Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Rational and site-selective formation of coordination polymer consisting of d^{10} coinage metal ions with thiolate ligands using a metal ion-doped polymer substrate

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Contents:

1. Experimental

Chemicals. Silver nitrate, copper nitrate trihydrate and potassium hydroxide were purchased from FUJIFILM Wako Pure Chemical Co., Ltd. 4-Mercaptobenzoic acid (*p*-HSPhCOOH) was purchased from Tokyo Chemical Industry Co., Ltd. Polymethyl methacrylate was purchased from Sigma-Aldrich Co., Ltd. Ethanol were purchased from Kanto Chemical, Ltd. All chemicals were used as received. Pyromellitic dianhydride oxydianiline-type polyimide films (50 μm thick, Kapton 200H, Du Pont-Toray Co., Ltd.) were used as polymer substrates. The films were cleaned prior to use by ultrasonication in ethanol at 25 ºC for 5 min.

Preparation of CPs on polyimide films. The polyimide films (1×2 cm^2) were initially immersed in a 5 M aqueous KOH solution at 50 °C for various times, followed by thorough rinsing with copious amounts of distilled water. The modified films were then immersed in a 100 mM aqueous metal precursor solution at 25 ºC for 20 min. After rinsing with distilled water, the ion-doped polymer films were immersed in an aqueous solution containing organic ligands (10 mM, 10 mL), followed by heating at 80 ºC using aluminum heating block under hydrothermal condition.

Patterning of CPs on polyimide films. A poly(methyl methacrylate) (PMMA) thin film was fabricated on the hydrolyzed polyimide substrate by spin-coating, using a toluene/chloroform (1:1) solution containing 3 mass% PMMA. After drying, vacuum ultraviolet (VUV) photolithography (λ = 172 nm) through a photomask was used to expose the PMMA layer in the desired pattern. The unexposed PMMA was removed away by dipping in a chloroform solution for 10 min. The resulting substrate with PMMA patterns was immersed in an aqueous solution of copper nitrate at room temperature for 20 min to achieve the exchange of potassium ions with copper ions. After being rinsed, the ion-doped polyimide films were immersed in a solution of organic ligands, followed by heating at 80 ºC using aluminum heating block under hydrothermal condition, in order to form CP crystals on the polyimide surface

Characterization. The surface morphology of the obtained CP films was observed by scanning electron microscopy (SEM; JSM-7001FA, JEOL). In addition, the cross-sectional EDX mapping images of the obtained samples were also collected by SEM equipped with an EDX system. X-ray diffraction (XRD) data were collected using a diffractometer (RINT-2200 Ultima IV, Rigaku) with Cu Kα radiation. The number of metal ions added into the nylon films was quantified using inductively coupled plasma atomic emission spectroscopy (ICP AES; SPS 7800, Seiko Instruments). Emission spectra were recorded using a spectrofluorometer (FP-6500, Jasco).

2. Effect of hydrolysis time on amounts of doped copper ion

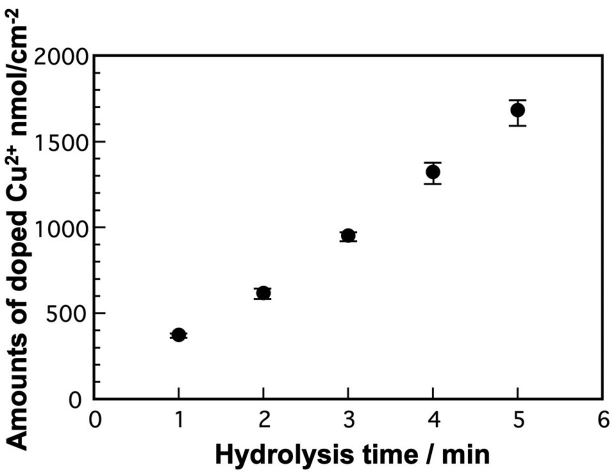

Figure S1. Effect of KOH treatment time of polyimide films on the number of adsorbed metal ions.

3. XRD patterns of the obtained sample and polyimide substrate

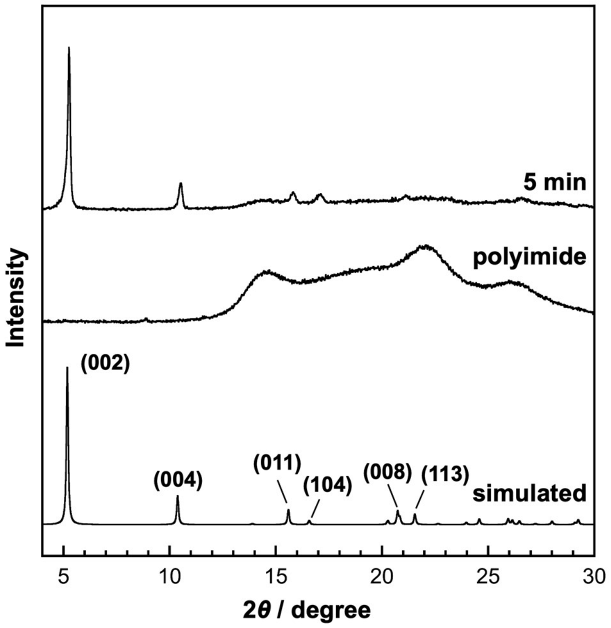

Figure S2. XRD patterns of polyimide substrate and the obtained sample using metal ion-doped substrate prepared by hydrolysis time of 5 min.

4. Luminescent property of the obtained samples

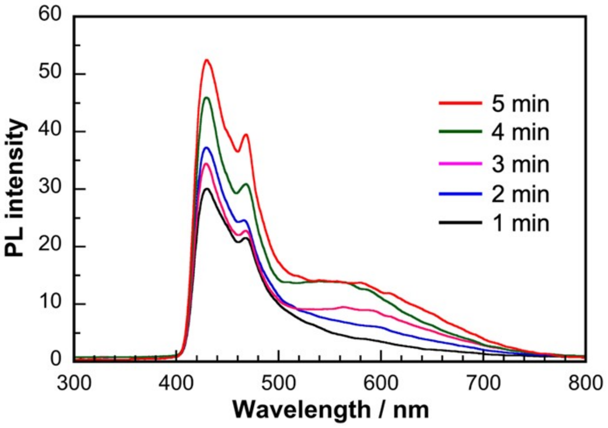

Figure S3. Emission spectra of the obtained [Cu(p-SPhCOOH)]$_n$ CPs (at 298 K, λ_{ex} = 365 nm) using metal ion-doped substrate prepared by different hydrolysis time.

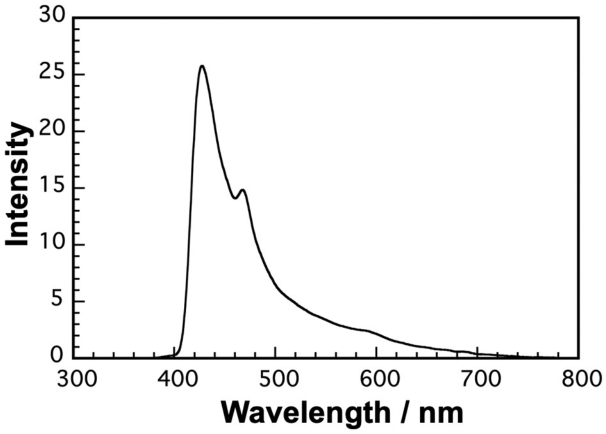

Figure S4. Emission spectrum of a methanol solution containing p-HSPhCOOH (at 298 K, λ_{ex} = 365 nm).

5. Formation of $[Ag(p\text{-SPhCOOH})]_n$ CP and mixed-metal $[Cu_xAg_{1-x}(p\text{-SPhCOOH})]_n$ CPs on substrate

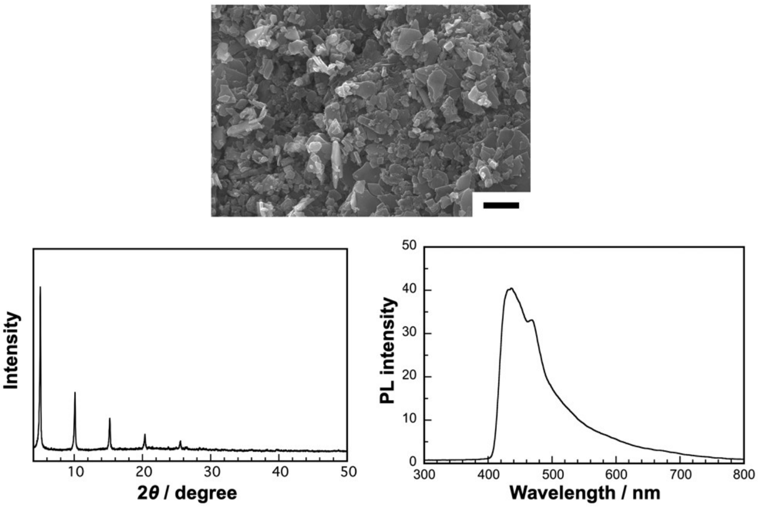

Figure S5. SEM image, XRD pattern, and emission spectrum of the obtained samples (at 298 K, λ_{ex} = 365 nm) using silver ion-doped substrate. Scale bar is 1 μm.

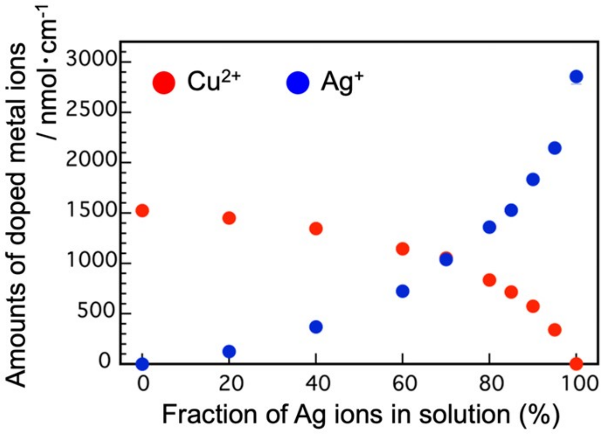

Figure S6. Effect of the concentration of reaction solution during ion-exchange reaction on amount of adsorbed copper and silver ions in polyimide films.

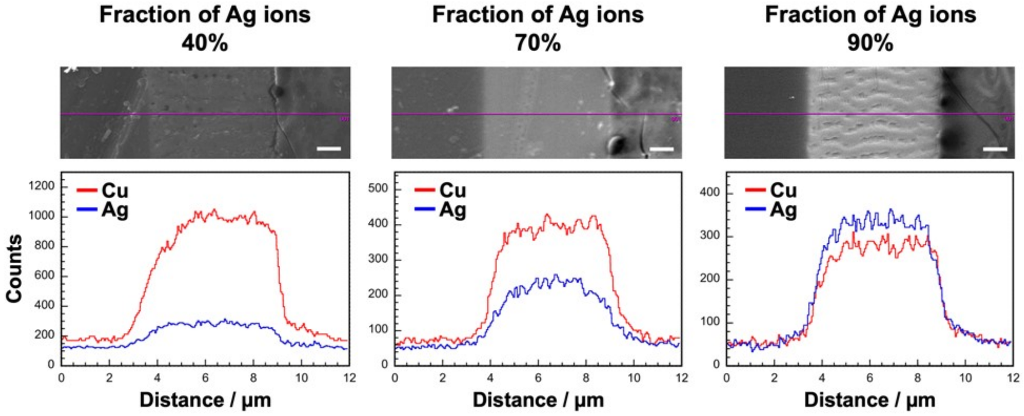

Figure S7. EDX line profiles of polyimide films after ion-exchange reaction with different fraction of Ag ions in reaction solution. Scale bars are 1 μm.

6. High-resolution SEM image and XRD pattern of patterned-$[\mathrm{Cu}(p\text{-}\mathrm{SPhCOOH})]_n$ CP on substrate

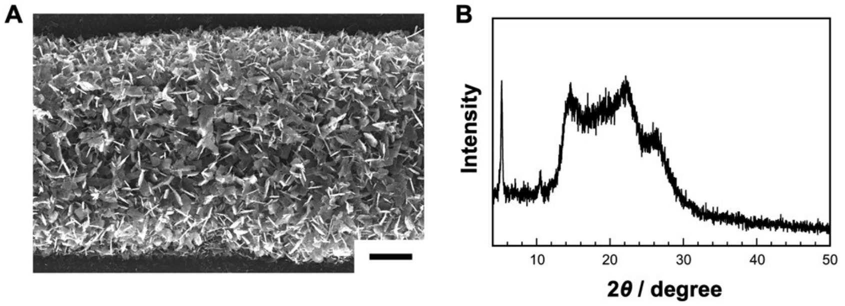

Figure S8. (A) SEM image and (B) XRD pattern of the obtained samples (at 298 K, λ_{ex} = 365 nm) using a PMMA-patterned polyimide films. Scale bar is 5 μm.