Electronic Supplementary Information (ESI)

# Aggregation-induced emission (AIE) behavior and thermochromic luminescent property of a new gold(I)

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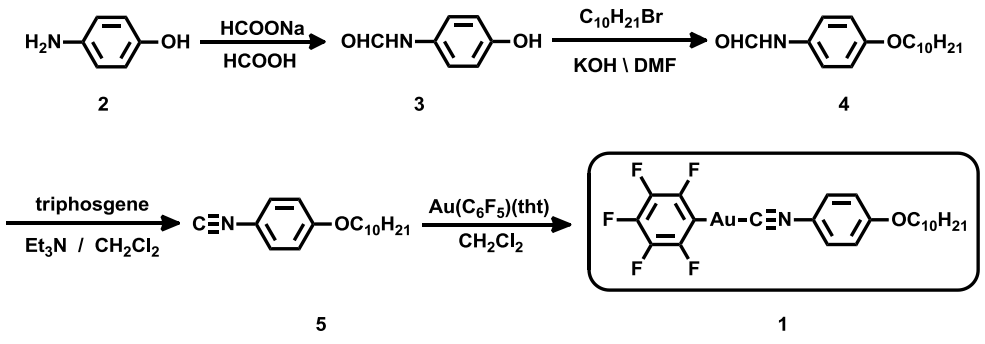
## 1. Experimental Section

### Materials and measurements

All manipulations were carried out at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were predried, distilled, and degassed prior to use, except those for spectroscopic measurements, which were of spectroscopic grade. The starting material 4-aminophenol (**2**) purchased from Alfa Aesar was used as received. All other reagents and solvents were purchased as analytical grade from Shen Shi Hua Gong Company (China) and used without further purification. Ethanol (EtOH) was distilled from magnesium powder/iodine. Dichloromethane ($CH_2Cl_2$) was distilled from $CaH_2$. Ultra-pure water was used in the experiments. Intermediates *N*-(4-hydroxyphenyl)formamide (**3**)[1] and $C_6F_5Au(tht)$[2] were prepared according to the literature methods. Elemental analyses (C, H, N) were performed by the Microanalytical Services, College of Chemistry, CCNU. $^1H$ and $^{13}C$ NMR spectra were collected on American Varian Mercury Plus 400 spectrometer (400 MHz). $^1H$ and $^{13}C$ NMR chemical shifts are relative to TMS. $^{19}F$ NMR chemical shifts are relative to $C_6F_6$ ($\delta$ = -163.00). UV-vis spectra were obtained on U-3310 UV spectrophotometer. Fluorescence spectra were recorded on a Hitachi-F-4500 fluorescence spectrophotometer. Dynamic light scattering (DLS) measurements were performed on the Zetasizer instrument ZEN3600 (Malvern, UK) with a 173° back scattering angle and He–Ne laser ($\lambda$ = 633 nm).

The water/EtOH mixtures with different water fractions were prepared by slowly adding ultra-pure water into the EtOH solution of samples.




**Scheme S1.** Synthesis of the gold(I) compound **1**.

**General procedure for the synthesis**

N-(4-(decyloxy)phenyl)formamide (**4**). A EtOH suspension (10 mL) of **3** (549 mg, 4.0 mmol) and KOH (292 mg, 5.2 mmol) was refluxed. To the mixture was added dropwise a 1-bromodecane (1060 mg, 4.8mmol). The mixture was refluxed for 12h. The mixture was extracted several times with $CH_2C1_2$. The combined extract was washed with water, dried over magnesium sulfate and the solvent was evaporated. The residue was subjected to column chromatography on silica gel (eluent: $CH_2C1_2$) to give a pink solid. Yield: 683 mg, 75%. mp. 81-83°C. $^1$H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.2 Hz, 3H, $CH_3$), 1.30 (m, 14H, $CH_2$), 1.43-1.44 (br, 2H, $CH_2$), 1.75 (m, 2H, $CH_2$), 3.93 (t, *J* = 6.0 Hz, 2H, $OCH_2$), 6.85 (d, *J* = 9.2 Hz, 4H, Ar-H), 7.01 (d, *J* = 10.0 Hz, 1H, *o*-H, *cis*), 7.26 (bs, 0.5H, NH, trans), 7.42 (d, *J* = 10.0 Hz, 1H, *o*-H, *trans*), 7.92 (bs, 0.5H, NH, trans), 8.32 (s, 0.5H, *CHO*, *trans*), 8.49 (d, *J* = 12.0 Hz, 0.5H, *CHO*, *cis*). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): δ 14.1 (s, $CH_3$), 22.6, 26.0, 29.2, 29.3, 29.7, 31.8, 68.3 (s, $OCH_2$), 114.8, 115.4, 121.7, 129.5, 158.7(s, Ar), 162.9 (s, CHO). Anal. Calcd for $C_{17}H_{27}NO_2$: C, 73.61; H, 9.81; N, 5.05. Found: C, 73.47; H, 9.75; N, 5.18.

1-(decyloxy)-4-isocyanobenzene (**5**). A $CH_2C1_2$ suspension (10 mL) of **4** (682 mg, 3.0 mmol) and triethylamine (2.9 mL, 14.1 mmol) was cooled to 0℃. To the mixture was added dropwise a $CH_2C1_2$ solution (2 mL) of triphosgene (475 mg, 1.6 mmol) The mixture was refluxed for 3 h, At room temperature, 10% aq. $Na_2CO_3$ (50 mL) was added dropwise. The mixture was extracted several times with $CH_2C1_2$. The combined extract was washed with water, dried over magnesium sulfate and the solvent was evaporated. The residue was subjected to column chromatography on silica gel (eluent: petroleum ether / $CH_2C1_2$ = 4 : 1) to give a yellowish oily liquid. Yield: 567 mg, 73%. $^1$H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.2 Hz, 3H, $CH_3$), 1.23 (m, 14H, $CH_2$), 1.26-1.27 (br, 2H, $CH_2$), 1.79 (m, 2H, $CH_2$), 3.94 (t, *J* = 6.4 Hz, 2H, $OCH_2$), 6.84 (d, *J* = 9.2 Hz, 4H, Ar-H), 7.27 (d, *J* = 9.2 Hz, 4H, Ar-H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): δ 14.0 (s, $CH_3$), 22.7, 25.9, 28.9, 29.3, 29.5, 31.9, 68.8 (s, $OCH_2$), 114.9, 119.5, 127.7, 159.4 (s, Ar), 162.4 (s, N≡C). Anal. Calcd for $C_{17}H_{25}NO$: C, 78.72; H, 9.72; N, 5.40. Found: C, 78.61; H, 9.65; N, 5.53.

[($C_6F_5Au$)($\mu$-1-(decyloxy)-4-isocyanophenyl] (**1**). A mixture of $C_6F_5Au$(tht) (185 mg, 0.41 mmol) and 1-(decyloxy)-4-isocyanobenzene **5** (103 mg, 0.4mmol) was stirred in $CH_2Cl_2$ (8 mL) over night under an argon atmosphere at room temperature. The solvent was evaporated. The residue was subjected to column chromatography on silica gel (eluent: petroleum ether / $CH_2C1_2$ = 1 : 1) to give a white solid. Yield: 162 mg, 65%. mp. 56-58 $^oC$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 0.88 (t, $J$ = 7.6 Hz, 3H, $CH_3$), 1.27 (m, 14H, $CH_2$), 1.43-1.45 (br, 2H, $CH_2$), 1.80 (m, 2H, $CH_2$), 4.00 (t, $J$ = 7.2 Hz, 2H, $OCH_2$), 6.95 (d, $J$ = 10.0 Hz, 4H, Ar-H), 7.45 (d, $J$ = 9.6 Hz, 4H, Ar-H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 14.1 (s, $CH_3$), 22.7, 25.9, 28.9, 29.3, 29.5, 31.9 (s, $CH_2$), 68.8 (s, $OCH_2$), 115.7, 116.3, 128.3, 128.9 (s, Ar), 136.9 (dm, $J_{C-F}$ = 248 Hz, *C*F), 139.3 (dm, $J_{C-F}$ = 242 Hz, *C*F), 149.4 (dm, $J_{C-F}$ = 227 Hz, *C*F), 156.4 (s, Ar), 161.3 (s, N≡C). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ -116.0 (m, 2F, *m*-F), -158.0 (m, 1F, *p*-F), -162.6 (m, 2F, *o*-F). IR(KBr): 2219 ν(C≡N) $cm^{-1}$. Anal. Calcd for $C_{23}H_{25}AuF_5NO$: C, 44.31; H, 4.04; N, 2.25. Found: C, 44.19; H, 4.03; N, 2.24.

**Crystallographic Details.**

Single crystals of complexes **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 0.20 × 0.13 × 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)[3] and Fourier difference techniques and refined by full-matrix least-squares (SHELXL-97)[4]. All non-H atoms were refined anisotropically. The hydrogen atoms were placed in the ideal positions and refined as riding atoms. Further crystal data and details of the data collection are summarized in Table S1. Selected bond distances and angles is given in Tables S2.

## 2. References

1. M. Hosseini-Sarvari, H. Sharghi. *J. Org. Chem.* 2006, **71**, 6652.

2. R. Uson, A. Laguna, M. Laguna. *Inorg. Synth.* 1989, **26**, 85.

3. G. M. Sheldrick, SHELXS-97: Program for crystal structure solution, University of Götingen, Götingen, Germany, **1997**.
4. G. M. Sheldrick, SHELXS-97: Program for crystal structure refinement, University of Götingen, Götingen, Germany, **1997**.

### 3. Figs. S1-S8

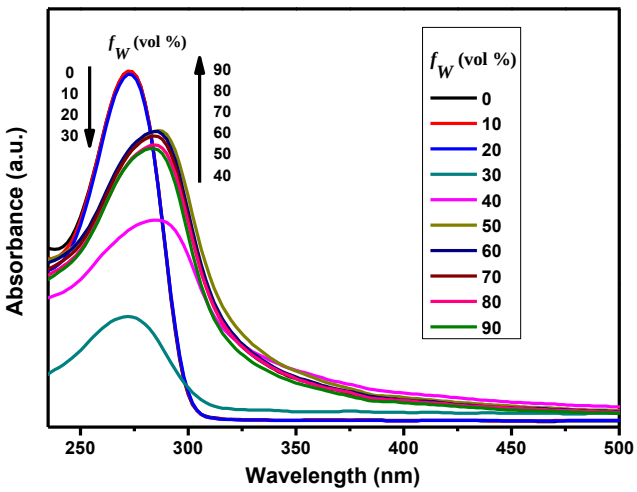



**Fig. S1** UV spectra of compound **1** ($2.0\times10^{-5}$ mol/L) in water–EtOH mixtures with different volume fractions of water (0 -90%).

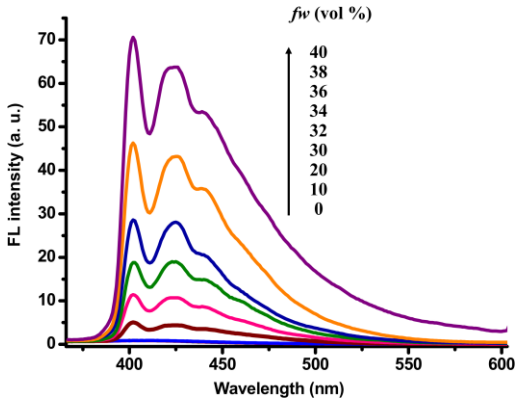



**Fig. S2** PL spectra of compound **1** ($2.0\times10^{-5}$ mol/L) in water–EtOH mixtures with different volume fractions of water (0 -40%). Excitation wavelength = 310 nm

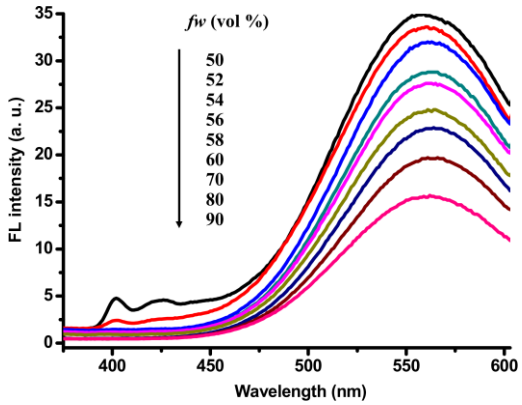



**Fig. S3** PL spectra of compound **1** ($2.0\times10^{-5}$ mol/L) in water–EtOH mixtures with different volume fractions of water (50% -90%). Excitation wavelength = 310 nm

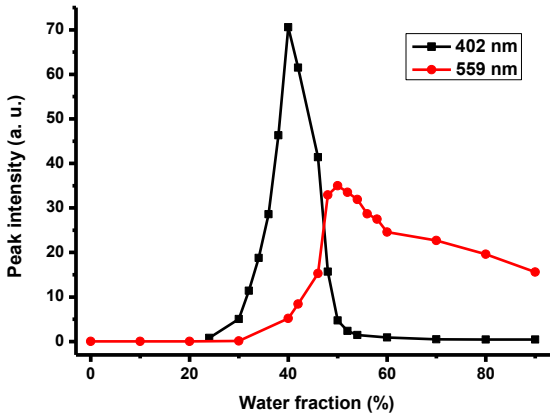



**Fig. S4** The PL intensity (at 402 nm and 559 nm) of compound **1** ($2.0\times10^{-5}$ mol/L) in water -EtOH mixtures with different volume fractions of water (0% -90%).

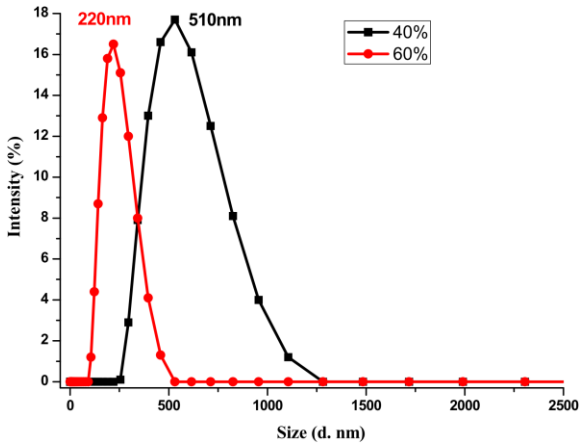



**Fig. S5** Size distribution curves of compound **1** ($2.0\times10^{-5}$ mol/L) in water–EtOH mixtures with different volume fractions of water (40% and 60%).

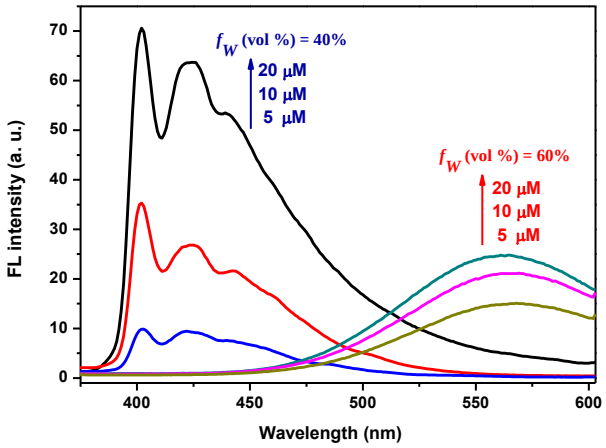



**Fig. S6** PL spectra of compound **1** (5μM, 10 μM and 20 μM) in water–EtOH mixtures with different volume fractions of water (40% and 60%).

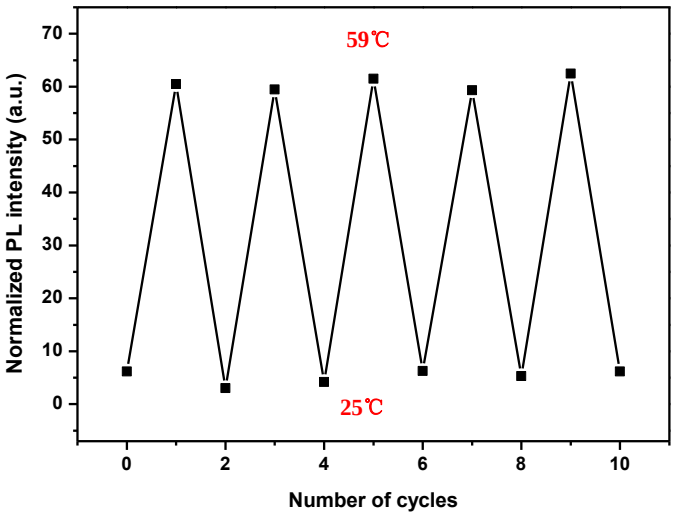



**Fig. S7** Reversible temperature-dependence of the PL of **1** at 530 nm.

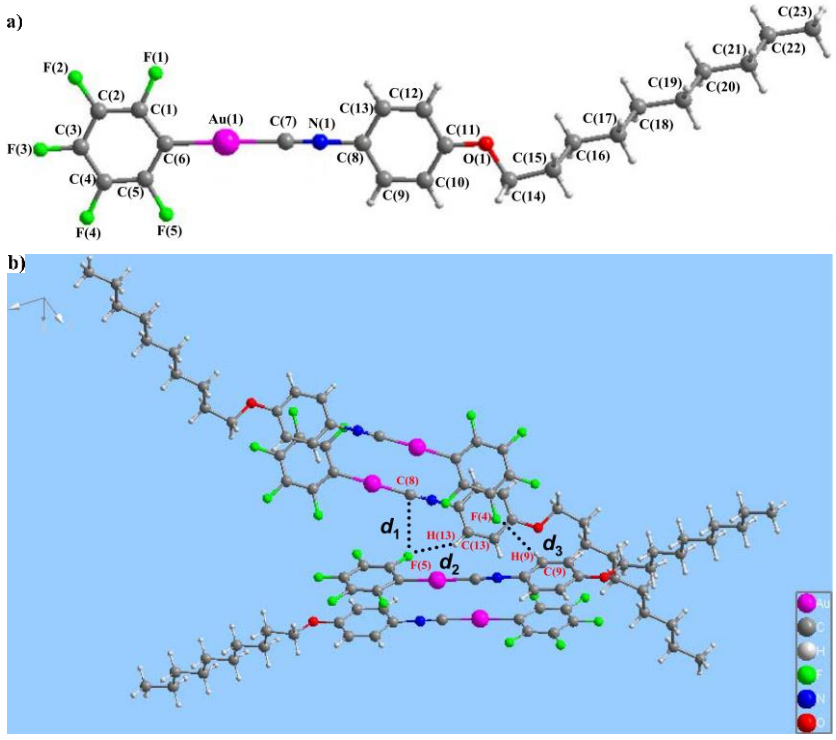



**Fig. S8** a) The single crystal structure of complex **1**. b) Crystal packing diagram of gold(I) complex **1**. It showed multiple weak interactions, including intermolecular C-H···F ($d_2$ = $d_{C(13)\text{-}H(13)\cdots F(5)}$ = 2.459Å, $d_3$ = $d_{C(9)\text{-}H(9)\cdots F(4)}$ = 2.646 Å) and C···F ($d_1$ = $d_{C(8)\cdots F(5)}$ =3.122 Å).

## 4. Table S1-S2.

**Table S1.** Crystal Data, Data Collection, and Refinement Parameter for **1.**

| | **1** |
|---|---|
| formula | C23 H25 Au F5 N O |
| Fw | 623.41 |
| temp(K) | 298(2) |
| cryst syst | Monoclinic |
| Space group | P2(1)/c |
| *a* (Å) | 24.7588(17) |
| *b* (Å) | 7.4380(5) |
| *c* (Å) | 12.7956(9) |
| $\alpha$(deg) | 90.00 |
| $\beta$(deg) | 98.2370(10) |
| $\gamma$(deg) | 90.00 |
| *V* (Å$^{-3}$) | 2332.1(3) |
| *Z* | 4 |
| $D_{calcd}$ (Mg cm$^{-3}$) | 1.776 |
| cryst size (mm$^3$) | 0.20 x 0.13 x 0.10 |
| *F*(000) | 1208 |
| diffractometer | KappaCCD |
| radiation | Mo Ka |
| $\theta$ range (deg) | 2.86 to 26.00 |
| *hkl* range | -23 to 30, -9 to 9, -15 to 14 |
| Reflections collected | 14447 |
| Independent reflections[$R_{(int)}$] | 4563 (0.0304) |
| Data / restraints / parameters | 4563 / 0 / 281 |
| final *R* | 0.0496 |
| $R_w$ | 0.0956 |
| *R* (all date) | 0.0543 |
| $R_w$ (all date) | 0.0974 |
| goodness of fit/$F^2$ | 1.284 |
| largest diff peak, hole (e Å$^{-3}$) | 1.715 and -1.655 |

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

| | | | |
|---|---|---|---|
| Au(1)-C(7) | 1.977(7) | C(13)-C(8)-N(1) | 119.2(7) |
| Au(1)-C(6) | 2.024(6) | C(9)-C(8)-N(1) | 120.1(7) |
| C(1)-F(1) | 1.361(8) | C(10)-C(9)-C(8) | 119.4(7) |
| C(1)-C(2) | 1.367(10) | C(10)-C(9)-H(9) | 120.3 |
| C(1)-C(6) | 1.387(10) | C(8)-C(9)-H(9) | 120.3 |
| C(2)-F(2) | 1.347(8) | C(9)-C(10)-C(11) | 120.3(8) |
| C(2)-C(3) | 1.352(10) | C(9)-C(10)-H(10) | 119.9 |
| C(3)-F(3) | 1.344(8) | C(11)-C(10)-H(10) | 119.9 |
| C(3)-C(4) | 1.376(11) | O(1)-C(11)-C(12) | 115.5(7) |
| C(4)-F(4) | 1.343(8) | O(1)-C(11)-C(10) | 124.6(7) |
| C(4)-C(5) | 1.379(9) | C(12)-C(11)-C(10) | 119.9(7) |
| C(5)-F(5) | 1.351(8) | C(13)-C(12)-C(11) | 120.3(7) |
| C(5)-C(6) | 1.378(9) | C(13)-C(12)-H(12) | 119.9 |
| C(7)-N(1) | 1.128(9) | C(11)-C(12)-H(12) | 119.9 |
| C(8)-C(13) | 1.384(10) | C(12)-C(13)-C(8) | 119.4(7) |
| C(8)-C(9) | 1.385(11) | C(12)-C(13)-H(13) | 120.3 |
| C(8)-N(1) | 1.414(9) | C(8)-C(13)-H(13) | 120.3 |
| C(9)-C(10) | 1.358(10) | O(1)-C(14)-C(15) | 107.6(7) |
| C(9)-H(9) | 0.9300 | O(1)-C(14)-H(14A) | 110.2 |
| C(10)-C(11) | 1.395(10) | C(15)-C(14)-H(14A) | 110.2 |
| C(10)-H(10) | 0.9300 | O(1)-C(14)-H(14B) | 110.2 |
| C(11)-O(1) | 1.360(8) | C(15)-C(14)-H(14B) | 110.2 |
| C(11)-C(12) | 1.373(10) | H(14A)-C(14)-H(14B) | 108.5 |
| C(12)-C(13) | 1.368(10) | C(16)-C(15)-C(14) | 113.3(8) |
| C(12)-H(12) | 0.9300 | C(16)-C(15)-H(15A) | 108.9 |
| C(13)-H(13) | 0.9300 | C(14)-C(15)-H(15A) | 108.9 |
| C(14)-O(1) | 1.421(10) | C(16)-C(15)-H(15B) | 108.9 |
| C(14)-C(15) | 1.518(11) | C(14)-C(15)-H(15B) | 108.9 |
| C(14)-H(14A) | 0.9700 | H(15A)-C(15)-H(15B) | 107.7 |
| C(14)-H(14B) | 0.9700 | C(15)-C(16)-C(17) | 113.4(8) |
| C(15)-C(16) | 1.515(13) | C(15)-C(16)-H(16A) | 108.9 |
| C(15)-H(15A) | 0.9700 | C(17)-C(16)-H(16A) | 108.9 |
| C(15)-H(15B) | 0.9700 | C(15)-C(16)-H(16B) | 108.9 |
| C(16)-C(17) | 1.518(11) | C(17)-C(16)-H(16B) | 108.9 |
| C(16)-H(16A) | 0.9700 | H(16A)-C(16)-H(16B) | 107.7 |
| C(16)-H(16B) | 0.9700 | C(18)-C(17)-C(16) | 114.8(8) |

| | | | |
|---|---|---|---|
| C(17)-C(18) | 1.490(13) | C(18)-C(17)-H(17A) | 108.6 |
| C(17)-H(17A) | 0.9700 | C(16)-C(17)-H(17A) | 108.6 |
| C(17)-H(17B) | 0.9700 | C(18)-C(17)-H(17B) | 108.6 |
| C(18)-C(19) | 1.515(12) | C(16)-C(17)-H(17B) | 108.6 |
| C(18)-H(18A) | 0.9700 | H(17A)-C(17)-H(17B) | 107.5 |
| C(18)-H(18B) | 0.9700 | C(17)-C(18)-C(19) | 114.5(8) |
| C(19)-C(20) | 1.504(13) | C(17)-C(18)-H(18A) | 108.6 |
| C(19)-H(19A) | 0.9700 | C(19)-C(18)-H(18A) | 108.6 |
| C(19)-H(19B) | 0.9700 | C(17)-C(18)-H(18B) | 108.6 |
| C(20)-C(21) | 1.531(13) | C(19)-C(18)-H(18B) | 108.6 |
| C(20)-H(20A) | 0.9700 | H(18A)-C(18)-H(18B) | 107.6 |
| C(20)-H(20B) | 0.9700 | C(20)-C(19)-C(18) | 114.1(9) |
| C(21)-C(22) | 1.505(15) | C(20)-C(19)-H(19A) | 108.7 |
| C(21)-H(21A) | 0.9700 | C(18)-C(19)-H(19A) | 108.7 |
| C(21)-H(21B) | 0.9700 | C(20)-C(19)-H(19B) | 108.7 |
| C(22)-C(23) | 1.495(14) | C(18)-C(19)-H(19B) | 108.7 |
| C(22)-H(22A) | 0.9700 | H(19A)-C(19)-H(19B) | 107.6 |
| C(22)-H(22B) | 0.9700 | C(19)-C(20)-C(21) | 114.7(9) |
| C(23)-H(23A) | 0.9600 | C(19)-C(20)-H(20A) | 108.6 |
| C(23)-H(23B) | 0.9600 | C(21)-C(20)-H(20A) | 108.6 |
| C(23)-H(23C) | 0.9600 | C(19)-C(20)-H(20B) | 108.6 |
| | | C(21)-C(20)-H(20B) | 108.6 |
| C(7)-Au(1)-C(6) | 177.8(3) | H(20A)-C(20)-H(20B) | 107.6 |
| F(1)-C(1)-C(2) | 117.4(7) | C(22)-C(21)-C(20) | 113.6(9) |
| F(1)-C(1)-C(6) | 118.6(7) | C(22)-C(21)-H(21A) | 108.8 |
| C(2)-C(1)-C(6) | 124.0(7) | C(20)-C(21)-H(21A) | 108.8 |
| F(2)-C(2)-C(3) | 119.2(7) | C(22)-C(21)-H(21B) | 108.8 |
| F(2)-C(2)-C(1) | 120.8(7) | C(20)-C(21)-H(21B) | 108.8 |
| C(3)-C(2)-C(1) | 119.8(7) | H(21A)-C(21)-H(21B) | 107.7 |
| F(3)-C(3)-C(2) | 121.1(7) | C(23)-C(22)-C(21) | 113.9(10) |
| F(3)-C(3)-C(4) | 119.0(7) | C(23)-C(22)-H(22A) | 108.8 |
| C(2)-C(3)-C(4) | 119.9(7) | C(21)-C(22)-H(22A) | 108.8 |
| F(4)-C(4)-C(3) | 120.6(7) | C(23)-C(22)-H(22B) | 108.8 |
| F(4)-C(4)-C(5) | 121.3(7) | C(21)-C(22)-H(22B) | 108.8 |
| C(3)-C(4)-C(5) | 118.1(7) | H(22A)-C(22)-H(22B) | 107.7 |
| F(5)-C(5)-C(6) | 119.8(6) | C(22)-C(23)-H(23A) | 109.5 |
| F(5)-C(5)-C(4) | 115.4(6) | C(22)-C(23)-H(23B) | 109.5 |
| C(6)-C(5)-C(4) | 124.7(7) | H(23A)-C(23)-H(23B) | 109.5 |

| | | | |
|---|---|---|---|
| C(5)-C(6)-C(1) | 113.4(6) | C(22)-C(23)-H(23C) | 109.5 |
| C(5)-C(6)-Au(1) | 121.9(5) | H(23A)-C(23)-H(23C) | 109.5 |
| C(1)-C(6)-Au(1) | 124.7(5) | H(23B)-C(23)-H(23C) | 109.5 |
| N(1)-C(7)-Au(1) | 178.0(7) | C(7)-N(1)-C(8) | 178.5(7) |
| C(13)-C(8)-C(9) | 120.7(7) | C(11)-O(1)-C(14) | 118.0(6) |