Electronic Supplementary Information (ESI)

A novel fluorene-based aggregation-induced emission (AIE)-active gold(I) complex with crystallization-induced emission enhancement (CIEE) and reversible mechanochromism characteristics

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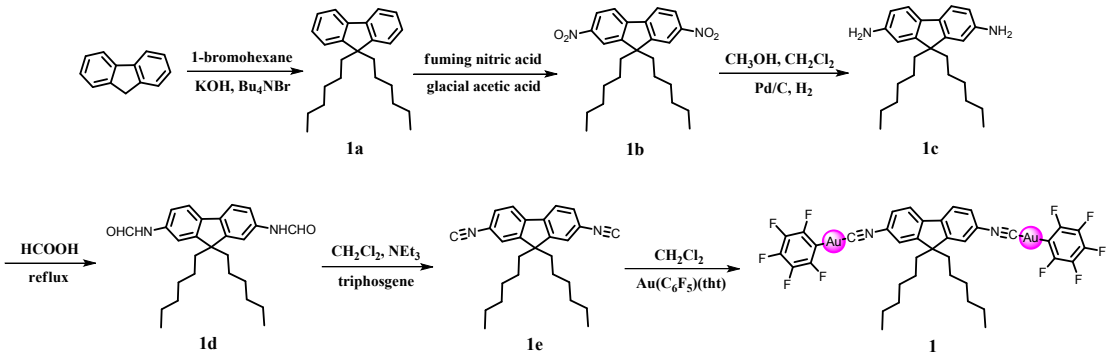
Contents

1. Experimental Section

Materials and measurements

The starting material fluorene purchased from Alfa Aesar was used as received. CH_2Cl_2 was dried with CaH_2 then distilled, and ultra-pure water was used in the experiments. All other starting materials and reagents were purchased as analytical-grade from Shen Shi Hua Gong Company (China) and used without further purification. Compounds **1a**[1], **1b**[2], **1c**[2] and $Au(C_6F_5)(tht)$[3] (tht = tetrahydrothiophene) were prepared by procedures described in the corresponding literatures. ^1H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). ^1H NMR spectra are reported as followed: chemical shift in ppm (δ) relative to the chemical shift of TMS at 0.00 ppm, integration, multiplicities (s=singlet, d=doublet, t=triplet, m=multiplet), and coupling constant (Hz). ^{13}C NMR chemical shifts reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. ^{19}F NMR chemical shifts are relative to C_6F_6 (δ= -163.00). EI-MS was obtained using Thermo scientific DSQ Ⅱ. Elemental analyses (C, H, N) were performed by the Microanalytical Services, College of Chemistry, CCNU. UV-Vis spectra were obtained on U-3310 UV Spectrophotometer. Fluorescence spectra were recorded on a Hitachi-F-4500 fluorescence spectrophotometer and Fluoromax-P luminescence spectrometer (HORIBA JOBIN YVON INC.). XRD studies were recorded on a Shimadzu XRD-6000 diffractometer using Ni-filtered and graphite- monochromated Cu Kα radiation (λ = 1.54 Å, 40 kV, 30 mA). the absolute fluorescence quantum yield was measured by Edinburgh Instruments FLS900. The DMF/water mixtures with various water fractions were prepared by slowly adding ultra-pure water into the DMF solution of samples. Dynamic light scattering (DLS) measurements were performed on the Zetasizer instrument ZEN3600 (Malvern, UK) with a 173° back scattering angle and He-Ne laser (λ =633 nm). The X-ray crystal-structure determinations of complex **1** was obtained on a Bruker APEX DUO CCD system.



Scheme S1. Synthesis of the complex **1**

General procedure for the synthesis

Synthesis of **1d:** A mixture of compound **1c** (1.0 g, 2.7 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 (3×20 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 pale solid product in a yield of 87%. ^{1}H NMR (400 MH_Z, $CDCl_3$): δ (ppm)= 8.78-8.74 (m, 1H), 8.43 (t, J= 2 Hz, 2H), 7.63-7.58 (m, 3H), 7.48-7.46 (m, 2H), 7.09-7.03 (m, 2H), 1.97-1.92 (m, 4H), 1.14-1.01 (m, 12H), 0.79-0.73 (m, 6H), 0.59 (s, 4H). ^{13}C NMR (100 MH_Z, $CDCl_3$): δ (ppm)= 163.19, 159.31, 152.52, 152.28, 151.76, 151.54, 137.98, 137.57, 137.16, 136.76, 136.32, 136.04, 135.79, 135.49, 120.46, 120.30, 119.77, 119.64, 118.60, 117.78, 114.48, 113.28, 55.39, 40.25, 31.38, 29.50, 23.59, 22.45, 13.89. EI-MS: m/z= 420.55$[M]^+$. Anal. Calcd. for $C_{27}H_{36}N_2O_2$: C, 77.10; H, 8.63; N, 6.66. Found: C, 77.14; H, 8.66; N, 6.61.

Synthesis of **1e:** A CH_2Cl_2 suspension (15 ml) of **1d** (0.3 g, 0.7 mmol) and triethylamine (5 ml) was cooled to 0℃. To the mixture was added dropwise a CH_2Cl_2 solution (10 ml) of triphosgene (0.5 g, 1.7 mmol). The mixture was refluxed under an argon atmosphere for 3 h, then 10% aq. Na_2CO_3 (50 ml) was added dropwise at room temperature. the mixture was extracted with dichloromethane (3×20 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 green solid product in a yield of 75%. ^{1}H NMR (400 MH_Z, $CDCl_3$): δ (ppm)= 7.70 (d, J= 8 Hz, 2H), 7.38 (t, J= 10 Hz, 4H), 1.98-1.94 (m, 4H), 1.15-1.02 (m, 12H), 0.78 (t, J= 8 Hz, 6H), 0.57-0.49 (m, 4H). ^{13}C NMR (100 MH_Z, $CDCl_3$): δ (ppm)= 164.45, 152.31, 140.26, 125.68, 120.96, 55.74, 39.86, 31.28, 29.31, 23.51, 22.38, 13.83. EI-MS: m/z= 384.42[M]$^+$. Anal. Calcd. for $C_{27}H_{32}N_2$: C, 84.33; H, 8.39; N, 7.28. Found: C, 84.35; H, 8.35; N, 7.25.

Synthesis of **1:** A mixture of $C_6F_5Au(tht)$ (0.29 g, 0.64 mmol) and **1e** (0.12 g, 0.31 mmol) was stirred in CH_2Cl_2 (20 ml) over night under an argon atmosphere 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= 93%. ^{1}H NMR (400 MH_Z, $CDCl_3$): δ (ppm)= 7.89 (d, J= 8 Hz, 2H), 7.61 (t, J= 8 Hz, 4H), 2.03 (s, 4H), 1.15-1.02 (m, 12H), 0.79 (t, J= 8 Hz, 6H), 0.57-0.51 (m, 4H). ^{19}F NMR ($CDCl_3$): δ (ppm)= -117.01, -158.12, -163.22. Anal. Calcd. for $C_{39}H_{32}Au_2F_{10}N_2$: C, 42.10; H, 2.90; N, 2.52. Found: C, 42.15; H, 2.87; N, 2.55.

Crystallographic Details

Single crystals of complex **1** suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a solution of dichloromethane. A crystal of **1** with approximate dimensions of 0.12 × 0.10 × 0.10 mm^3 for **1** was mounted on a glass fiber for diffraction experiment. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature. The structures were solved by a combination of direct methods (SHELXS-97)[4] and Fourier difference techniques and refined by full-matrix least-squares (SHELXL-97)[5]. All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Further crystal data is provided in Table S1. Bond distances and angles is given in Table S2. Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data

Centre as supplemental publication CCDC 1023090.

2. References

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3. Figs. S1-S4

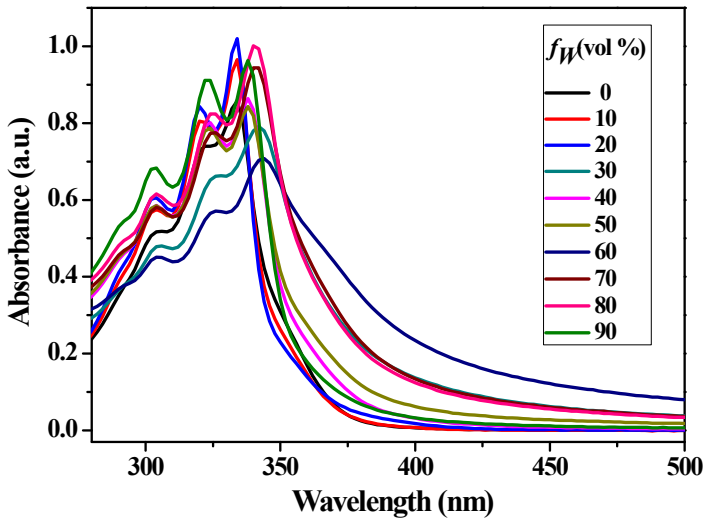


Fig. S1 UV spectra of complex **1** (2.0×10^{-5} mol L^{-1}) in DMF-water mixtures with various water contents (0-90%).

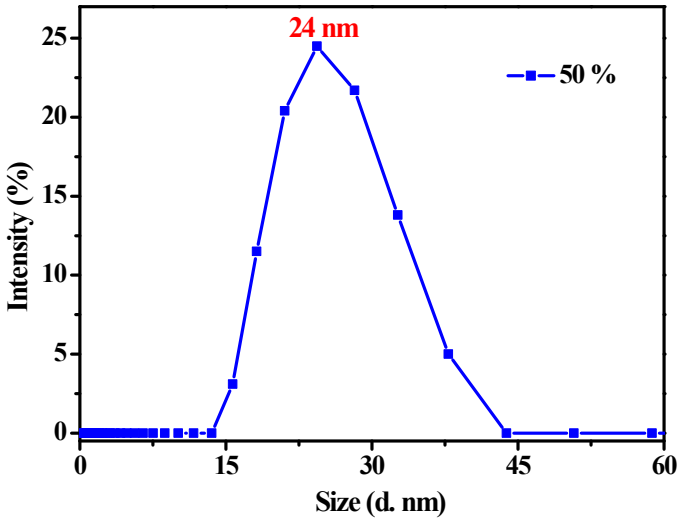


Fig. S2 Size distribution curve of complex **1** (2.0×10^{-5} mol L^{-1}) in DMF-water mixtures with 50% volume fraction of water.

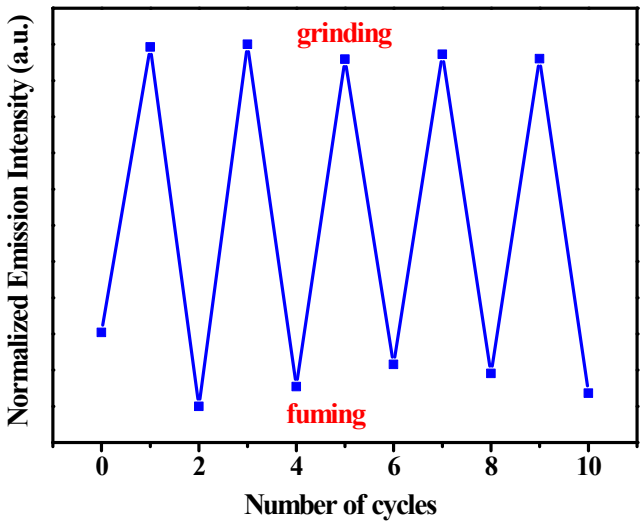


Fig. S3 Invertible grinding-fuming processes of the photoluminescence of complex **1** at 559 nm.

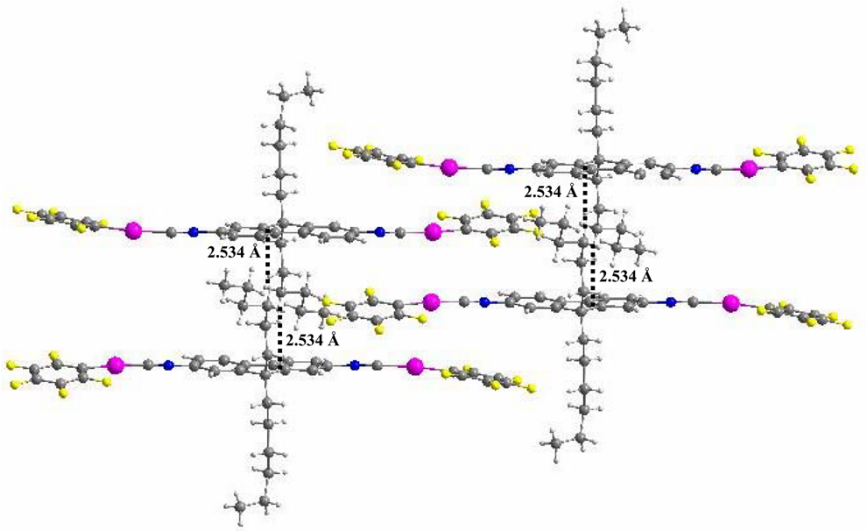


Fig. S4 Crystal packing diagram of complex **1**. It showed weak intermolecular C-H··· π interactions.

4. Table S1-S2

Table S1. Structure determination summary for the complex **1**.

Empirical formula	C_{39} H_{32} Au_2 F_{10} N_2
Formula weight	1112.60
Temperature (K)	296(2)
Crystal system	Triclinic
Space group	P-1
a (Å)	12.3529(19)
b (Å)	12.613(2)
c (Å)	12.950(2)
α (deg)	99.282(2)
β (deg)	107.229(2)
γ (deg)	100.920(2)
V (Å^3)	1840.7(5)
Z	2
Absorption coefficient (mm^{-1})	8.043
F (000)	1056
Theta range for data collection (deg)	2.00 to 25.01
Index ranges	-14<=h<=14, -14<=k<=12, -15<=l<=15

Reflections collected/unique	11843/6339 (R_{int}= 0.0468)
Final R indices [I>2sigma(I)]	R_1= 0.0733, wR_2= 0.2189
R indices (all data)	R_1= 0.0839, wR_2= 0.2359
Goodness-of-fit on F^2	1.053
Largest difference peak and hole(e $Å^{-3}$)	2.642, -4.113

Table S2. Bond lengths [Å] and angles [°] of **1**.

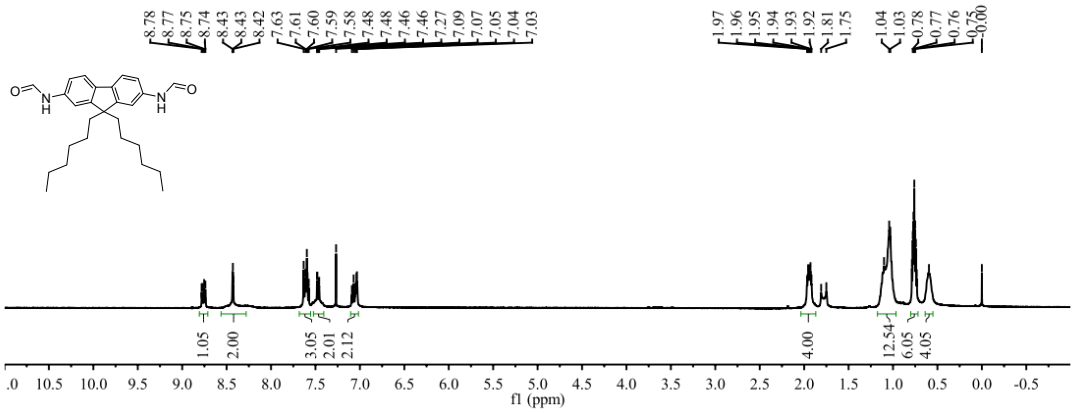
Au(1)-C(14)	1.968(12)	C(12)-N(2)	1.396(15)
Au(1)-C(28)	2.036(11)	C(13)-H(13)	0.9300
Au(1)-Au(2)	3.3788(8)	C(14)-N(1)	1.145(15)
Au(2)-C(15)#1	1.957(15)	C(15)-N(2)	1.162(17)
Au(2)-C(34)	2.030(12)	C(15)-Au(2)#2	1.957(15)
C(1)-C(2)	1.358(16)	C(16)-C(17)	1.560(16)
C(1)-C(6)	1.401(15)	C(16)-H(16A)	0.9700
C(1)-N(1)	1.419(14)	C(16)-H(16B)	0.9700
C(2)-C(3)	1.405(15)	C(17)-C(18)	1.544(16)
C(2)-H(2)	0.9300	C(17)-H(17A)	0.9700
C(3)-C(4)	1.377(15)	C(17)-H(17B)	0.9700
C(3)-H(3)	0.9300	C(18)-C(19)	1.51(2)
C(4)-C(5)	1.424(14)	C(18)-H(18A)	0.9700
C(4)-C(9)	1.449(15)	C(18)-H(18B)	0.9700
C(5)-C(6)	1.380(16)	C(19)-C(20)	1.56(2)
C(5)-C(7)	1.506(14)	C(19)-H(19A)	0.9700
C(6)-H(6)	0.9300	C(19)-H(19B)	0.9700
C(7)-C(22)	1.534(14)	C(20)-C(21)	1.47(3)
C(7)-C(8)	1.536(13)	C(20)-H(20A)	0.9700
C(7)-C(16)	1.544(13)	C(20)-H(20B)	0.9700
C(8)-C(13)	1.381(15)	C(21)-H(21A)	0.9600
C(8)-C(9)	1.386(16)	C(21)-H(21B)	0.9600
C(9)-C(10)	1.405(16)	C(21)-H(21C)	0.9600
C(10)-C(11)	1.376(16)	C(22)-C(23)	1.525(15)
C(10)-H(10)	0.9300	C(22)-H(22A)	0.9700
C(11)-C(12)	1.393(17)	C(22)-H(22B)	0.9700
C(11)-H(11)	0.9300	C(23)-C(24)	1.544(17)
C(12)-C(13)	1.364(17)	C(23)-H(23A)	0.9700

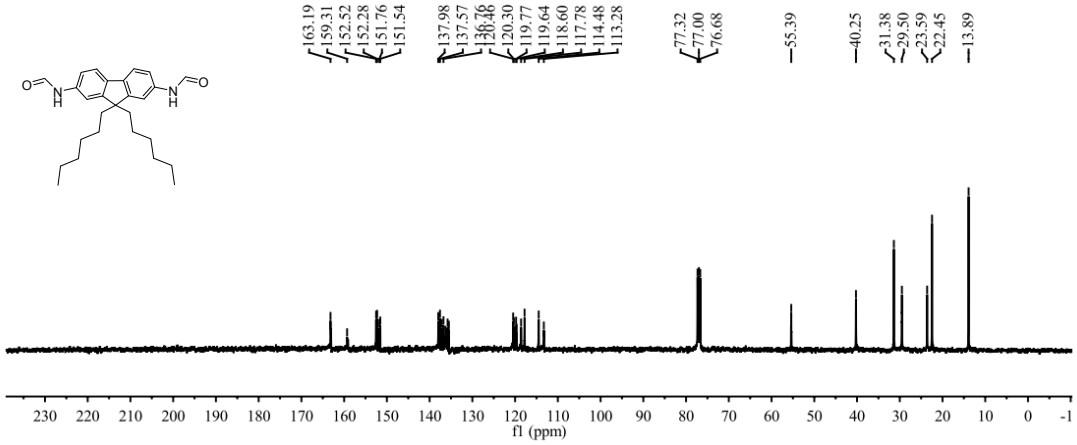
C(23)-H(23B)	0.9700	C(15)#1-Au(2)-C(34)	176.1(5)
C(24)-C(25)	1.517(17)	C(15)#1-Au(2)-Au(1)	104.6(3)
C(24)-H(24A)	0.9700	C(34)-Au(2)-Au(1)	72.5(3)
C(24)-H(24B)	0.9700	C(2)-C(1)-C(6)	123.8(10)
C(25)-C(26)	1.51(2)	C(2)-C(1)-N(1)	118.7(10)
C(25)-H(25A)	0.9700	C(6)-C(1)-N(1)	117.5(10)
C(25)-H(25B)	0.9700	C(1)-C(2)-C(3)	118.7(10)
C(26)-C(27)	1.41(3)	C(1)-C(2)-H(2)	120.7
C(26)-H(26A)	0.9700	C(3)-C(2)-H(2)	120.7
C(26)-H(26B)	0.9700	C(4)-C(3)-C(2)	119.5(10)
C(27)-H(27A)	0.9600	C(4)-C(3)-H(3)	120.3
C(27)-H(27B)	0.9600	C(2)-C(3)-H(3)	120.3
C(27)-H(27C)	0.9600	C(3)-C(4)-C(5)	120.8(10)
C(28)-C(29)	1.365(16)	C(3)-C(4)-C(9)	131.1(10)
C(28)-C(32)	1.386(17)	C(5)-C(4)-C(9)	108.0(9)
C(29)-F(1)	1.345(14)	C(6)-C(5)-C(4)	119.6(10)
C(29)-C(30)	1.389(17)	C(6)-C(5)-C(7)	129.1(9)
C(30)-F(2)	1.349(14)	C(4)-C(5)-C(7)	111.2(9)
C(30)-C(31)	1.368(19)	C(5)-C(6)-C(1)	117.6(10)
C(31)-F(3)	1.351(14)	C(5)-C(6)-H(6)	121.2
C(31)-C(33)	1.361(18)	C(1)-C(6)-H(6)	121.2
C(32)-F(5)	1.338(15)	C(5)-C(7)-C(22)	111.0(8)
C(32)-C(33)	1.363(17)	C(5)-C(7)-C(8)	100.3(8)
C(33)-F(4)	1.365(15)	C(22)-C(7)-C(8)	112.1(8)
C(34)-C(35)	1.366(18)	C(5)-C(7)-C(16)	112.0(9)
C(34)-C(39)	1.379(18)	C(22)-C(7)-C(16)	109.6(8)
C(35)-F(6)	1.367(14)	C(8)-C(7)-C(16)	111.7(8)
C(35)-C(36)	1.411(19)	C(13)-C(8)-C(9)	121.2(10)
C(36)-F(7)	1.304(18)	C(13)-C(8)-C(7)	127.2(10)
C(36)-C(37)	1.35(2)	C(9)-C(8)-C(7)	111.6(9)
C(37)-F(8)	1.332(15)	C(8)-C(9)-C(10)	119.8(10)
C(37)-C(38)	1.37(2)	C(8)-C(9)-C(4)	108.7(9)
C(38)-F(9)	1.343(15)	C(10)-C(9)-C(4)	131.4(11)
C(38)-C(39)	1.376(18)	C(11)-C(10)-C(9)	118.4(11)
C(39)-F(10)	1.358(16)	C(11)-C(10)-H(10)	120.8
C(14)-Au(1)-C(28)	174.5(5)	C(9)-C(10)-H(10)	120.8
C(14)-Au(1)-Au(2)	100.9(3)	C(10)-C(11)-C(12)	120.6(11)
C(28)-Au(1)-Au(2)	84.3(3)	C(10)-C(11)-H(11)	119.7

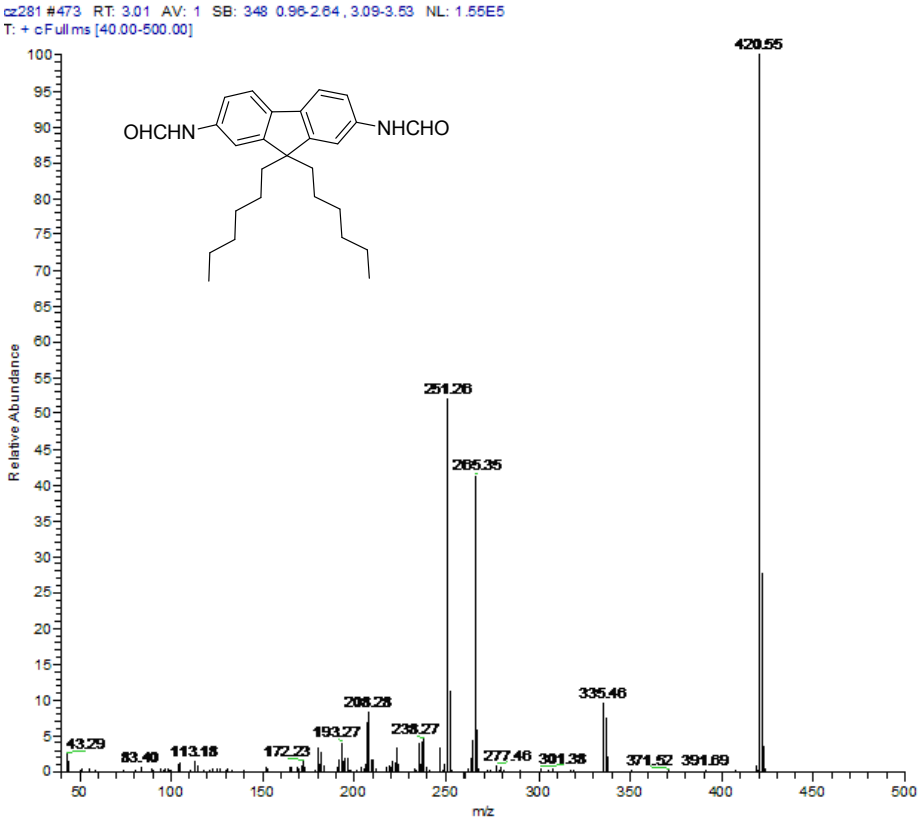
C(12)-C(11)-H(11)	119.7	H(20A)-C(20)-H(20B)	107.8
C(13)-C(12)-C(11)	121.2(11)	C(20)-C(21)-H(21A)	109.5
C(13)-C(12)-N(2)	118.1(12)	C(20)-C(21)-H(21B)	109.5
C(11)-C(12)-N(2)	120.6(11)	H(21A)-C(21)-H(21B)	109.5
C(12)-C(13)-C(8)	118.7(11)	C(20)-C(21)-H(21C)	109.5
C(12)-C(13)-H(13)	120.6	H(21A)-C(21)-H(21C)	109.5
C(8)-C(13)-H(13)	120.6	H(21B)-C(21)-H(21C)	109.5
N(1)-C(14)-Au(1)	175.5(11)	C(23)-C(22)-C(7)	114.4(9)
N(2)-C(15)-Au(2)#2	175.1(12)	C(23)-C(22)-H(22A)	108.7
C(7)-C(16)-C(17)	113.9(9)	C(7)-C(22)-H(22A)	108.7
C(7)-C(16)-H(16A)	108.8	C(23)-C(22)-H(22B)	108.7
C(17)-C(16)-H(16A)	108.8	C(7)-C(22)-H(22B)	108.7
C(7)-C(16)-H(16B)	108.8	H(22A)-C(22)-H(22B)	107.6
C(17)-C(16)-H(16B)	108.8	C(22)-C(23)-C(24)	112.2(10)
H(16A)-C(16)-H(16B)	107.7	C(22)-C(23)-H(23A)	109.2
C(18)-C(17)-C(16)	113.5(10)	C(24)-C(23)-H(23A)	109.2
C(18)-C(17)-H(17A)	108.9	C(22)-C(23)-H(23B)	109.2
C(16)-C(17)-H(17A)	108.9	C(24)-C(23)-H(23B)	109.2
C(18)-C(17)-H(17B)	108.9	H(23A)-C(23)-H(23B)	107.9
C(16)-C(17)-H(17B)	108.9	C(25)-C(24)-C(23)	111.2(11)
H(17A)-C(17)-H(17B)	107.7	C(25)-C(24)-H(24A)	109.4
C(19)-C(18)-C(17)	112.7(11)	C(23)-C(24)-H(24A)	109.4
C(19)-C(18)-H(18A)	109.0	C(25)-C(24)-H(24B)	109.4
C(17)-C(18)-H(18A)	109.0	C(23)-C(24)-H(24B)	109.4
C(19)-C(18)-H(18B)	109.0	H(24A)-C(24)-H(24B)	108.0
C(17)-C(18)-H(18B)	109.0	C(26)-C(25)-C(24)	115.1(14)
H(18A)-C(18)-H(18B)	107.8	C(26)-C(25)-H(25A)	108.5
C(18)-C(19)-C(20)	109.7(13)	C(24)-C(25)-H(25A)	108.5
C(18)-C(19)-H(19A)	109.7	C(26)-C(25)-H(25B)	108.5
C(20)-C(19)-H(19A)	109.7	C(24)-C(25)-H(25B)	108.5
C(18)-C(19)-H(19B)	109.7	H(25A)-C(25)-H(25B)	107.5
C(20)-C(19)-H(19B)	109.7	C(27)-C(26)-C(25)	116.4(17)
H(19A)-C(19)-H(19B)	108.2	C(27)-C(26)-H(26A)	108.2
C(21)-C(20)-C(19)	113.1(17)	C(25)-C(26)-H(26A)	108.2
C(21)-C(20)-H(20A)	109.0	C(27)-C(26)-H(26B)	108.2
C(19)-C(20)-H(20A)	109.0	C(25)-C(26)-H(26B)	108.2
C(21)-C(20)-H(20B)	109.0	H(26A)-C(26)-H(26B)	107.3
C(19)-C(20)-H(20B)	109.0	C(26)-C(27)-H(27A)	109.5

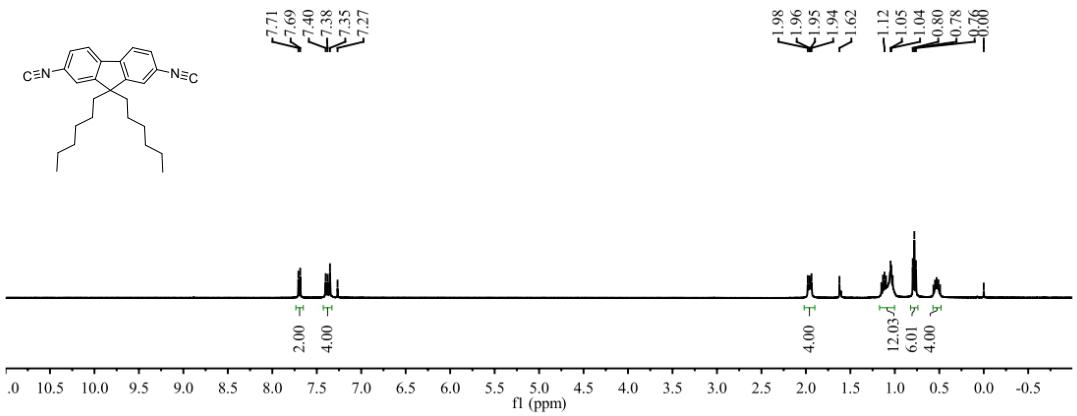
C(26)-C(27)-H(27B)	109.5	C(32)-C(33)-F(4)	121.3(12)
H(27A)-C(27)-H(27B)	109.5	C(35)-C(34)-C(39)	113.3(11)
C(26)-C(27)-H(27C)	109.5	C(35)-C(34)-Au(2)	121.5(9)
H(27A)-C(27)-H(27C)	109.5	C(39)-C(34)-Au(2)	124.8(10)
H(27B)-C(27)-H(27C)	109.5	C(34)-C(35)-F(6)	119.7(11)
C(29)-C(28)-C(32)	116.1(11)	C(34)-C(35)-C(36)	124.4(12)
C(29)-C(28)-Au(1)	122.4(9)	F(6)-C(35)-C(36)	115.9(13)
C(32)-C(28)-Au(1)	121.5(9)	F(7)-C(36)-C(37)	122.0(13)
F(1)-C(29)-C(28)	122.6(11)	F(7)-C(36)-C(35)	119.7(14)
F(1)-C(29)-C(30)	115.9(11)	C(37)-C(36)-C(35)	118.2(14)
C(28)-C(29)-C(30)	121.5(11)	F(8)-C(37)-C(36)	121.0(14)
F(2)-C(30)-C(31)	118.8(11)	F(8)-C(37)-C(38)	118.5(12)
F(2)-C(30)-C(29)	120.7(12)	C(36)-C(37)-C(38)	120.4(12)
C(31)-C(30)-C(29)	120.6(11)	F(9)-C(38)-C(37)	120.4(11)
F(3)-C(31)-C(33)	121.2(12)	F(9)-C(38)-C(39)	121.1(13)
F(3)-C(31)-C(30)	120.0(12)	C(37)-C(38)-C(39)	118.5(12)
C(33)-C(31)-C(30)	118.8(11)	F(10)-C(39)-C(38)	116.2(11)
F(5)-C(32)-C(33)	116.7(11)	F(10)-C(39)-C(34)	118.7(11)
F(5)-C(32)-C(28)	120.4(11)	C(38)-C(39)-C(34)	125.0(13)
C(33)-C(32)-C(28)	122.9(11)	C(14)-N(1)-C(1)	176.3(12)
C(31)-C(33)-C(32)	120.0(12)	C(15)-N(2)-C(12)	173.9(13)
C(31)-C(33)-F(4)	118.6(11)		

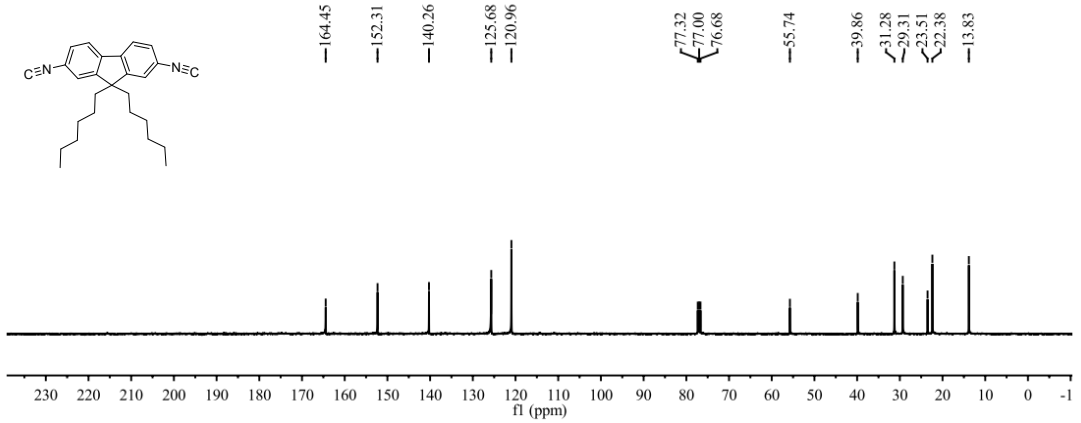
5. Copies of NMR spectra and Mass spectra

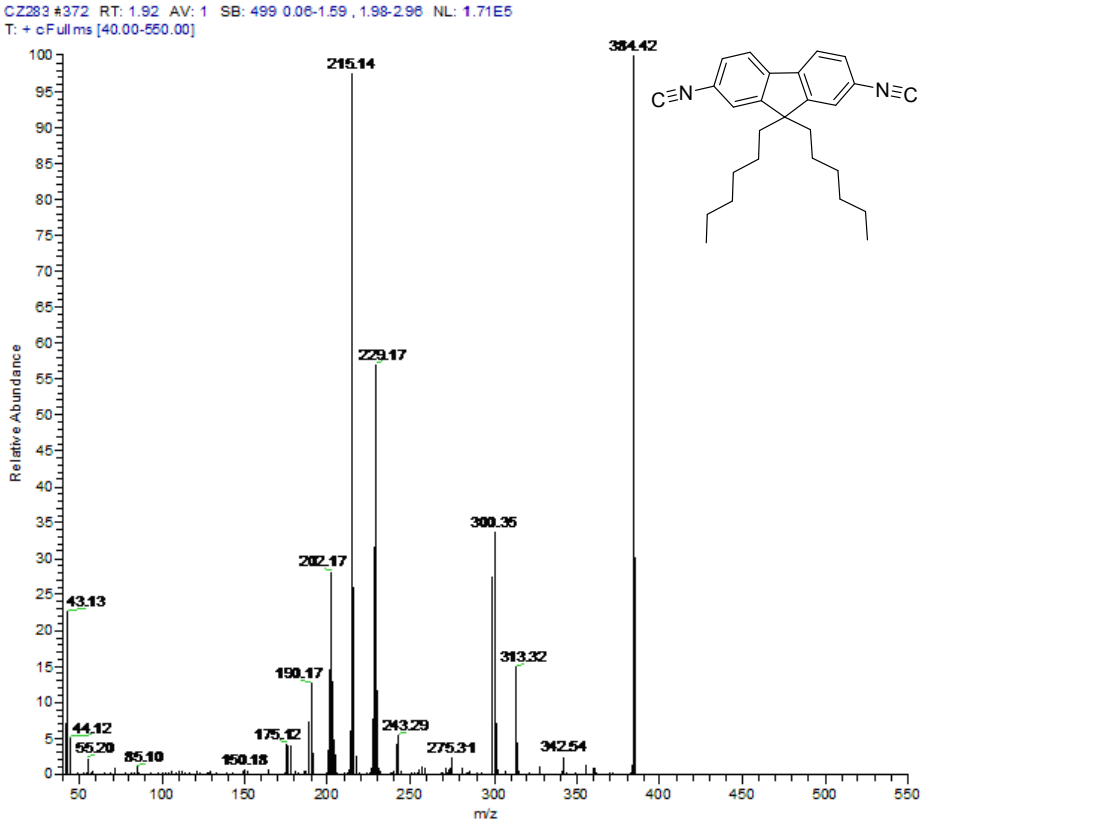


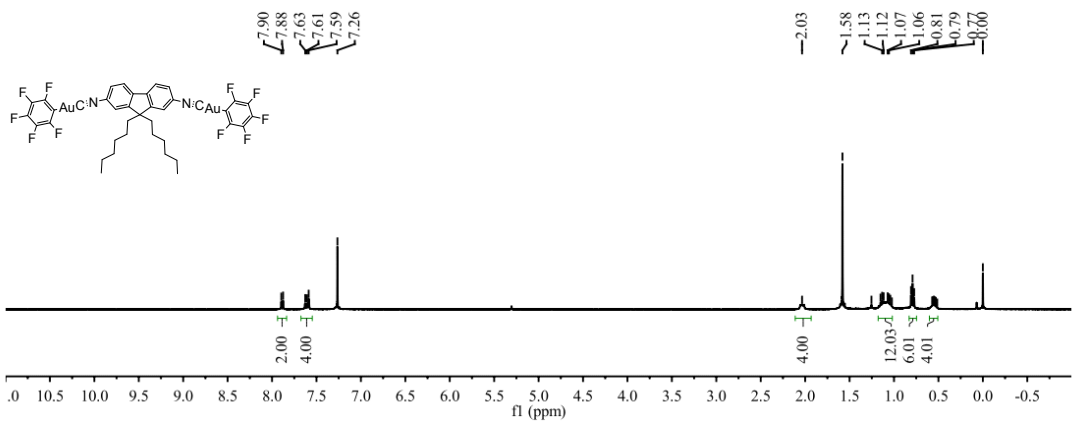

163.19
159.31
152.52
152.28
151.76
151.54
137.98
137.57
136.76
120.46
120.30
119.77
119.64
118.60
117.78
114.48
113.28
77.32
77.00
76.68
55.39
40.25
31.38
29.50
23.59
22.45
13.89
f1 (ppm)

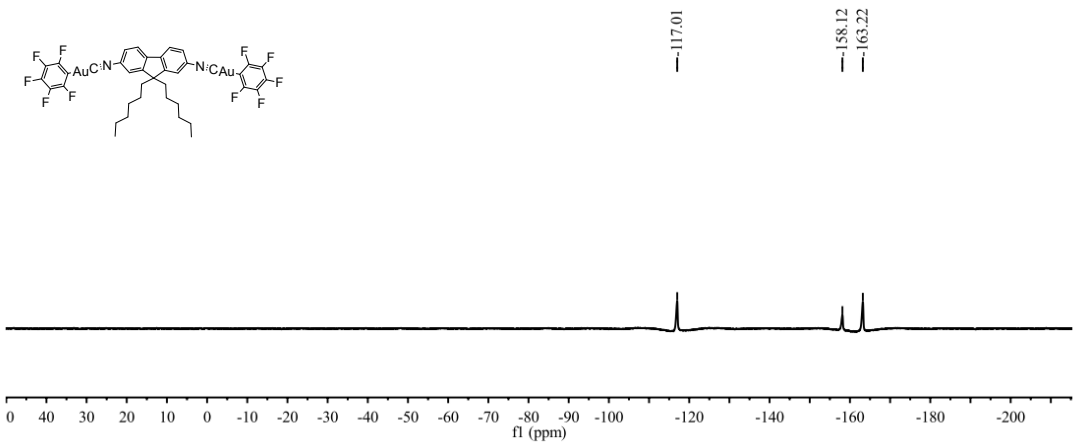

cz281 #473 RT: 3.01 AV: 1 SB: 348 0.96-2.64 , 3.09-3.53 NL: 1.55E5
T: + c Full ms [40.00-500.00]
OHCHN
NHCHO
420.55
251.26
265.35
335.46
208.28
193.27
238.27
43.29
83.40
113.18
172.23
277.46
301.38
371.52
391.69
Relative Abundance
m/z


7.71
7.69
7.40
7.38
7.35
7.27
1.98
1.96
1.95
1.94
1.62
1.12
1.05
1.04
0.80
0.78
0.76
0.00
2.00
4.00
4.00
12.03
6.01
4.00
f1 (ppm)


C≡N
N≡C
164.45
152.31
140.26
125.68
120.96
77.32
77.00
76.68
55.74
39.86
31.28
29.31
23.51
22.38
13.83
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


CZ283 #372 RT: 1.92 AV: 1 SB: 499 0.06-1.59 , 1.98-2.96 NL: 1.71E5
T: + c Full ms [40.00-550.00]
C≡N
N≡C
384.42
215.14
229.17
300.35
202.17
43.13
313.32
190.17
243.29
44.12
175.12
55.20
85.10
150.18
275.31
342.54
Relative Abundance
m/z


7.90
7.88
7.63
7.61
7.59
7.26
2.03
1.58
1.13
1.12
1.07
1.06
0.81
0.79
0.77
0.00
2.00
4.00
4.00
12.03
6.01
4.01
f1 (ppm)


-117.01
-158.12
-163.22
0 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)