Supporting information:

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

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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-Tespc spectrometer. 31P NMR data were recorded on a Bruker Avance II spectrometer (400MHz) using H$_3$PO$_4$ (85%) as external standards. The thermogravimetric analysis (TGA) were recorded under nitrogen atmosphere in the range 30-1000°C with a NETZSCH TG-209F1 instrument.

X-ray Crystallography and Data Collection

Intensity data of compounds were collected on an Oxford Gemini S Ultra system (Mo 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 CH$_3$CN, Et$_2$O, (CH$_3$)$_2$CO and CH$_3$OH 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$_3$Ag(Ph$_2$P-4-Mepy)$_3$](BF$_4$)$_2$ (1). The ligand Ph$_2$P-4-Mepy (L1) was prepared in a similar synthetic procedure as literature method$^1$ and the ligand Ph$_2$Ppym (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$_2$Cl$_2$) 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$_2$O = 1 : 1 (v / v) at 4°C 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$_2$N$_3$F$_8$P$_3$SAgAu$_3$·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. $\lambda_{\text{em max}} = 475$ nm; $\tau = 26.12 \pm 1.22 \mu$s. 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 30 min with exclusion of light. The resulting mixture was then filtered and the solvent (CH$_2$Cl$_2$) 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$_2$O into a dry MeCN solution of the sample after one week. The crystals emitted green light when radiated by UV light. Yield: 262.7 mg, 67.4%.

Anal. Calcd for C$_{51}$H$_{42}$B$_2$N$_3$F$_8$P$_3$SAgAu$_3$·0.5MeCN: C, 36.15; N, 2.48; H, 2.50. Found: C, 36.42; N, 2.86; H, 2.56. $^{31}$P NMR (CDCl$_3$, ppm): 37.00. $\lambda_{\text{em max}} = 503$ nm; $\tau = 3.37 \pm 0.14 \mu$s. 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 light. The resulting mixture was then filtered and the solvent (CH$_2$Cl$_2$) 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: 194.1 mg, 71.5%.

Anal. Calcd for C$_{48}$H$_{39}$B$_2$N$_6$F$_8$P$_3$SAgAu$_3$·0.5OCMe$_2$·0.5H$_2$O: C, 34.26; N, 4.84; H, 2.50. Found C, 34.17; N, 4.61; H, 2.77. $^{31}$P NMR ((CD$_3$)$_2$CO, ppm): 39.82. $\lambda_{\text{em max}} = 502$ nm; $\tau = 11.59 \pm 0.12 \mu$s. IR (KBr, cm$^{-1}$): 3065(w), 1628(m), 1560(s), 1479(m), 1437(m), 1385(s), 1082(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$_2$Cl$_2$:CH$_3$OH = 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$_2$N$_6$F$_8$P$_3$SAgAu$_3$: C, 33.43; N, 4.87; H, 2.45. Found C, 33.58; N, 4.96; H, 2.02. $^{31}$P NMR (CD$_2$Cl$_2$/CD$_3$OD=1:1, ppm): 41.66. $\lambda_{\text{em max}} = 541$ nm; $\tau = 6.75 \pm 0.32 \mu$s. 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
III. Characterization

Figure S1. $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of 1a in CD$_3$CN.
**Figure S2.** $^{31}P\{^1H\}$ NMR spectrum of $2a$ in CDCl$_3$.

![Figure S2 NMR spectrum of 2a](image1)

**Figure S3.** $^{31}P\{^1H\}$ NMR spectrum of $3a$ in (CD$_3$)$_2$CO.

![Figure S3 NMR spectrum of 3a](image2)
Figure S4. $^{31}$P$^1$H NMR spectrum of 3b in CD$_2$Cl$_2$/CD$_3$OH.

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

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