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Electronic Supplementary Information

Ionic additive strategy to control nucleation and generate larger single crystals of 3D covalent organic frameworks

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1. Sample preparation procedure and list of chemicals used

All chemicals and solvents used in this report are listed in Table S1, and were used as received. The glass containers used for sample preparations described below were exclusively scientific screw-top glass vials (MPL, SR-21x40; capacity, 6 mL). Prior to use, the interior of the vials was blown with a jet of high-purity dry nitrogen gas (purity, >99.998%) passed through a hollow fiber filter unit. The vials were then washed once with ultrapure water (resistivity, 18.2 MΩ·cm) and then twice with high-purity methanol (purity, ≥99.9%) using an ultrasonic bath (Branson, 3510-DTH) for 2 min per washing step to ensure particulate removal from the inner vial wall. The vials were then dried at 70 °C before further use.

The entire sample preparation process is shown in Fig. 1 in the main text. First, BDA (**1**, 1 equiv.) and aniline (**3**, 13.2 equiv.) were dissolved in 1,4-dioxane, assisted by ultrasonication for 5 min, to achieve a concentration of 0.05 M for **1**. The resulting solution was then passed through a PTFE filter with a pore size of 200 nm (Merck-LG, SLLGX13NL) to remove any floating particulates from the liquid, which was denoted as "solution **A**". Separately, TAM (**2**, 0.5 equiv.) was dissolved in 1,4-dioxane in another vial, assisted by ultrasonication for 5 min, to obtain a concentration of 0.025 M for **2**. The resulting solution was then passed through a PTFE filter (same as above) to obtain "solution **B**". In a third vial, the additive (2.8 equiv. of the respective additive for #1–#8; 90 equiv. of H_2O (ultrapure water) for #0; nothing for #0′; 2.8 equiv. of decane for #0″) was uniformly mixed with glacial acetic acid (112 equiv.), assisted by ultrasonication for 5 min, to obtain "mixture **C**". Note that the volume of mixture **C** varied depending on the type of additive.

To grow COF crystals, solution **A** (0.28 mL) was added to the vial of mixture **C**, which was then subjected to ultrasonication for 5 min to homogenize the solution and promote the formation of precursor **4** (see Fig. 1 in the main text). Solution **B** (0.25 mL) was then added to the vial. The vial was immediately closed with a cap and gently shaken by hand for a few seconds. The mixture was transparent without turbidity and light scattering, as described in the main text. The vial was then stored in a dark and noiseless Peltier incubator kept at 22±0.5 °C until grown crystals were observed in the vial.

Table S1. List of chemicals used in this study.

Chemical name[a]	**Supplier**	**Purity (Supplier product #)**	**Descriptions**
Tetrakis(4-aminophenyl)methane, TAM	Accela ChemBio	99.2 % (NMR) (SY027348)	Building block, **1**
Terephthaldehyde, BDA	TCI	> 98.0 % (GC) (T0010)	Building block, **2**
Aniline	Sigma-Aldrich	≥ 99.5 % (GC) (242284)	Modulator, **3**
Acetic acid	Wako	> 99.5 % (HPLC) (010-19112)	Catalyst
1,4-dioxane	Wako	99.5+ % (GC) (048-03763)	Solvent
Decane	TCI	> 99.5 % (GC) (S0282)	Additive #0″
Na[NTf$_2$]	Sigma-Aldrich	97 % (NMR) (762377)	Additive #1
EIM[NTf$_2$]	Iolitec	> 98 % (NMR) (IL-0269-SG)	Additive #2
[C$_2$mim][NTf$_2$]	Iolitec	99 % (NMR) (IL-0023-HP)	Additive #3
[C$_2$mim][acetate]	Iolitec	> 98 % (NMR) (IL-0189-HP)	Additive #4
[C$_6$mim][NTf$_2$]	Sigma-Aldrich	≥ 99 % (HPLC) (490031)	Additive #5
[C$_{10}$mim][NTf$_2$]	Iolitec	> 98 % (NMR) (IL-0100-HP)	Additive #6
[N$_{8881}$][NTf$_2$]	Iolitec	99 % (NMR) (IL-0017-HP)	Additive #7
[N$_{8881}$]Cl	Sigma-Aldrich	≥ 97 % (AT) (69485)	Additive #8

[a] [EIM], 1-ethylimidazolium; [C$_n$mim], 1-*alkyl*-3-methylimidazolium; [N$_{8881}$], methyltrioctylammonium; [NTf$_2$], bis(trifluoromethylsulfonyl)amide.

2. Quantum chemical calculations of 4

To understand the properties of precursor species **4**, which was the expected product from mixing **1** and **3** (see Fig. 1a in the main text), quantum-chemical calculations were conducted using Gaussian 16® software.

The optical absorption spectrum of **4** was calculated at the CAM-B3LYP/6-31G++(d,p) level (CAM, Coulomb-attenuating method)[S1] specifying 1,4-dioxane as the solvent and setting the number of states to 50. The calculated spectrum (Fig. S1a) had an absorption peak at 344 nm, corresponding to the transition from the ground state to the lowest singlet state, supporting the attribution of the absorption feature observed at around 350 nm, as shown in Fig. 2a in the main text.

Furthermore, the charge distribution of **4** in the ground state was calculated at the B3LYP/6-31G++(d,p) level specifying 1,4-dioxane as the solvent. The result is shown in Fig. S1b, with red and blue colors representing negative and positive charges, respectively. As expected, considerable electronic polarization was observed around the imine bonds.

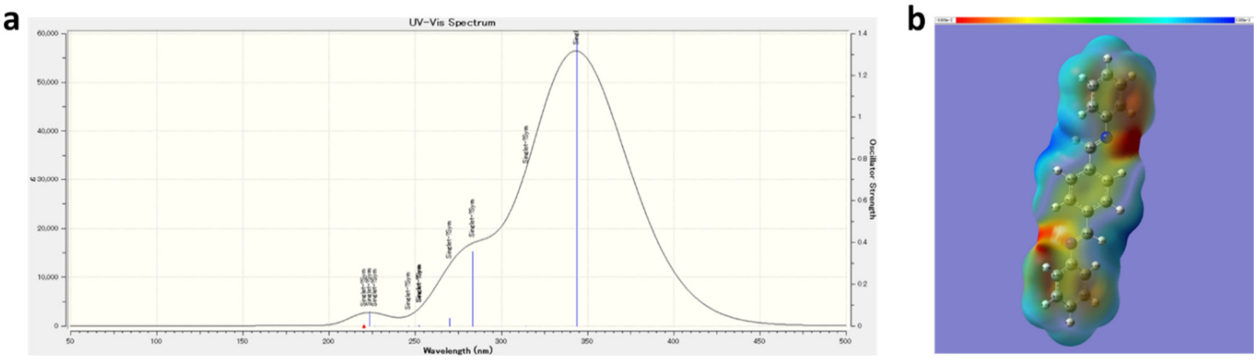

Figure S1. (a) Optical absorption spectrum and (b) electronic charge distribution (red, negative; blue, positive) of precursor species **4** calculated by Gaussian 16 specifying 1,4-dioxane as solvent.

3. Optical absorption spectra of all samples before adding 2

Figure S2 shows the optical absorption spectra of all samples before adding **2**. This confirmed that the initial amount of **4** formed by exothermic reaction between **1** and **3** (see Fig. 1a in the main text) was similar in all samples, suggesting that the reaction to generate **4** was almost quantitative.

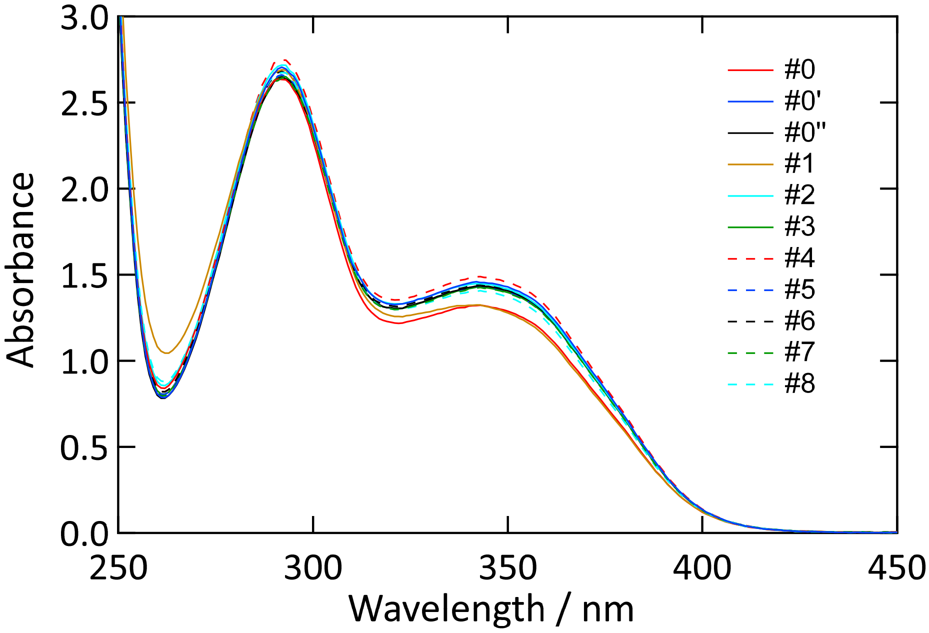

Figure S2. Optical adsorption spectra (path length, 1 mm) of all samples before adding **2**. To lower the absorbance magnitudes to a measurable range, all liquids were diluted 60-fold with dioxane before measurement.

4. Comparisons of crystal size distributions on days 7 and 20

Figure S3 compares the crystal size distributions of some representative samples on days 7 and 20. These results indicated that prolonging the growth time beyond 7 days did not greatly enhance the size. Accordingly, a growth time of 7 days was determined to be sufficient and applied in the present study.

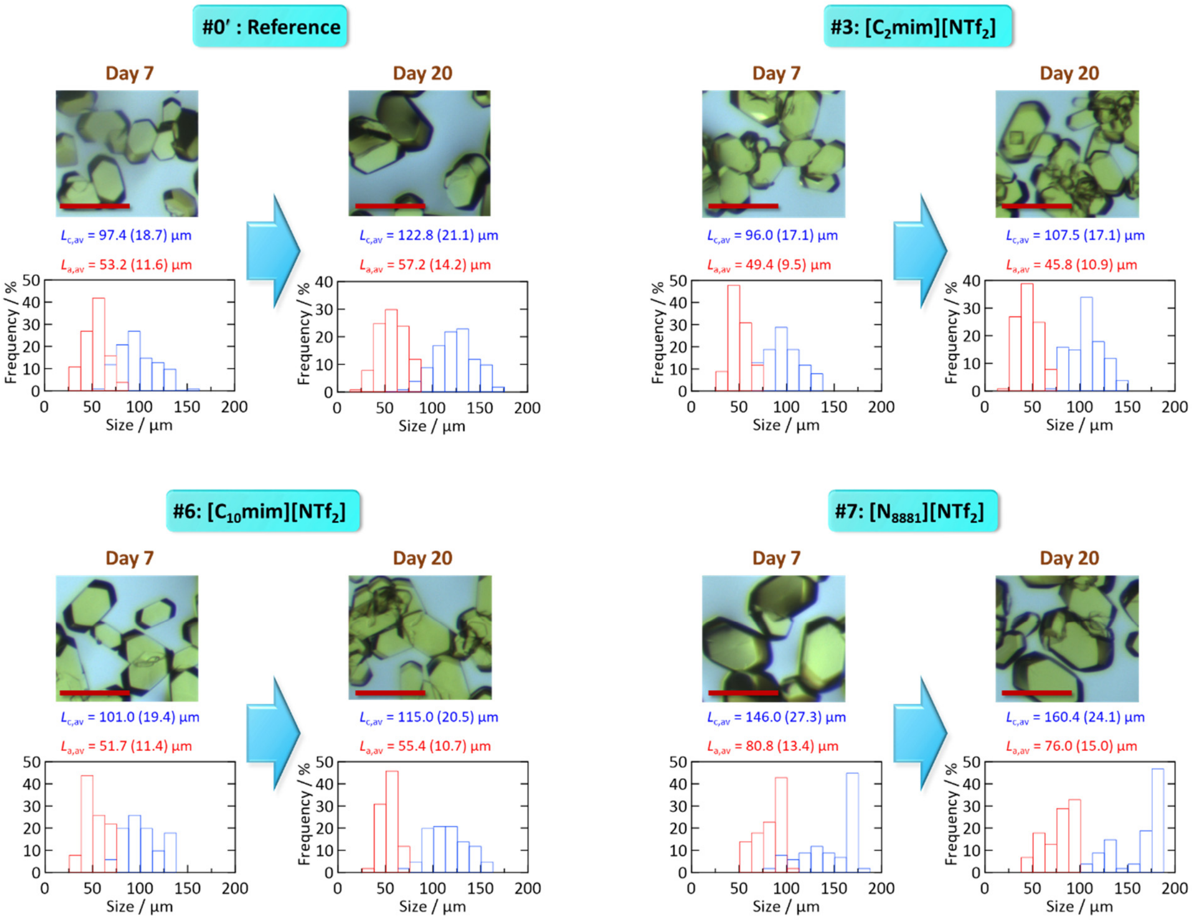

Figure S3. Optical micrographs and crystal size histograms (blue, c-axis, red, a-axis) for several representative samples, comparing days 7 and 20. Each histogram was constructed by measuring 100 crystals. Scale bars in the optical micrographs represent 150 μm.

5. Size distribution histograms for all experiments conducted three times

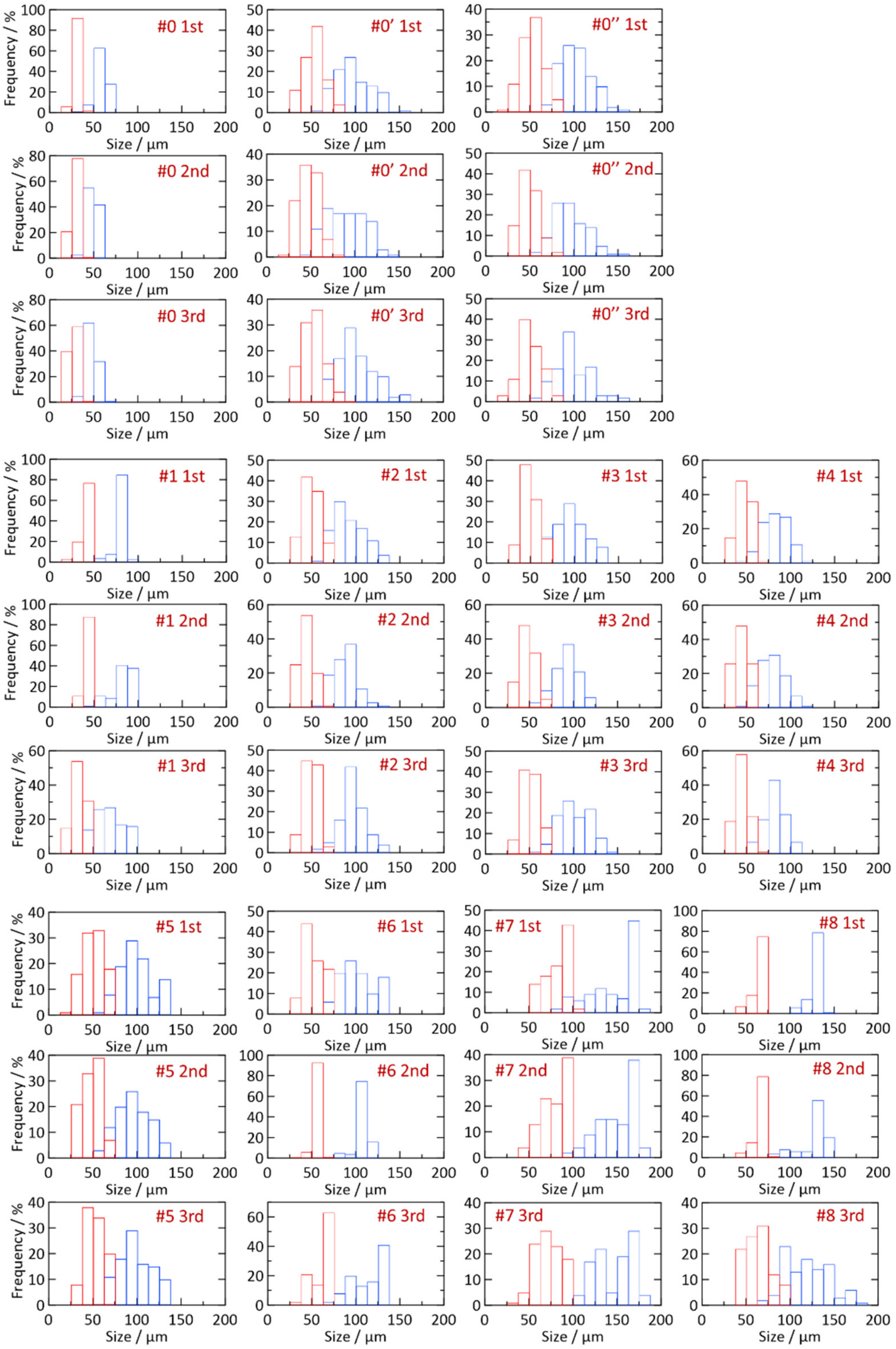

Figure S4. Size distribution histograms (blue, c-axis, red, a-axis) for all experiments conducted three times. Each histogram was constructed by counting 100 crystals.

6. Powder X-ray diffraction data

Figure S5 shows the typical powder X-ray diffraction (PXRD) pattern measured for COF crystals in this study, acquired after activation using Cu-Kα line (Rigaku, SmartLab). This pattern was in excellent agreement with the PXRD pattern of single crystals of ***dia-c7*** COF-300 created from the CIF data reported by Ma et al.[S2] as compared in this figure.

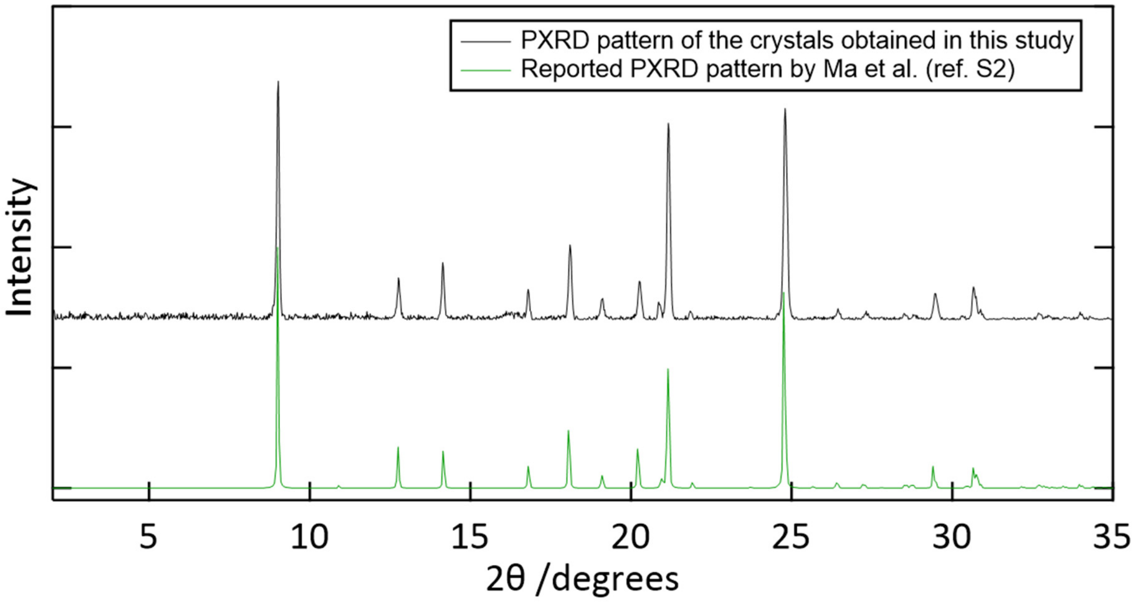

Figure S5. PXRD pattern for typical single crystals generated in this study after activation by vacuum-drying at 100 °C for 5 h (black), compared with the PXRD pattern of single crystals of ***dia-c7*** COF-300 reported in ref. S2 (green).

7. Check of single crystallinity by polarized light microscopy

In Fig. S6, the single crystallinity of a typical crystal for #7 generated in 7 days was confirmed using a polarized light microscope (Olympus, BX53).

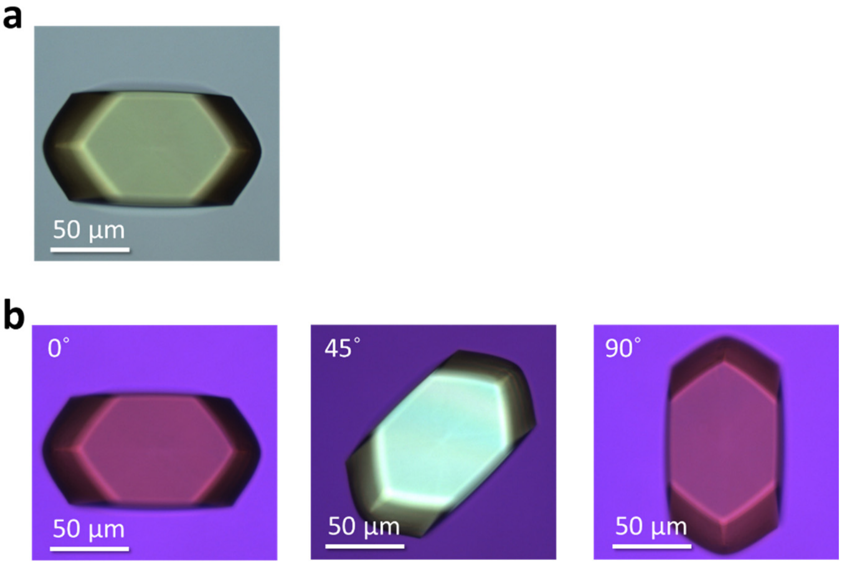

Figure S6. (a) Optical microscope image of a typical crystal generated in sample #7. (b) Polarized light microscope images of the same crystal, indicating the single crystallinity consisting of a single domain.

8. Porosity data

To investigate whether the large size COF-300 crystals grown with ionic liquid additives can be activated similar to those grown without additive, and hence to elucidate whether or not the ionic liquid additive remained in the pores even after washing and activation, we conducted nitrogen (N_2) adsorption measurements at 77 K and compared the porosities of COF-300 crystals prepared with and without ionic liquid additive.

Specifically, we compared the porosities of the samples generated in #0′ (grown without additives) and #7 (grown with additive) after they were washed and activated by the following method. First, the as-grown crystals were immersed in dioxane for 10 h and then in acetone for 10 h, during which each solvent was decanted and freshly replenished three times. Then, the crystals were immersed in toluene for about 5 h. Subsequently, the crystals were collected and dried in vacuum (less than 5 Pa) under a flow of N_2 gas (50 sccm) at 120 °C for 12 h. In this treatment, the temperature of 120 °C and vacuum state were gradually attained spending ca. 1.5 h from the room temperature and atmospheric pressure to change the temperature and pressure mildly.

After the dried crystals (ca. 30 mg) were loaded in a glass tube cell and the cell was mounted to an adsorption analyzer (Micromeritics, 3Flex), an additional activation was carried out under ultra-high vacuum ($\sim 10^{-5}$ mmHg) at 120 °C for 5 h. After this activation, adsorption measurements started at 77 K with ultra-high-purity N_2 gas (over 99.9995% purity).

The adsorption isotherms for these samples are shown in Fig. S7, from which the following two points are recognized. First, both samples showed very small N_2 uptake of less than 10 cm^3 g^{-1}. This small uptake agreed well with the results of a recent report[S3] that revealed a monotonous decrease of N_2 uptake with increasing the crystal size of COF-300. In that paper, N_2 uptake decreased from 400 cm^3 g^{-1} for COF-300 crystals with the size of 500 nm to below 100 cm^3 g^{-1}

for the crystals with the size of 30 μm owing to the increased rigidity of the activated COF-300 crystal.[S3] Therefore, the very small N_2 uptakes found in Fig. S7 are quite reasonable considering the fact that the sizes of our COF-300 crystals were far larger (cf. Table 1 in the main text) than those used in ref. S3. Second, the isotherm of #7 was quantitatively very similar to that of #0′, suggesting that the use of the additives did not alter the porosity of the crystals after activation. Therefore, the results here indicate that the crystals grown with the additive can be activated similar to the crystals grown without additives after proper washing treatments were taken.

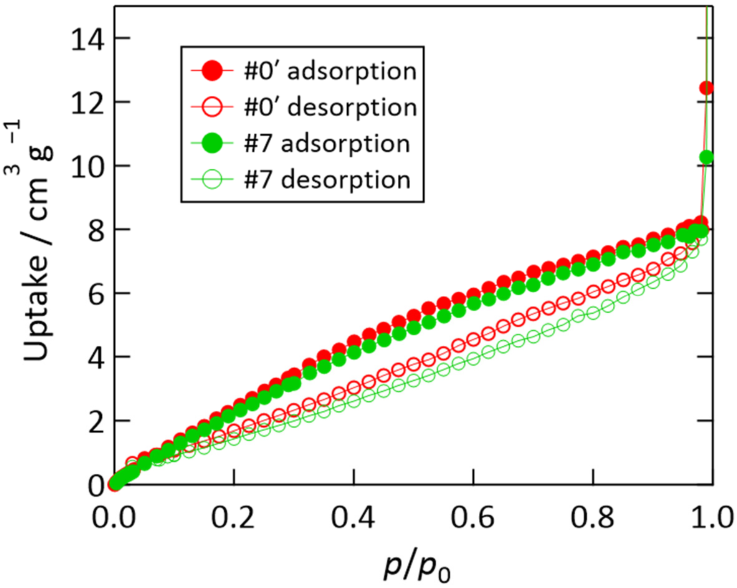

Figure S7. N_2 adsorption isotherms acquired at 77 K for the activated crystals generated in #0′ (red) and #7 (green).

9. X-ray fluorescence data

In a previous paper from Qianrong Fan's group,[S4] ionic liquids were used as solvent for 3D-COF growth, succeeded in formations of ionic-liquid-containing 3D-COFs termed as "3D-IL-COFs". These authors showed that ionic liquids remained in the pores of their COFs even after washing with ethanol and acetone.[S4] In contrast, the present study used ionic liquids as additives, whose amount was only 2.8 equiv. of **2** and 2.5 mol% of acetic acid (see the main text). Here, we investigate whether or not the ionic liquid additives used in this study remain captured by the channels of COF-300 crystals even after washing treatment with organic solvents.

For this investigation, we employed two types of washing processes, **method 1** and **method 2**. In **method 1**, as-grown COF crystals (3−5 mg) was separated on a round PTFE filter (ADVANTEC, T100A025A, diameter: 25 mm). Then, using a Pasteur pipette, dioxane (2 mL), ethanol (10 mL), and finally acetone (10 mL) were slowly dropped onto the crystals on the PTFE filter. In **method 2**, the liquid in the glass vial, where the COF crystals had grown (see Section 1 of this ESI), was decanted and then the vial was replenished with dioxane (ca. 2 mL) and held for 10 h. Subsequently, the dioxane was decanted and replenished with acetone (ca. 3 mL) and held for 10 h. Finally, the crystals were separated on a PTFE filter.

The crystals washed by either of these methods were naturally dried on the filter in atmospheric environment. Finally, they were ground in a quartz mortar to obtain fine powders. Thereby prepared COF powders were analyzed with an X-ray fluorescence (XRF) spectrometer (Rigaku, NEX DE) to find out whether the ionic liquids were captured in these COF-300 crystals.

Figure S8 shows the XRF spectra obtained for the samples #2, #3, and #7. For all of them, signal of sulfur, which is an indicator of [NTf_2^-] anion of the ionic liquids, was not detected at all. Therefore, the ionic liquids, regardless of their molecular size, were not strongly captured by the pores of the COF-300 crystals and thus could readily be removed by washing treatments using organic solvents.

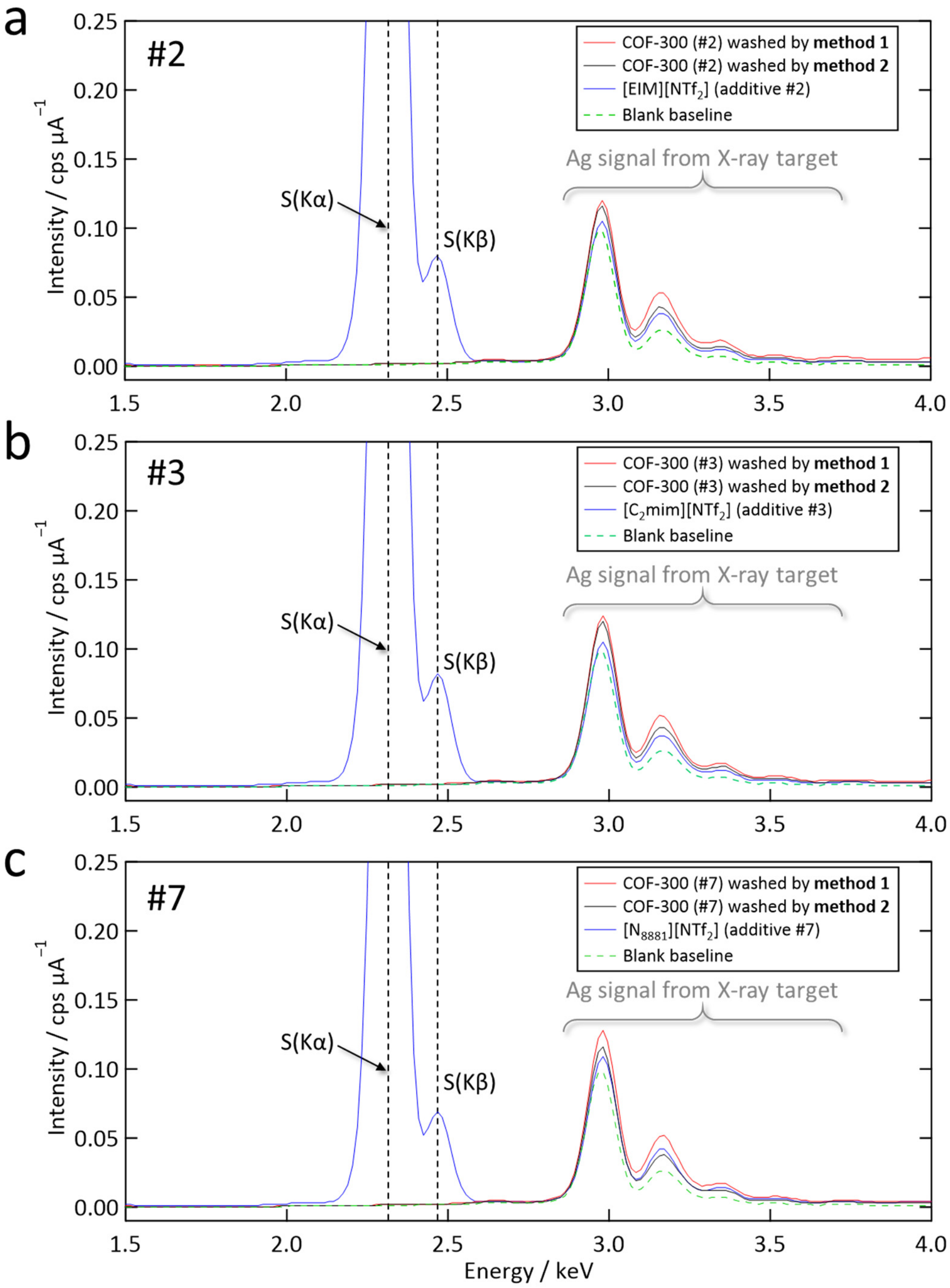

Figure S8. XRF spectra acquired for the samples (a) #2, (b) #3, and (c) #7 washed by **method 1** (red) and **method 2** (black). Spectra of neat ionic liquids (blue) and blank baseline (green) are also shown.

10. Results when previously reported concentration conditions were used

Figure S9 shows the results of crystal growth for 7 days conducted for selected additives using almost the same concentrations of the reactants (0.1 M for **1** and 0.05 M for **2** in 0.5 mL dioxane), aniline modulator (0.06 mL, 13.2 equiv. to **1**), and acetic acid (0.1 mL of 6 M aqueous solution) as those originally used by Ma et al.[S2] Although the crystal sizes were much smaller, the tendencies in the crystal sizes over the additive type were consistent with the tendencies found in Fig. 3a of the main text.

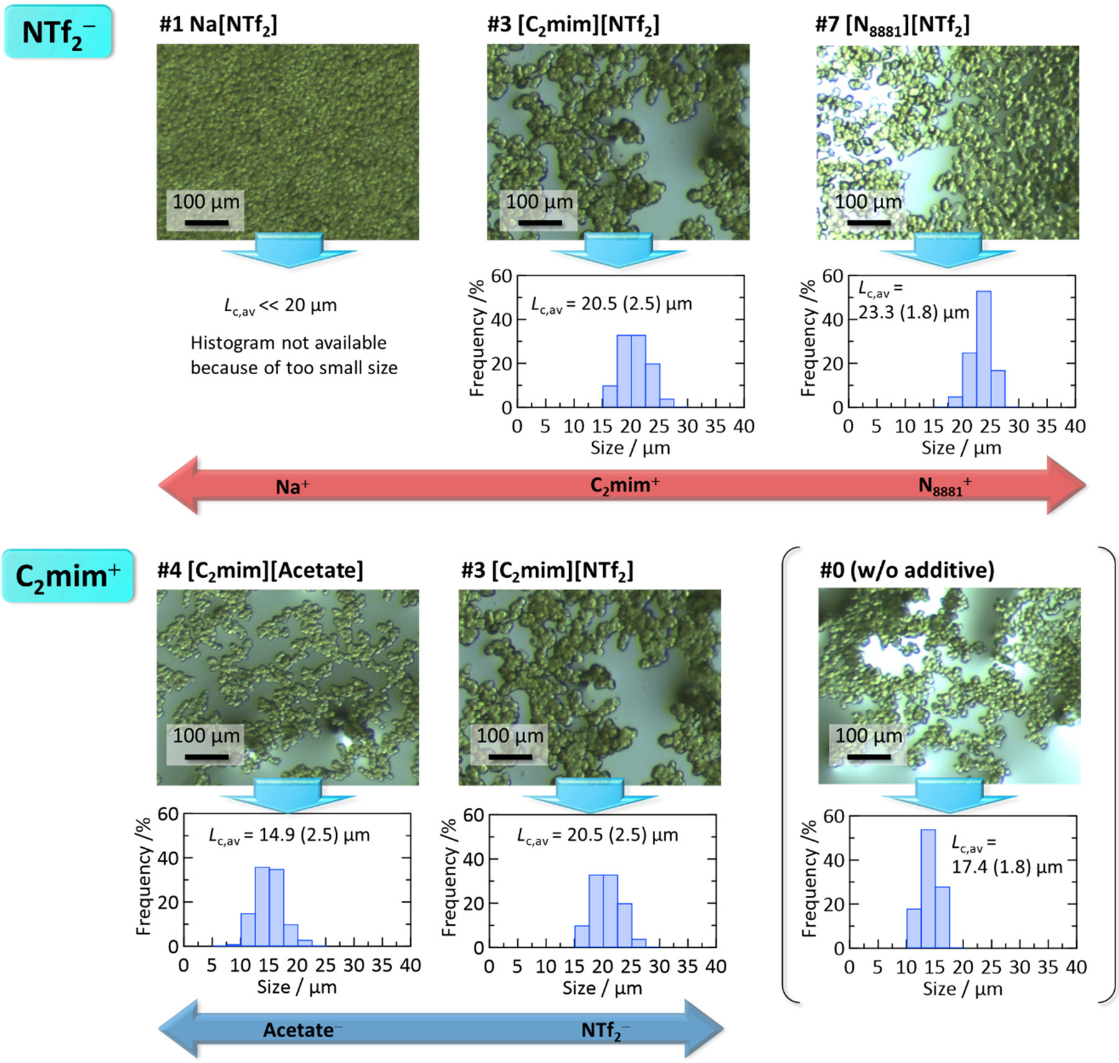

Figure S9. Optical micrographs and size distribution histograms of the crystals grown for 7 days using the original concentrations of the reactants and aqueous acetic acid employed in ref. S2. Each histogram was constructed by counting 100 crystals.

11. Correlation with acceptor number

Figure S10 shows the plot of average crystal size along the c-axis ($L_{c,av}$) against Gutmann acceptor number (AN), where no clear correlation was found. Owing to the highly limited availability of experimental AN values, the only experimentally determined ANs were those of [C_2mim][NTf_2][S5] and water.[S6] Other ANs were calculated from experimentally determined Kamlet–Taft parameters of respective species using the conversion relation reported by Marcus.[S6] Specifically, ANs of [C_2mim][acetate] and decane were calculated from their Kamlet–Taft parameters reported in refs. S5 and S6, respectively. The ANs of [C_6mim][NTf_2], [C_{10}mim][NTf_2], and [N_{8881}][NTf_2] were calculated from their Kamlet–Taft parameters reported in ref. S7. The AN of [N_{8881}][Cl] was calculated from the Kamlet–Taft parameter reported in ref. S8.

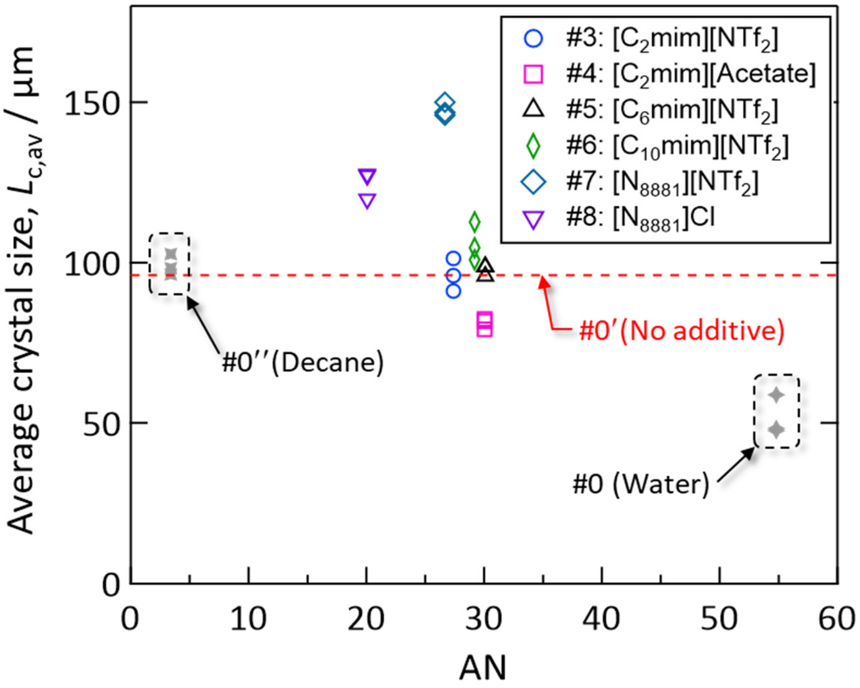

Figure S10. Plot of average crystal sizes along the c-axis after 7 days of growth against ANs of the additives, with three data points shown for each condition. Each datapoint is an average for 100 crystals (see Fig. S4).

12. Dependence of crystal size on the amount of [N_{8881}][NTf_2]

Figure S11 shows the dependence of the average crystal size after 7 days of growth on the amount of [N_{8881}][NTf_2] added. Although the dependence was rather weak, a moderate maximum was observed at around 1.9 equiv.

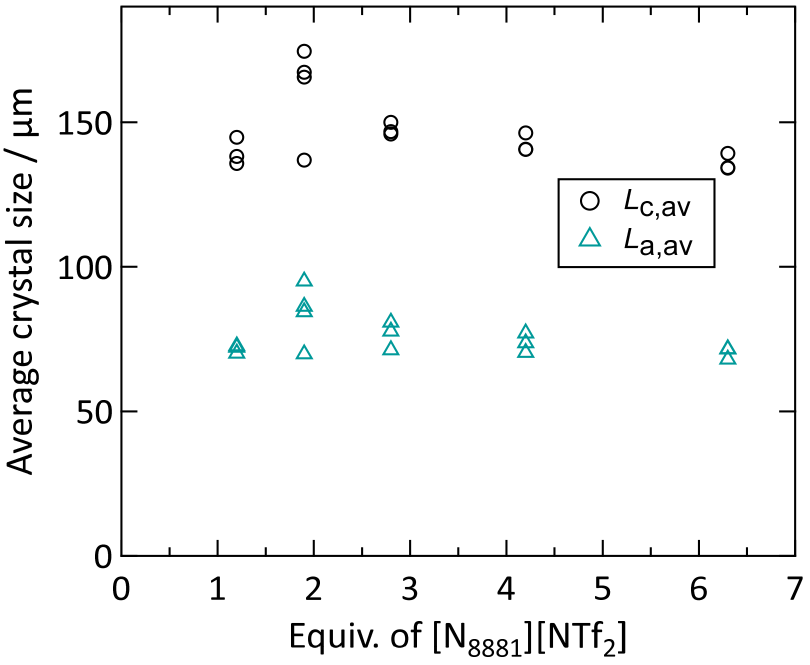

Figure S11. Dependence of average crystal size after 7 days of growth on amount of [N_{8881}][NTf_2] added. Molar equivalence is relative to BDA (**1**). Three or four data points are shown for each condition to demonstrate reproducibility, with each data point an average for 100 crystals.

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