

## Supporting information

### Luminescent gold(I)-copper(I) cluster with unprecedented carbon-centered trigonal prismatic hexagold

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**Figure S22.** Emission spectrum of **3** in solid state.

## I. Physical measurements

The C, H, N microanalyses were carried out with a Vario EL III elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400  $\text{cm}^{-1}$  with a Nicolet Avatar FT-IR330 spectrometer. UV-Vis spectra were recorded on a Varian Cary5000 UV-VIS-NIR Spectrophotometer. Luminescence and quantum yield using Rhodamine B as standard substance were measured on a Hitachi F-7000 spectrometer.<sup>1</sup> Lifetime was measured on Horiba Jobin Yvon Fluoromax-4P-Tcspc spectrometer. NMR data were recorded on a Bruker Avance II spectrometer (400MHz) and Avance III (500M). Chemical shifts,  $\delta$ , are reported with the external standard 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  NMR. The ESI-MS spectra were recorded on a Bruker Daltonics Esquire-LC ESI ion trap mass spectrometer (Bremen Germany).

### X-ray Crystallography.

Intensity data of compounds **1**·6 $\text{CH}_2\text{Cl}_2$ · $\text{C}_6\text{H}_{14}$ , **2**· $\text{CH}_2\text{Cl}_2$ · $\text{Et}_2\text{O}$  and **3**·6 $\text{CH}_2\text{Cl}_2$  were collected on an Oxford Gemini S Ultra system (Mo  $\text{K}\alpha$ ) at 173K. Absorption corrections were applied by using the program CrysAlis (multi-scan). The structures were solved by direct methods, and non-hydrogen atoms except disordered components were refined anisotropically by least-squares on  $F^2$  using the SHELXTL program. Some of the  $\text{CH}_2\text{Cl}_2$ , n-hexane and  $\text{Et}_2\text{O}$  solvent molecules are disordered. The hydrogen atoms of organic ligands were generated geometrically, while no attempt was made to locate hydrogen atoms of the disordered solvent molecules.

## II. Synthesis

### Materials and Reagents.

All reagents employed were commercially available and used without further purification. The reactions were carried out under dry nitrogen atmosphere using Schlenk techniques. The solvents were purified and distilled by standard procedures prior to use. Triethylamine ( $\text{Et}_3\text{N}$ ) was dried and distilled from  $\text{CaH}_2$ . Trimethylsilyldiazomethane ( $\text{Me}_3\text{SiCHN}_2$ ) was purchased from Alfa Aesar as a 2 M hexane solution, and  $\text{LiBu}^n$  was obtained from Acros. Diphenyl-2-pyridylphosphine (dppy) and 2-chloro-5-methylpyridine were obtained from J&K Chemical.  $\text{Ph}_2\text{PH}$  was purchased from Shanghai Boka-Chem Tech Inc..  $[\text{Cu}(\text{MeCN})_4]\text{BF}_4$ <sup>2</sup> and precursor  $[\text{Au}_6(\text{C})(\text{dppy})_6](\text{BF}_4)_2$ <sup>3</sup> were prepared by literature methods, and  $\text{LAuBF}_4$  was prepared by reacting  $\text{LAuCl}$  with  $\text{AgBF}_4$ .

### Diphenylphosphino-5-methyl-pyridine (L)

This compound was prepared in a synthetic procedure similar to the literature method<sup>4</sup>.  $\text{LiBu}^n$  in hexane (1.6 M, 18 mL) was added dropwise to a solution of  $\text{Ph}_2\text{PH}$  (4.5 mL, 25.3 mmol) in THF (20 mL) at 0 °C. The resulting mixture was added dropwise to a solution of 2-chloro-5-methylpyridine (3.2 mL, 26 mmol) in THF (10 mL) at -78 °C, after the mixture was stirred for 1h then it was allowed to warm slowly to room temperature. The solvents were removed under vacuum and water (50 mL) was added. The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  (3 × 20 mL) and the organic phase was dried with anhydrous  $\text{Na}_2\text{SO}_4$  overnight. Most of the  $\text{CH}_2\text{Cl}_2$  was removed under vacuum and hexane (100 mL) was added to deposit a light yellow solid, which upon recrystallization from  $\text{CH}_2\text{Cl}_2$  / hexane afforded a colorless product. Yield: 5.2 g, 74.3%.

<sup>1</sup>H NMR (500.2 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$ 8.60 (s, 1H, Py),  $\delta$ 8.18 (m, 1H, Py),  $\delta$ 7.86 (m, 4H, Ph),  $\delta$ 7.65 (d, 1H, Py),  $\delta$ 7.52 (t, 2H, Ph),  $\delta$ 7.44 (t, 4H, Ph),  $\delta$ 2.38 (s, 3H,  $\text{CH}_3$ ).  
<sup>31</sup>P {<sup>1</sup>H} NMR (202.5 MHz,  $\text{CDCl}_3$ , ppm): 21.27 (s).

### **[(LAu)<sub>3</sub>O]BF<sub>4</sub>**

This compound was prepared in a modified literature procedure<sup>5</sup>. To a solution of LAuBF<sub>4</sub> (575 mg, 0.33 mmol) in dichloromethane (10 mL), a solution of KOH (65 mg, 1.16 mmol) and NaBF<sub>4</sub> (500 mg, 4.55 mmol) in methanol (120 mL) was added and the mixture was stirred overnight. The solvent was removed under vacuum and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 40 mL). The combined CH<sub>2</sub>Cl<sub>2</sub> extracts were filtered, concentrated and to which excess ethyl ether was added to precipitate a light yellow solid. Yield: 415 mg, 81.6%.

Anal. Calcd for C<sub>54</sub>H<sub>48</sub>BN<sub>3</sub>OF<sub>4</sub>P<sub>3</sub>Au<sub>3</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub>: C, 41.74; H, 3.15; N, 2.68. Found: C, 41.79; H, 3.08; N, 2.53. <sup>1</sup>H NMR (500.2 MHz, CDCl<sub>3</sub>, ppm): δ8.52 (s, 3H, Py), δ7.72-7.30 (m, 30+6H, Ph+Py), δ2.36 (s, 9H, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.5 MHz, CDCl<sub>3</sub>, ppm): 22.43 (s).

### **[CAu<sub>6</sub>Cu<sub>2</sub>(dppy)<sub>6</sub>](BF<sub>4</sub>)<sub>4</sub>·6CH<sub>2</sub>Cl<sub>2</sub>·C<sub>6</sub>H<sub>14</sub> (1·6CH<sub>2</sub>Cl<sub>2</sub>·C<sub>6</sub>H<sub>14</sub>)**

To a solution of [CAu<sub>6</sub>(dppy)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> (68 mg, 0.023 mmol) in dichloromethane (15 mL) were added [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> (15 mg, 0.048 mmol) and the red mixture was stirred for 12h. After filtration, the resulting mixture was evaporated under reduced pressure to obtain a red crude solid. Red prism crystals were obtained from CH<sub>2</sub>Cl<sub>2</sub> / MeOH / n-Hexane (v : v : v = 6 : 1 : 2) in refrigerator at 4°C. Yield: 46 mg (61.3%, based on gold).

Anal. Calcd for C<sub>103</sub>H<sub>84</sub>B<sub>4</sub>N<sub>6</sub>F<sub>16</sub>P<sub>6</sub>Cu<sub>2</sub>Au<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 37.48; H, 2.60; N, 2.52. Found: C, 37.50; H, 2.75; N, 2.47. ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, v:v = 1:5): [Au(dppy)<sub>2</sub>]<sup>+</sup>, m/z (%) = 722.8 (100); [Au(dppy)]<sup>+</sup>, m/z (%) = 459.7 (10). IR (KBr, cm<sup>-1</sup>): ν1082 (br, B-F). <sup>1</sup>H NMR (400.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>OD, ppm): δ7.76-6.86 (m, 6+72+6H, Py+Ph). <sup>31</sup>P{<sup>1</sup>H} NMR (162MHz, CD<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>OD, ppm): 30.23 (s). Lifetime: In CH<sub>2</sub>Cl<sub>2</sub> solution: τ = 2.1 ± 0.2μs; in solid-state: τ = 12.3 ± 0.3μs. Φ(CH<sub>2</sub>Cl<sub>2</sub>) = 4.3%.

### **[CAu<sub>6</sub>L<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>·Et<sub>2</sub>O (2·CH<sub>2</sub>Cl<sub>2</sub>·Et<sub>2</sub>O)**

This compound was prepared in a synthetic procedure similar to the literature method<sup>2</sup>. To a solution of [(LAu)<sub>3</sub>O]BF<sub>4</sub> (242 mg, 0.16 mmol) in dichloromethane (3

mL) were added Et<sub>3</sub>N (0.02 mL, 0.16 mmol) and a 2 M hexane solution of Me<sub>3</sub>SiCHN<sub>2</sub> (0.08 mL, 0.16 mmol). The resulting mixture was stirred for 3h. After filtration, a layer of Et<sub>2</sub>O (5 mL) was then allowed to diffuse into the filtrate, which gave the product as colorless block-like crystals after several days. Yield: 185 mg (76.3%, based on gold).

Anal. Calcd for C<sub>109</sub>H<sub>96</sub>B<sub>2</sub>N<sub>6</sub>F<sub>8</sub>P<sub>6</sub>Au<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 42.40; H, 3.17; N, 2.70. Found: C, 42.21; H, 3.10; N, 2.59. <sup>1</sup>H NMR (400.1MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ8.16 (s, 6H, py), 7.66-7.50 (m, 24+6H, Ph+py), 7.32 (t, 12H, Ph), 7.01 (m, 24H, Ph), 6.96 (d, 6H, py), 2.13 (s, 18H, CH<sub>3</sub>). <sup>31</sup>P NMR (162MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): 25.39 (s).

#### [CAu<sub>6</sub>Cu<sub>2</sub>L<sub>6</sub>](BF<sub>4</sub>)<sub>4</sub>·6CH<sub>2</sub>Cl<sub>2</sub> (3·6CH<sub>2</sub>Cl<sub>2</sub>)

To a solution of [Au<sub>6</sub>(C)L<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> (140 mg, 0.046 mmol) in dichloromethane (15 mL) were added [Cu(MeCN)<sub>4</sub>]BF<sub>4</sub> (36 mg, 0.114 mmol) and the mixture was stirred for 4h. When the reaction was complete (monitored by <sup>31</sup>P-NMR), the solution was filtered, and the filtrate was precipitated with Et<sub>2</sub>O to afford a red crude solid. Orange octahedral crystals were obtained from CH<sub>2</sub>Cl<sub>2</sub> / MeOH / n-Hexane (v : v : v = 24 : 1 : 6) in refrigerator at 4°C after one week. Yield: 85 mg (55.6%, based on gold).

Anal. Calcd for C<sub>109</sub>H<sub>96</sub>B<sub>4</sub>N<sub>6</sub>F<sub>16</sub>P<sub>6</sub>Cu<sub>2</sub>Au<sub>6</sub>·3CH<sub>2</sub>Cl<sub>2</sub>: C, 37.50; H, 2.86; N, 2.34. Found: C, 37.69; H, 2.50; N, 2.40. IR (KBr, cm<sup>-1</sup>): ν1085 (br, B-F). <sup>1</sup>H NMR (500.2MHz, CDCl<sub>3</sub> / CD<sub>3</sub>OD, ppm): δ7.50 (d, 6H, Py); δ7.46-7.28 (m, 30+6H, Ph+Py); δ7.24-7.10 (m, 30+6H, Ph+Py); δ1.78 (s, 18H, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202.5MHz, CDCl<sub>3</sub> / CD<sub>3</sub>OD, ppm): 29.2 (s). Lifetime: In CH<sub>2</sub>Cl<sub>2</sub>: τ = 7.76 ± 0.16μs; in solid-state: τ = 25.52 ± 1.06μs. Φ(CH<sub>2</sub>Cl<sub>2</sub>) = 2.2%.

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- (1) Parker, C. A.; Rees, W. T. *Analyst* **1960**, *85*, 587-600.
- (2) Ho, D. M.; Bau, R. *Inorg. Chem.* **1983**, *22*, 4079-4083.
- (3) Jia, J.-H.; Wang, Q.-M. *J. Am. Chem. Soc.* **2009**, *131*, 16634-16635.
- (4) Kuang, S.-M.; Zhang, Z.-Z.; Wang, Q.-G.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1998**, 2927-2929.
- (5) Yang, Y.; Ramamoorthy, V.; Sharp, P. R. *Inorg. Chem.* **1993**, *32*, 1946-1950.

### III. Characterization

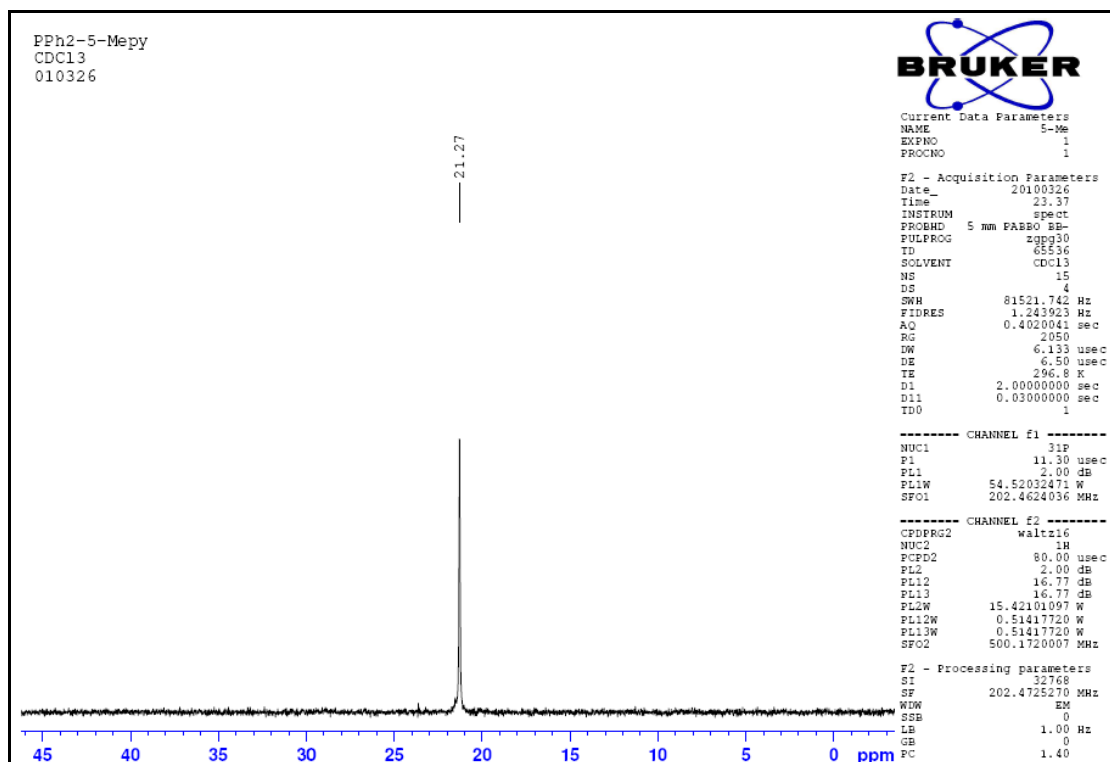


Figure S1.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of L in  $\text{CDCl}_3$ .

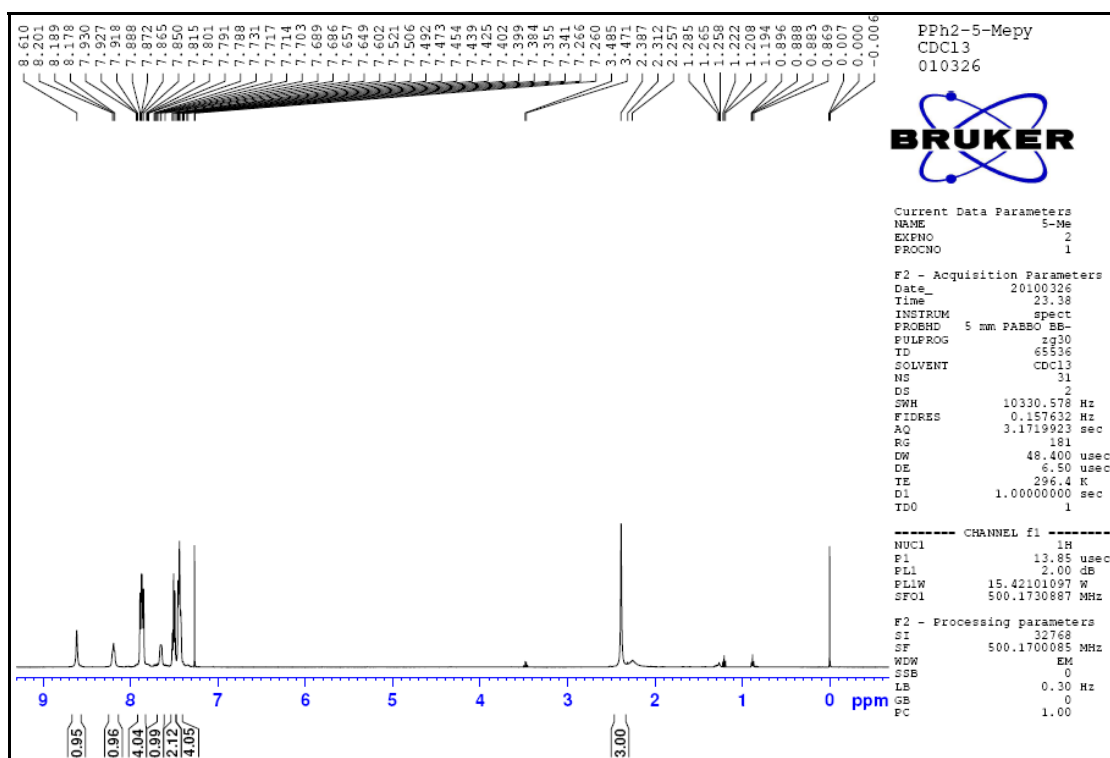


Figure S2.  $^1\text{H}$  NMR spectrum of L in  $\text{CDCl}_3$ .

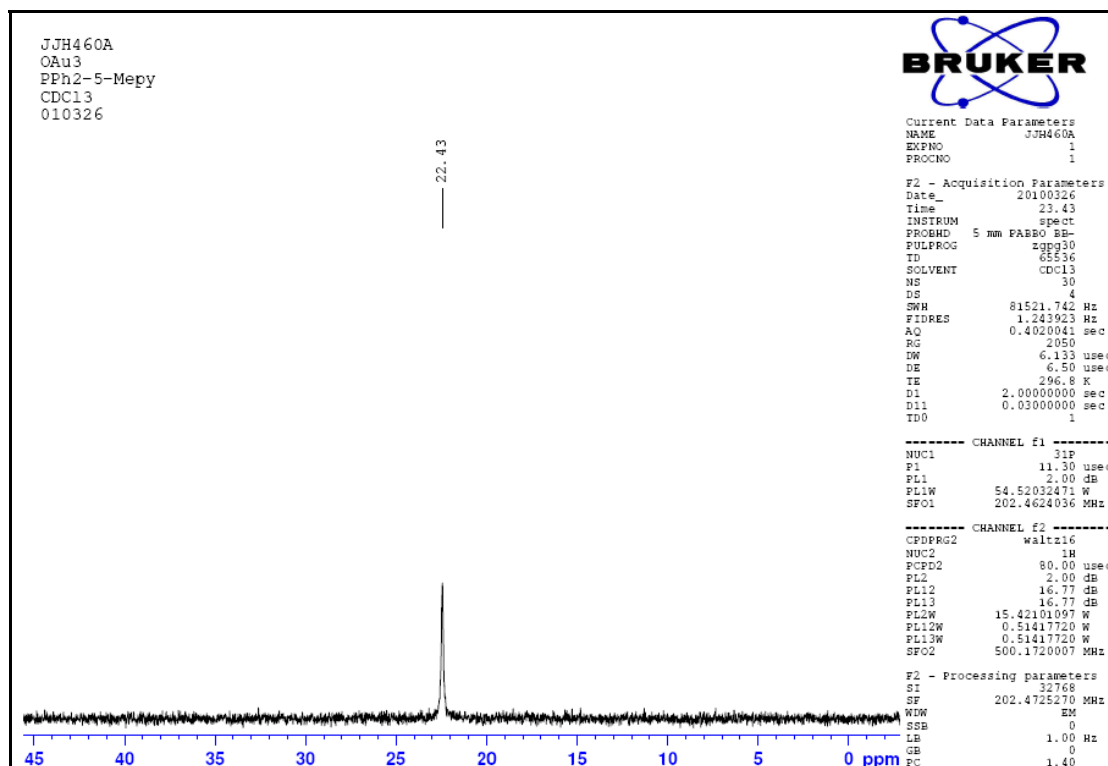


Figure S3.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[(\text{LAu})_3\text{O}]\text{BF}_4$  in  $\text{CDCl}_3$ .

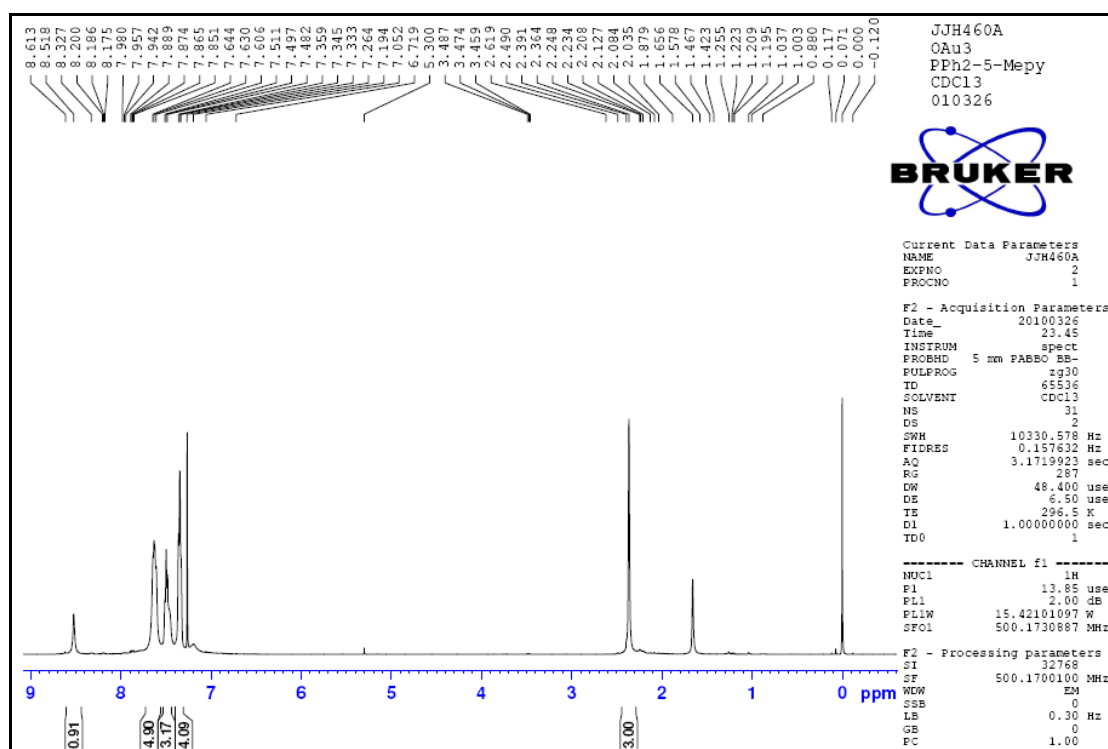
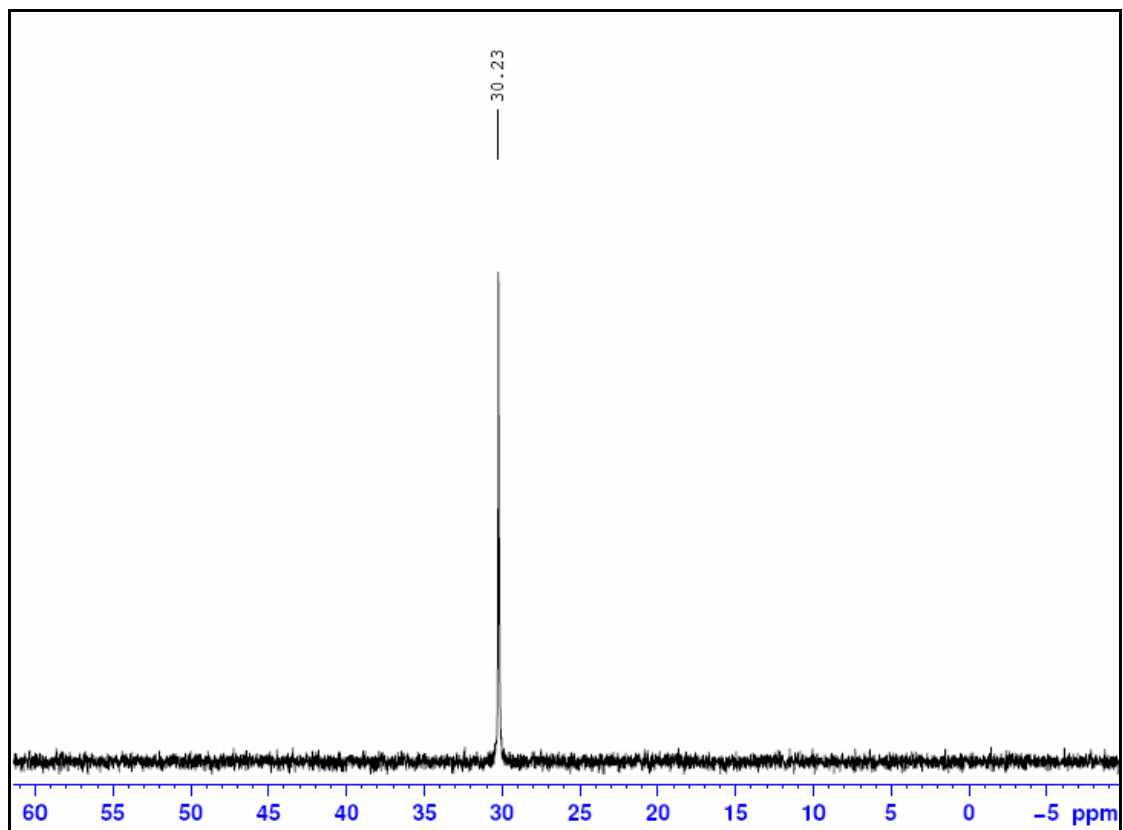
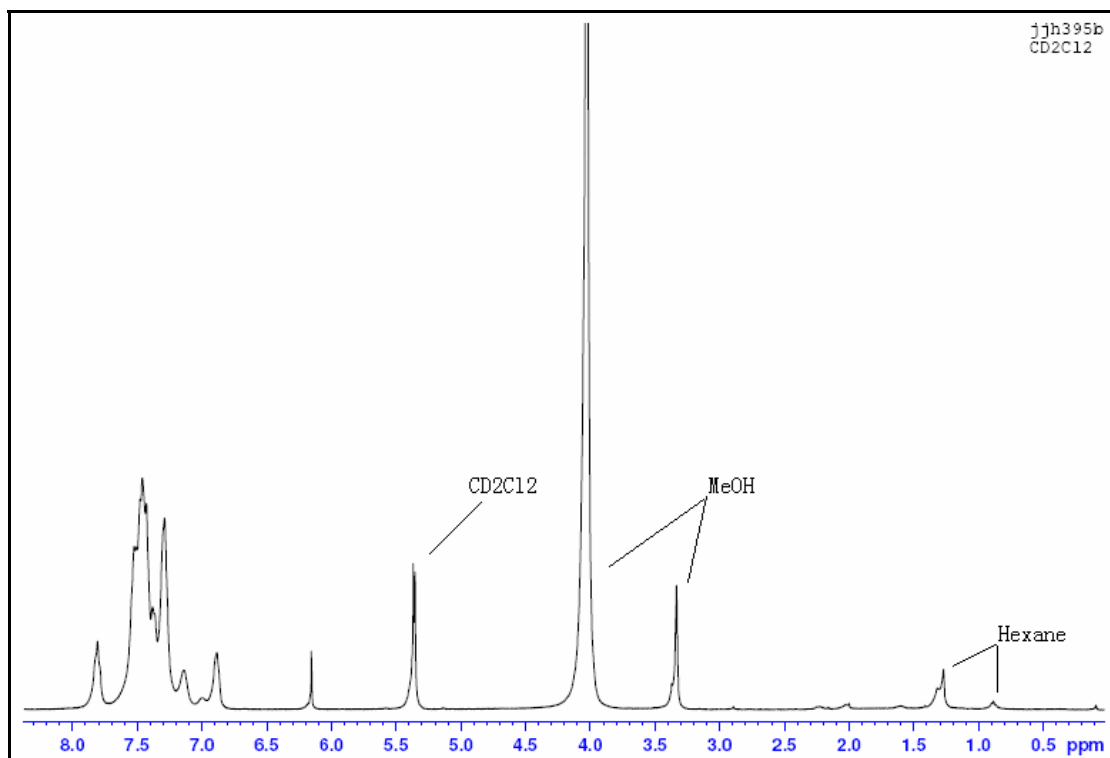


Figure S4.  $^1\text{H}$  NMR spectrum of  $[(\text{LAu})_3\text{O}]\text{BF}_4$  in  $\text{CDCl}_3$ .

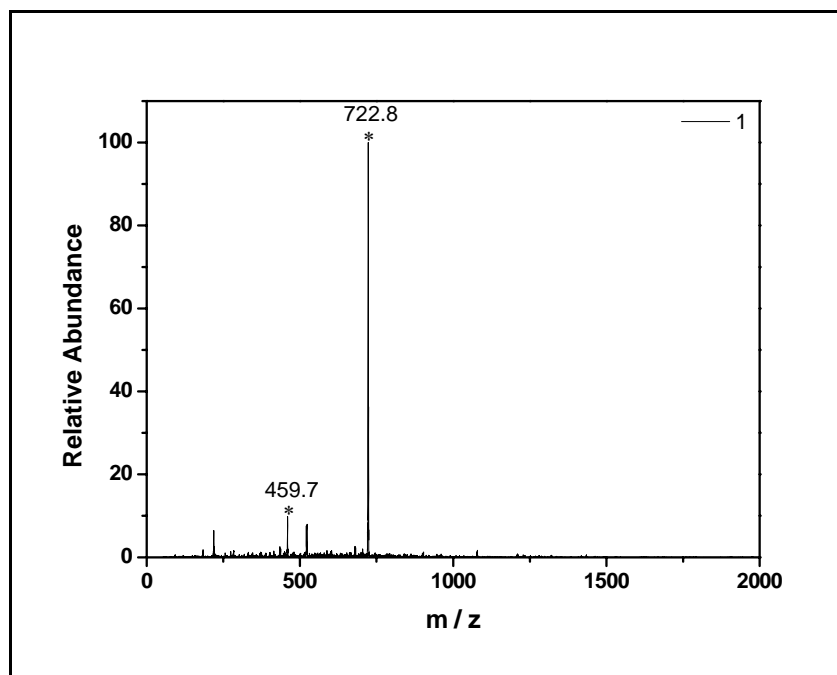




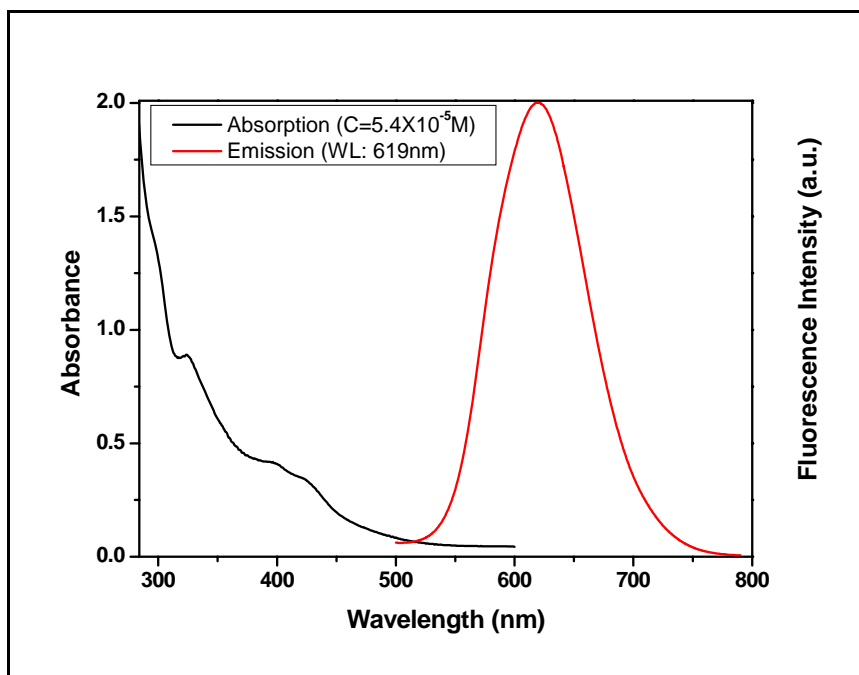
**Figure S5.**  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{OD}$  (v/v = 5:1).



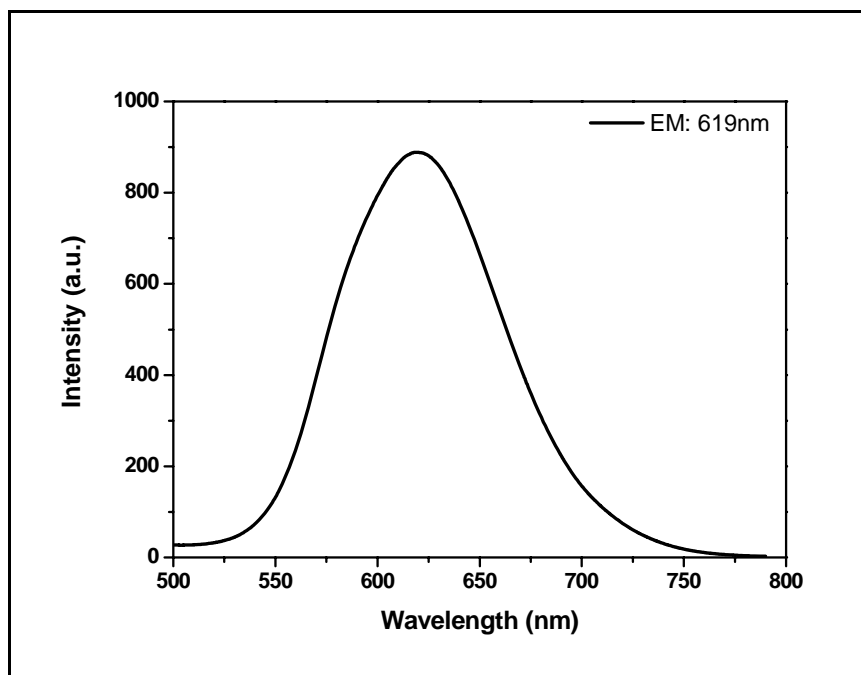
**Figure S6.**  $^1\text{H}$  NMR spectrum of **1** in  $\text{CD}_2\text{Cl}_2:\text{CD}_3\text{OD}$  (v/v = 5:1).



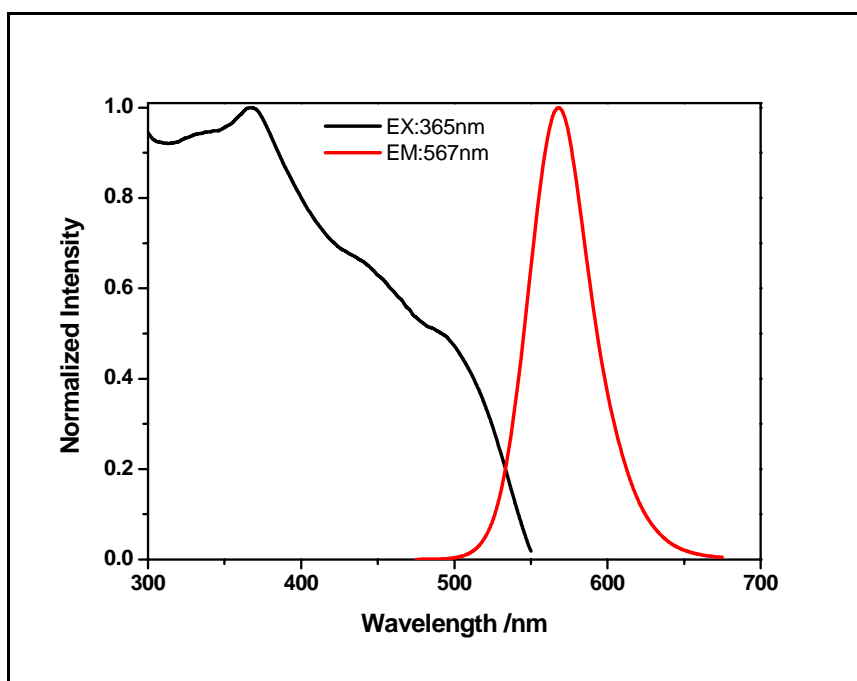
**Figure S7.** ESI-MS spectrum of **1** in CH<sub>2</sub>Cl<sub>2</sub>:MeOH (v/v = 1:5).



**Figure S8.** Absorption ( $C=5.4 \times 10^{-5} M$ ) and emission spectra of **1** in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S9.** Emission spectrum of **1** in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S10.** Excitation and emission spectra of **1** in solid state.

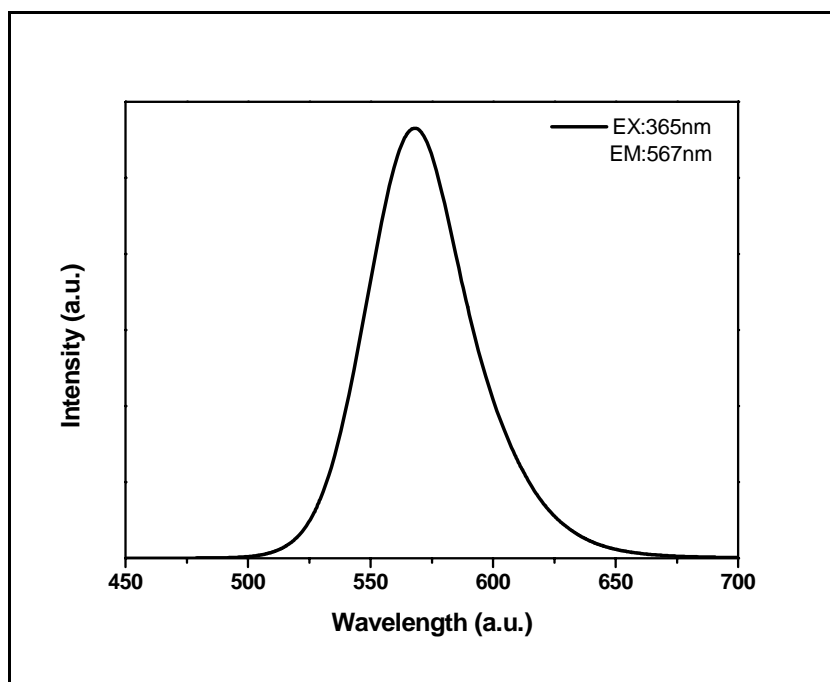


Figure S11. Emission spectrum of **1** in solid state.

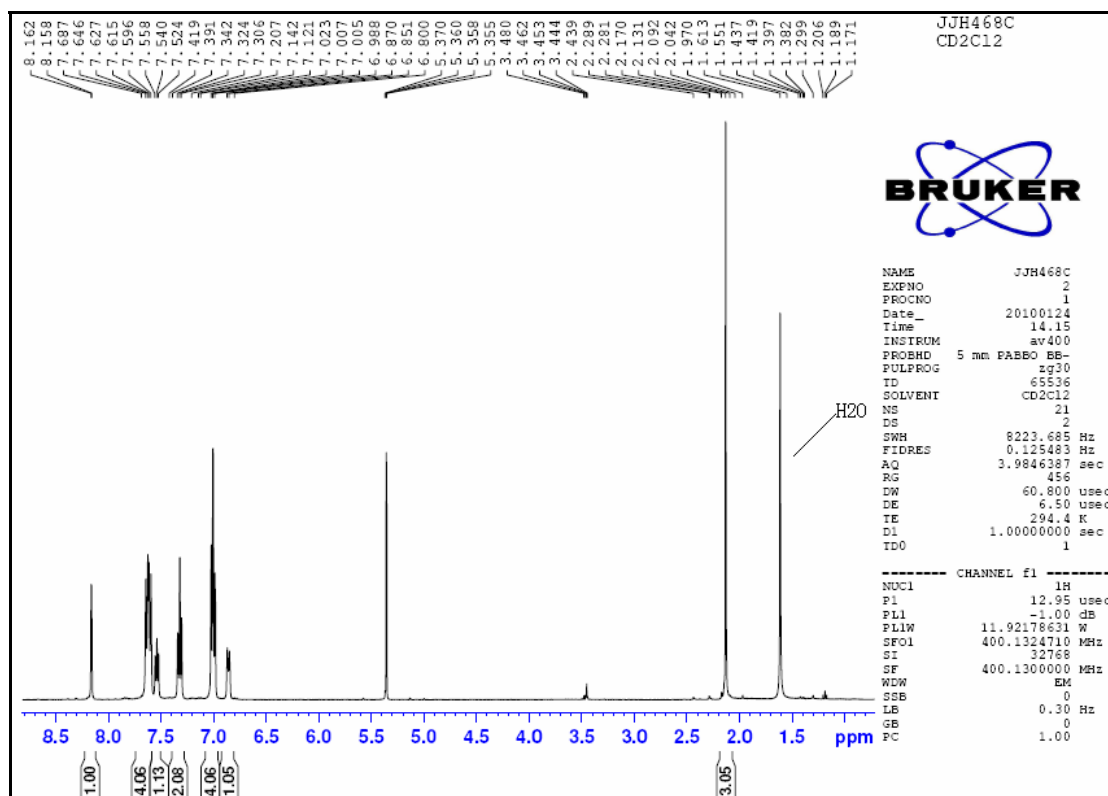


Figure S12.  $^1\text{H}$  NMR spectrum of **2** in  $\text{CD}_2\text{Cl}_2$ .

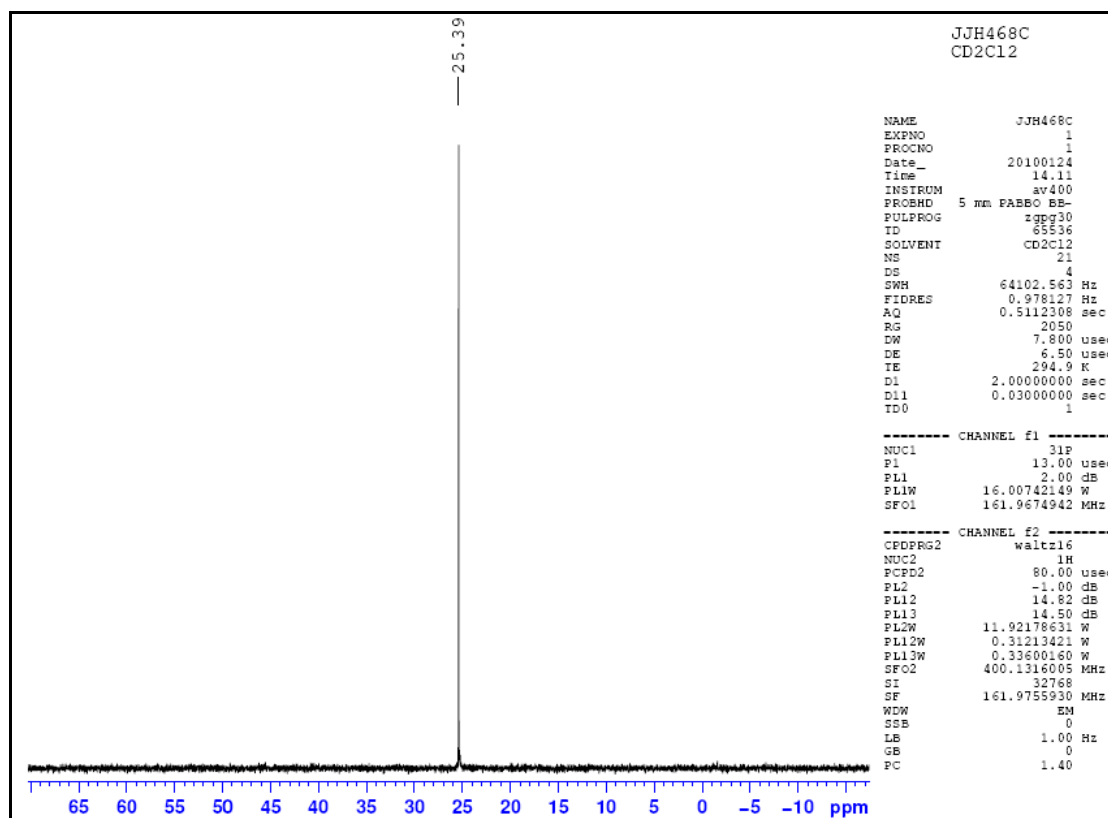


Figure S13.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{CD}_2\text{Cl}_2$ .

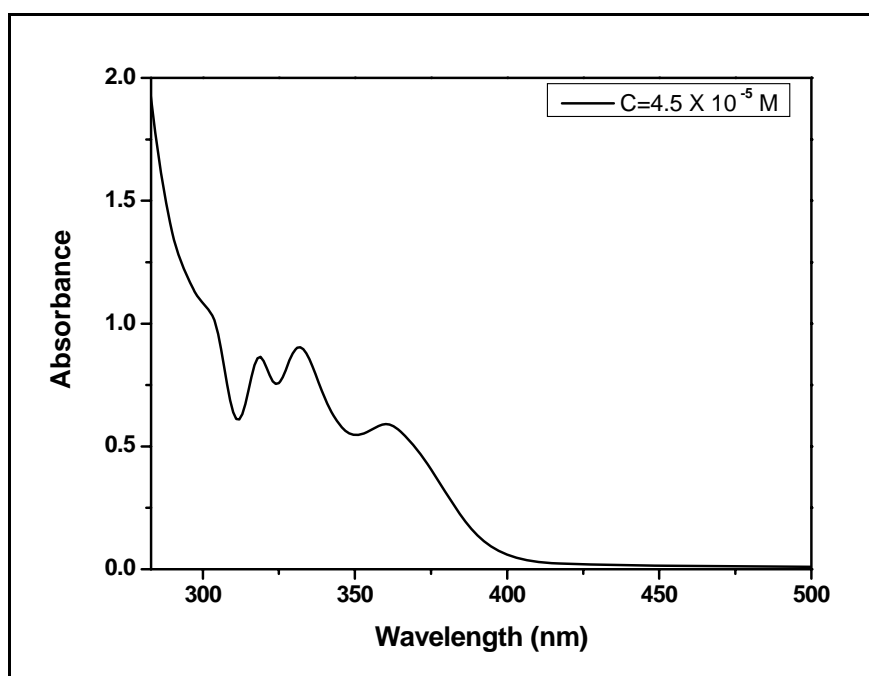
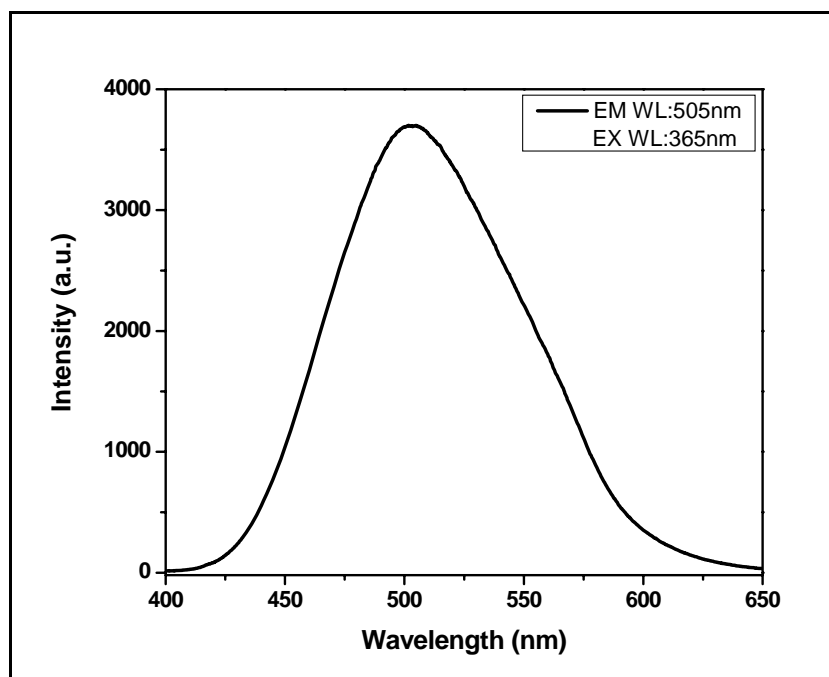
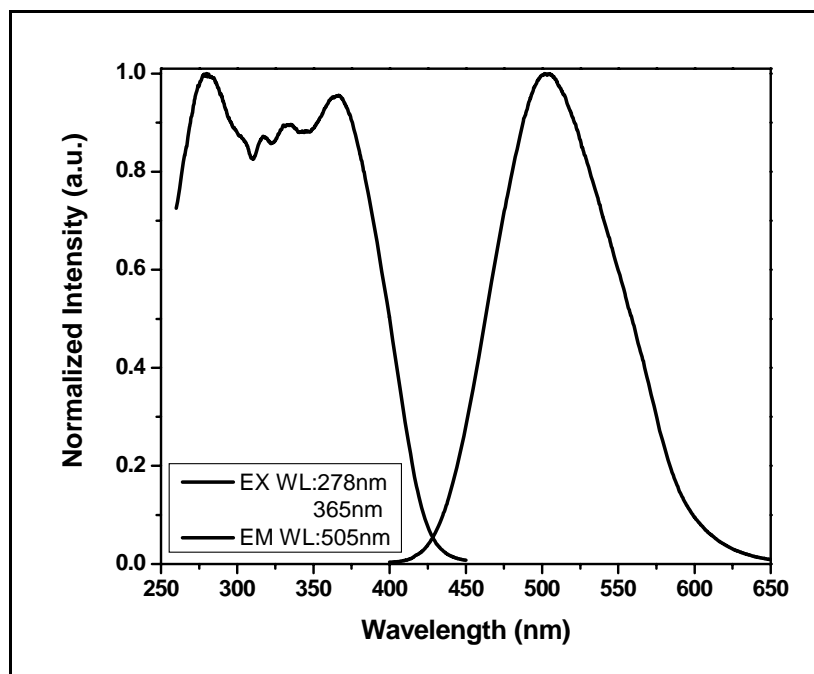


Figure S14. Absorption ( $C=4.5 \times 10^{-5}\text{M}$ ) spectrum of **2** in  $\text{CH}_2\text{Cl}_2$ .



**Figure S15.** Emission spectrum of **2** in solid state.



**Figure S16.** Excitation and emission spectra of **2** in solid state.

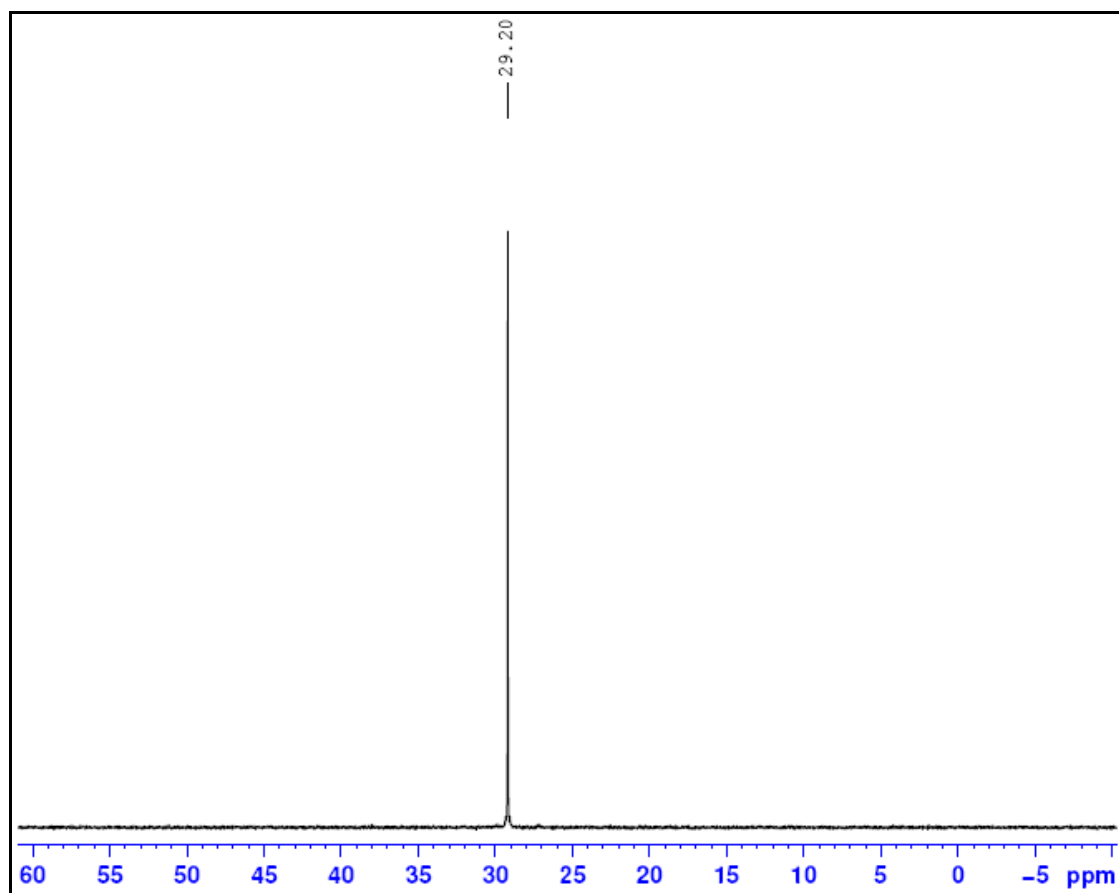


Figure S17. <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **3** in CDCl<sub>3</sub>: CD<sub>3</sub>OD(v/v = 50/4).

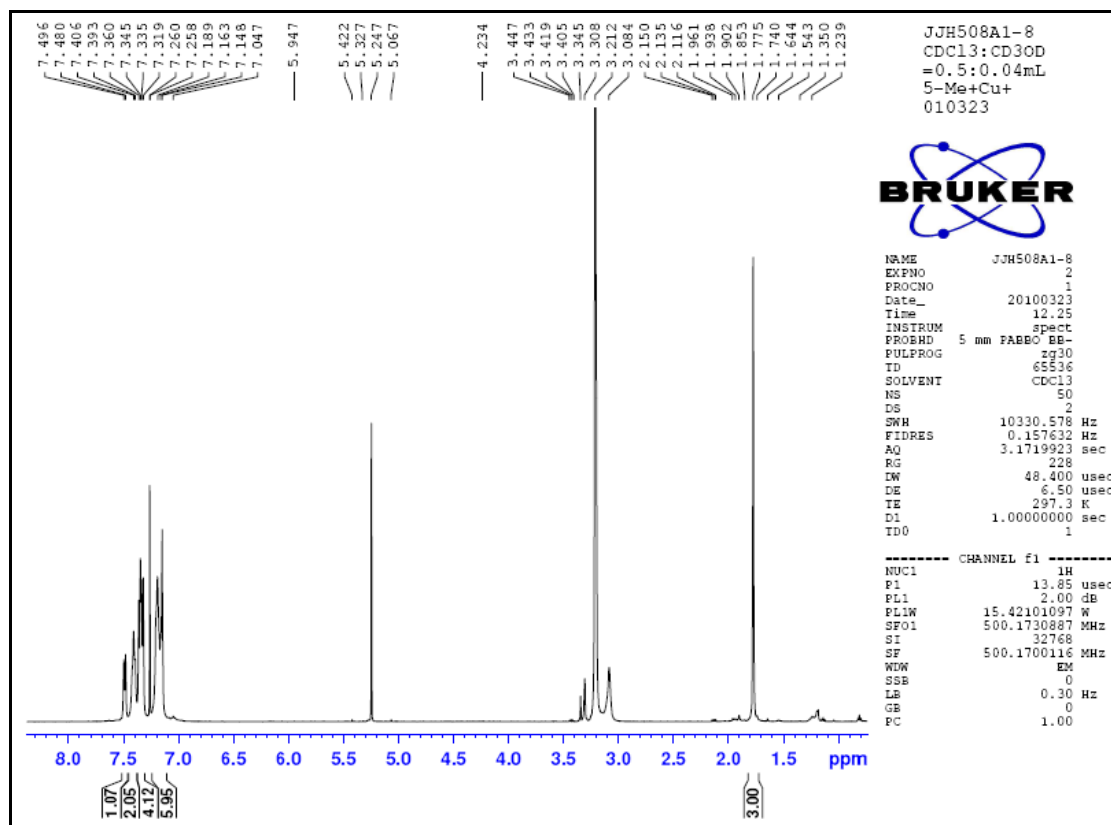
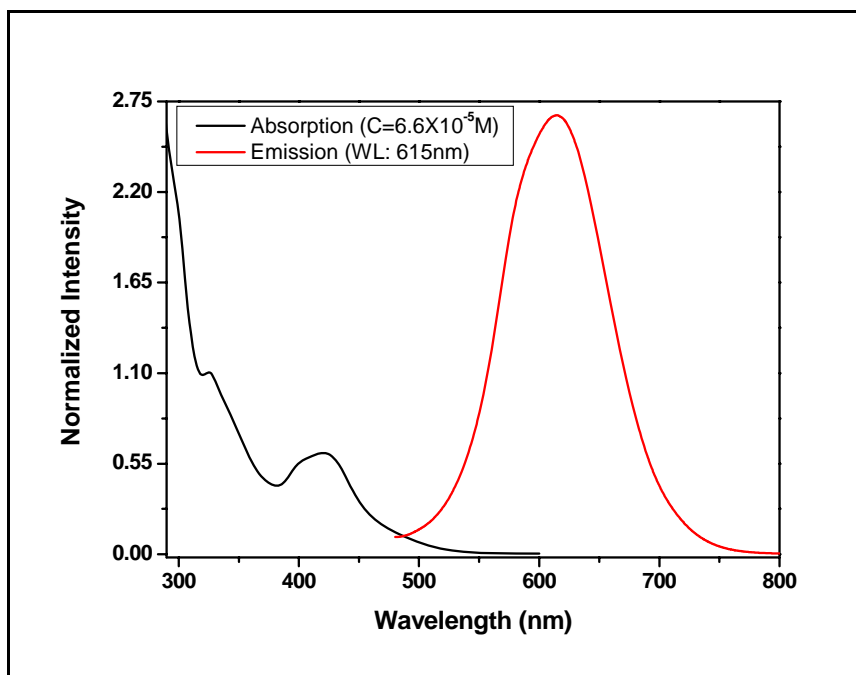
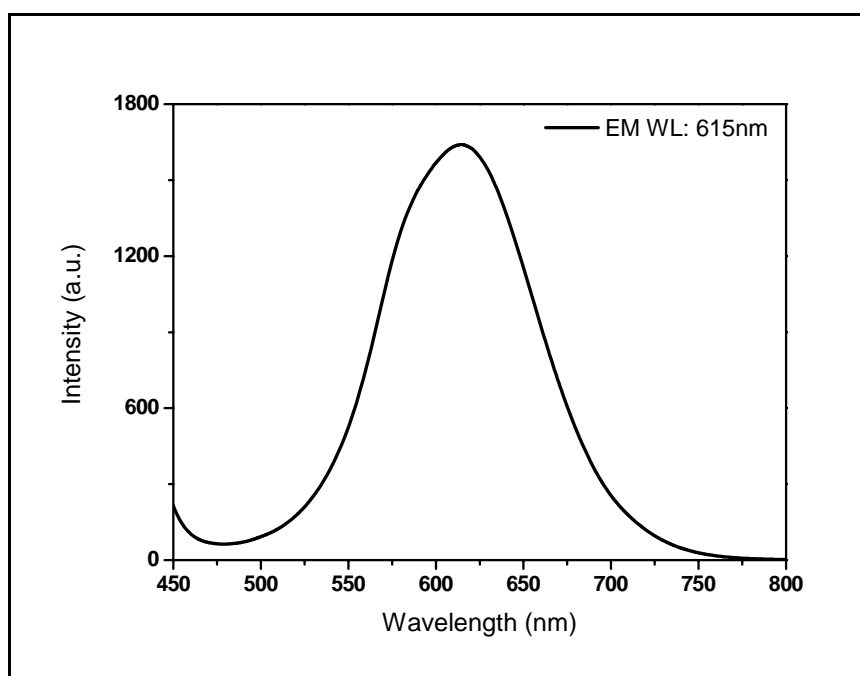


Figure S18. <sup>1</sup>H NMR spectrum of **3** in CDCl<sub>3</sub>: CD<sub>3</sub>OD(v/v = 50/4).

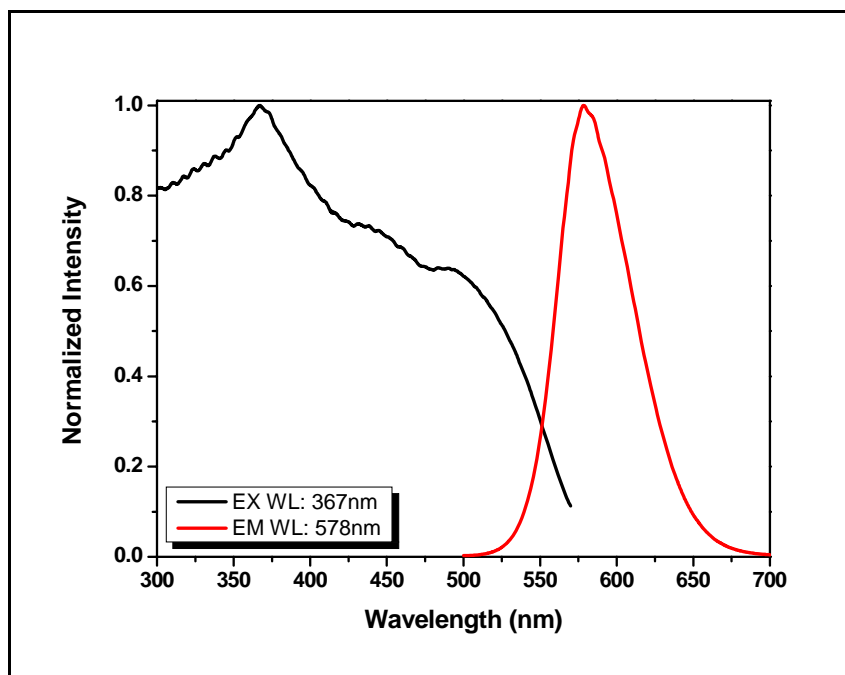


**Figure S19.** Absorption ( $C=6.6 \times 10^{-5} \text{M}$ ) and emission spectra of **3** in  $\text{CH}_2\text{Cl}_2$ .

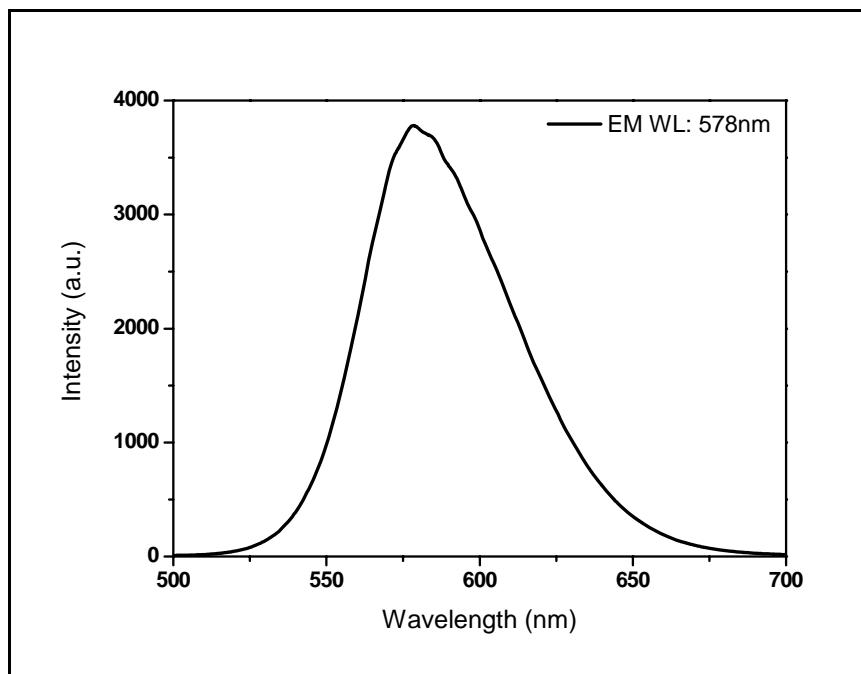


**Figure S20.** Emission spectrum of **3** in  $\text{CH}_2\text{Cl}_2$ .





**Figure S21.** Excitation and emission spectra of **3** in solid state.



**Figure S22.** Emission spectrum of **3** in solid state.