

Post-Synthetic Modification of Aerogels Made of Covalent Cross-linked Metal-Organic Polyhedra

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Aerogels are porous ultralight materials known for their high porosity, wide range of pore sizes, low density, and good macroscopic mechanical properties, all of which make them promising candidates for shaped adsorbents, catalysts, and insulators, among other applications. Here, this work reports a new approach that enables both the formation of modular aerogels, via dynamic covalent chemistry, and their post-synthetic modification, via coordination chemistry. To demonstrate this strategy, this work first polymerizes porous amino-functionalized Rh(II)-based metal-organic polyhedra (MOPs) with aldehydes, which afforded robust imine-gel networks that is then converted into aerogels. Next, this work functionalizes these aerogels through the coordination of ligands on the axial site of Rh(II) paddlewheels of the MOP. Interestingly, in this chemistry, the local changes in the coordination site of the MOPs are transferred to the overall aerogel, thereby altering its macroscopic physicochemical properties. Importantly, this feature enables the synthesis of optimized adsorbents tailored to specific guests, as this work demonstrates through a series of experiments using ligands of different electrostatic and hydrophobic characters.

1. Introduction

Aerogels are a fascinating class of highly porous materials that are among the lightest known materials: typically, 90% to 99% of an aerogel is air.^[1] Despite their low density, aerogels are also known for their exceptional mechanical strength and thermal insulation properties.^[2] Given these features, aerogels have become a subject of intense research interest, with potential applications including aerospace engineering,^[3] energy storage,^[4] biomedical engineering,^[5] and environmental remediation.^[6] The first aerogel was discovered by Samuel Kistler in 1931. He studied the use of the supercritical drying method on gels, which led to gentle liquid removal and aerogel formation.^[7] Since then, many different material precursors have been successfully used to create aerogels, including metal oxides, carbides,

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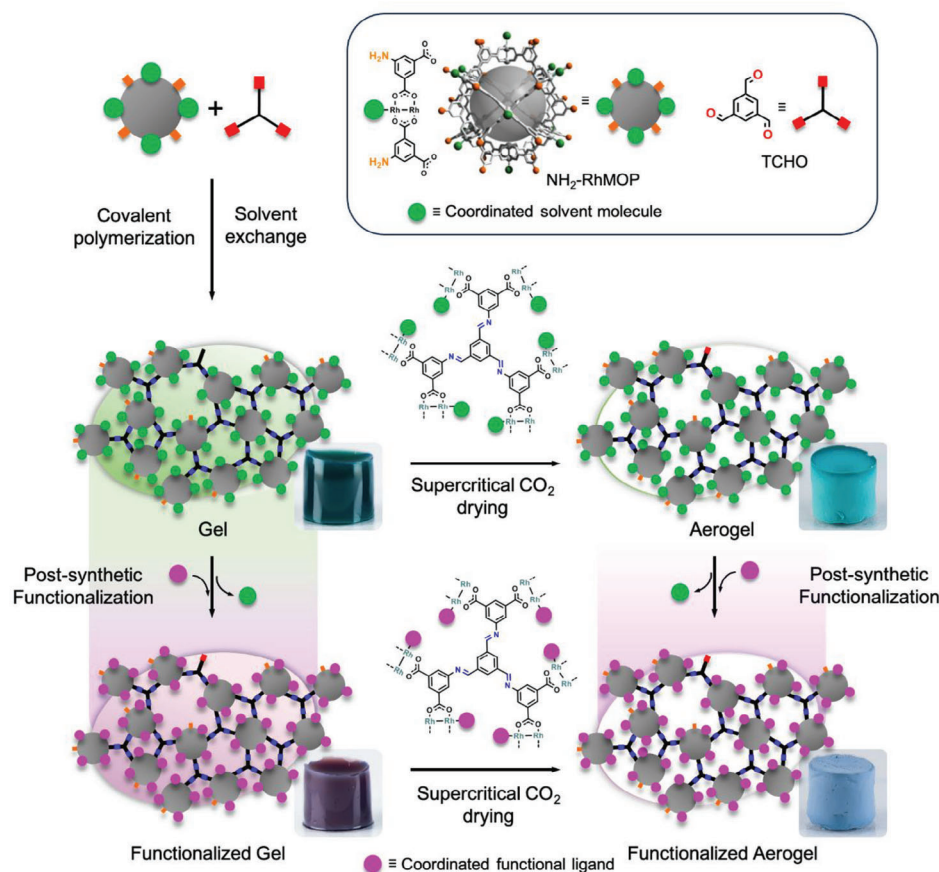


Figure 1. Schematic of the synthesis of imine cross-linked gels and aerogels, and their respective post-synthetic functionalization.

polymers, cellulose, carbon nanotubes, and graphene.^[8] It is important to stress that these materials have low crystallinity and tunability.^[1] Further progress in aerogel chemistry has related to the utilization of various metal and semiconductor nanoparticles. This approach bridges the nanoscopic and macroscopic worlds, enabling facile processability of nanomaterials at the macroscale without any concomitant loss of nanoscale properties.^[9] Furthermore, the devices derived from aerogels benefit from the increased mass transfer provided by the hierarchical structure of porous aerogels. Therefore, aerogels-based devices have been applied in different application fields, such as pollutant removal,^[10] gas sensing/storage,^[11,12] catalysis,^[13] and delivery,^[14] among others.

Among the latest types of materials applied to aerogel chemistry are molecular porous reticular materials, including metal-organic frameworks (MOFs),^[15–17] and covalent organic frameworks (COFs).^[18–20] These materials are employed so that their diverse microporosity and chemical functionalities can be incorporated into aerogels. Recently, metal-organic cages/polyhedra (MOCs/MOPs) have also been used as porous building blocks for the creation of aerogels.^[21,22] In particular, Furukawa et al. reported the formation of aerogels by crosslinking cuboctahedral $[\text{Rh}_2(\text{bdc})_2]_{12}$ (where *bdc* is benzene-1,3-dicarboxylate and its derivatives) MOPs using the ditopic 1,4-bis(imidazol-1-ylmethyl)benzene (bix) linker.^[23–25] This linker

can bridge/polymerize RhMOPs by coordinating two unsaturated Rh(II) sites of two different RhMOPs, forming gels and their corresponding aerogels. Remarkably, these coordinative soft aerogels incorporate the microporosity of the RhMOPs, with Brunauer–Emmett–Teller surface areas (S_{BET}) in the range of ≈ 500 to $\approx 750 \text{ m}^2 \text{ g}^{-1}$.

Herein, we explore a new strategy to synthesize aerogels using such cuboctahedral RhMOPs as microporous building units, and then functionalize the resultant aerogels via post-synthetic modification (**Figure 1**). Our synthesis is based on using dynamic covalent chemistry—rather than coordination chemistry—to crosslink the RhMOPs, which provides several advantages.^[26,27] First, covalent bonds tend to be stronger than coordination bonds. Accordingly, we expected that they would generate aerogels with greater chemical stability than those built from coordinative bonds. Second, we planned to introduce an NH_2 group at the 5-position of each of the 24 *bdc* linkers that form the RhMOP. We envisioned that these groups could react with aldehydes to form imine bonds, thereby polymerizing the RhMOPs. We reasoned that our strategy would allow use of 24 reactive sites per MOP rather than the 12 available reactive Rh(II) ions per MOP, as in the case of using coordinative bonds. Our aim was to increase the connectivity of the synthesized aerogels to make them more robust. Interestingly, this covalent chemistry has recently been demonstrated in the crosslinking of CuMOPs to form soft

gel-like materials.^[28] Finally, and most importantly, we expected that formation of MOP-based aerogels through covalent chemistry would leave the 12 available, outer, coordinatively unsaturated Rh(II) metal sites in each MOP untouched. Thus, we imagined that these sites could be exploited for post-synthetic functionalization of the hierarchical pores of the aerogels, using functional ligands: for example, to tune the macroscopic properties of the aerogels and therefore, optimize their sorption capabilities.

Herein, we report the preparation of a series of monolithic aerogels, made by crosslinking cuboctahedral RhMOPs through imine bond formation, and their subsequent post-synthetic functionalization, using the coordination chemistry described above. Our methodology comprised four steps (Figure 1). First, a gel is formed by a sol-gel process involving the imine crosslinking of the cuboctahedral $[\text{Rh}_2(5\text{-NH}_2\text{-bdc})_2]_{12}$ MOP (hereafter named $\text{NH}_2\text{-RhMOP}$) via the 3-connected benzene-1,3,5-tricarbaldehyde (TCHO). Second, the MOP-based gel undergoes solvent exchange. Third, it is subsequently dried under supercritical CO_2 (scCO_2) to form the desired monolithic aerogel, which maintains the microporosity of the constituent RhMOP and exhibits a hierarchical porous structure that features both meso- and macroporosity and exhibits interesting mechanical properties. Finally, this monolithic aerogel is functionalized by immersion into a solution containing the desired functional ligand. As proof of concept, we demonstrated the post-synthetic modification of these aerogels by tuning their electrostatic or hydrophobic character for the synthesis of optimized adsorbents toward charged or hydrophobic pollutants, respectively.

2. Results and Discussion

2.1. Synthesis of Cross-Linked MOP-Based Aerogels

First, we followed our previously reported protocol to synthesize the $\text{NH}_2\text{-RhMOP}$, which has 24 accessible amino groups on its outer surface.^[29] Next, we reacted NH_2 -terminated MOP with TCHO in dimethyl sulfoxide (DMSO) at 85 °C for 24 h to make the iminic MOP-based gels. Finally, we dried these gels with scCO_2 to afford the desired aerogels. This began with a solvent-exchange process with tetrahydrofuran (THF), to remove the coordinated DMSO that had become trapped after the gel synthesis. During this solvent-exchange step, the gels changed from red to green, indicating that a change in the coordination sphere of Rh(II) ions had occurred (Figure S1, Supporting Information). Next, THF was exchanged with liquid CO_2 and then, with scCO_2 . Finally, we removed CO_2 from the pores by gradually decreasing the pressure until atmospheric pressure was reached. This procedure afforded stable, porous iminic MOP-based aerogels containing unsaturated Rh(II) metal sites.

Next, to maximize crosslinking between the TCHO and the $\text{NH}_2\text{-RhMOP}$ in the final aerogels, we systematically varied the molar ratio of TCHO/ $\text{NH}_2\text{-RhMOP}$ in the initial gelation process: from 2:1 to 4:1 to 8:1 to 16:1 and finally, to 32:1. Remarkably, for all these molar ratios studied, we were able to synthesize the iminic MOP-based gels and their corresponding aerogels. Note that, for maximizing crosslinking between a 3-connected TCHO and a 24-connected $\text{NH}_2\text{-RhMOP}$, the expected ideal molar ratio is 8:1. This is because the network able to satisfy the 24 and 3 extension sites of the $\text{NH}_2\text{-RhMOP}$ and TCHO, respectively,

is the 3,24-rht topology in which the two building blocks are at a molar ratio of 8:1.^[30] Therefore, when the number of TCHO building blocks is greater or less than 8 in the gelation reaction, the $\text{NH}_2\text{-RhMOP}$ s are expected to be less interconnected. During gel formation, we found that, consistent with theoretical expectations, the gel resulting from the reaction of $\text{NH}_2\text{-RhMOP}$ with 8 equivalents of TCHO exhibited the highest shear storage modulus of the series (value: 503 Pa; Table S1 and Figure S2, Supporting Information). This trend corroborates a higher degree of crosslinking being achieved when $\text{NH}_2\text{-RhMOP}$ is reacted with 8 equivalents of TCHO to form a highly interconnected gel. The gels corresponding to these lower or higher molar ratios did indeed exhibit lower shear storage modulus values. Moreover, we also observed that the transparency of the gels increased with the number of TCHO equivalents, indicating a possible decrease in the size of the particles comprising the gel network (Figure S3, Supporting Information). We confirmed this correlation by analyzing the five resultant aerogels by field-emission scanning electron microscopy (FE-SEM). The FE-SEM micrographs revealed that all the aerogels comprise a colloidal network made of fused nanoparticles (Figure 2a, Figures S4–S8, Supporting Information). Statistical analysis of these SEM images confirmed that, as the amount of TCHO used increased (range: 2 to 32 mol eq.), the size of the nanoparticles decreased (range: 29 ± 2 to 20 ± 2 nm) (Table S1, Supporting Information).

Next, we characterized our MOP-based aerogels through solid-state cross-polarized magic angle spinning (CP/MAS) ^{13}C -NMR and Fourier-Transform infrared (FT-IR) spectroscopy to confirm the crosslinking of $\text{NH}_2\text{-RhMOP}$ and TCHO through the formation of imine bonds (Figure 2b,c). Solid-State CP/MAS ^{13}C -NMR confirmed the presence of the characteristic imine carbon signal at ≈ 150 ppm for all aerogels (Figure 2b). Moreover, for the aerogels that were fabricated using TCHO/ $\text{NH}_2\text{-RhMOP}$ ratios of 8:1, 16:1, and 32:1, a peak at 190 ppm was observed, which we attributed to the presence of free aldehyde groups in the network. Interestingly, the intensity of this peak increased as the TCHO/ $\text{NH}_2\text{-RhMOP}$ ratio increased. The corresponding FT-IR spectra corroborated these findings. The signals attributed to the presence of carbonyl groups ($\text{C}=\text{O}$, stretching bands) of the TCHO monomer were detected at ≈ 1690 cm^{-1} for all aerogels, as well as the characteristic band attributed to the imine bond ($\text{C}=\text{N}$ stretching band) at ≈ 1625 cm^{-1} (Figure 2c). However, as the TCHO/ $\text{NH}_2\text{-RhMOP}$ ratio increased, the intensity of the peak corresponding to free aldehyde also increased, indicating that as the molar ratio of TCHO increased in the reaction, its connectivity decreased. Interestingly, these differences in the connectivity of the MOP network did not translate to differences in overall thermal stability, as ascertained by thermogravimetric analysis (TGA) measurements, which showed that thermal decomposition of all five MOP-based aerogels do not start until reaching $\approx 300\text{--}320$ °C (Figure S11, Supporting Information).

We analyzed the stoichiometric composition of the fabricated aerogels by first digesting the samples under acidic conditions and then, analyzing the resulting solutions by ^1H -NMR. Under acidic conditions, the MOP-based aerogels decompose, releasing imine molecules that, upon hydrolyzation, form the corresponding $\text{NH}_2\text{-bdc}$ and TCHO. We calculated the conversion rate by comparing the integration of one peak at 8.42 ppm corresponding to $\text{NH}_2\text{-bdc}$ and that peak at 10.10 ppm corresponding to

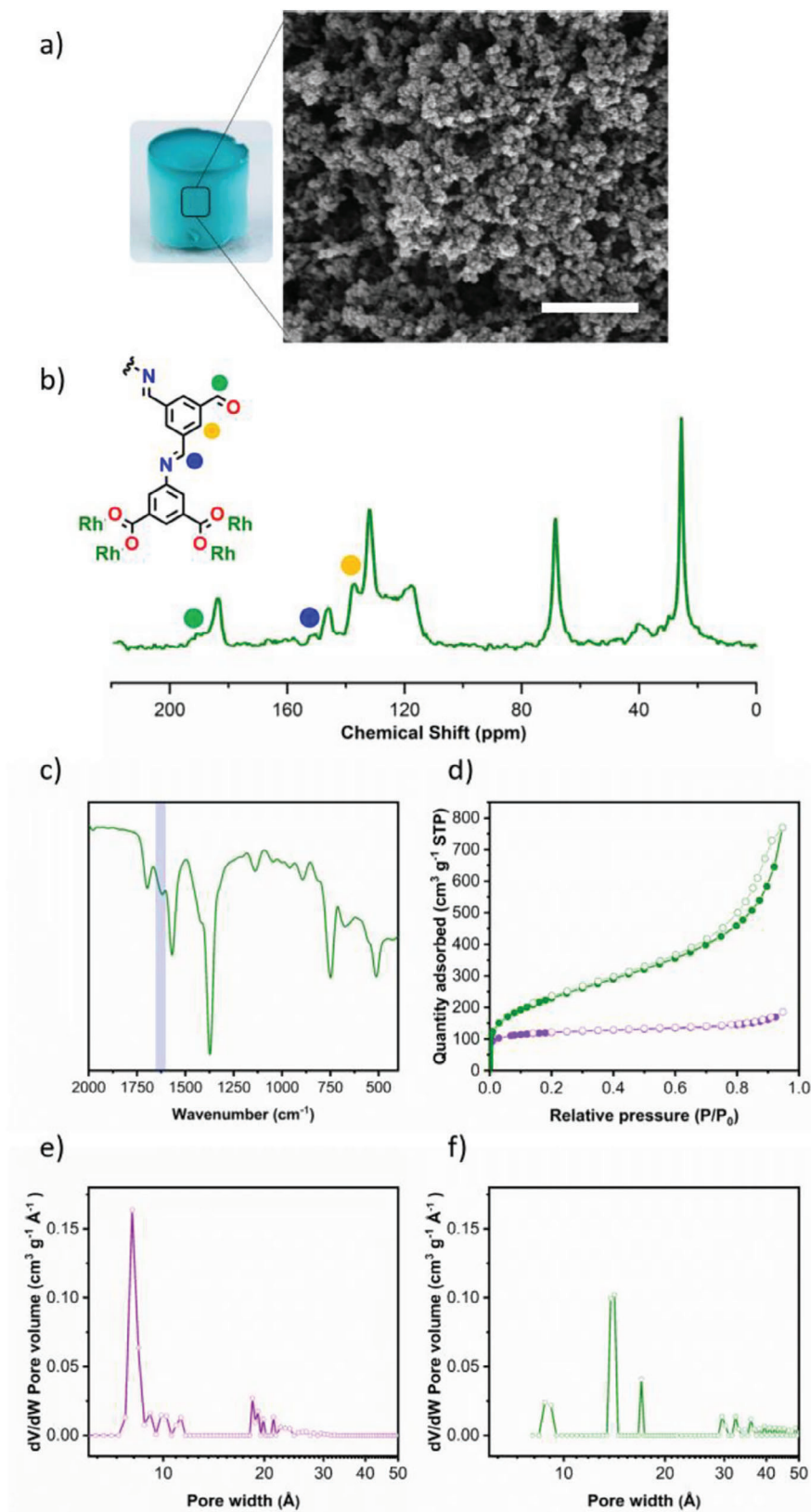


Figure 2. a) Photograph and corresponding FESEM image of BCN-1, Scale bar: 500 nm. b) Solid-State CP/MAS ^{13}C -NMR of BCN-1. c) FT-IR spectra of BCN-1. d) N_2 -sorption isotherm at 77 K for NH_2 -RhMOP (purple) and BCN-1 (green). e, f) Pore size distribution estimated by DFT for e) NH_2 -RhMOP and f) BCN-1.

TCHO (SI). Table S1, Supporting Information, lists the stoichiometric composition calculated for the five aerogels. From these data, we found that the final compositions of the three first aerogels closely agree with the TCHO/NH₂-RhMOP ratios of 2:1 (ratio found: 2:1), 4:1 (ratio found: 4:1) and 8:1 (ratio found: 7:1) used in the initial gelation reaction. However, for the other two aerogels, the final compositions were far from the initial TCHO/NH₂-RhMOP ratios used: the final values were $\approx 10:1$ (ratio used: 16:1) and $\approx 14:1$ (ratio used: 32:1).

Seeking to evaluate the porosity of these aerogels, we next performed N₂ adsorption experiments at 77 K, which confirmed that all samples were indeed porous (Figure 2d and Figure S17, Supporting Information). The isotherms for all aerogels exhibited a trend typical of porous materials that contain a wide range of porosity: a sharp increase in the quantity of N₂ adsorbed at low relative pressures, followed by a monotonic increase. From these isotherms, we calculated Brunauer–Emmett–Teller (S_{BET}) surface areas, obtaining values in the range of ≈ 700 to ≈ 865 m² g⁻¹, the highest of which were found for the aerogels synthesized using TCHO/NH₂-RhMOP ratios of 16:1 (865 m² g⁻¹) and 8:1 (824 m² g⁻¹) (Figure 2d, Table S1, Supporting Information). To verify that the inner cavity of RhMOPs remained accessible to guest molecules, we calculated the pore-size distribution (PSD) based on NLDFT models, and compared it with that of the prototypical [Rh₂(bdc)₂]₁₂ MOP.^[31,32] The PSD revealed the presence of pores of 0.9, 1.3, and 1.7 nm for all synthesized MOP-based aerogels (Figure 2e). The pore of 0.9 nm corresponds to the inner space of the MOP cavity,^[25] as revealed by the PSD of the NH₂-RhMOP, which was maintained and fully accessible after the MOP crosslinking and activation of the samples. In contrast, we attributed the pores of 1.3 and 1.7 nm to the inter-MOP space created due to the polymerization of NH₂-RhMOPs and TCHO. Additionally, the PSD also revealed the presence of meso- and macro-porosity, which we ascribed to the larger cavities formed by the colloidal network.

Finally, we analyzed the aqueous stability of the MOP-based aerogels, given that some of the main applications of aerogels require their use in water. To this end, we incubated the different aerogels in deuterium oxide for 72 h at room temperature. In all cases, the macroscopic shape of the aerogel was preserved. After the incubation, we analyzed the supernatants and the digested aerogels by ¹H-NMR, finding that the composition of the aerogels having a TCHO/NH₂-RhMOP ratio of 2:1, 4:1, or 7:1 had not changed (Figures S29–S34, Supporting Information). However, the aerogels whose TCHO/NH₂-RhMOP ratios were 10:1 and 14:1 changed in composition, to 7:1 and 11:1, respectively, due to leaching of the TCHO in water. These results correlate well with the average connectivity of TCHO for each aerogel. Thus, those gels prepared with more than 8 mol. eq. of TCHO contained a higher percentage of di- or mono-connected TCHO groups, which are susceptible to leaching upon incubation in water. Based on these aqueous stability findings, and the aforementioned properties, we concluded that the aerogel obtained from the polymerization of NH₂-RhMOP with 8 equivalents of TCHO (hereafter named BCN-1) was the optimal material.

Finally, we assessed the mechanical stiffness of BCN-1 (density = 0.11 g cm⁻³) through a uniaxial quasi-static compression test. The aerogel behaves as a brittle material, exhibiting a Young's modulus value of 500 $\pm$ 50 kPa and withstanding a maximum

stress of 115 kPa (Figure S39, Supporting Information). The material could be compressed to $\approx 75\%$ before reaching the densification region, where the stress increases rapidly with increasing strain. However, the aerogel showed partial splitting on the edges, resulting in reduced contact area with the compression platens and thus underestimating its compressive strength. Nonetheless, Young's modulus of BCN-1 is higher than other previously reported MOP gels ($E = 1\text{--}3.5$ kPa) or aerogels of reticular materials such as COFs ($E = 0.8\text{--}4.1$ kPa) or COF composites ($E = 260$ kPa), but smaller than those measured for monolithic MOF composites ($E = 12\,000\text{--}25\,000$ kPa).^[18,33–35]

2.2. Post-Synthetic Functionalization of MOP-Based Aerogels

Having synthesized the five MOP-based aerogels and chosen BCN-1 as the optimal one for further development, we next functionalized its pores by linking functional organic ligands to the coordinatively unsaturated Rh(II) sites. For this, we selected monodentate ligands having different functional groups (Figure 3): heptyl-4-(4-pyridyl) pyridinium (HPP), to impart positive charge; 4-(4-pyridyl) benzoic acid (PBA), to confer negative charge; and tris(4-trifluoromethylphenyl) phosphine (TFP), to provide hydrophobicity. The pyridyl and phosphine functionalities were used to anchor the desired functionality onto the Rh(II) axial sites, based on the well-documented reactivity of such sites in dirhodium paddlewheels toward N- or P- donor ligands.^[36–38]

The aerogel BCN-1 was functionalized with either pyridyl ligand and separately by incubating the aerogel in a solution containing an excess of HPP or PBA. Specifically, for HPP, this was done in a mixture of THF/MeOH (3:1) containing 24 molar equivalents (mol. eq.) of HPP (per MOP within the network) at room temperature for 4 h. For PBA, the reaction was run in the same conditions, except using PBA instead of HPP, and water as solvent. Remarkably, after few minutes of incubation, the aerogels changed from greenish-blue to either purple (PBA) or wine red (HPP) (Figure 3). This was the first indication of the coordination of the pyridyl ligands to the Rh(II) metal ions (vide infra). Interestingly, both aerogels maintained their shape throughout incubation (Figure 3). Afterward, the functionalized aerogels (hereafter named HPP@BCN-1 and PBA@BCN-1) were thoroughly washed to remove non-coordinated ligands.

We began characterizing HPP@BCN-1 and PBA@BCN-1 by diffuse reflectance UV–vis spectroscopy. Importantly, the Rh–Rh bond has a characteristic adsorption band centered at 500–600 nm (band I), which corresponds to the $\pi^* \rightarrow \sigma^*$ transition and is highly sensitive to axial coordination, enabling us to track the functionalization spectroscopically.^[39,40] Solid-state UV–vis analysis revealed a shift in band I from 599 nm to either 570 nm (for HPP@BCN-1) or 576 nm (for PBA@BCN-1) (Figure S40, Supporting Information). These results confirmed that in each aerogel, the respective pyridyl ligand was coordinated to the open metal sites of the MOP, rather than merely being attached by weak interactions within the network. Next, we evaluated the degree of functionalization by digesting the aerogels and analyzing the resulting solutions by ¹H-NMR. From these experiments, we found that BCN-1 was functionalized with 10 molecules of HPP or PBA per MOP unit (Figures S41 and S42, Supporting Information). Considering that only the outer Rh(II) axial sites

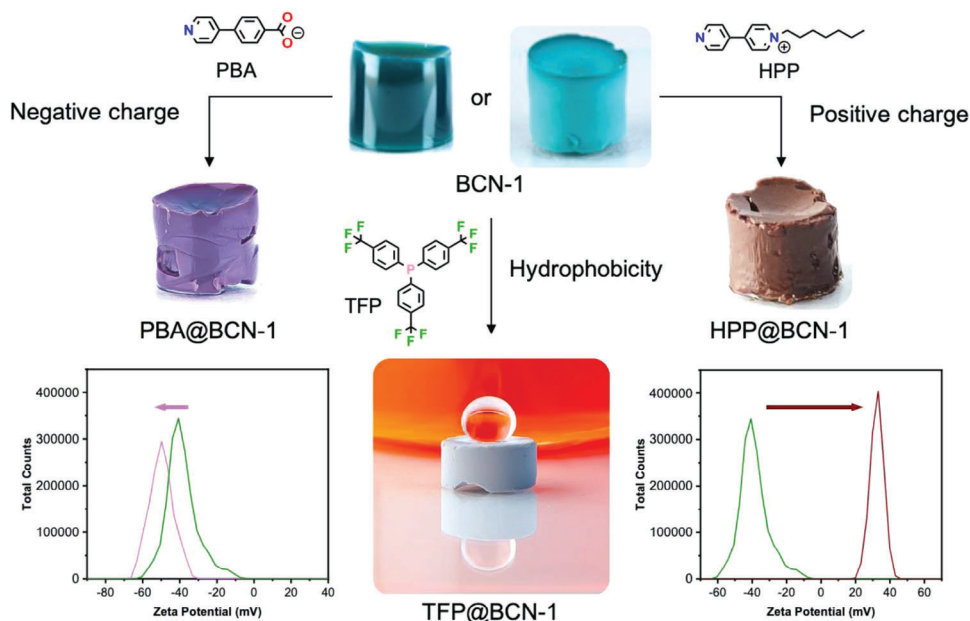


Figure 3. Schematic of the post-synthetic coordinative functionalization of BCN-1 with either PBA (to impart negative charge) or HPP (to provide positive charge). Shown are photographs of the precursor BCN-1 gel (left) and aerogel (right), and the resultant functionalized aerogels PBA@BCN-1, HPP@BCN-1, and TFP@BCN-1. Moreover, for both PBA@BCN-1 and HPP@BCN-1, the charge of the Z-potential before and after functionalization is shown. For TFP@BCN-1, its hydrophobicity is demonstrated in its photo, in which a water droplet rests on its surface.

are available for such bulky ligands,^[41–44] the percentage of occupancy of the outer Rh(II) axial sites was 83% in both cases. Interestingly, we achieved a similar degree of functionalization by performing the post-synthetic coordinative reaction on the gel precursor, and then converting it to the aerogel (Figures S41 and S42, Supporting Information).

We then evaluated the porosity of activated HPP@BCN-1 and PBA@BCN-1 in N_2 adsorption experiments run at 77 K. The corresponding isotherms revealed that, despite their high degree of functionalization, each aerogel preserved its hierarchical porosity. The S_{BET} values found were $449 \text{ m}^2 \text{ g}^{-1}$ (for HPP@BCN-1) and $630 \text{ m}^2 \text{ g}^{-1}$ (for PBA@BCN-1) (Figures S43–S48, Supporting Information).

To assess the influence of each pyridine on the macroscopic electrostatic character of each functionalized aerogel, we measured the Z-potential of BCN-1 and compared it to that of PBA@BCN-1 and HPP@BCN-1 (Figure 3). The non-functionalized aerogel had a negative Z-potential (-40 mV), which we ascribed to the Lewis acidic character of its internal and external Rh(II) axial sites. Interestingly, functionalization with PBA correlated to a decrease in Z-potential, with PBA@BCN-1 showing a value of -50 mV . Conversely, HPP@BCN-1 exhibited a Z-potential of $+32 \text{ mV}$.

As mentioned above, to impart hydrophobicity to BCN-1, we functionalized it with TFP, a bulky fluorinated ligand. This was done by immersing the BCN-1 gel precursor in a THF solution of TFP containing 12 equivalents of TFP per MOP present in the network for 4 h. This process induced a rapid color change in the aerogel, from greenish-blue to dark purple. Subsequently, the gel was repeatedly washed with THF, and then transformed into the corresponding aerogel (hereafter named TFP@BCN-1) by drying with scCO_2 obtaining a pale purple aerogel (Figure 3). Solid-

state UV-vis analysis confirmed the coordinative attachment of TFP on the Rh(II) axial sites, as the adsorption of Band I shifted from 599 to 562 (Figure S49, Supporting Information). The final TFP/MOP ratio in TFP@BCN-1 was found to be 11:1, as determined by the ^1H -NMR spectrum of the digested aerogel, which corresponds to an occupancy of 92% at the outer Rh(II) axial sites. The hierarchical porosity of TFP-BCN-1 was confirmed by N_2 adsorption at 77 K, which revealed an S_{BET} of $687 \text{ m}^2 \text{ g}^{-1}$ and a wide distribution of pore size (Figures S51–S54, Supporting Information).

Finally, we studied the impact of TFP functionalization on the hydrophobicity of BCN-1 through contact-angle experiments. Whereas BCN-1 exhibited extreme hydrophilicity, with a water contact angle of $\approx 0^\circ$, TFP@BCN-1 was found to be highly hydrophobic, with a contact angle of 145° (Figure 3 and Figures S55 and S56, Supporting Information). The same trend was observed in water-vapor adsorption experiments, where the maximum water uptake at 1 bar for BCN-1 was 0.31 g g^{-1} , and for TFP@BCN-1, 0.12 g g^{-1} (Figure S57, Supporting Information).

2.3. Sorption of Organic Pollutants from Water: Non-Functionalized Versus Functionalized BCN-1 Aerogels

Inspired by our finding that local changes at the Rh(II) axial sites induced by the coordination of charged pyridine ligands influence the electrostatic properties of the hierarchically porous aerogel BCN-1, we envisaged that such transformations could be used to modulate the affinity of BCN-1 toward charged molecules. To demonstrate this hypothesis, we studied the performance of BCN-1, HPP@BCN-1 and PBA@BCN-1 toward the uptake of two representative charged organic pollutants: the

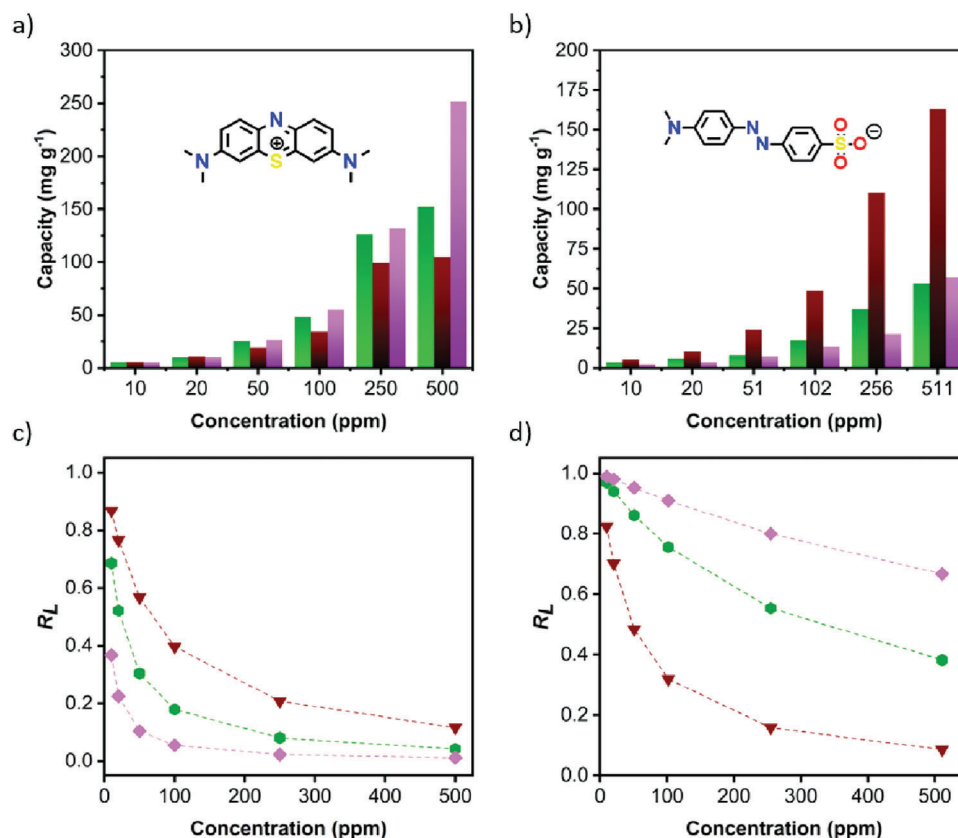


Figure 4. a,b) Bar diagrams representing the respective removal capacity of BCN-1 (green), HPP@BCN-1 (wine red), and PBA@BCN-1 (magenta) for either a) the cationic dye methylene blue (MB) or b) the anionic dye methyl orange (MO), and at various concentrations of MB or MO. c,d) The variation of separation factor (R_L) for BCN-1 (green), HPP@BCN-1 (wine red), and PBA@BCN-1 (magenta) at different concentrations of c) MB or d) MO.

anionic dye methyl orange (MO), and the cationic dye methylene blue (MB). We initially determined the uptake capacity of BCN-1, HPP@BCN-1, and PBA@BCN-1 for either MO or MB at different concentrations of pollutant (range: 10 to 500 ppm) after 72 h of incubation in water (pH = 7) (Figure 4a,b). For uptake of MB above a concentration of 50 ppm, we found the following trend: PBA@BCN-1 > BCN-1 > HPP@BCN-1 (Figure 4a). For example, when challenged to a MB concentration of 500 ppm, the maximum capacities were 250 (PBA@BCN-1), 150 (BCN-1), and 100 mg g⁻¹ (HPP@BCN-1). We ascribed the higher maximum uptake and removal of (cationic) MB by PBA@BCN-1 compared to BCN-1 and HPP@BCN-1 to its highly negative electrostatic character. As expected, we observed the opposite trend for uptake of (anionic) MO: HPP@BCN-1 > BCN-1 ≈ PBA@BCN-1 (Figure 4b). Thus, at a MO concentration of 500 ppm, the maximum uptake capacities of these aerogels were 150 mg g⁻¹ (HPP@BCN-1) and ≈50 mg g⁻¹ for both BCN-1 and PBA@BCN-1. Therefore, in terms of maximum capacity, the functionalized BCN-1 aerogels exhibit a dye removal performance that falls within the range of the current state-of-the-art aerogel adsorbents (Table S2, Supporting Information).

Next, we fitted the dye adsorption isotherms of BCN-1, HPP@BCN-1, and PBA@BCN-1 to the Langmuir and Freundlich models to elucidate the main adsorption mechanism for each adsorbent and pollutant. The Langmuir model revealed a stronger correlation (i.e., higher R^2 value) with experimental data

than did the Freundlich model, indicating that the adsorption process is best described by the formation of a monolayer of the adsorbate on the surface of the adsorbent, which contains uniformly distributed active adsorptive sites (Figures S58 and S59, Supporting Information). From the Langmuir constant obtained for each isotherm, one can estimate the separation factor (R_L), which is a parameter that indicates to what extent an adsorption process is favored. Therefore, the nature of the adsorption process can be described from its respective value of R_L , whether it is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).^[45] In the case of the adsorption of MB, which tends to be irreversible at high MB concentration, R_L is enhanced upon functionalization of BCN-1 with PBA but decreased upon functionalization with HPP (Figure 4c). The impact of functionalization on BCN-1 was even more drastic in the case of MO (Figure 4d), whereby the degree of adsorption was markedly higher for HPP@BCN-1 than for BCN-1 throughout the entire concentration range studied. Conversely, functionalization of BCN-1 with PBA induced a strong decrease in MO adsorption.

As reflected in the results above, the observed trends in maximum uptake capacities and degree of favorability for the adsorption of MO or MB by our synthesized MOP-based aerogels correlate well with the electrostatic repulsion/attraction for each adsorbent-adsorbate pair. Encouraged by this correlation, we sought to further characterize the aerogel-dye adsorption

mechanism by elucidating the kinetics of the process. To this end, time-dependent adsorption curves were acquired for each aerogel and dye at the aforementioned concentrations (from 10 to 500 ppm). The experiment was done by monitoring the remaining concentrations of dye at different time intervals (2, 4, 6, 24, 48 and 72 h) for each concentration studied. Thereafter, the dye uptake was plotted against time, and the plot was fitted with a pseudo-second order kinetic model. In all cases, the fittings revealed good correlation (i.e., R^2 values) between the experimental data and the pseudo-second order kinetic model (Figures S61–S71, Supporting Information).

This observation led us to conclude that, for all pollutants and aerogels studied, the main parameter determining the removal performance is the relative amount of adsorbent and dye. Furthermore, the maximum capacity (q_{max}) value for each adsorbent obtained from the kinetic model fittings closely agreed with the experimentally obtained value for each pollutant, further confirming the accuracy of the fitting (Table S3, Supporting Information).

Next, we employed the kinetic data to gain a deeper understanding of the diffusion of dye guest molecules throughout the aerogel adsorbent and investigate the impact of aerogel functionalization on this phenomenon. To this end, we fitted the time-dependent adsorption data for each dye and adsorbent to the Weber-Morris kinetic model using the following equation:

$$q_t = K_{id} t^{0.5} + C \quad (1)$$

Therefore, by plotting q_t (amount adsorbed at each time) as a function of $t^{0.5}$, one can determine the intra-particle diffusion rate constant (K_{id}) and constant C that is proportional to the thickness of the boundary layer. In this model, $C = 0$ (i.e., the line passes through the origin) indicates that intra-particle diffusion is the rate-limiting step, whereas $C \neq 0$ indicates that the adsorption process is controlled by a combination of the intra-particle diffusion and one or more other steps. We found that, for the majority of our materials, the intraparticle diffusion was the rate-limiting step in the adsorption (Table S4, Supporting Information). This would correspond to the diffusion of the dye throughout the colloidal particle to reach the inner adsorptive sites generated by the MOP network. However, the kinetics of this process (K_{id}) can be tuned by selective post-synthetic functionalization of BCN-1. Thus, the intraparticle diffusion rates for MB and for MO were higher in PBA@BCN-1 and in HPP@BCN-1, respectively, than in the parent BCN-1 (Figures S72–S83 / Table S4, Supporting Information). For example, at 500 ppm of MB, the K_{id} increased from 15.2 to 28.7 $\text{mg g}^{-1} \text{min}^{-1/2}$ upon PBA functionalization. Analogously, for MO at 511 ppm, the K_{id} increased from 6.25 to 18.7 $\text{mg g}^{-1} \text{min}^{-1/2}$ upon HPP functionalization.

2.4. Oil-Water Separation Properties of the Hydrophobic TFP@BCN-1 Aerogel

Next, the strong hydrophobic character of TFP-BCN-1 (water contact angle = 145°) prompted us to study its performance as a selective adsorbent of lipophilic solvents. Thus, we compared the uptake capacities of BCN-1 and of TFP@BCN-1 for toluene, dichloromethane, hexane, paraffin oil, diesel, and water (Figure 5a). BCN-1 demonstrated high sorption efficiency

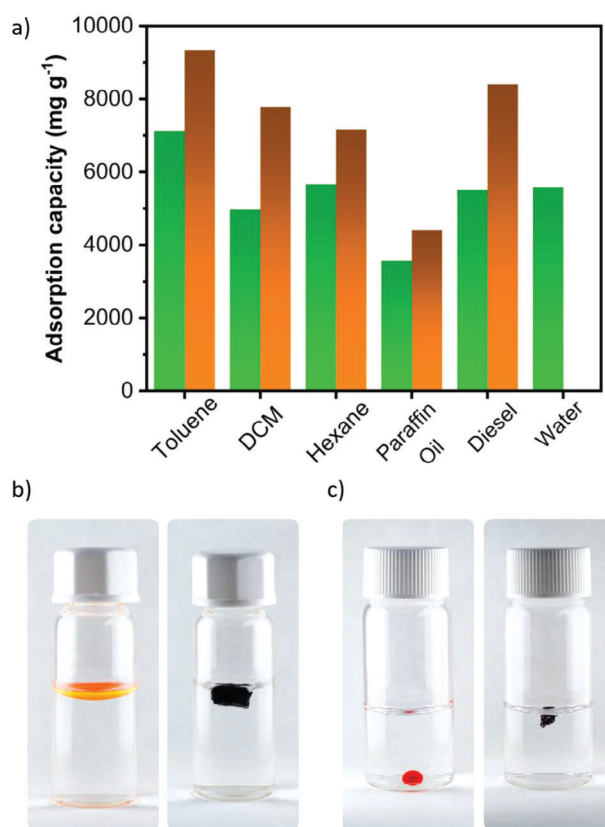


Figure 5. a) Adsorption capacities of BCN-1 (green) and of TFP@BCN-1 (orange) toward toluene, dichloromethane (DCM), hexane, paraffin oil, diesel, or water. b,c) Photographs represent mixtures of toluene and dichloromethane with water (both organic solvents were stained with Nile red dye for better visibility).

toward the aforementioned solvents, oil and water, yet without any selectivity. Conversely, TFP@BCN-1 showed greater sorption capacity for organic solvents and a negligible sorption capacity for water (Figure 5a). Therefore, the TFP-functionalization on the Rh(II)-site of the aerogel led to a higher selectivity for sorption of the lipophilic solvents over water, owing to its hydrophobicity. Encouraged by this observation, we sought to perform an oil-water separation experiment with the hydrophobic TFP@BCN-1 adsorbent. To this end, we challenged TFP@BCN-1 toward the selective removal of organic solvents, toluene, diesel or dichloromethane, from biphasic mixtures of each with water. The organic solvents were selected because they are immiscible in water, with the DCM layer located below of the water layer, and the toluene and diesel layers located above the water layer. In a typical experiment, when a portion of the hydrophobic TFP@BCN-1 aerogel was introduced into a biphasic mixture of toluene and water, the top layer of toluene was immediately adsorbed by TFP@BCN-1 (Figure 5b and Video S1, Supporting Information). The same behavior was observed for diesel (Video S2, Supporting Information). When the same adsorbent was placed in a biphasic mixture of water and DCM, the TFP@BCN-1 and the respective organic solvent remained separated by water due to the high hydrophobicity of TFP-BCN-1, causing it to float on top of the water layer. However, the DCM layer could be completely

removed by pushing the TFP@BCN-1 to the bottom of the mixture. Indeed, once the aerogel had touched the DCM, it immediately adsorbed it (Figure 5c and Video S3, Supporting Information). These experiments showed that (hydrophobic) TFP@BCN-1 can remove organic solvents from either above or below the water layer in biphasic mixtures of these solvents with water.

3. Conclusions

Herein we have reported a methodology for the synthesis of robust aerogels from MOPs via covalent chemistry. This approach enables to polymerize MOPs into shaped aerogels preserving the reactivity of the Rh(II) axial site. Therefore, our strategy enables to integrate properties of Rh(II) opened metal sites into hierarchically porous aerogels that might find application in fields such as catalysis^[46,47] and removal of toxic pollutants including hazardous gases such as NH₃, SO₂ and H₂S.^[48–50] We exploited the latent reactivity of the Rh(II) sites in BCN-1 aerogel as anchoring sites for functional ligands with the aim of changing its physicochemical properties. We observed that the functionality of the attached ligands is transferred to the overall aerogel, enabling the post-synthetic modification of its physicochemical properties toward the development of optimized adsorbents for targeted guests. We demonstrated this concept by imparting our optimal aerogel, BCN-1, with negative or positive electrostatic surface charges (using the ligands PBA or HPP, respectively), or hydrophobicity (using the ligand TFP), enabling us to tune the adsorption properties of the resultant functionalized aerogels. Thus, compared to BCN-1, the positively charged aerogel HPP@BCN-1 adsorbed more of the anionic dye MO; the negatively charged PBA@BCN-1 adsorbed more of the cationic dye MB; and the hydrophobic TFP@BCN-1 exhibited greater selectivity for sorption of organic solvents and oils over water. We believe that the methodology herein described will enable the structuration of myriad functionalities (i.e., organocatalysts, chiral (bio)molecules, polymers) on robust aerogels by virtue of the rich surface reactivity of MOPs toward the development of novel shaped adsorbents, sensors and catalysts.^[51]

4. Experimental Section

Synthesis of NH₂-RhMOP: NH₂-RhMOP was synthesized according to a previously described methodology.^[29]

General Synthesis of Iminic MOP-Based Gels of TCHO:NH₂-RhMOP: In a typical experiment, 30 mg (4.4 μmol) of NH₂-RhMOP were dissolved in 1.5 mL of DMSO resulting in a clear red solution. Then, the corresponding amount of benzene-1,3,5-tricarbaldehyde (TCHO) was added to the NH₂-RhMOP solution. Specifically, the following amounts of TCHO were added for each of the gels formed: 1.5 mg (8.8 μmol, 2 mol. eq.); 2.9 mg (17.7 μmol, 4 mol. eq.); 5.7 mg (35.2 μmol, 8 mol. eq.); 11.5 mg (70.7 μmol, 16 mol. eq.); and 22.9 mg (141.3 μmol, 32 mol. eq.). The red solutions were placed inside a syringe and heated at 85 °C for 24 h. The obtained red gels were carefully removed from the syringe to undergo a solvent exchange process. The solvent exchange process entailed the washing of the gels with tetrahydrofuran (THF) (ca. 20 mL) every day until the color of the gel changed from red to green.

Synthesis of Iminic MOP-Based Aerogels through Supercritical CO₂ Drying: The THF-exchanged gels were first exchanged with liquid CO₂ at 25 °C and 60 bar for 30 min. Next, the liquid CO₂ was transformed into supercritical CO₂ (scCO₂) by increasing the pressure to 140 bar at 40 °C. The sample

was kept under scCO₂ for 2 h. Finally, the CO₂ was slowly vented during 1 h to reach 1 bar. After this process, the green MOP-based aerogel was obtained.

Synthesis of PBA@BCN-1 Starting from the MOP-Based Gel: The gel synthesized with 8 mol. eq. of TCHO and containing 30 mg (4.4 μmol) of NH₂-RhMOP was incubated in a mixture of MeOH:THF (2:1) (6 mL) containing 21.1 mg (105.9 μmol) of PBA for 4 h. After the incubation time, the gel was thoroughly washed with a mixture of THF:MeOH (2:1) (x3), and MeOH (x3). Finally, the functionalized gel was dried with scCO₂, as explained above to yield PBA@BCN-1.

Synthesis of PBA@BCN-1 Starting from BCN-1 Aerogel: BCN-1 aerogel containing 30 mg (4.4 μmol) of NH₂-RhMOP was incubated in a water solution (6 mL) containing 21.1 mg (105.9 μmol) of PBA for 4 h. After the incubation time, the aerogel was thoroughly washed with water (x5), and was ready to be used for the sorption of organic pollutants from water.

Synthesis of HPP@BCN-1 Starting from the MOP-Based Gel: The gel synthesized with 8 mol. eq. of TCHO and containing 30 mg (4.4 μmol) of NH₂-RhMOP was incubated in a mixture of THF:MeOH (3:1) (6 mL) containing 35.5 mg (105.9 μmol) of HPP for 4 h. After the incubation time, the gel was thoroughly washed with a mixture of THF:MeOH (3:1) (x3), and MeOH (x3). Finally, the functionalized gel was converted into an aerogel through scCO₂ drying, as detailed above.

Synthesis of HPP@BCN-1 Starting from BCN-1 Aerogel: BCN-1 aerogel containing 30 mg (4.4 μmol) of NH₂-RhMOP was incubated in a mixture of THF:MeOH (3:1) (6 mL) containing 35.5 mg (105.9 μmol) of HPP for 4 h. After the incubation time, the aerogel was thoroughly washed with a mixture of THF:MeOH (3:1) (x3), and MeOH (x3). Finally, the functionalized aerogel was thoroughly washed with water (x5) before performing the pollutant removal experiments.

Synthesis of TFP@BCN-1 Starting from the MOP-Based Gel: The gel synthesized with 8 mol. eq. of TCHO and containing 30 mg (4.4 μmol) of NH₂-RhMOP was incubated in a THF solution (6 mL) containing 24.7 mg (52.9 μmol) of TFP for 4 h. After the incubation time, the gel was thoroughly washed THF (x5). Finally, it was dried with scCO₂ to yield TFP@BCN-1.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aerogels, hydrophobicity, metal-organic polyhedra, porosity, post-synthetic modification

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- [1] N. Hüsing, U. Schubert, *Angew. Chem., Int. Ed.* **1998**, *37*, 22.
- [2] R. Baetens, B. P. Jelle, A. Gustavsen, *Energy Build.* **2011**, *43*, 761.
- [3] N. Bheekhun, A. R. Abu Talib, M. R. Hassan, *Adv. Mater. Sci. Eng.* **2013**, *2013*, 406065.
- [4] J. Mao, J. Iocozzia, J. Huang, K. Meng, Y. Lai, Z. Lin, *Energy Environ. Sci.* **2018**, *11*, 772.
- [5] S. Karamikamkar, E. P. Yalcintas, R. Haghniaz, N. R. De Barros, M. Mecwan, R. Nasiri, E. Davoodi, F. Nasrollahi, A. Erdem, H. Kang, J. Lee, Y. Zhu, S. Ahadian, V. Jucaud, H. Maleki, M. R. Dokmeci, H.-J. Kim, A. Khademhosseini, *Adv. Sci.* **2023**, *10*, 2204681.
- [6] H. Maleki, *Chem. Eng. J.* **2016**, *300*, 98.
- [7] S. S. Kistler, *Nature* **1931**, *127*, 741.
- [8] A. C. Pierre, G. M. Pajonk, *Chem. Rev.* **2002**, *102*, 4243.
- [9] C. Ziegler, A. Wolf, W. Liu, A.-K. Herrmann, N. Gaponik, A. Eychmüller, *Angew. Chem., Int. Ed.* **2017**, *56*, 13200.
- [10] M. Peydayesh, M. K. Suter, S. Bolisetty, S. Boulos, S. Handschin, L. Nyström, R. Mezzenga, *Adv. Mater.* **2020**, *32*, 1907932.
- [11] G. Shao, O. Ovsianyskyi, M. F. Bekheet, A. Gurlo, *Chem. Commun.* **2020**, *56*, 450.
- [12] J. E. Amonette, J. Matyáš, *Micropor. Mesopor. Mat.* **2017**, *250*, 100.
- [13] D. R. Rolison, J. J. Pietron, E. R. Glaser, T. H. Brintlinger, J. P. Yesinowski, P. A. Desario, J. S. Melinger, A. D. Dunkelberger, J. B. Miller, C. L. Pitman, J. C. Owrutsky, R. M. Stroud, M. D. Johannes, *ACS Appl. Mater. Interfaces* **2020**, *12*, 41277.
- [14] C. A. García-González, A. Sosnik, J. Kalmár, I. De Marco, C. Erkey, A. Concheiro, C. Alvarez-Lorenzo, *J. Controlled Release* **2021**, *332*, 40.
- [15] M. R. Lohe, M. Rose, S. Kaskel, *Chem. Commun.* **2009**, 6056.
- [16] J. Reboul, S. Furukawa, N. Horike, M. Tsotsalas, K. Hirai, H. Uehara, M. Kondo, N. Louvain, O. Sakata, S. Kitagawa, *Nat. Mater.* **2012**, *11*, 717.
- [17] N. Moitra, S. Fukumoto, J. Reboul, K. Sumida, Y. Zhu, K. Nakanishi, S. Furukawa, S. Kitagawa, K. Kanamori, *Chem. Commun.* **2015**, *51*, 3511.
- [18] J. Á. Martín-Illán, D. Rodríguez-San-Miguel, O. Castillo, G. Beobide, J. Perez-Carvajal, I. Imaz, D. Maspoch, F. Zamora, *Angew. Chem., Int. Ed.* **2021**, *60*, 13969.
- [19] D. Zhu, Y. Zhu, Q. Yan, M. Barnes, F. Liu, P. Yu, C.-P. Tseng, N. Tjahjono, P.-C. Huang, M. M. Rahman, E. Egap, P. M. Ajayan, R. Verduzco, *Chem. Mater.* **2021**, *33*, 4216.
- [20] J. Á. Martín-Illán, J. A. Suárez, J. Gómez-Herrero, P. Ares, D. Gallego-Fuente, Y. Cheng, D. Zhao, D. Maspoch, F. Zamora, *Adv. Sci.* **2022**, *9*, 2104643.
- [21] A. Khobotov-Bakishchev, L. Hernández-López, C. Von Baeckmann, J. Albalad, A. Carné-Sánchez, D. Maspoch, *Adv. Sci.* **2022**, *9*, 2104753.
- [22] E. Sánchez-González, M. Y. Tsang, J. Troyano, G. A. Craig, S. Furukawa, *Chem. Soc. Rev.* **2022**, *51*, 4876.
- [23] A. Carné-Sánchez, G. A. Craig, P. Larpent, T. Hirose, M. Higuchi, S. Kitagawa, K. Matsuda, K. Urayama, S. Furukawa, *Nat. Commun.* **2018**, *9*, 2506.
- [24] Z. Wang, G. A. Craig, A. Legrand, F. Haase, S. Minami, K. Urayama, S. Furukawa, *Chem. Asian J.* **2021**, *16*, 1092.
- [25] Z. Wang, C. Villa Santos, A. Legrand, F. Haase, Y. Hara, K. Kanamori, T. Aoyama, K. Urayama, C. M. Doherty, G. J. Smales, B. R. Pauw, Y. J. Colón, S. Furukawa, *Chem. Sci.* **2021**, *12*, 12556.
- [26] G. Lal, M. Derakhshandeh, F. Akhtar, D. M. Spasyuk, J.-B. Lin, M. Trifkovic, G. K. H. Shimizu, *J. Am. Chem. Soc.* **2019**, *141*, 1045.
- [27] J. Zhao, L. Cheng, K. Liu, Z. Zhang, W. Yu, X. Yan, *Chem. Commun.* **2020**, *56*, 8031.
- [28] M. L. Schneider, J. A. Campbell, A. D. Slattery, W. M. Bloch, *Chem. Commun.* **2022**, *58*, 12122.
- [29] J. Albalad, A. Carné-Sánchez, T. Grancha, L. Hernández-López, D. Maspoch, *Chem. Commun.* **2019**, *55*, 12785.
- [30] F. Nouar, J. F. Eubank, T. Bousquet, L. Wojtas, M. J. Zaworotko, M. Eddaoudi, *J. Am. Chem. Soc.* **2008**, *130*, 1833.
- [31] S. Furukawa, N. Horike, M. Kondo, Y. Hijikata, A. Carné-Sánchez, P. Larpent, N. Louvain, S. Diring, H. Sato, R. Matsuda, R. Kawano, S. Kitagawa, *Inorg. Chem.* **2016**, *55*, 10843.
- [32] A. Carné-Sánchez, J. Albalad, T. Grancha, I. Imaz, J. Juanhuix, P. Larpent, S. Furukawa, D. Maspoch, *J. Am. Chem. Soc.* **2019**, *141*, 4094.
- [33] A. Legrand, L.-H. Liu, P. Royla, T. Aoyama, G. A. Craig, A. Carné-Sánchez, K. Urayama, J. J. Weigand, C.-H. Lin, S. Furukawa, *J. Am. Chem. Soc.* **2021**, *143*, 3562.
- [34] A. K. Mohammed, S. Usgaonkar, F. Kanheerampockil, S. Karak, A. Halder, M. Tharkar, M. Addicoat, T. G. Ajithkumar, R. Banerjee, *J. Am. Chem. Soc.* **2020**, *142*, 8252.
- [35] H. Thakkar, S. Eastman, Q. Al-Naddaf, A. A. Rownaghi, F. Rezaei, *ACS Appl. Mater. Interfaces* **2017**, *9*, 35908.
- [36] S. Takamizawa, T. Hiroki, E.-I. Nakata, K. Mochizuki, W. Mori, *Chem. Lett.* **2002**, *31*, 1208.
- [37] E. Warzecha, T. C. Berto, J. F. Berry, *Inorg. Chem.* **2015**, *54*, 8817.
- [38] E. Warzecha, T. C. Berto, C. C. Wilkinson, J. F. Berry, *J. Chem. Educ.* **2019**, *96*, 571.
- [39] E. B. Boyar, S. D. Robinson, *Coord. Chem. Rev.* **1983**, *50*, 109.
- [40] K. Sanada, H. Ube, M. Shionoya, *J. Am. Chem. Soc.* **2016**, *138*, 2945.
- [41] M. W. Schneider, I. M. Oppel, H. Ott, L. G. Lechner, H.-J. S. Hauswald, R. Stoll, M. Mastalerz, *Chem. -Eur. J.* **2012**, *18*, 836.
- [42] E. V. Perez, K. J. Balkus, J. P. Ferraris, I. H. Musselman, *J. Membr. Sci.* **2014**, *463*, 82.
- [43] T.-H. Chen, L. Wang, J. V. Trueblood, V. H. Grassian, S. M. Cohen, *J. Am. Chem. Soc.* **2016**, *138*, 9646.
- [44] P. S. Reiss, M. A. Little, V. Santolini, S. Y. Chong, T. Hasell, K. E. Jelfs, M. E. Briggs, A. I. Cooper, *Chem. -Eur. J.* **2016**, *22*, 16547.
- [45] B. Kiran, A. Kaushik, *Biochem. Eng. J.* **2008**, *38*, 47.
- [46] J. Adams, D. M. Spero, *Tetrahedron* **1991**, *47*, 1765.
- [47] V. Boquet, A. Nasrallah, A. L. Dana, E. Brunard, P. H. Di Chenna, F. J. Duran, P. Retailleau, B. Darses, M. Sircoglou, P. Dauban, *J. Am. Chem. Soc.* **2022**, *144*, 17156.
- [48] S. G. Dunning, N. K. Gupta, J. E. Reynolds, M. Sagastuy-Breña, J. G. Flores, E. Martínez-Ahumada, E. Sánchez-González, V. M. Lynch, A. Gutiérrez-Alejandro, J. Aguilar-Pliego, K.-S. Kim, I. A. Ibarra, S. M. Humphrey, *Inorg. Chem.* **2022**, *61*, 15037.
- [49] A. Carné-Sánchez, J. Martínez-Esaín, T. Rookard, C. J. Flood, J. Faruqi, K. C. Stylianou, D. Maspoch, *ACS Appl. Mater. Interfaces* **2023**, *15*, 6747.
- [50] A. López-Olvera, S. Pioquinto-García, J. Antonio Zárate, G. Díaz, E. Martínez-Ahumada, J. L. Obeso, V. Martis, D. R. Williams, H. A. Lara-García, C. Leyva, C. V. Soares, G. Maurin, I. A. Ibarra, N. E. Dávila-Guzmán, *Fuel* **2022**, *322*, 124213.
- [51] J. Albalad, L. Hernández-López, A. Carné-Sánchez, D. Maspoch, *Chem. Commun.* **2022**, *58*, 2443.