Electronic Supplementary Information

HKUST-1 MOF in reline deep eutectic solvent: synthesis and phase transformation

Renata A. Maia, Benoît Louis* and Stéphane A. Baudron*

Abstract: The fate of HKUST-1 ($Cu_3(BTC)_2$, BTC = 1,3,5-benzenetricarboxylate) in the green Deep Eutectic Solvent (DES) reline (choline chloride/urea 1:2) was investigated, highlighting that not only reline can be used to make this MOF but also to transform it into another crystalline material. The synthesis of HKUST-1(reline) showing good textural properties and a particular rose morphology was indeed successfully achieved in this solvent. However, upon optimizing the reaction conditions such as concentration and metal/ligand ratio, it was found that another structure $Cu_2(BTC)Cl$ also forms. It was unequivocally demonstrated that, upon heating in reline, HKUST-1 behaves as a metastable architecture, converting to the non-porous chloride-incorporating material. Hence, a novel feature of DES in MOF synthesis is uncovered: its role as a structure-directing agent, triggering the transformation between two different MOF structures.

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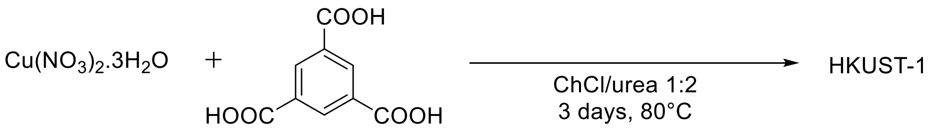
S1. Materials and Instrumentation

The commercially available reagents choline chloride 99% (Acros), urea 99.5% (Acros), trimesic acid 95% (Sigma-Aldrich) and $Cu(NO_3)_2.3H_2O$ (Carlo Erba) were used as received. The reactions were set in either a Chemglass® high-pressure vessel (o.d. x i.d. = 2.5 x 1.6 cm^2 and 10 cm length, 48 mL, model CG-1880-04) or VWR 8 mL vials. VWR digital heatblocks were used as dry baths and sonication was performed in a Branson 5510 ultrasonic cleaner. PXRD patterns were recorded on a Bruker D8 Advance diffractometer with LynxEye detector, Cu K_α wavelength in a 2θ interval of 4° – 40°, step size of 0.007° and time/step of 0.35 s. The textural properties of the samples were obtained by N_2 adsorption-desorption isotherms at 77 K in a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. The Brunauer-Emmett-Teller (BET) method was used for obtaining the specific surface area, and the total pore volume (V_{Total}) was obtained by single point adsorption at p/p_0 = 0.97363. The t-plot method was employed for obtaining the micropore volume (V_{Micro}) and the specific surface area related to the micropores ($S_{BET,micro}$). The samples were pre-treated, prior to the N_2 adsorption-desorption analysis, by heating the sample under vacuum at 150°C for 8 h, and the MicroActive Software was used to analyze the data. The infrared spectra were obtained in a FTIR-UATR PerkinElmer Spectrum Two, in the wavenumber interval of 4.000 cm^{-1} – 400 cm^{-1}. The thermal stability of the samples was accessed in a PerkinElmer Thermogravimetric Analyzer TGA 4000 under N_2 flow of 20 mL/min, and a heating rate of 5°C/min up to 800°C. Elemental analyses (CHN) of vacuum dried samples were performed in duplicate, employing a ThermoFischer Flash 2000 equipment, whereas the reported values for the CHN was taken as the average of two measurements. SEM images were obtained with a Zeiss GeminiSEM 500 microscope with a FEG Schottky source and an Everhart–Thornley detector.

S2. General preparation of reline

In a round bottom flask, equipped with a stirring bar, it was added, in a molar ratio, choline chloride (1 equiv.) and urea (2 equiv.). The flask was placed in a pre-heated oil bath at 100°C and the mixture was stirred until it became a clear liquid solution (usually a few minutes). Due to its viscosity, reline was kept at 100°C during the process of addition to the HKUST-1 reaction vessel. Note that the reline was freshly prepared for every reaction.

S3. Synthesis of HKUST-1(reline)



In a Chemglass® high-pressure vessel, it was added $Cu(NO_3)_2.3H_2O$ (1 equiv., 0.3 mmol, 0.0725 g) and trimesic acid (6 equiv., 1.8 mmol, 0.3982 g). Freshly prepared reline (8 mL) was added into the vessel with the aid of a syringe: the solvent was added in small portions and, in these intervals, mixed gently with a spatula in order to better incorporate the reagents, affording a bright yellow mixture. Then, the vessel was sealed with its Teflon cork and sonicated for 1 h at room temperature (25°C), which dissolved most of the remaining non-incorporated solid. Finally, the vessel was placed in a pre-heated oil bath at 80°C and reacted for 3 days. After the completion of the reaction, the resulting mixture appeared as a green suspension. The vessel was cooled down to room temperature and its content was filtered off and washed with distilled water (100 mL), which immediately turned the green suspension into a blue one (most likely associated with ligand exchange at the axial positions of the Cu_2 paddle wheel), and anhydrous ethanol (100 mL). The remaining blue solid (20 mg) was air-dried and collected into a vial.

FT-IR (ATR, cm^{-1}): 3700-2700 (s); 1651 (s); 1617 (s); 1550 (s); 1451 (s); 1374 (s); 1111 (m); 938 (m); 760 (s); 729 (s); 493 (s).

Elemental analysis (CHN) for $C_{18}H_{18}Cu_3O_{18}$ ($[Cu_3(BTC)_2(H_2O)_6]$), calculated: 30.32% C, 2.54% H; found: 30.31% C, 2.68% H, 0% N.

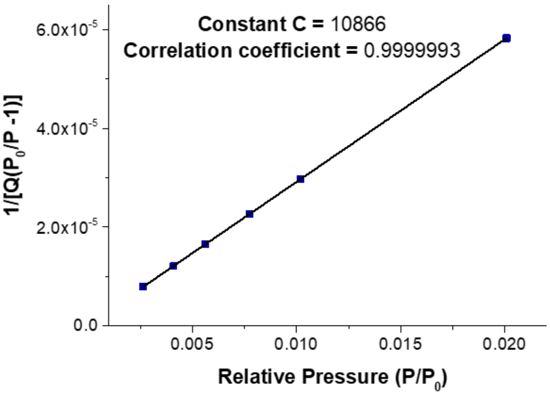


Fig. S1. Plot of $1/[Q(P_0/P - 1)]$ versus relative pressure for HKUST-1**(reline)**.

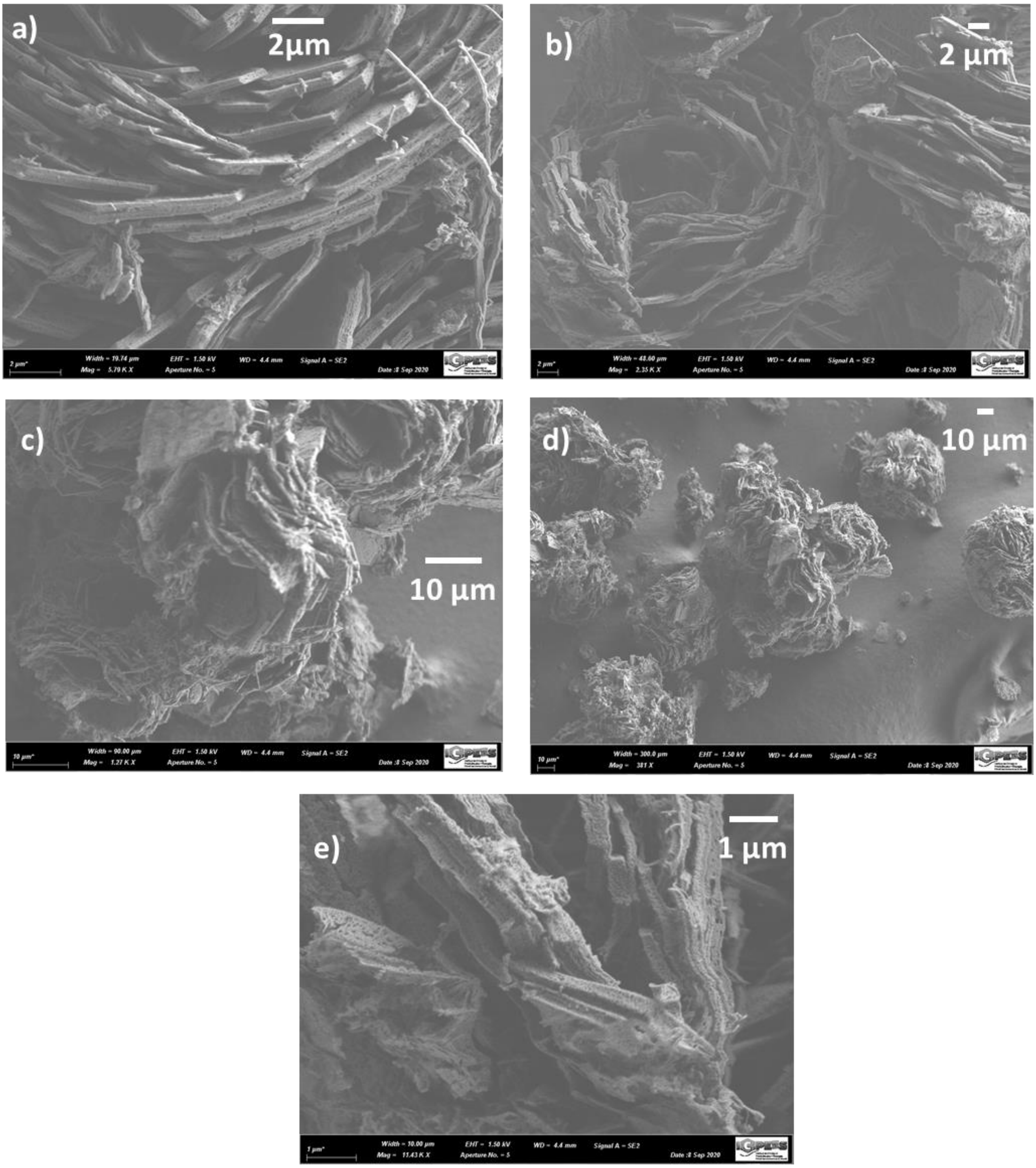
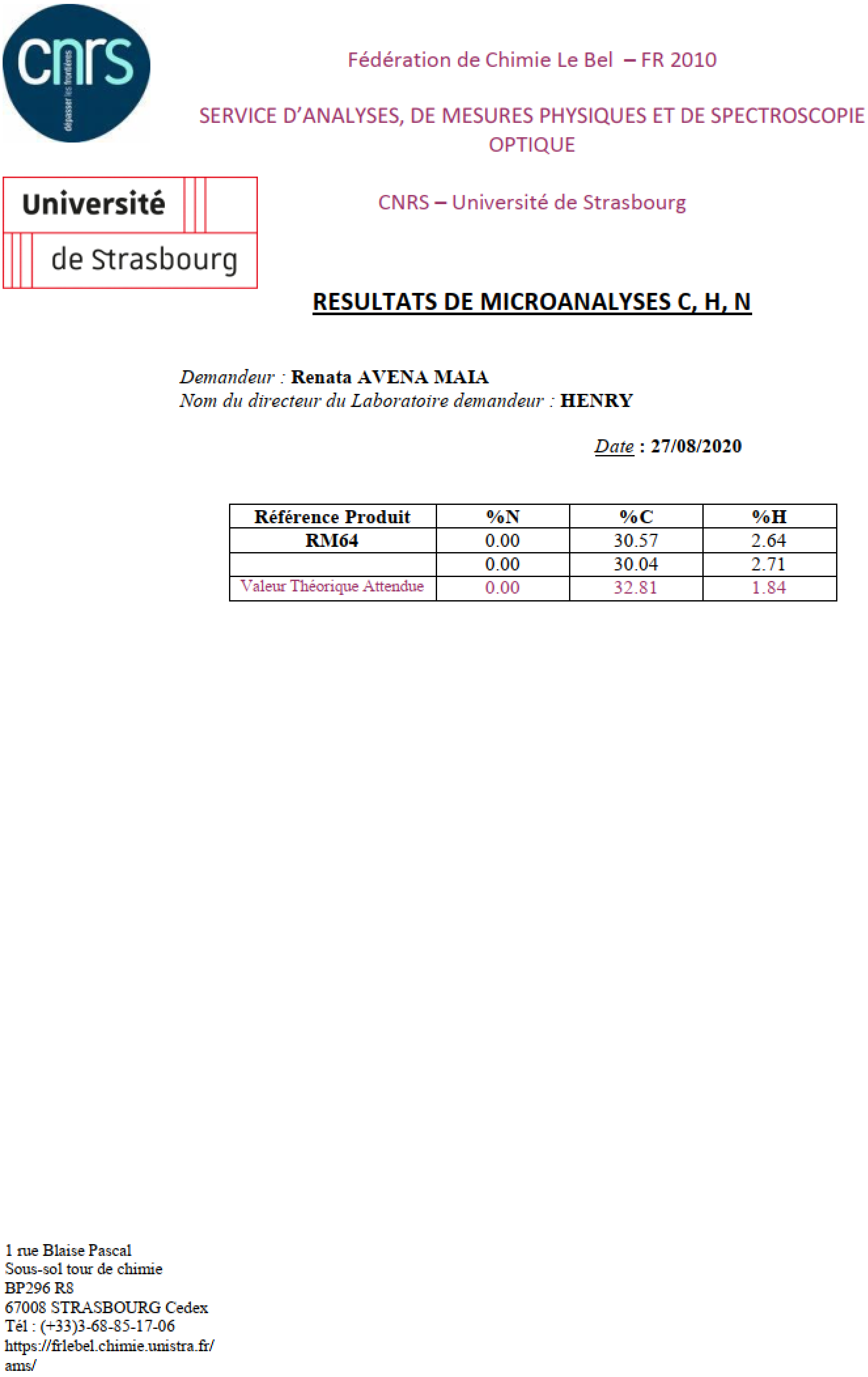


Fig. S2. SEM micrographs of HKUST-1**(reline)**.



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RESULTATS DE MICROANALYSES C, H, N

Demandeur : **Renata AVENA MAIA**
Nom du directeur du Laboratoire demandeur : **HENRY**

Date : **27/08/2020**

Référence Produit	%N	%C	%H
RM64	0.00	30.57	2.64
	0.00	30.04	2.71
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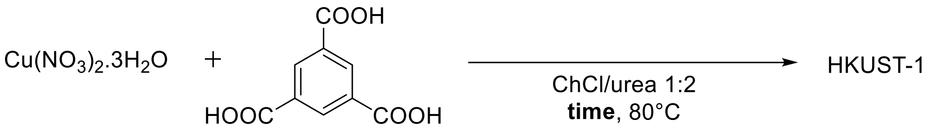
1 rue Blaise Pascal
Sous-sol tour de chimie
BP296 R8
67008 STRASBOURG Cedex
Tél : (+33)3-68-85-17-06
https://frlebel.chimie.unistra.fr/ams/

Fig. S3. Elemental analysis of HKUST-1**(reline)**.

S3.1 Kinetic study for HKUST-1(reline): 1 and 2 days



In a Chemglass® high-pressure vessel, it was added $Cu(NO_3)_2.3H_2O$ (1 equiv., 0.3 mmol, 0.0725 g) and trimesic acid (6 equiv., 1.8 mmol, 0.3982 g). Freshly prepared reline (8 mL) was added into the vessel with the aid of a syringe: the solvent was added in small portions and, in these intervals, mixed gently with a spatula in order to better incorporate the reagents, affording a bright yellow mixture. Then, the vessel was sealed with its Teflon cork and sonicated for 1 h at room temperature (25°C), which dissolved most of the remaining non-incorporated solid. Finally, the vessel was placed in a pre-heated oil bath at 80°C and reacted for either 1 or 2 days. After the completion of the reaction, the resulting mixture appeared as a green suspension. The vessel was cooled down to room temperature and its content was filtered off and washed with distilled water (100 mL), which immediately turned the green suspension into a blue one, and anhydrous ethanol (100 mL). The remaining blue solid (33 mg for the 1 day reaction, and 30 mg for the 2 days reaction) was air-dried and collected into a vial.

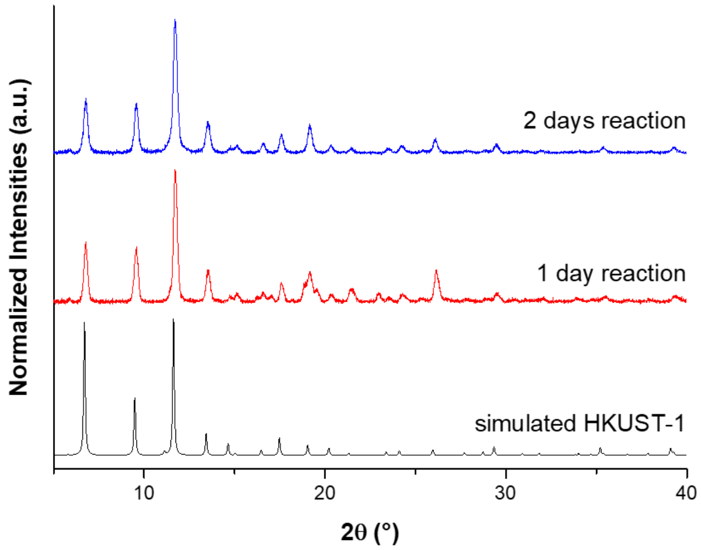


Fig. S4. PXRD diffractogram for the products obtained after 1 day (red) and 2 days (blue).

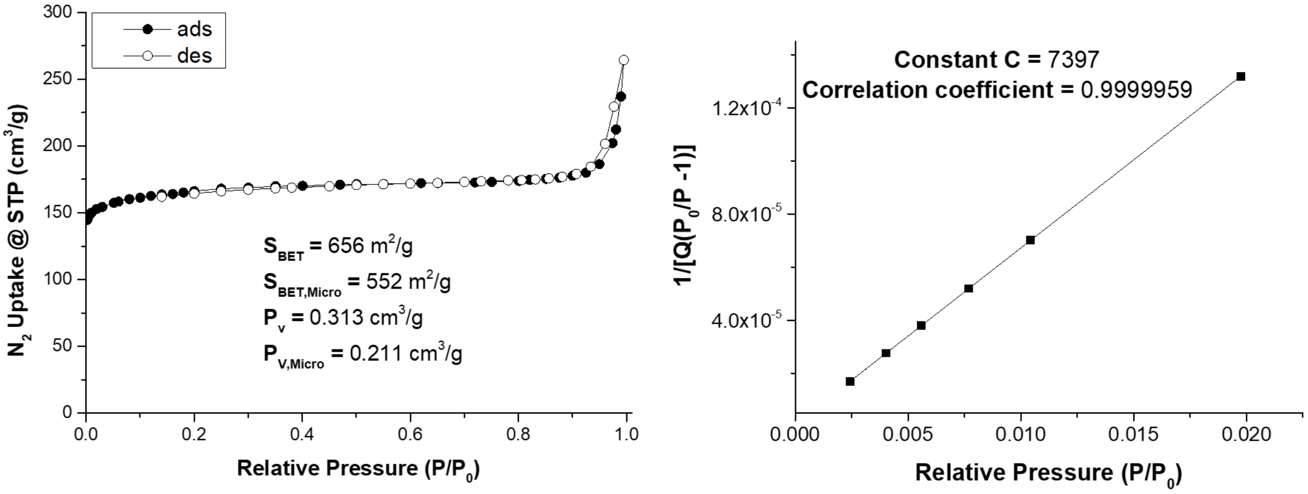


Fig. S5. N_2 adsorption-desorption isotherms at 77 K (left) and plot of $1/[Q(P_0/P - 1)]$ versus relative pressure (right) for the product obtained after 1 day of reaction.

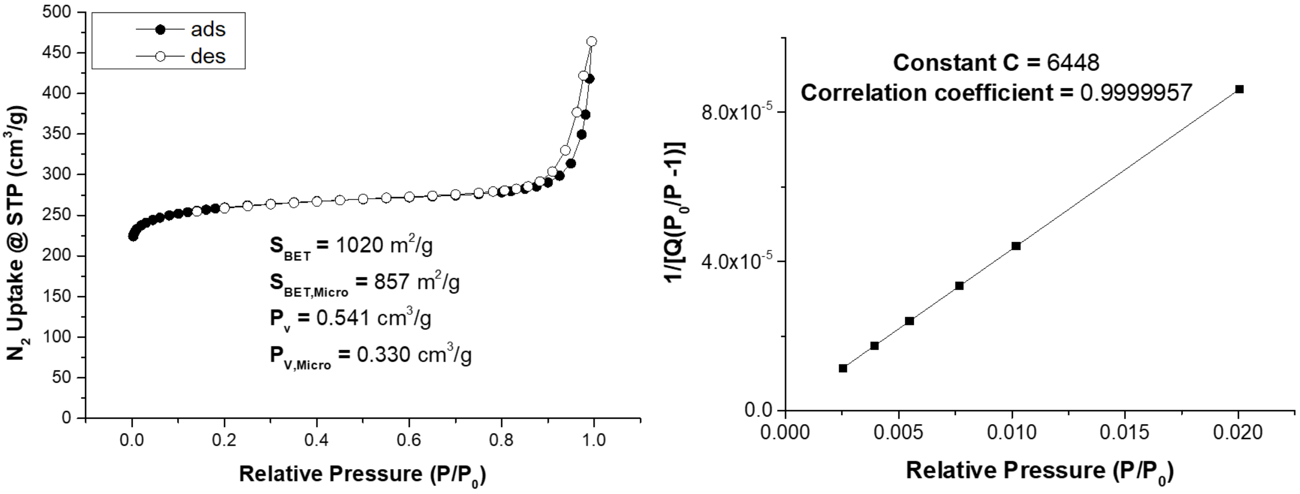


Fig. S6. N_2 adsorption-desorption isotherms at 77 K (left) and plot of 1/[Q(P_0/P - 1)] versus relative pressure (right) for the product obtained after 2 days of reaction.

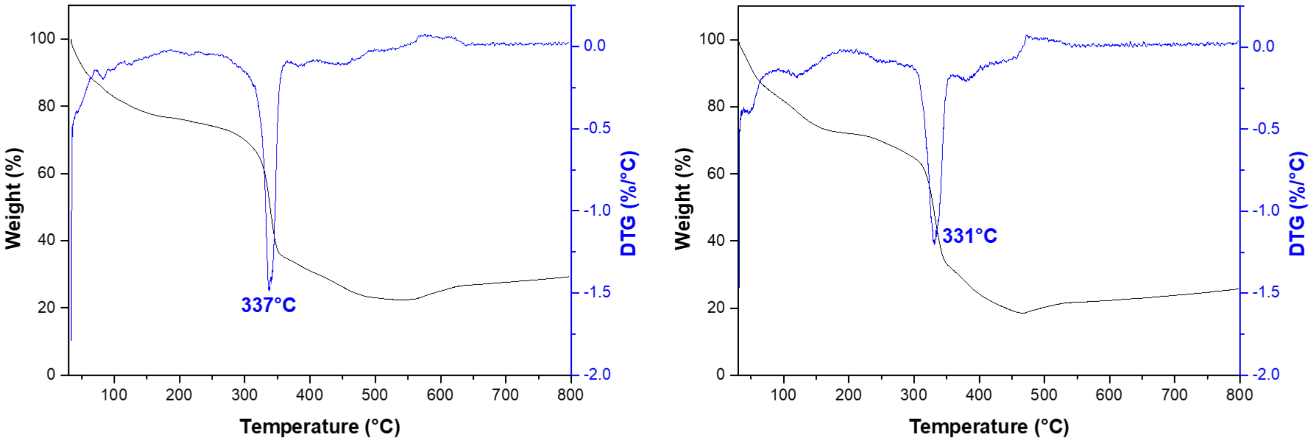


Fig. S7. TGA for the product obtained after 1 day reaction (left) and after 2 days reaction (right).

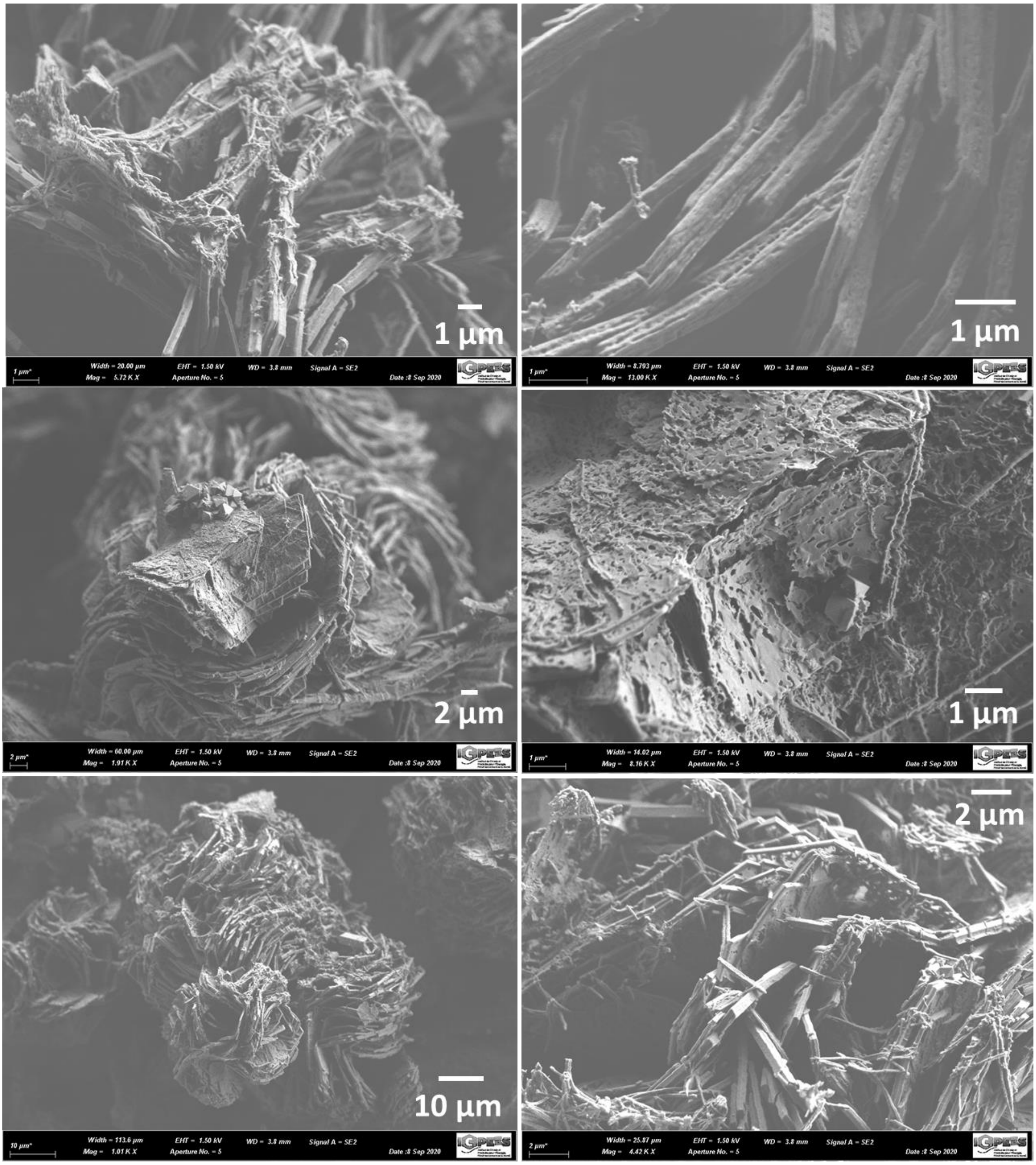


Fig. S8. SEM micrographs for the product obtained after 1 day of reaction.

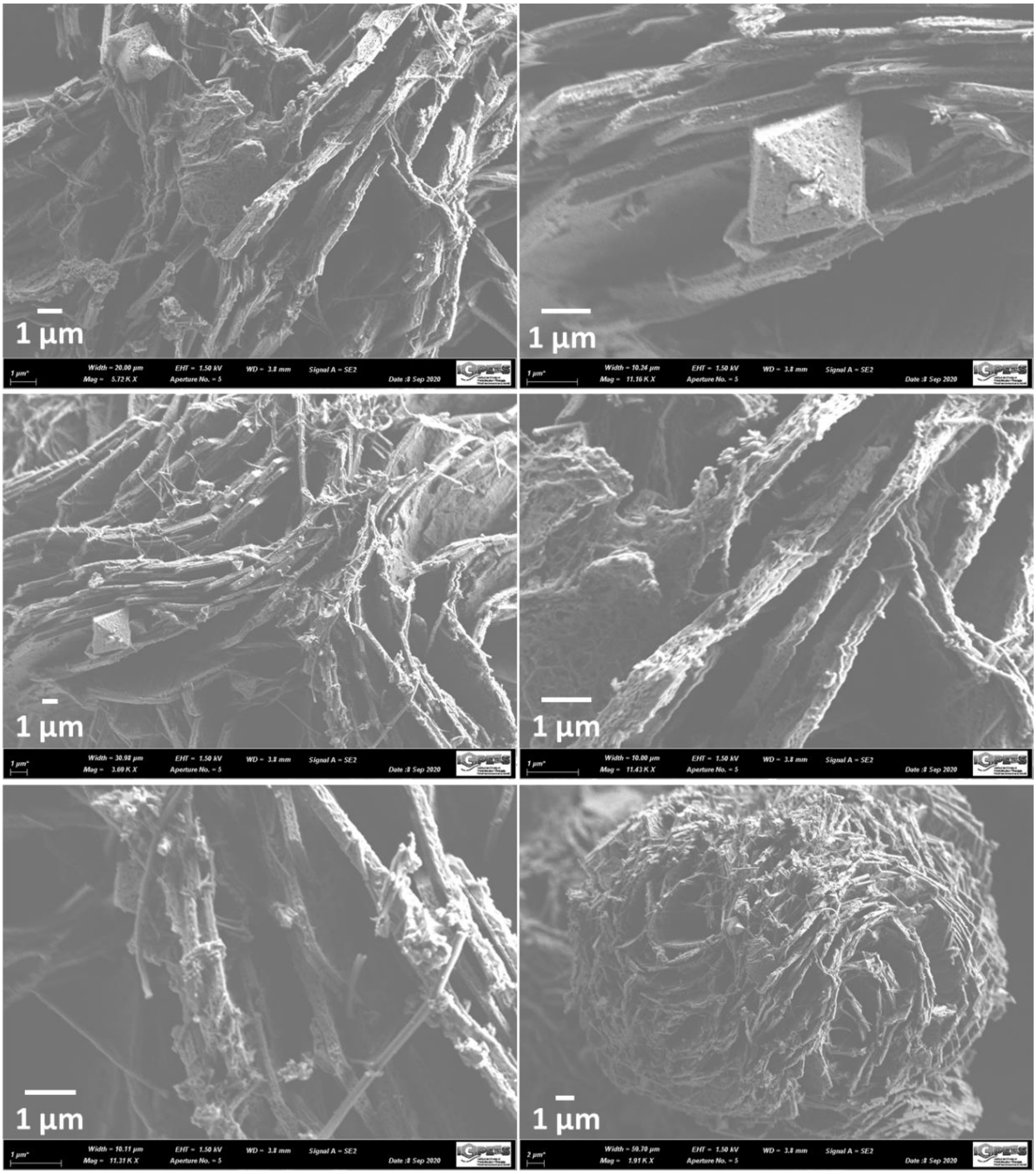


Fig. S9. SEM micrographs for the product obtained after 2 days of reaction.

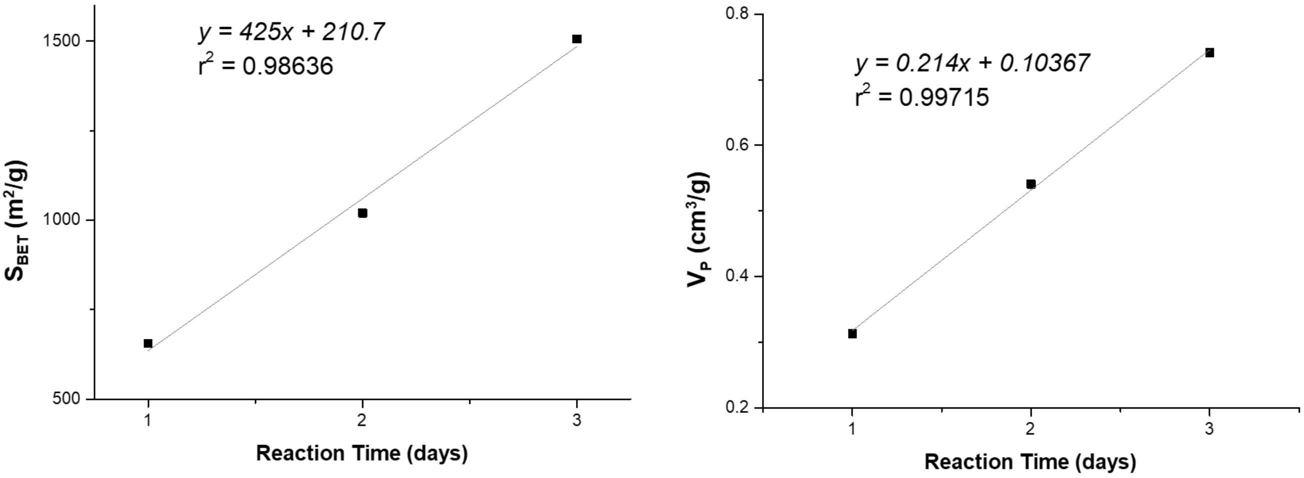


Fig. S10. Linear correlation between reaction time and (left) S_{BET} and (right) total pore volume, V_P.

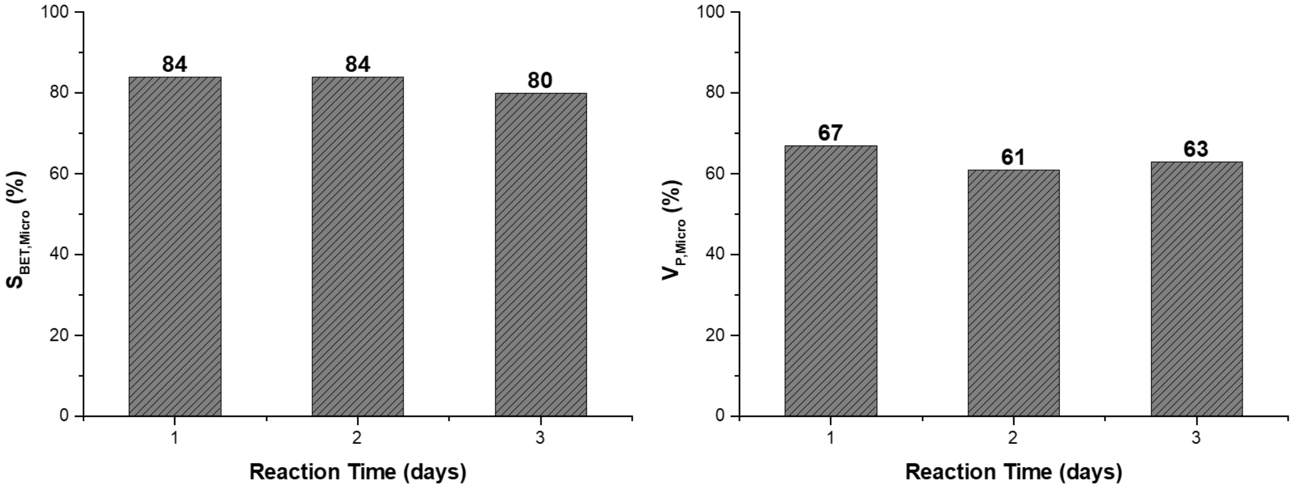


Fig. S11. Correlation between reaction time and $S_{BET,Micro}$ (left) and micropore pore volume (right).

S4. Homogenization study of HKUST-1(reline)

As the next step in our synthetic scope, we turned our efforts towards synthesizing HKUST-1**(reline)** in a greater order of magnitude and evaluating the differences regarding homogenization tools (Table S1). By attempting to synthesize HKUST-1**(reline)** in a 4-fold scale of the parent reaction conditions, a material with a S_{BET} of 1538 m^2/g was found (method SU1), which evidenced the reliability of our methodology at a greater scale. It is worth to mention that even though the pristine condition was increased by a 4-fold, the product mass increased by one order of magnitude, indicating a 10-fold increase of the desired product in a mass basis (from 20 mg to 212 mg). Employing continuous stirring during the course of the reaction, besides the pre-sonication step (method SU2), decreased *ca*. 20% of the S_{BET}, although the product mass remained similar. Moreover, when no sonication was performed and the stirring was the only homogenization tool (method SU3), the resulting product afforded a S_{BET} of only 314 m^2/g. Finally, when neither stirring nor sonication were used (method SU4), the S_{BET} was insignificant (~1 m^2/g). Attempts to exclusively sonicate the reaction mixture for 8 h did not afford any product.

Regarding their morphologies, the product from method SU1 exhibited nano-roses upon SEM analysis (Fig. **S15**). Conversely, nanorods were found for the products of methods SU2 (Fig. **S18**) and SU3 (Fig. **S22**), while a dense sintered-like morphology was found for SU4 (Fig. **S24**). This implies that continuous stirring during the HKUST-1 synthesis breaks apart the platelets that assemble into nano-roses, which were only observed upon sonication. The latter is supported by our optimization studies: when no sonication was employed, the typical octahedral morphology for the HKUST-1 materials was found (Fig. S34-39).

Thus, it can be stated that the sonication affects greatly the morphology outcome of a highly porous HKUST-1 in reline. Importantly, ultrasonic irradiation distinguishes itself as a distinct homogenizing tool due to the phenomenon of acoustic cavitation. This feature of sonication may enable a very efficient dispersion of the starting materials, and even the early formation of critical nuclei of HKUST-1 material, as the dynamic of cavity growth and its collapse depends immensely on the local environment.[1]

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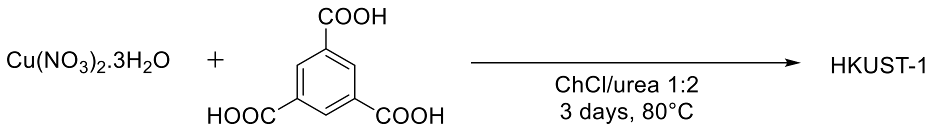
[1] K. S. Suslick, *Science* 1990, **247**, 1439–1445

Table S1. Comparison of the reference HKUST**(reline)** synthesis with different homogenization tools.

Method	Homogenization Tool	Product mass (mg)	S_{BET} (m^2/g)
HKUST-1**(reline)**[a]	1 h of sonication[c]	20	1506
SU1[b]	1 h of sonication[c]	212	1538
SU2[b]	1 h sonication,[c] stirring[d]	217	1270
SU3[b]	stirring[d]	231	315
SU4[b]	None	370	~1[e]

[a] 0.3 mmol of $Cu(NO_3)_2.3H_2O$, 1.8 mmol of BTC, and 8 mL of reline were heated at 80°C for 3 days. [b] 1.2 mmol of $Cu(NO_3)_2.3H_2O$, 7.2 mmol of BTC, and 30 mL of reline were heated at 80°C for 3 days. [c] prior to the start of the reaction. [d] continuously during the reaction time. [e] obtained by single point adsorption ($p/p_0 = 0.01026$).

S4.1 Method SU1 (sonication, no stirring)



In a Chemglass® high-pressure vessel, it was added $Cu(NO_3)_2.3H_2O$ (1 equiv., 1.2 mmol, 0.2899 g) and trimesic acid (6 equiv., 7.2 mmol, 0.3982 g). Freshly prepared reline (30 mL) was added into the vessel with the aid of a syringe: the solvent was added in small portions and, in these intervals, mixed gently with a spatula in order to better incorporate the reagents, affording a bright yellow mixture. Then, the vessel was sealed with its Teflon cork and sonicated for 1 h at room temperature (25°C), which dissolved most of the remaining non-incorporated solid. Finally, the vessel was placed in a pre-heated oil bath at 80°C and reacted for 3 days. After completion of the reaction, the resulting mixture appeared as a green suspension. The vessel was cooled down to room temperature and its content was filtered off and washed with distilled water (400 mL), which immediately turned the green suspension into a blue one, and anhydrous ethanol (400 mL). The remaining blue solid (212 mg) was air-dried and collected into a vial.

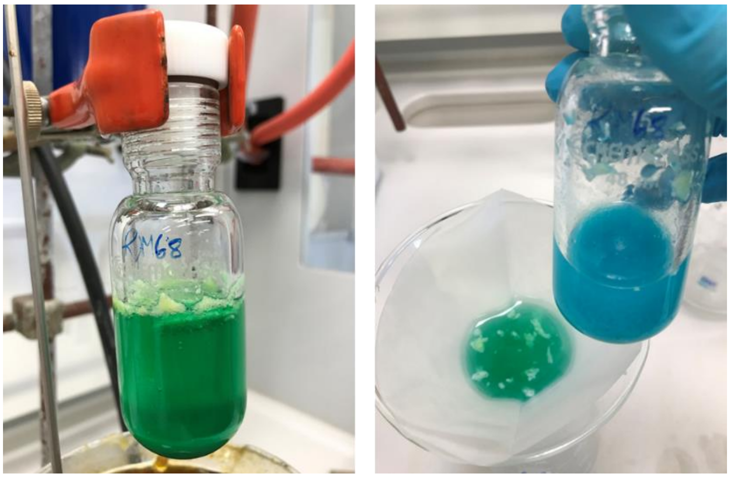


Fig. S12. Green suspension right after the completion of the reaction (left), which immediately turned blue upon addition of water upon the filtering process (right).

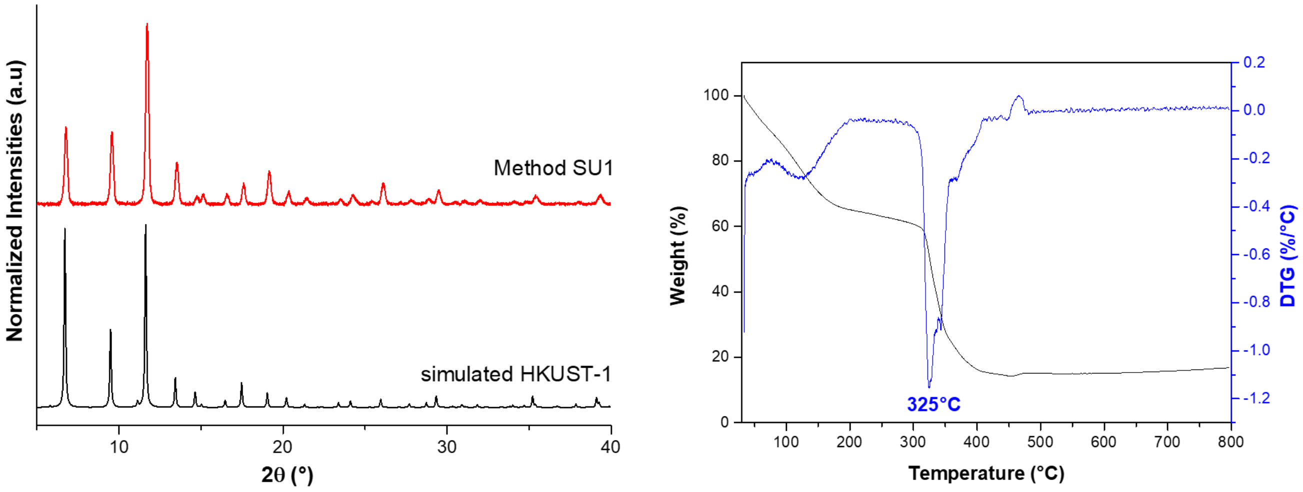


Fig. S13. PXRD diffractogram (left) and TGA (right) for the product obtained by the Method SU1.

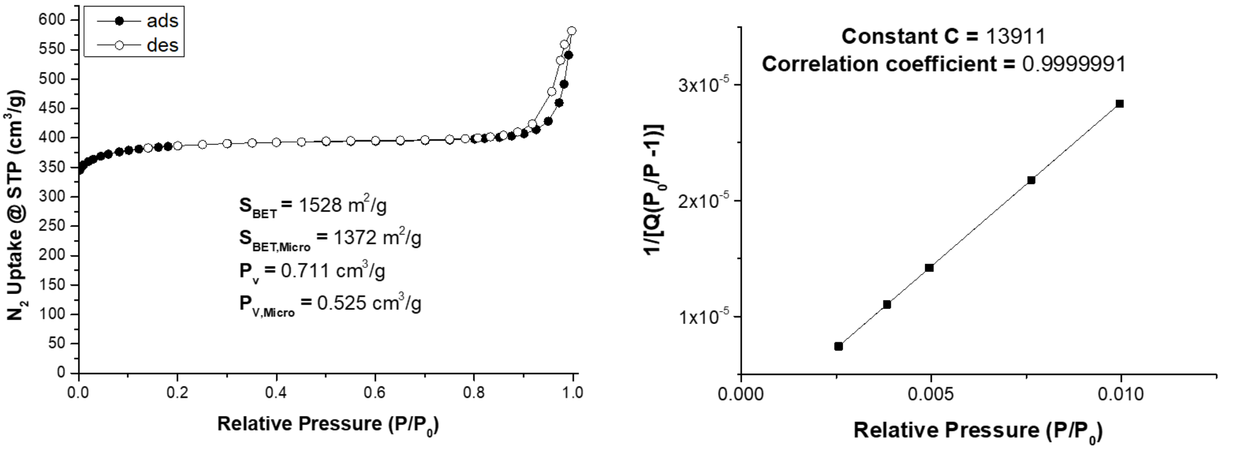


Fig. S14. N_2 adsorption-desorption isotherms at 77 K (left) and plot of $1/[Q(P_0/P - 1)]$ versus relative pressure (right) for the product obtained by the Method SU1.

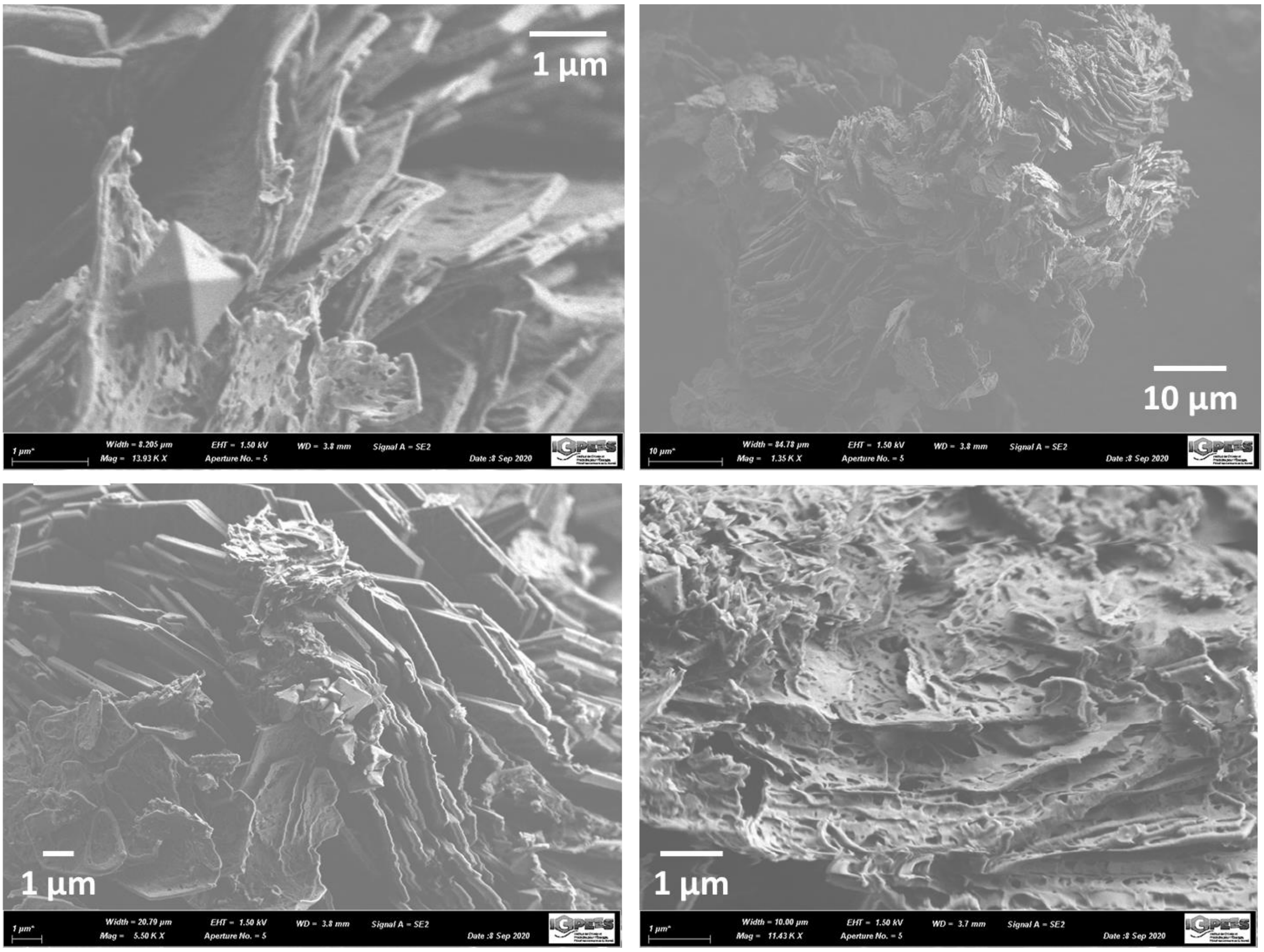
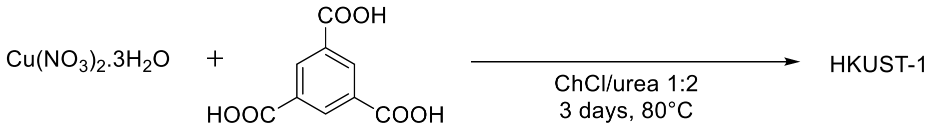


Fig. S15. SEM for the product obtained by the Method SU1.

S4.2 Method SU2 (sonication and stirring)



In a Chemglass® high-pressure vessel equipped with a magnetic stirring bar, it was added $Cu(NO_3)_2.3H_2O$ (1 equiv., 1.2 mmol, 0.2899 g) and trimesic acid (6 equiv., 7.2 mmol, 0.3982 g). Freshly prepared reline (30 mL) was added into the vessel with the aid of a syringe: the solvent was added in small portions and, in these intervals, mixed gently with a spatula in order to better incorporate the reagents, affording a bright yellow mixture. Then, the vessel was sealed with its Teflon cork and sonicated for 1 h at room temperature (25°C), which dissolved most of the remaining non-incorporated solid. Finally, the vessel was placed in a pre-heated oil bath at 80°C and reacted for 3 days with continuous stirring. After the completion of the reaction, the resulting mixture appeared as a green suspension. The vessel was cooled down to room temperature and its content was filtered off and washed with distilled water (400 mL), which immediately turned the green suspension into a blue one, and anhydrous ethanol (400 mL). The remaining blue solid (217 mg) was air-dried and collected into a vial.

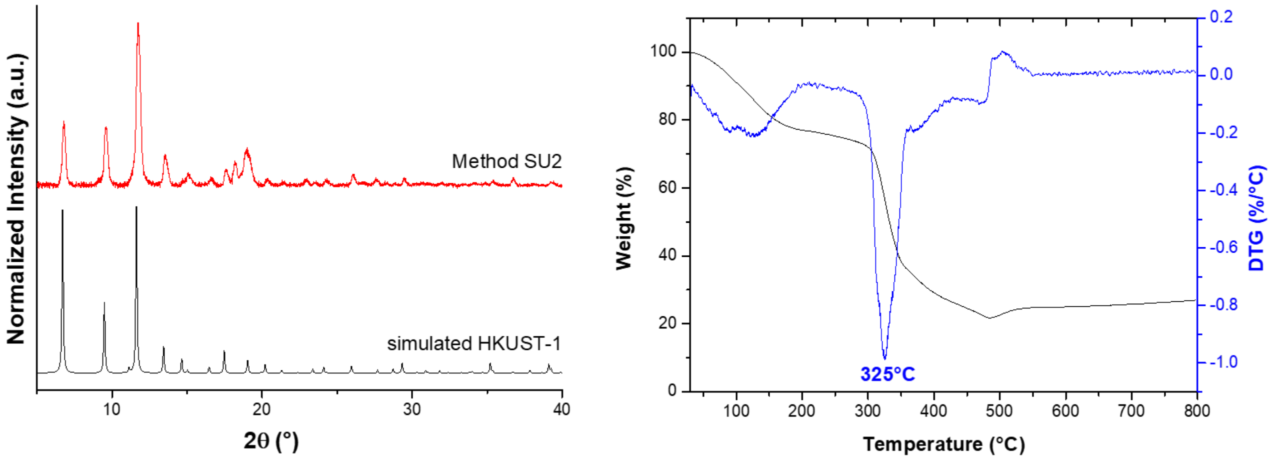


Fig. S16. PXRD diffractogram (left) and TGA (right) for the product obtained by the Method SU2.

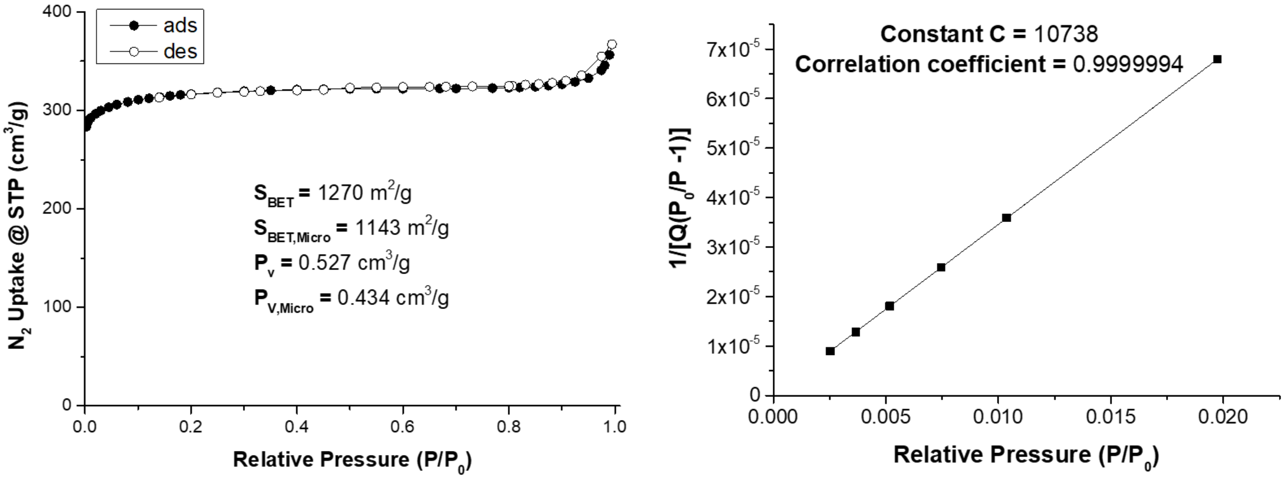


Fig. S17. N_2 adsorption-desorption isotherms at 77 K (left) and plot of $1/[Q(P_0/P - 1)]$ versus relative pressure (right) for the product obtained by the Method SU2.

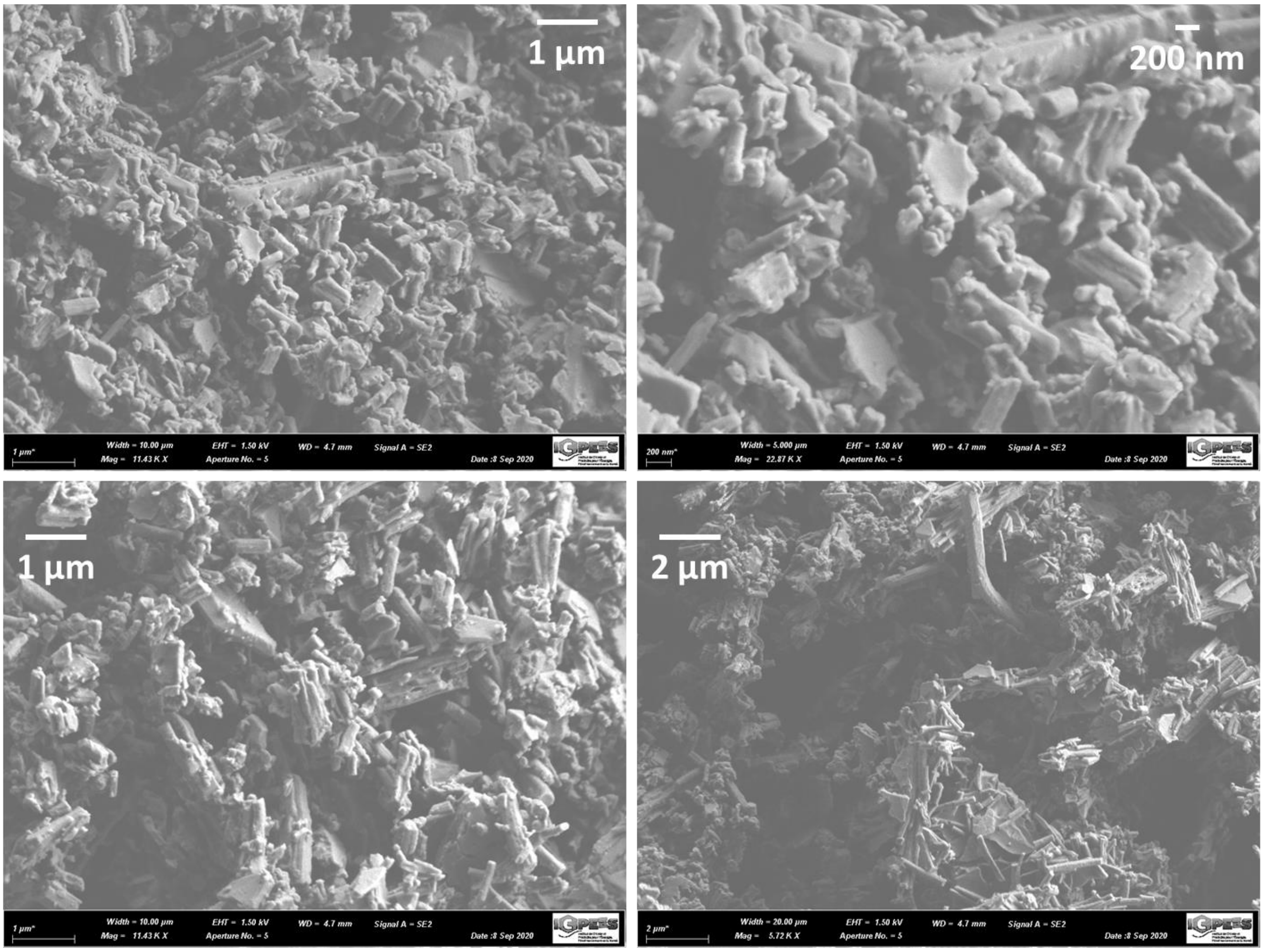
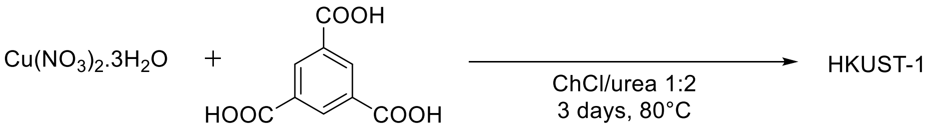


Fig. S18. SEM for the product obtained by the Method SU2.

S4.3 Method SU3 (stirring, no sonication)



In a Chemglass® high-pressure vessel equipped with a magnetic stirring bar, it was added $Cu(NO_3)_2.3H_2O$ (1 equiv., 1.2 mmol, 0.2899 g) and trimesic acid (6 equiv., 7.2 mmol, 0.3982 g). Freshly prepared reline (30 mL) was added into the vessel with the aid of a syringe: the solvent was added in small portions and, in these intervals, mixed gently with a spatula in order to better incorporate the reagents, affording a bright yellow mixture. Finally, the vessel was placed in a pre-heated oil bath at 80°C and reacted for 3 days with continuous stirring. After the completion of the reaction, the resulting mixture appeared as a blue suspension. The vessel was cooled down to room temperature and its content was filtered off and washed with distilled water (400 mL), which immediately turned the green suspension into a blue one, and anhydrous ethanol (400 mL). The remaining blue solid (231 mg) was air-dried and collected into a vial.

Fig. S19. Blue suspension after the completion of the reaction.

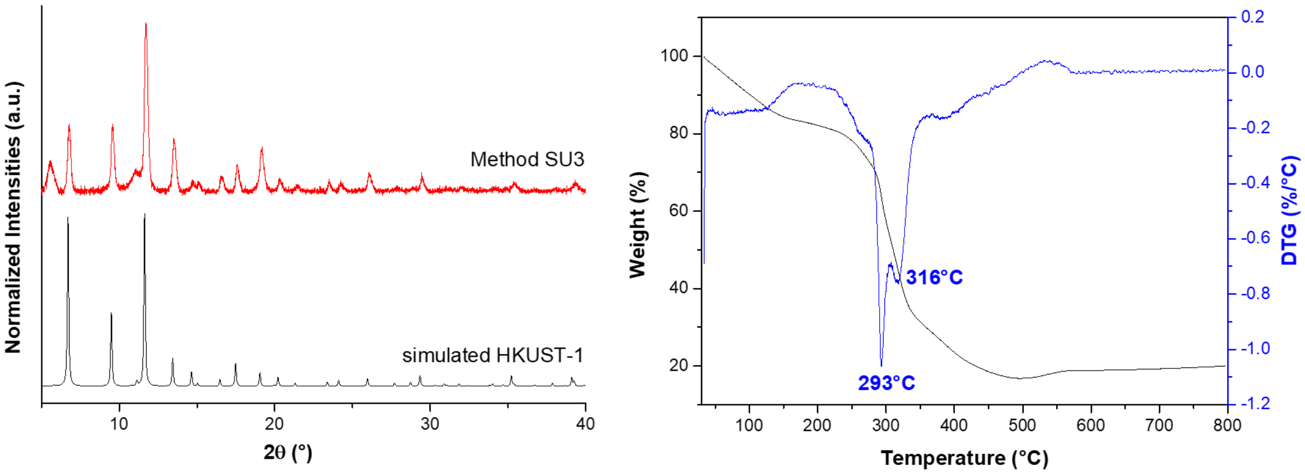


Fig. S20. PXRD diffractogram (left) and TGA (left) for the product obtained by the Method SU3.

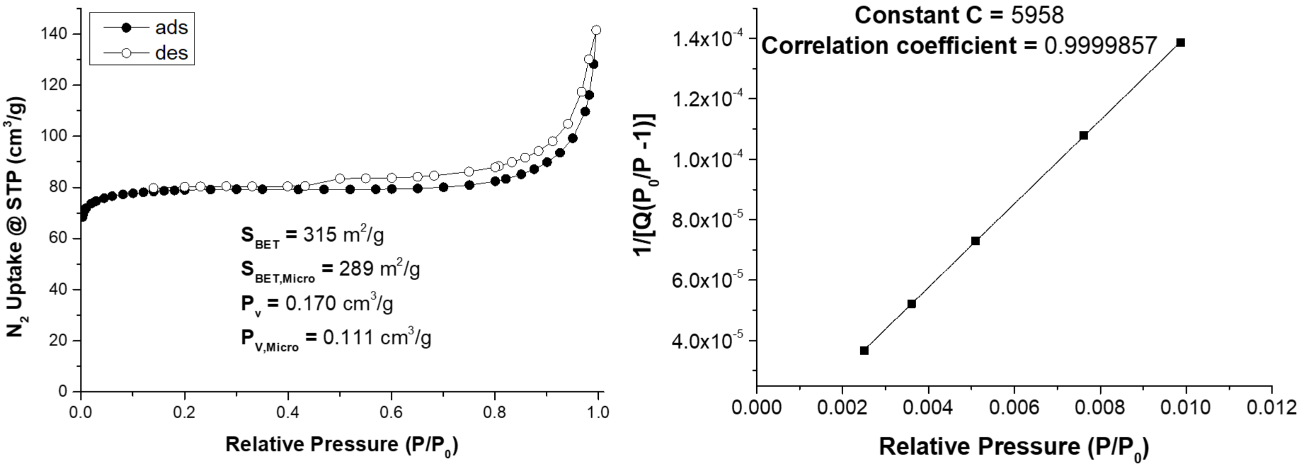


Fig. S21. N_2 adsorption-desorption isotherms at 77 K (left) and plot of $1/[Q(P_0/P - 1)]$ versus relative pressure (right) for the product obtained by the Method SU3.

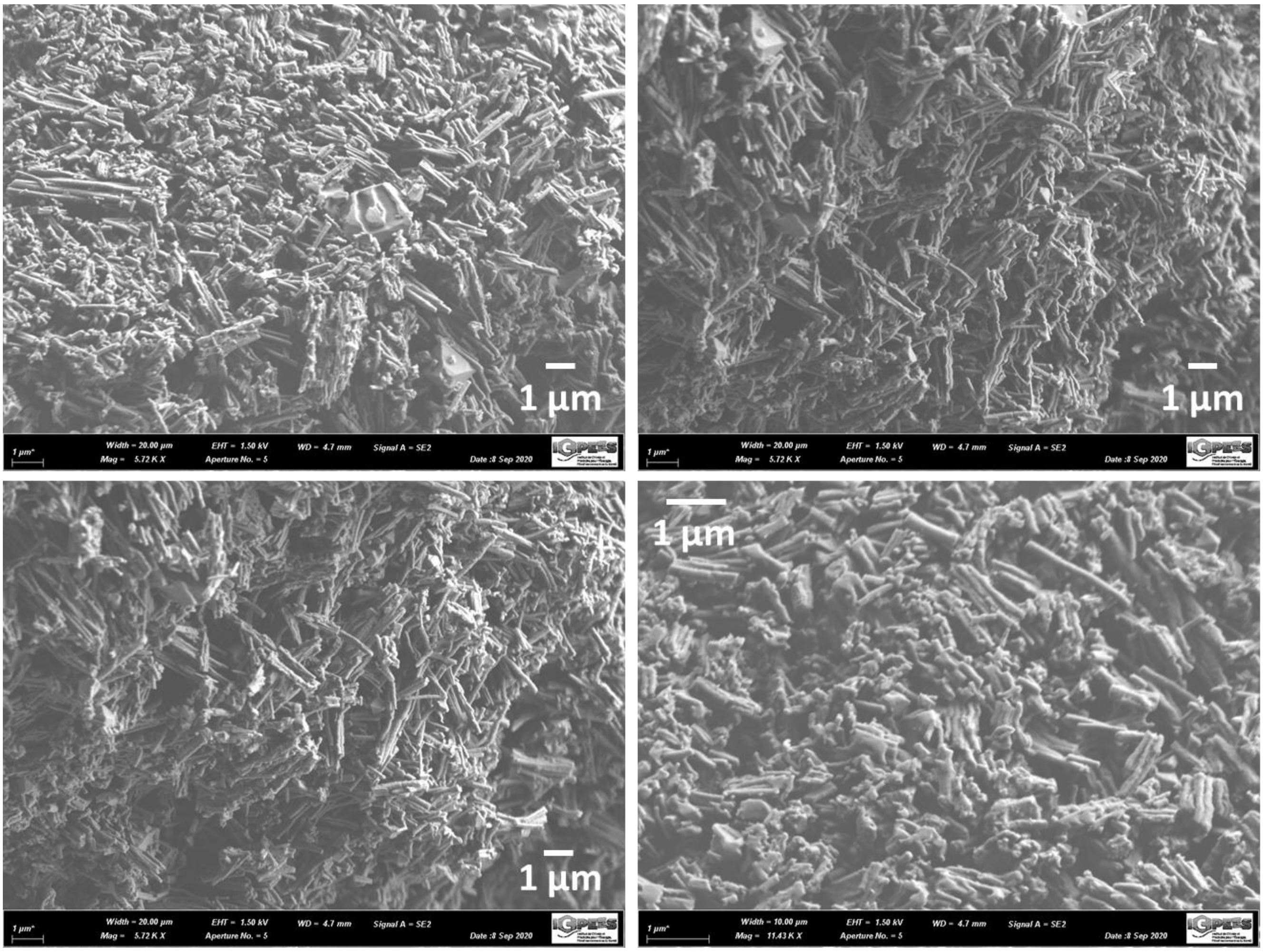
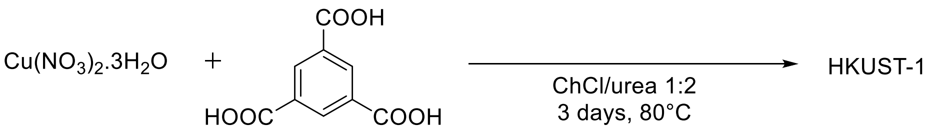


Fig. S22. SEM for the product obtained by the Method SU3.

S4.4 Method SU4 (neither sonication, nor stirring)



In a Chemglass® high-pressure vessel, it was added $Cu(NO_3)_2.3H_2O$ (1 equiv., 1.2 mmol, 0.2899 g) and trimesic acid (6 equiv., 7.2 mmol, 0.3982 g). Freshly prepared reline (30 mL) was added into the vessel with the aid of a syringe: the solvent was added in small portions and, in these intervals, mixed gently with a spatula in order to better incorporate the reagents, affording a bright yellow mixture. Finally, the vessel was placed in a pre-heated oil bath at 80°C and reacted for 3 days. After the completion of the reaction, the resulting mixture appeared as a blue suspension. The vessel was cooled down to room temperature and its content was filtered off and washed with distilled water (400 mL), which immediately turned the green suspension into a blue one, and anhydrous ethanol (400 mL). The remaining blue solid (370 mg) was air-dried and collected into a vial.

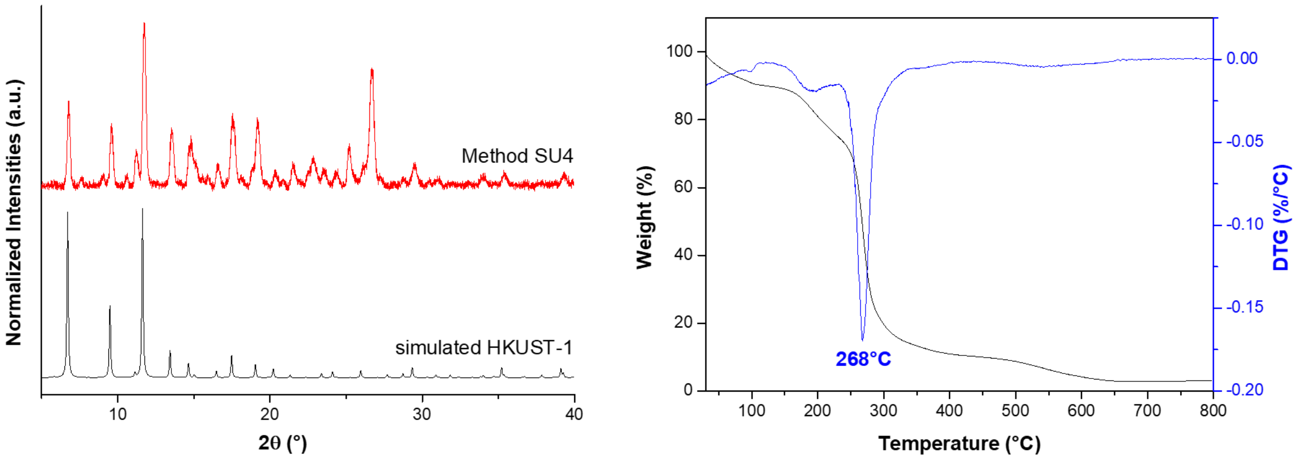


Fig. S23. PXRD diffractogram (left) and TGA (right) for the product obtained by the Method SU4.

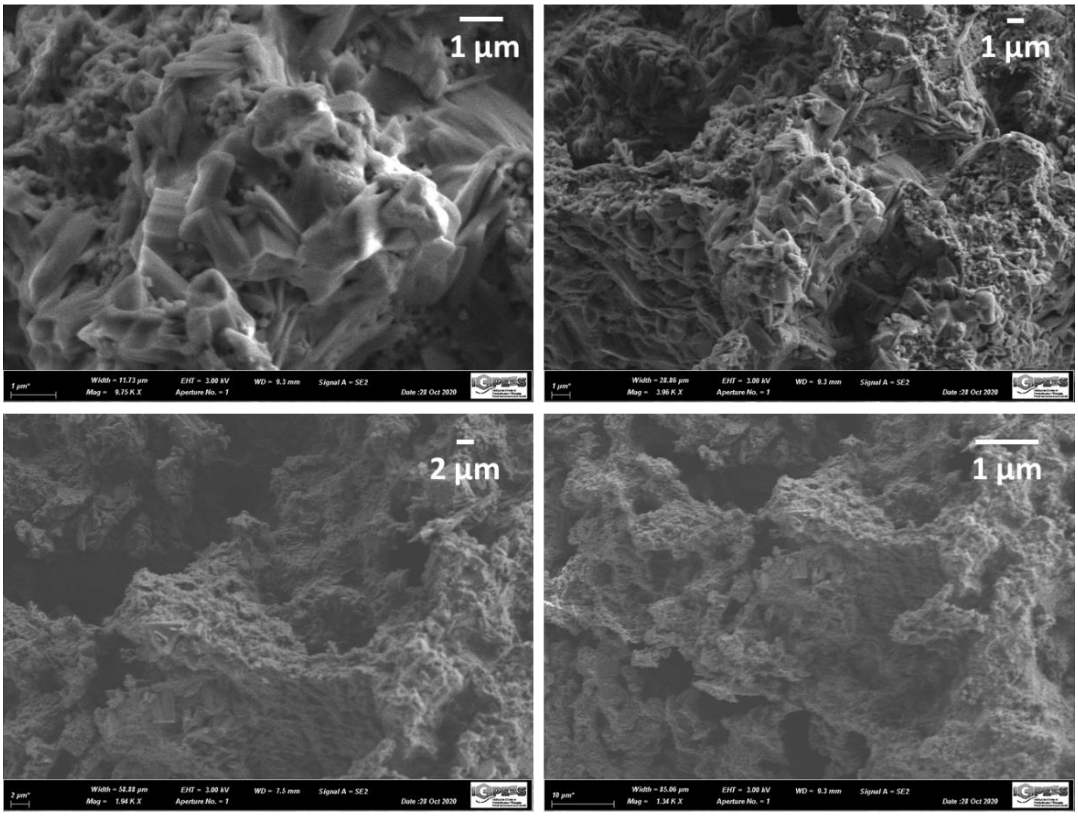
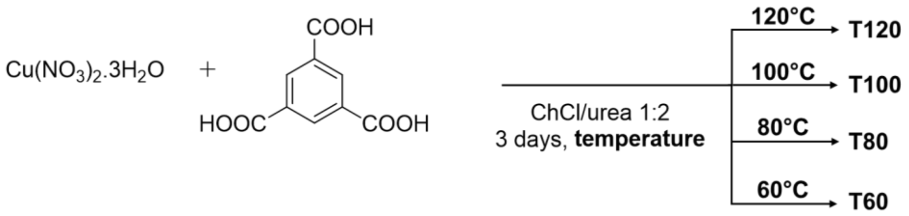


Fig. S24. SEM for the product obtained by the Method SU4.

S5. Optimization of the Reaction Conditions for HKUST-1(reline)

S5.1 Temperature (no sonication)



In an 8 mL vial, it was added $Cu(NO_3)_2.3H_2O$ (1 equiv., 0.3 mmol, 0.0725 g) and trimesic acid (6 equiv., 1.8 mmol, 0.3982 g). Freshly prepared reline (2 mL) was added at once into the vial with the aid of a syringe. After that, the vial was sealed and placed in a pre-heated dry bath at the chosen temperature (either 60°C, 80°C, 100°C, or 120°C) and reacted for 3 days. After the completion of the reactions, they were cooled down to room temperature. Right after, each vial content was filtered off and washed with distilled water (100 mL) and anhydrous ethanol (100 mL). The remaining blue solid was air-dried and collected into a vial, affording the products **T60**, **T80**, **T100**, and **T120**.

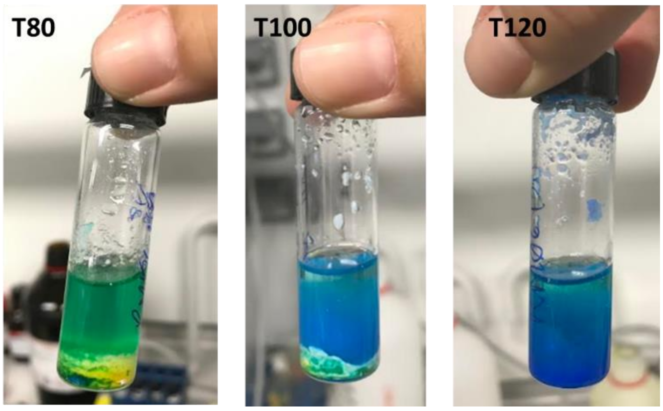


Fig. S25. Different temperature reaction vials after 3 days of reaction at 80°C (left), 100°C (center), and 120°C (right).

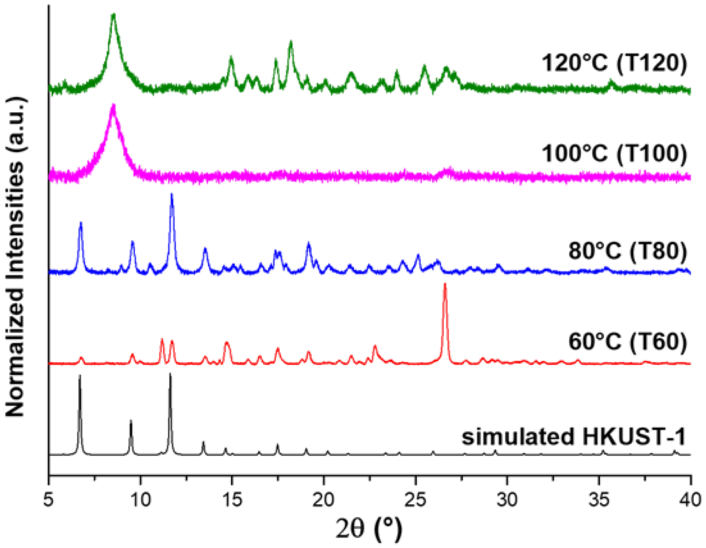
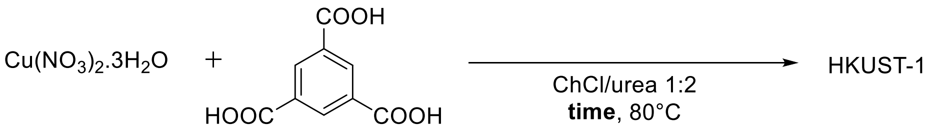


Fig. S26. PXRD profile of **T60**, **T80**, **T100**, and **T120** samples for temperature optimization at 60°C, 80°C, 100°C and 120°C, respectively.

S5.2 Reaction Time (no sonication)



In an 8 mL vial, it was added $Cu(NO_3)_2.3H_2O$ (1 equiv., 0.3 mmol, 0.0725 g) and trimesic acid (6 equiv., 1.8 mmol, 0.3982 g). Freshly prepared reline (2 mL) was added at once into the vial with the aid of a syringe. After that, the vial was sealed and placed in a pre-heated dry bath at 80°C and reacted either for 1h, 3h, 8h, and 1 to 7 days (Table S2). After the completion of the reactions, they were cooled down to room temperature. Right after, each vial content was filtered off and washed with distilled water (100 mL) and anhydrous ethanol (100 mL). The remaining blue solid was air-dried and collected into a vial.

Table S2. Summary of the results for the kinetic experiments (from 1 h to 7 days) at 80°C: obtained mass (mg), temperature of decomposition (T_d, °C) and specific surface area (S_{BET}, m^2/g).

Entry	Time	Mass (mg)	T_d (°C)	S_{BET} (m^2/g)[a]
1	1 h	-[b]	-[b]	-[b]
2	3 h	traces	-[c]	-[c]
3	8 h	15	300	-[c]
4	1 day	13	331	-[c]
5	2 days	31	337	504
6	3 days	45	338	555
7	4 days	33	343	67
8	5 days	20	338	122
9	6 days	82	344	119
10	7 days	88	330	98

[a] Single point surface area at p/p_0 at 0.0077; [b] No product was obtained; [c] No sufficient amount of material for this analysis.

Besides the 1 hour experiment – in which no product was obtained (Table S2, entry 1) – all the experiments resulted in the formation of the $Cu_3(BTC)_2$ material (Fig. S27 and S28).

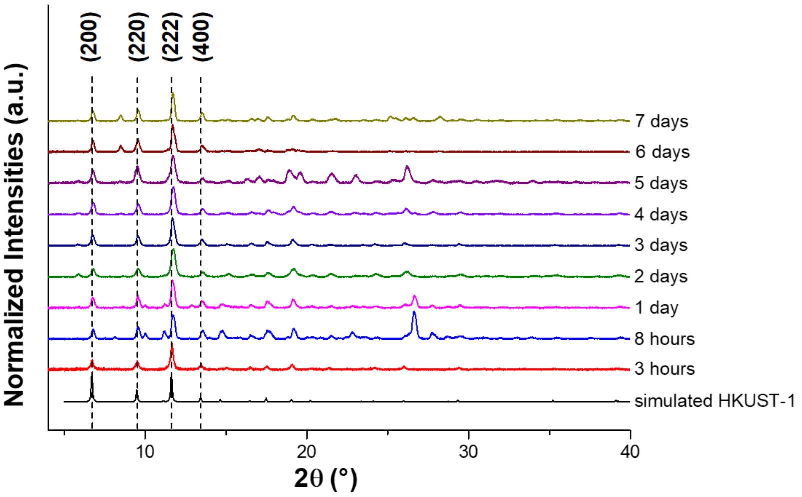


Fig. S27. PXRD diffractogram of the products obtained at 80°C under different reaction times.

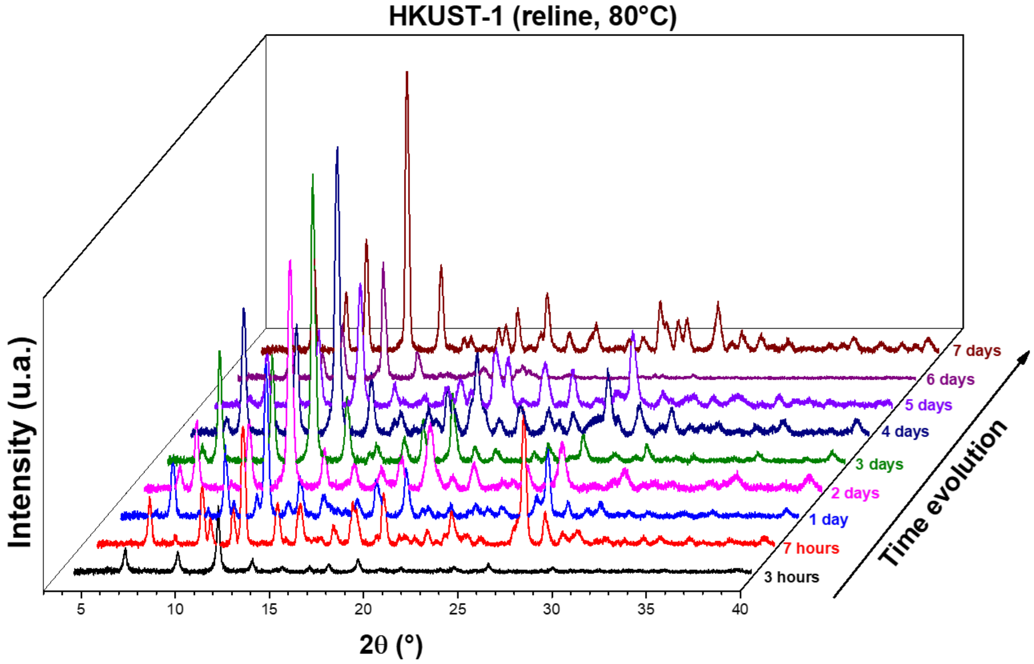


Fig. S28. PXRD diffractogram of the products obtained at 80°C under different reaction times (non-normalized scale).

Aiming to further investigate those obtained materials, other factors were taken under consideration for electing the optimum reaction time, such as the product mass, the decomposition temperature, and the S_{BET} (summarized in Table S2). In Fig. S29, it is shown that both thermal stability and product mass increase up to 3 days of reaction. For the latter, the highest S_{BET} was obtained, with the value of 555 m^2/g (Table S2, entry 6). By analyzing longer reaction times, it was noticed that the T_d increased slightly for the 4 days experiment, and further decreased for longer reaction times. This decline in the T_d was also accompanied by lower values of S_{BET} (<125 m^2/g). Therefore, taking into account all these factors – accessible porosity, thermal stability and product mass – the reaction time of 3 days was elected as optimal, as it displayed a better combination of such features.

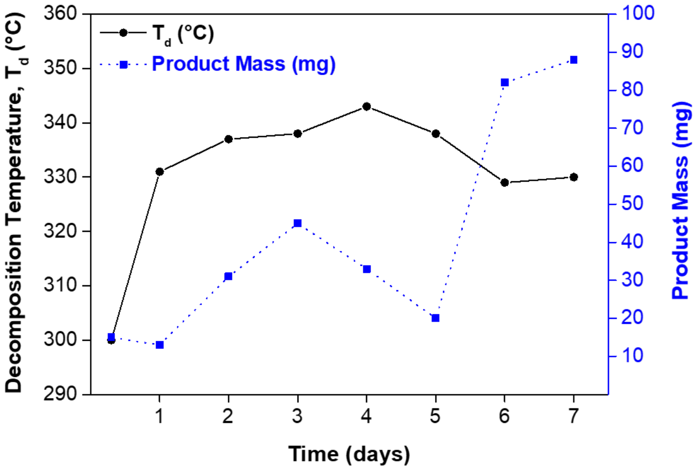


Fig. S29. Plot of decomposition temperature (T_d) and product mass vs. the reaction time for the kinetic experiments of HKUST-1.

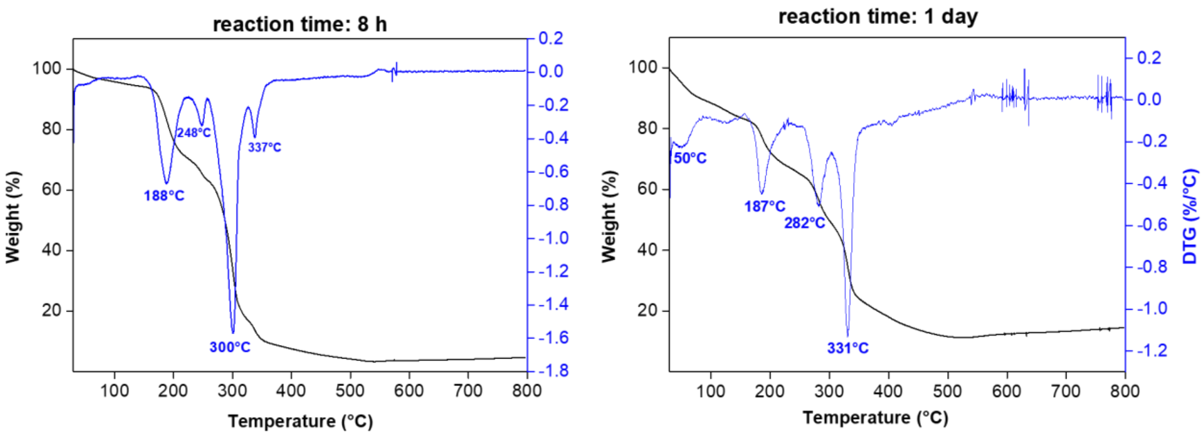


Fig. S30. TGA for the experiments reacted for 8 h (left) and 1 day (right).

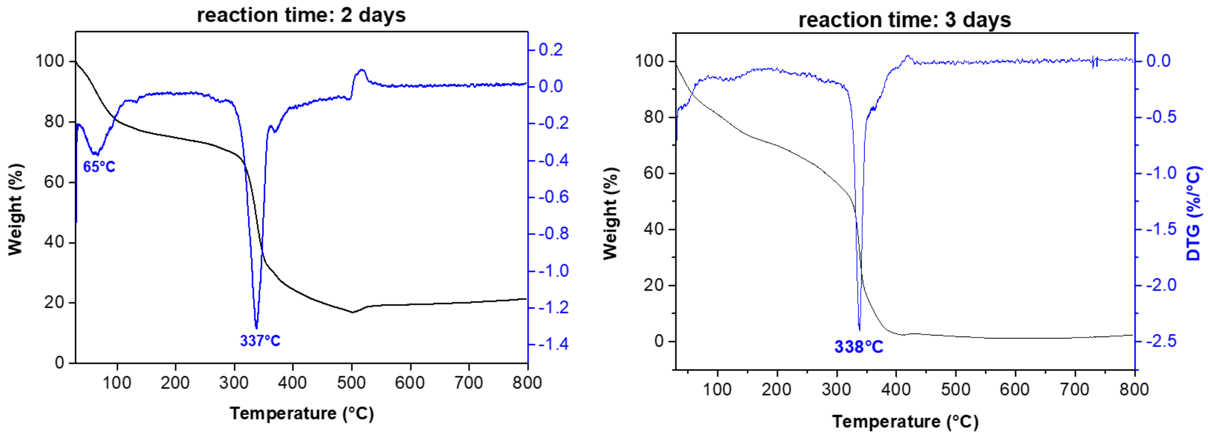


Fig. S31. TGA for the experiments reacted for 2 days (left) and 3 days (right).

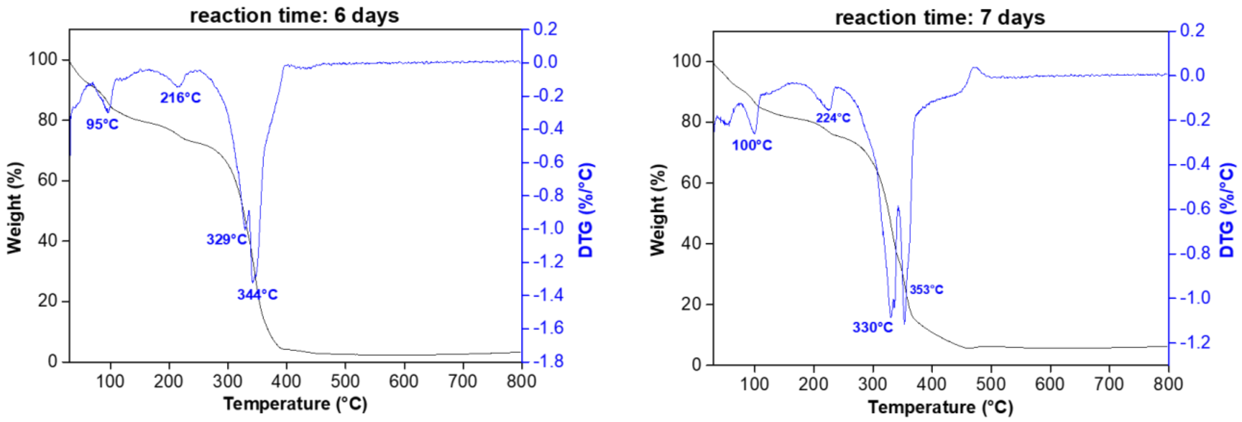


Fig. S32. TGA for the experiments reacted for 4 day (left) and 5 days (right).

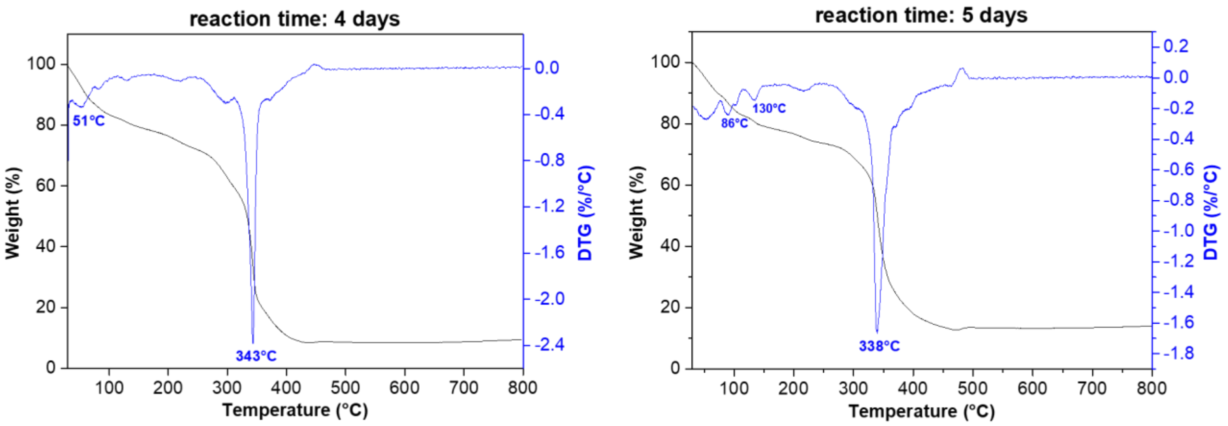


Fig. S33. TGA for the experiments reacted for 6 day (left) and 7 days (right).

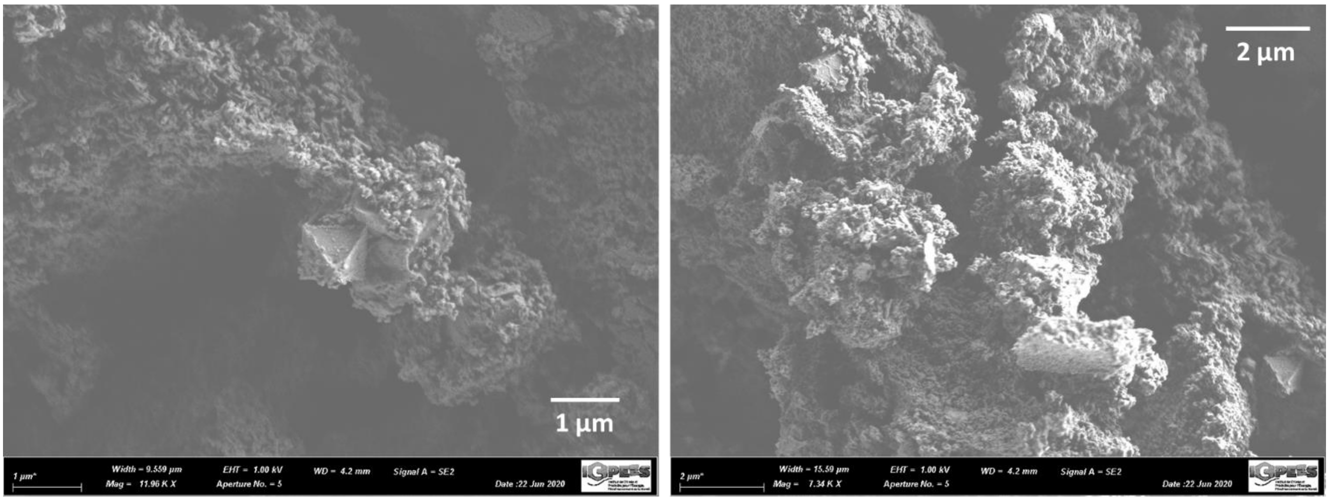


Fig. S34. SEM for reaction time of 3 h. (Table S1, entry 2).

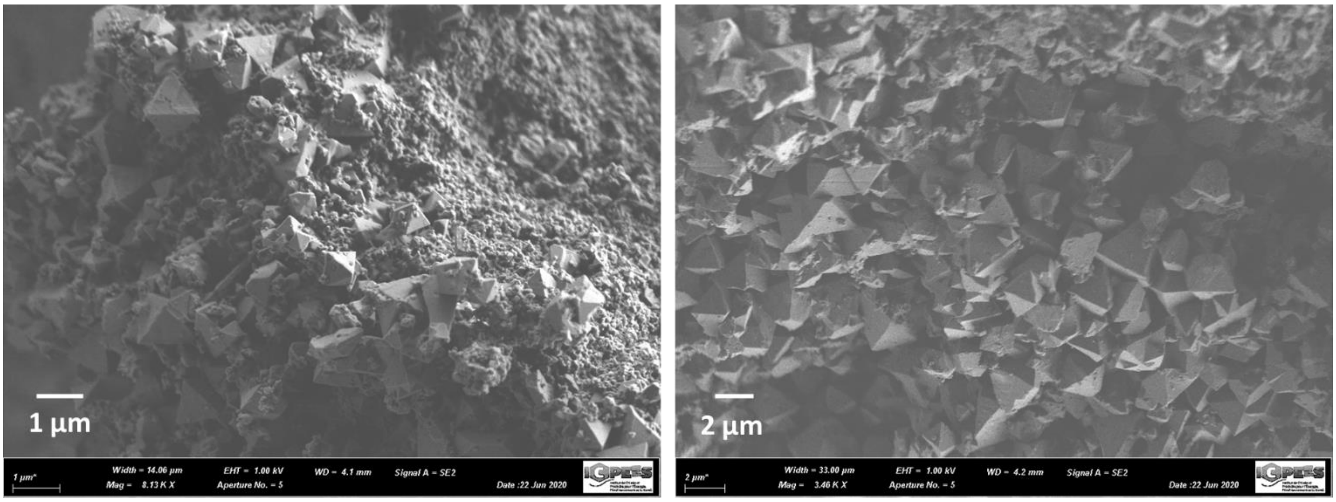


Fig. S35. SEM for reaction time of 8 h. (Table S1, entry 3).

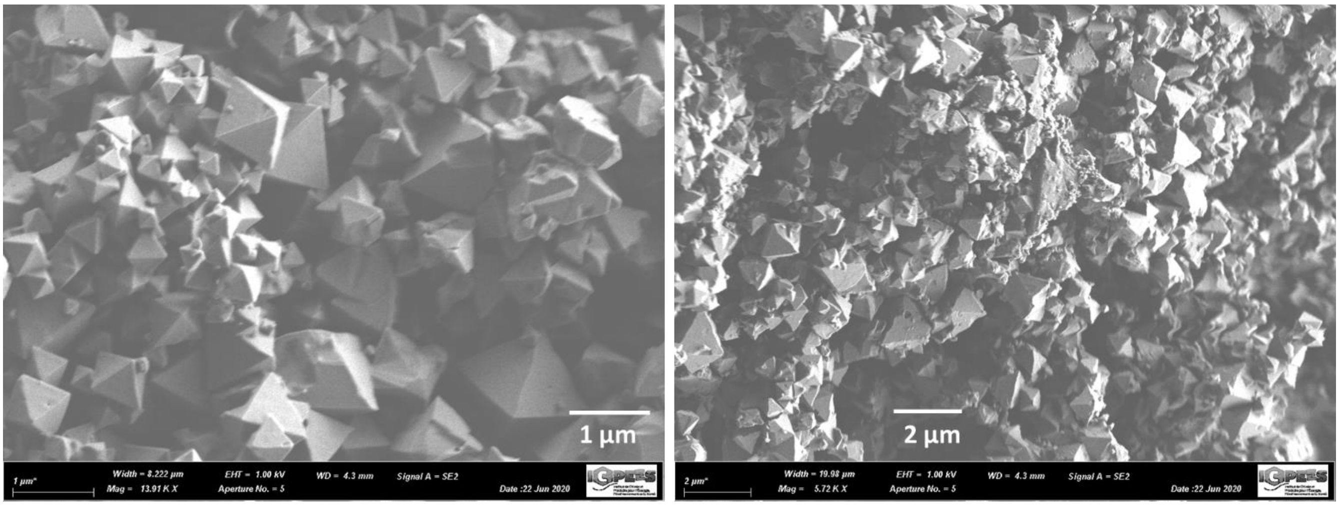


Fig. S36. SEM for reaction time of 1 day. (Table S1, entry 4).

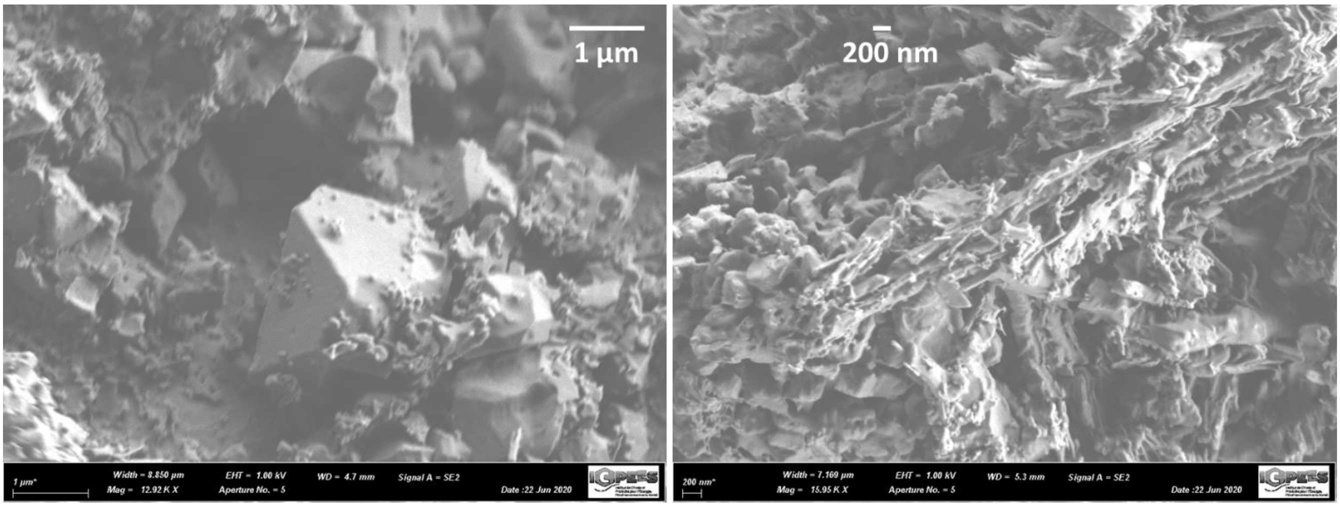


Fig. S37. SEM for reaction time of 2 days. (Table S1, entry 5).

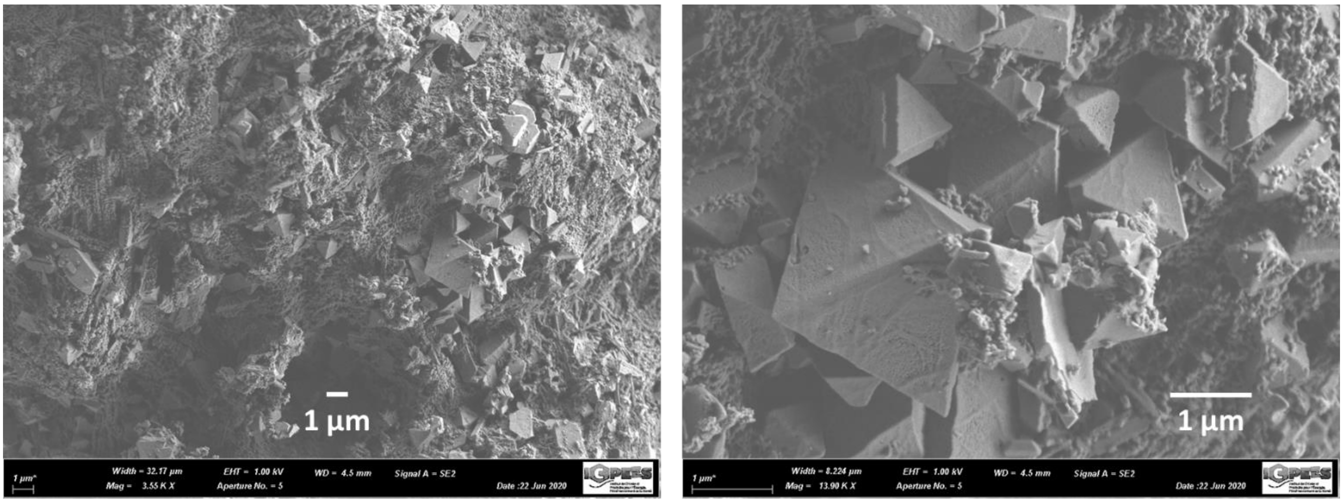


Fig. S38. SEM for reaction time of 3 days. (Table S1, entry 6).

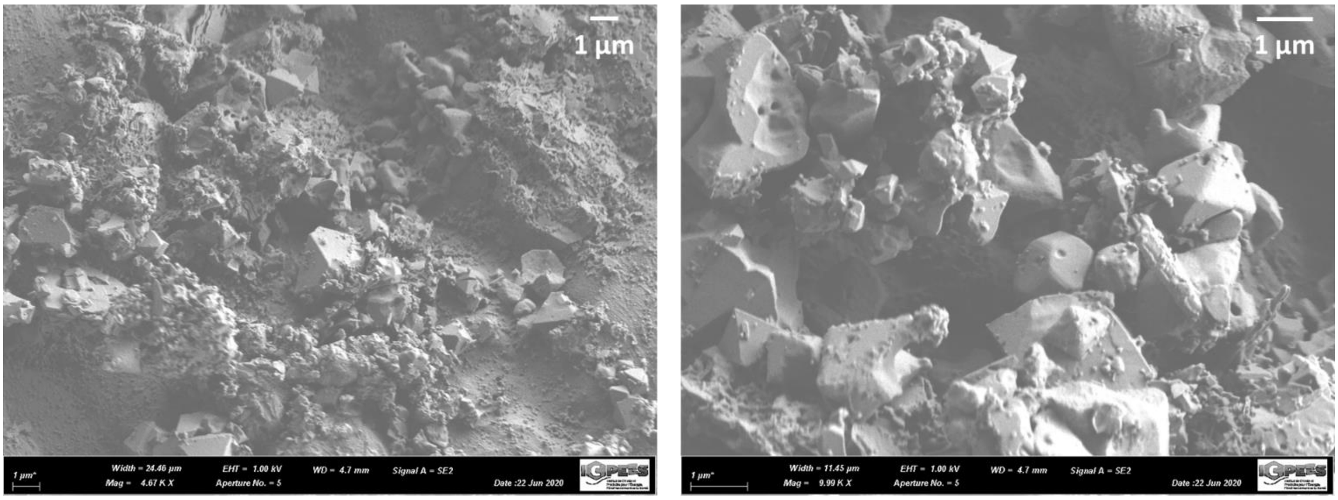
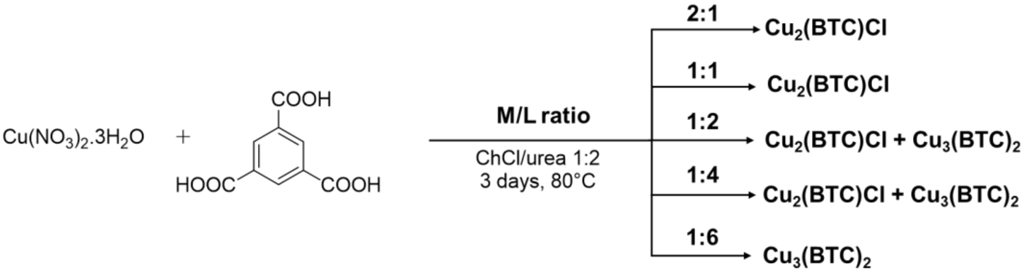


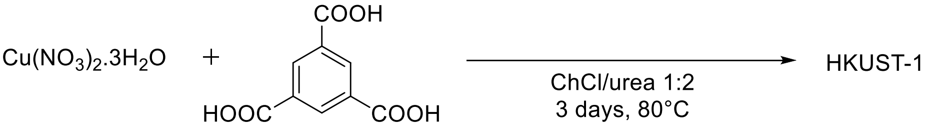
Fig. S39. SEM for reaction time of 7 days. (Table S1, entry 10).

S5.3 Ligand/Metal Ratio



In 8 mL vials, it was added $Cu(NO_3)_2.3H_2O$ and trimesic acid in the respective Metal/Ligand (M/L) molar ratio: 2:1 (0.60 mmol of copper nitrate and 0.30 mmol of BTC), 1:1 (0.30 mmol of copper nitrate and 0.30 mmol of BTC), 1:2 (0.30 mmol of copper nitrate and 0.60 mmol of BTC), 1:4 (0.30 mmol of copper nitrate and 1.2 mmol of BTC), and 1:6 (0.30 mmol of copper nitrate and 1.8 mmol of BTC). Freshly prepared reline (2 mL) was added at once into the vial with the aid of a syringe. After that, the vial was sealed and placed in a pre-heated dry bath at 80°C and reacted for 3 days. After the completion of the reactions, the vials were cooled down to room temperature. Right after, each vial content was filtered off and washed with distilled water (100 mL) and anhydrous ethanol (100 mL). The remaining blue solid was air-dried and collected into a vial, the remaining product was analyzed by PXRD.

S5.4 Concentration (no sonication)



In 8 mL vials, it was added $Cu(NO_3)_2.3H_2O$ (1 equiv., 0.3 mmol, 0.0725 g) and trimesic acid (6 equiv., 1.8 mmol, 0.3982 g). Freshly prepared reline was added into the vessels with the aid of a syringe, in the volumes of 2 mL, 4 mL or 8 mL (for the 8 mL reaction, the reaction was set in a Chemglass® high-pressure vessel). The solvent was added in small portions and, in these intervals, mixed gently with a spatula in order to better incorporate the reagents, affording a bright yellow mixture. After that, the vessels were sealed and placed in a pre-heated dry bath at 80°C and reacted for 3 days. After the completion of the reactions, they were cooled down to room temperature. Right after, each vial content was filtered off and washed with distilled water (100 mL) and anhydrous ethanol (100 mL). The remaining blue solid was air-dried and collected into a vial.

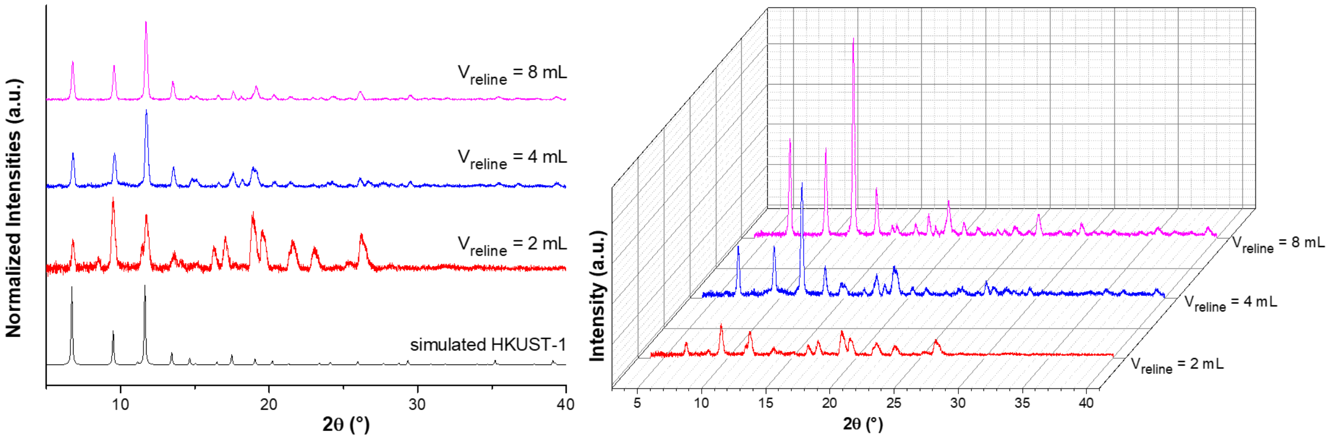


Fig. S40. PXRD of the samples reacted with different volumes of reline. Diffractograms in normalized (left) and non-normalized (right) scales.

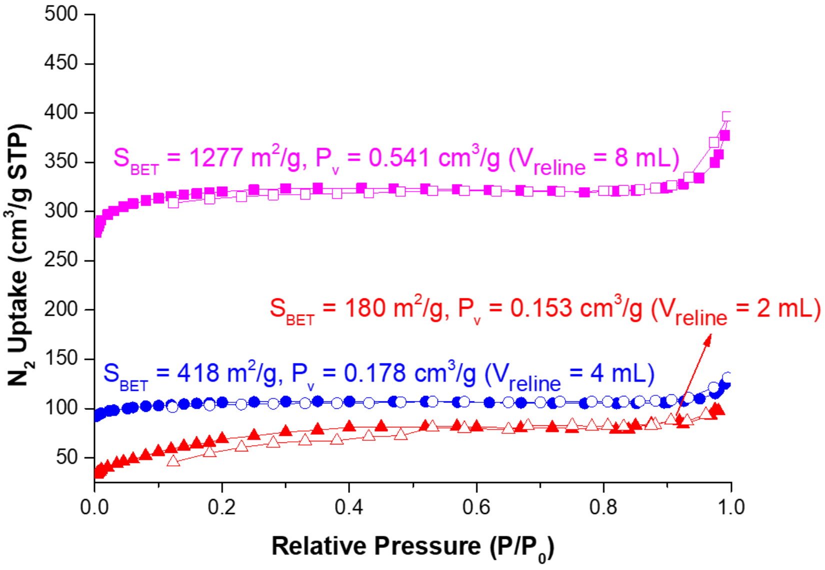


Fig. S41. N_2 adsorption-desorption isotherms at 77 K, along with their BET specific surface areas (S_{BET}) and total pore volumes (P_V). Closed and open symbols stand for adsorption and desorption, respectively.

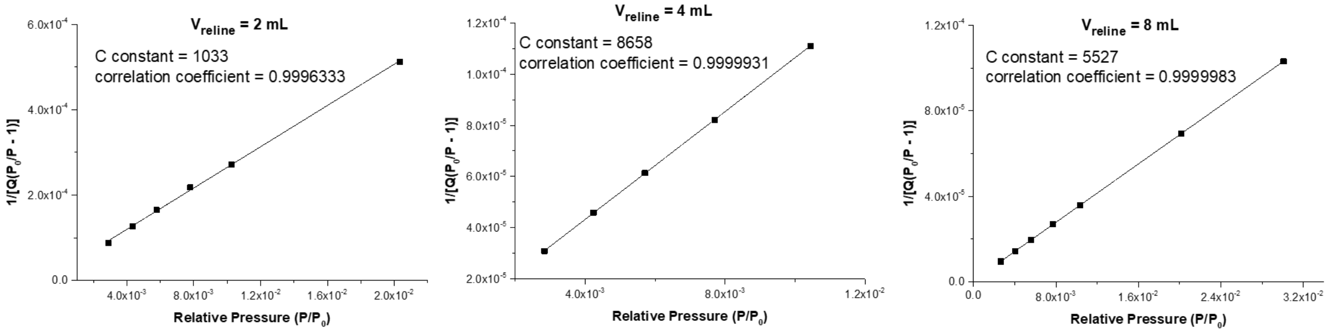


Fig. S42. Plot of $1/[Q(P_0/P - 1)]$ versus relative pressure for V_{reline} = 2 mL (left), V_{reline} = 4 mL (center), and V_{reline} = 8 mL (right).

S5.4.1 Detection of $Cu_2(BTC)Cl$

In 8 mL vials, it was added $Cu(NO_3)_2.3H_2O$ (1 equiv., 0.1 mmol, 0.0242 g) and trimesic acid (6 equiv., 0.6 mmol, 0.1327 g). Freshly prepared reline (5 mL) was added into the vessels with the aid of a syringe. The solvent was added in small portions and, in these intervals, mixed gently with a spatula in order to better incorporate the reagents, affording a bright yellow mixture. After that, the vessels were sealed and placed in a pre-heated dry bath at either 60°C or 80°C and reacted for 6 days. After the completion of the reactions, they were cooled down to room temperature. The vials kept at 60°C and 80°C appeared as a green and a blue mixture, respectively. Right after, each vial content was filtered off and washed with distilled water (100 mL) and anhydrous ethanol (100 mL). The remaining blue solid of both vials were air-dried and collected into a vial.

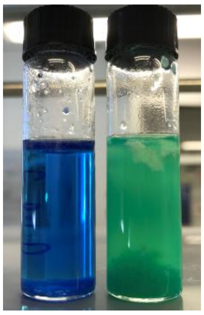


Fig. S43. Reaction kept at 80°C (blue, left) and at 60°C (green, right), after 6 days.

S6. Structure transformation of $Cu_3(BTC)_2$ into $Cu_2(BTC)Cl$

S6.1 From HKUST-1(reline)

In 8 mL vials, it was added 50 mg of the HKUST-1(**reline**). Immediately after, 5 mL of freshly prepared reline was added. When the material got in contact with the solvent, its color changed immediately from light blue to light green. The vial was closed and placed in a pre-heated dry bath at 80°C for either 3 days, 5 days, and 7 days. After the completion of the reactions, the content of the vials had a blue supernatant and blue needles, which were observed by an optical microscope. The vessels were cooled down to room temperature and their content was filtered off and washed with distilled water (100 mL), and anhydrous ethanol (100 mL). The remaining blue solid (~5 mg) was air-dried and collected into a vial.
FT-IR (ATR, cm^{-1}): 3315 (s); 3176 (w); 1615 (s); 1557 (s); 1436 (s); 1363 (s); 1216 (s); 1103 (w); 1092 (w); 925 (w); 834 (m); 754 (m); 722 (m); 667 (m); 597 (w); 454 (s).

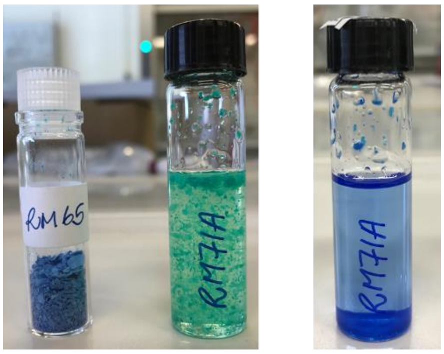


Fig. S44. HKUST-1(**reline**) change of color from blue to green when immersed in reline (left), and the resulting mixture after 3 days at 80°C.

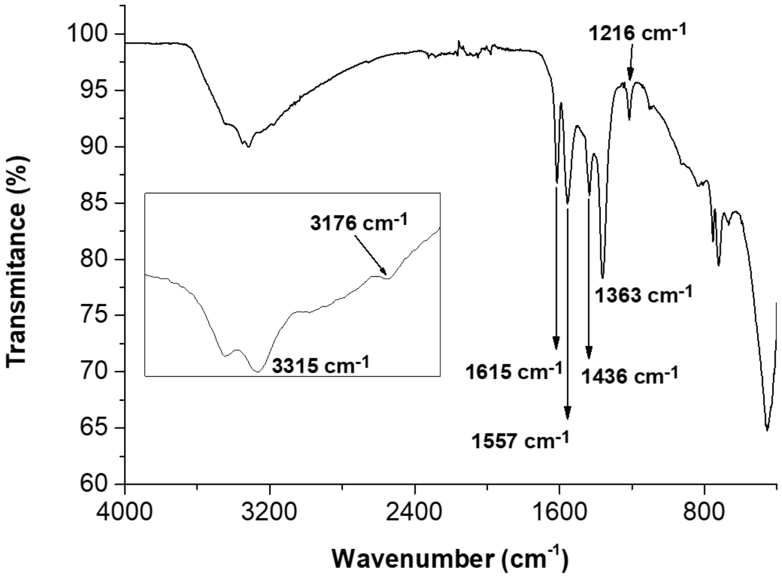


Fig. S45. FT-IR of HKUST-1**(reline)** after 5 days immersed in reline at 80°C.

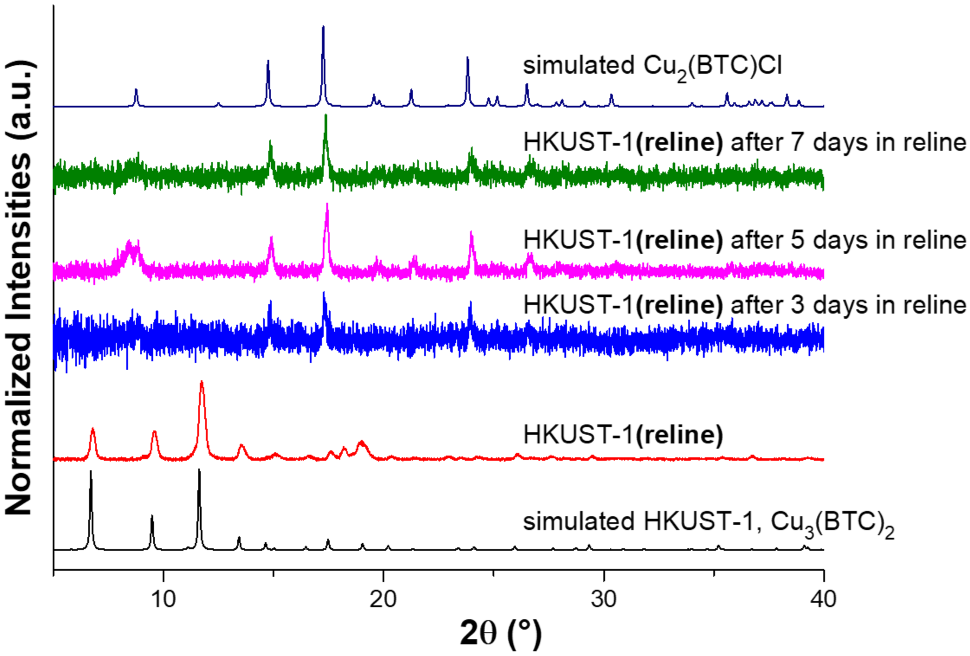


Fig. S46. PXRD diffractogram of HKUST-1**(reline)** (red), immersed in reline after 3 days (blue), 5 days (pink), and after 7 days (green) at 80°C.

S6.2 From HKUST-1c

In 8 mL vials, it was added 50 mg of the HKUST-1**c** material, obtained from the typical solvothermal synthesis in EtOH/water.[2] Immediately after, 5 mL of freshly prepared reline was added. The vial was closed and placed in a pre-heated dry bath at 80°C for either 3 days, 5 days, and 8 days. After the completion of the reactions, the content of the vials presented blue needles, but only after the 8 days reaction they were unanimously present, which was observed by an optical microscope. The vessels were cooled down to room temperature and their content was filtered off and washed with distilled water (100 mL), and anhydrous ethanol (100 mL). The remaining blue solid (~5 mg) was air-dried and collected into a vial.

Elemental analysis (CHN):

- HKUST-1**c**, $C_{18}H_{16}Cu_3O_{17}$ ($[Cu_3(BTC)_2(H_2O)_5]$), calculated: 31.11% C, 2.32% H; found: 31.46% C, 2.09% H, 0% N.

FT-IR (ATR, cm^{-1}):

- HKUST-1**c**, $C_{18}H_{16}Cu_3O_{17}$ ($[Cu_3(BTC)_2(H_2O)_5]$): 3700-2700 (s); 1646 (s); 1447 (s); 1451 (s); 1368 (s); 1111 (w); 1081 (w); 1042 (w); 941 (w); 875 (m); 761 (s); 729 (s); 488 (s).
- HKUST-1**c** after 8 days in reline, $Cu_2(BTC)Cl$: 3315 (m); 3176 (w); 1615 (s); 1562 (s); 1436 (s); 1363 (s); 1216 (s); 1103 (w); 1092 (w); 931 (w); 828 (w); 809 (m); 754 (s); 724 (s); 669 (m); 577 (w); 461 (s).

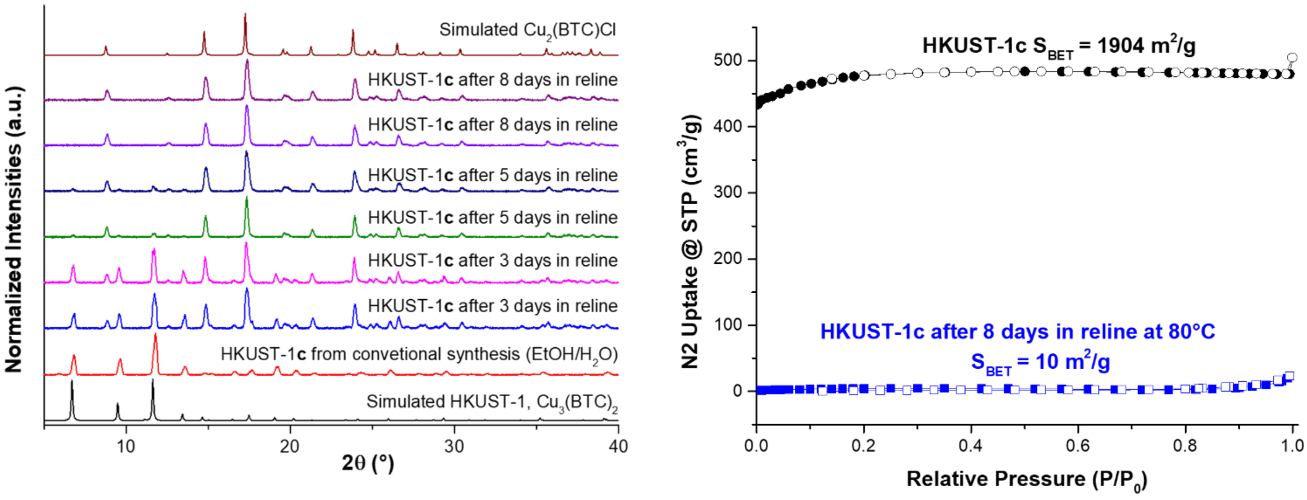


Fig. S47. PXRD diffractogram of HKUST-1**c** (red), immersed in reline after 3 days, 5 days, and 8 days at 80°C, in duplicate (left). N_2 adsorption-desorption isotherms of HKUST-1**c** before immersion (black) and after immersion for 8 days in reline at 80°C (right). Closed and open symbols stand for adsorption and desorption, respectively.

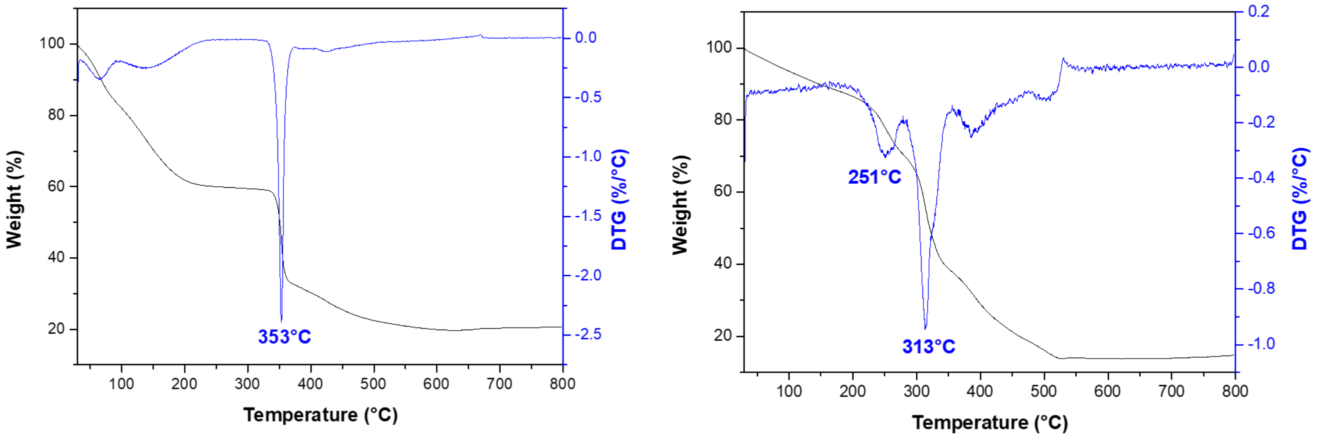


Fig. S48. TGA of HKUST-1**c** before immersion (left) and after immersion for 8 days in reline at 80°C (right).

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[2] Q. M. Wang, D. Shen, M. Bülow, M. L. Lau, S. Deng, F. R. Fitch, N. O. Lemcoff and J. Semanscin, *Micropor. Mesopor.Mat.* 2002, **55**, 217-230.

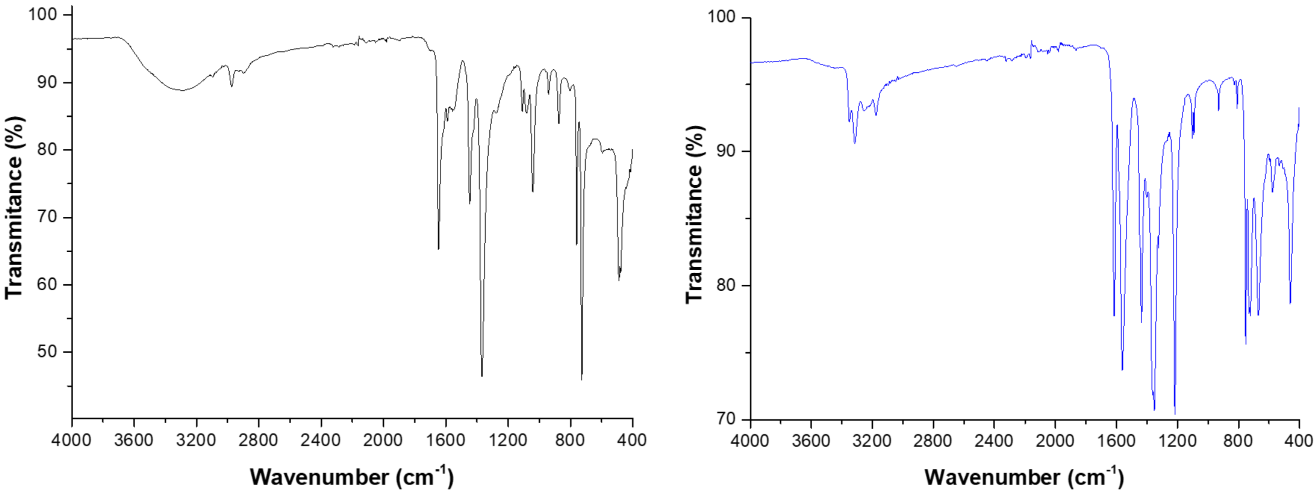


Fig. S49. FT-IR of HKUST-1**c** before immersion (left) and after immersion for 8 days in reline at 80°C (right).

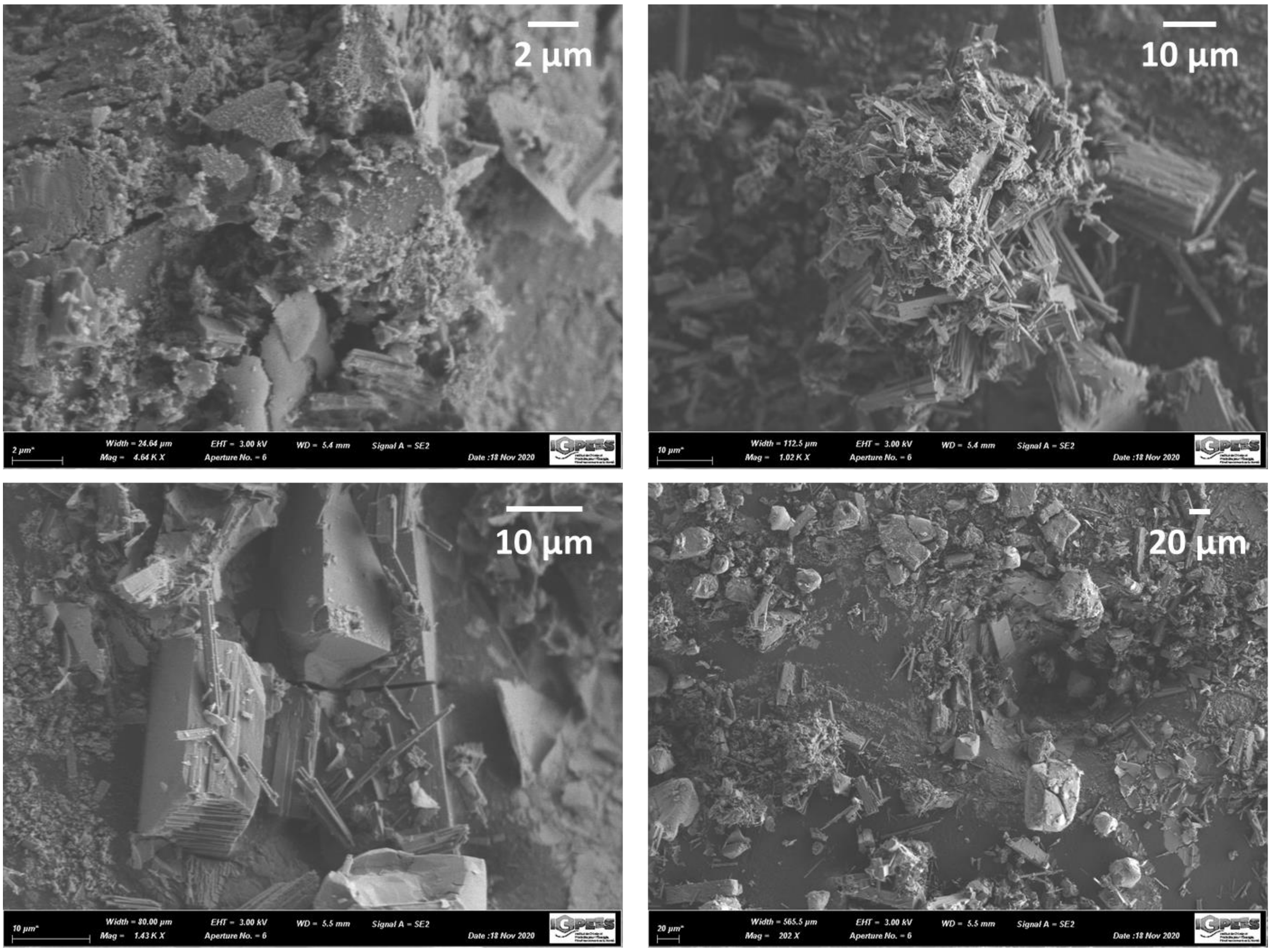


Fig. S50. SEM of HKUST-1**c** after immersion in reline for 3 days at 80°C.

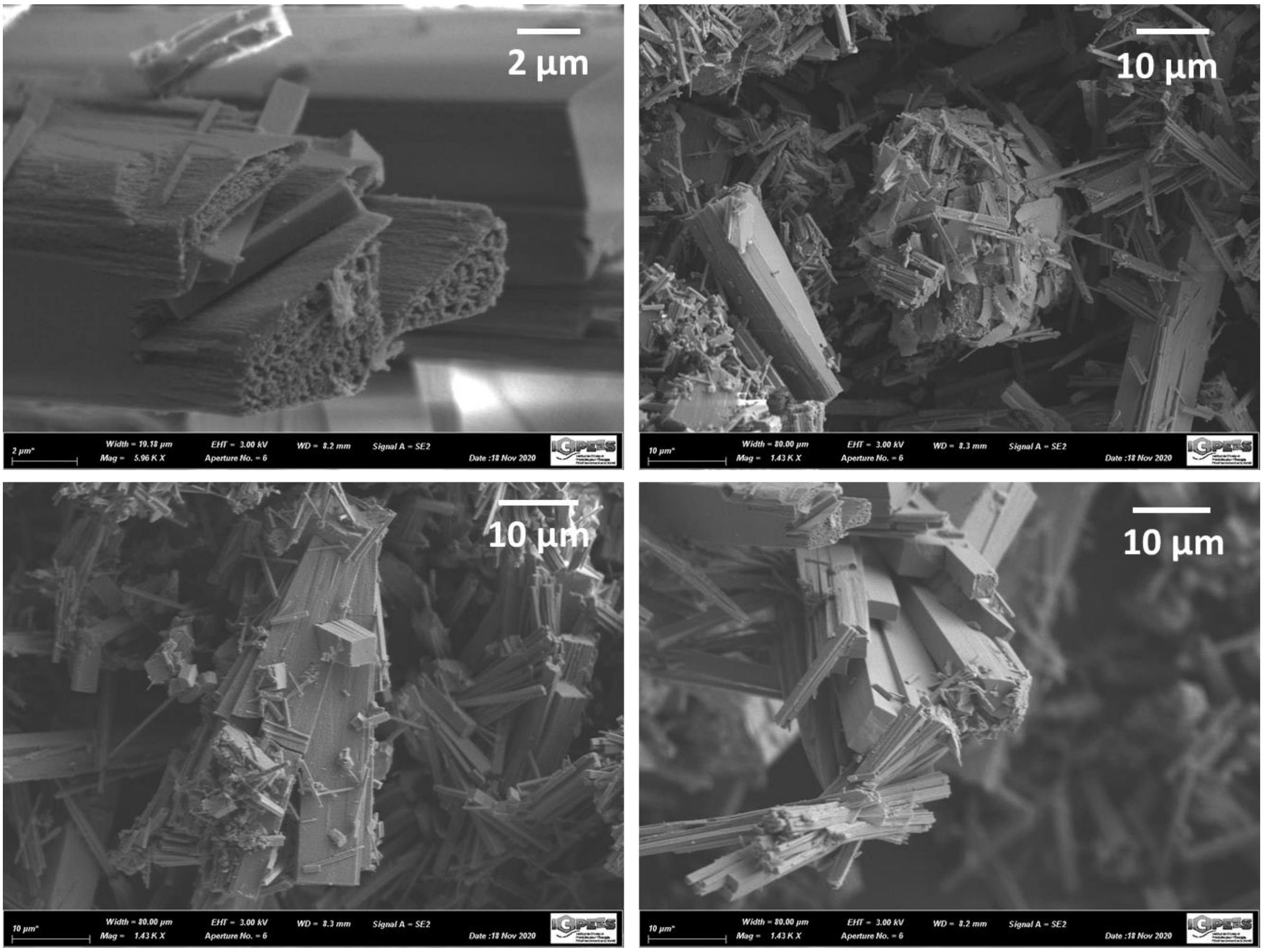


Fig. S51. SEM of HKUST-1**c** after immersion in reline for 5 days at 80°C.

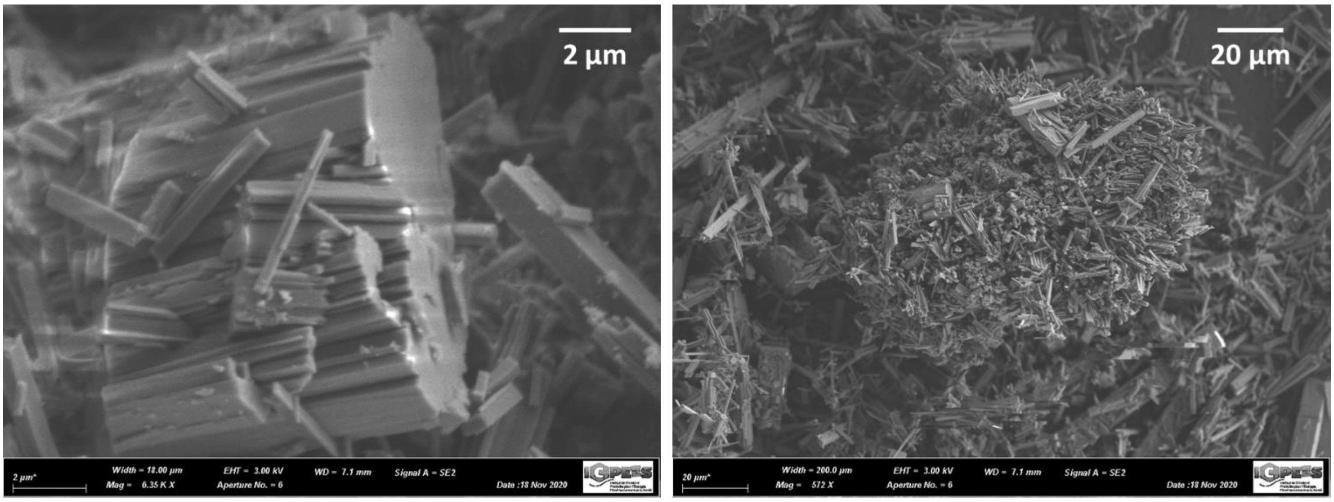
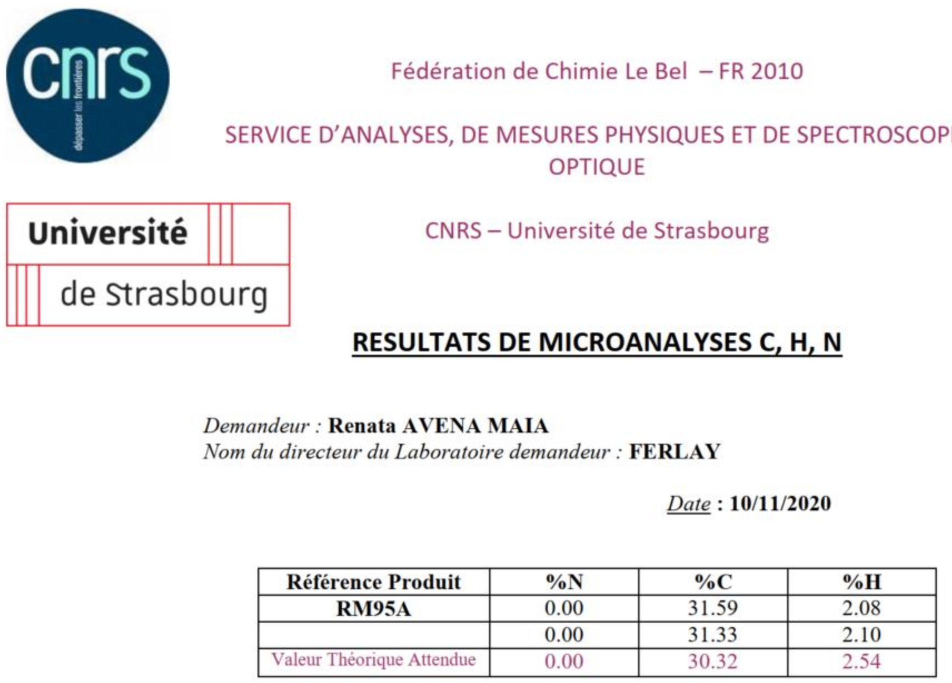


Fig. S52. SEM of HKUST-1**c** after immersion in reline for 8 days at 80°C.



Fédération de Chimie Le Bel – FR 2010

SERVICE D'ANALYSES, DE MESURES PHYSIQUES ET DE SPECTROSCOPIE OPTIQUE

CNRS – Université de Strasbourg

RESULTATS DE MICROANALYSES C, H, N

Demandeur : **Renata AVENA MAIA**
Nom du directeur du Laboratoire demandeur : **FERLAY**

Date : **10/11/2020**

Référence Produit	%N	%C	%H
RM95A	0.00	31.59	2.08
	0.00	31.33	2.10
Valeur Théorique Attendue	0.00	30.32	2.54

Fig. S53. Elemental analysis for the sample of HKUST-1**c**.

S7. Structure transformation evaluation of $Cu_3(BTC)_2$/$Cu_2(BTC)Cl$ in H_2O/EtOH

S7.1 From $Cu_3(BTC)_2$ to $Cu_2(BTC)Cl$

In an 8 mL vial, it was added 50 mg of the HKUST-1**c** material (0.07 mmol, based on the chemical formula $[Cu_3(BTC)_2(H_2O)_4]$), and choline chloride (6 equiv., 0.42 mmol, 0.059 g). Immediately after, 5 mL of EtOH/H_2O was added. The vial was closed and placed in a pre-heated dry bath at 80°C for 7 days. After the reaction was over, the vial was cooled down to room temperature. The content of the vial was thoroughly washed with distilled water and ethanol. The remaining product (blue powder, 37 mg) was analyzed by PXRD, showing that no phase transformation occurred in H_2O/EtOH in the presence of excess of ChCl, and that the crystalline nature of the HKUST-1**c** material still remained.

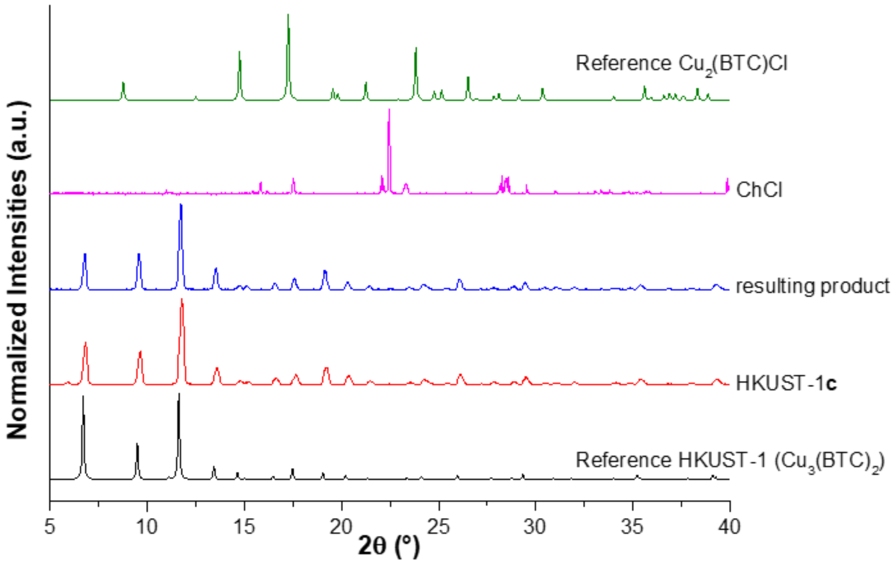


Fig. S54. PXRD diffractogram of HKUST-1**c** (red) immersed in H_2O/EtOH in the presence of ChCl after 7 days at 80°C (blue).

S7.2 From $Cu_2(BTC)Cl$ to $Cu_3(BTC)_2$

In an 8 mL vial, it was added 40 mg of the $Cu_2(BTC)Cl$ material (0.09 mmol, based on the chemical formula $[Cu_2(BTC)Cl(H_2O)_4]$) and trimesic acid (6 equiv., 0.54 mmol, 0.1134 g). Immediately after, 5 mL of EtOH/H_2O was added. The vial was closed and placed in a pre-heated dry bath at 80°C for 7 days. After the reaction was over, the vial was cooled down to room temperature. The content of the vial was thoroughly washed with distilled water and ethanol. The remaining product (5 mg) was analyzed by PXRD, showing that no phase transformation occurred in H_2O/EtOH in the presence of excess of trimesic acid.

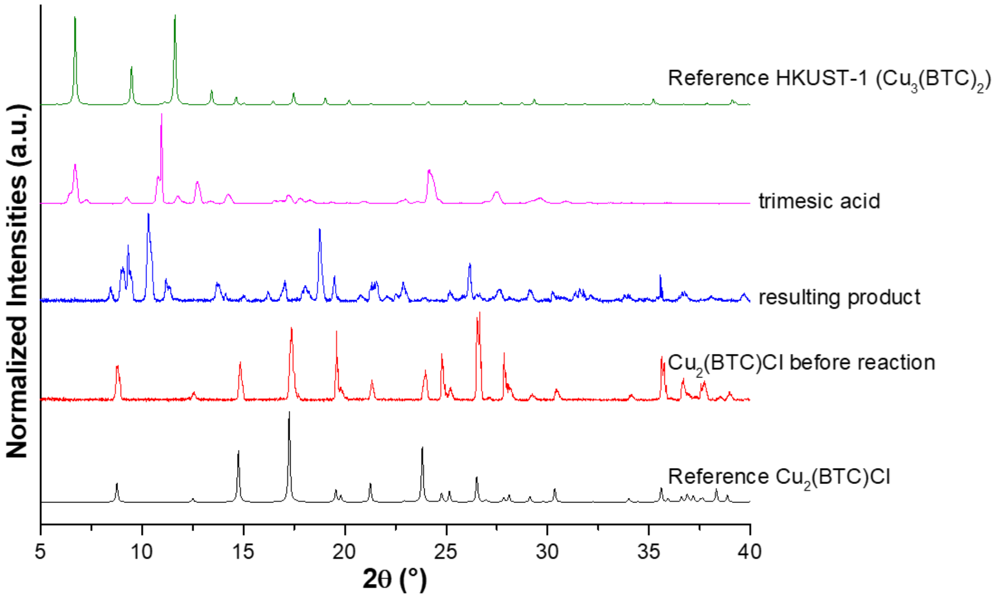


Fig. S55. PXRD diffractogram of Cu2(BTC)Cl material (red) immersed in H_2O/EtOH in the presence of trimesic acid after 7 days at 80°C (blue).