Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Luminescence on-Off switching via reversible interconversion between inter- and intramolecular aurophilic interactions

Semi Han,[a] Yu Young Yoon,[a] Ok-Sang Jung[b] and Young-A Lee*[a]

[a] *Department of Chemistry and Research Institute of Physics and Chemistry, Chonbuk National University, Jeonju 561-756, Korea. Fax: +82 63 270 3408; Tel: +82 63 270 3347; E-mail: ylee@jbnu.ac.kr*

[b] *Department of Chemistry, Pusan National University, Pusan 609-735, Korea.*

S1. Experimental details of **1a** and **1b**

S2. TGA/DSC overlay of **1a** and **1b**

S3. FT-IR spectra of **1a** and **1b** in KBr

S4. ^{1}H NMR spectrum of **1a** and **1b** in $CDCl_3/CD_3OD$

S5. ^{13}C NMR spectrum of **1a** and **1b** in $CDCl_3/CD_3OD$

S6. ^{31}P NMR spectrum of **1a** and **1b** in $CDCl_3/CD_3OD$

S7. ^{19}F NMR spectrum of **1a** in $CDCl_3/CD_3OD$

S8. Emission spectra of **1a** and **1b** in solid state at RT

S9. Emission spectra of **1a** and **1b** in solid state at 77 K

S10. Time-dependent emission spectra of **1a** in CF_3CO_2H and NEt_3 chamber at RT

S11. Time-dependent emission spectra of **1a** in HCl and NEt_3 chamber at RT

S1. Experimental details of 1a and 1b

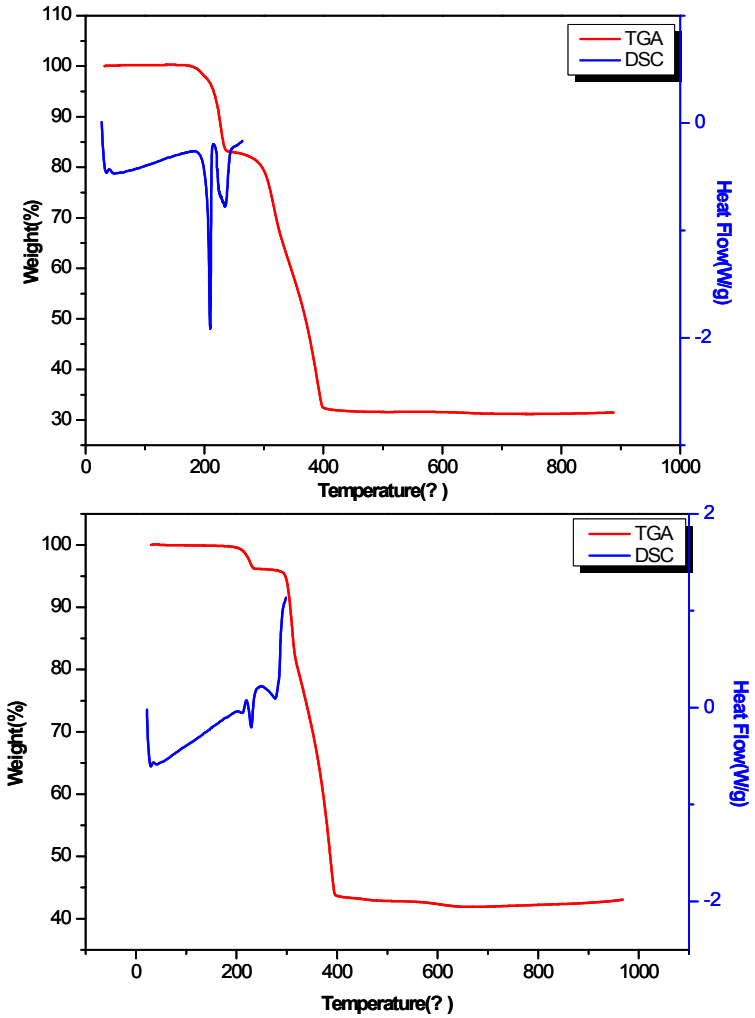
Materials and Instrumentation: $Au_2(dppp)Cl_2$ were prepared according to the literature procedure. 2-benzimidazolethiol (BIT) was purchased from Aldrich and was used without further purification. Elemental analyses were performed on crystalline samples by using a Vario-EL analyzer at Center for University-Wide Research Facilities, CBNU. Infrared spectra were obtained with a Thermo Nicolet AVATAR 330 FT-IR spectrophotometer as KBr pellets. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a JEOL JNM AL-400 instrument relative to $SiMe_4$. ^{19}F NMR (376 MHz) and ^{31}P NMR (162 MHz) spectra were reported relative to external CF_3CO_2H (100%) and H_3PO_4 (85%), respectively, with a JEOL JNM AL-400 spectrometer. Emission spectra were obtained using a JASCO FP-6500 spectrofluorometer corrected for instrument response with monochromators positioned with a 2 nm band-pass. Solid-state emission samples were prepared as a 10% (w/w) mixture of the complex in a matrix of finely ground KBr. The melting points were determined with a SRS EZ-Melt MPA-120 melting point apparatus and were uncorrected. Thermal analyses were carried out under a dinitrogen atmosphere at a scan rate of 10 °C/min using a TA Instruments SDT Q20 and DSC Q20.

$Au_2(dppp)(BIT)_2{\cdot}2CF_3CO_2H$ (1a): To a solution of $Au_2(dppp)Cl_2$ (310 mg, 0.35 mmol) in CH_2Cl_2 (15 mL) was added $AgCF_3CO_2$ (156 mg, 0.71 mmol), and the reaction mixture was stirred at RT for 30 min. The suspension was filtered through a pad of celite to remove the AgCl precipitate, and into a suspension of 2-benzimidazolethiol (BIT) (106 mg, 0.71 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred 2 h at RT. The resulting solution was concentrated to 5 mL, and the addition of Et_2O (75 mL) gave an off-white precipitate. The precipitate was collected by filtration and washed with Et_2O. Recrystallization by slow diffusion of Et_2O into a CH_2Cl_2 solution gave a white colored product. Yield 76%. Mp 197.6 °C. Anal. Calcd for $C_{41}H_{36}N_4P_2S_2Au_2{\cdot}2CF_3CO_2H$: C, 40.55; H, 2.87; N, 4.20; S, 4.81. Found: C, 40.91; H, 3.03; N, 4.56; S, 5.88. IR (KBr): ν = 1201(s), 1460(m), 1661(s) cm^{-1} (C=O). ^1H NMR (400 MHz, $CDCl_3/CD_3OD$, 25 °C, TMS): δ = 7.57 (dd, *J*=12.7, 6.8 Hz, 8H), 7.38 (d, *J*=5.9 Hz, 12H), 7.13 (dd, *J*=6.1, 3.2 Hz, 4H), 6.95 (dd, *J*=6.1, 3.2 Hz, 4H), 2.79 (br, 4H), 2.08 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3/CD_3OD$, 25 °C, TMS): δ = 20.4, 27.2, 27.6, 111.5, 115.1, 118.1, 123.8, 127.7, 128.2, 129.0, 129.1, 131.8, 131.9, 132.7, 132.8, 156.5,

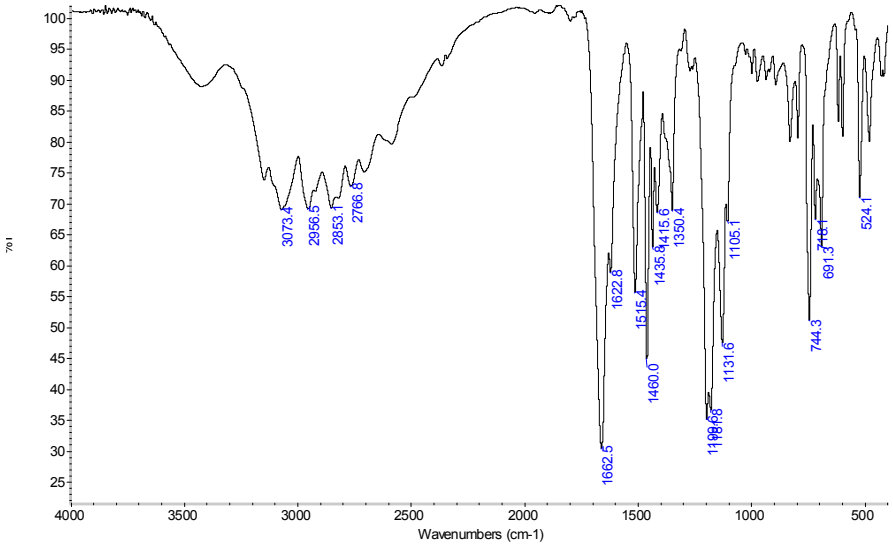
161.1, 161.5, 161.8. ^{19}F NMR (376 MHz, $CDCl_3/CD_3OD$, 25 °C, CF_3CO_2H): δ = -75.5. ^{31}P NMR (162 MHz, $CDCl_3/CD_3OD$, 25 °C, PCl_3): δ = 32.3.

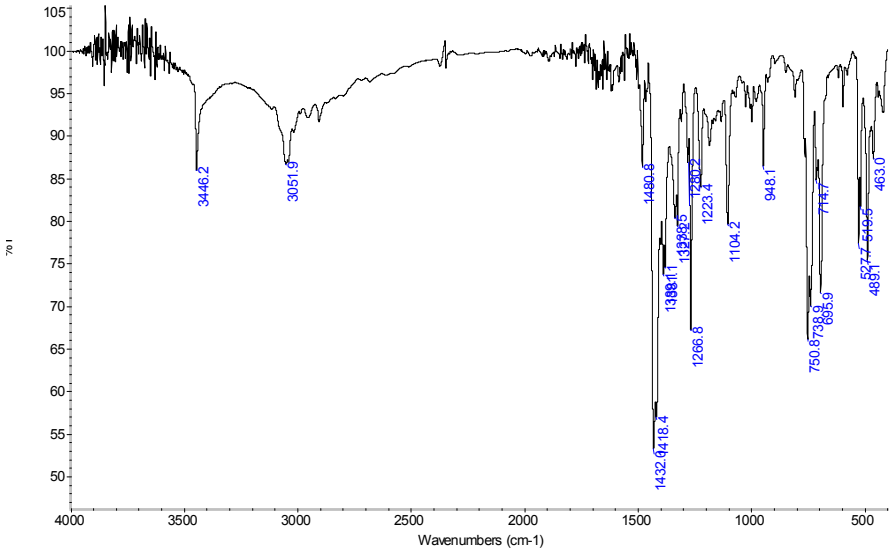
$Au_2(dppp)(BIT)_2\cdot 2.5CH_3OH\cdot 0.5H_2O$ (1b): Method A This compound was prepared by the similar method as for **1a**, except for using basic reaction condition. To a solution of $[Au_2(dppp)(CF_3CO_2)_2]$ in CH_2Cl_2 was added excess K_2CO_3 and two equivalent BIT at once, and the resulting suspensions were then stirred 12 h at RT. After excess K_2CO_3 and other precipitate were filtered off, the filtrate was evaporated to dryness. The crude white solid was recrystallized from a solvent pair of CH_2Cl_2 and hexane (10:1) to obtain colorless crystals. Yield 88%. **Method B** To a solution of $[Au_2(dppp)(CF_3CO_2)_2]$ in CH_2Cl_2 was added two equivalent $K(BIT)\cdot H_2O$ in methanol, and the resulting solution was then stirred 2 h at RT. After KCF_3CO_2 was filtered off, the filtrate was evaporated to dryness. The crude white solid was recrystallized from a solvent pair of CH_2Cl_2 and hexane to obtain colorless crystals. Yield 85%. Mp 280.7 °C. Anal. Calcd for $C_{41}H_{36}N_4P_2S_2Au_2\cdot 2.5CH_3OH\cdot 0.5H_2O$: C, 43.76; H, 3.97; N, 4.69; S, 5.37. Found: C, 44.18; H, 3.44; N, 5.04; S, 6.27. IR (KBr): ν = 1431 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$, 25 °C, TMS): δ = 7.32 (t, J=10.2 Hz, 9H), 7.14 (d, J=7.3 Hz, 5H), 7.09 (d, J=7.3 Hz, 9H), 7.01 (s, 4H), 6.78 (s, 4H), 2.53 (br, 4H), 1.80 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3/CD_3OD$, 25 °C, TMS): δ = 121.3, 128.4, 129.0, 129.2, 131.7, 132.8, 132.9. ^{31}P NMR (162 MHz, $CDCl_3/CD_3OD$, 25 °C, PCl_3): δ = 33.6.

S2. TGA/DSC overlay of 1a (top) and 1b (down)

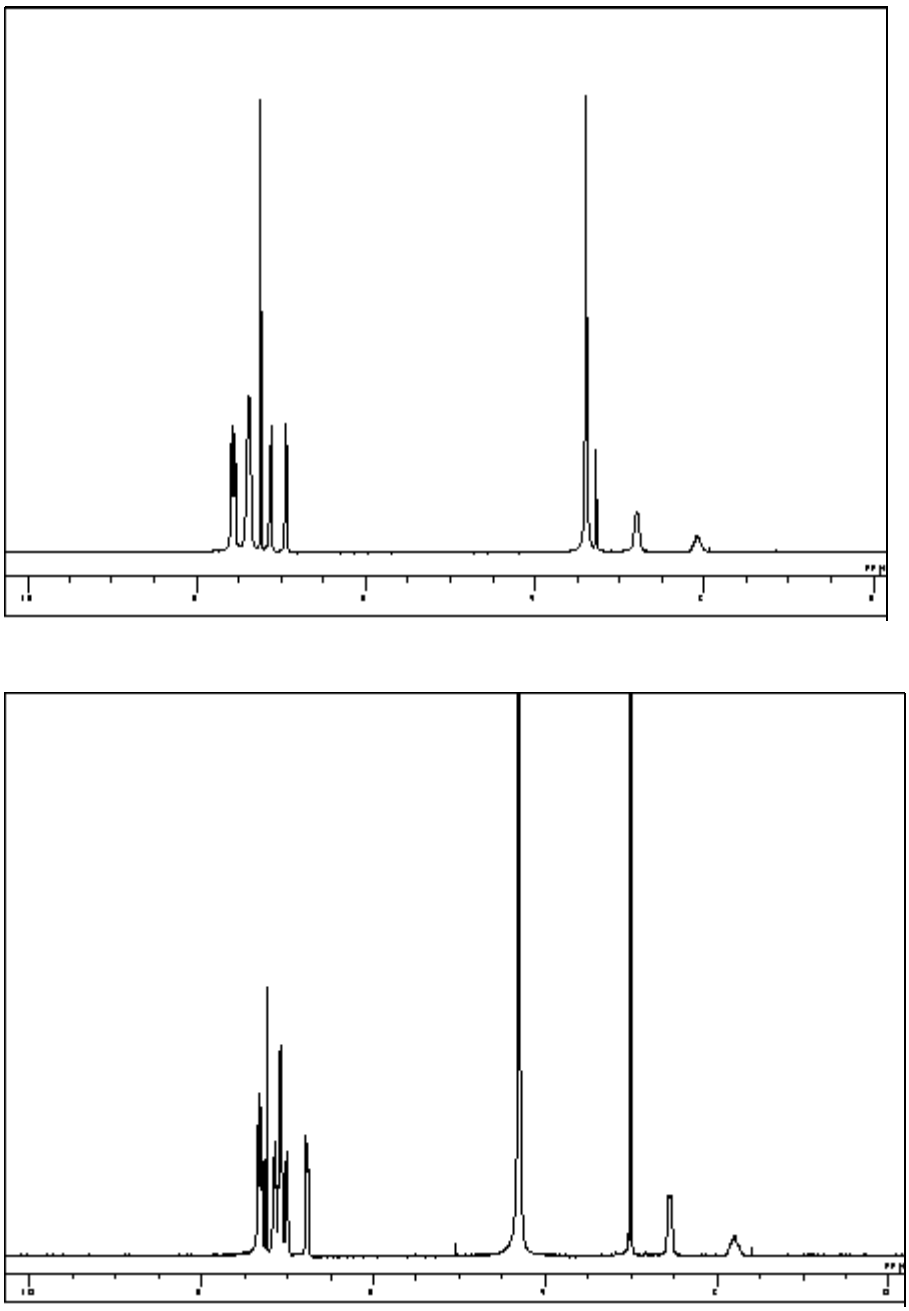


S3. FT-IR spectra of 1a (top) and 1b (down) in KBr

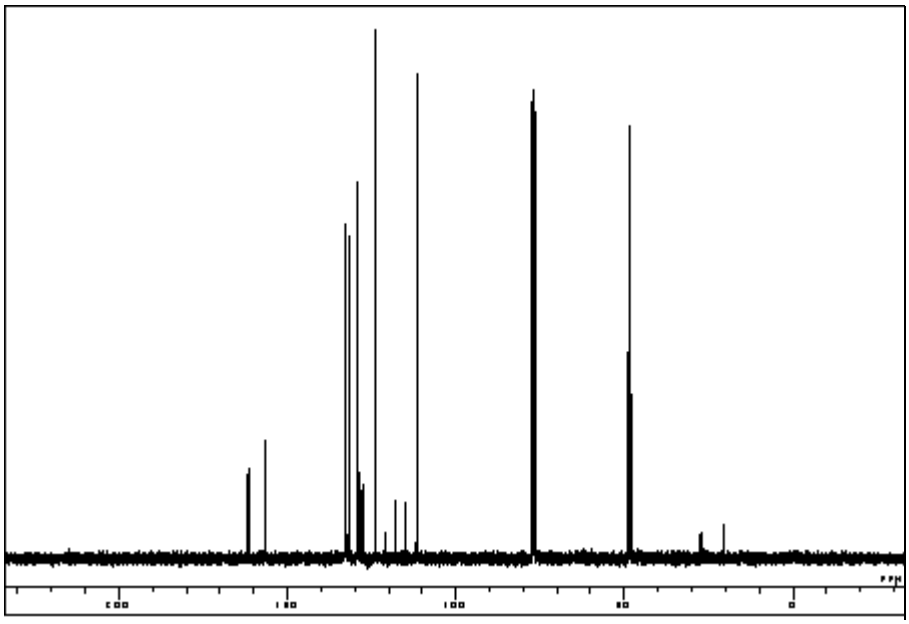


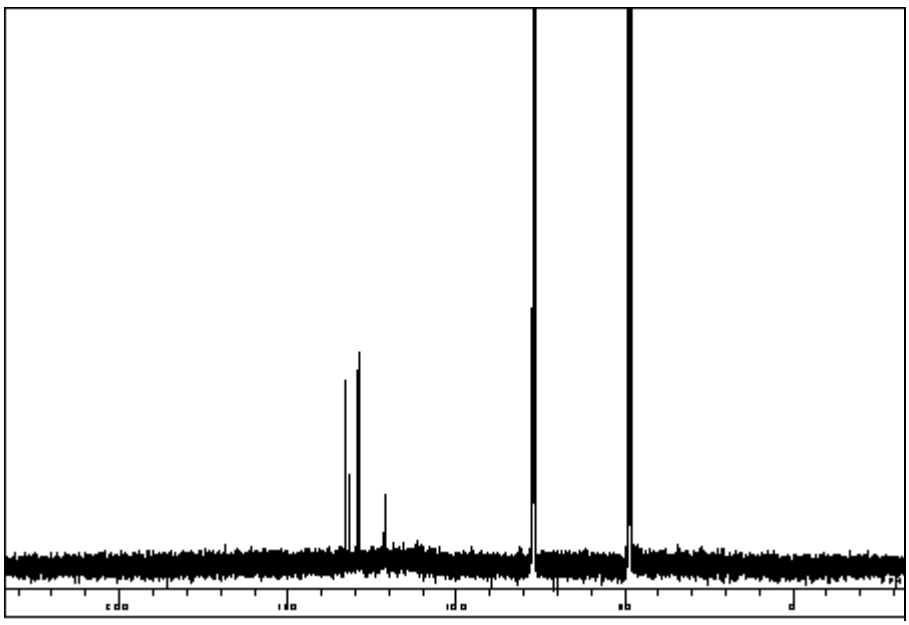


S4. ^{1}H NMR spectrum of 1a (top) and 1b (down) in $CDCl_3/CD_3OD$

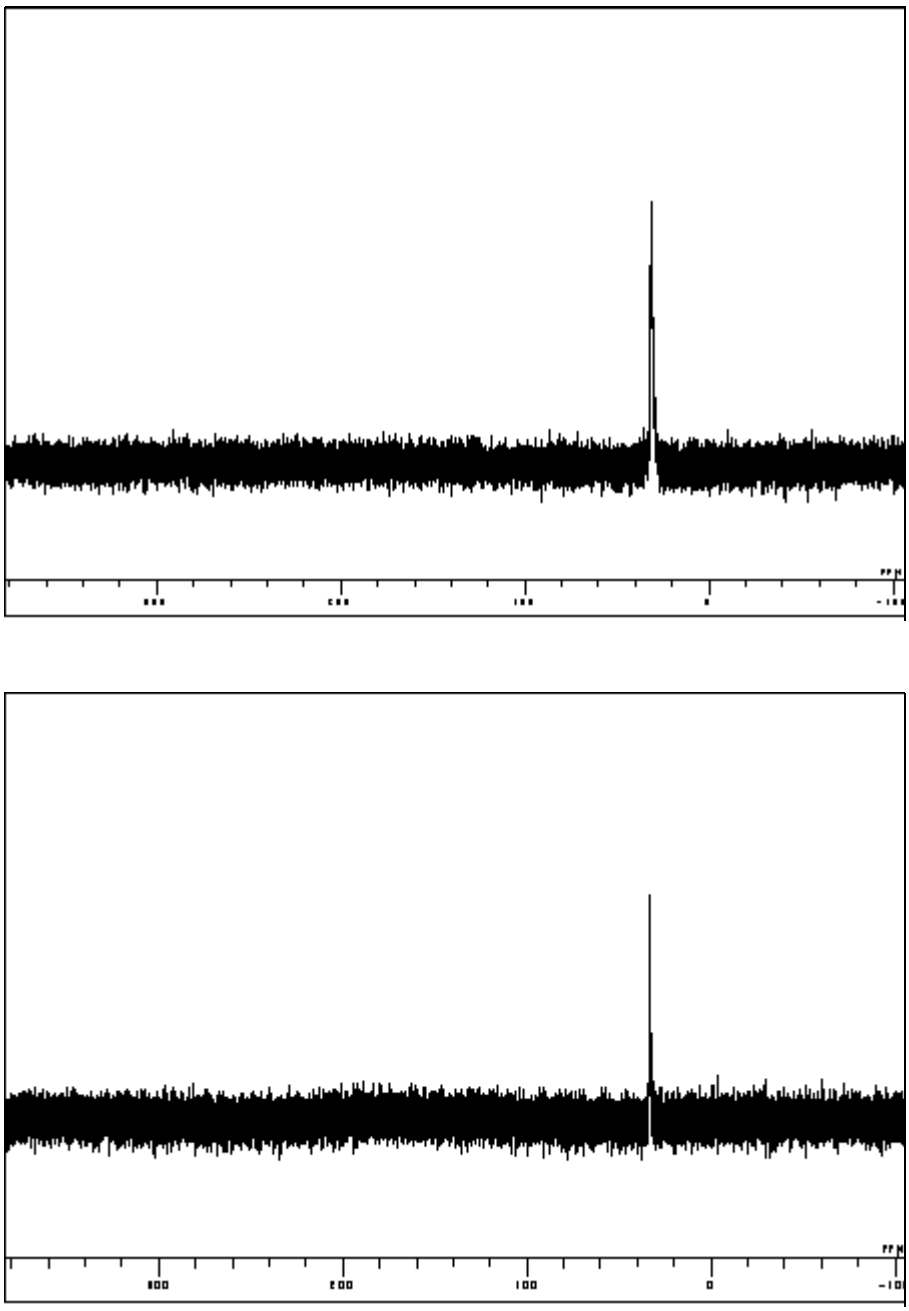


S5. ^{13}C NMR spectrum of 1a (top) and 1b (down) in $CDCl_3/CD_3OD$

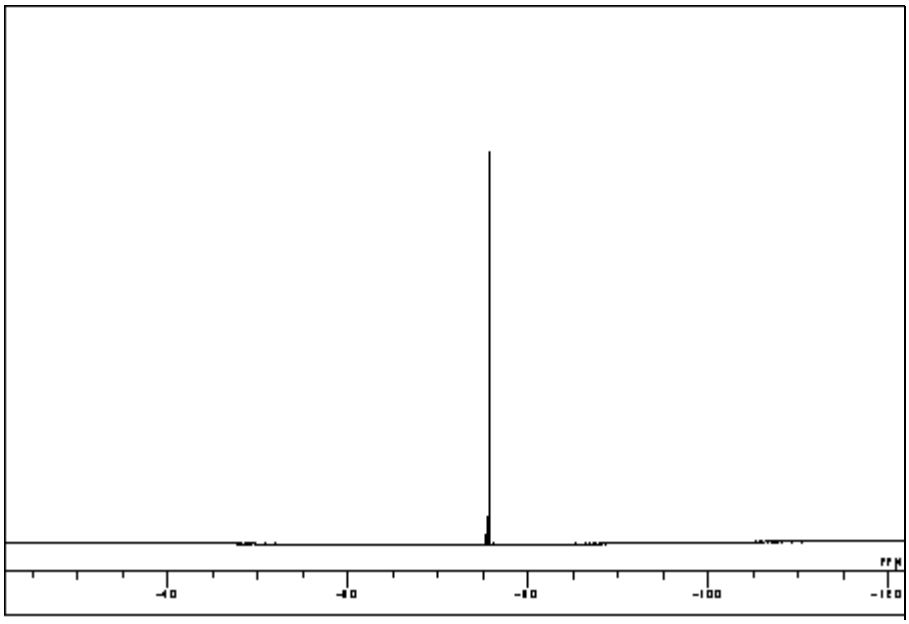




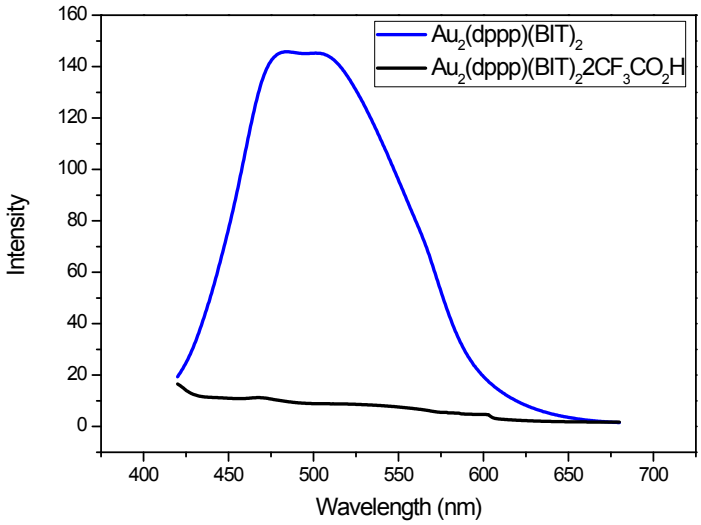
S6. ^{31}P NMR spectrum of 1a (top) and 1b (down) in $CDCl_3/CD_3OD$



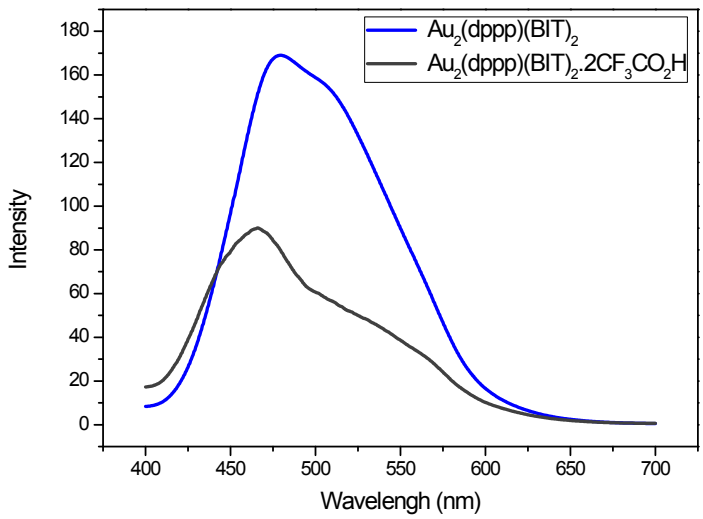
S7. ^{19}F NMR spectrum of 1a in $CDCl_3/CD_3OD$



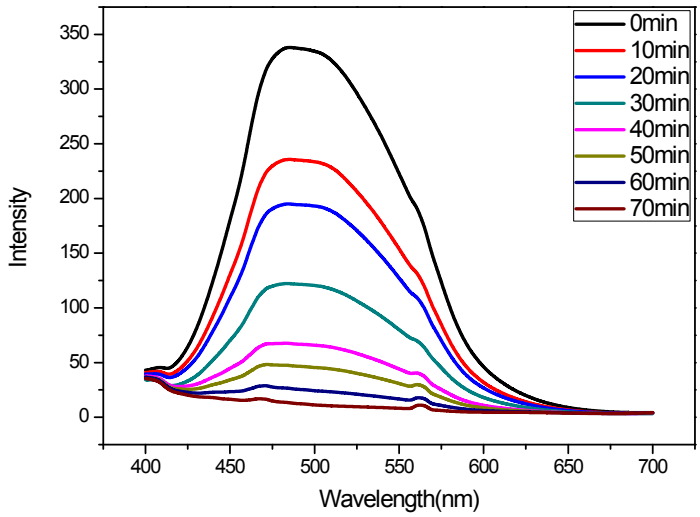
S8. Emission spectra of 1a and 1b in solid state at RT

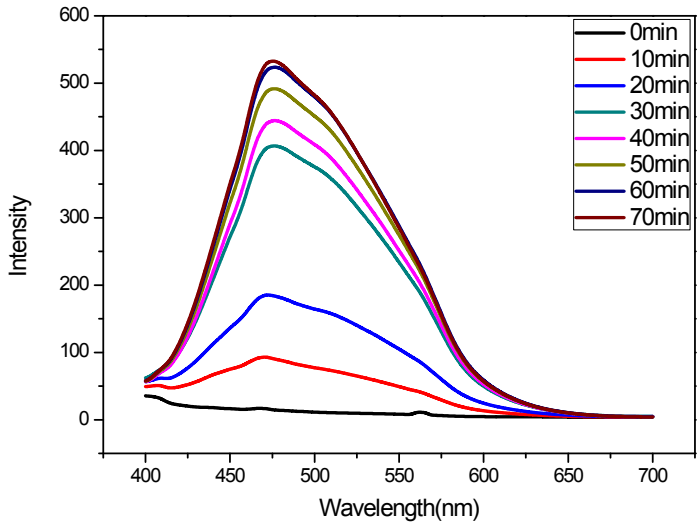


S9. Emission spectra of 1a and 1b in solid state at 77K



S10. Time-dependent emission spectra of 1a in CF_3CO_2H (top) and NEt_3 (down) chamber at RT





S11. Time-dependent emission spectra of 1a in HCl (top) and NEt_3 (down) chamber at RT