CHEMISTRY
AN ASIAN JOURNAL

Supporting Information

Supramolecular Porphyrin-Based Metal–Organic Frameworks with Fullerenes: Crystal Structures and Preferential Intercalation of C_{70}

Tetsushi Ohmura,*[a] Arimitsu Usuki,[a] Yusuke Mukae,[a] Hirofumi Motegi,[a] Shuji Kajiya,[a] Masami Yamamoto,[a] Shunsuke Senda,[b] Tsuyoshi Matsumoto,[c] and Kazuyuki Tatsumi[b]

asia_201501422_sm_miscellaneous_information.pdf

1. Single-crystal X-ray Diffraction (XRD)

2. Powder XRD

3. TGA

4. TD-MS

5. HPLC

6. SEM

1. Single-crystal X-ray Diffraction (XRD)

ORTEP view of **1** and **2** are shown in Fig.1S-1 and Fig. 1S-2, respectively. Crystallographic data can be obtained in 'Complex 1_Report.pdf' and 'Complex 2_Report.pdf'.

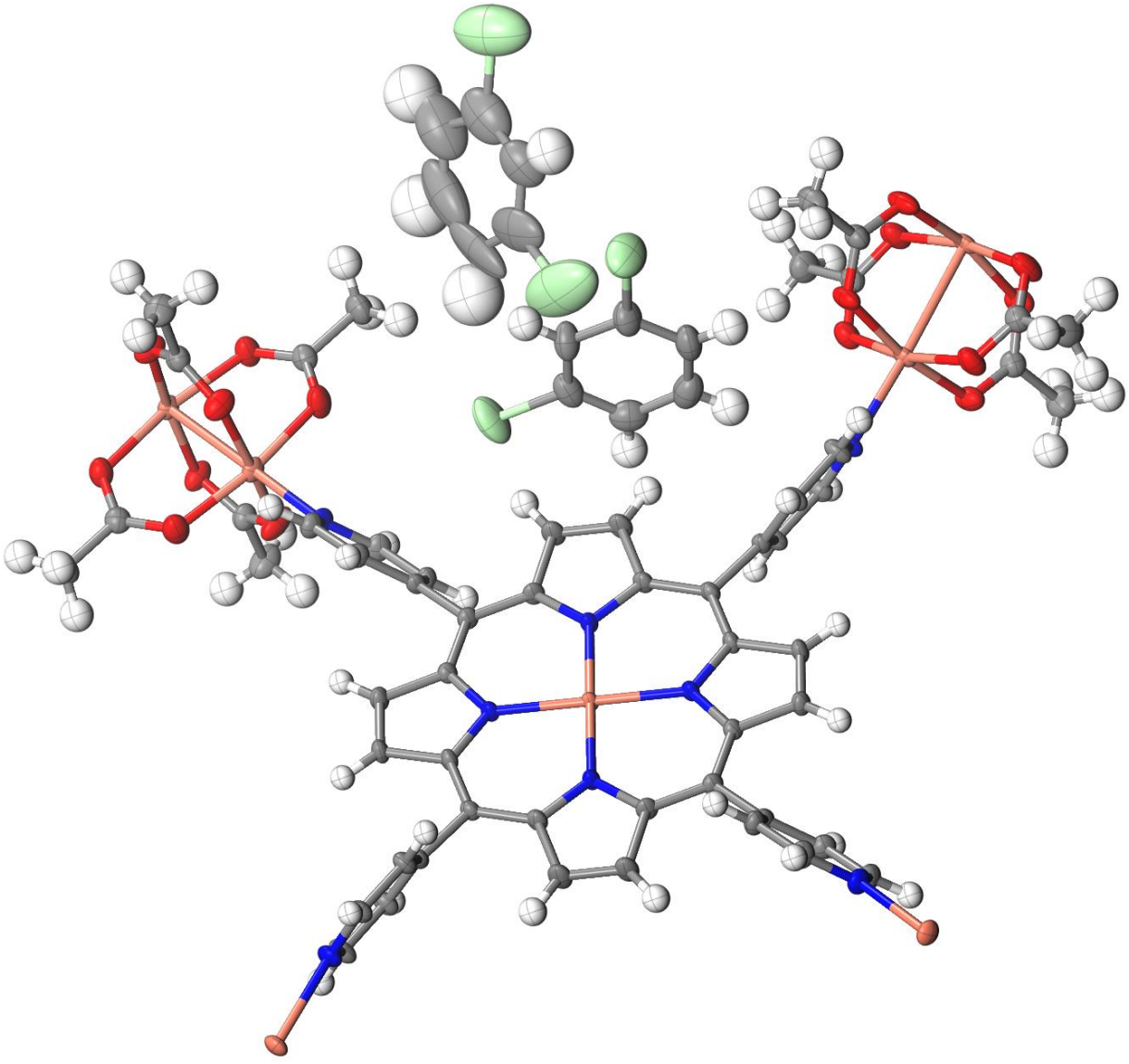

Fig. 1S-1. ORTEP view of **1**. Color scheme: C, gray; N, blue; O, red; Cl, green; and Cu, brown color.

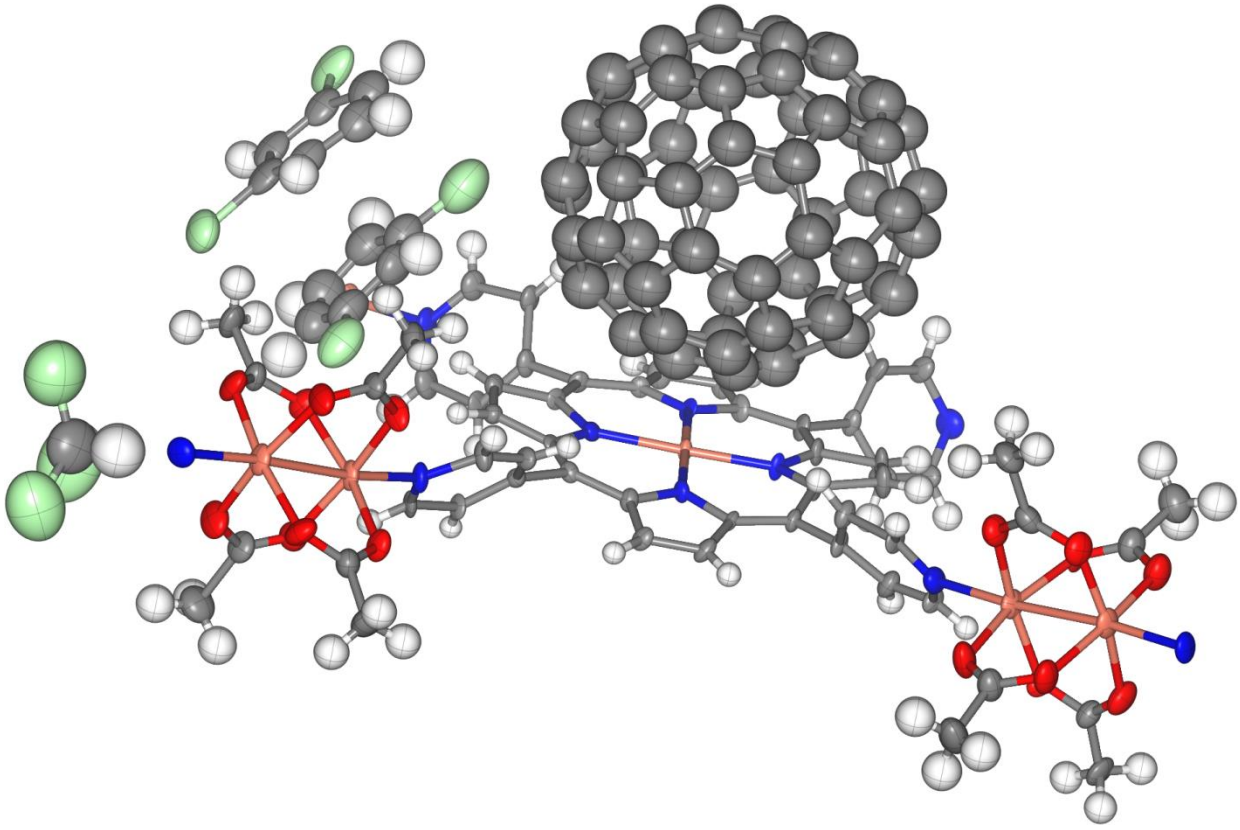

Fig. 1S-2. ORTEP view of **2**. Color scheme: C, gray; N, blue; O, red; Cl, green; and Cu, brown color.

2. Powder XRD

An *m*-DCB solution of C_{70} was added to a $CHCl_3$ solution of H_2TPyP and a MeOH solution of CuAcO was added to this mixture. The resultant mixture was stirred for 12 h. The crystals were filtered, CuAcO−CuTPyP·C_{70} ⊃ solvent (**2'**). A *m*-DCB solution that contained a 1 : 1 mixture of C_{60} and C_{70} was added to a $CHCl_3$ solution of H_2TPyP and a MeOH solution of CuAcO was added to this mixture. The resultant mixture was stirred for 12 h. The crystals were filtered, CuAcO-CuTPyP·0.23C_{60}·0.77C_{70} ⊃ solvent (**3'**).

Powder XRD patterns were obtained by a Rigaku Ultima IV using Mo Kα radiation at room temperature. The following conditions were used: 40 kV, 40 mA, increment = 0.02 deg, scan speed = 2.0 deg/min. The XRD patterns for **2'** and **3'** are shown in Fig. 2S.

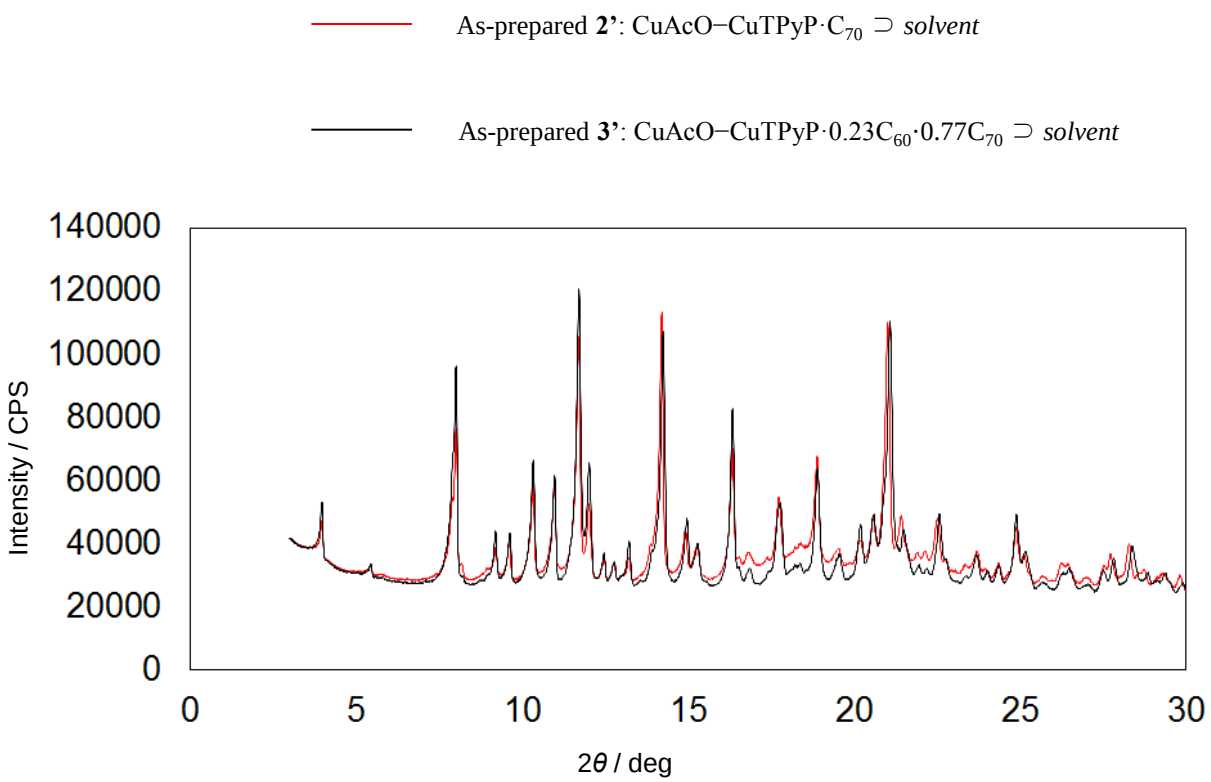

Fig. 2S. Powder XRD patterns for as-prepared **2'** and **3'**.

3. TGA

TGA data were obtained using a Rigaku Thermo Plus TGA. The experiment was carried out with 2.118 mg of **2'** placed in an Al pan and heated at 10 ºC/min up to 400 ºC in a flow of N_2 (Fig. 3S).

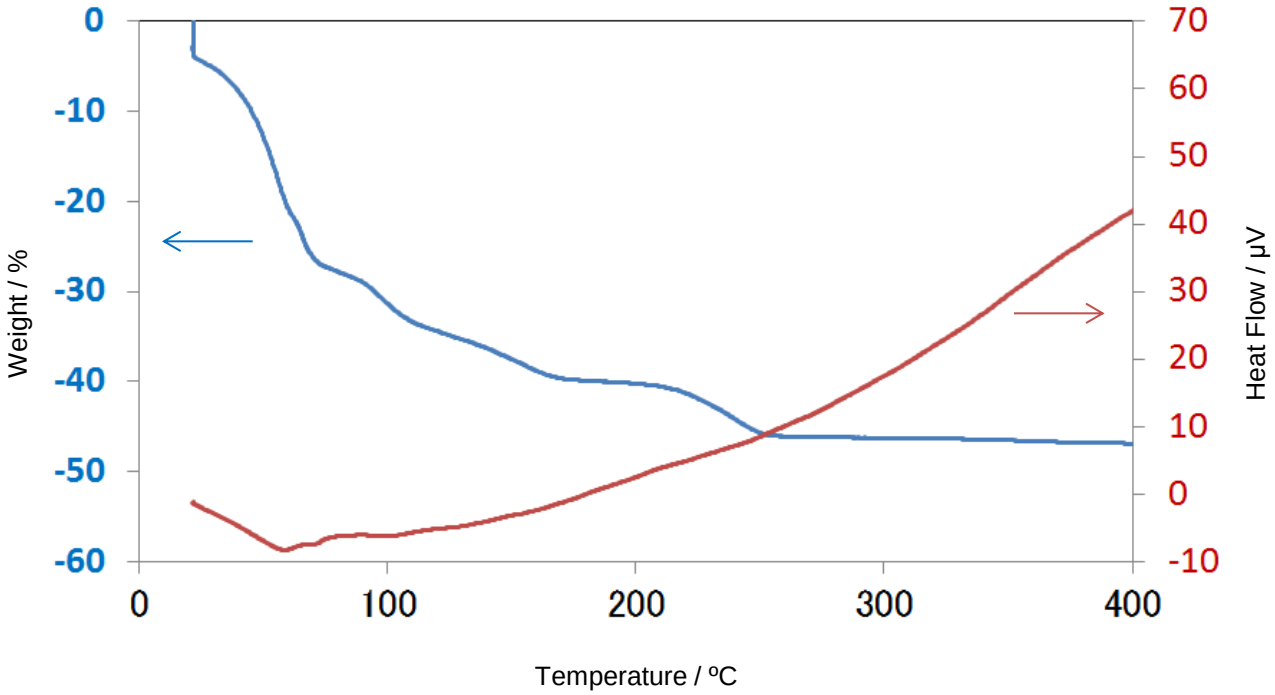

Fig. 3S. TGA plot of as-prepared **2'**.

4. TD-MS

TD-MS data were obtained on a Frontier Lab PY-2020D and Agilent 6890-5970 GC-MS. The experiment was carried out with 0.5 mg of **2'** and **3'** and heated at 10 ºC/min up to 400 ºC in a flow of He (Fig. 4S). The evolution curves were obtained for the parent ions or fragment ions of *m*-DCB (m/z = 146), $CHCl_3$ radical (m/z = 83, 85), CH_3COOH radical (m/z = 60), CO_2 radical (m/z = 44), and MeOH radical (m/z = 31).

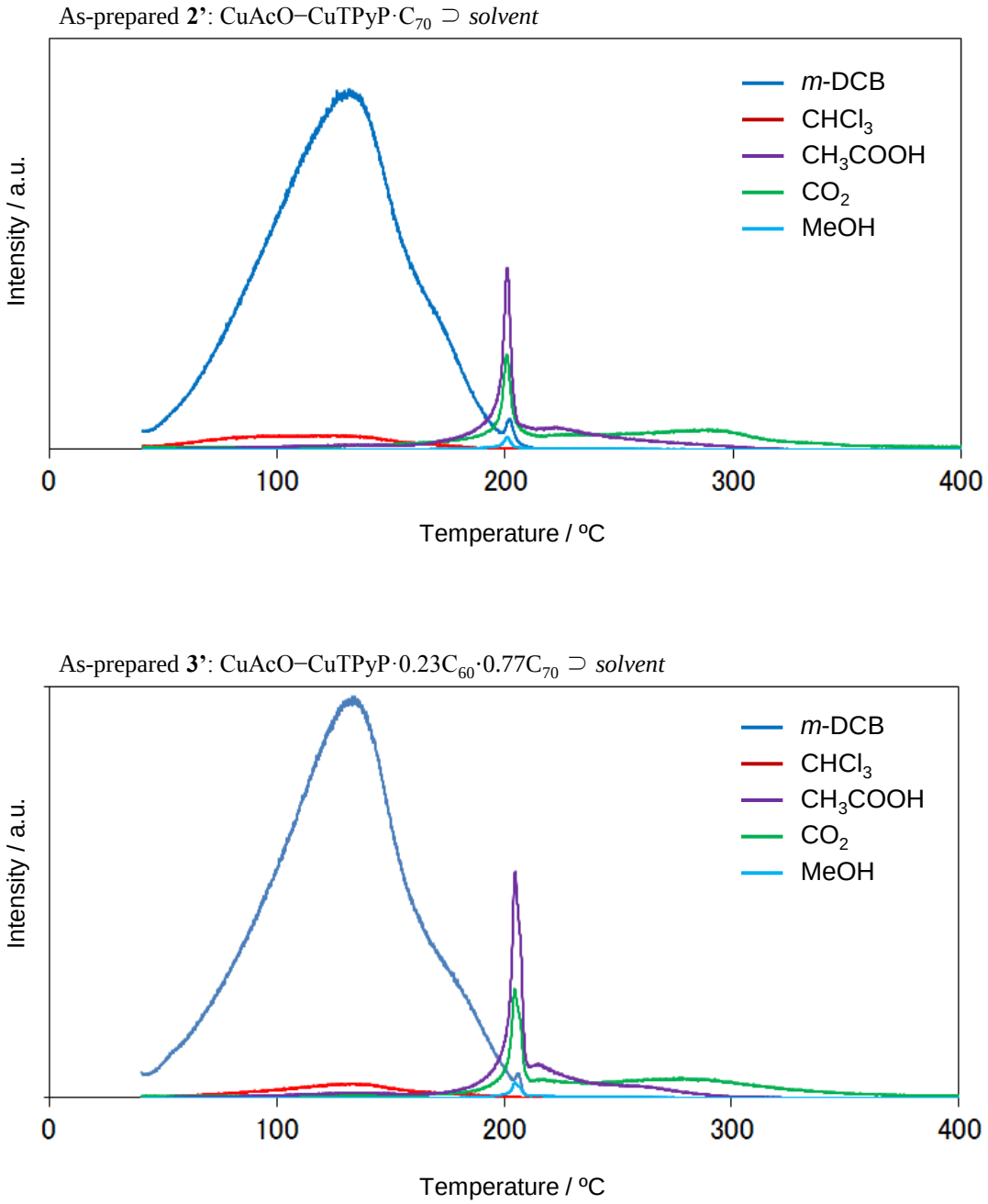

Fig. 4S. TD-MS plot of as prepared **2'** and **3'** .

5. HPLC

A *m*-DCB solution that contained a 1 : 1 mixture of C_{60} and C_{70} was add to a $CHCl_3$ solution of H_2TPyP and a MeOH solution of CuAcO was add to this mixture. The resultant mixture was stirred for 1 week. The crystals were filtered, decomposed with HCl and extracted with *m*-DCB. High-performance liquid chromatography (HPLC) analysis revealed an enriched C_{70} content (C_{60} : C_{70} = 19 : 81). When a *m*-DCB solution containing a 19:81 mixture of C_{60} and C_{70} was used, the C_{70} was enriched further to a 8:92 C_{60}:C_{70} ratio (Fig. 5S).

HPLC measurement conditions:
Solvent: toluene/acetone = 6:4
Columm: Agilent Eclipse XDB-C18; inner diameter 4.6mm × length 150mm)
Detector: UV at 350 nm
Flow rate: 1.0 mL/min

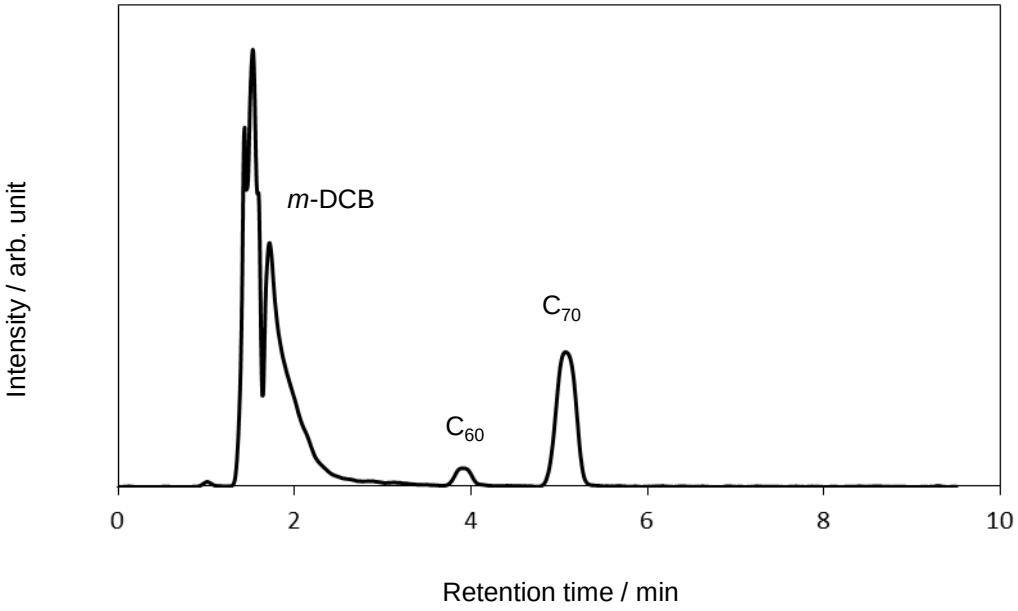

Fig. 5S. HPLC plot of as-prepared **3'**.

6. SEM images

Scanning electron microscopy (SEM) was performed using a Hitachi SU-3500 scanning electron microscope (Hitachi, Tokyo, Japan) at an acceleration voltage of 5 kV.

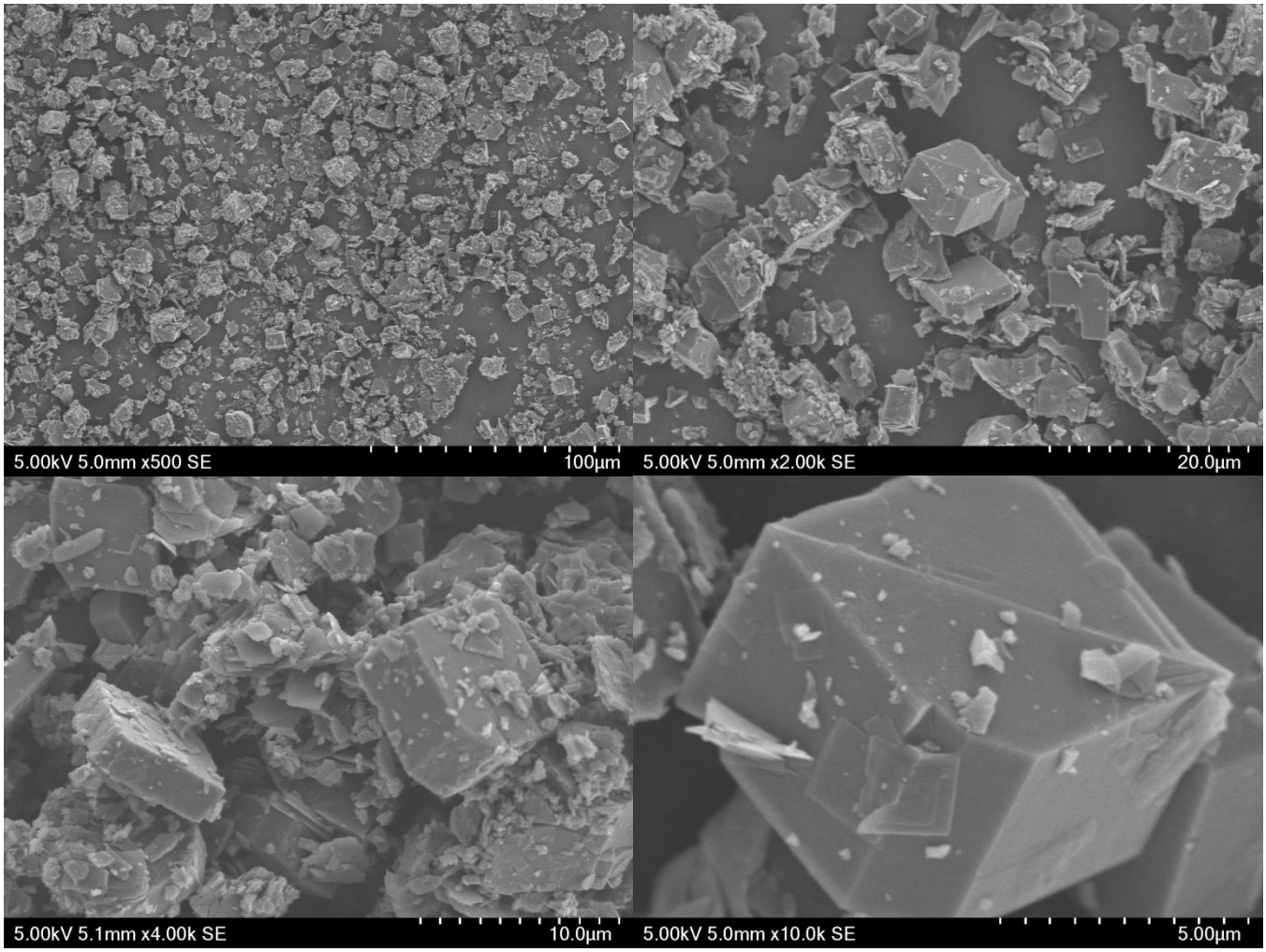

Fig. 6S-1. SEM images of **2'**.

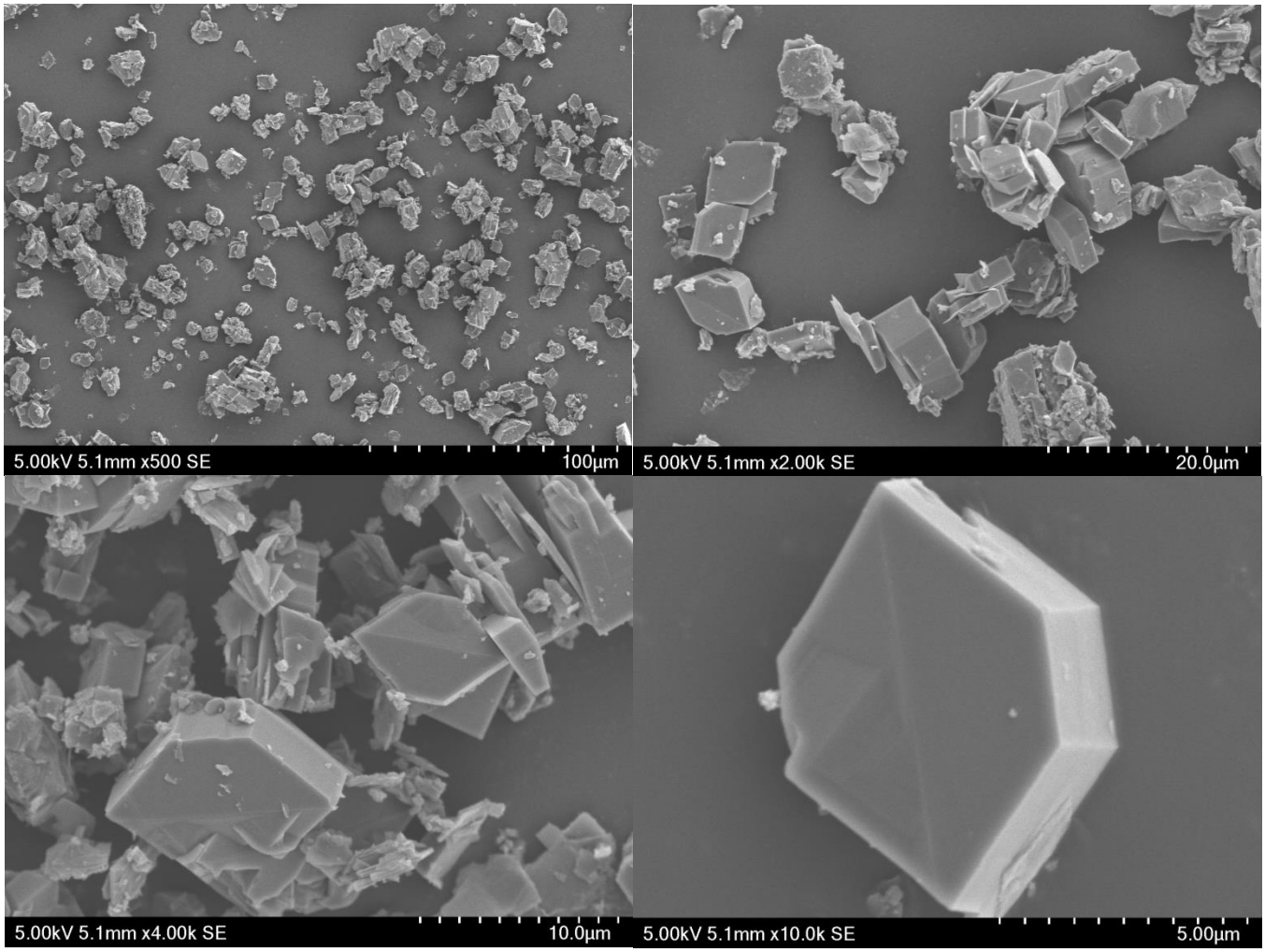

Fig. 6S-2. SEM images of **3'**.