Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Control of the nucleation and growth processes of metal-organic frameworks using a metal ion-doped polymer substrate for the construction of continuous films

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Experimental Procedure

Materials:

Potassium hydroxide, zinc nitrate hexahydrate, and sodium nitrate were purchased from Wako Chemical Ldt. Methanol and ethanol were purchased from Kanto Chemical Ltd. 2-Methylimidazole was purchased from Tokyo Chemical Industry Co. Ltd. All chemicals were used as-received. Pyromelitic 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 ZIF-8 crystals:

The polyimide films (1×2 cm^2) were initially immersed into a 5 M aqueous KOH solution at 50 ºC for 5 min, followed by through rinsing with copious amounts of distilled water. The modified films were then immersed into a 50 mM aqueous $Zn(NO_3)_2$ solution at room temperature for 20 min. After rinsing with distilled water, the ion-doped polymer films were immersed into a water/methanol (1/1) mixture solution (1000 mL) of 2-methylimidazole and $NaNO_3$ (500 mM and 100 mM, respectively) at room temperature for 72 h.

Characterization:

The surface morphology and thickness of the obtained ZIF-8 films were observed by 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

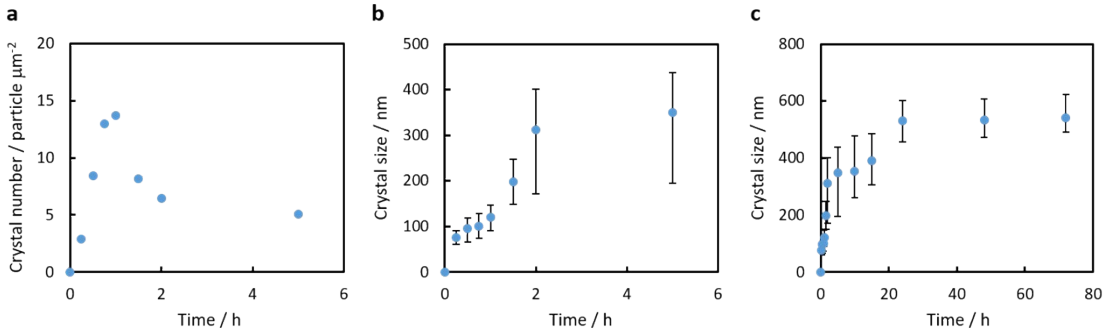

Figure S1 Variation in (a) crystal number, (b) crystal size of the samples in the early stage of the reaction within 5 h of the reaction, and (c) crystal size of the samples during reaction for 80 h.

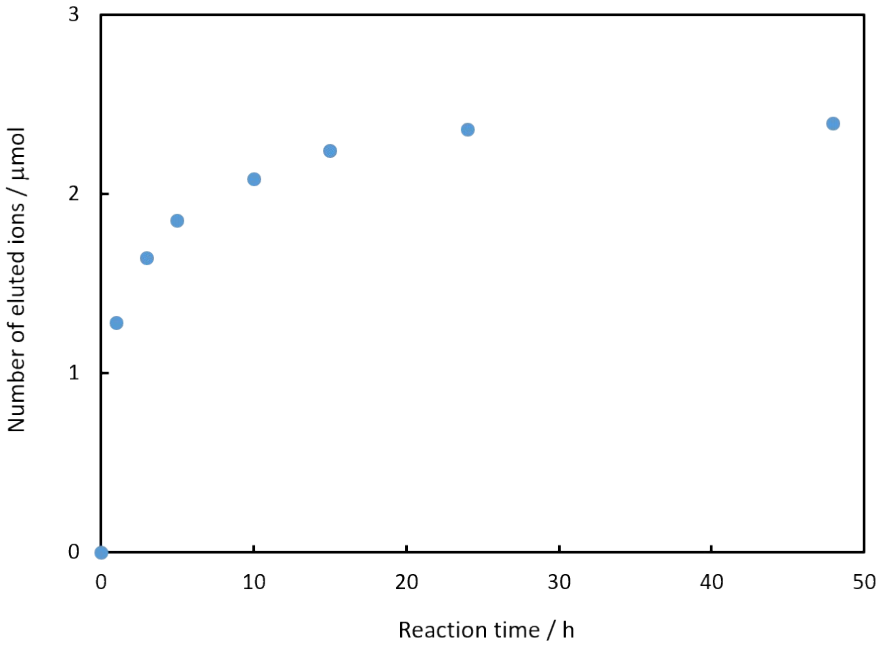

Figure S2. Elution rate of doped Zn^{2+} ions from polyimide film in H_2O/MeOH mixed solution at $NaNO_3$ concentration of 50 mM.

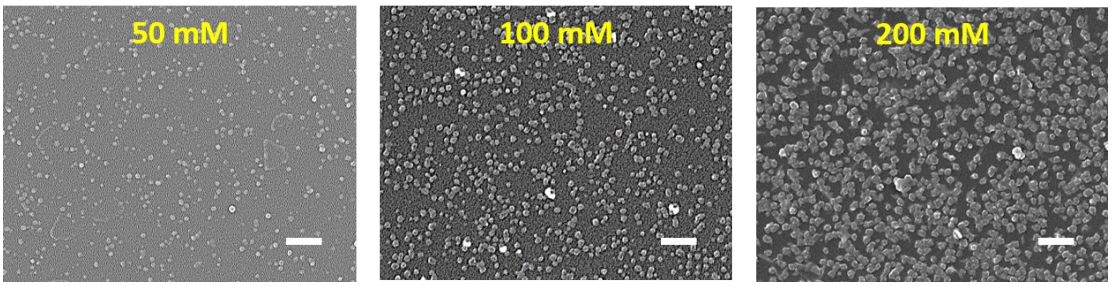

Figure S3. SEM images of ZIF-8 films obtained after 1 h reaction for $NaNO_3$ concentration of 50-200 mM. The MeIM ligand concentration was fixed at 500 mM. Scale bars are 500 nm.

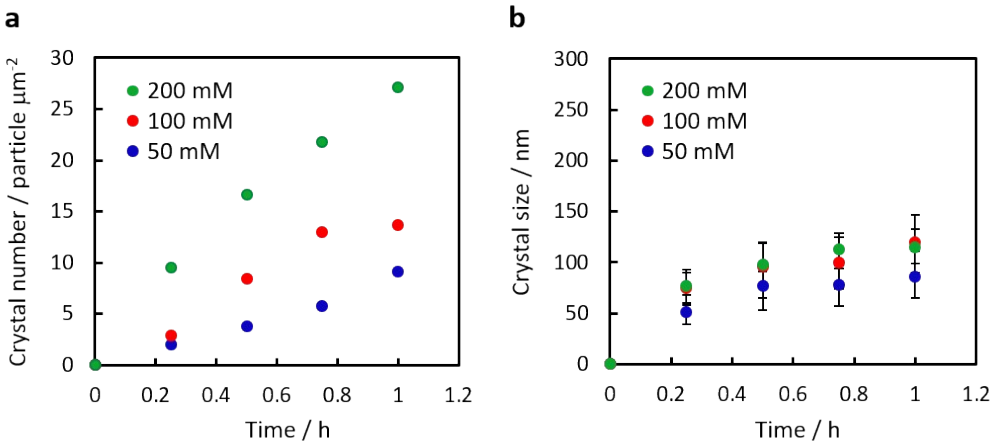

Figure S4. Variation in (a) crystal number and (b) crystal size of the samples obtained at initial reaction stage for $NaNO_3$ concentration of 50-200 mM. The MeIM ligand concentration was fixed at 500 mM.

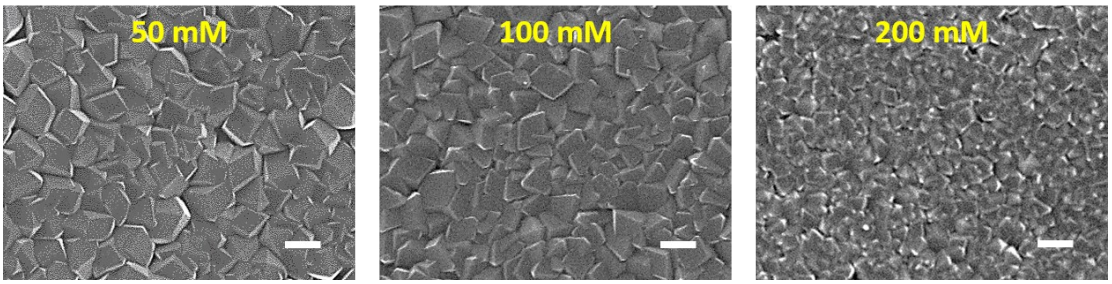

Figure S5. SEM images of ZIF-8 films obtained after 72 h reaction for $NaNO_3$ concentration of 50-200 mM. The MeIM ligand concentration was fixed at 500 mM. Scale bars are 500 nm.

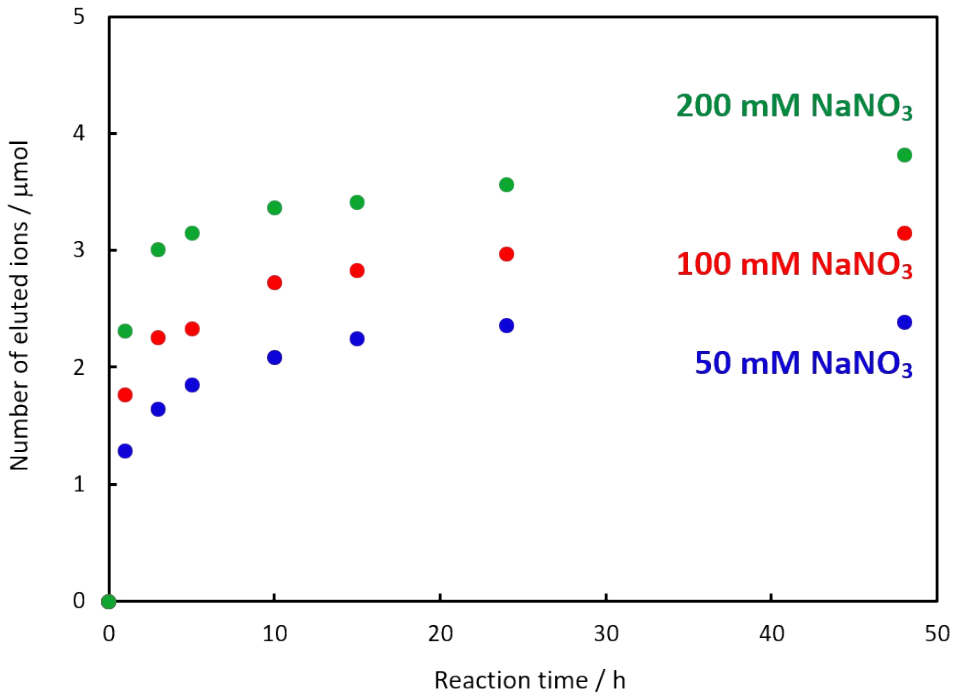

Figure S6. Elution rate of doped Zn^{2+} ions from polyimide film in H_2O/MeOH mixed solution including different $NaNO_3$ concentration of 50-200 mM.

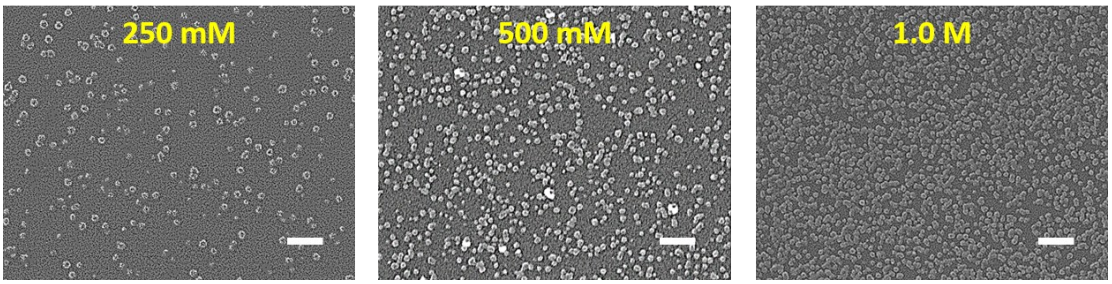

Figure S7. SEM images of ZIF-8 films obtained after 1 h reaction for MeIM ligand concentration of 250 mM-1.0 M. The $NaNO_3$ concentration was fixed at 100 mM. Scale bars are 500 nm.

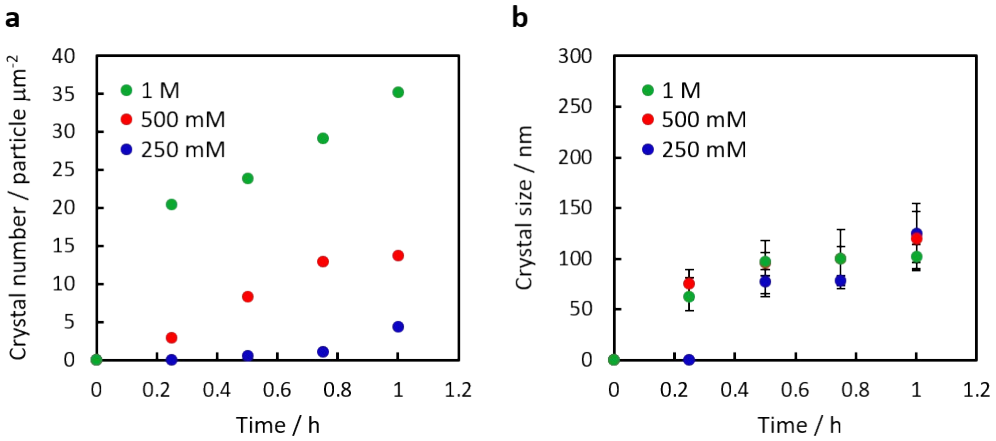

Figure S8. Variation in (a) crystal number and (b) crystal size of the samples obtained at initial reaction stage for MeIM ligand concentration of 250 mM-1.0 M. The $NaNO_3$ concentration was fixed at 100 mM.

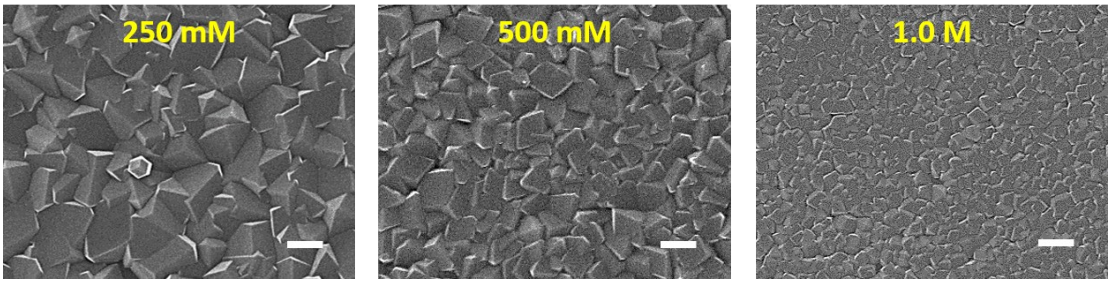

Figure S9. SEM images of ZIF-8 films obtained after 72 h reaction for MeIM ligand concentration of 250 mM-1.0 M. The $NaNO_3$ concentration was fixed at 100 mM. Scale bars are 500 nm.

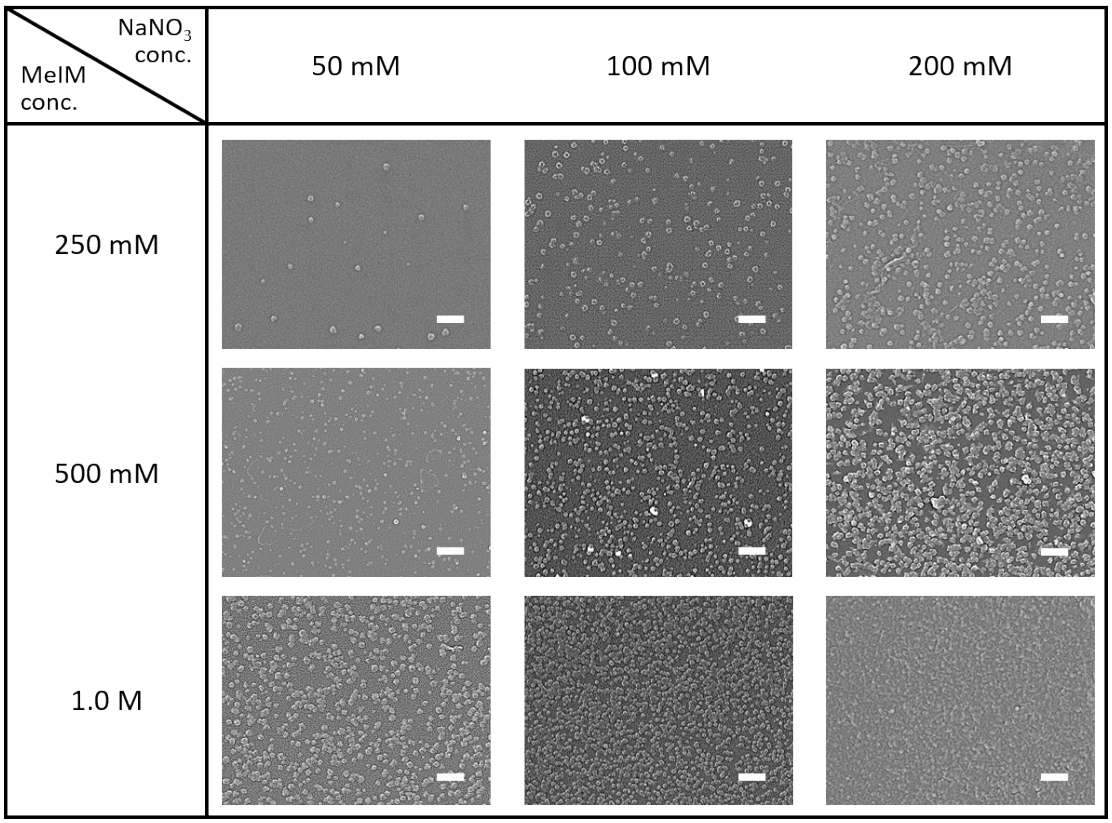

Figure S10. SEM images of ZIF-8 films obtained after 1 h reaction at different concentration of $NaNO_3$ and MeIM ligands. Scale bars are 500 nm.

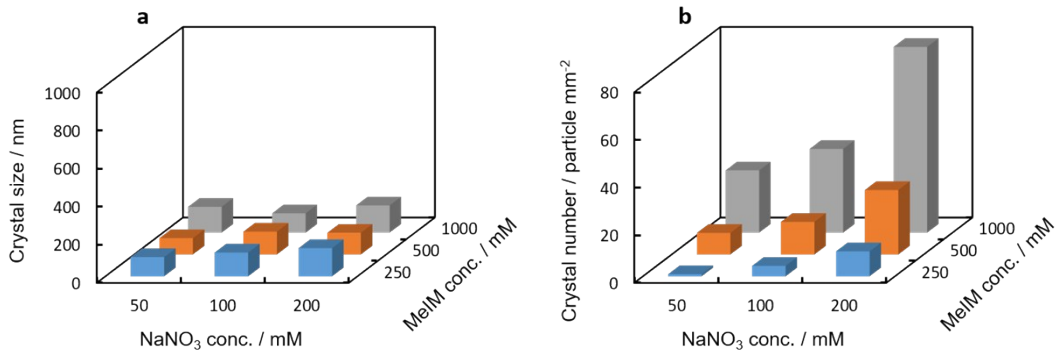

Figure S11. Variation in (a) crystal size and (b) crystal number of the samples obtained after 1 h reaction at different concentration of $NaNO_3$ and MeIM ligands.

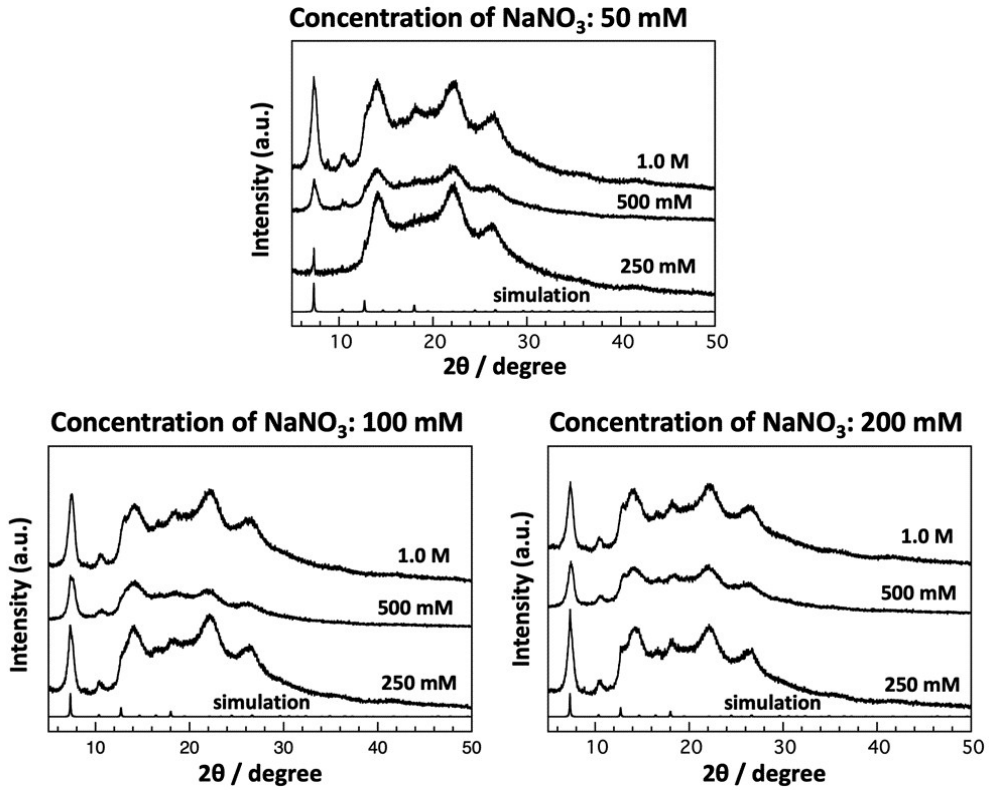

Figure S12. XRD pattern of the ZIF-8 films obtained after 72 h of reaction at different concentrations of $NaNO_3$ and MeIM.

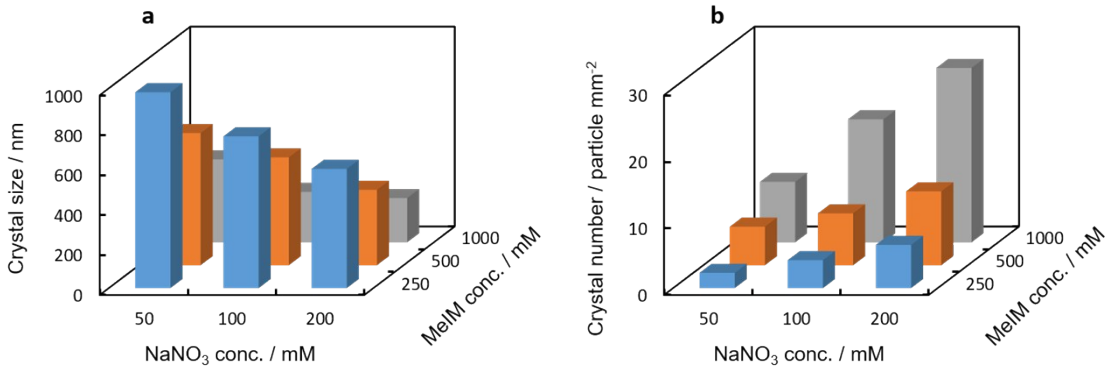

Figure S13. Variation in (a) crystal size and (b) crystal number of the samples obtained after 72 h reaction at different concentration of $NaNO_3$ and MeIM ligands.