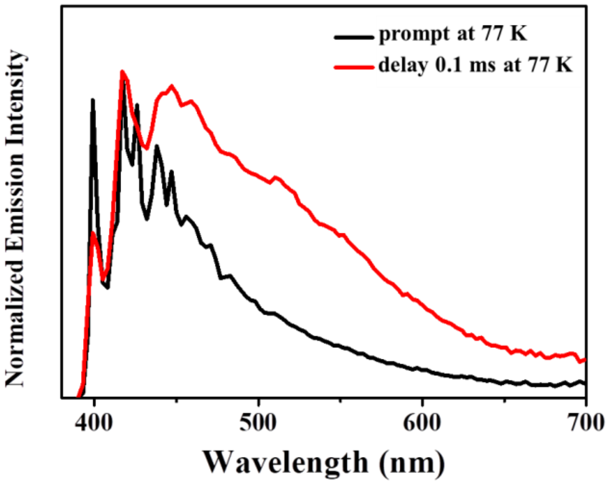


Figure S1. Normalized steady-state (black) and delayed (red) emission spectra of polymorph **1B** at 77 K.

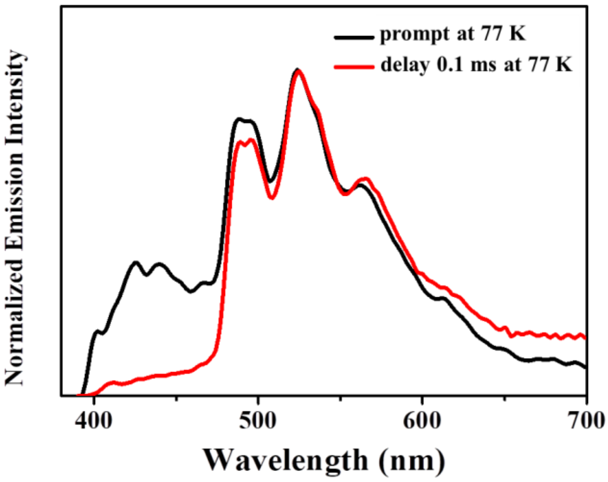


Figure S2. Normalized steady-state (black) and delayed (red) emission spectra of polymorph **1YG** at 77 K.

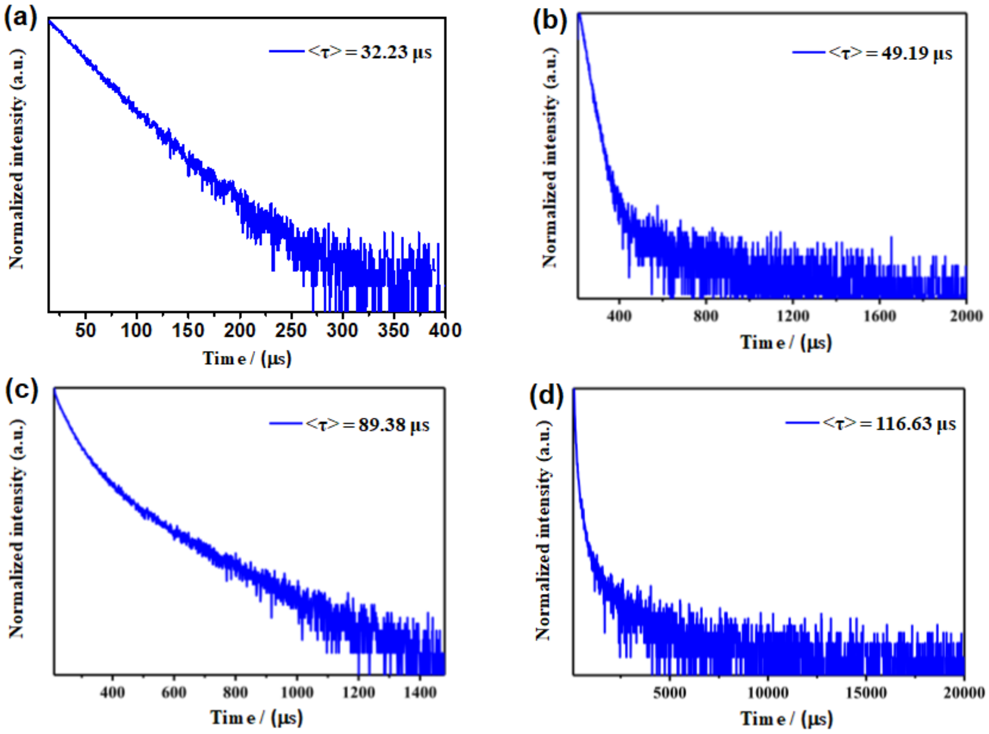


Figure S3. (a) Decay curve of **1B** at the peak emission wavelength of 423 nm at room temperature; (b) Decay curve of **1B** at the peak emission wavelength of 510 nm at room temperature; (c) Decay curve of **1B** at the peak emission wavelength of 417 nm at 77 K; (d) Decay curve of **1B** at the peak emission wavelength of 510 nm at 77 K.

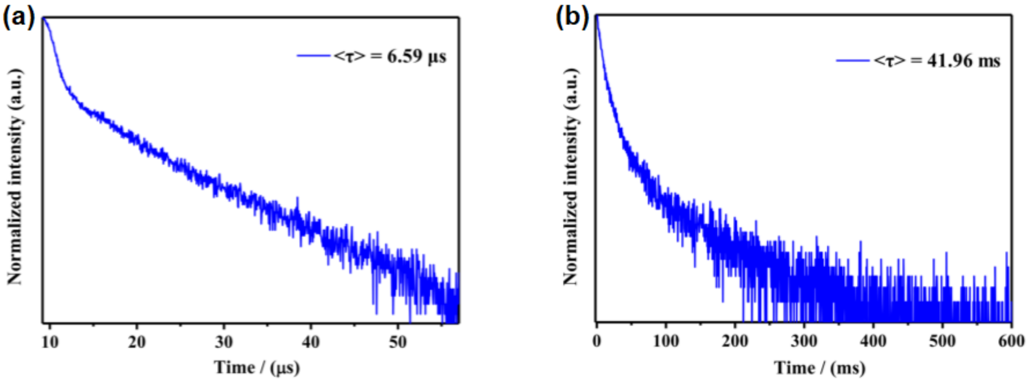


Figure S4. (a) Decay curve of **1YG** at the peak emission wavelength of 436 nm at room temperature; (b) Decay curve of **1YG** at the peak emission wavelength of 534 nm at room temperature.

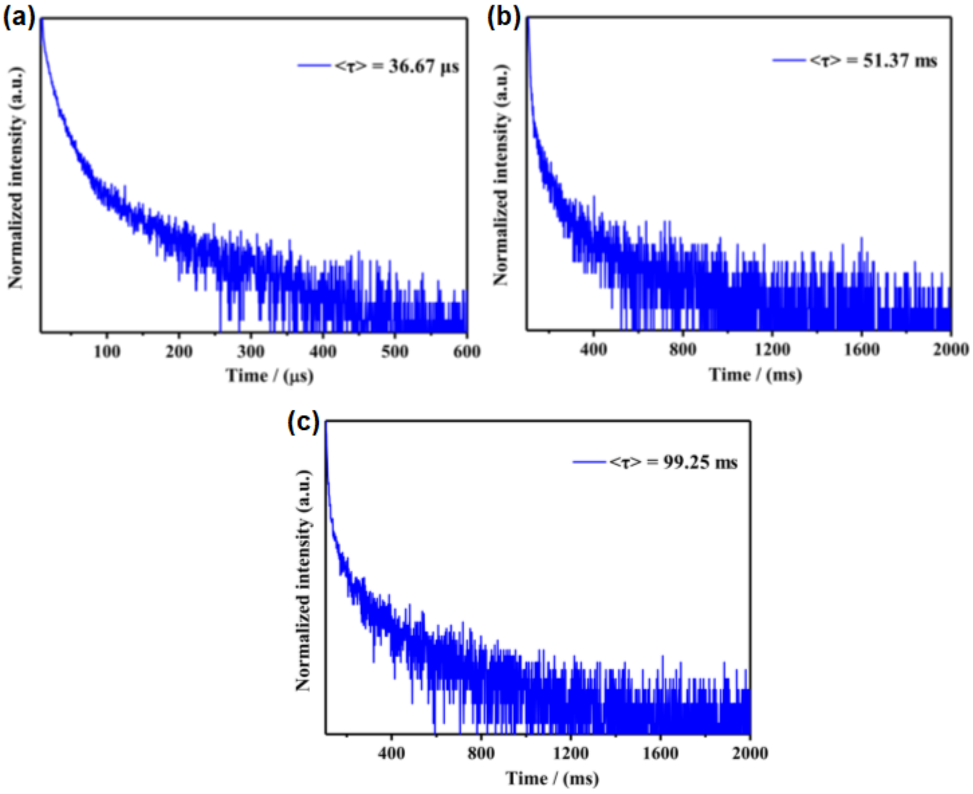


Figure S5. (a) Decay curve of **1YG** at the peak emission wavelength of 422 nm at 77 K; (b) Decay curve of **1YG** at the peak emission wavelength of 487 nm at 77 K; (c) Decay curve of **1YG** at the peak emission wavelength of 527 nm at 77 K.

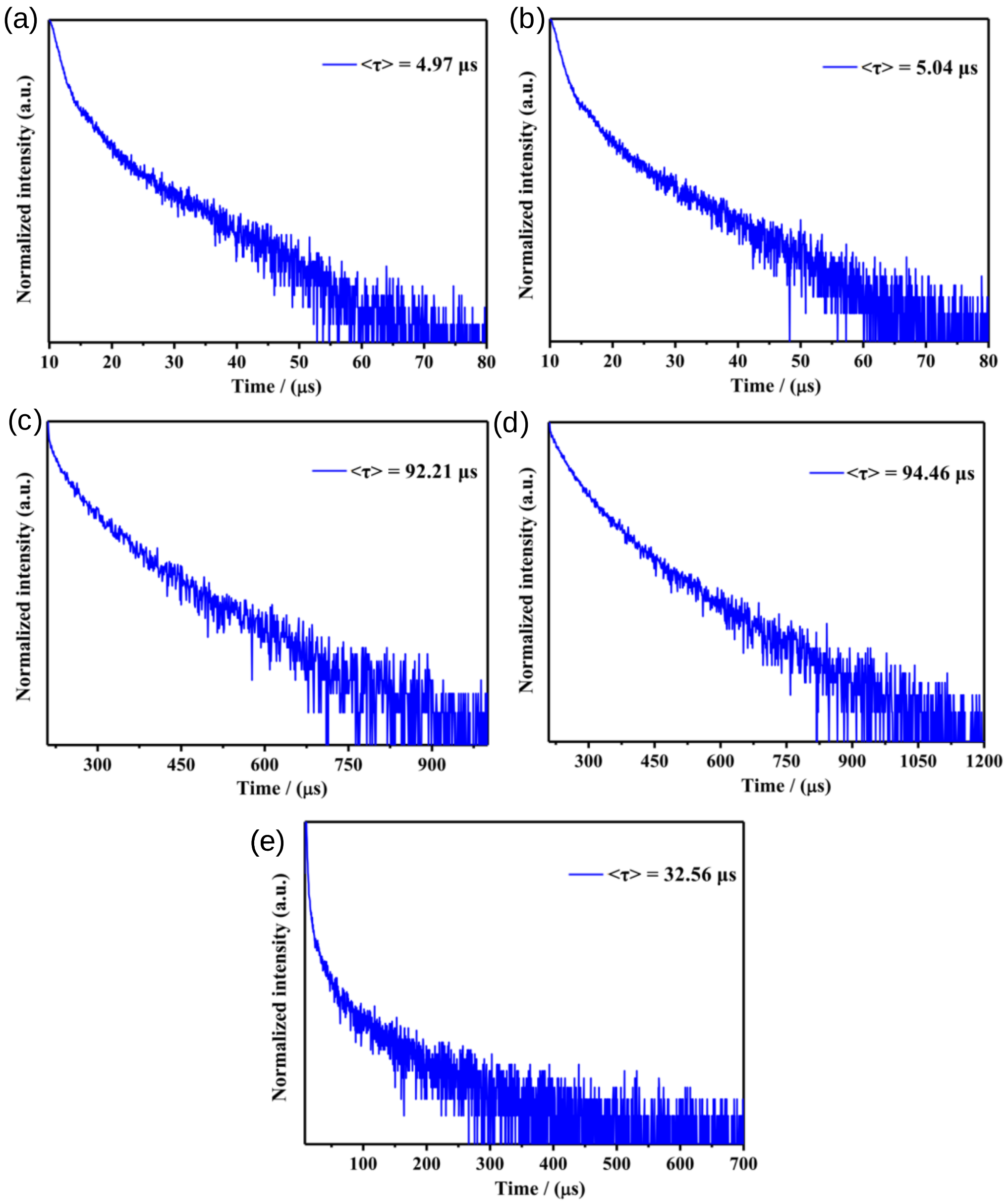


Figure S6. (a) Decay curve of the ground **1YG** at the peak emission wavelength of 507 nm at room temperature; (b) Decay curve of the ground **1YG** at the peak emission wavelength of 531 nm at room temperature; (c) Decay curve of the ground **1YG** at the peak emission wavelength of 412 nm at 77 K; (d) Decay curve of the ground **1YG** at the peak emission wavelength of 435 nm at 77 K; (e) Decay curve of the ground **1YG** at the peak emission wavelength of 494 nm at 77 K.

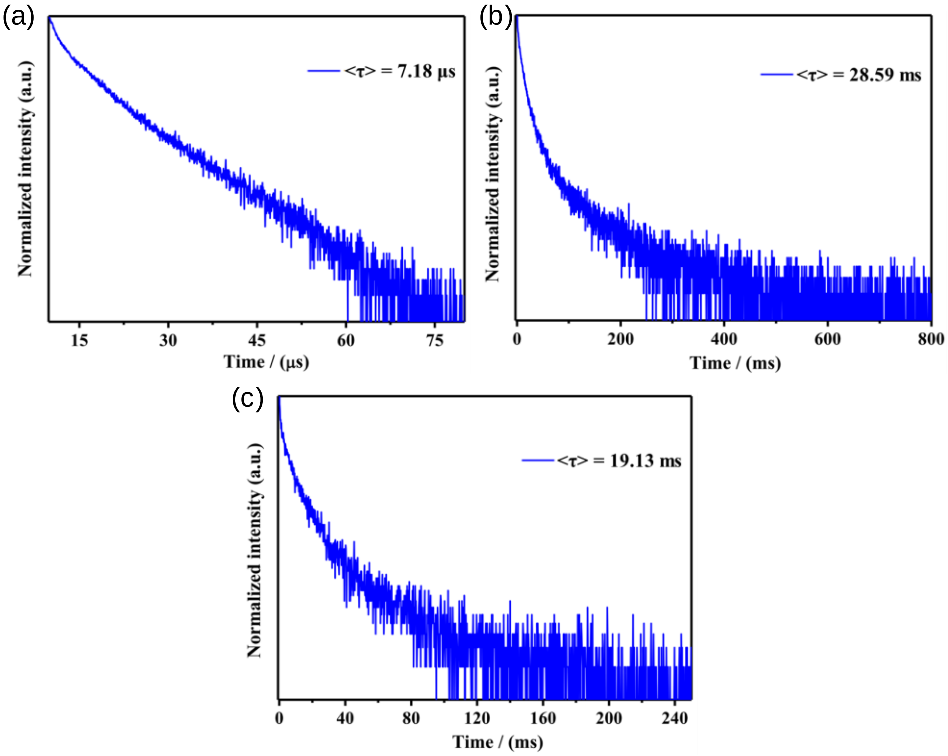


Figure S7. (a) Decay curve of **1YG** after treating with CH_2Cl_2 at the peak emission wavelength of 422 nm at room temperature; (b) Decay curve of **1YG** after treating with CH_2Cl_2 at the peak emission wavelength of 494 nm at room temperature; (c) Decay curve of **1YG** after treating with CH_2Cl_2 at the peak emission wavelength of 537 nm at room temperature.

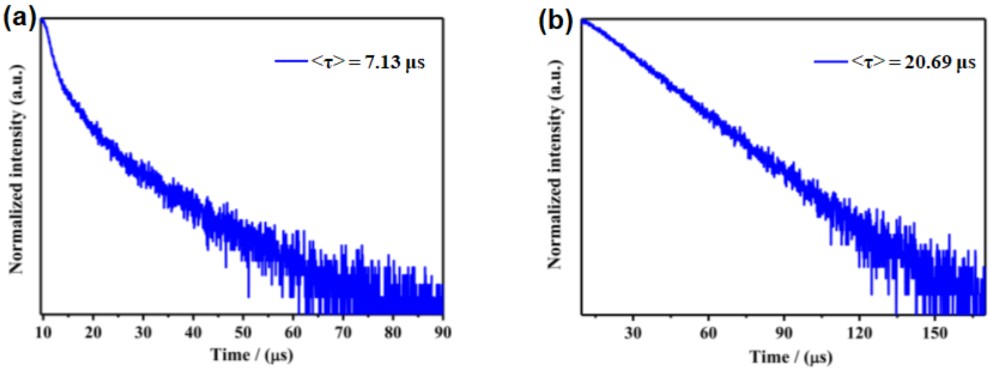


Figure S8. (a) Decay curve of the ground **1B** at the peak emission wavelength of 495 nm at room temperature; (b) Decay curve of **1B** after treating with CH_2Cl_2 at the peak emission wavelength of 423 nm at room temperature.

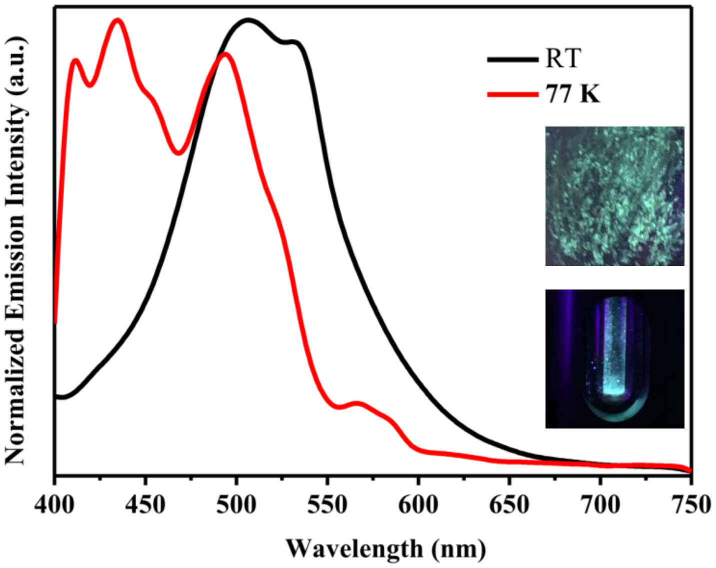


Figure S9. Normalized emission spectra of the ground **1YG** at room temperature and 77 K. The pictures were taken at room temperature (above) and 77 K (below) under a 365 nm portable UV lamp.

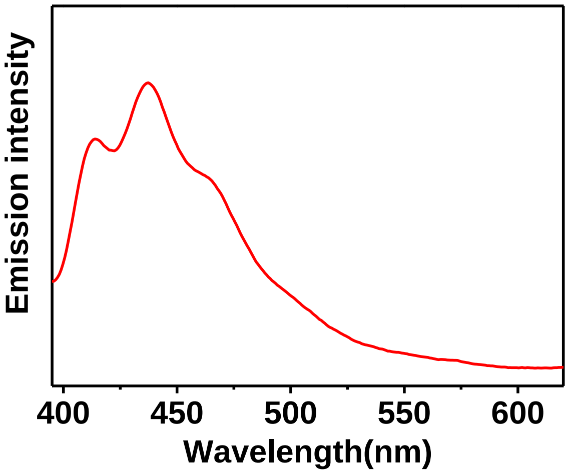


Figure S10. The emission spectrum of complex **1** in dilute DMF solution. Concentration: 20 μM. Excitation wavelength: 365 nm.

4. Tables S1-S4

Table S1. Structure determination summary of polymorph **1B**.

Crystal data	
Chemical formula	$C_{19}H_{16}AuClF_5NO_3$
M_r	633.75

Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	296
a, b, c (Å)	4.7449 (7), 10.8014 (16), 39.937 (6)
b (°)	93.174 (2)
V (Å^3)	2043.7 (5)
Z	4
Radiation type	Mo *K*a
m (mm^{-1})	7.40
Crystal size (mm)	0.2 × 0.1 × 0.1
Data collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	Multi-scan *SADABS2008*/1 (Bruker,2008) was used for absorption correction. wR2(int) was 0.0977 before and 0.0479 after correction. The Ratio of minimum to maximum transmission is 0.5863. The l/2 correction factor is 0.0015.
T_{min}, T_{max}	0.437, 0.745
No. of measured, independent and observed [I ? 2u(I)] reflections	15922, 4238, 3831
R_{int}	0.042
(sin q/l)$_{\text{max}}$ (Å^{-1})	0.632
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.047, 0.097, 1.06
No. of reflections	4238
No. of parameters	271
H-atom treatment	H-atom parameters constrained
	$w = 1/[s^2(F_o^2) + (0.P)^2 + 20.5973P]$ where $P = (F_o^2 + 2F_c^2)/3$
Dρ$_{\text{max}}$, Dρ$_{\text{min}}$ (e Å^{-3})	2.47, -4.08

Computer programs: *SAINT* v7.68A (Bruker, 2009), XS (Sheldrick, 2008), olex2.refine (Bourhis *et al.*, 2015), Olex2 (Dolomanov *et al.*, 2009).

Table S2. Selected geometric parameters (Å, °) of polymorph **1B**.

Au1—C7	1.969 (8)	C5—C4	1.355 (11)
Au1—C1	2.017 (7)	C5—F4	1.356 (9)
C7—N1	1.142 (9)	C2—C3	1.371 (11)
N1—C8	1.403 (9)	C2—F1	1.359 (9)
C10—C9	1.377 (10)	C3—C4	1.381 (11)
C10—C11	1.383 (10)	C3—F2	1.341 (9)
C8—C13	1.366 (10)	C4—F3	1.342 (8)
C8—C9	1.382 (10)	O2—C15	1.423 (9)
C13—C12	1.387 (10)	O2—C16	1.410 (9)
C11—C12	1.382 (9)	C14—C15	1.506 (10)
C11—O1	1.356 (8)	O3—C17	1.404 (10)
O1—C14	1.431 (8)	O3—C18	1.420 (11)
C1—C6	1.378 (10)	C16—C17	1.510 (12)
C1—C2	1.388 (10)	C18—C19	1.461 (14)
C6—C5	1.384 (11)	C19—Cl1	1.773 (10)
C6—F5	1.347 (8)		

C1—Au1—C7	177.6 (3)	C4—C5—C6	120.5 (7)
N1—C7—Au1	176.5 (7)	F4—C5—C6	120.4 (7)
C8—N1—C7	174.3 (7)	F4—C5—C4	119.1 (7)
C11—C10—C9	120.6 (7)	C3—C2—C1	124.5 (7)
C13—C8—N1	118.8 (6)	F1—C2—C1	119.1 (7)
C9—C8—N1	119.9 (7)	F1—C2—C3	116.3 (7)
C9—C8—C13	121.4 (7)	C4—C3—C2	118.8 (7)
C12—C13—C8	119.7 (7)	F2—C3—C2	121.9 (7)
C8—C9—C10	118.8 (7)	F2—C3—C4	119.3 (7)
C12—C11—C10	119.9 (7)	C3—C4—C5	119.1 (7)
O1—C11—C10	115.7 (6)	F3—C4—C5	120.1 (7)
O1—C11—C12	124.4 (6)	F3—C4—C3	120.8 (7)
C11—C12—C13	119.6 (7)	C16—O2—C15	113.0 (6)
C14—O1—C11	118.3 (5)	C15—C14—O1	107.2 (6)
C6—C1—Au1	122.7 (5)	C14—C15—O2	113.1 (6)
C2—C1—Au1	123.1 (5)	C18—O3—C17	111.1 (7)
C2—C1—C6	114.0 (7)	C17—C16—O2	108.6 (7)
C5—C6—C1	123.1 (7)	C16—C17—O3	110.4 (7)
F5—C6—C1	120.0 (7)	C19—C18—O3	110.1 (9)

F5—C6—C5	116.9 (7)	Cl1—C19—C18	113.4 (8)

Table S3. Structure determination summary of polymorph **1YG**.

Crystal data	
Chemical formula	$C_{19}H_{16}AuClF_5NO_3$
M_r	633.74
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	297
a, b, c (Å)	4.6528 (12), 10.670 (3), 39.493 (10)
b (°)	93.086 (4)
V (Å^3)	1957.8 (8)
Z	4
Radiation type	Mo Ka
m (mm^{-1})	7.72
Crystal size (mm)	0.12 × 0.12 × 0.10
Data collection	
Diffractometer	Bruker *APEX*-II CCD
Absorption correction	–
No. of measured, independent and observed [I > 2s(I)] reflections	15724, 4447, 3567
R_{int}	0.138
(sin q/l)$_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.079, 0.205, 1.10
No. of reflections	4447
No. of parameters	271
H-atom treatment	H-atom parameters constrained

$D\rho_{max}$, $D\rho_{min}$ (e Å^{-3})	6.25, -5.59

Computer programs: Bruker *APEX2*, Bruker *SAINT*, *SHELXS97* (Sheldrick, 2008), *SHELXL2014*/7 (Sheldrick, 2014), Bruker *SHELXTL*.

Table S4. Selected geometric parameters (Å, °) of polymorph **1YG**.

Au1—C7	1.984 (14)	C8—N1	1.401 (13)
Au1—C1	2.028 (12)	C9—C10	1.402 (15)
C1—C2	1.366 (18)	C10—C11	1.373 (15)
C1—C6	1.386 (17)	C11—O1	1.361 (13)
C2—F1	1.338 (13)	C11—C12	1.365 (16)
C2—C3	1.389 (16)	C12—C13	1.398 (17)
C3—F2	1.316 (13)	C14—O1	1.445 (14)
C3—C4	1.368 (17)	C14—C15	1.516 (15)
C4—F3	1.329 (14)	C15—O2	1.411 (14)
C4—C5	1.369 (18)	C16—O2	1.410 (13)
C5—F4	1.343 (13)	C16—C17	1.486 (18)
C5—C6	1.350 (18)	C17—O3	1.411 (15)
C6—F5	1.338 (14)	C18—O3	1.423 (14)
C7—N1	1.100 (15)	C18—C19	1.469 (19)
C8—C13	1.382 (16)	C19—Cl1	1.800 (12)
C8—C9	1.387 (15)		
C7—Au1—C1	177.1 (5)	C9—C8—N1	117.2 (10)
C2—C1—Au1	121.9 (8)	C13—C8—C9	123.1 (10)
C2—C1—C6	115.7 (11)	C13—C8—N1	119.7 (10)
C6—C1—Au1	122.3 (10)	C8—C9—C10	117.0 (10)
C1—C2—C3	123.1 (10)	C11—C10—C9	120.4 (10)
F1—C2—C1	119.8 (10)	C12—C11—C10	121.4 (11)
F1—C2—C3	117.0 (10)	O1—C11—C10	124.0 (10)
C4—C3—C2	118.8 (11)	O1—C11—C12	114.5 (10)
F2—C3—C2	121.7 (10)	C11—C12—C13	120.0 (12)
F2—C3—C4	119.5 (11)	C8—C13—C12	117.9 (11)
C3—C4—C5	118.9 (11)	O1—C14—C15	105.3 (9)
F3—C4—C3	118.8 (12)	O2—C15—C14	113.6 (9)
F3—C4—C5	122.3 (11)	O2—C16—C17	107.6 (10)
C6—C5—C4	121.0 (11)	O3—C17—C16	110.3 (11)
F4—C5—C4	118.7 (11)	O3—C18—C19	108.8 (11)
F4—C5—C6	120.3 (11)	C18—C19—Cl1	112.4 (10)
C5—C6—C1	122.3 (12)	C7—N1—C8	173.5 (12)
F5—C6—C1	119.2 (12)	C11—O1—C14	117.2 (9)

F5—C6—C5	118.4 (11)	C16—O2—C15	113.3 (9)
N1—C7—Au1	177.6 (11)	C17—O3—C18	111.7 (10)

C6—C1—C2—F1	−176.3 (10)	C4—C5—C6—F5	177.0 (12)
C6—C1—C2—C3	3.3 (18)	C4—C5—C6—C1	−1 (2)
Au1—C1—C2—F1	7.8 (16)	N1—C8—C9—C10	−178.3 (11)
Au1—C1—C2—C3	−172.6 (9)	C13—C8—C9—C10	0.2 (18)
C2—C1—C6—F5	−179.2 (11)	N1—C8—C13—C12	179.0 (10)
C2—C1—C6—C5	−1.7 (18)	C9—C8—C13—C12	0.5 (18)
Au1—C1—C6—F5	−3.3 (16)	C8—C9—C10—C11	−0.3 (18)
Au1—C1—C6—C5	174.2 (10)	C9—C10—C11—O1	−177.9 (11)
F1—C2—C3—F2	−1.3 (17)	C9—C10—C11—C12	−0.3 (18)
F1—C2—C3—C4	176.9 (11)	C10—C11—O1—C14	−4.6 (16)
C1—C2—C3—F2	179.1 (11)	C12—C11—O1—C14	177.6 (10)
C1—C2—C3—C4	−2.7 (18)	O1—C11—C12—C13	178.8 (10)
F2—C3—C4—F3	−1.5 (18)	C10—C11—C12—C13	1.0 (17)
F2—C3—C4—C5	178.5 (11)	C11—C12—C13—C8	−1.1 (17)
C2—C3—C4—F3	−179.7 (11)	C15—C14—O1—C11	−173.7 (9)
C2—C3—C4—C5	0.2 (18)	O1—C14—C15—O2	−69.7 (12)
F3—C4—C5—F4	−1.0 (19)	C14—C15—O2—C16	−77.1 (12)
F3—C4—C5—C6	−178.8 (12)	C17—C16—O2—C15	175.2 (9)
C3—C4—C5—F4	179.1 (11)	O2—C16—C17—O3	69.7 (12)
C3—C4—C5—C6	1.3 (19)	C16—C17—O3—C18	−166.4 (11)
F4—C5—C6—F5	−0.8 (18)	C19—C18—O3—C17	−177.9 (11)
F4—C5—C6—C1	−178.3 (12)		

5. Copies of NMR spectra

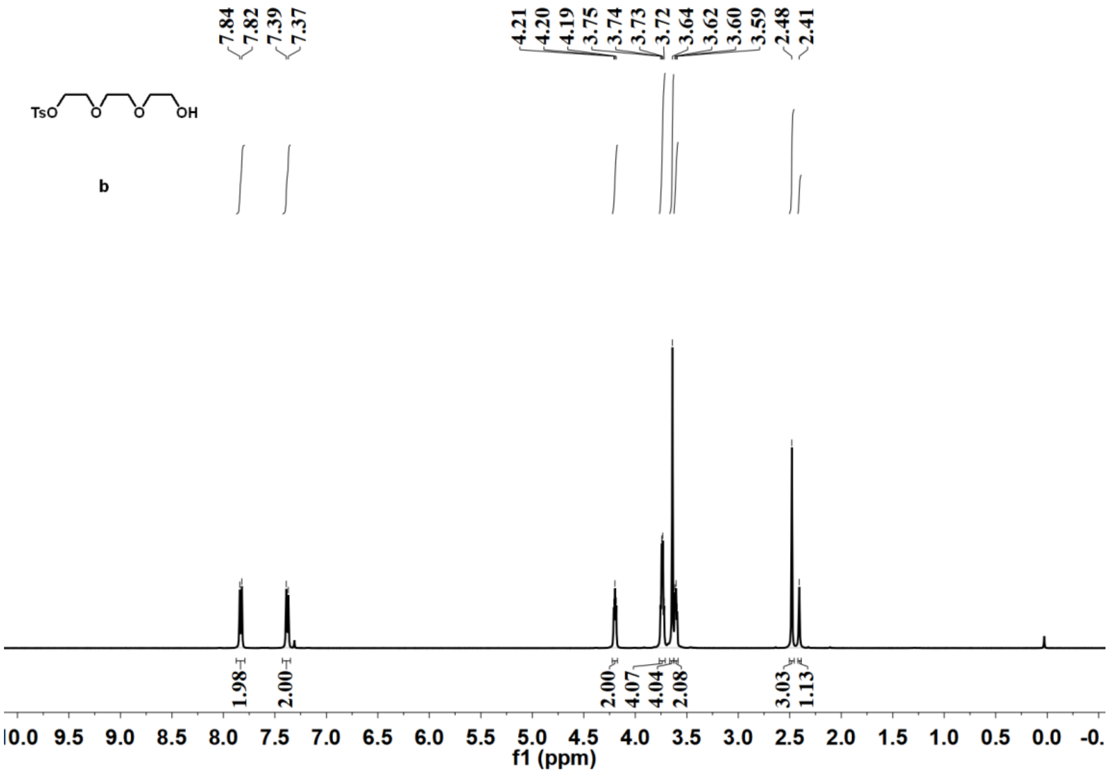


Figure S11. ^{1}H NMR spectrum of **b** in $CDCl_3$ at room temperature.

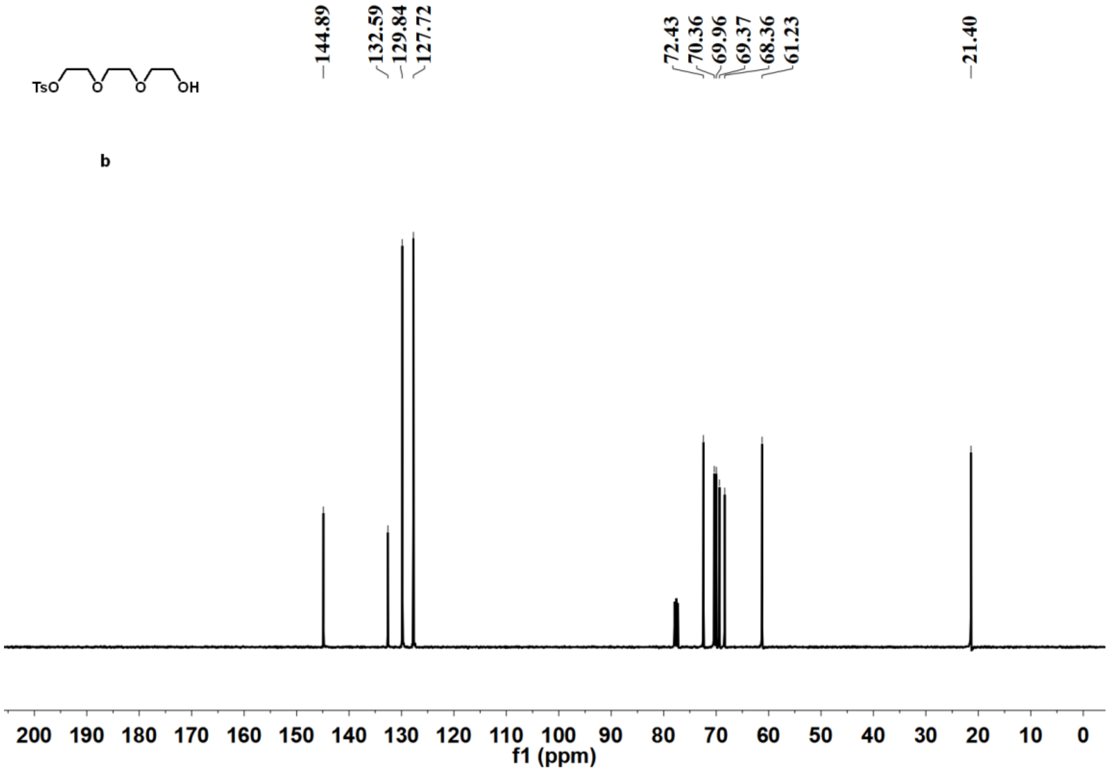


Figure S12. ^{13}C NMR spectrum of **b** in $CDCl_3$ at room temperature.

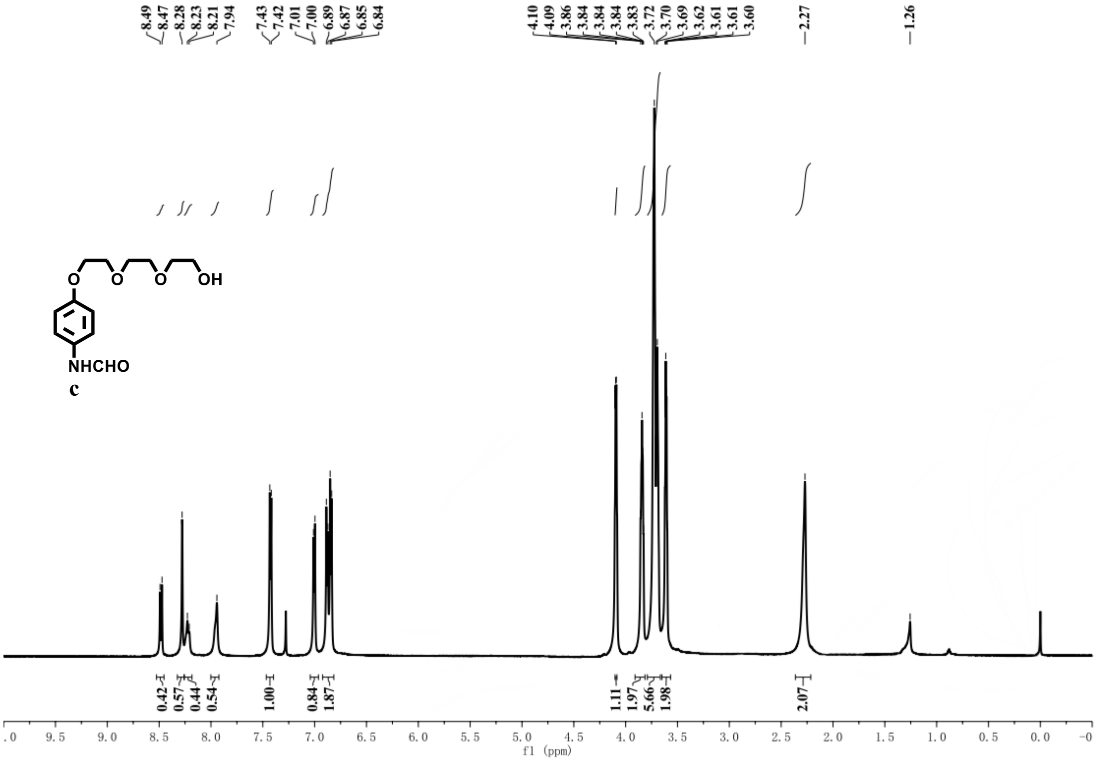


Figure S13. ^{1}H NMR spectrum of **c** in $CDCl_3$ at room temperature.

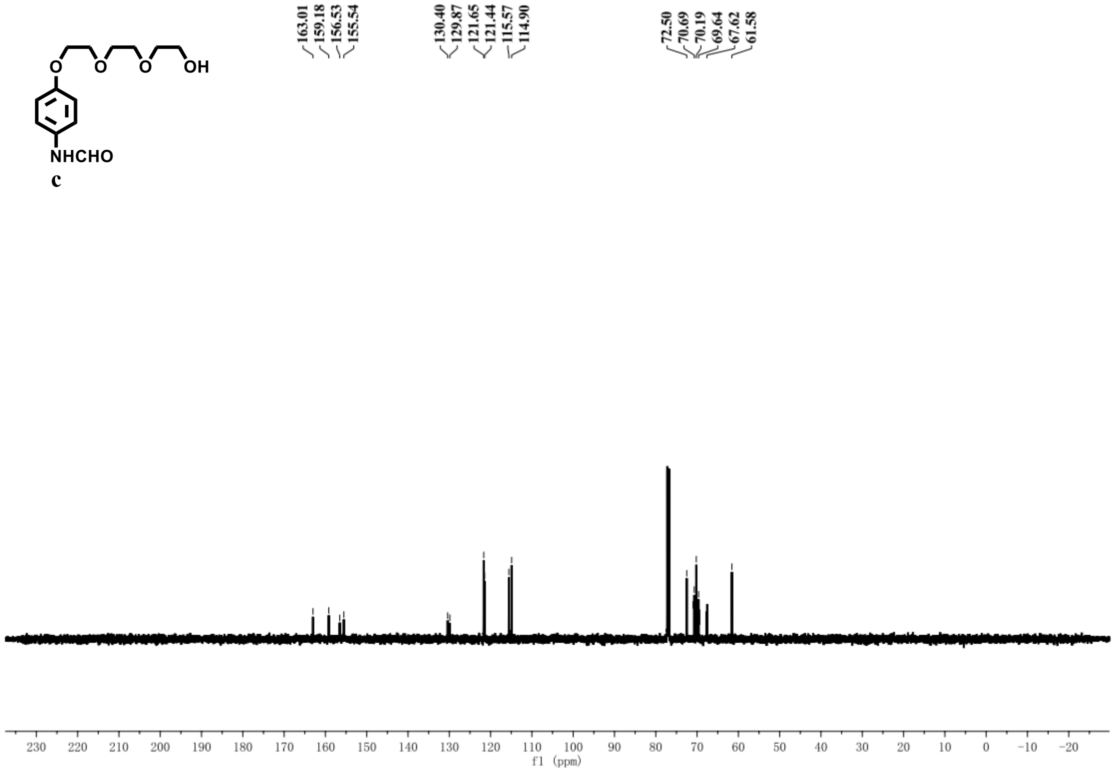


Figure S14. ^{13}C NMR spectrum of **c** in $CDCl_3$ at room temperature.

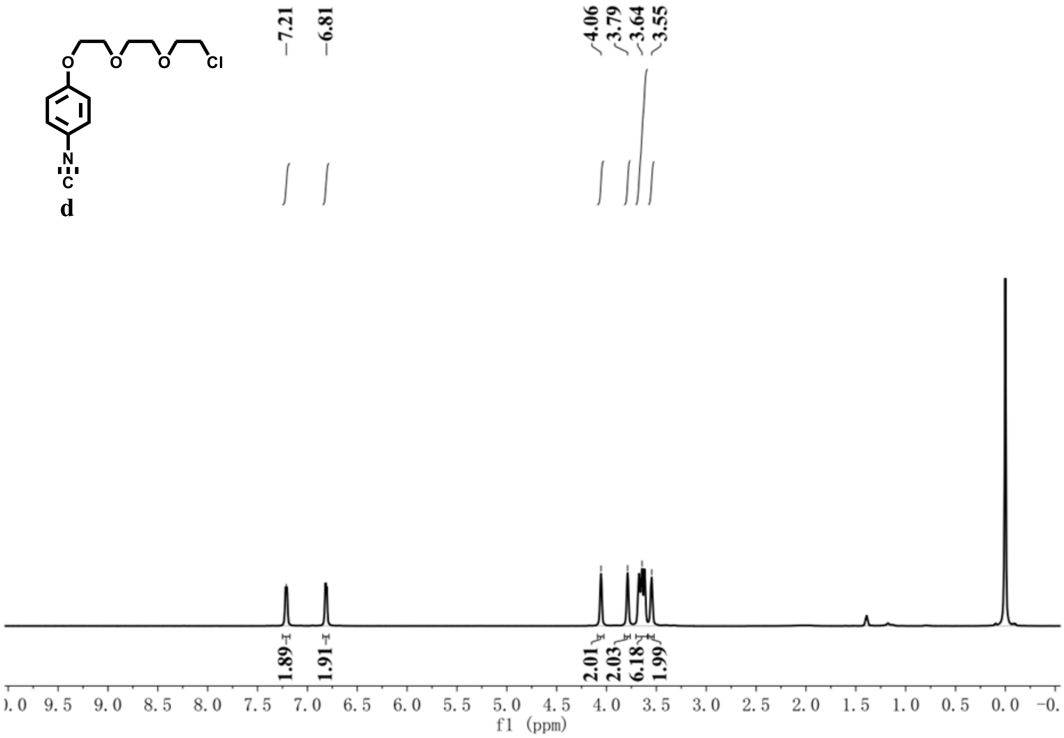


Figure S15. ^{1}H NMR spectrum of **d** in $CDCl_3$ at room temperature.

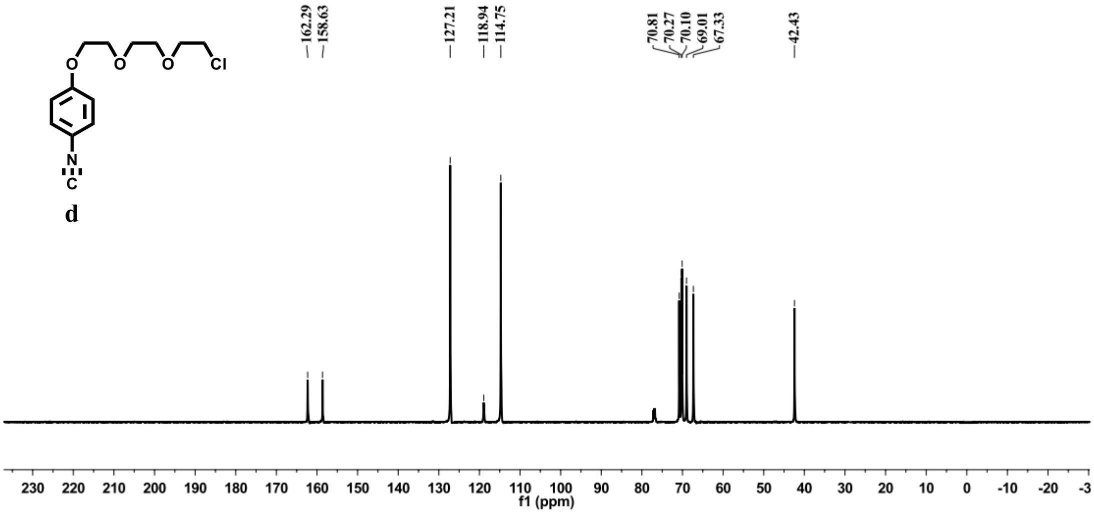


Figure S16. ^{13}C NMR spectrum of **d** in $CDCl_3$ at room temperature.

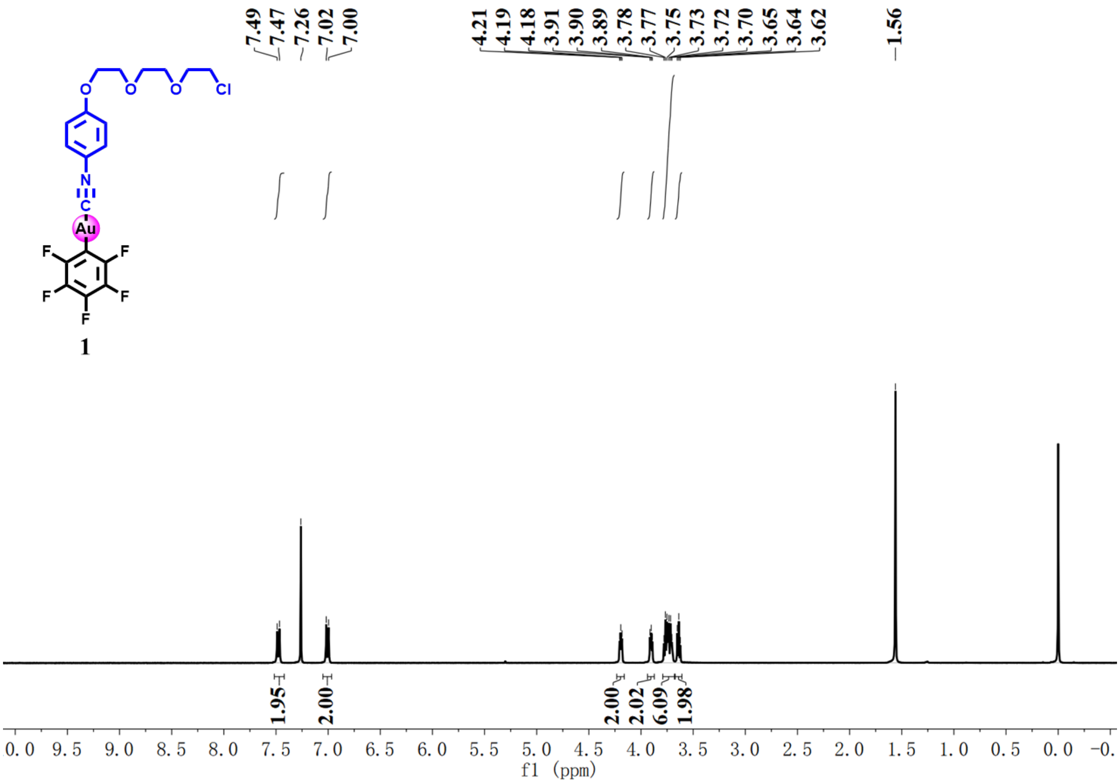


Figure S17. ^{1}H NMR spectrum of **1** in $CDCl_3$ at room temperature.

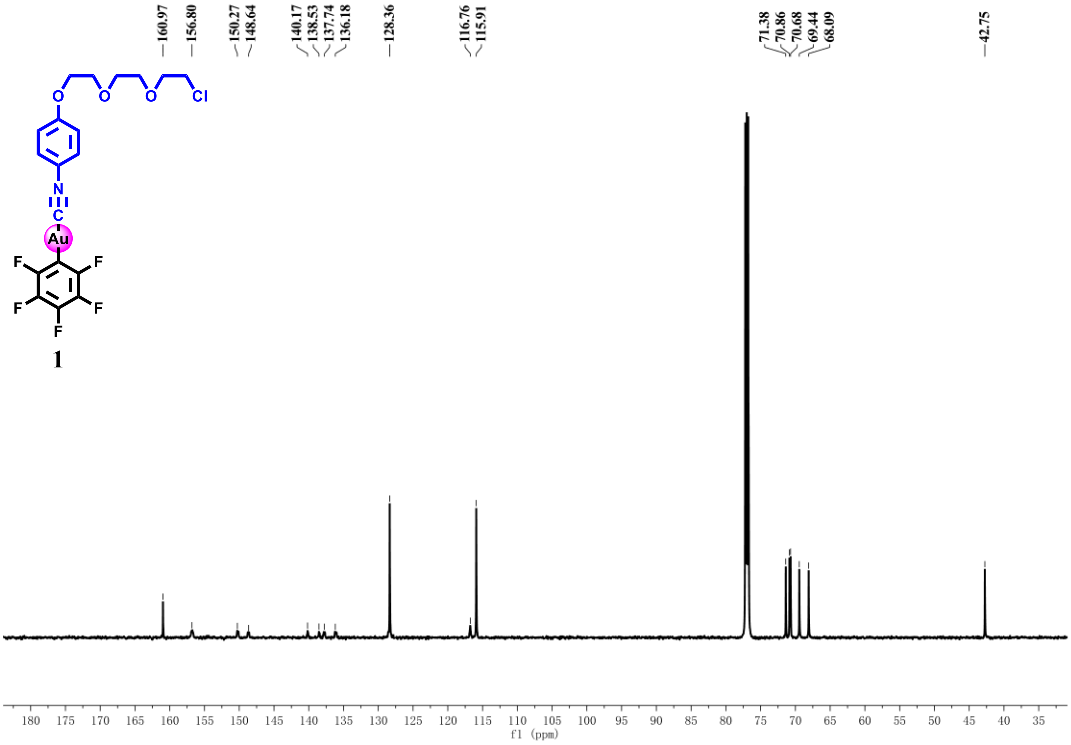


Figure S18. ^{13}C NMR spectrum of **1** in $CDCl_3$ at room temperature.

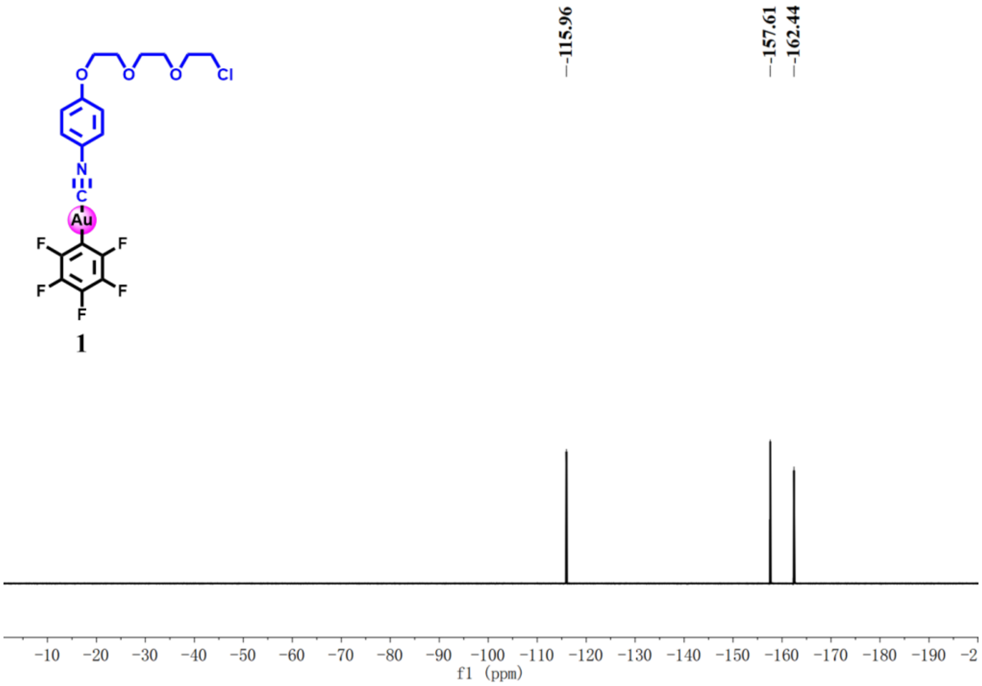


Figure S19. ^{19}F NMR spectrum of **1** in $CDCl_3$ at room temperature.