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Understanding of the multiscale self-assembly of metal-organic polyhedra towards functionally graded porous gels

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Spatial heterogeneity and gradients within porous materials are key for controlling their mechanical properties and mass/energy transport, both in biological and synthetic materials. However, it is still challenging to induce such complexity in well-defined microporous materials such as crystalline metal-organic frameworks (MOFs). Here we show a method to generate a continuous gradient of porosity over multiple length scales by taking advantage of the amorphous nature of supramolecular polymers based on metal-organic polyhedra (MOPs). First, we use time-resolved dynamic light scattering (TRDLS) to elucidate the mechanism of hierarchical self-assembly of MOPs into colloidal gels and to understand the relationship between the MOP concentrations and the architecture of the resulting colloidal networks. These features directly impact on the viscoelastic response of the gels and their mechanical strength. We then show that gradients of stiffness and porosity can be created within the gel by applying centrifugal force at the point of colloidal aggregation. These results with the creation of asymmetric and graded pore configuration in soft materials could lead to the emergence of advanced properties that are coupled to asymmetric molecule/ion transport as seen in biological systems.
Introduction

Natural organisms often have hierarchical structures spanning multiple length scales that present heterogeneities or gradients – in this way it is possible for complex functions to emerge from a relatively limited set of building blocks.\textsuperscript{1, 2} The spatial distribution of biological materials particularly affects local mechanical properties, with continuous gradients tuning the stiffness;\textsuperscript{3} for instance, the combination of rigidity and flexibility found in squid sucker ring teeth arises from a gradient in porous materials made from supramolecular networks of semi-crystalline proteins.\textsuperscript{4} Inspired by biological systems, synthetic materials with such gradients have been designated as functionally graded materials (FGM),\textsuperscript{5} and porous materials containing gradients can give unique mechanical properties and permeability, with applications in various fields from tissue engineering\textsuperscript{6} to the aerospace industry.\textsuperscript{7} In most cases, the fabrication procedures to engineer porosity have been limited to top-down approaches including microfluidics\textsuperscript{8} or 3D printing technologies;\textsuperscript{9} indeed, inducing gradients of porosity over the mesoporous and microporous regimes remains a challenge.

Recent developments in metal-organic frameworks (MOFs) or covalent-organic frameworks (COFs) allow us to finely tune the size and shape of micropores;\textsuperscript{10, 11} however, because of the crystalline nature of the materials there are only a few methods that could potentially induce gradients in the porosity. One method is to use post-synthetic ligand exchange to change the pore size by introducing longer ligands, thus creating larger pores than those found in the parent MOF structure.\textsuperscript{12} In this case the resulting materials intrinsically possess a core-shell configuration such that this method leads only to radial gradients. Another approach is to build up the MOF structure from a substrate using layer-
by-layer methods,\textsuperscript{13} which allows for hybridizing several MOFs but with sharp interfaces, rather than continuous and gradual changes of function. While there are also several synthetic strategies to use nano-sized crystalline MOFs as building blocks to obtain hierarchical superstructures over the mesoscopic and macroscopic scale, most focus on localizing the assembly of metal ions and organic linkers, meaning that there is no general strategy to generate a graded distribution of the material.\textsuperscript{14}

Very recently we used metal-organic polyhedra (MOPs), which are discrete molecules self-assembled from organic linkers and metal clusters and are recognized as potentially the smallest porous unit, to introduce a new class of microporous material. This material was synthesized by simply assembling pre-synthesized MOP molecules [Rh\textsubscript{2}(bdc-C\textsubscript{12})\textsubscript{2}]\textsubscript{12} (C\textsubscript{12}RhMOP; bdc-C\textsubscript{12} = 5-dodecoxybenzene-1,3-dicarboxylate) with the ditopic linker, 1,4-bis(imidazole-1-ylmethyl)benzene (bix) by coordination-driven supramolecular polymerization.\textsuperscript{15} Unlike crystalline metal-organic frameworks, the resulting amorphous MOP network is shaped into colloidal particles at the mesoscale, followed by connecting particles leading to the formation of macroscale colloidal gels. Such structural hierarchy is automatically generated during the self-assembly processes. Hence, we envisaged that by unveiling the multistep assembly, one could then influence specific stages of polymerization by applying external stimuli and induce functional gradients in the porous gels.

Here we show that the detailed evaluation of the hierarchical self-assembly process of MOPs is an essential step to then create continuous gradients of porosities and mechanical properties within the colloidal gels. First, we reveal the correlation of the gel formation with the resulting macroscopic architecture using time-resolved dynamic light scattering
(TRDLS) techniques and with the mechanical property of gels. The TRDLS can be used to gain insight into (i) the dynamics of the self-assembly near the gelation threshold \( t_g \); (ii) the mechanism of gelation; and (iii) the final architecture of the supramolecular gel based on \( \text{C}_{12}\text{RhMOP} \). Finally, we show that applying centrifugal force only at the onset of colloidal aggregation leads to the formation of the density gradient of colloidal networks, which induces the gradual change of mechanical properties.
Results and discussion

In order to induce gradients of porosities over the microporous and mesoporous regimes, initial design of materials is essential. As summarized in Figure 1, metal-organic materials system can be categorized into four distinct configurations from the viewpoint of gradients. As discussed above, heterostructural MOFs with sharp chemical interfaces can be created in crystalline MOF system by stepwise framework growth. On the other hand, colloidal gel materials based on MOP possess continuous networks of hierarchical colloidal structures. By controlling the mesoscale assembly of colloids, we get a new opportunity to induce nonuniform colloidal architectures, leading to graded porosities. First, we investigate the hierarchical assembling process of MOPs.

Study of the gel formation dynamics. The axial coordination sites of the dirhodium paddlewheel nodes embedded in C_{12}RhMOP are initially occupied by solvent molecules, but are labile to ligand-exchange reactions and can easily be replaced by N-donor ligands like the imidazole moieties of bix. This coordination reaction between C_{12}RhMOP and bix leads to the formation of supramolecular coordination polymers. The formation of a colloidal gel requires kinetic control of the polymerization reaction: this is achieved by isolation of a kinetically trapped cage molecule in which all of the twelve exohedral axial sites of the dirhodium clusters are coordinated by twelve bix molecules in a monodentate fashion, with a composition of (C_{12}RhMOP)(bix)_{12}. At this stage, UV-visible spectroscopy can be used to reveal the coordination of bix to C_{12}RhMOP, which induces a shift of the absorption maximum from 593 to 553 nm (Figure S2a).

Thanks to the solubility of the MOPs, their solution phase dynamics can be monitored
using spectroscopic techniques.\textsuperscript{16,17} The size of the discrete MOP is ca. 3 nm, and therefore, detectable by dynamic light scattering (DLS) measurements. These characteristics allow us to follow the hierarchical self-assembly process that occurs during gelation with in situ monitoring of the scattering elements. DLS analysis gives a particle size for the kinetically trapped MOP \((C_{12}RhMOP)(bix)_{12}\) of 3.2 ± 1.4 nm (Figure S2b). Supramolecular polymerization is induced by heating the solution of \((C_{12}RhMOP)(bix)_{12}\) at 80°C, driving the coordination equilibrium toward dissociation of bix and creating a vacant axial site, which can be occupied by a bix attached to a neighboring kinetically trapped MOP. Indeed, this reaction resulted in the formation of a gel (I) over the course of several hours. The self-assembly process was followed by TRDLS; Figure 2a shows the evolution of particle size as a function of time for an initial MOP concentration of 0.93 mM. Once polymerization begins, the system hierarchically assembles into colloidal particles as observed in the TRDLS measurements, where a steep increase in particle size occurs during stage II to reach a maximum of 30.5 ± 4.5 nm after 250 minutes. As the infinite coordination network forms and immobilizes the DMF solvent molecules, the general mobility of the particles is frozen due to topological constraints and the diffusion becomes null, rendering reliable measurement of the particle size impossible (represented as the gray region, stage III). Rather than following particle size evolution, changes in the time-averaged scattering intensity, \(\langle I \rangle_T\), can give a clearer indication of sol-gel transitions as shown in Figure 2b.\textsuperscript{18,19} Indeed, the plot of \(\langle I \rangle_T\) as a function of time shows that random fluctuations appear at 270 min, corresponding to the onset of the gelation point \(t_g\). These changes in the particle size and the \(\langle I \rangle_T\) are characteristic of the loss of ergodicity and homogeneity that occurs upon
Mechanism of gelation. Each DLS measurement recorded during the gelation has an associated time-averaged intensity correlation function (ICF), \( g^{(2)}(\tau) - 1 \), that is derived from the time dependence of the decay in scattered light by a randomly diffusing object.\(^{20,22}\) Because the diffusion will depend on the nature of the particles in solution, the analysis of ICF can give insight into the gelation mechanism of 1. Figure 2c shows the ICF at three stages of the gelation process, for \( t = 3, 270 \) and 300 min, i.e. at the beginning of the reaction, at \( t_g \), and beyond the gelation point, respectively. In the solution regime (pregel, \( 0 < t < 270 \)), the ICF can be fitted as a sum of single and stretched exponentials (equation 1):

\[
g^{(2)}(\tau) - 1 = \sigma_1^2 \left\{ A e^{-(\tau/\tau_f)} + (1 - A) e^{-\tau/\tau_s} \right\}^2
\]

where \( \sigma_1^2 \) is the initial amplitude of the ICF, \( A \) is the fraction of the fast diffusion mode, \( \beta \) is the stretched exponent, and \( \tau_f \) and \( \tau_s \) are the relaxation times of the fast and slow components, respectively.\(^{22}\) Here, \( \beta \) reflects the distribution of relaxation times of the slow mode,\(^{23}\) and \( \tau_f \) is inversely proportional to the diffusion \( D \) (see SI for further details). The two-step relaxation observed at 3 min is attributed to the combination of a fast mode due to translational diffusion of the MOP cages with a slow mode attributed to the stretched dodecoxy chains on the isophthalate linker. In order to confirm the appearance of the slow mode, the temperature dependence of ICF of the pristine \( \text{C}_{12}\text{RhMOP} \) was measured (Figure S3a). Similar to what is observed for polymer chains grafted on spherical particles,\(^{24,25}\) at room temperature the ICF of the solubilized \( \text{C}_{12}\text{RhMOP} \) in DMF shows only a monotonic
decay without the slow mode, which is attributed to the compacted dodecoxy chain (Figure S3a). On the other hand, increasing the temperature of the C\textsubscript{12}RhMOP solution to 80°C leads to the appearance of the slow relaxation mode stemmed from the collective motion of thermally agitated chains extended away from the MOP (Figure S3a). The same trend is observed for the kinetically trapped phase, (C\textsubscript{12}RhMOP)(bix)\textsubscript{12}, at 25 and 80°C (Figure S3b). This indicates that the appearance of the slow mode relies on a thermal effect.

Figure 2d shows the variation with time of $A$ and $\beta$ obtained from the fits of the ICF of the pregel sample using equation 1. At the beginning of the reaction at 80°C, the low $A$ value reflects the large contribution of the slow mode as discussed above. With continuous heating the $A$ value increases, which implies that the fast relaxation mode becomes the dominant factor. We attribute this change to the closer proximity of the MOPs caused by polymerization, which hinders the stretched alkyl chains and therefore quenches the slow mode associated with isolated MOPs. During this reaction time, the increase in particle size is only a few nanometers (growth from ~5 to ~10 nm as shown in Figure 2a) and is ascribed to nuclei formation (oligomer formation) as (C\textsubscript{12}RhMOP)(bix)\textsubscript{12} are linked to each other by the bix molecules (stage I) during supramolecular polymerization. At $t = 168$ min the value of $A$ begins to decrease as another slow diffusion mode starts to contribute, caused by the loss of mobility of the nuclei as they fuse into colloidal particles and behave as local oscillators (stage II’). As shown in Figure S4, the ICF shows that this slow mode ($t = 249$ min) is different from the one at the stage I ($t = 3$ min): the shape of exponential decay is more stretched at stage II’ compared to the two-step decay seen at stage I. In addition, the slow relaxation mode, $\tau_s$, plateaued around 150 $\mu$s during stage I and starts to increase in
stage II (Figure S5, $\tau_s = 526$ µs at the end of stage II' at $t = 249$ min). Meanwhile, $\beta$ shows a continuous increase towards unity, indicating a lower distribution of the relaxation times;\textsuperscript{23} we propose that this reflects the formation of colloidal particles of uniform size and hence similar relaxation times (stage I and II'), as supported by subsequent SEM measurements (see below). After 249 min, the colloidal particles begin to aggregate and form the premise of the gel network that will be assembled at the gelation threshold ($t_g = 270$ min). Finally, as the colloids randomly aggregate, the distribution of relaxation times of the particles increases, shown by the decrease in $\beta$ (stage II'').\textsuperscript{23} This decrease indicates the wider size distribution of colloidal aggregates.

From these data, we propose the mechanism shown in Figure 2e. First, heating pushes the coordination equilibrium between MOP and bix towards dissociation, creating a vacant site to be occupied by a free imidazole moiety of bix attached to neighboring \((C_{12}RhMOP)(bix)_{12}\) molecules. As the supramolecular polymerization progresses, the MOPs self-assemble into small nuclei, which cause the initial slow growth in particle size shown in Figure 2a (stage I). Stage II' occurs when the nuclei fuse into colloidal particles driving (i) a faster increase in the particle size, (ii) a decrease in the fraction of the fast diffusion, $A$, (Figure 2d) and (iii) a lower size-distribution of colloidal particles with reaching their maximum size. Beyond this point, attractive interactions drive the aggregation of the colloidal particles (stage II'').\textsuperscript{26, 27} On the surface of the particles many monodentate bix molecules are immobilized, which helps to keep the particles within short proximity of each other. The simultaneous removal of those bix molecules from the surface induces the exposure of reaction sites, leading to the linkage of colloidal particles by the Rh-bix
coordination bonds. Finally, the aggregates form a percolating elastic network spanning the liquid medium, yielding the supramolecular gel (stage III). The $^1$H NMR experiments on the digested gels revealed the composition of the gel to be $(\text{C}_{12}\text{RhMOP})(\text{bix})_{9.7}$, indicating that there are also monodentate bix incorporated in the gels.

*Architecture and mechanical properties of the colloidal gel.* The mechanical properties of a gel, such as its viscoelasticity, are governed by the network architecture, which is in turn defined by (i) the correlation length $\xi$, which reflects the evolution of the density of the network during the reaction time in the solution phase (Figure S1); and (ii) the degree of branching $n$, which is determined at the sol-gel transition. $\xi$ is obtained from equation 1 as it is directly related to the diffusion $D$ through the Stokes-Einstein equation (see the SI for details). The value for $\xi$ was observed to only diverge just before gelation (Figure S6). At the gelation threshold the characteristic correlation length, $\xi^*$, is expected to be a measure of the density of the network of the gel and is estimated to be $113 \pm 3$ nm. Meanwhile, the degree of branching, $n$, can be obtained from equation 2, which reflects the change of the ICF shape from a stretched exponential to a power-law function at $t_g$ due to the transition from sol to gel. Macroscopic quantities and physical properties characterizing a system follow a power law behavior when the critical point is approached in agreement with the prediction of the theory of critical phenomena. Indeed, at the gelation threshold the ICF can no longer be fitted by the equation 1, but instead by the sum of a single exponential and power-law according to equation 2:
\[ g^{(2)}(\tau) - 1 = \sigma_1^2 \left\{ A e^{(-\tau/\tau^*)} + (1 - A)(1 + \tau/\tau^*)^{(n-1)/2} \right\}^2 \]  \tag{2}

where \( \tau^* \) is the characteristic time where the power-law behavior begins and the power-law exponent \( n \) is related to the degree of branching.\textsuperscript{32} Beyond the gelation point, the appearance of nonergodicity and the decrease in the magnitude of the fluctuations of the scattering elements are reflected by the appearance of small amplitude variations in the ICF, which makes the fitting of the ICF with equation 2 more difficult (Figure 2c, 300 min).

To understand how the correlation length and the degree of branching affect the structure and mechanical properties of our system, gels with initial \( \text{C}_{12}\text{RhMOP} \) concentrations of 0.23, 0.63, 0.93, 1.37, 1.83, 2.20 and 2.40 mM (1a, 1b, 1c, 1d, 1e, 1f and 1g, respectively) were prepared. The dynamics of gel formation at each concentration were followed using TRDLS (Figure S7-S10) to extract \( \xi^* \) and \( n \) by fitting the equations described above. Increasing the MOP concentration of the gels induces an increase of the degree of branching and a decrease in the correlation length. This tendency means that the connectivity and density of the network of colloidal particles increase with increasing the concentration of MOPs (Figure 3a).

Changes in the gel architecture should affect the viscoelasticity of soft matter. To elucidate the mechanical properties of 1a-g, the fully matured gel samples were characterized by dynamic mechanical analysis using a rheometer with compression geometry to determine the resistance to elastic deformation (stiffness). Measurements of the storage and loss Young’s moduli, \( E' \) and \( E'' \), respectively, were carried out as a function of the oscillatory deformation frequency \( \omega \), at a fixed strain amplitude (1%) within the linear viscoelastic regime. At 10 rad/s, for a gel concentration of 2.40 mM, \( E' \) and \( E'' \) are 11.0 x \( 10^3 \) and 1.9 x \( 10^3 \)
Pa, respectively, while at a concentration of 0.93 mM those values are 1.4 x 10^3 and 0.1 x 10^3 Pa, respectively (Figure 3b). Over the entire frequency range, these values are essentially constant and $E'$ is approximately one order magnitude higher than $E''$. The samples are confirmed as behaving as elastic solids (Full data set shown in Figure S11; the lower concentration gels 1a and 1b were too weak to sustain the applied strain and to be measured). Over the entire frequency range, these values are essentially constant and $E'$ is approximately one order magnitude higher than $E''$. The samples are confirmed as behaving as elastic solids (Full data set shown in Figure S11; the lower concentration gels 1a and 1b were too weak to sustain the applied strain and to be measured). Over the entire frequency range, these values are essentially constant and $E'$ is approximately one order magnitude higher than $E''$. The samples are confirmed as behaving as elastic solids (Full data set shown in Figure S11; the lower concentration gels 1a and 1b were too weak to sustain the applied strain and to be measured). Over the entire frequency range, these values are essentially constant and $E'$ is approximately one order magnitude higher than $E''$. The samples are confirmed as behaving as elastic solids (Full data set shown in Figure S11; the lower concentration gels 1a and 1b were too weak to sustain the applied strain and to be measured). Over the entire frequency range, these values are essentially constant and $E'$ is approximately one order magnitude higher than $E''$. The samples are confirmed as behaving as elastic solids (Full data set shown in Figure S11; the lower concentration gels 1a and 1b were too weak to sustain the applied strain and to be measured).

Figure 3c shows the evolution of the storage modulus $E'$, at $\omega = 10$ rad/sec, as a function of the MOP concentration in the gel. As the MOP concentration increases, $E'$ increases almost exponentially indicating mechanically stronger gels. The macroscopic behavior of the gels is directly correlated to the change in the gel architecture. Higher degrees of branching and shorter correlation lengths in the colloidal network result in the formation of stiffer gels.

Aerogel structure and porosity. The gels of 1a-g were converted to the corresponding aerogel forms of 2a-g, after solvent exchange and supercritical CO$_2$ treatment, for field emission scanning electron microscopy (FESEM) and gas adsorption measurements. The FESEM images of the aerogel with the lowest (2a: 0.23 mM) and highest (2g: 2.40 mM) C$_{12}$RhMOP concentrations (Figure 3d) show distinct features corresponding to the observations made from the evolution of the correlation length and the degree of branching with the concentration. Indeed, Figure 3a shows almost linear chains of colloidal particles forming a light network structure for 2a. In contrast, the network is denser and build from more highly interconnected particles in the case of 2g. The statistical analysis of size distribution of colloidal particles in the network revealed that the concentration did not strongly influence
the size (38.3 ± 6.4 nm for 2a and 34.4 ± 4.3 nm for 2g), which correspond to the sizes derived from TRDLS measurements (Figure S12) and implies that the number of particles rather than the size of the particles increases with concentration.

$N_2$ and $CO_2$ adsorption experiments prior activation at 120°C for 12h, performed on aerogels of 2a-g at 77 K and 195 K, respectively, show that the intrinsic porosity of MOP cages is still accessible even after assembly into 3D colloidal networks (Figure S13). In addition, the maximum CO$_2$ uptake remain within the similar range of 60-72 cm$^3$/g at $P/P_0=0.95$ for all of the aerogels (Figure S13a), higher than the bulk powder of pristine C$_{12}$RhMOP (46.01 cm$^3$/g as previously reported$^{15}$). The fact that there is no significant change to the sorption properties among the samples prepared with different MOP concentrations is attributed to the similar size of colloidal particles in the network observed by FESEM. However, increasing the concentration of MOPs causes a slight decrease in the N$_2$ uptake at $P/P_0=0.95$, which is ascribed to the increased density of the aerogel networks leading to a reduction in the macroporosity (Figure S13b).

Functionally graded porous material. Understanding the correlation between the mechanism of gel formation and the resulting network structure is fundamental to then be able to increase complexity at the macroscale by, for example, creating gradients of properties within the material. It is known that colloidal gels compact under their own weight with aging due to gravity, ultimately leading to the collapse of the structure.$^{41,42}$ However, it has been shown for depletion gels that before collapse, gradients can be created by using gravitational stress to compress the gel.$^{43}$ Given that centrifugation has been used to create gradients in
polyvinylpyrrolidone-coated silica nanoparticles\textsuperscript{44} and to tune the compressive yield response of suspended particles,\textsuperscript{45} we hypothesized that it could be used to modify the mechanical properties of colloidal gels containing MOPs.

From the analysis of the TRDLS measurements, we concluded that the mechanical property of the gels is dictated during stage II’’, when the correlation length and degree of branching are determined. We then supposed it ought to be possible to increase the complexity of the system over longer length scales by perturbing this out-of-equilibrium stage. Thus, we used TRDLS to monitor the evolution of the diffusion coefficient $D$ of a gelating solution at 80°C at a concentration of 1.37 mM of $\text{C}_{12}\text{RhMOP}$. When the diffusion coefficient reached a value of 7.82 μm$^2$/s, corresponding to the maximum particle size reached (Figure S14a), the sample was centrifuged for 5 minutes at 3500 rpm at room temperature, before further heating at 80°C to continue gelation, yielding the gradient gel $3\text{d}_{\text{GG}}$. The gradient gel was sliced into two parts, $3\text{d}_{\text{GG}}$-A and $3\text{d}_{\text{GG}}$-B, the top and bottom parts, respectively, as shown in Figure 4a. The rheology measurements of these two parts were carried out, together with a control experiment, which was not centrifuged (1d) (Figure S15). $3\text{d}_{\text{GG}}$-B has an increased storage modulus (6.0 x10$^3$ Pa), compared to the control experiment (2.0 x10$^3$ Pa). In contrast, the top part $3\text{d}_{\text{GG}}$-A presents a lower storage modulus $E’$ (1.0 x10$^3$ Pa) as shown in Figure 4b. The difference in stiffness between the top and bottom parts suggests the creation of a gradient of network density in $3\text{d}_{\text{GG}}$. The FESEM images support this claim as a less dense network of colloidal particles is observed for the gel formed at the top compared to the gel formed at the bottom (Figure 4c). The same trend was observed for a sample with an initial MOP concentration of 2.40 mM for $3\text{g}_{\text{GG}}$ (Figure S14b for
TRDLS analysis, Figure 4b for the rheology experiments and Figure S16 for the FESEM images). In order to clarify the importance of the time at which the centrifugal force is applied, a control experiment was performed on a 1.37 mM \((C_{12}RhMOP)(bix)_{12}\) solution following a similar protocol as described above. The only difference is that the sample was centrifuged in the early stage of the supramolecular polymerization reaction (Stage I, t = 60 min), when colloidal particles have not yet formed. The FESEM images of the top \((3\text{neg}_GGA)\) and bottom \((3\text{neg}_GB)\) part of the aerogel samples show no difference in their network structures (Figure S17). In addition, a partial sedimentation of the sample occurred during the centrifugation step. The FESEM images show a dense material with no specific network structure (Figure S18), which highlights the importance of understanding the mechanism of hierarchical self-assembling processes as a first step towards functionally graded soft materials.

Conclusions. In this work, we have shown that the use of TRDLS gives us a better understanding of the mechanism underlying the assembly of colloidal gels formed from porous building blocks, in this case MOPs. TRDLS measurements can be used to determine features of the network and its formation, such as the correlation length between the particles, the degree of branching, and the duration of the distinct stages of polymerization. These analyses show the initial formation of nuclei from the linking of a few MOPs during stage I, which further fuse into colloidal particles with approximately the size of 35 nm during the stage II’. The duration of stage I and II’ depend on the concentration of MOPs because the supramolecular polymerization reaction is the main kinetic factor directing the formation of
colloidal particles. On the other hand, the duration of stage II”, which corresponds to the time necessary for the colloidal particles to aggregate before reaching the gelation point, is almost constant for all of the samples with different concentrations. However, stage II” affects the architecture of the colloidal network. A higher concentration of MOPs in the gel leads to an increase in the density and the degree of branching of colloidal backbone. This last stage is critical for the determination of the macroscopic behavior of the gel system such as the mechanical strength as demonstrated by the increase of stiffness with concentration. From this understanding, we demonstrated the fabrication of functionally graded porous gels using centrifugation during stage II”. The gradual change of viscoelasticity in the resulting gels, determined by rheology experiments, is explained by the density gradient of colloidal networks formed with the gravitational stress applied during centrifugation. Such functionally graded materials, which possess a property gradient within a material, in particular, asymmetric configuration of porosities, could lead to the emergence of advanced materials functions such as separation, catalysis and energy storage, which can be related to the controlled transport of molecules/ions as seen in biomimetic systems.46-48
Methods

Materials. All chemical reagents and solvents were purchased (Wako, Japan) and used without further purification. The detail protocols for ligand and crosslinker synthesis can be found elsewhere.\textsuperscript{15}

Gels characterization. The rheological measurements of the gels were made using a stress-controlled AR-G2 (TA Instruments, New Castle, DE, USA) rheometer. The measurements were conducted with a 1\% strain amplitude that was well inside the linear regime. Gelation was performed in a syringe during the night before rheological measurement in order to minimize solvent evaporation. After the reaction, the gel was removed from the syringe and viscoelastic properties directly measured.

The hydrodynamic diameter ($R_H$), collective diffusion ($D$), time-averaged autocorrelation function (ICF) and scattering intensity ($\langle I \rangle_T$) were measured using time-resolved dynamic light scattering (TRDLS) performed on a Zetasizer Nano ZS instrument (Malvern Instruments, Malvern, UK). The light source was a HeNe laser working at $\lambda = 633\text{nm}$. The observations were made at the backscattering angle $\theta = 173^\circ$. The time dependence of $R_H, D, \langle I \rangle_T$ and ICF, during gelation process of solution 2a, 2b, 2c, 2d, 2e, was evaluated at $80 \pm 0.5^\circ\text{C}$ for 360 min. Every 1 min, the data of 10 independent measurements over 12 s were averaged. Note that the data thus obtained represent time-averaged characteristics where only one position of the sample is probed. After gelation, the system becomes nonergodic and the ICF becomes dependent of the sample position. However, when using long enough data collection time, a relative spatial homogeneity just after the gelation threshold can be assumed by considering the heterogeneities to be partially
frozen-in and having still some mobility.\textsuperscript{21}

**Aerogels characterization.** The gas sorption isotherms of the aerogels were recorded on a BELSORP-mini volumetric adsorption instrument from BEL Japan Inc.. Aerogels samples were observed using a field-emission scanning electron microscope (FE-SEM) with a JEOL Model JSM-7001F4 system operating at 10 kV and 5 mA current. \textsuperscript{1}H-NMR spectra were recorded on a Bruker Biospin DRX-600 (600 MHz) spectrometer. For \textsuperscript{1}H-NMR analysis, 5-10 mg of aerogel samples were digested in a mixture of DMSO-d\textsubscript{6} (750 µl) and DCl (50 µl). The mixture was heated at 100 °C overnight to obtain a yellow solution.

**Synthesis of C\textsubscript{12}RhMOP.** The cuboctahedral MOP cage was synthesized as reported previously.\textsuperscript{15,49}

**Synthesis of the kinetically trapped phase, (C\textsubscript{12}RhMOP)(bix)\textsubscript{12}.** The metastable state of the MOP was synthesized by solubilizing C\textsubscript{12}RhMOP in 1.5 mL of DMF at 80°C. The solution was added to 12 mol. eq. of 1,4-bis(imidazole-1-ylmethyl)benzene (bix) in 1.5 mL at 80°C followed by a rapid cooling to room temperature which formed isolated MOP molecules with the composition of (C\textsubscript{12}RhMOP)(bix)\textsubscript{12}. Seven solutions with different MOP concentration were prepared ((C\textsubscript{12}RhMOP)(bix)\textsubscript{12}: 0.23/ 0.67/ 0.93/ 1.37/ 1.83/ 2.20/ 2.40 mM).

**Synthesis of supramolecular colloidal gel (1).** The gel was formed by putting 3 mL of the kinetically trapped phase, (C\textsubscript{12}RhMOP)(bix)\textsubscript{12}, into a plastic syringe from which the top part was cut in order to remove easily the gel for rheology measurement. The solution was kept in the oven at 80°C for 12h to give 1, a supramolecular colloidal gel. Seven gels were prepared using one of the solutions with a MOP “gelator” concentration of 0.23, 0.67, 0.93,
1.37, 1.83, 2.20 and 2.40 mM to give 1a, 1b, 1c, 1d, 1e, 1f and 1g respectively.

Aerogel preparation (2). The gel samples were exchanged with fresh acetone for 3 days. The supercritical CO\textsubscript{2} drying process of the gels, to form the aerogels, was carried out on a SCLEAD-2BD autoclave (KISCO) using super-critical CO\textsubscript{2} at 14 MPa and 50 °C to give 2a, 2b, 2c, 2d, 2e, 2f and 2g.

Gradient gel preparation (3). TRDLS was used to monitor the evolution of the diffusion coefficient $D$ of a gelating solution at 80°C at a concentration of 2.40 mM and 1.37 mM of (C\textsubscript{12}RhMOP)(bix)\textsubscript{12}. When the diffusion coefficient reached a value of 7.8 µm\textsuperscript{2}/s, corresponding to the maximum particle size reached, the sample was centrifuged for 5 minutes at 3500 rpm at room temperature, and then heating at 80°C was continued for gelation to proceed, yielding the gradient gel 3g\textsubscript{GG} and 3d\textsubscript{GG}, respectively.

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Author contributions
A. L and S. F. conceived and designed the experiments. A. L. and G. A. C. performed all synthetic and characterization experiments. A. L., S. F., S. M. and K. U. performed and analyzed TRDLS experiments. A. L. and M. B. performed sorption experiments. A. L., S. M. and K. U. performed rheological measurements. A. L., G. A. C. and S. F. analyzed the data and 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.
**Figures:**

![Diagram showing structural complexity of porous materials](image)

**Figure 1. Illustration of structural complexity of porous materials.** Crystalline MOF materials provide uniform pore distribution throughout the entire material due to their crystallinity. Layer-by-layer growth methods allow for the fabrication of heterostructure of MOFs with sharp interfaces. On the other hand, amorphous porous materials of polymeric MOP gels intrinsically generate more complex hierarchical structures, thanks to the formation of colloidal particles based on MOP polymerization, followed by linking particles to form colloidal architectures. This study further induces the gradient of distribution of MOP colloidal particles to synthesize functionally graded porous materials.
Figure 2. Time-resolved dynamic light scattering experiment (TR-DLS) to elucidate the mechanism of hierarchical self-assembly of MOPs into colloidal gels. TRDLS measurement during the supramolecular polymerization of $(C_{12}RhMOP)(bix)_{12}$ at 80°C at a concentration of 0.93 mM, showing (a) the particle size evolution and (b) the time-averaged scattering intensity. (c) Log-log plot of the intensity-time correlation function (ICF) for different reaction times during the supramolecular polymerization reaction at a concentration of 0.93 mM. The solid lines represent the fitted ICF using a stretched exponential and power-law function for the solution state (at 3 min) and gel threshold (270 min) respectively. The
ICF, beyond the gel point, is shown in cyan (300 min). (d) Variation of the fraction of the fast diffusion mode ($A$) and stretched exponent ($\beta$) as a function of the reaction time. The gelation threshold is represented by the blue dotted line. The gray region highlights the effect of the frozen mobility of particles due to gel formation on the DLS response. The fraction of the fast diffusion mode ($A$) and stretched exponent ($\beta$) are fitted parameters obtained from (d). (e) Proposed mechanism for the supramolecular polymerization of the kinetically trapped phase into a colloidal gel.
Figure 3. Relationship between the MOP concentrations and the resulting colloidal network architectures on the viscoelastic response of the gels and its mechanical strength. Effect of the concentration of MOPs on (a) the characteristic correlation length ($\xi^*$) and degree of branching ($n$) for the gels 1a-g obtained from the fitted ICF using a stretched exponential and power-law functions. (b) Storage and loss modulus, $E'$ and $E''$ respectively, for gels prepared with concentration of MOP of 2.40 (1g, black) and 0.93 mM (1c, green). The measurements were performed at a fixed strain amplitude (1%) within the linear viscoelastic regime. The lower concentration gels 1a and 1b were too weak to sustain the applied strain and to be measured. (c) Effect of the MOP concentration on the storage modulus ($E'$) of the gels at 10 rad/sec. (d) FE-SEM images of the aerogels 2a (0.23 mM) and
2g (2.40 mM). The right part images are magnification of the corresponding white square. The scale bars for lower and highest magnification are 1 µm and 100 nm, respectively.
Figure 4. Creation of a gradients of stiffness and porosity within the gel by applying centrifugal force at the specific moment of colloidal aggregation. (a) Gelation of the
(C\textsubscript{12}RhMOP)(bix\textsubscript{12} solution(1.37 mM) prepared with applying centrifugal forces during the beginning of stage II’” corresponding to the onset of colloidal aggregation. The sample was centrifuged for 5 minutes at 3500 rpm at room temperature, and then heating at 80°C was continued for gelation to proceed, yielding the gradient gel 3d\textsubscript{GG}. The sample was cut into two equal parts for further dynamic mechanical analysis. The same gelation procedure was performed without centrifugation, which serve as control experiment (1d). (b) Histogram of the storage modulus E’ at 10 rad / sec of the bottom (3g\textsubscript{GG}-B, black and 3d\textsubscript{GG}-B, black stripes) and top part (3g\textsubscript{GG}-B, blue and 3d\textsubscript{GG}-B, blue stripes) of 2.40 and 1.37 mM MOP-based gel prepared using centrifugation method to create a concentration gradient. As comparison the same gel was prepared without applying centrifugation as reference (red). (c) FE-SEM images of the top (3d\textsubscript{GG}-A) and bottom part (3d\textsubscript{GG}-B) of 3d\textsubscript{GG} (1.37mM) MOP-based aerogels prepared using centrifugation method. The scale bars for lower and highest magnification are 1 µm and 100 nm, respectively.
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Supporting Information

Understanding the formation mechanism of colloidal gels based on metal-organic polyhedra towards functionally gradient porous gels

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Theory Background of dynamic light scattering (DLS)

In DLS, time-intensity correlation function (ICF) allow to extract time dependence of the diffusion of scattering element in the presence of noise. The function represents, the delay, in μs, necessary for the diffusion speed of scattering particles to decay after interacting with incident light. In the solution state the ICF is best described by the sum of a single and stretched exponential functions:

\[
g^{(2)}(\tau) - 1 = \sigma_1^2 \left\{ A e^{-\tau/\tau_f} + (1 - A) e^{-\tau/\tau_s} \right\}^2
\]

\[
\sigma_1^2 \text{ is the initial amplitude of ICF with value close to the instrumental coherence factor (usually } \approx 1\text{). During the gelation process, the system tends towards nonergodicity resulting in a decrease in } \sigma_1^2. A \text{ (}0 < A < 1\text{) is the fraction of the collective diffusion mode, } \beta \text{ (}0 < \beta < 1\text{) is the stretched exponent and reflects the distribution of relaxation times of the slow mode. } \tau_f \text{ and } \tau_s \text{ are the characteristic relaxation times of the fast and slow modes respectively. } \tau_f \text{ is also called the gel mode and is related to the collective diffusion of local motions, } D, \text{ by:}
\]

\[
\tau_f = 1/(q^2 D)
\]

with q the wave vector defined as:

\[
q = \frac{4\pi r_D}{\lambda} \sin(\theta/2)
\]

where \( r_D \) is the refractive solvent index, \( \lambda \) is the incident wavelength and \( \theta \) is the angle at which the detector is placed. Here, the detector position is fixed at 173° (backscattering mode) to reduce multiple scattering.

The collective diffusion \( D \) is also related to the correlation length through the Stokes-Einstein equation:

\[
\xi = \frac{k_B T}{6\pi\eta D}
\]

with \( k_B \) the Boltzmann constant, \( T \) the temperature and \( \eta \) the viscosity of the solvent. In polymer gel system, the correlation length corresponds to the distance between two cross-link sites (mesh size depicted in Figure S1) and is equivalent in our colloidal gel system to the distance between two branching units.

During the supramolecular polymerization reaction, the particles grow into colloids and their aggregation hindered their free diffusion. Hence, the characteristic times for the decays to start are shifted to higher delay time. At gelation threshold, the ICF became best described by a single exponential and power law functions:

\[
g^{(2)}(\tau) - 1 = \sigma_1^2 \left\{ A e^{-\tau/\tau_f} + (1 - A)(1 + \tau/\tau^*)^{(n-1)/2} \right\}^2
\]

That change of shape of the ICF is a characteristic feature of gels and it is due to the apparition of connectivity divergence as colloids form domains during the dynamic formation of the gel network.
Figure S1. Schematic representation of the correlation length in case of low (left) and high (right) branching colloidal particles network
Figure S2. (a) UV-visible spectra of \( \text{C}_{12}\text{RhMOP} \) (black) and \( \text{(C}_{12}\text{RhMOP})(\text{bix})_{12} \) (red). (b) DLS measure of \( \text{C}_{12}\text{RhMOP} \) (black) and \( \text{(C}_{12}\text{RhMOP})(\text{bix})_{12} \) particle sizes.
Figure S3. Temperature effect on the ICF decay for (a) 0.93 mM \((\text{C}_{12}\text{RhMOP})\) in DMF from 30°C to 80°C and (b) 0.93 mM \((\text{C}_{12}\text{RhMOP})(\text{bix})_{12}\) in DMF at 25°C and 80°C at the beginning of the reaction and after 6 min. Both show the appearance of a 2\text{nd} relaxation time at higher temperature. The one of \((\text{C}_{12}\text{RhMOP})(\text{bix})_{12}\) decrease after 6 min of reaction at 80°C. The insert scheme is the possible mechanism explaining the variation observed in the ICF, which is the thermal agitation of the extended C12 alkyl chains of the MOP’s linkers (in red).
Figure S4. Variation of ICF as function of characteristic reaction time representative of transition between the different stages of the gelation process.
Figure S5. Variation of the correlation length of 1 as function of time during the supramolecular reaction at 80°C. The data were obtained from the fit of the ICF using equation 1 and using equation 2, 3 and 4.
Figure S6. Variation of the correlation length of 1 as function of time during the supramolecular reaction at 80°C. The data were obtained from the fit of the ICF using equation 1 and using equation 2, 3 and 4.
Figure S7. TRDLS measurement during the supramolecular polymerization of \((\text{C}_12\text{RhMOP})(\text{bix})_{12}\) at 80°C at a concentration of 0.93 mM, showing the particle size evolution and the time-averaged scattering intensity as a function of time. System with different concentrations were prepared, (a): 0.23 mM, (b) 0.63 mM, (c) 1.37mM, (d) 1.83 mM, (e) 2.20mM, (f) 2.40 mM. The gelation threshold is represented by the blue dotted line. The gray region highlights the effect of the frozen mobility of particles due to gel formation on the DLS response.
Figure S8. Variation of the fraction of fast diffusion mode (A) and stretched exponent ($\beta$) as a function of the reaction time for samples prepared with concentration of MOPs of (a) 0.23 mM, (b) 0.63 mM, (c) 1.37 mM, (d) 1.83 mM, (e) 2.20 mM and (f) 2.40 mM.
Figure S9. Evolution of the fast ($\tau_f$) and slow ($\tau_s$) relaxation time modes as a function of the reaction time for samples prepared with concentration of MOPs of (a) 0.23 mM, (b) 0.63 mM, (c) 1.37 mM, (d) 1.83 mM, (e) 2.20 mM and (f) 2.40 mM.
Figure S10. Variation of the correlation length of 1 as function of the supramolecular reaction time at 80°C for different concentration of MOPs. For clarity, samples prepared with concentration of MOPs of 0.23, 0.67 and 0.93 mM are shown in (a) while concentration of MOPS of 0.93, 1.37, 1.83, 2.20 and 2.40 mM in (b). The data were obtained from the fit of the ICF using equation 1 and using equation 2, 3 and 4.
Figure S11. Storage and loss modulus, $E'$ (close symbol) and $E''$ (open symbol) respectively, for gels prepared with concentration of MOP of 2.40 (black), 2.20 (blue), 1.83 (pink), 1.37 (orange) and 0.93 (green) mM. The measurements were performed at a fixed strain amplitude (1%) within the linear viscoelastic regime.
Figure S12. (a) FE-SEM images and (b) the corresponding size distribution of colloid particles determined for the aerogel 2a-g.
Figure S13. (a) CO$_2$ uptake (195K) and (b) N$_2$ uptake (77K) for aerogel samples prepared with concentration of MOP of 0.23 mM (black), 1.37 mM (dark cyan) and 2.40 mM (red).
Figure S14. TRDLS measurement during the supramolecular polymerization of $(C_{12}RhMOP)(bix)_{12}$ at 80°C at a concentration of (a) 1.37 mM and (b) 2.40 mM, showing the particle size evolution and the diffusion coefficient as a function of the reaction time. When the diffusion coefficient reached a value of 7.82 μm$^2$/s (green region), corresponding to the formation of the colloidal particles, the sample was centrifuged for 5 minutes at 3500 rpm, and then heating was continued for gelation to proceed, yielding the gradient gels $3_{GG}$. 
Figure S15. Storage moduli $E'$ of the bottom ($3g_{GG}$-B, black circle and $3d_{GG}$-B, black triangle) and top part ($3g_{GG}$-B, blue circle and $3d_{GG}$-B, blue triangle) of 2.40 and 1.37 mM MOP-based gel prepared using centrifugation method to create a concentration gradient. As comparison the same gel was prepared without applying centrifugation as reference (2.40 mM, red circle and 1.37 mM, red triangle). The measurements were performed at a fixed strain amplitude (1%) within the linear viscoelastic regime.
Figure S16. FE-SEM images of the top (3g_{GG}-A) and bottom part (3g_{GG}-B) of 3d_{GG} (1.37 mM) MOP-based aerogels prepared using centrifugation method. The scale bars for lower and highest magnification are 1 μm and 100 nm, respectively.
**Figure S17.** FE-SEM images of the $3\text{neg}_{GG}$ (1.37 mM) MOP-based aerogels prepared using centrifugation method during the early stage of the supramolecular polymerization (Stage I, $t = 60$ min) showing the top ($3\text{neg}_{GG}$-A) and the bottom ($3\text{neg}_{GG}$-B) part of the sample. The right part images are magnification of the corresponding white square. The scale bars for lower and highest magnification are 1 μm and 100 nm, respectively.
Figure S18. FE-SEM images of the sedimentation part of 3neg_{66} (1.37 mM) MOP-based aerogels formed when centrifugation method is applied during the early stage of the supramolecular polymerization (Stage I, t = 60 min) showing different magnification of the sample. The scale bars of (a)-(b) and (c)-(d) are 1 μm and 100 nm, respectively.
