Supporting Information for

Transformation of Metal-Organic Framework to Polymer Gel by Cross-Linking the Organic Ligands Pre-organized in Metal-Organic Framework

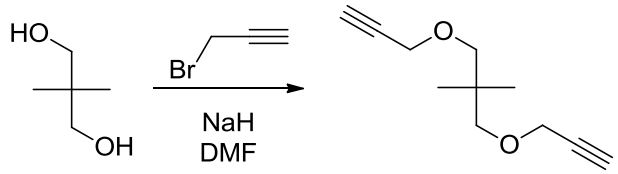
Takumi Ishiwata[1], Yuki Furukawa[1], Kouta Sugikawa[2], Kenta Kokado[1,3], and Kazuki Sada[1,3]

[1]Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, 060-0810, Japan

[2]Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka, 819-0395, Japan

[3]Department of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, 060-0810, Japan

Synthesis of CL2



Anhydrous DMF (10mL) was added to a 50 mL round-bottom flask containing neopentyl glycol (1.00g, 9.6 mmol) and sodium hydride (60% oil dispersion, 1.80g, 45 mmol) at 0 °C, and the mixture was stirred at room temperature for 3 h. After cooled to 0 °C again, propargyl bromide (5.70mL, 77 mmol) was added to the mixture, and it was stirred at room temperature for 24 h. The reaction was quenched by addition of small quantity of methanol at 0 °C, and dissolved in ether. The organic phase was washed with water, and dried over $MgSO_4$. The solvent was removed by rotary evaporator, and the residue was purified by silica gel column chromatography (EtOAc/hexane = 1/4) to obtain **CL2** as a yellow oil (0.91 g, 52%). ^{1}H NMR (300 MHz, $CDCl_3$, TMS standard, r.t.): δ (ppm) 0.93 (s, 6H, -C*H*$_3$), 2.40 (t, *J* = 2.33 Hz, 2H, -C≡C*H*), 3.29 (s, 4H, -O-C*H*$_2$-), 4.13 (d, *J* = 2.22 Hz, 4H, -C≡C-C*H*$_2$-). HRMS (ESI) [M+Na] Calcd: m/z 203.1043, Found: m/z 203.1051.

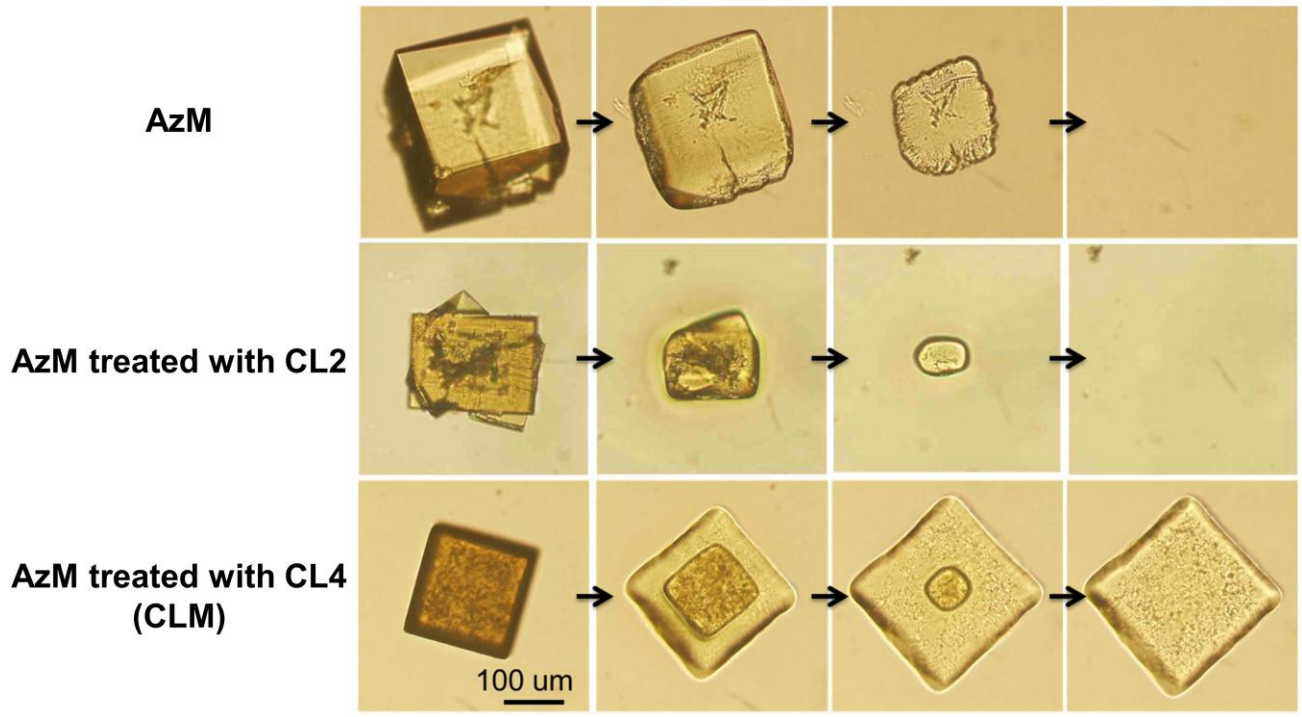


Figure S1. Optical microscopy images following the hydrolysis reaction of **AzM**, **AzM** treated with **CL2**, **AzM** treated with **CL4**.

Figure S2. Photograph of sample vial containing resulting powdery product after simultaneous click reaction during the crystallization process of **AzM**.

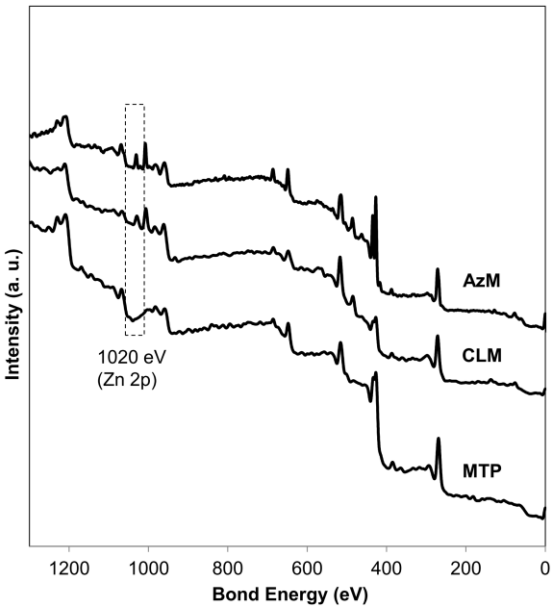


Figure S3. XPS charts of **AzM**, **CLM**, and **MTP**.

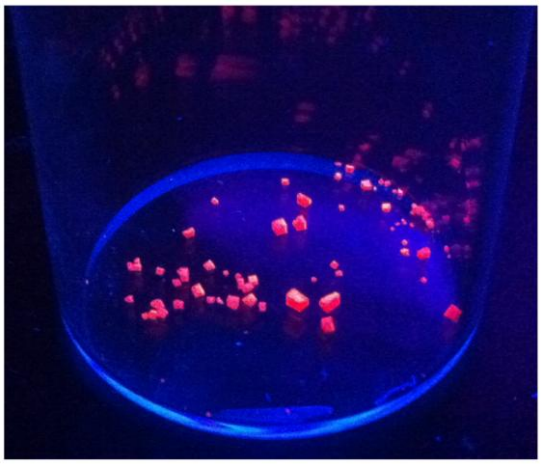


Figure S4. A photograph of **MTP** after immersion in 40 mM $EuNO_3 \cdot 6H_2O$ aq. under UV light (365 nm) irradiation.

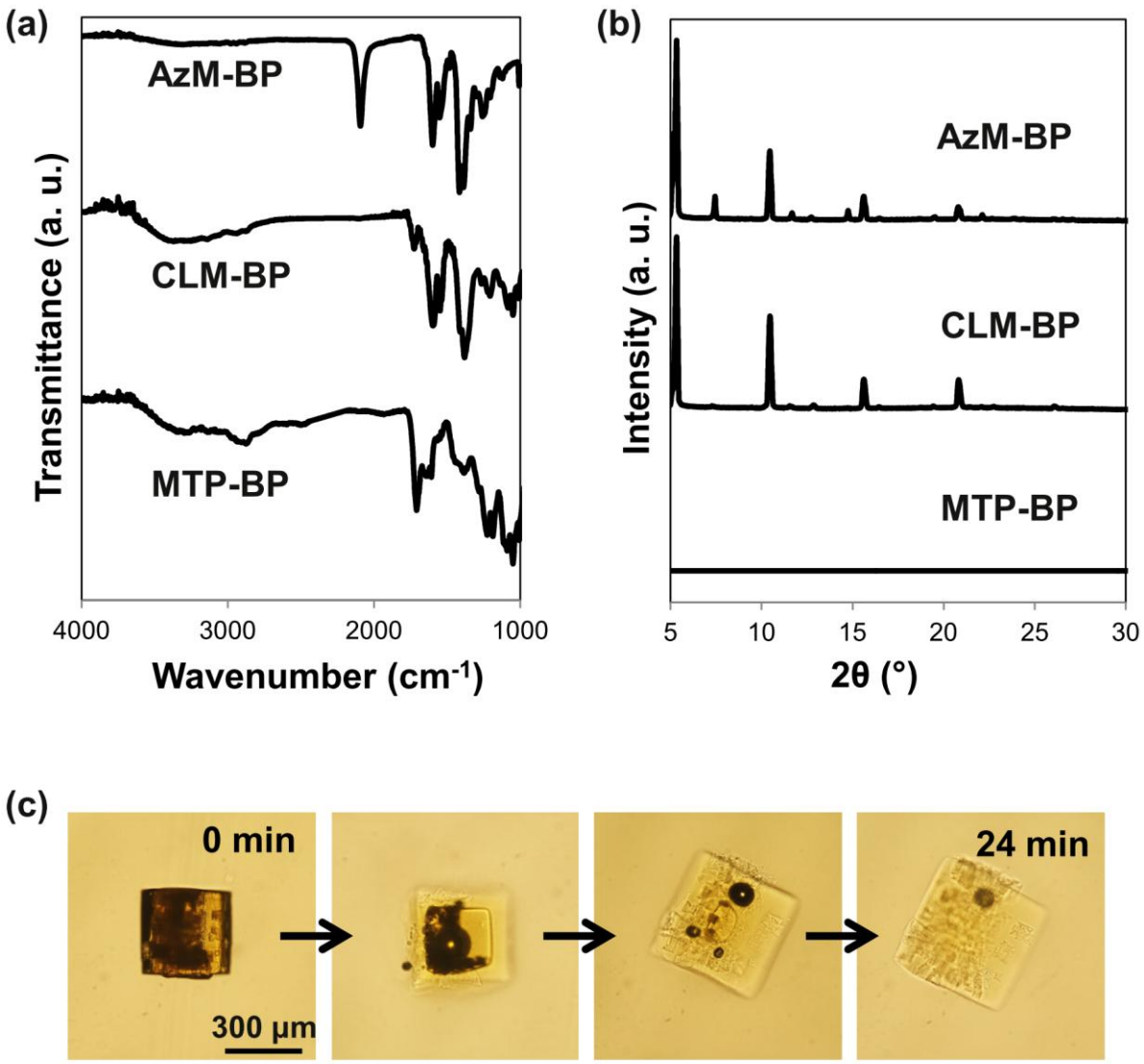


Figure S5. (a) IR spectra and (b) XRD patterns of **AzM-BP**, **CLM-BP**, and **MTP-BP**. (c) Optical microscopy images following the hydrolysis reaction of **CLM-BP**

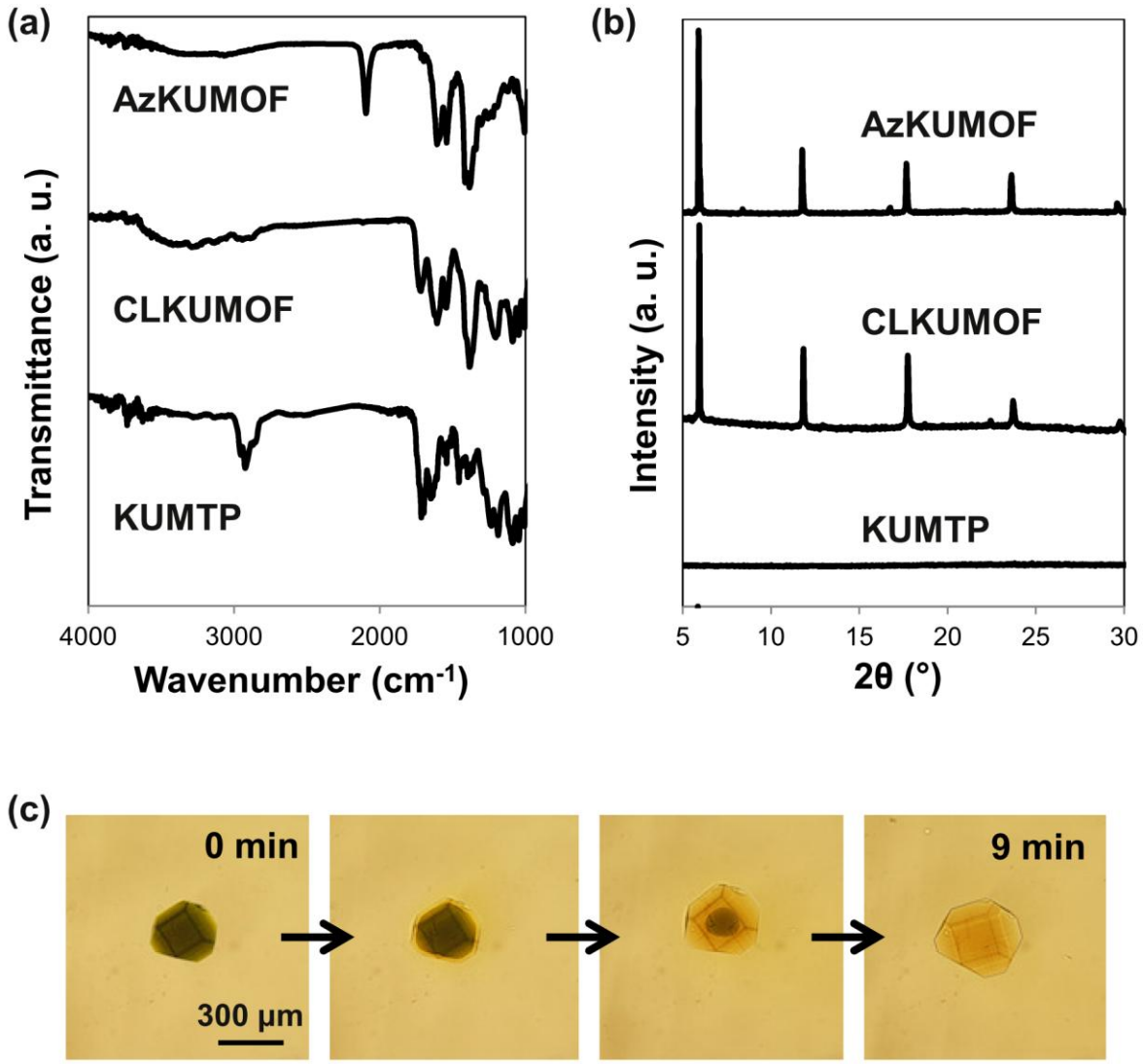


Figure S6. (a) IR spectra and (b) XRD patterns of **AzKUMOF**, **CLKUMOF**, and **KUMTP**. (c) Optical microscopy images following the hydrolysis reaction of **CLKUMOF**

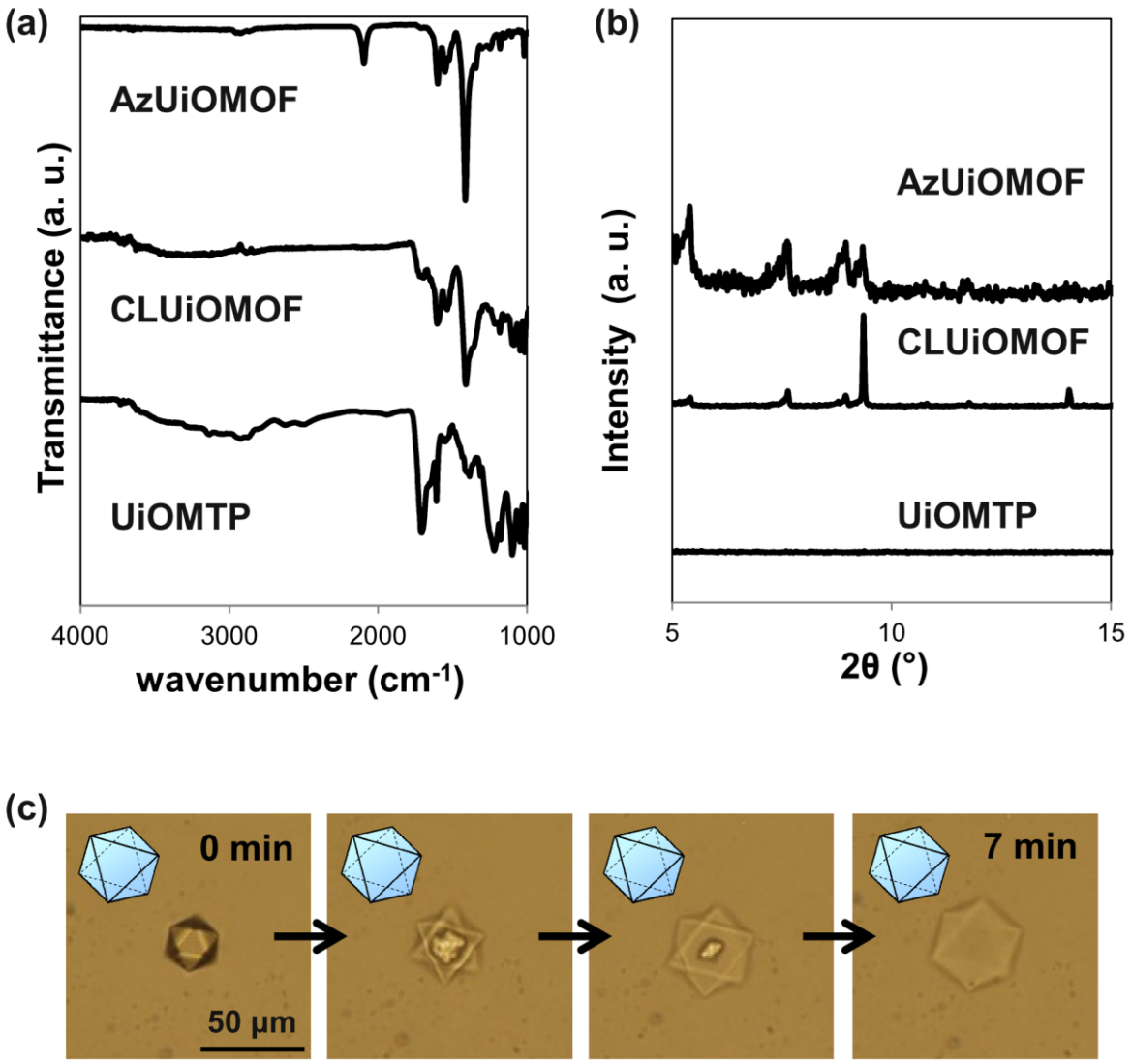


Figure S7. (a) IR spectra and (b) XRD patterns of **AzUiOMOF**, **CLUiOMOF**, and **UiOMTP**. (c) Optical microscopy images following the hydrolysis reaction of **CLUiOMOF**.