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Journal Article

Kyoto University
Mesoscopic architectures of porous coordination polymers fabricated by pseudomorphic replication

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The spatial organisation of porous coordination polymer (PCP) crystals into higher-order structures is critical for their integration into separation systems, heterogeneous catalysts, ion/electron transport and photonic devices. Here, we demonstrate a rapid method to spatially control the nucleation site, leading to the formation of mesoscopic architecture in PCPs, in both two and three dimensions. Inspired by geological processes, this method relies on the morphological replacement of a shaped sacrificial metal oxide used both as a metal source and as an “architecture-directing agent” by an analogous PCP architecture. Spatiotemporal harmonisation of the metal oxide dissolution and the PCP crystallisation allowed for preservation of very fine mineral morphological details of periodic alumina inverse opal structures. The replication of randomly structured alumina aerogels resulted in a PCP architecture with hierarchical porosity in which the hydrophobic micropores of the PCP and the mesopores/macropores inherited from the parent aerogels synergistically enhanced the material’s selectivity and mass transfer for water/ethanol separation.
Pseudomorphic mineral replacement events consist in the transformation of a mineral phase that is out of equilibrium into a more thermodynamically stable phase, involving dissolution and reprecipitation sub-processes. This natural phenomenon is characterised by the preservation of the shape and dimensions of the replaced parent phase whenever the kinetics of its dissolution are coupled with the kinetics of nucleation and crystallisation of the new phase. The initiation and spatiotemporal harmonisation of these re-equilibration reactions rely on parameters that are controllable in the laboratory. Therefore, the application of this natural process using pre-shaped sacrificial supports is an attractive strategy for introducing structural hierarchy and hence for improving the range of properties of various functional materials. However, although the pseudomorphic replacement process is responsible for the generation of a variety of mineral phases in natural environments, this phenomenon has so far been rarely used as a strategy for the synthesis of functional materials and its application was limited to the production of purely mineral materials, for instance, complex metal sulfides, hydroxyapatites and zeolites.
Porous coordination polymers (PCPs), constructed via the assembly of metal centres with organic linkers, are an intriguing class of crystalline microporous materials.\textsuperscript{8-13} While PCPs demonstrate a range of properties that make them ideal for applications in gas storage,\textsuperscript{14} catalysis,\textsuperscript{15,16} sensing,\textsuperscript{17} proton-conduction\textsuperscript{18} and adsorptive separation,\textsuperscript{19} their utilisation in practical applications is limited due to the poor processability of PCPs that are produced as bulk powders or single crystals through homogeneous crystallisation. The increasing number of reports that focus on the processing of PCPs into thin films,\textsuperscript{20} two-dimensional patterns\textsuperscript{21} and spheres\textsuperscript{22} accounts for the significance of their integration into directly applicable materials. Control of the crystallisation processes is traditionally performed on substrates by the induction of heterogeneous nucleation\textsuperscript{23,24} or by the direct deposition\textsuperscript{25,26} of PCP crystals. However, the limitations of these techniques, in terms of the lack of control over the spatial localisation of the heterogeneous crystallisation, hinder the construction of designable higher-order architectures. Here, we demonstrate a coordination replication method by applying the pseudomorphic replacement process to introduce organic elements into a pre-shaped dense metal oxide phase. This process leads to the
Because of its ubiquitous nature, processability and well-studied dissolution behaviour in the presence of organic acid molecules in natural environments (chemical weathering), the alumina phase was selected as metal reservoir and mesoscale architecture-directing agent. A two-dimensional honeycomb pattern and a three-dimensional inverse opal structure were first constructed as model parent architectures to emphasise the potential of our strategy in terms of the construction of a mesoscopic PCP architecture. By taking advantage of the unique characteristic of PCPs, whereby a suitable choice of both metal ions and organic ligands allows for a tailored pore size, pore surface functionality and framework flexibility, we constructed mesoscopic PCP architectures with different pore characteristics. We also showed the potential use of this strategy for the preparation of materials with enhanced functionality compared with conventional powders. After coordination replication, the selection of both
1,4-naphthalenedicarboxylic acid (H$_2$ndc) as an organic ligand and a randomly structured alumina aerogel as the parent architecture led to the formation of a hierarchical, porous system constructed from highly hydrophobic PCP crystals with efficient mass transport properties for water/ethanol vapour-phase separation.

Assemblies of 1 μm polystyrene (Ps) beads were used as hard templates for the synthesis of two-dimensional honeycomb patterns or three-dimensional inverse opal structures\(^2^9\) (Fig. 2). After the reaction of the pattern at 180°C for 10 min in an aqueous solution of H$_2$ndc under microwave conditions, synchrotron X-ray diffraction measurements unambiguously confirmed the formation of an aluminium naphthalene dicarboxylate framework\(^3^0\) [Al(OH)(ndc)$_n$ based on one-dimensional inorganic chains of [Al(OH)(COO)$_2$]$_n$ (Figs. 2a-c). Characterisation by field-emission scanning electron microscopy (FESEM) showed that the two-dimensional alumina patterns were composed of well-ordered hexagonal arrangements of macro-voids and alumina walls approximately 50-nm thick (Fig. 2d). After the reaction, FESEM revealed that a perfect PCP replica of the
alumina pattern was obtained (Fig. 2e). Intergrown PCP crystals of 10 to 200 nm with a nearly cubic shape replaced the 50-nm-thick alumina walls.

The coordination replication of a three-dimensional alumina inverse opal structure (Fig. 2f) led to the formation of a PCP-based material with a hierarchical porosity (Figs. 2g and 2h), combining the microporosity of the PCP and the macroporosity of the inverse opal structure. The PCP replica exhibited macropores with a diameter of 800 nm connected by windows of 100 to 200 nm in width (Fig. 2g). Similar to the two-dimensional hexagonal pattern, the walls of the PCP macroporous materials were composed of well-intergrown crystals ranging from 10 to 200 nm in size.

The PCP product inherits a shape that is identical to that of the alumina parent architecture. Careful observation of the FESEM images revealed that even the fine morphological details of the parent product were preserved after transformation into the PCP crystals (Supplementary Figs. S1 and S2). Such preservation strongly suggests a coupled “dissolution-reprecipitation” mechanism,\(^1\) in which the metastable parent product dissolves in the fluid at the solid-liquid interface and immediately crystallises as a new
stable daughter phase at the same site as the dissolved precursor. This mechanism was confirmed via an FESEM analysis obtained from time course experiments with the reaction at 140°C (Fig. 3). After a 1 s reaction time, the smooth surfaces of the alumina pattern (Fig. 3a) became rougher (Fig. 3b) due to the coating of small ill-defined nuclei with lengths of approximately 10 nm. From 4 s to 10 s (Figs. 3c-e), the number of crystals with a size between 10 and 100 nm increased. Simultaneously, the reaction front at the interface between the alumina and the PCP crystal progressively disappeared with time, providing evidence of alumina consumption to form the PCP crystals (Fig. 3e). As shown in Figures 3d-g, the crystals were not connected to each other, and voids of a few nanometres were clearly visible between them. The presence of porosity within the new material formed is a classic feature of the coupled dissolution-reprecipitation mechanism.\textsuperscript{1,31} After a reaction time of 60 s, the PCP replica of the alumina parent pattern, composed of densely packed crystals, was finally formed (Fig. 3h). Based on these observations, the mechanism of pseudomorphic mineral replacement reactions can hence be adapted to our coordination replication process, as shown in Figure 4 and Supplementary Figure S3.
The coordination replication was then applied with two other dicarboxylic acids (Supplementary Fig. S4-7). A three-dimensional alumina inverse opal crystal architecture composed of inter-grown octahedral $\{[\text{Al}_3\text{O(OH)(H}_2\text{O)}_2][\text{btc}]_2\}_n$ crystals, also known as MIL-100, was synthesised via the replication of the analogous alumina architecture in a solution of benzene tricarboxylic acid (H$_2$btc), used as an organic ligand (Supplementary Figs. S4 and S5). Instead, the use of benzene dicarboxylic acid (H$_2$bdc) led to the formation of a PCP replica of the inverse opal structure based on an assembly of $[\text{Al(OH)(bdc)}]_n$ crystals (known as MIL-53) with a plate-like morphology (Supplementary Figs. S6 and S7). Hence, the utilisation of three different organic ligands resulted in the construction of a three-dimensional PCP architecture, presenting three remarkable porous properties based on the stiff and hydrophobic $[\text{Al(OH)(ndc)}]_n$ framework, the mesoporous $\{[\text{Al}_3\text{O(OH)(H}_2\text{O)}_2][\text{btc}]_2\}_n$ framework and the $[\text{Al(OH)(bdc)}]_n$ framework that is well-known for its flexible behaviour under hydration/dehydration.

Here, we focused on the hydrophobic micropores of $[\text{Al(OH)(ndc)}]_n$ to implement a new water/ethanol separation system. Extraction of bioethanol from its aqueous synthesis
media is important for the development of the next generation of fuel systems.\textsuperscript{34} However, suitable porous materials that combine a high selectivity for ethanol against water with a high adsorption capacity are still rare, and such separation has never been performed by molecule-based porous materials. The selective vapour adsorption of $[\text{Al(OH)(ndc)}]_n$ for ethanol versus water was confirmed by a single-component adsorption isotherm obtained at 298 K (Supplementary Fig. S8). After packing the powders of $[\text{Al(OH)(ndc)}]_n$ crystals into a glass tube, we demonstrated for the first time the water/ethanol separation capacity of PCPs by means of a binary vapour-phase breakthrough experiment for an equimolar mixture of water/ethanol with a separation selectivity of 2.26 (Supplementary Fig. S9). However, when integrated into the chemical engineering processes, the dimensions of the equipment, the attainable product recovery and the resulting power consumption are tightly linked to the macroscopic architecture of the microporous material, which affects decisive parameters such as the mass transfer properties and the pressure drop.\textsuperscript{35}

We explored the prospective application of the coordination replication method by the inclusion of $[\text{Al(OH)(ndc)}]_n$ crystals as an integral part of an architectural design.
containing a multimodal porosity. To maximise the adsorption area, mechanical strength and flow and transport through the structure of the mesoscopic PCP architectures, the highly open and disordered alumina networks of two aerogels with distinct pore properties were chosen as parent structures. As indicated by nitrogen sorption measurements (Supplementary Figs. S10-12) and FESEM (Supplementary Figs. S13 and S14), one aerogel contains an intrinsic mesoporosity with a median mesopore size of 94 nm, and the other one is a hierarchically porous aerogel composed of both mesopores (38 nm) and macropores (1 μm). After replication of the parent structures, two mesoscopic PCP architectures with two types of hierarchical porosity were obtained (Fig. 5 and Supplementary Fig. S15). Replication of the mesoporous alumina aerogel results in the formation of the microporous/mesoporous PCP architecture called Meso-PCP. Replication of the mesoporous/macroporous alumina aerogel results in the microporous/mesoporous/macroporous PCP architecture called Macro-PCP.

The entire architectures of Meso-PCP and Macro-PCP are unambiguously composed of thoroughly intergrown crystals of \([\text{Al(OH)(ndc)}]_n\) (Figs. 5b and 5c and
Supplementary Figs. S16-S18). As shown by the nitrogen sorption measurements (Supplementary Figs. S10 and S11), the characteristic mesopores of the parent aerogels were maintained even after replication into the corresponding mesoscopic PCP architectures of **Meso-PCP** and **Macro-PCP**, which additionally possess microporosity based on the framework \[\text{Al(OH)(ndc)}\_n\] structure. The formation of the PCP microporosity was confirmed with a carbon dioxide sorption isotherm (Supplementary Figs. S19), in which a significant increase of adsorption at a low relative pressure, ranging from 0 to 0.1, was observed after replication (Supplementary Figs. S20). Note that the unique Type 1 sorption profile and the saturation capacity (up to 143 cm\(^3\) (STP)·g\(^{-1}\)) of the mesoscopic PCP architectures are comparable to those of the \[\text{Al(OH)(ndc)}\_n\] powders synthesised from the aluminium salt, as reported in the literature (138 cm\(^3\) (STP)·g\(^{-1}\)).

Breakthrough experiments performed with **Meso-PCP** or **Macro-PCP** for the separation of an equimolar binary water/ethanol mixture demonstrated the effect of the adsorbent architecture over the separation efficiency (Fig. 6). Importantly, the shape, size (Supplementary Fig. S21), crystallinity (Supplementary Figure S18) and microporosity
(Supplementary Figure S19) of PCP crystals that construct both Meso-PCP and Macro-PCP were shown to be analogous. An equal bed voidage was guaranteed by packing columns with pieces of Meso-PCP and Macro-PCP of the same size (approximately 200 μm, Supplementary Fig. S22). Also, the weights of packed materials and the procedures applied for packing Meso-PCP and Macro-PCP into the glass tubes were rigorously identical. Therefore, difference in separation efficiency observed between Meso-PCP and Macro-PCP in the following section can be exclusively explained by their distinct mesoscopic architectures. In contrast with the parent alumina aerogel (Supplementary Fig. S23), both mesoscopic PCP architectures enabled a significant water/ethanol separation with a separation selectivity of 2.56 for Meso-PCP and 1.84 for Macro-PCP. Importantly, we observed a reduction in the breakthrough time and lower pressures at the inlet of the column with Meso-PCP and Macro-PCP compared with the powder samples (inlet pressure = 54, 33 and 256 kPa; water breakthrough time = 12.1, 8.6 and 15 min; ethanol breakthrough time = 24, 14.5 and 40 min for Meso-PCP, Macro-PCP and the powder, respectively). In addition, steeper breakthrough fronts were observed when
the separation process was performed with Meso-PCP and Macro-PCP compared with the powder, indicating more uniform water and ethanol vapour-phase velocities through the column. These results show the beneficial effect of the mesoporosity and macroporosity of the PCP architecture on the performance of the separation column, which provide short diffusion paths towards the adsorption sites located within the microporosity of the PCP crystals.

We also observed a significant difference between Meso-PCP and Macro-PCP for the separation performance. As a consequence of the macroporosity, the use of Macro-PCP led to a lower separation time and a lower pressure at the inlet than that of Meso-PCP. In contrast, the smaller pore size of Meso-PCP and the higher exposed surface area of PCP within this architecture (Supplementary Fig. S12) allowed for higher ethanol retention and improved separation selectivity. The loss of adsorbent loading observed with Macro-PCP due to its large diffusion paths can be avoided by the design of the mesoscopic PCP architecture.

These results demonstrate a new method for designing mesoscopic architecture
based on PCP crystals in two and three dimensions using a reliable and extremely fast coordination replication protocol. The kinetics and spatial coupling between the dissolution of a metastable alumina phase and the crystallisation of aluminium-based PCPs enables the production of both periodic and random mesoscopic PCP architectures through a pseudomorphous replacement mechanism. Assisted by the well-established processing of metal oxide, the precise localisation of parent metal oxide phases should permit the design of PCP architectures with a great variety of useful geometries. We believe that the construction of mesoscopic PCP architectures, achieved here through the conversion of an alumina phase into PCPs, can be extended to other metal oxide phases, such as iron oxide, zirconium oxide or nickel oxide, because the natural weathering processes of these metal oxides were studied\textsuperscript{39,40} and because these mineral phases can be used for the formation of PCPs\textsuperscript{41} once the condition of spatiotemporal coupling between dissolution and crystallisation is established.
Methods

Preparation of the two-dimensional hexagonal alumina patterns and three-dimensional alumina-based inverse opal structure. For preparation of the two-dimensional hexagonal patterns, a suspension of Ps beads with a diameter of 1 μm in ethanol was spread by spin coating (1000 rpm) on an amorphous silica plate previously treated for 24 h in a piranha solution. After drying for 10 h at room temperature, the colloidal film was annealed by a short thermal treatment of 1 min at 100°C and then placed for 3 h in a horizontally face-up configuration in a solution composed of 0.820 g of aluminium tri-sec-butoxide (Al[OCH(CH3)C2H5]3), 2.37 g of ethanol and 1.72 g of 60% nitric acid. After drying for 48 h at room temperature, the colloidal mask was calcined for 7 h at 580°C under nitrogen. The three-dimensional alumina-based inverse opal materials were obtained by the formation of multilayered colloidal crystal films on the silica plate at slow spinning rate (500 rpm).

Preparation of the two- and three-dimensional PCP-based replicates. Replication of the alumina pattern was performed with a microwave reactor (Initiator 2.5, Biotage). The
alumina pattern and inverse opal crystals on silica substrates (width = 0.5 cm, length = 1 cm) were placed in a 2 ml microwave container with 0.08 g 1,4-naphthalenedicarboxylic acid and 2 ml water. The microwave treatment was performed at 180°C for 10 min. The PCP-based replicate obtained was washed with water and dimethylformaldehyde. Time dependence experiments were performed at 140°C.

The comparative time dependence study with hydrothermal treatment was performed in 10 mL Teflon-lined autoclaves at 140°C for various times on samples, which were prepared using the same procedure.

For the application of the coordination replication with benzene tricarboxylic acid and benzene dicarboxylic acid, the inverse opal crystals on silica substrates (width = 0.5 cm, length = 1 cm) were placed in a 2 ml microwave container with 0.077 g benzenetricarboxylic acid or 0.061 g of benzene dicarboxylic acid and 2 ml water. The microwave treatment was performed at 220°C for 10 s with the benzenetricarboxylic acid and 180°C for 3 min with the benzenedicarboxylic acid. The PCP-based replicates obtained were washed with dimethylformaldehyde, water and ethanol.
**Preparation of the alumina aerogel.** 649 mg of aluminum chloride hexahydrate (AlCl₃·6H₂O) were dissolved in a mixture of 0.6 ml of distilled H₂O and 0.740 ml of ethanol. Then, 0.560 ml of propylene oxide (PO) was added under ambient conditions (25°C). After being stirred for 1 min, the resultant homogeneous solution was kept for gelation and aging in an incubator at 40°C for 24h. The transparent solution turned into a translucent gel. After threefold solvent exchange with 2-propanol at 60°C for 24h, the wet gels were dried by a supercritical drying process in a SCLEAD-2BD autoclave from KISCO using supercritical carbon dioxide at 80°C and 14.0 MPa. The recovered aerogel preserved the dimensions of the corresponding wet gel.

**Preparation of the alumina macroporous aerogel.** The same procedure as for the synthesis of the mesoporous alumina aerogel was applied to obtain the macroporous alumina aerogel. 9 mg of poly(ethylene oxide) (PEO) was added to the 649 mg of aluminum chloride hexahydrate (AlCl₃·6H₂O) within the initial reagent mixture.

**Preparation of the mesoscale PCP-based architectures (Meso-PCP and Macro-PCP).** The alumina aerogel or the macroporous alumina aerogel was placed in a 2 ml microwave
container with 0.08 g of 1,4-naphthalenedicarboxylic acid and 2 ml water. The microwave
treatment was performed at 180°C for 1 min. The PCP-based replicate obtained was
washed with water and dimethylformaldehyde.

**Preparation of the [Al(OH)(ndc)]\(_n\) crystal powder.** 375 mg of aluminum nitrate
nonahydrate (Al(NO\(_3\))\(_3\).6H\(_2\)O) and 108 mg of 1,4-naphthalenedicarboxylic acid were mixed
in 10 mL of water. A microwave treatment was performed at 180°C for 10 min. The white
PCP powder obtained was washed with water and dimethylformaldehyde.

**Breakthrough measurements in vapor phase.** Breakthrough experiments in vapor phase
for the equimolar water/ethanol gas mixture were performed using the experimental setup
described in Supplementary Fig. S24. Briefly, 0.09 g of the [Al(OH)(ndc)]\(_n\) PCP crystal
powder or grinded **Meso-PCP** or grinded **Macro-PCP** were packed in a glass tube (\(L = 5\)
cm; \(d_i = 3\) mm). The adsorption column was then placed in an oven at 80°C and operated
by introducing continuously an equimolar water/ethanol vapor mixture generated by
BELFlow-3 from BEL JAPAN. The composition history of the mixtures collected at the
outlet of the column was evaluated by a gas chromatographer GC-2014 from SHIMADZU
equipped with TPA 60-80/PEG 6000 columns. A thermal conductivity detector was connected to the GC column outlet. Peaks were identified by reference injections using series of different water or ethanol concentrations and by drawing calibration curves.
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Author Contributions:

S.F., J.R., and S.K. conceived and designed the experiments. J.R. N.H. and M.T. performed all synthetic and characterization experiments. S.F., K.H., H.U., M.K., N.L., and O.S. carried out synchrotron XRD measurements. J.R. carried out water/ethanol separation experiments. J.R. and S.F. analyzed the data and co-wrote the manuscript. All authors discussed the results and commented on the manuscript.

Competing Financial Interests:

The authors declare that they have no competing financial interests.
Figure Legends:

**Figure 1. The coordination replication and mesoscopic architecture concept.** The coordination replication method is based on the replacement of a metastable dense metal oxide phase (illustrated as a red honeycomb pattern) by more stable PCP crystals (as a blue honeycomb pattern). Local dissolution of the metal oxide phase provides the metal ions, which are immediately consumed by the formation of coordination frameworks with organic ligands (as yellow sticks) at metal oxide-solution interfaces. Therefore, morphological details are preserved. As the metal oxide is shaped in the first step using sol-gel process involving metal ions (depicted as red spheres), it acts not only as a metal source through its dissolution but also as an “architecture-directing agent”. Here, the term “mesoscopic architecture” refers to architectural motifs hierarchically organised both at the macroscale (PCP crystalline architectures inherited from the parent metal oxide structure) and at the molecular scale (PCP frameworks composed of subunits organised at the molecular scale).
Figure 2. Coordination replication to form two- and three-dimensional mesoscopic architectures based on a porous aluminium coordination polymer. a. The crystal structure of the aluminium naphthalenedicarboxylate framework, [Al(OH)(ndc)]$_n$, reveals a three-dimensional framework composed of infinite chains of Al(OH)$_2$O$_4$ units connected with 1,4-naphthalenedicarboxylate ligands. b. A chain composed of corner-sharing octahedral Al(OH)$_2$O$_4$ units. c. Synchrotron X-ray diffraction pattern of the replica and the simulated pattern of [Al(OH)(ndc)]$_n$. d. Top-view FESEM images of the alumina hexagonal pattern. e. Top-view FESEM images of the aluminium PCP replica obtained after microwave treatment for 10 min at 180°C. f. Top-view FESEM image of the three-dimensional alumina inverse opal crystal before transformation. g and h. FESEM images of the PCP replica after transformation (top and side views, respectively). All scale bars = 1 µm.
Figure 3. Time-course monitoring of the coordination replication by FESEM. Images of (a) the alumina pattern and of the same sample after replication for (b) 1 s, (c) 4 s, (d) 6 s, (e) 10 s, (f) 20 s, (g) 40 s and (h) 60 s. All scale bars = 1 µm. This series of experiments was performed at 140°C, compared to 180°C for the sample shown in Fig. 2, because replication was completed at 180°C after 1 s, which made a time dependence study difficult. By performing the experiments at 140°C, the reaction was slowed down, allowing us to carefully follow the alumina transformation at different stages.
Figure 4. Schematic view of the coordination replication mechanism. We adapt the mechanism of pseudomorphic mineral replacement reactions that is well described in geochemistry to the coordination replication. a. Dissolution of alumina forms the interface layer supersaturated with respect to aluminium aqua complexes. A coordination reaction between dissolved aluminium cations and dicarboxylate ligands promotes the formation of PCP-nuclei composed of aluminium hydroxide oligomers connected with each other by the ligands. b. The PCP crystal grows from the crystal surfaces in contact with the supersaturated interface layer. As the alumina dissolves, the interface layer is enriched with freshly released aluminium cations that feed the crystal growth, together with the organic ligand. Alumina dissolution induces the creation of voids below the crystals, providing pathways for ligand diffusion from the solution to the reaction front. The crystal grows towards the alumina surface as indicated by the red arrow. Localisation of the supersaturated layer only at the interface between the alumina surface and the ligand solution is allowed by the fast crystallization kinetics compare to the alumina dissolution kinetics. Hence PCP crystal formation is maintained at the solid-liquid interface that
enables coordination replication. The crystal structure of Al-based PCP is simplified for clarity.
Figure 5. Replication of randomly structured alumina aerogels for the formation of mesosopic PCP architectures used as water/ethanol separation systems. a. Schematic illustration of coordination replication from alumina aerogel and macroporous alumina aerogel parent structures to Meso-PCP and Macro-PCP analogous architectures, respectively. The different types of porosity composing the parent aerogels and the PCP-based replicas are indicated below each scheme. b. FESEM images of Meso-PCP. c. FESEM images of Macro-PCP. Scale bars = 10 μm for the main images. Scale bars = 1 μm for the images in inset.
Figure 6. Water/ethanol separation with the mesoscopic PCP architecture, Meso-PCP or Macro-PCP. Binary breakthrough separation profiles for the equimolar separation of mixture of ethanol (circle) /water (triangle) at T=80°C obtained with Macro-PCP (red), Meso-PCP (blue) and powders (black). Compared to the PCP powder, mesoscale architectures enhance the mass transfer kinetics, resulting in lower breakthrough times of water and ethanol while keeping significant separation efficiency.
Metal ions

Sol-gel process

Organic ligands

Coordination replication

Metal oxide parent phase as "architecture-directing agent"

PCP

Mesoscopic PCP architecture