Supporting information:

# Solvent-induced intercluster rearrangements and the reversible luminescence responses in sulfide bridged gold(I)-silver(I) clusters

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## Contents

## Ⅰ. Physical Measurements

The C, H, N analyses were carried out with a Vario EL III elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 $cm^{-1}$ with a Nicolet Avatar FT-IR330 spectrometer. Luminescence was measured on a Hitachi F-7000 spectrometer. Lifetime was measured on Horiba Jobin Yvon Fluoromax-4P-Tcspc spectrometer. $^{31}P$ NMR data were recorded on a Bruker Avance II spectrometer (400MHz) using $H_3PO_4$ (85%) as external standards. The thermogravimetric analysis (TGA) were recorded under nitrogen atmosphere in the range 30-1000℃ with a NETZSCH TG-209F1 instrument.

## X-ray Crystallagraphy and Data Collection

Intensity data of compounds were collected on an Oxford Gemini S Ultra system (Mo Kα) 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 $CH_3CN$, $Et_2O$, $(CH_3)_2CO$ and $CH_3OH$ 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 of the reagents employed were commercially available and used without further purification. Literature method was used to prepare compound $[SAu_3Ag(Ph_2P\text{-}4\text{-}Mepy)_3](BF_4)_2$(**1**). The ligand $Ph_2P$-4-Mepy (L1) was prepared in a similar synthetic procedure as literature method[1] and the ligand $Ph_2Ppym$ (L3) was also prepared according the literature method.[2] The precursors LAuCl, $LAu(BF_4)$ and $S(AuL)_2$ were pumped under vacuum for 2h before use.

### 1a

To a solution of L1AuCl (40 mg, 0.08 mmol) in dichloromethane (4 mL) was added $S(AuL1)_2$ (78 mg, 0.08 mmol) in dichloromethane (6 mL) and the mixture was stirred for 30 min at room temperature. $AgBF_4$ (35 mg, 0.18 mmol) was added and stirred for 4h with exclusion of light. The resulting mixture was then filtered and the solvent ($CH_2Cl_2$) was removed under vacuum to give a brown crude solid. Light yellow block-like crystals suitable for X-ray crystallography were obtained from a solution of MeCN : $Et_2O$ = 1 : 1 (v / v) at 4℃ in refrigerator after three weeks. The afforded crystals emitted blue light when radiated by UV light. Yield: 62 mg, 44.3%.

Anal. Calcd for $C_{54}H_{48}B_2N_3F_8P_3SAgAu_3\cdot MeCN$: C, 37.84; H, 2.89; N, 3.15. Found:

C, 37.48; H, 3.07; N, 2.93. $^{31}$P NMR (CD3CN, ppm): 35.43. $\lambda_{em}$max = 475 nm; τ = 26.12 ± 1.22 µs. IR (KBr, cm$^{-1}$): 3046(w), 2917(w), 1595(m), 1436(m), 1384(m), 1083(br, B-F), 750(m), 693(m).

**2a**

To a solution of L2AuCl (116.5 mg, 0.24 mmol) in dichloromethane (4 mL) was added S(AuL2)$_2$ (218.4 mg, 0.23 mmol) in dichloromethane (12 mL) and the mixture was stirred for 5 min at room temperature. $AgBF_4$ (113.4 mg, 0.58 mmol) was added and stirred for 30min with exclusion of light. The resulting mixture was then filtered and the solvent ($CH_2Cl_2$) was removed under vacuum to give a yellow-green crude solid. Green flake crystals suitable for X-ray crystallography were obtained from the diffusion of $Et_2O$ into a dry MeCN solution of the sample after one week. The crystals emitted green light when radiated by UV light. Yield: 262.7mg, 67.4%.

Anal. Calcd for $C_{51}H_{42}B_2N_3F_8P_3SAgAu_3\cdot0.5MeCN$: C, 36.15; N, 2.48; H, 2.50. Found: C, 36.42; N, 2.86; H, 2.56. $^{31}$P NMR (CDCl3, ppm): 37.00. $\lambda_{em}$max = 503 nm; τ=3.37 ± 0.14 µs. IR (KBr, cm-1): 3057(w), 2966(w), 2920(w), 2851(w), 1630(m), 1430(m), 1382(w), 1083(br, B-F), 749(m), 693(m).

**3a**

To a solution of L3AuCl (80.3 mg, 0.16 mmol) in dichloromethane (6 mL) was added S(AuL3)$_2$ (157.1 mg, 0.16 mmol) in dichloromethane (6 mL) and the mixture was stirred for 5 min at room temperature. $AgBF_4$ (74.3 mg, 0.38 mmol) was added and stirred for 30 min with exclusion of the light. The resulting mixture was then filtered and the solvent ($CH_2Cl_2$) was removed under vacuum to give a yellow-green crude solid. Light yellow block-like crystals suitable for X-ray crystallography were obtained from an acetone solution of the sample after four days. The crystals emitted green light when radiated by UV light. Yield: 194.1mg, 71.5%.

Anal. Calcd for $C_{48}H_{39}B_2N_6F_8P_3SAgAu_3\cdot0.5OCMe_2\cdot0.5H_2O$: C, 34.26; N, 4.84; H, 2.50. Found C, 34.17; N, 4.61; H, 2.77. $^{31}$P NMR ($(CD_3)_2CO$, ppm): 39.82. $\lambda_{em}$max = 502 nm; τ = 11.59 ± 0.12 µs. IR (KBr, cm-1): 3065(w), 1628(m), 1560(s), 1479(m), 1437(m), 1385(s), 1080(br, B-F), 748(m), 693(m).

**3b**

Light yellow block-like crystals suitable for X-ray crystallography were obtained from a solution of the sample in $CH_2Cl_2$:$CH_3OH$ = 1:1 (v/v) after two days, which emitted yellow-green light when radiated by portable UV light.

Anal. Calcd for $C_{48}H_{39}B_2N_6F_8P_3SAgAu_3\cdot1.5H_2O$: C, 33.43; N, 4.87; H, 2.45. Found C, 33.58; N, 4.96; H, 2.02. $^{31}$P NMR ($CD_2Cl_2/CD_3OD$=1:1, ppm): 41.66. $\lambda_{em}$max = 541 nm; τ = 6.75 ± 0.32 µs. IR (KBr, cm-1): 2923(w), 2848(w), 1632(m), 1557(m), 1436(w), 1384(m), 1082(br, B-F), 746(m), 694(m).

## References

(1) Kuang, S.-M.; Zhang, Z.-Z; Wang, Q.-G.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans*. **1998**, 2927-2929.

(2) Li, S.-L.; Zhang, Z.-Z.; Mak, T. C. W. *J.Organomet. Chem.* **1997**, *536-537,* 73-86.

## Ⅲ. Characterization

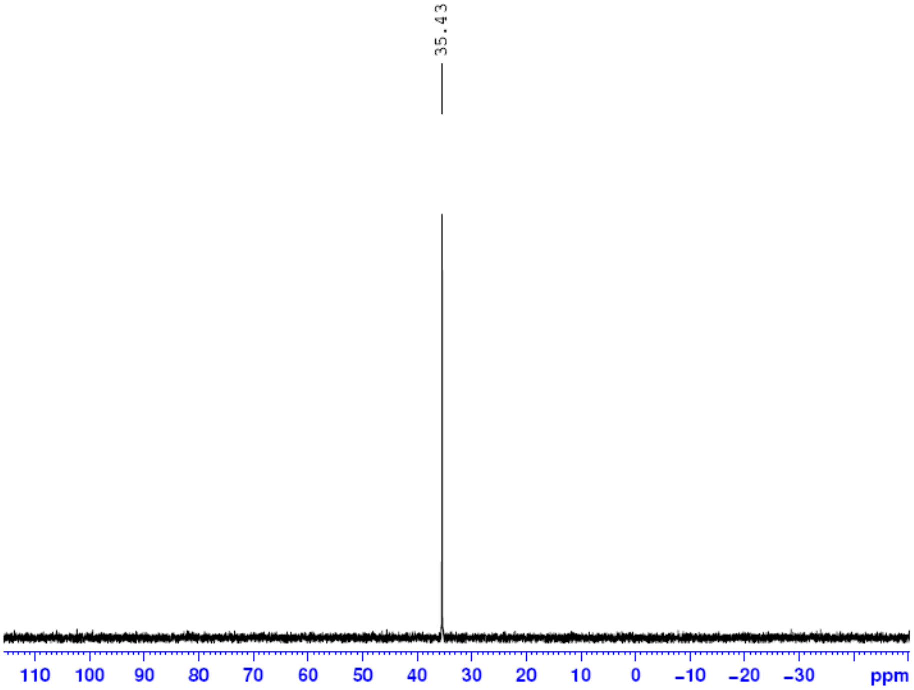

**Figure S1.** $^{31}P\{^1H\}$ NMR spectrum of **1a** in $CD_3CN$.

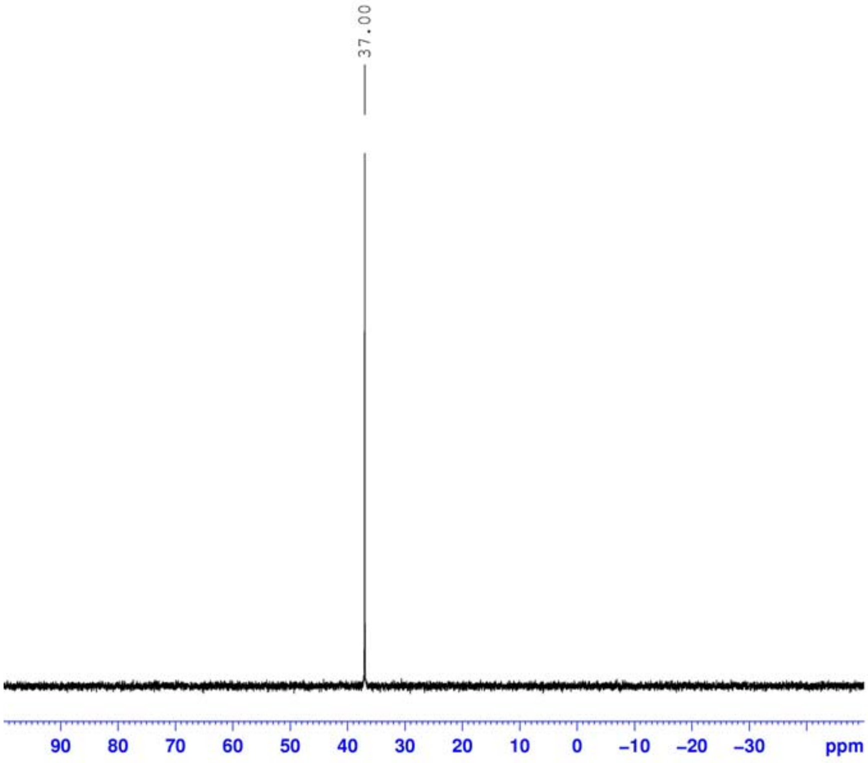

**Figure S2.** $^{31}P\{^1H\}$ NMR spectrum of **2a** in $CDCl_3$.

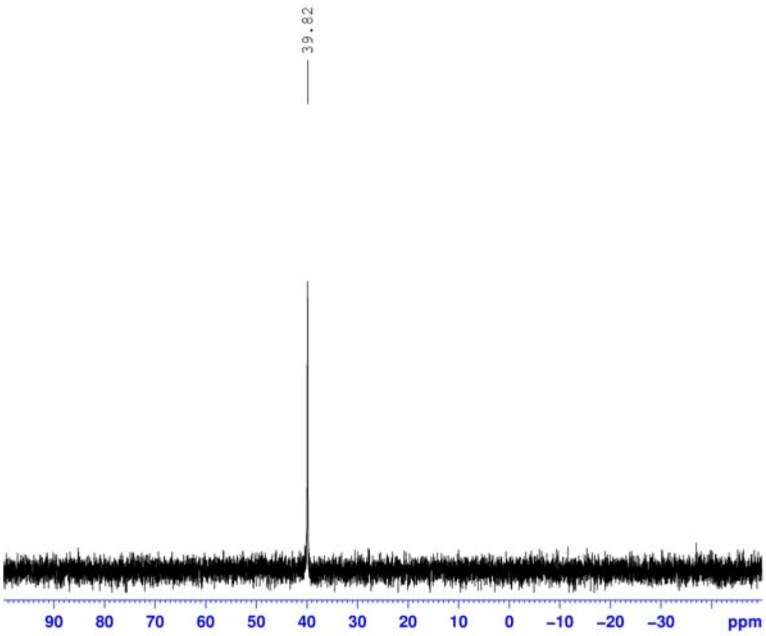

**Figure S3.** $^{31}P\{^1H\}$ NMR spectrum of **3a** in $(CD_3)_2CO$.

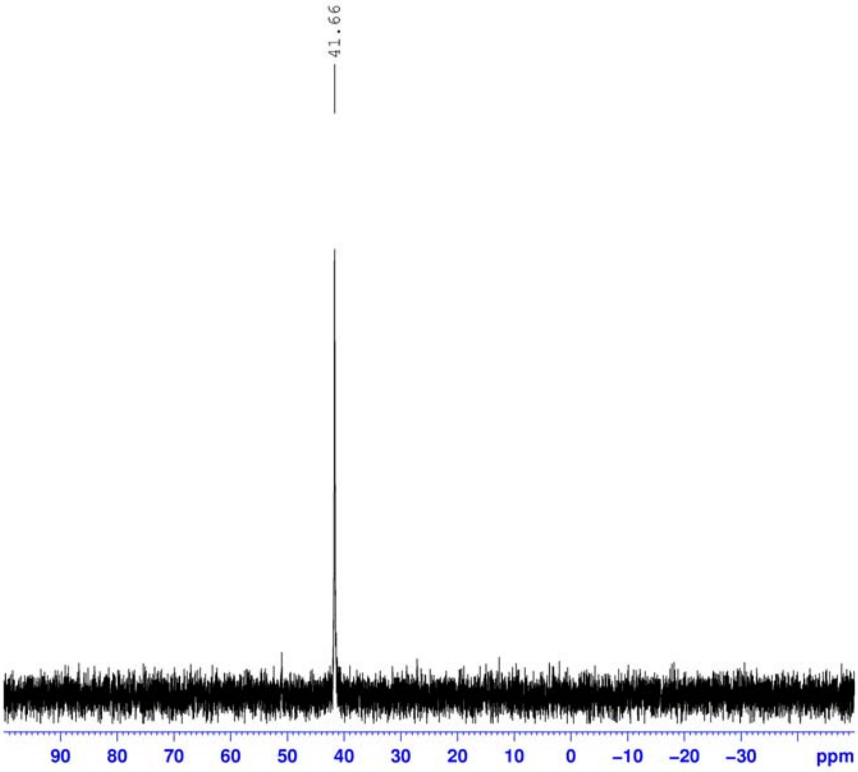

**Figure S4.** $^{31}P\{^1H\}$ NMR spectrum of **3b** in $CD_2Cl_2/CD_3OH$.

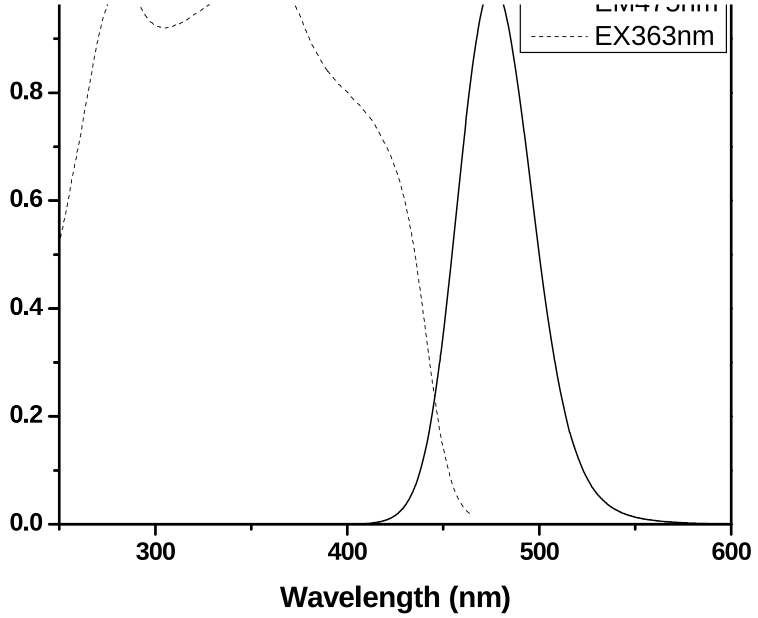

**Figure S5.** Excitation and emission spectra of **1a** in solid state

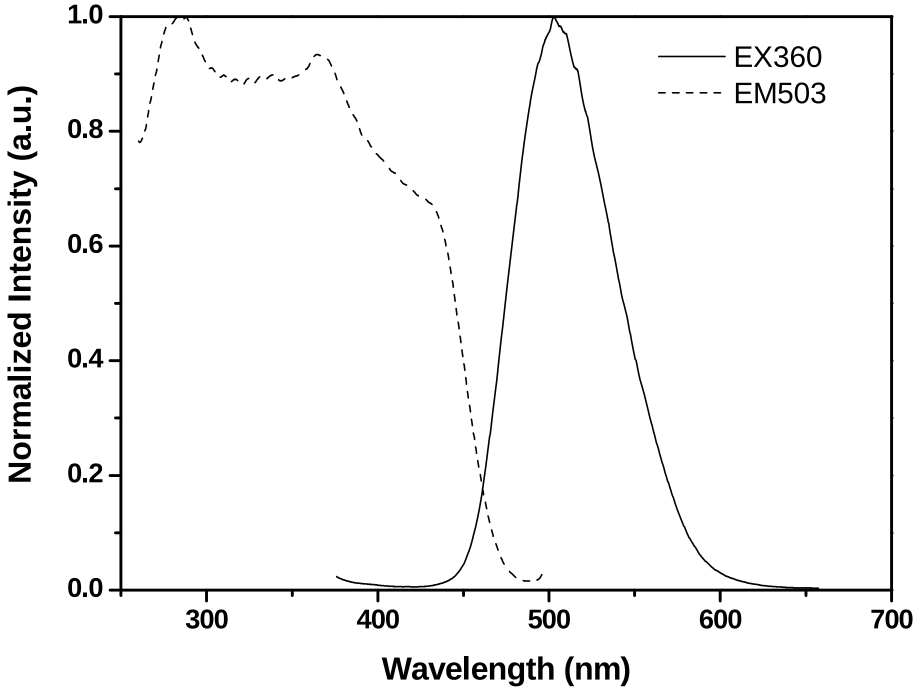

**Figure S6.** Excitation and emission spectra of **2a** in solid state

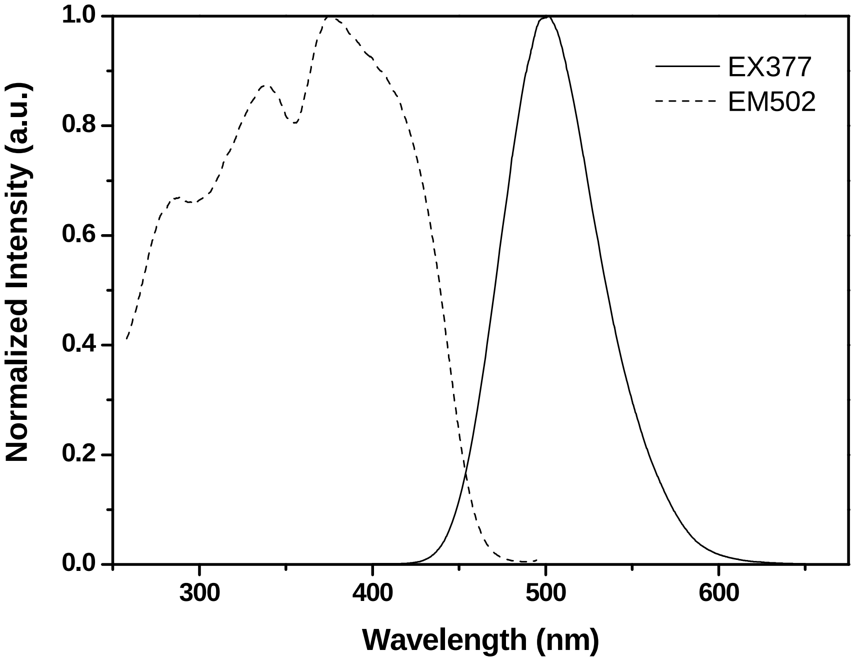

**Figure S7.** Excitation and emission spectra of **3a** in solid state

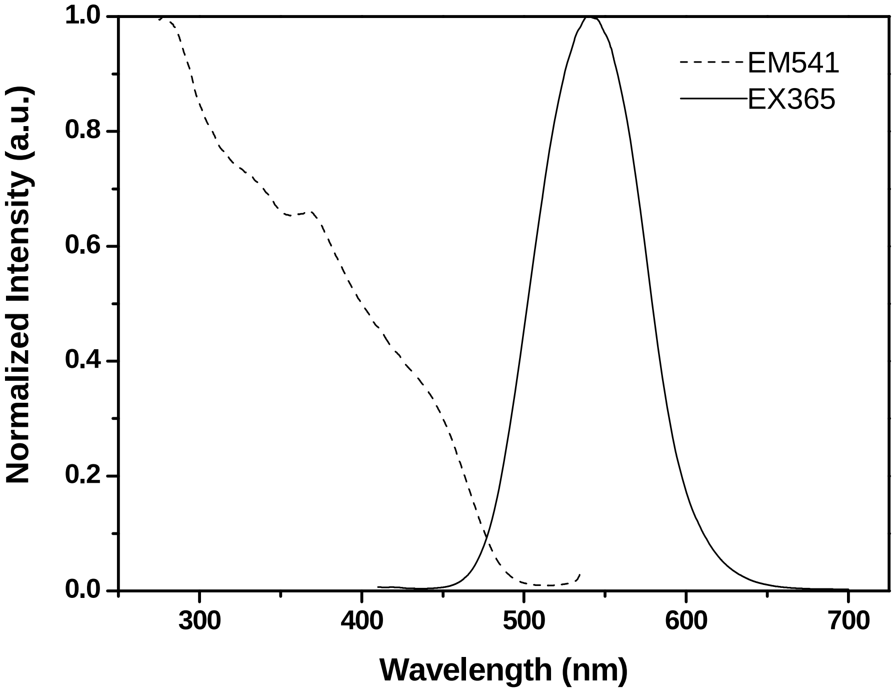

**Figure S8.** Excitation and emission spectra of **3b** in solid state

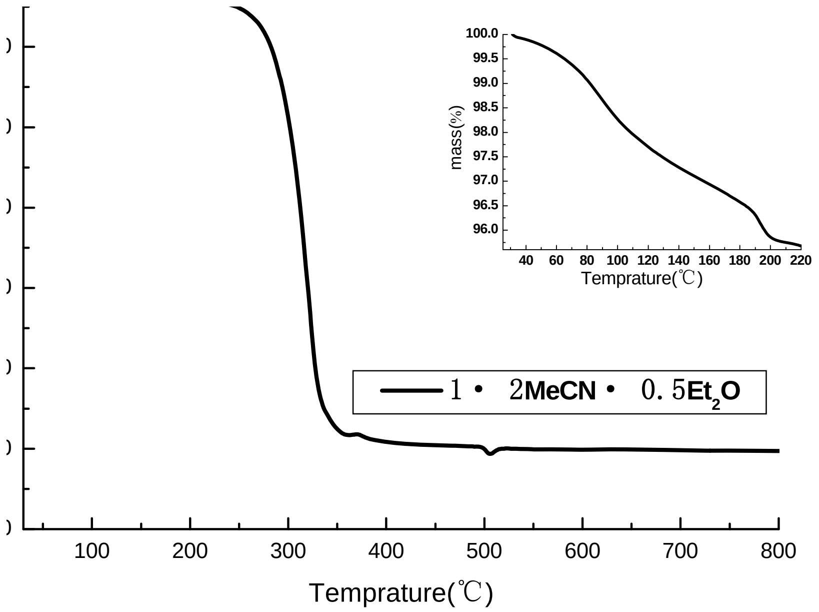

**Figure S9.** TGA of **1a**.

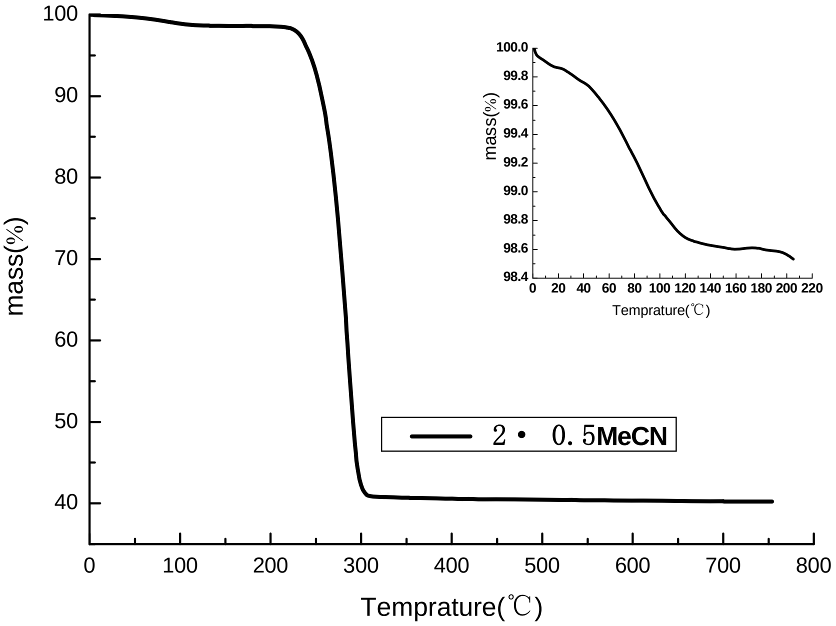

**Figure S10.** TGA of **2a**.

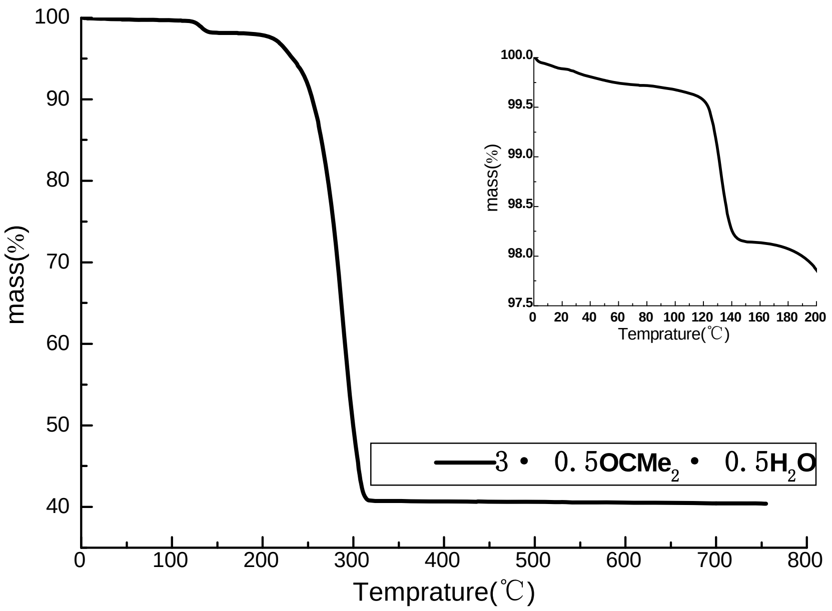

**Figure S11.** TGA of **3a**.

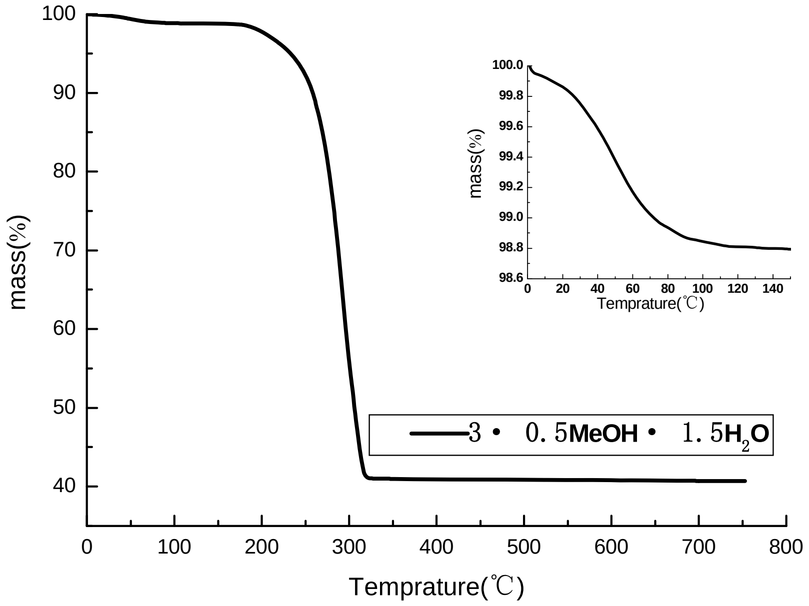

**Figure S12.** TGA of **3b**

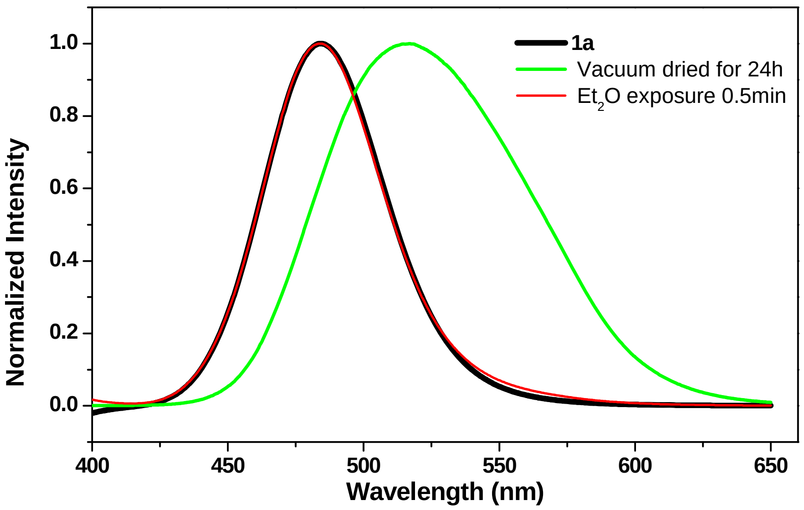

**Figure S13**. Normalized emission spectra of **1a,** after being dried in vacuum for 24 h, and then exposure to saturated $Et_2O$ vapor for 0.5 min.