Supplementary Information (SI) for CrystEngComm.
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Supplementary Information

Structural transformation of silver(I)-thiolate coordination polymer film at solid–liquid interfaces

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Contents:

1. Experimental

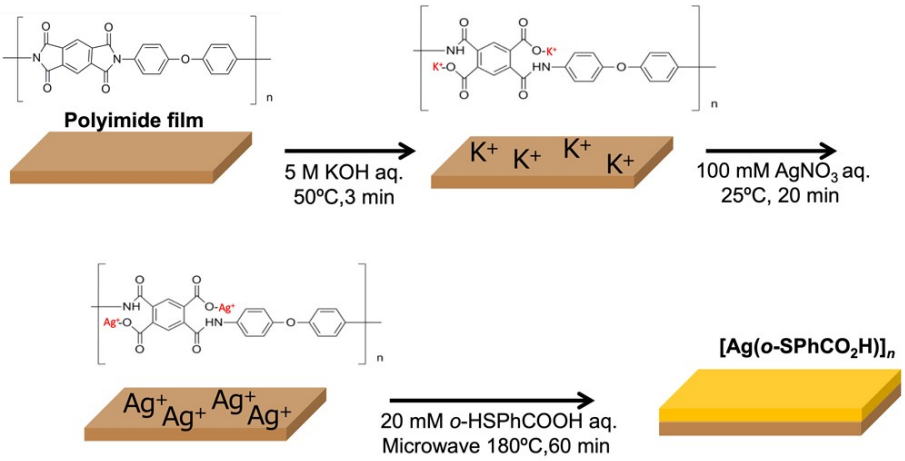
Chemicals. Potassium hydroxide, silver nitrate, 2-mercaptobenzoic acid, methanol, ethanol, and DMF were purchased from FUJIFILM Wako Pure Chemical Corp. 4-mercaptobenzoic acid was purchased from Tokyo Chemical Industry Co., Ltd. Pyromellitic dianhydride- and oxydianiline-type polyimide films (50 μm thick, Kapton 200H, Toray-Du Pont Co. Ltd.) were used as polymer substrates. The films were cleaned by ultrasonication in ethanol at 25ºC for 5 min before use.

Preparation of $[Ag(o\text{-}SPhCO_2H)]_n$ using Ag^+-doped polymer substrate. The polyimide films (1 × 2 cm) were initially immersed into a 5 M aqueous KOH solution at 50ºC for 3 min followed by rinsing with distilled water. Next, the modified films were immersed in a 100 mM aqueous $Ag(NO_3)$ solution at 25ºC for 20 min. After rinsing with distilled water, the ion-doped polymer films were immersed in an aqueous solution containing *o*-HSPhCOOH (20 mM), transferred to a microwave oven, and heated for 60 min at 180 ºC under microwave irradiation (Initiator+; Biotage). The obtained samples were rinsed three times with methanol.

Ligand exchange from $[Ag(o\text{-}SPhCO_2H)]_n$ to $[Ag(p\text{-}SPhCO_2H)]_n$ CPs. The obtained $[Ag(o\text{-}SPhCO_2H)]_n$ CP-based films were then immersed into a methanol solution containing *p*-HSPhCOOH (10 mM) and left standing for 120 min at 25 ºC. The obtained samples were rinsed three times with methanol.

Characterization. The surface morphologies of the obtained films were observed using scanning electron microscopy (SEM; JSM-7001FA, JEOL). X-ray diffraction (XRD) data were collected using a diffractometer (RINT-2200 Ultima IV, Rigaku) with Cu Kα radiation. The emission spectra were recorded using a spectrofluorometer (FP-6500, Jasco). The ratio of *p*-SPhCOOH to all the ligands (*o*-SPhCOOH and *p*-SPhCOOH) in the crystals was characterized using nuclear magnetic resonance (NMR; JNM-ECA500, JEOL). NMR samples were prepared by immersing the crystal films into the mixture solution containing DMSO-d_6 (1 mL) and 60% (v/v) HNO_3 (80 μL).

2. Preparation of [Ag(*o*-SPhCO$_2$H)]$_n$ using Ag$^+$-doped polymer substrate



Scheme S1. Schematic illustration of the formation of [Ag(*o*-SPhCO$_2$H)]$_n$ CPs.

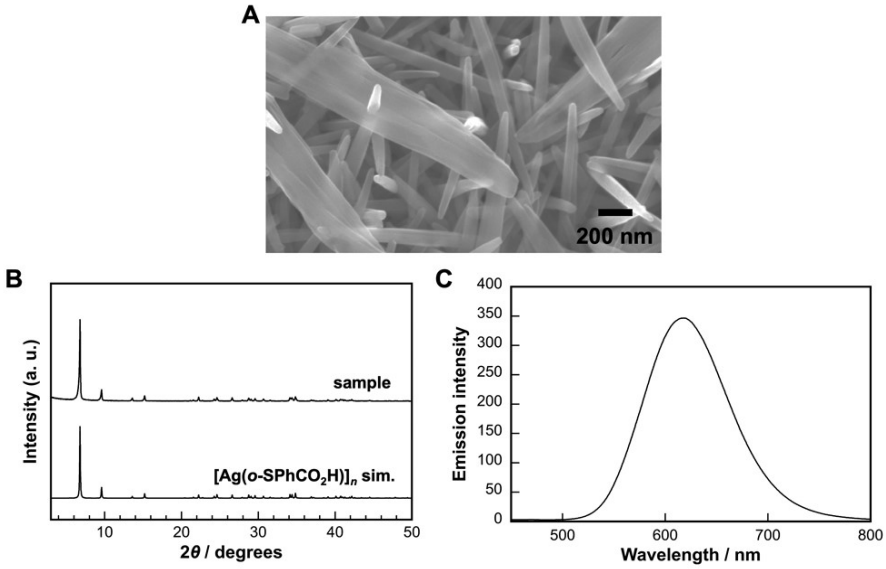


Figure S1. (A) SEM image, (B) XRD pattern, and (C) emission spectrum of the obtained samples by microwave irradiation using the Ag$^+$-doped polyimide film.

3. Influence of ligand concentrations on ligand-exchange rate and surface morphology of the obtained samples

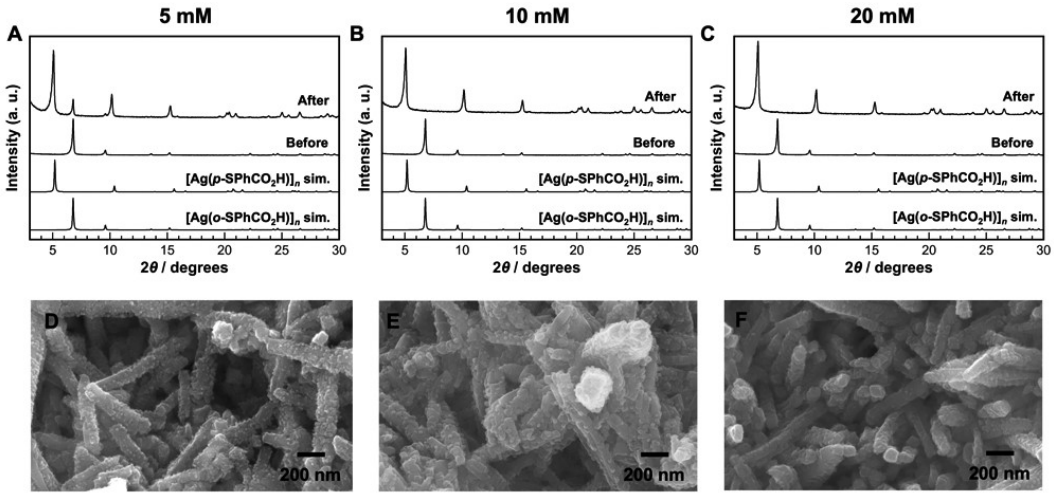
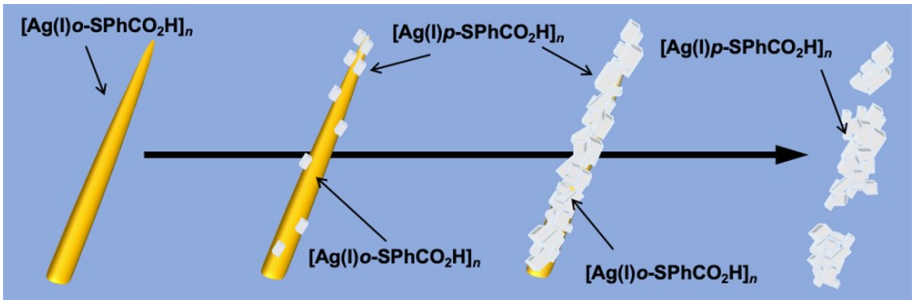


Figure S2. (A–C) XRD patterns and (D–F) SEM images of the obtained samples prepared by using ligand exchange solutions containing different ligand concentrations.

4. Schematic illustration of the crystal conversion by the ligand exchange



Scheme S2. Schematic illustration of the crystal conversion between [Ag(*p*-$SPhCO_2H$)]$_n$ and [Ag(*o*-$SPhCO_2H$)]$_n$ CPs by the present approach.