



HAL
open science

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

Renata Maia, Benoît Louis, Stéphane Baudron

► **To cite this version:**

Renata Maia, Benoît Louis, Stéphane Baudron. HKUST-1 MOF in reline deep eutectic solvent: synthesis and phase transformation. Dalton Transactions, 2021, 50 (12), pp.4145-4151. 10.1039/D1DT00377A . hal-03215927

HAL Id: hal-03215927

<https://hal.science/hal-03215927>

Submitted on 19 Aug 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Renata A. Maia,^a Benoît Louis^{*,b} and Stéphane A. Baudron^{*,a}

^a CNRS, CMC UMR 7140, Université de Strasbourg, 4 rue Blaise Pascal, F-67000 Strasbourg, France, E-mail: sbaudron@unistra.fr

^b CNRS, ICPEES UMR 7515, Université de Strasbourg, 25 rue Becquerel, F-67087 Strasbourg, France, E-mail: blouis@unistra.fr

The fate of HKUST-1 ($\text{Cu}_3(\text{BTC})_2$, 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 $\text{Cu}_2(\text{BTC})\text{Cl}$ also forms. It was unequivocally demonstrated that, upon heating in reline, HKUST-1 converts 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.

Introduction

Metal-Organic Frameworks (MOFs),¹ a class of crystalline, porous, and hybrid reticular materials constructed by complexation of metallic cations by polytopic linkers incite increasing interests academically and industrially, mainly in the fields of adsorption,²⁻⁴ heterogeneous catalysis,^{5,6} and electrical conductivity,⁷ to cite a few. The conventional and most common strategy for MOF synthesis remains the solvothermal approach, consisting in the reaction taking place in a closed vessel under autogenous pressure.^{8,9} Nonetheless, alternative synthetic routes have been progressively introduced in the MOF field, aiming at more sustainable techniques and environmentally friendly reaction media or as a mean to obtain novel materials. Additionally, the use of different synthetic methods could even result in materials with unusual features, such as different morphologies, particle sizes, and textural properties. These features could influence the MOF performance towards a certain application, as they contribute to the physico-chemical properties of a given material.⁸ One alternative methodology for the preparation of MOFs worth mentioning is ionothermal synthesis.^{8,10} This approach consists in providing an ionic environment for the reaction, and, ideally, eliminates the competition between template-framework and solvent-framework interactions that takes place in hydro/solvo-thermal synthesis.¹¹ Whereas ionic liquids (IL) have been widely and successfully employed with this approach,¹¹⁻¹⁴ the use of Deep Eutectic Solvents (DES) as alternative reaction media remains under-explored.¹²

DES are a class of non-toxic, biodegradable, low vapor-pressure and inexpensive solvents, usually made from renewable sources.¹⁵⁻¹⁹ They consist in a mixture of two or more solid components, with a melting point substantially lower than the one of its individual components. Coined in 2003 by Abbott and co-workers,²⁰ the term “deep eutectic solvents” was employed to address the low melting point of choline chloride (ChCl) and urea mixtures. Reline, the usual name for this DES, is a liquid at room temperature and has a melting point of 12°C,^{20,21} while

its individual pure components exhibit melting points at 302°C and 135°C, respectively. This depression of the melting point is attributed to the formation of hydrogen bonds between a hydrogen-bond acceptor (HBA) and a hydrogen-bond donor (HBD), whereas the free energy of the solid phase is modified due to the supramolecular complex that is formed.^{15,16} The individual components of a particular DES determine not only its melting point, but other physical properties, such as viscosity and conductivity, allowing the tunability of such properties.²¹ Often compared to ionic liquids, DES differ by usually incorporating at least one neutral component, and more importantly, due to their atom economy of 100%. Since DES are prepared by the straightforward mixture of its commercially available components by heating or grinding, they need neither further purification by organic solvents nor subsequent treatments, as they are used as-synthesized, and therefore are truly green solvents.²²

Interestingly, in addition to being reaction media for the preparation of MOFs, DES can play multiple other roles as reported by Bu and co-workers in their study of the synthesis of $[\text{In}_3(\text{BTC})_4]_n^{3n-}$ (BTC = 1,3,5-benzenetricarboxylate, trimesate) in ChCl/ethylene-urea (e-urea)²³ and a series of trivalent metal MOFs (In^{3+} , Y^{3+} , Nd^{3+} , Sm^{3+} , Gd^{3+} , Dy^{3+} , Ho^{3+} , Yb^{3+}) employing several ChCl/urea derivative mixtures.²⁴ In the latter, the authors observed (i) the incorporation of both cations and anions, with cholinium acting as a structure-directing agent (SDA) and Cl^- ions bound to the framework; (ii) the incorporation of both cations and neutral molecules, with cholinium ions acting as SDA and neutral ligands bound to the framework, or the opposite, where (iii) neutral ligands act as SDA and cholinium ions are bound directly to the framework; and finally, (iv) the direct bonding of neutral compounds in the MOF structure. Furthermore, a fifth alternative is possible, where neither choline nor the neutral DES component are incorporated, but only the chloride anion, as evidenced in the study of $\text{Zn}_2(\text{im})\text{Cl}_2[\text{B}(\text{im})_4]$ (im = imidazolate) material in ChCl/1,3-dimethylurea (m-urea).²⁵ Additionally, Liao *et al.*²⁶ synthesized the coordination polymer $[\text{Zn}(\text{O}_3\text{PCH}_2\text{CO}_2)]_n \cdot \text{NH}_4$ in reline, in which the authors suggest that $(\text{NH}_4)^+$, formed by thermal decomposition of urea, acts as an SDA, since a higher temperature was essential for product formation. Therefore, DES can transcend the solvent role, as they may intrinsically participate in the formation of those extended structures.

In light of these unique features, it appeared interesting to further investigate DES for the synthesis of other MOFs such as well-established materials. In the present study, the synthesis of HKUST-1 ($\text{Cu}_3(\text{BTC})_2$, Fig. 1 left) in the DES reline was explored. A preliminary report by Liu *et al.*²⁷ addressed the synthesis of this MOF, by employing copper nitrate/trimesic acid in a 2.1:1 molar ratio, either in ChCl/e-urea or ChCl/m-urea at 100°C for 36 h. They obtained pure $\text{Cu}_3(\text{BTC})_2$ material, evidenced by PXRD and SEM showing typical octahedral micro-crystals. The same morphology was evidenced by Kim *et al.*,²⁸ who investigated the synthesis of this material in ChCl/e-urea by sonication. They were able to obtain the pure HKUST-1 material after 1 h, with excellent thermal and textural properties by reacting copper nitrate/trimesic acid in a 2.6:1 molar ratio. Interestingly, Jiao and co-workers²⁹ reported the obtention of $\text{Cu}_2(\text{BTC})\text{Cl}$ single-crystals (Fig. 1 right), when reacting copper nitrate/trimesic acid (1:1 molar ratio) in reline for 3 days at 100°C. The 2D layered $\text{Cu}_2(\text{BTC})\text{Cl}$ structure was isolated instead of the traditional $\text{Cu}_3(\text{BTC})_2$ one.

Considering the peculiar roles of DES in the synthesis of MOFs, these results raise the question of whether the tunability of the reaction conditions could favor one material or the other, as well as the nature of the relationship between these materials. Seeking to address this issue, we report herein the optimized preparation of HKUST-1 in reline and its in-depth characterisation by powder X-ray diffraction, infrared spectroscopy, N_2 adsorption-desorption isotherms,

elemental analysis, thermogravimetric analysis and scanning-electron microscopy. Importantly, we describe the unprecedented phase transformation of HKUST-1 in this medium. Indeed, the HKUST-1 material, either prepared in DES or solvothermally, was found to transform unequivocally into the non-porous $\text{Cu}_2(\text{BTC})\text{Cl}$ structure, upon heating in reline. This highlights that this solvent can not only be used to make HKUST-1 but also to break it and convert it. Hence, a sixth role of DES in MOF synthesis is uncovered: its ability to act as a structure-directing agent, triggering the transformation between two different MOF architectures.

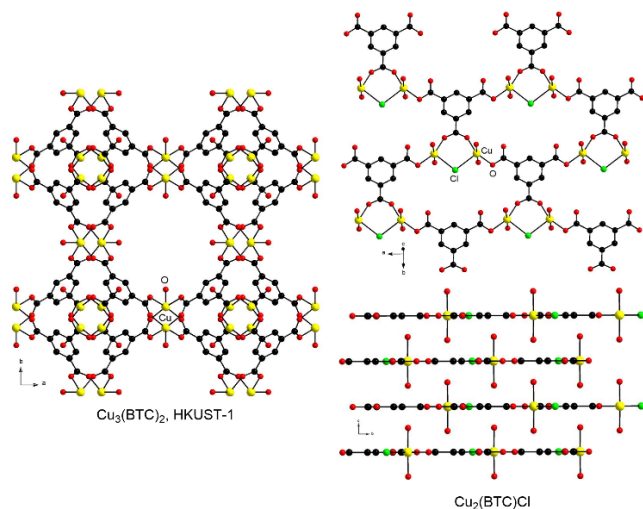


Fig. 1. Representation of the 3D network in $\text{Cu}_3(\text{BTC})_2$ (HKUST-1) (left) and of the 2D network in $\text{Cu}_2(\text{BTC})\text{Cl}$ and its packing (right), as described in the literature.^{29,31}

Results and discussion

Synthesis and characterisation of HKUST-1(reline)

Aiming at synthesizing HKUST-1 in deep eutectic solvents, we based our initial reaction parameters on an already optimized procedure performed in classical solvents.³⁰ The temperature, reaction duration, ligand/metal ratio, and concentration were thoroughly investigated in the green DES reline (Sections 3-5 of Electronic Supplementary Information, ESI). As a result, HKUST-1 was successfully synthesized and reproduced consistently several times. Briefly, 0.3 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 1.8 mmol of trimesic acid (H_3BTC), and 8 mL of freshly prepared reline were added in a high-pressure vessel. The mixture was firstly sonicated for 1 h and subsequently heated at 80°C for 3 days. The remaining blue solid was filtered off and washed with distilled water, ethanol, and air dried. The final product, named HKUST-1(reline), was analyzed by powder X-ray diffraction (PXRD), Fourier-transform infrared spectroscopy (FT-IR), elemental analysis, N_2 adsorption-desorption isotherm, scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). It can be noted that, during this process, the presence of another structure was detected in addition to the expected $\text{Cu}_3(\text{BTC})_2$ MOF (*vide infra*).

PXRD of HKUST-1(reline) presented in Fig. 2a demonstrates that the pattern of HKUST-1(reline) successfully matches the one obtained from the simulation based on its single crystal data,³¹ thus confirming the crystalline structure of the as-obtained MOF. The FT-IR spectrum of HKUST-1(reline) (Fig. 2b) shows the expected characteristic bands for this MOF. The asymmetric and symmetric stretching modes of the carboxylate functional groups are observed in the ranges of $1700\text{--}1500\text{ cm}^{-1}$ and $1500\text{--}1300\text{ cm}^{-1}$, respectively. The band at 1451 cm^{-1} is related to benzene ring stretching and deformation modes, while its C-H bending mode is

located around 729 cm^{-1} . Additionally, the band associated with the Cu-O stretching mode is seen at 493 cm^{-1} , and the presence of water molecules in the sample is evidenced by a broad band in the region of $2700\text{-}3700\text{ cm}^{-1}$.^{32,33}

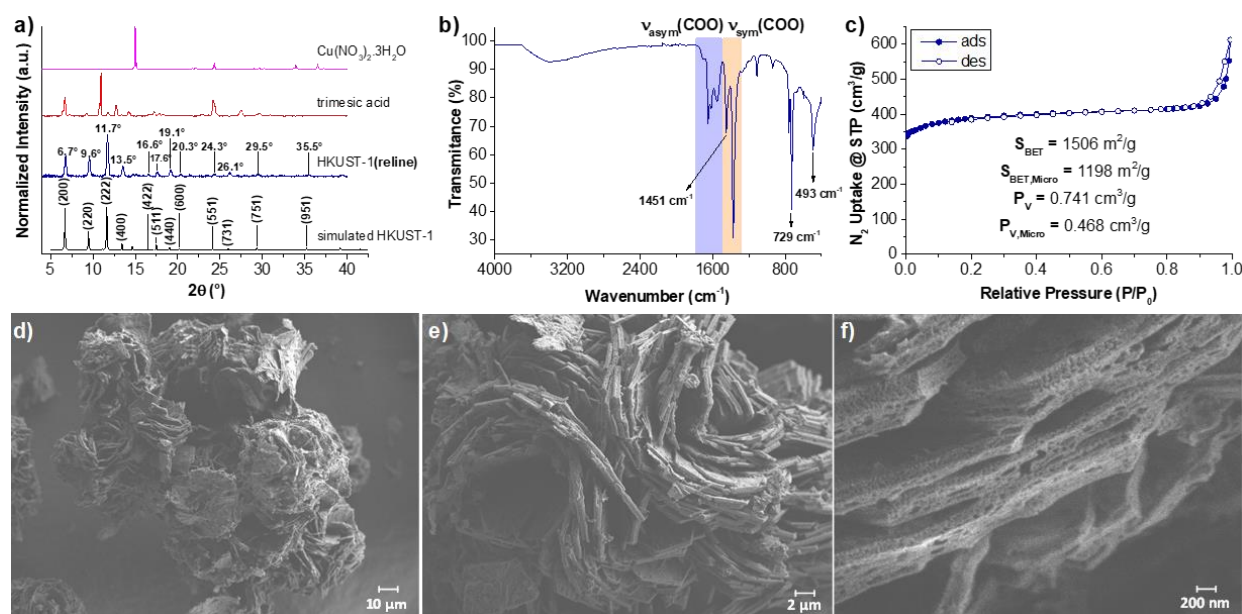


Fig. 2. a) Powder X-ray diffraction pattern for the obtained HKUST-1(**reline**) material, comparison with simulated pattern from literature single crystal data and starting materials, b) Infrared spectrum, c) N₂ adsorption-desorption isotherm at 77 K, and d-f) Scanning electron microscopy micrographs of HKUST-1(**reline**).

Elemental analysis (CHN) further confirmed the chemical composition of vacuum activated HKUST-1(**reline**) as $[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_6]$ (Fig. S3). This result is in agreement with the reported $[\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_{3.x}(\text{H}_2\text{O})]$ formula for this MOF, whereas the degree of hydration may vary due to moisture exposure.^{31,34,35} Indeed, this hydration can be qualitatively perceived visually: the activated dark blue HKUST-1(**reline**) product turns immediately turquoise upon air exposure.^{36,37} Additionally, elemental analysis did not detect any nitrogen, meaning that neither cholinium nor urea are incorporated in the resulting HKUST-1(**reline**).

The textural properties were analyzed by N₂ adsorption-desorption isotherm at 77 K (Fig. 2c). The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method (S_{BET}), and the total pore volume (P_V) was obtained by single point adsorption ($p/p_0 = 0.97363$). The t-plot method was used to determine the micropore volume ($P_{V,\text{Micro}}$) and the specific surface area related to the micropores ($S_{\text{BET},\text{Micro}}$). Prior to analysis, the sample was kept under vacuum at 150°C for 8 h. The material HKUST-1(**reline**) presented a type I isotherm, characteristic of a microporous material. The subtle hysteresis loop at the desorption branch ($0.85\text{-}1.0\ p/p_0$) is an indication of some mesopore contribution. HKUST-1(**reline**) presented a S_{BET} of $1506\text{ m}^2/\text{g}$, $S_{\text{BET},\text{Micro}}$ of $1198\text{ m}^2/\text{g}$, P_V of $0.74\text{ cm}^3/\text{g}$, and $P_{V,\text{Micro}}$ of $0.47\text{ cm}^3/\text{g}$. Interestingly, the increase in the S_{BET} and the V_P with the reaction time (1-3 days) (Fig. S5-S6) was evidenced as a linear correlation (Fig. S10), while the contribution of microporosity to the surface area ($S_{\text{BET},\text{Micro}}$) and to the pore volume ($V_{P,\text{Micro}}$) remained overall constant (Fig. S11). The usual S_{BET} values reported for HKUST-1 vary between $700\text{-}1100\text{ m}^2/\text{g}$, whereas P_V varies between $0.42\text{-}0.69\text{ cm}^3/\text{g}$,^{33,38-42} though few exceptions reported the S_{BET} as $\geq 1500\text{ m}^2/\text{g}$.^{37,40,43,44} Thus, comparing

our data with the literature, it was possible to evidence the relevance of our material in terms of its textural properties.

The SEM micrographs for HKUST-1(**reline**) are shown in Fig. 2d-f and Fig. S2. This sample presents the morphology of roses (Fig. 2d), which are assembled by platelets stacking (Fig. 2e). These platelets are clearly porous, whereas macropores (> 50 nm) can be visualized in Fig. 2f. Even for shorter reaction times, *e.g.* 1 day (Fig. S8) and 2 days (Fig. S9), the morphology is consistent with what was found for HKUST-1(**reline**). This type of morphology is rather unusual for the HKUST-1 MOF, as typically octahedral shapes are reported for this material.^{45–49} Occasionally, ill-defined or spherical shapes^{30,46,49–52} have been described in the literature, which are usually correlated with an elevated synthesis temperature^{30,52} or with longer reaction duration.^{46,52} As far as we know, this is the first report of a rose-like morphology for this MOF, which we infer is majorly influenced by the nature of the synthesis solvent. Reline bears a remarkably higher viscosity (*ca.* 700 cP)^{18,53} than the usual solvents employed for HKUST-1 synthesis, *e.g.* water and ethanol (*ca.* 1.0 cP).⁵⁴ Besides, optimization studies showed that a pre-sonication step of the reaction mixture is crucial for a high-quality material and for its unusual morphology, while continuous stirring is detrimental regarding those aspects (see Section S3-5 in ESI). These factors may account for differences in diffusivity processes, which could generate such peculiar rose morphology.

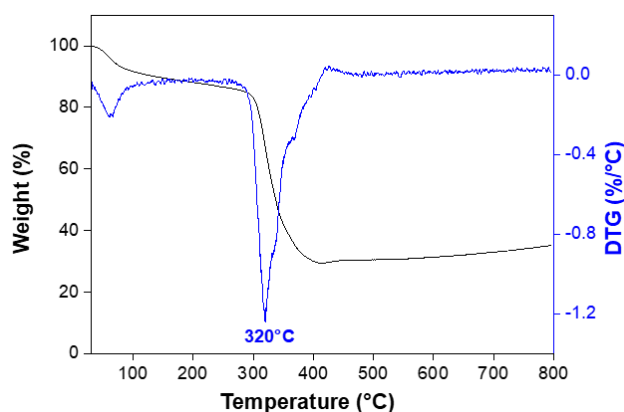


Fig. 3. Thermogravimetric analysis under N_2 flow for HKUST-1(**reline**).

Finally, TGA analysis demonstrated the thermal stability of the as-synthesized HKUST-1(**reline**) (Fig. 3), in which the sample was heated up to 800°C under N_2 flow. The first weight loss between 30°C and 110°C (~ 9 wt.%) was attributed to desorbed solvent, as the elemental analysis previously confirmed the absence of cholinium and urea in the final product. The second and most prominent weight loss (57 wt.%) evidenced the decomposition temperature (T_d) at 320°C , which was associated with framework disintegration, being in agreement with T_d values reported for high purity HKUST-1.^{37,40,43,51,52}

Structure competition and transformation

Interestingly, while optimizing the metal/ligand (M/L) ratio for obtaining HKUST-1 ($\text{Cu}_3(\text{BTC})_2$), the presence of another structure, $\text{Cu}_2(\text{BTC})\text{Cl}$, was detected (Fig. 4, and Section 5.4.1 of ESI). Jiao's group²⁹ reported the formation of this structure when reacting copper nitrate and trimesic acid in a M/L ratio of 1:1 in reline at 100°C for 3 days. Initially, our M/L ratio corresponded to 1:6 (0.3 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 1.8 mmol of H_3BTC in *ca.* 2 mL of reline), and our exploratory M/L ratio scope was set to 2:1, 1:1, 1:2 and 1:4 (Fig. 4). Reasonably, the $\text{Cu}_2(\text{BTC})\text{Cl}$ material was obtained when the M/L ratio was 1:1. However,

when the M/L ratio was 1:2 and 1:4, a mixture of both structures, $\text{Cu}_2(\text{BTC})\text{Cl}$ and $\text{Cu}_3(\text{BTC})_2$, was obtained. Furthermore, when the ratio was 2:1, solely the $\text{Cu}_2(\text{BTC})\text{Cl}$ structure was detected. It is worth noting that using the same 2:1 stoichiometry but in either $\text{ChCl}/e\text{-urea}$ or $\text{ChCl}/m\text{-urea}$, Liu *et al.* obtained HKUST-1.²⁷ For the M/L 1:6, only the $\text{Cu}_3(\text{BTC})_2$ was formed, even when the reaction time was extended to 7 days (Section S5.2). While the HKUST-1 ($\text{Cu}_3(\text{BTC})_2$) structure is known for its paddlewheel-based SBU composed by dimeric cupric tetracarboxylate units, $\text{Cu}_2(\text{BTC})\text{Cl}$ presents a dimeric copper unit bridged by one carboxylate group and one chloride ion, forming a small 6-membered ring (Fig. 1). The coordination sphere of the Cu atoms is completed by a monodentate carboxylate moiety. The extended structure of the latter gives rise to a 2D layered structure, which is quite different from the 3D framework of HKUST-1. Consistently with these different coordination spheres around the Cu centers, the observed M/L ratio dependence (Fig. 4) on which phase is obtained shows that the BTC ligand concentration with respect to the chloride plays a key role in structure formation.

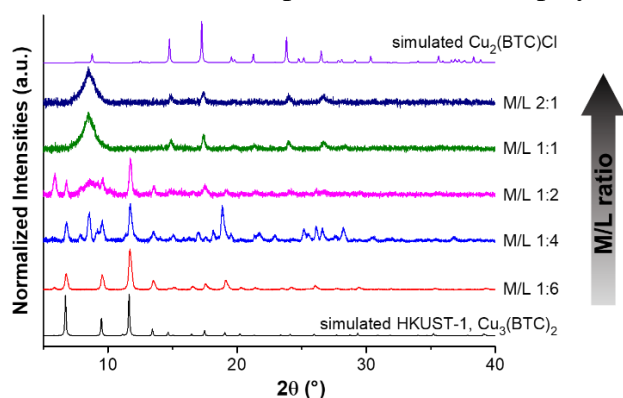


Fig. 4. PXRD patterns of the materials obtained from different metal/ligand (M/L) ratios, which were reacted for 3 days at 80°C.

This is confirmed by performing the synthesis with the same 1:6 M/L ratio however under more diluted conditions. Indeed, 0.1 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 0.6 mmol of H_3BTC (M/L 1:6) in *ca.* 5 mL of *reline* were reacted at 80°C for 6 days (Fig. 5, Section S5.4.1). The PXRD pattern of the reaction product unquestionably indicated the formation of the $\text{Cu}_2(\text{BTC})\text{Cl}$ structure (Fig. 5).

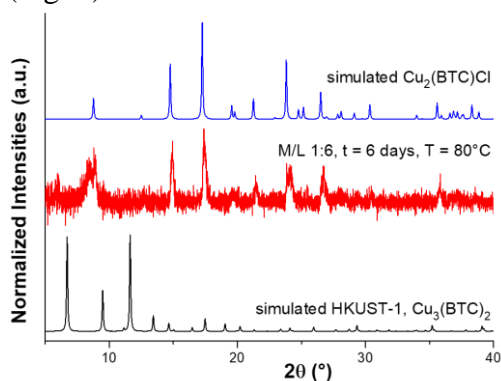


Fig. 5. PXRD pattern of the material obtained from the metal/ligand (M/L) ratio 1:6, under diluted conditions.

To further highlight the structure-directing role of chloride anion from the DES on the formation of these different phases, another experiment was performed: an already synthesized HKUST-1 (**reline**) material was placed in reaction vials *only* in the presence of *reline*, and heated at 80°C

for 3, 5 and 7 days (Section S6.1). The PXRD pattern (Fig. S46) assesses the transformation from the $\text{Cu}_3(\text{BTC})_2$ toward the $\text{Cu}_2(\text{BTC})\text{Cl}$ structure. In order to broaden the scope of this structure transformation and to show that this phenomenon is independent from the origin of HKUST-1, this material was prepared according to the conventional synthesis in EtOH/ H_2O (HKUST-1c)⁵⁵ and was then heated in reline at 80°C for several days (Section S6.2). Clearly, the PXRD patterns of the resulting samples (Fig. 6) show that the HKUST-1 crystalline structure is completely absent after 8 days, and instead the $\text{Cu}_2(\text{BTC})\text{Cl}$ diffraction pattern arises. Additionally, the octahedral morphology drastically changes from 20 μm octahedral crystals of HKUST-1c to elongated square-base rods with transversal dimensions smaller than 2 μm (Fig. 7, and Fig. S50-52). Moreover, the FT-IR spectrum and S_{BET} of HKUST-1c after 8 days in reline further supports the PXRD results. The IR bands of the reline-immersed samples (Fig. S49) present an overall bathochromic shift in relation to the parent HKUST-1, which matches the IR data reported by Jiao's group for the $\text{Cu}_2(\text{BTC})\text{Cl}$ structure.²⁹ Likewise, the S_{BET} decreases drastically in comparison with the pristine material, evidencing the non-porous feature of the $\text{Cu}_2(\text{BTC})\text{Cl}$ material (Fig. S47), which also presented a lower thermal stability (Fig. S48). Hence, it can be concluded that structure transformation indeed occurs from $\text{Cu}_3(\text{BTC})_2$ to $\text{Cu}_2(\text{BTC})\text{Cl}$, and it is independent from the parent $\text{Cu}_3(\text{BTC})_2$ synthesis conditions. Nevertheless, attempts to obtain the chemical composition of the transformed material by elemental analysis were unfruitful, which may be attributed to some amorphous impurity in the resulting sample.

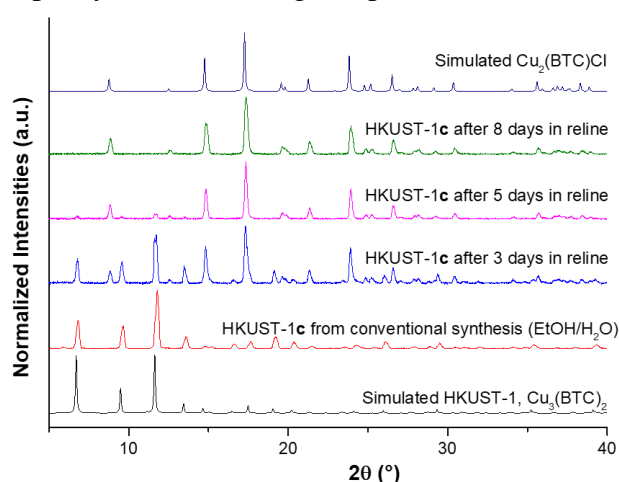


Fig. 6. PXRD patterns of HKUST-1c synthesized in EtOH/ H_2O (red), and after its immersion in reline at 80°C for 3 days (blue), 5 days (pink), and 8 days (green).

The chemical degradation of a MOF is strongly related to the medium to which it is exposed, and it has been widely reported that such event can happen in the presence of water, acid, bases or coordinating ions.⁵⁶ In the present case, several factors may be at stake such as the excess chloride as well as the reported tendency of reline to decompose upon heating, generating traces of ammonia.⁵⁸ In the presence of larger amount of H_3BTC ligand (for example in the M/L 1:6 conditions), the traces of ammonia may be neutralized, whereas under more diluted conditions or when the M/L ratio is higher this effect may be attenuated, potentially leading to ammonia acting as a decomposition agent. Another potential key component in the process is the chloride anion which competes with the H_3BTC ligand to favor one phase or the other. Further studies are necessary to confirm the mechanism of conversion that may involve only one of these agents or their combined effect. However, it is clear that chloride anions are necessary for the

formation of the $\text{Cu}_2(\text{BTC})\text{Cl}$ phase. This conversion to a chloride-incorporating material is consistent with the reported observation that metal-halogen bonds are stabilized in DES, as described for the Cl-Co bond in SIZ-13 ,⁵⁷ the Cl-Zn bond in ZBIF-1 ²⁵ and in the coordination polymer $\text{C}_5\text{H}_{14}\text{NO}\cdot\text{ZnCl}(\text{HPO}_3)$.⁵⁹ It is worth highlighting that our attempts at performing the HKUST-1 synthesis under conventional conditions (EtOH/ H_2O) with great excess of choline chloride afforded neither material. Also, upon immersion of HKUST-1c in EtOH/ H_2O in the presence of six equivalents of ChCl at 80°C for 7 days, no phase transformation was detected (Fig. S54). Finally, our attempts at performing the reverse process by immersing $\text{Cu}_2(\text{BTC})\text{Cl}$ in EtOH/ H_2O in the presence of six equivalents of H_3BTC at 80°C for 7 days did not lead to the formation of HKUST-1 (Fig. S55).

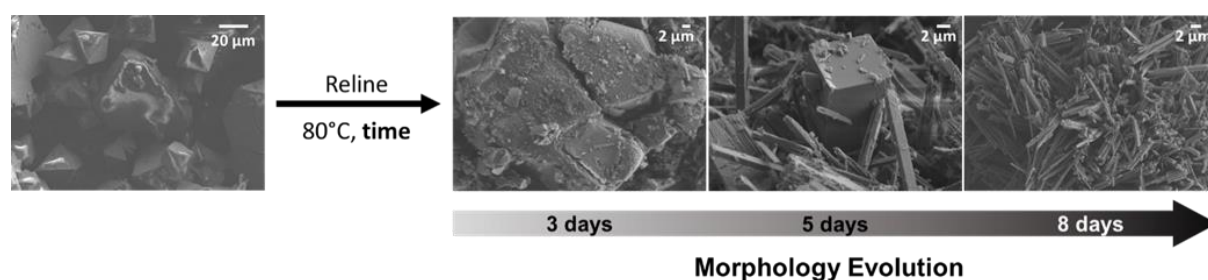


Fig. 7. Morphology evolution of octahedral HKUST-1c to elongated square-based rods, when immersed in reline at 80°C for 3, 5, and 8 days.

Conclusions

The synthesis of the MOF HKUST-1 was successfully achieved in the non-toxic, biodegradable and low vapor-pressure reline Deep Eutectic Solvent (DES). The obtained material, HKUST-1(**reline**), exhibited good textural properties, a peculiar rose-like morphology, and its synthesis was optimized with yields consistent with those reported in the literature for solvothermal conditions³⁰ (Fig. 8). Furthermore, it was shown that, upon changes in the reaction conditions such as concentration, and metal/ligand ratio, another material is formed. It was demonstrated that the HKUST-1 structure, when heated post-synthetically in the chloride-rich reline, is transformed into the $\text{Cu}_2(\text{BTC})\text{Cl}$ structure, granted by the stabilization of the halogen-metal bond (Fig. 8). Thus, in a broader view, one can draw a parallel with metastable systems observed in zeolite synthesis.⁶⁰

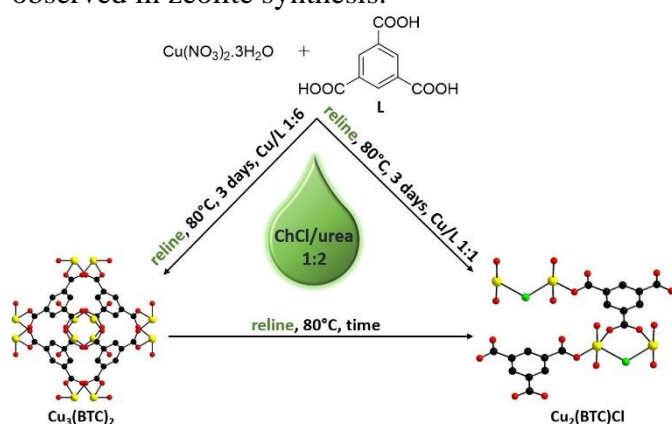


Fig. 8. Schematic representation of the role of reline in the synthesis and transformation of HKUST-1.

The foregoing results demonstrate a new feature of DES in MOF synthesis: its role as a structure-directing agent, triggering the transformation between two different MOF structures. Hence, it would be of interest to further explore DES for the preparation of MOFs, as it could represent an alternative method to design new MOF architectures based on the SDA roles of its components.

Author Contributions

Funding acquisition: S.A.B. and B.L.; experiments and data curation: R.A.M.; investigation and interpretation of the results: R.A.M., S.A.B. and B.L. writing of original draft: R.A.M.; revision of the manuscript and additional contributions: S.A.B. and B.L.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work has benefited from support provided by the University of Strasbourg Institute of Advanced Study (USIAS) for a fellowship, within the French national program “Investment for the Future” (IdEx–Unistra). We also thank the Université de Strasbourg, the C.N.R.S., and the Ministère de l’Enseignement Supérieur, de la Recherche et de l’Innovation for financial support.

References

- 1 H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.* 2012, **112**, 673–674.
- 2 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.* 2012, **112**, 724–781.
- 3 M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.* 2012, **112**, 782–835.
- 4 S. Rojas and P. Horcajada, *Chem. Rev.* 2020, **120**, 8378–8415.
- 5 L. Zhu, X.-Q. Liu, H.-L. Jiang and L.-B. Sun, *Chem. Rev.* 2017, **117**, 8129–8176.
- 6 A. Corma, H. García and F. X. Llabrés i Xamena, *Chem. Rev.* 2010, **110**, 4606–4655.
- 7 L. S. Xie, G. Skorupskii and M. Dincă, *Chem. Rev.* 2020, **120**, 8536–8580.
- 8 N. Stock and S. Biswas, *Chem. Rev.* 2012, **112**, 933–969.
- 9 A. Rabenau, *Angew. Chem. Int. Ed. Engl.* 1985, **24**, 1026–1040.
- 10 P. Li, F.-F. Cheng, W.-W. Xiong and Q. Zhang, *Inorg. Chem. Front.* 2018, **5**, 2693–2708.
- 11 E. R. Parnham and R. E. Morris, *Acc. Chem. Res.* 2007, **40**, 1005–1013.
- 12 R. E. Morris, *Chem. Commun.* 2009, 2990–2998.
- 13 A. Dhakshinamoorthy, A. M. Asiri, M. Alvaro and H. Garcia, *Green Chem.* 2018, **20**, 86–107.
- 14 F. P. Kinik, A. Uzun and S. Keskin, *ChemSusChem* 2017, **10**, 2842–2863.
- 15 A. Paiva, R. Craveiro, I. Aroso, M. Martins, R. L. Reis and A. R. C. Duarte, *ACS Sustain. Chem. Eng.* 2014, **2**, 1063–1071.
- 16 C. Florindo, F. S. Oliveira, L. P. N. Rebelo, A. M. Fernandes and I. M. Marrucho, *ACS Sustain. Chem. Eng.* 2014, **2**, 2416–2425.
- 17 N. Rodriguez Rodriguez, A. van den Bruinhorst, L. J. B. M. Kollau, M. C. Kroon and K. Binnemans, *ACS Sustain. Chem. Eng.* 2019, **7**, 11521–11528.
- 18 Q. Zhang, K. De Oliveira Vigier, S. Royer and F. Jérôme, *Chem. Soc. Rev.* 2012, **41**, 7108–7146.

- 19 B. B. Hansen, St. Spittle, B. Chen, D. Poe, Y. Zhang, J. M. Klein, A. Horton, L. Adhikari, T. Zelovich, B. W. Doherty, B. Gurkan, E. J. Maginn, A. Ragauskas, M. Dadmun, T. A. Zawodzinski, G. A. Baker, M. E. Tuckerman, R. F. Savinell and J. R. Sangoro, *Chem. Rev.*, 2021, **121**, 1232-1285.
- 20 A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chem. Commun.* 2003, 70–71.
- 21 B. Gurkan, H. Squire and E. B. Pentzer, *J. Phys. Chem. Lett.* 2019, **10**, 7956-7964.
- 22 I. Wazeer, M. Hayyan and M. K. Hadj-Kali, *J. Chem. Technol. Biotechnol.* 2018, **93**, 945–958.
- 23 S. Chen, J. Zhang, T. Wu, P. Feng and X. Bu, *J. Am. Chem. Soc.* 2009, **131**, 16027–16029.
- 24 J. Zhang, T. Wu, S. Chen, P. Feng and X. Bu, *Angew. Chem. Int. Ed.* 2009, **48**, 3486–3490.
- 25 S. Chen, J. Zhang, T. Wu, P. Feng and X. Bu, *Dalton Trans.* 2010, **39**, 697–699.
- 26 J.-H. Liao, P.-C. Wu and Y.-H. Bai, *Inorg. Chem. Commun.* 2005, **8**, 390–392.
- 27 L. Liu, H. Wei, L. Zhang, J. Li and J. Dong, *Stud. Surf. Sci. Catal.*, 2008, **174**, 459-462.
- 28 S.-H. Kim, S.-T. Yang, J. Kim and W.-S. Ahn, *Bull. Korean Chem. Soc.* 2011, **32**, 2783–2786.
- 29 Q. Q. Xu, B. Liu, L. Xu and H. Jiao, *J. Solid State Chem.* 2017, **247**, 1–7.
- 30 E. Biemmi, S. Christian, N. Stock and T. Bein, *Microporous Mesoporous Mater.* 2009, **117**, 111–117.
- 31 S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science* 1999, **283**, 1148–1150.
- 32 E. Borfecchia, S. Maurelli, D. Gianolio, E. Groppo, M. Chiesa, F. Bonino and C. Lamberti, *J. Phys. Chem. C* 2012, **116**, 19839–19850.
- 33 F. Wang, H. Guo, Y. Chai, Y. Li and C. Liu, *Microporous Mesoporous Mater.* 2013, **173**, 181–188.
- 34 K. Schlichte, T. Kratzke and S. Kaskel, *Micropor. Mesopor. Mater.* 2004, **73**, 81–88.
- 35 Z. Liang, M. Marshall and A. L. Chaffee, *Energy Fuels* 2009, **23**, 2785–2789.
- 36 S. Bordiga, L. Regli, F. Bonino, E. Groppo, C. Lamberti, B. Xiao, P. S. Wheatley, R. E. Morris and A. Zecchina, *Phys. Chem. Chem. Phys.* 2007, **9**, 2676.
- 37 G. Majano and J. Pérez-Ramírez, *Adv. Mater.* 2013, **25**, 1052–1057.
- 38 K.-Y. A. Lin and Y.-T. Hsieh, *J. Taiwan Inst. Chem. Eng.* 2015, **50**, 223–228.
- 39 K.-S. Lin, A. K. Adhikari, C.-N. Ku, C.-L. Chiang and H. Kuo, *Int. J. Hydrog. Energy* 2012, **37**, 13865–13871.
- 40 Y. Chen, X. Mu, E. Lester and T. Wu, *Prog. Nat. Sci.* 2018, **28**, 584–589.
- 41 Y. Li and R. T. Yang, *AIChE J.* 2008, **54**, 269–279.
- 42 P. Chowdhury, C. Bikkina, D. Meister, F. Dreisbach and S. Gumma, *Microporous Mesoporous Mater.* 2009, **117**, 406–413.
- 43 W. Zhang, M. Kauer, P. Guo, S. Kunze, S. Cwik, M. Muhler, Y. Wang, K. Epp, G. Kieslich and R. A. Fischer, *Eur. J. Inorg. Chem.* 2017, 925–931.
- 44 J. Huo, M. Brightwell, S. El Hankari, A. Garai and D. Bradshaw, *J. Mater. Chem. A* 2013, **1**, 15220–15223.
- 45 Z. Zhao, S. Wang, Y. Yang, X. Li, J. Li and Z. Li, *Chem. Eng. J.* 2015, **259**, 79–89.
- 46 N. Al-Janabi, P. Hill, L. Torrente-Murciano, A. Garforth, P. Gorgojo, F. Siperstein and X. Fan, *Chem. Eng. J.* 2015, **281**, 669–677.

- 47 X. Sun, H. Li, Y. Li, F. Xu, J. Xiao, Q. Xia, Y. Li and Z. Li, *Chem. Commun.* 2015, **51**, 10835–10838.
- 48 M. Shöâè, J. R. Agger, M. W. Anderson and M. P. Attfield, *CrystEngComm* 2008, **10**, 646–648.
- 49 H. Du, J. Bai, C. Zuo, Z. Xin and J. Hu, *CrystEngComm* 2011, **13**, 3314–3316.
- 50 X. Cai, Z. Xie, M. Pang and J. Lin, *Cryst. Growth Des.* 2019, **19**, 556–561.
- 51 C. Y. Chuah, K. Goh and T.-H. Bae, *J. Phys. Chem. C* 2017, **121**, 6748–6755.
- 52 X. Mu, Y. Chen, E. Lester and T. Wu, *Microporous Mesoporous Mater.* 2018, **270**, 249–257.
- 53 E. L. Smith, A. P. Abbott and K. S. Ryder, *Chem. Rev.* 2014, **114**, 11060–11082.
- 54 M.-J. Lee and T.-K. Lin, *J. Chem. Eng. Data* 1995, **40**, 336–339.
- 55 Q. Min Wang, D. Shen, M. Bülow, M. Ling Lau, S. Deng, F. R. Fitch, N. O. Lemcoff and J. Semanscin, *Microporous Mesoporous Mater.* 2002, **55**, 217–230.
- 56 L. Feng, K. Wang, G. S. Day, M. R. Ryder and H. Zhou, *Chem. Rev.* 2020, **123**, 13087–13133.
- 57 E. A. Drylie, D. S. Wragg, E. R. Parnham, P. S. Wheatley, A. M. Z. Slawin, J. E. Warren and R. E. Morris, *Angew. Chem. Int. Ed.* 2007, **46**, 7839–7843.
- 58 S. P. Simeonov and C. A. M. Alonso, *RSC Adv.*, 2016, **6**, 5485–5490.
- 59 W. T. A. Harrison, *Inorg. Chem. Commun.* 2007, **10**, 833–835.
- 60 B. Louis, E. S. Gomes, P. Losch, G. Lutzweiler, T. Coelho, A. Faro, J. F. Pinto, C. S. Cardoso, A. V. Silva and M. M. Pereira, *ChemCatChem* 2017, **9**, 2065–2079.