Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Site-selective growth of metal-organic frameworks using an interfacial growth approach combined with VUV photolithography

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Contents:

1. Experimental procedure

Materials:

Potassium hydroxide, copper nitrate trihydrate, aluminum chloride, 1,4-naphtalenedicarboxylic acid, 1,4-diazabicyclo[2.2.2]octane, 1,4-benzendicarboxylic acid, and disodium 1,4-dicarboxylate were purchased from Wako Chemicals Ldt. Terbium nitrate hexahydrate, 1-butanol, and ethanol were purchased from Kanto Chemical Ltd. All chemicals were used as-received. Pyromellitic dianhydride oxydianiline (PMDA-ODA) type polyimide films (50 μm thick, Kapton 200H, Toray-Du Pont Co. Ltd.) were used as polymer substrates. The films were cleaned prior to use by ultrasonication in ethanol at room temperature for 5 min.

Construction of MOF crystals:

The ion-doped polymer films with PMMA resist patterns were immersed into reaction solutions (5 mL) of organic ligands ($[Cu_2(ndc)_2(dabco)]_n$ framework: 1-butanol solution of 1,4-naphtalenedicarboxylic acid (10 mM) and 1,4-diazabicyclo[2.2.2]octane (5 mM), MIL-53 (Al) framework: aqueous solution of 1,4-benzenedicarboxylic acid (10 mM), and $[Tb_2(bdc)_3(H_2O)_4]_n$ framework: aqueous solution of disodium 1,4-benzenedicarboxylate (10 mM)), followed by heating for 1 h at 200 ºC with microwave irradiation (Initiator+; Biotage).

Characterization

AFM image of the obtained samples was collected by atomic force microscopy (AFM; VN-8000, KEYENCE). The surface morphology and thickness of the obtained MOF crystals were observed by scanning electron microscopy (SEM; JSM-7001FA, JEOL). X-ray diffraction data were collected on a Rigaku RINT-2200 Right System (Ultima IV) diffractometer with CuKα radiation. Elemental analysis of the obtained samples was perfomed using SEM equipped with an energy-dispersive X-ray (EDX) microanalyzer operating at 15 kV. Emission and excitation spectra were recorded using a spectrofluorometer (FP-6500, Jasco). Fluorescence image was obtained by fluorescence microscope (BX51, Olympus).

2. AFM Analysis of PMMA Resist Pattern

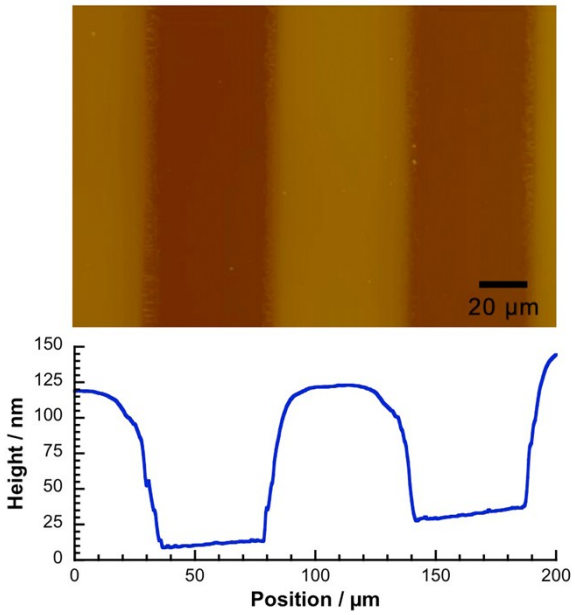

Figure S1. AFM image and height profile of PMMA pattern on the substrate.

3. XRD Pattern of $[Cu_2(ndc)_2(dabco)]_n$ Crystals

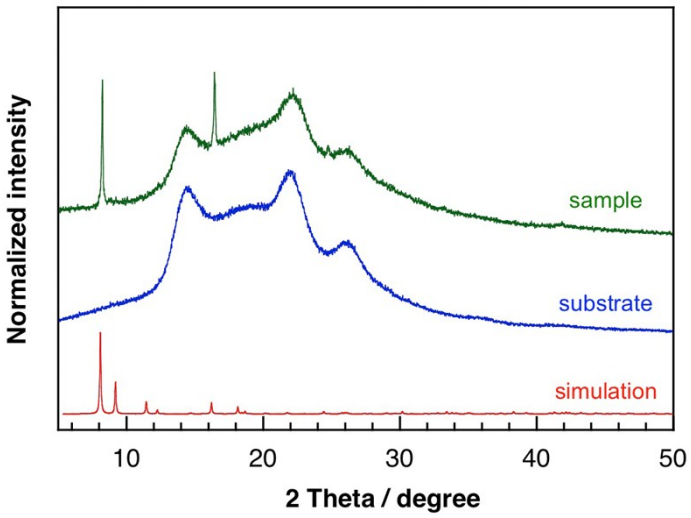

Figure S2. XRD pattern of $[Cu_2(ndc)_2(dabco)]_n$ crystals on a PMDA-ODA polyimide substrate with PMMA resist patterns.

4. XRD Pattern of MIL-53 (Al) Crystals

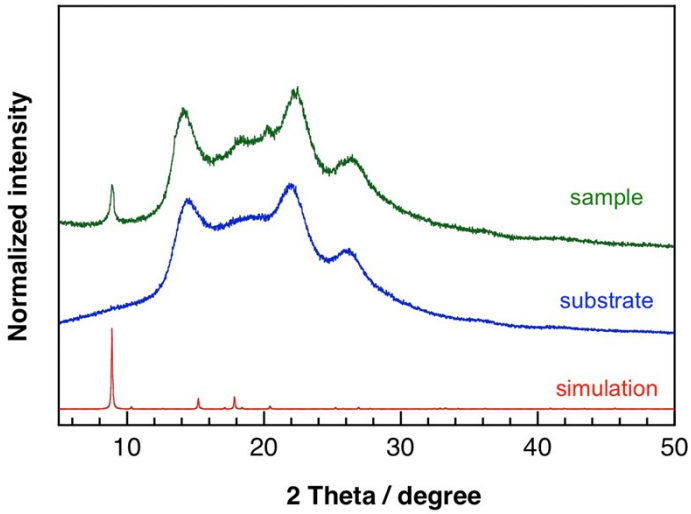

Figure S3. XRD pattern of MIL-53 (Al) crystals on a PMDA-ODA polyimide substrate with PMMA resist patterns.

5. EDX Mapping Image of $[Cu_2(ndc)_2(dabco)]_n$ Crystals

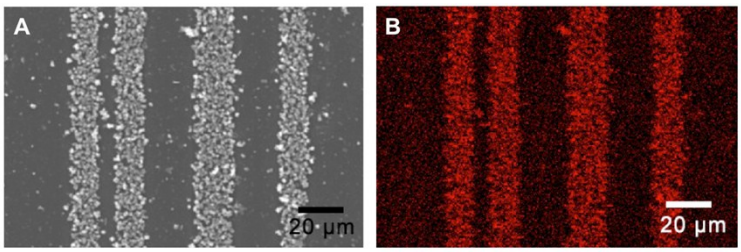

Figure S4. EDX mapping of Cu element (red color) of $[Cu_2(ndc)_2(dabco)]_n$ crystals on a PMDA-ODA polyimide substrate with PMMA resist patterns.

6. XRD Pattern and EDX Mapping Image of $[Tb_2(bdc)_3(H_2O)_4]_n$ Crystals

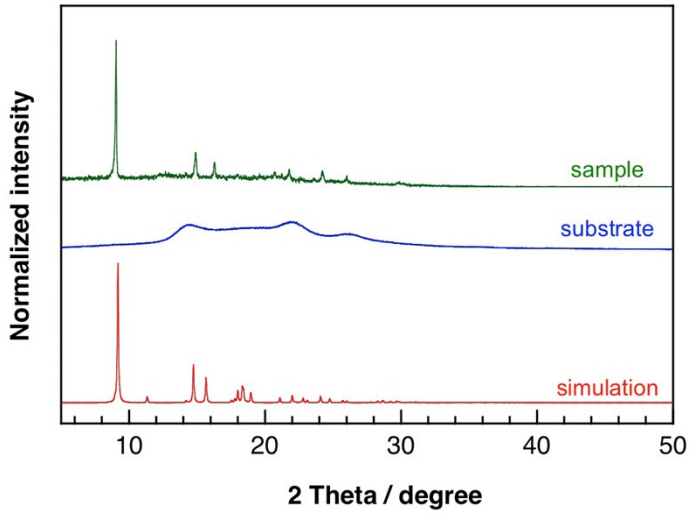

Figure S5. XRD pattern of $[Tb_2(bdc)_3(H_2O)_4]_n$ crystals on a PMDA-ODA polyimide substrate.

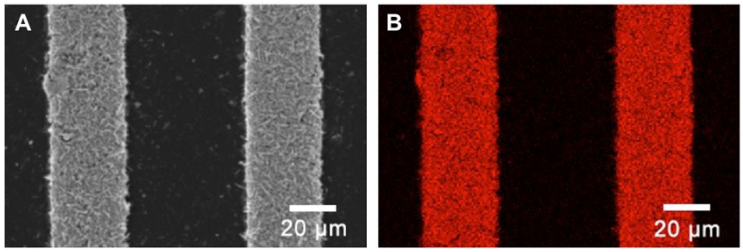

Figure S6. EDX mapping of Tb element (red color) of $[Tb_2(bdc)_3(H_2O)_4]_n$ crystals on a PMDA-ODA polyimide substrate with PMMA resist patterns.