Supporting Information for

Photoluminescent Coordination Polymer Bulk Glass and Laser Induced Crystallization

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Table of contents

- Experimental section \quad S2-S5
- Supplementary figures and table \quad S6-S20
Experimental Materials

All chemicals were obtained from chemical companies and used without further purification. Gold(I) cyanide (AuCN), copper(I) cyanide (CuCN), silver(I) cyanide (AgCN), triphenylphosphine (PPh$_3$), hexane, and dichloromethane were obtained from FUJIFILM Wako Pure Chemical Corporation (Japan).

Synthesis of $\left\{ \text{[Ag(PPh}_3\text{)]}_2\text{[Au(CN)_2]} \right\}_n \text{(AgAu)}$

AgAu was synthesized according to previous literature with a slight modification. AuCN (0.223 g, 1 mmol) was added to a dichloromethane (40 mL) containing PPh$_3$ (0.524 g, 2 mmol). The mixture was stirred for 30 min to obtain a clear solution. Then, AgCN (0.134 g, 1 mmol) was added to the solution and further stirred for 24 h. After filtration, hexane (30 mL) was added to the filtrate to obtain white crystalline powder. The powder collected by filtration was washed with hexane several times and then dried in vacuo at room temperature overnight. Yield: 0.620 g (70%).

Elemental analysis calculated for C$_{38}$H$_{30}$AgAuN$_2$P$_2$ (AgAu): C, 51.73; H, 3.40; N, 3.18; experimental: C, 51.64; H, 3.40; N, 3.18.

Synthesis of $\left\{ \text{[Ag(PPh}_3\text{)]}_2\text{[Cu(CN)_2]} \right\}_n\cdot x\text{H}_2\text{O} \text{(AgCu-xH}_2\text{O)}$

AgCu·xH$_2$O was synthesized according to previous literature with a slight modification. AgCN (0.134 g, 1 mmol) was added to a CH$_2$Cl$_2$ (40 mL) containing PPh$_3$ (0.524 g, 2 mmol). The mixture was stirred for 30 min to obtain a clear solution. Then, CuCN (0.090 g, 1 mmol) was added to the solution with magnetically stirring for 24 h. After filtration, hexane (30 mL) was added to the filtrate to obtain white crystalline powder. The powder collected by filtration was washed with hexane several times and dried in vacuo at room temperature overnight. Yield: 0.685 g (92%).

Synthesis of $\left\{ \text{[Cu(PPh}_3\text{)]}_2\text{[Au(CN)_2]} \right\}_n\cdot x\text{H}_2\text{O} \text{(CuAu-xH}_2\text{O)}$

CuAu·xH$_2$O was synthesized according to previous literature with a slight modification. AuCN (0.223 g, 1 mmol) was added to a CH$_2$Cl$_2$ (45 mL) containing PPh$_3$ (0.524 g, 2 mmol). The mixture was stirred for 0.5 h to obtain a clear solution. Then, CuCN (0.090 g, 1 mmol) was added to the solution with magnetically stirring for 24 h to obtain white crystalline powder. The powder collected by filtration was washed with CH$_2$Cl$_2$ several times and dried in vacuo at room temperature overnight. Yield: 0.597 g (68%).

Degas of CuAu·xH$_2$O and AgCu·xH$_2$O

CuAu·xH$_2$O and AgCu·xH$_2$O were heat under vacuum overnight at 140 °C and 100 °C, respectively to obtain the guest free phase CuAu and AgCu. Elemental analysis calculated for C$_{38}$H$_{30}$CuAuN$_2$P$_2$ (CuAu): C, 54.47; H, 3.59; N, 3.35; experimental: C, 55.43; H, 3.60; N, 3.39. Elemental analysis calculated for C$_{38}$H$_{30}$AgCuN$_2$P$_2$ (AgCu): C, 61.02; H, 4.04; N, 3.74; experimental: C, 60.78; H, 4.05; N, 3.83.

Glass formation of AgAu, CuAu, and AgCu
120 mg of polycrystalline powder was transferred into a 20 mL agate vessel with ten agate balls (10 mm in diameter) under argon atmosphere. The sample was ball-milled at 400 rpm which involves 10 min run and 10 min pause for 48 cycles produced AgAu-g, CuAu-g and AgCu-g.

**Preparation of bulk glass monolith**

100 mg of CuAu-g/AgCu-g powder was first pressed into pellet by a pellet DIE with 13 mm diameter. The pellet was set between two pieces of metal support and this setup was then transferred into a vacuum hot-press machine. The sample was preheated at 100/105 °C in a vacuum for 30 min and then 60 kN pressure was added. The pressure was maintained for 60 min. Transparent monolith was obtained after pressure was released and the system cooled to room temperature.

**Physical measurements**

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku MiniFlex 600 operated at 40 kV and 15 mA with Cu Kα radiation (λ = 1.54 Å). Synchrotron PXRD was measured at SPring-8 at 25 °C (BL02B2, λ = 0.799617 Å). The synchrotron PXRD data were used for Rietveld refinement of CuAu and AgCu. The initial structures for Rietveld refinement were constructed from the reported crystal structure of AgAu. The refinement was carried out using EXPO2014 software.

Thermogravimetric and differential thermal analyses (TG/DTA) were carried out using a Rigaku Thermoplus 8120 for measurement under nitrogen atmospheres. A weighed sample in an aluminum pan was heated from 30 to 500 °C with heating rate of 10 °C min⁻¹. The samples in the pan were observed in real-time.

Differential scanning calorimetry (DSC) was measured with Hitachi High-Tech Science Corporation DSC7020. A weighed sample in an aluminum pan was heated or cooled with a rate of 10 °C min⁻¹.

Scanning electronic microscopy (SEM) observation was carried out by JEOL Model JSM-7001F4 SEM system operating at 15.0 kV. The samples were deposited on carbon tape and coated with osmium prior to the measurement.

Microscope images were taken by a wide-range zoom lens VH-Z100T.

Fourier-transform infrared spectroscopy (IR) measurements were carried out using JASCO FTIR-6700 under air between the wavelength of 500 and 3500 cm⁻¹.

Raman spectra were collected by using Raman spectra was collected at room temperature by using Horiba Jobin Yvon LabRAM HR800 with semiconductor laser at 488 nm.

Diffusion reflectance spectrum and transmittance of glass monolith were recorded with a Shimadzu UV-3600 spectrophotometer with an ISR-3100 integral sphere unit.

Photoluminescence spectra were recorded using a JASCO FP-6600DS spectrofluorometer at 25 °C.
Photoluminescence lifetime measurement was measured by Quantaurus-Tau-C11367, Hamamatsu Photonics at 25 °C. The excitation wavelength was set as 365 nm.

Extended X-ray Absorption Fine-Structure Spectroscopy were collected on beamline BL01B1 at SPring-8. X-ray absorption spectra in the energy region of the Cu K-edge were measured in transmission mode. Fourier transformation was $k^3$-weighted in the k range from 3.0 to 12.5 Å$^{-1}$. The data processing and coordination number fitting were performed with Athena and Artemis software, respectively. All samples were measured in air at 25 °C. The resulting $k^3$-weighted radial distribution function was fitted by a FEFF calculation using single crystal data of CuAu·xH$_2$O.

X-ray total scattering data of samples in a quartz glass capillary ($\phi = 2$ mm) filled with argon were collected at 25 °C with four CdTe and two Ge detectors covering the Q range up to 25 Å$^{-1}$ at the BL04B2 beamline (61.377 keV) at SPring-8. The incident beam was monochromated at $\lambda = 0.2020$ Å. $G(r)$ is obtained from the Fourier transformation of $S(Q)$ with a Lorch modification function through Igor Pro software.

$^{31}$P solid-state MAS NMR was performed on a JNM-ECZ600R (JEOL RESONANCE Inc.) solid-state NMR spectrometer at 14.1 T at 25 °C at 20 kHz (3.2 mm rotor).

**Setup for laser irradiation**

The setup for laser irradiation is shown as below. A concentrator was placed 7 cm in front of sample to ensure the highest laser power. The PhoxX® 730 nm diode laser was used for experiment.

The focused beam size is calculated by using the following equation:

$$d = \frac{4\lambda M^2f}{\pi D} = \frac{4 \times 730 \times 10^{-9} \times 1.052 \times 0.07}{\pi \times 1 \times 10^{-3}} \approx 47 \, \mu\text{m}$$
Parameters:

\(d\): beam size after concentration

\(D\): beam size before concentration

\(f\): focus distance of concentrator

\(\lambda\): wavelength

\(M\): quality of the beam
**Fig. S1** (A) PXRD patterns of simulated AgAu from single crystal structure, synthesized AgAu, AgAu-g, and AgAu-g by heating above its $T_c$. (B) TGA profiles of AgAu and AgAu-g with a heating rate of 10 °C min$^{-1}$ in N$_2$ atmosphere. Inset figure is the melt state of AgAu at $T_m$ of 218 °C.

**Fig. S2** (A) PXRD patterns of simulated AgCu xH$_2$O from the single crystal structure, synthesized AgCu xH$_2$O, AgCu, AgCu-g, and AgCu-g heated above its $T_c$. (B) TGA profile of AgCu and AgCu-g with a heating rate of 10 °C min$^{-1}$ in N$_2$ atmosphere. Insert figure is melt state of AgCu at $T_m$ of 197 °C.
Fig. S3 (A) PXRD patterns of simulated CuAu\textsubscript{x}H\textsubscript{2}O from the single crystal structure, synthesized CuAu\textsubscript{x}H\textsubscript{2}O, CuAu, CuAu-g, and CuAu-g heated above its T\textsubscript{c}. (B) TGA profile of CuAu and CuAu-g with a heating rate of 10 °C min\textsuperscript{-1} in N\textsubscript{2} atmosphere. Insert figure is melt state of CuAu at T\textsubscript{m} of 198 °C.

Fig. S4 (A) Result of Rietveld refinement of CuAu. Space group is P2\textsubscript{1}/n. a = 9.56660 Å, b = 20.52415 Å, c = 16.99206 Å, β = 96.370°. R\textsubscript{p} = 2.846%, R\textsubscript{wp} = 3.703%. (B) Result of Rietveld refinement of AgCu. Space group is P2\textsubscript{1}/n. a = 9.60682 Å, b = 20.23585 Å, c = 17.18036 Å, β = 95.931°. R\textsubscript{p} = 5.523%, R\textsubscript{wp} = 6.128%. λ = 0.799617 Å.
**Table S1.** Calculated $\Delta H_m$ and $\Delta S_m$ during melting of three $M^\text{N}M^\text{C}$s by DSC.

|        | $T_m$/°C | $\Delta H$ / kJ mol | $\Delta S$ / J mol K$^{-1}$ |
|--------|----------|----------------------|-----------------------------|
| CuAu   | 198      | 50                   | 105                         |
| AuAg   | 218      | 65                   | 130                         |
| AgCu   | 197      | 53                   | 114                         |

**Table S2.** Elemental analysis of $M^\text{N}M^\text{C}$s before and after the melt-quench process.

|       | C / %  | H / %  | N / %  |
|-------|--------|--------|--------|
| AgAu calculated | 51.73  | 3.40   | 3.18   |
| AgAu as-synthesized | 51.64  | 3.40   | 3.18   |
| AgAu after melt-quench | 51.61  | 3.38   | 3.01   |
| CuAu calculated | 54.47  | 3.59   | 3.35   |
| CuAu as-synthesized | 55.43  | 3.60   | 3.39   |
| CuAu after melt-quench | 54.94  | 3.59   | 3.46   |
| AgCu calculated | 61.02  | 4.04   | 3.74   |
| AgCu as-synthesized | 60.78  | 4.05   | 3.83   |
| AgCu after melt-quench | 60.20  | 3.94   | 3.73   |
Fig. S5 (A) DSC profile of AgAu. (B) PXRD pattern of AgAu after DSC measurement. (C) DSC profile of AgCu. (D) PXRD pattern of AgCu after DSC measurement. DSC was measured under N₂ atmosphere with a heating rate of 10 °C min⁻¹.

Fig. S6 DSC profile of ground CuAu-MQG with two heating-cooling cycles. DSC was measured under N₂ atmosphere with a heating rate of 10 °C min⁻¹.
Fig. S7 (A) FT-IR spectra of CuAu·xH₂O, CuAu, CuAu-g and PPh₃. (B) Zoomed FT-IR spectra of CuAu·xH₂O, CuAu, CuAu-g.

Fig. S8 (A) FT-IR spectra of AgAu, AgAu-g, and PPh₃. (B) Zoomed FT-IR spectra of AgAu, AgAu-g.
Fig. S9 (A) FT-IR spectra of AgCu·xH₂O, AgCu, AgCu-g, and PPh₃. (B) Zoomed FT-IR spectra of AgCu·xH₂O, AgCu, AgCu-g.

Fig. S10 Raman spectra of CuAu·xH₂O, CuAu, CuAu-g and PPh₃. (B) Zoomed Raman spectra of CuAu·xH₂O, CuAu, CuAu-g and PPh₃.
Fig. S11 (A) Raman spectra of AgAu, AgAu-g, and PPh₃. (B) Zoomed Raman spectra of AgAu, AgAu-g, and PPh₃.

Fig. S12 (A) Raman spectra of AgCu·xH₂O, AgCu, AgCu-g, and PPh₃. (B) Zoomed Raman spectra of AgCu·xH₂O, AgCu, AgCu-g, and PPh₃.
Fig. S13 Cu K-edge XANES spectra of CuAu and CuAu-g.

Fig. S14. $k^3$-weighted RDFs of (A) CuAu and (B) CuAu-g.

RDF fitting parameters for CuAu and CuAu-g.

| Coordinating Atoms | Coordination Number | $R$ / Å | $S_0^2$ | $\sigma^2$ | $\Delta E_0$ / eV | R-factor |
|--------------------|---------------------|---------|---------|-----------|-----------------|----------|
| N                  | 2.3 (±0.4)          | 1.98 (±0.02) | 0.9 | 0.008 | 8.424 | 0.006 |
| P                  | 2.0 (±0.2)          | 2.29 (±0.01) | 0.9 | 0.008 | 8.424 | 0.006 |

| Coordinating Atoms | Coordination Number | $R$ / Å | $S_0^2$ | $\sigma^2$ | $\Delta E_0$ / eV | R-factor |
|--------------------|---------------------|---------|---------|-----------|-----------------|----------|
| N                  | 2.2 (±0.8)          | 2.00 (±0.01) | 0.9 | 0.009 | 8.081 | 0.007 |
| P                  | 2.0 (±0.2)          | 2.28 (±0.01) | 0.9 | 0.009 | 8.081 | 0.007 |
**Fig. S15** PDF profiles of (A) AuAg-g and (B) AgCu-g compared with simulated PDF profiles of AgAu and AgCu from their crystal structures.

**Fig. S16** Solid state $^{31}$P MAS NMR of (A) CuAu·$x$H$_2$O, CuAu, CuAu-g and (B) AgCu·$x$H$_2$O, AgCu and AgCu-g at 25 °C.
Fig. S17 Excitation and emission spectra of (A) CuAu-MQG, (B) AgAu, AgAu-g and (C) AgCu·xH₂O, AgCu and AgCu-g at 25 °C.
Fig. S18 Photoluminescent lifetime measurements of $M^NMC$ and $M^NMC-g$ at 25 °C.
Fig. S19 (A) PXRD pattern of CuAu-g monolith made by hot-press. (B) Reflectance diffusion spectra of PPh₃.

Fig. S20 (A) Surface and (B) cross-section SEM images of CuAu-g monolith. (C) Microscope image of CuAu-g monolith. (D) Surface and (E) cross-section SEM images of CuAu pellet.
Fig. S21 Transmittance of AgCu-g monolith. Inset figure is the photo of AgCu-g monolith made by hot-press. The scale bar is 1 cm.
Fig. S22 (A) PXRD patterns of anhydrous CuSO₄ and AgCu-g-CuSO₄. (B) Reflectance diffusion spectra of AgCu-g-CuSO₄. (C) The transmittance of AgCu-g-CuSO₄ monolith made by hot press. (D) SEM image and (E) EDS mapping on the AgCu-g-CuSO₄ monolith.
Fig. S23 (A) Surface of the AgCu-g-CuSO₄ powder pellet under the microscope. Areas 1 and 2 are irradiated by 47 μm size of the laser. Other grey spots are also crystallized domain. (B) Confocal Raman spectra at areas 1 and 2, and the area without laser irradiation. Spectra of pure AgCu and AgCu-g are also shown.