Electronic Supplementary Information

In situ solvothermal growth of highly oriented Zr-based metal organic framework UiO-66 film with monocrystalline layer

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Experimental

Synthesis of UiO-66 films on Si substrates

$ZrCl_4$ (Sigma-Aldrich Japan K.K., Japan) and 1,4-benzenebicarboxylate (BDC; Sigma-Aldrich Japan K.K., Japan) were mixed with *N*,*N*-dimethylformamide (DMF; Nacalai Tesque Inc., Japan). Then, acetic acid (Nacalai Tesque Inc., Japan) and water were added to the solution and further mixed at room temperature for 20 min. The final composition of the precursor solution was 1 $ZrCl_4$: 1 BDC: 1 H_2O: 500 acetic acid: 1500 DMF. The silicon substrate (~1 cm × 1 cm) was horizontally introduced into a Teflon®-lined stainless steel autoclave, after which the precursor solution was added. Solvothermal reaction was carried out at 393 K for 24 h. After the solvothermal synthesis, the obtained film was immersed in water and rinsed with water several times. These steps were repeated up to three times. Then, the obtained films were dried at 373 K overnight. Furthermore, UiO-66 films were prepared in the absence of acetic acid or water accordingly by adjusting the composition of the precursor solutions using the same synthesis procedure. Additionally, to confirm the effect of acetic acid and water on the crystal growth of UiO-66, UiO-66 powder was synthesized using the same procedure, but in the absence of the Si substrate.

Chemical stability tests

Chemical stability of the UiO-66 film prepared in the presence of acetic acid and water was evaluated as follows. The UiO-66 film immersed in a 0.1M HCl aqueous solution for 6 h at an ambient temperature and rinsed by water and dried at 333 K. The crystallinity of the film was evaluated by the XRD measurement. Subsequently, the film post-treated by an acidic solution was immersed in a NaOH aqueous solution (pH= 11) for 6 h at an ambient temperature. After rinsing and drying, the film was evaluated again by the XRD measurement. The UiO-66 powder prepared in the same synthesis condition was tested according to the same procedure for comparison.

Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance (Bruker AXS K.K., Japan) using Cu Kα radiation. The crystalline morphology, and appearance and thickness of the films were assessed by scanning electron microscopy (SEM; Hitachi S-4800, Hitachi High-Technologies Corporation, Japan).

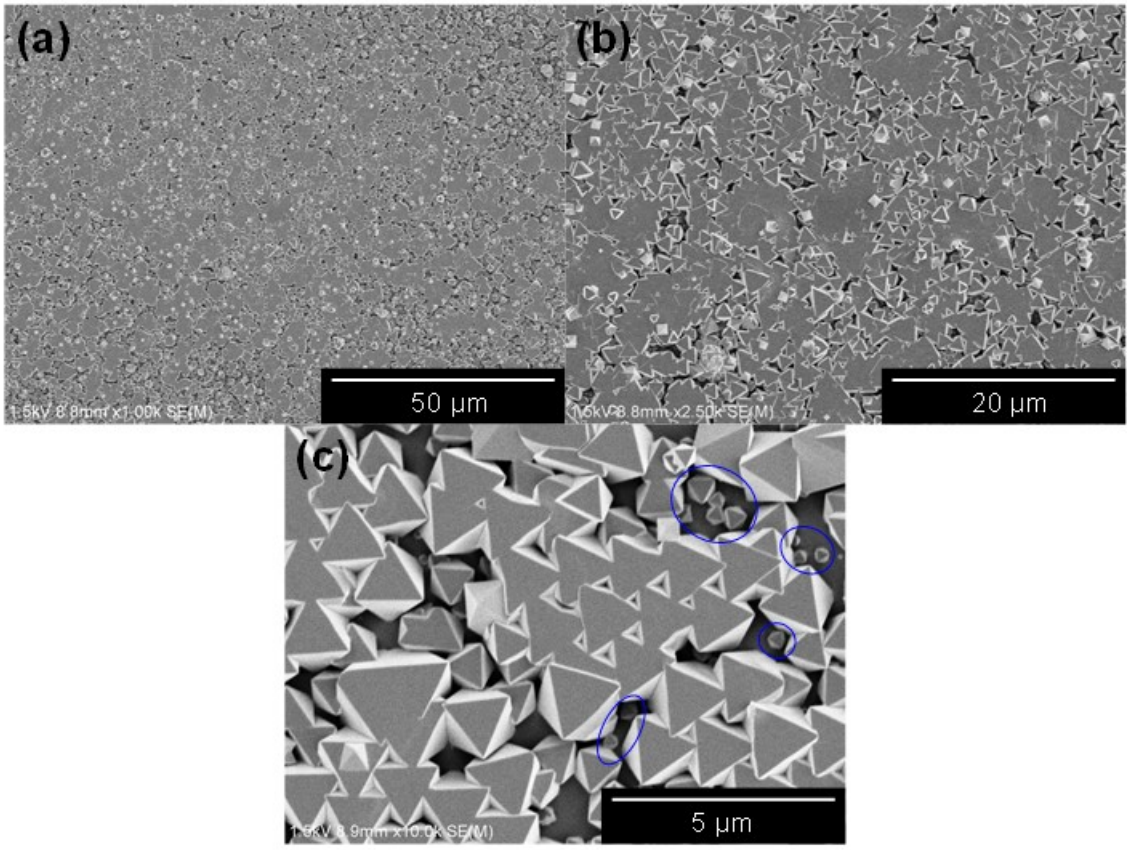

Fig. S1. SEM images of a UiO-66 film obtained after three solvothermal treatments in the presence of acetic acid and water. Nucleated small crystals obtained upon successive solvothermal treatments are indicated by the blue circles.

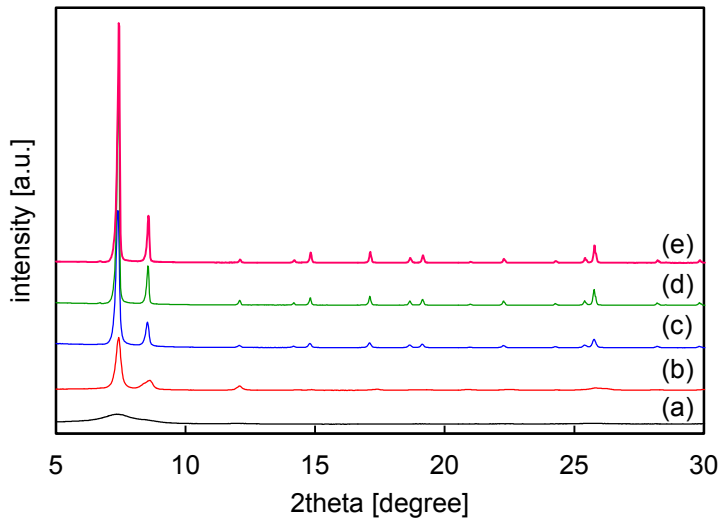

Fig. S2. XRD spectra of UiO-66 crystals synthesized at varying concentrations (*x* equivalents) of acetic acid. The molar composition of the precursor solution during synthesis was 1 $ZrCl_4$: 1 BDC: *x* acetic acid: 1500 DMF. (a) 0 equivalent, (b) 10 equivalent, (c) 100 equivalent, (d) 300 equivalent and (d) 500 equivalent.

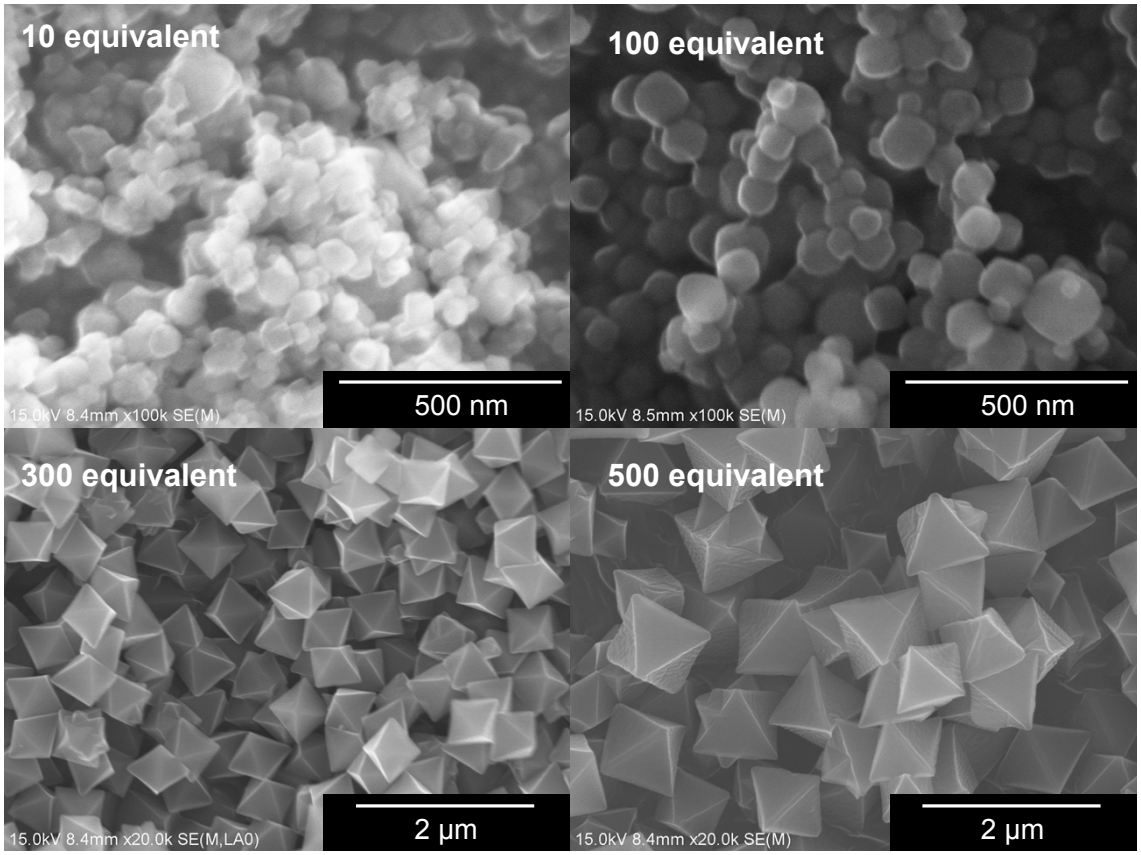

Fig. S3. SEM images of UiO-66 crystals synthesized at varying concentrations (*x* equivalents) of acetic acid. The molar composition of the precursor solution during synthesis was 1 $ZrCl_4$: 1 BDC: *x* acetic acid: 1500 DMF.

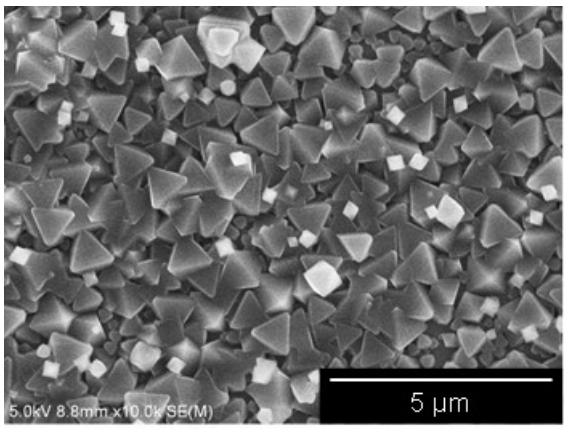

Fig. S4. SEM image of UiO-66 thin film on Si substrate obtained after three successive solvothermal treatments in the presence of acetic acid only.

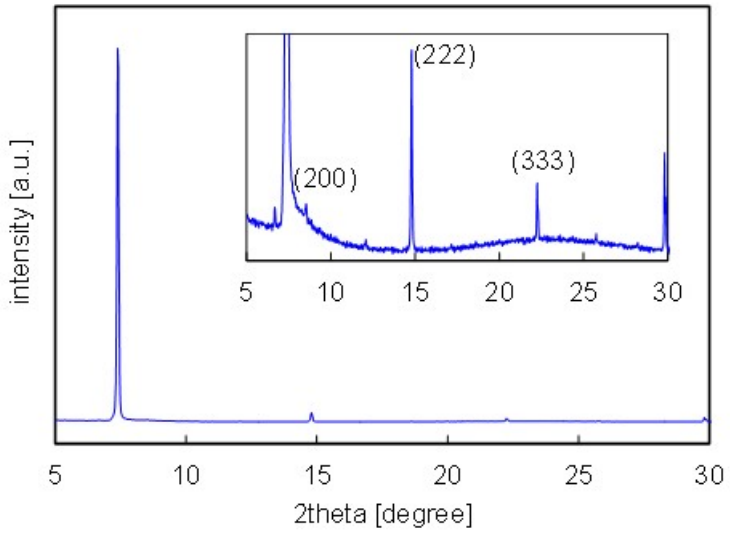

Fig. S5. XRD pattern of UiO-66 thin film on Si substrate obtained after three successive solvothermal treatments in the presence of acetic acid only.

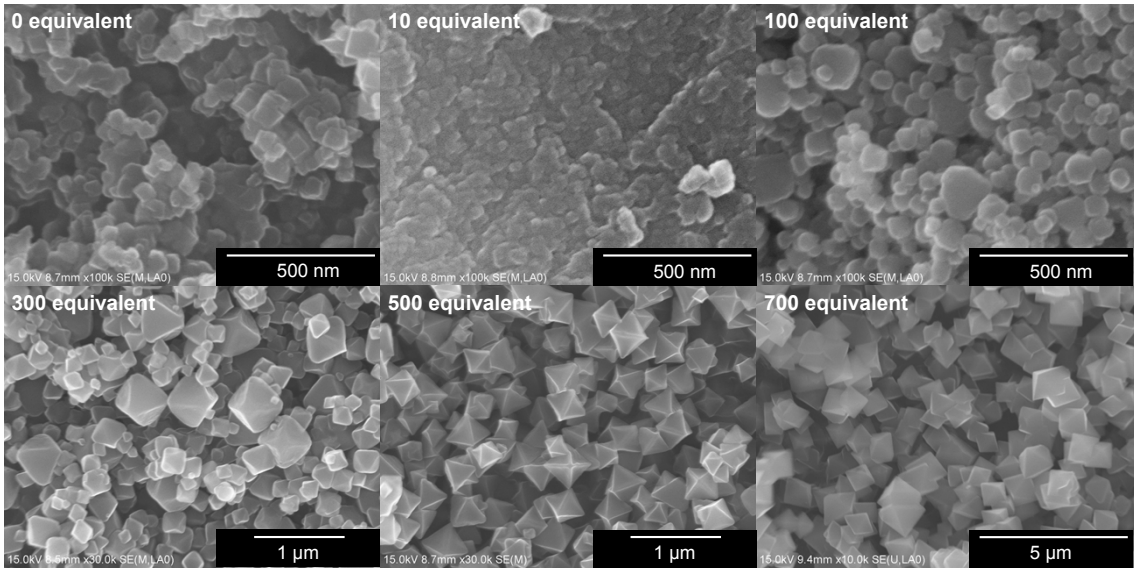

Fig. S6. SEM images of UiO-66 crystals synthesized at varying concentrations (*x* equivalents) of acetic acid in the presence of water. The molar composition of the precursor solution during synthesis was 1 $ZrCl_4$: 1 BDC: 1 H_2O: *x* acetic acid: 1500 DMF.

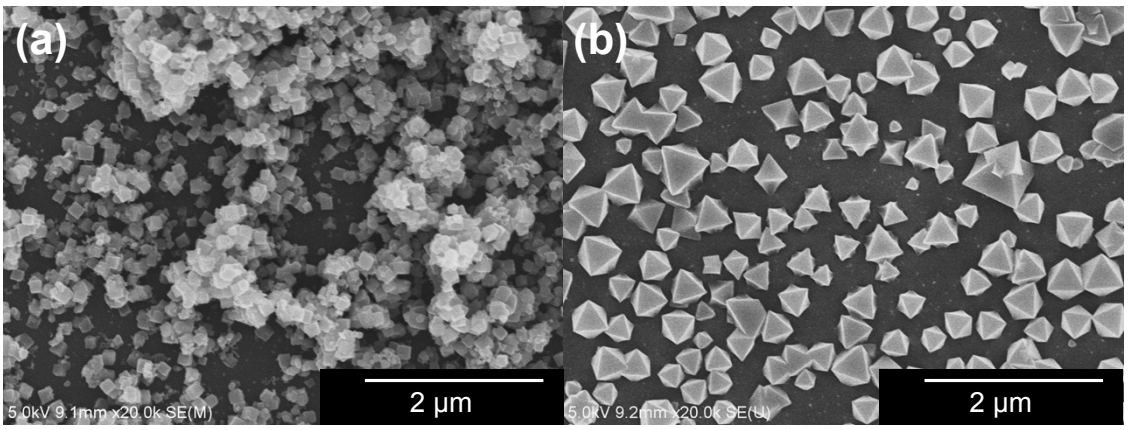

Fig. S7. SEM images of UiO-66 crystals on Si substrate obtained after one solvothermal treatment (a) in the presence of water only and (b) in the presence of acetic acid only.

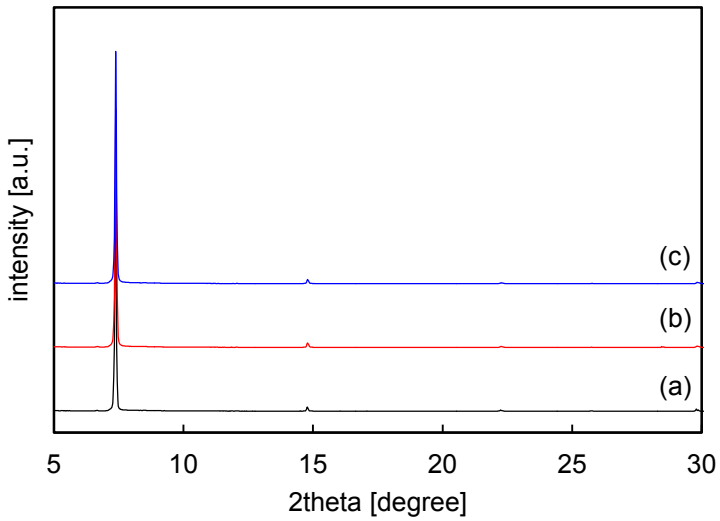

Fig. S8. XRD pattern of UiO-66 thin film on Si substrate obtained after three successive solvothermal treatments in the presence of acetic acid and water. a) as synthesized, b) 0.1M HCl aqueous solution for 6 h at an ambient temperature, c) NaOH aqueous solution (pH= 11) for 6 h at an ambient temperature.

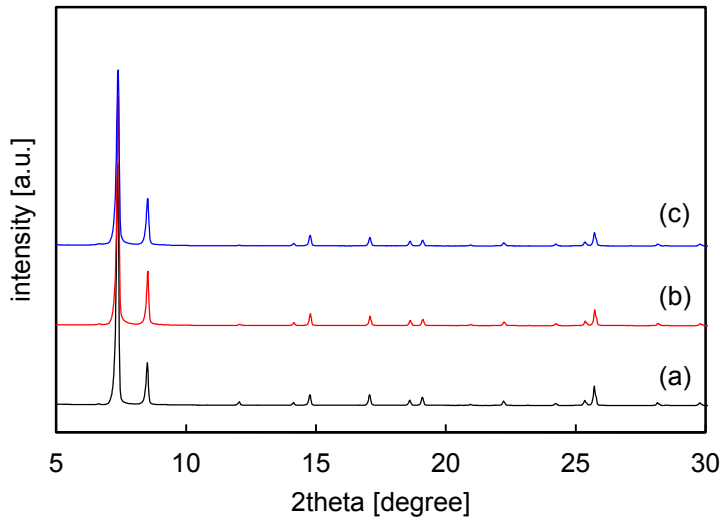

Fig. S8. XRD pattern of UiO-66 crystals prepared in the presence of acetic acid and water. a) as synthesized, b) 0.1M HCl aqueous solution for 6 h at an ambient temperature, c) NaOH aqueous solution (pH= 11) for 6 h at an ambient temperature.