Porous Organic Cage Thin Films and Molecular-Sieving Membranes

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Completely disordered packing of cage molecules, as visualized in Figure 1d, is also feasible by controlling the processing of cage molecules, for example by rapid removal of the guest solvent molecules. For example, we used a freeze drying approach to evaporate solvents and thus to render the CC3 in an amorphous state. The disordered packing of CC3 cage molecules still leads to interconnected microporosity that includes both intrinsic intracage cavities and extrinsic intercage voids (Figure 1f). These amorphous cage materials showed a high level of porosity and tunable gas selectivity. The Brunauer–Emmett–Teller (BET) surface area of amorphous CC3 reaches 898 m$^2$ g$^{-1}$, which is twice the surface area of highly crystalline CC3. Amorphous POCs can also be formed from cage molecules with different geometries and vertex groups. For example, we have demonstrated amorphous scrambled porous organic cage molecules (ASPOC), synthesized using a mixture of different diamines, which leads to a distribution of cage species that cannot pack efficiently, and therefore form amorphous solids rather than crystalline materials. These molecules are also much more soluble in organic solvents, and can be used to fabricate “porous liquids,” or used as a stabilizer for the dispersion of metal nanoparticle catalysts in solution.

We demonstrate here the solution-processing of porous organic cage molecules into thin films, showing potential for these materials as membranes for molecular separations. To the best of our knowledge, this is the first time that POCs are fabricated into continuous and defect-free microporous thin-film membranes with molecular sieving properties, without any other matrix-forming material, such as a polymer. The unique structure of POCs and their solid-state molecular packing differentiates our work from the known literature on other membrane materials such as zeolites, polymers, MOFs, carbon molecular sieves, graphene, glass, metals, ceramics, and liquids. Hence, these results open up a new field of research on the structure and properties of porous organic cage thin films and their potential technological applications.

We fabricated thin films of POC molecules on various substrates by solution processing techniques, for example, by spin coating. Spin coating is a common and established solution-processing method to coat uniform thin films from a variety of solutions on flat substrates. Compared to other solution-processing techniques, such as dip-coating and spray coating, spin-coating is the preferred method to deposit thin and uniform films on flat substrates. We start from cage molecular solids (Figure 1g) and dissolve them in organic solvents (Figure 1h),
then coat these cage molecules on various substrates. The dense packed cage film coated on the glass is transparent (Figure 1i), but can be visually observed by staining with iodine,[22] which immediately changes the film to a yellow-brown color upon adsorption. The spin coating process involves the equilibrium between the centrifugal forces generated at a high spinning speed and the viscous forces owing to the enhanced viscosity from solvent evaporation. In the case of small cage molecules with sizes down to 2 nm, noncovalent intermolecular forces, such as van der Waals forces, are dominant in attracting the molecules together to form continuous films. Therefore, as visualized in Figure 1j,k, the spin-coating of cage molecules on both nonporous substrates and porous substrates leads to the formation of thin films, where the cage molecules pack in a disordered state because of the rapid solvent removal. The microporosity of cage thin films allows rapid transport and diffusion of molecules; hence, cage thin films might be used as building blocks for functional materials and devices, such as molecular sensors and separation membranes.

To demonstrate the generality and transferability of this solution-processing approach, five different types of POCs were used to prepare thin films and membranes, including a representative crystalline cage CC3,[18] a related imine-cage, CC13,[20] an amorphous scrambled porous organic cage mixture (ASPOC) synthesized by dynamic scrambling covalent reactions,[20] a reduced amine cage (RCC3),[23] and a “tied” cage (FT-RCC3) by reaction of amine groups in RCC3 with carboxyls such as formaldehyde[23] that was shown previously to have exceptional stability to water, acids, and bases. More details of synthetic chemistry are given in Figure S1 in the Supporting Information. The morphology of three representative POCs, ASPOC, CC3, and FT-RCC3, are shown in Figure 2a–c. In the solid state, ASPOC shows a poorly ordered morphology, while CC3, CC13, and FT-RCC3 have a regular octahedral crystal morphology (Figure S2, Supporting Information). X-ray diffraction (XRD) patterns of the cage solids confirmed their crystalline structure (Figure S3, Supporting Information). FTIR spectra for cage films show a strong imine stretch at 1640 cm\(^{-1}\) (Figure S4, Supporting Information) for the imine cages.

Cage molecules were dissolved in volatile solvents, such as chloroform (boiling point, 61.15 °C) or dichloromethane (39.6 °C), to a predetermined concentration and purified by passing through PTFE filters (0.2 μm). In this study, the cage solution was dropped on to the substrate surface, with the liquid covering the whole surface up to the edges. The substrate was then accelerated to a very high angular velocity (>500–4000 rpm), resulting in a thin uniform layer coated on the surface. Continuous cage films were formed with no observable pinholes or defects, as shown in Figure 2d.f. Occasionally, we observed by SEM buckling and exfoliation from the substrate for ASPOC thin films (Figure 2e), which is likely due to stress upon fracture in liquid nitrogen. The buckling indicates that cage thin films are, to some extent, mechanically flexible. We further confirmed that similar continuous films could be fabricated from other cage molecules, including the CC13 and RCC3 cages (Figure S5, Supporting Information). These cage thin films are amorphous, whether they are spin-coated on silicon wafer or low-background silicon substrate, as confirmed by XRD (Figure 2m; Figure S6, Supporting Information).

The structure of cage thin films can be easily tuned by controlling the speed of spinning and the concentration of cage molecules in solution. For example, by varying the weight concentration of ASPOC molecules in chloroform from 1 to 5 wt%, we were able to change the thickness of the spin-cast film from 100 nm to nearly a micrometer (Figure S7, Supporting Information). The porosity of cage films can be tuned from microporous to hierarchically porous by changing the composition of cage solutions, for example, use of co-solvents of dichloromethane (DCM) and methanol at different fractions. For example, CC3 cage molecules were dissolved in a mixture of DCM and methanol, with the weight percentage of methanol in the mixture varying from 2 wt% to 40 wt%. In this case, the addition of a small amount of methanol into the solvent significantly enhanced the solubility of the CC3. The resulting spin-coated CC3 films show a significantly different morphology. As shown in Figure 2f–g and Figure S8 (Supporting Information), cage films spin-coated from co-solvent with low fraction of methanol (2–10 wt%) are densely packed and essentially microporous with no observable mesopores or macropores. By contrast, cage solutions containing excess methanol (>10 wt%) generate hierarchically porous films with interconnected nanoparticles with sizes at ~100 nm (Figure 2g), owing to the phase separation induced by solvent evaporation. XRD patterns confirmed that both dense and porous films are amorphous (Figure S8, Supporting Information). Similar phase separation phenomenon occurred for RCC3 cages and consequently macropores were formed in the films when the cage molecules were spin-coated at low speed (1000 rpm) (Figure S9, Supporting Information).

For the more rigid, tied cage, FT-RCC3, hierarchically porous thin films can also be formed. As the solubility of FT-RCC3 in chloroform or DCM was very low, a small amount of methanol was again added to the solvent to enhance the solubility of cage molecules (up to 4 wt%) so that thicker films could be prepared, but hierarchically porous films were then obtained (Figure 2h and Figure S10 Supporting Information). In this case, the weak peaks in the XRD pattern indicate the presence of small nanocrystals. These hierarchically porous cage thin films may be useful in a range of applications, such as templates for nanostructured films, or supports for catalysis.

These high-quality cage thin films have potential for absorption-based sensing based on optics or absorption spectroscopy.[43] Cage molecules were spin-coated on thin quartz glass substrates to form thin films with a thickness of 100 nm. Subsequently, the cage thin films were exposed to iodine solids in a glass vial. Some of the sublimed iodine was adsorbed in the cage thin films, as evidenced by a dark brown coloration in this film (Figure 1i). We tracked the UV–vis absorbance as a function of adsorption time. As shown in Figure S11 in the Supporting Information, the UV–vis spectra showed a strong absorbance peak at 400 nm upon exposure to iodine. The increase of absorbance corresponds to the amount of iodine molecules adsorbed in the cage films. The UV irradiation may induce halogenation reactions of iodine with POC molecules, and hence desorption of the iodine molecules is relatively slow and not complete even after 24 h, indicating that it is possible to utilize similar reaction strategy to modify the cage thin films.
Figure 2. Morphology and structure of POC thin films coated on nonporous and porous substrates. a) ASPOC powder. b) CC3 crystals. c) FT-RCC3 crystals. d) ASPOC thin film spin-coated from ASPOC solution in chloroform (4 wt%, weight percentage of cages in solvent). e) Buckling of ASPOC thin films occasionally occurred upon exposure to fracture in liquid nitrogen. f) CC3 thin film, spin-coated from CC3 cage solution (4 wt%, weight percentage of cages in solvent) in a mixture of co-solvent of MeOH (2 wt%)/DCM (98 wt%). g) CC3 film, spin-coated from CC3 cage solution (4 wt% in solvent) in a mixture of co-solvent of MeOH (15 wt%)/DCM (85 wt%). h) FT-RCC3 film, spin-coated from FT-RCC3 cage solution (4 wt% in solvent) in a mixture of co-solvent of MeOH (2 wt%)/DCM (98 wt%). i) Cross-sectional SEM of porous anodized aluminum oxide (AAO) support. j) Cross-sectional SEM of ASPOC cages coated on Al2O3 support. ASPOC cage solution (4 wt% in chloroform) was spin-coated at 2000 rpm for 1 min. k) Cross-sectional SEM of 50 nm thick CC3 thin film coated on Al2O3 support. CC3 cage solution (1 wt% in solvent) in a co-solvent of MeOH (2 wt%)/DCM (98 wt%) was spin-coated at 2000 rpm for 1 min. l) Cross-sectional SEM of 300 nm thick CC3 thin film coated on alumina support. CC3 cage solution (4 wt%) in a co-solvent of MeOH (2 wt%)/DCM (98 wt%) was spin-coated on alumina support at 2000 rpm for 1 min. m) X-ray diffraction of POC thin films coated on low-background silicon substrates.
We further fabricated POC thin-film composite (TFC) membranes by spin coating cage molecules on porous anodized aluminum oxide (AAO) filter discs. The films in this work were spin-coated directly on the membrane supports without any intermediate coating or sacrificial layer. The size of cage molecules are so small that they can potentially penetrate through the surface layer of AAO support (pore size of 20 nm) and enter into the larger nanochannels (pore size of 200 nm) (Figure 2i). Pinhole and defects lead to low selectivity (close to Knudsen diffusion selectivity) and a significant increase of permeance if a continuous film is not formed. Nevertheless, defect-free films could be prepared by simply spin coating cage solutions on the surface of the AAO substrates, as shown in Figure 2j,k, and Figure S12 in the Supporting Information. Some cage molecules seem to be embedded in the 20 nm nanochannels in the AAO support, but they do form a continuous and defect-free skin layer. We performed XRD analyses of these thin films and confirmed that they are amorphous (Figure S13, Supporting Information). The success rate of fabricating defect-free films was significantly enhanced by using more concentrated cage solutions (up to 4 wt%) (Figure 2l). Such higher concentration increases the viscosity of the cage solution and consequently results in thicker films while the penetration of the cage solution into the interior of the support was also limited during the spinning process. In some cases, it is relatively difficult to determine the accurate thickness for the thin-film composite membranes because of the penetration into the large channels in the alumina support that occurred for some cage molecules, including ASPOC, CC13, and RCC3. Interestingly, the degree of penetration of cage molecules into the substrates seems to be related to the structural flexibility of the cage molecules. For the most flexible RCC3 cages, the material cannot form a continuous film at the surface (Figure S14, Supporting Information). In contrast, the more rigid FT-RCC3 cages showed phase separation behavior, as also observed on nonporous substrates (Figure S14, Supporting Information). In addition, polymer thin films were also prepared from a low-free-volume polyimide (Matrimid 5218) and a microporous PIM-1 polymer (SEM images are given in Figure S15, Supporting Information), as good control for measurements of gas transport properties.

Gas transport in glassy polymeric materials follows the solution-diffusion model, where the gas molecules are adsorbed in the free volume elements and diffuse through the membrane. In the case of microporous cage thin films, gas transport can also be described by the solution-diffusion model. To have a better understanding of the gas solubility and diffusivity and their relationships with the structure, we measured gas sorption properties of cage solids using various techniques. As shown in Figure 3a, N₂ sorption isotherms of ASPOC and amorphous CC3 confirmed the presence of microporosity in these disordered solids. We also measured gas sorption isotherms at room temperature (Figure 3b) and derived the gas
solubility at 1 bar (Figure 3c). Detailed isotherms are given in Figure S16 (Supporting Information). The gas solubility follows the sequence of CO₂ > CH₄ > N₂ > H₂, corresponding well to the critical temperature of gas molecules. These values of gas solubility in cage molecules are comparable to those in PIM-1 polymer. Particularly, the high CO₂ sorption capacity in cage solids reflects the favorable solubility in micropores or free volume elements and intermolecular interactions between CO₂ gas molecules and cages.

We further demonstrated that cage thin-film composite membranes show molecular-sieving properties in terms of high permeance and molecular selectivity. Single gas transport properties of cage membranes were measured at 295 K with industrially important gas molecules with different kinetic diameters, including He (2.65 Å), H₂ (2.89 Å), CO₂ (3.3 Å), Ar (3.40 Å), O₂ (3.46 Å), N₂ (3.64 Å), and CH₄ (3.82 Å), using a time-lag apparatus. First, we proved the high gas permeance through the AAO support alone (Figure S17, Supporting Information), for example, H₂ and CO₂ permeance are 1.7 × 10⁻⁵ mol m⁻² s⁻¹ Pa⁻¹ and 4 × 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹, respectively. Therefore, the gas permeation resistance of the AAO support can be neglected in TFC membranes. In addition, we also measured the gas transport properties of polymer thin-film membranes spin-cast from a dense polyimide (Matrimid 5218) and a microporous PIM-1 polymer. For example, PIM-1 thin film gives an initial CO₂ permeability of 2960 Barrer while Matrimid 5218 gives a CO₂ permeability of about 10 Barrer. These gas transport properties are very close to those measured with thick polymer films in the same apparatus. Therefore, these polymer thin films serve as reliable controls for comparing the gas transport properties of cage thin films.

Gas permeation data for three representative cage thin-film membranes, CC₃, ASPOC, and CC₁₃, are shown in Figure 3d. The data reported here are the values measured at the point when the selectivity became stable. More detailed data are shown in Figure S18 and Table S1 in the Supporting Information. For a typical CC₃ membrane spin-coated with 1 wt% cage solution in a co-solvent of DCM and methanol (methanol concentration of 2 wt%) at 2000 rpm, the gas permeances follow the order of H₂ > CO₂ > O₂ > CH₄ > N₂. The initial permeance of H₂ is as high as 1.53 × 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹, with high H₂/N₂ selectivity of 30, and a H₂/CH₄ selectivity close to 20. The initial CO₂ permeance is up to 9.2 × 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ with CO₂/N₂ selectivity of ≈19 and a CO₂/CH₄ selectivity of ≈10. The measured gas permeances of CC₃ thin films are 10–20 times higher than that for reported MOF membranes (10–30 μm), or zeolite membranes (see Table S1 in the Supporting Information), presumably because our cage films are much thinner (down to 50 nm). In the case of ASPOC films, gas permeances are relatively lower owing to penetration of the cages into the substrates, even though a concentrated solution (4 wt% in chloroform) was used. CC₁₃, which has two methyl groups per vertex, shows much lower permeance, but still shows molecular sieving performance. For ASPOC, the ideal selectivity of CO₂/N₂ is surprisingly high (25–30), which is in agreement with its favorable adsorption of CO₂ (1.65 mmol g⁻¹) and high solubility selectivity of CO₂/N₂ (≈6.5). Such behavior is similar to that observed in glassy polymers, such as polyimides and PIMs.

We then calculated the gas permeability from permeance multiplied by thickness (P = J × L). We quantified the average penetration depth as observed in SEM and assumed this depth to be the effective thickness of the membrane. We then estimated the apparent permeability. We further compare the gas transport properties in the upper bound plot of selectivity versus permeability. A typical H₂/N₂ gas pair is shown in Figure 4. For a representative 50 nm-thick CC₃ membrane, the initial H₂ permeability is about 226 Barrer, while CC₁₃ cages show H₂ permeability of 48 Barrer. Certainly, these cage thin films have relatively low permeability compared to PIM-1 polymer thin films (H₂ permeability close to 2000–3000 Barrer), but they are still much more permeable than conventional low-free-volume polymers (e.g., H₂ permeability of Matrimid at about 20–30 Barrer). Similar results were found for other gas pairs as shown in Figure S18 in the Supporting Information. Based on the gas solubility and permeability, we derived the diffusion coefficients for various gas molecules (D = P/S). The gas diffusivities can be correlated with effective molecular size, as plotted in Figure 3f. For 24 h aged ASPOC, H₂ diffusivity was as high as 9.5 × 10⁻⁷ cm² s⁻¹, while N₂ and CH₄ diffusivities were 1.1 × 10⁻⁸ cm² s⁻¹ and 6.1 × 10⁻⁹ cm² s⁻¹, respectively. The cage thin films show high diffusivity selectivity for gas pairs H₂/CO₂ (≈20), H₂/N₂ (≈87), and H₂/CH₄ (≈155). Similar results were found for amorphous CC₃ thin films. These analyses confirm the molecular sieving properties of cage thin films, although their diffusion coefficients are relatively lower than those of rigid polymer networks.

Extensive studies on physical aging of glassy polymer thin films have shown that minor decreases of free volume with time result in significant loss of permeability. Here, we observed significant loss in gas permeability for all cage thin.
films (Figure S18 and S19, Supporting Information). Cages with different structures show varied aging behavior. As shown in Figure 4, ASPOC cages give high H2 permeability of 643 Barrer but with low selectivity of H2/N2 (5.8 initially). The permeability quickly decreased after aging for 24 h while selectivity increased for all gas pairs, e.g., H2 permeability decreased to 187 Barrer, while the H2/N2 selectivity unexpectedly increased to above 30. Similarly, CO2 permeability dropped to 160 Barrer with CO2/CH4 selectivity increasing up to 17. Afterward, the ideal gas selectivity maintained relatively stable but the gas permeability continued to decrease over 30 d. For thinner CC3 (~50 nm), the ideal selectivity was relatively stable, but the permeability also decreased significantly. In the case of thicker CC3 film (~300 nm), both permeability and selectivity showed immediate loss. These films remained amorphous even after aging for several months.

The complex aging phenomena of cage thin films are not yet fully understood. In this study, a very thin layer of cage molecules were coated on the alumina to form thin-film composite (TFC) membranes, instead of free-standing cage membranes. Therefore, unlike free-standing polymer films,[15] N2 sorption and surface areas of cage TFC membranes before and after use were not easily measured. While the permeability in cage membranes decreased significantly (e.g., ten times lower in 24 h for ASPOC membrane), gas sorption capacities of cage solids remained at high levels after being evacuated under vacuum for 24 h. Since permeability is a product of solubility and diffusivity, the loss of gas permeability may be attributed to decrease in diffusivity. From the materials perspective, these amorphous cage thin films are in metastable states that are kinetically trapped during the spin coating, which leads to an inhomogeneous density within the material. The lower density regions are in pseudo-equilibrium state and tend to pack more densely to minimize free volume over time. Previously, we designed a simulation methodology for generating amorphous cage models, and investigated gas diffusivities and diffusion mechanism in amorphous organic cage systems.[12] We found that the contribution of the extrinsic (between cages) and intrinsic (within cages) porosity to the total porosity has a significant effect on pore connectivity and gas diffusion pathway. Denser packing of cage molecules in the amorphous thin-film state would result in a loss of extrinsic voids, which hinders the gas diffusion pathways (e.g., lower degree of connectivity of free volume or micropores, whether intrinsic or extrinsic) and consequently decreased the gas permeability in the aged cage thin films.

The molecular-sieve membranes fabricated from porous organic cage molecules are insufficiently robust for many practical applications due to physical ageing, and limited chemical and thermal stability, for example, in CO2 separation of steam-containing flue gas, or separation of H2/CO2 at high temperatures. For example, hydrolysis of the imine-linkages in cage molecules may occur upon exposure to water, acidic, and basic conditions. Further work is in progress to produce more stable films, for example, transforming cage thin films to more chemically stable ones (such as FT-RCC3), or introducing stronger intermolecular forces into cages to form rigid and stable networks (e.g., by designing specific hydrogen bonding interactions between cages, or covalent crosslinking). On the other hand, the flexible property of cage solids and thin films may be useful in other applications, for example, controlled release of guest molecules (e.g., drug molecules), or adaptive materials.

In conclusion, we have demonstrated that porous organic cages can be solution-processed into coherent thin films with tunable structure and porosity. The thin films show potential in molecular sensing and selective molecular-sieve membranes for molecular-level separations. The fabrication technique via spin coating is a simple, reproducible, and easily controlled process that yields uniform and defect-free thin films with excellent thickness control. Such ease of fabrication is achievable by the solution processability of POC molecules as building blocks. Our work also leads to better understandings of the factors that determine the phase-separation and microstructure in these systems, with which we could generate hierarchically porous cage thin films that may serve as platform for functional materials. We further demonstrate the proof-of-concept viability of molecular-sieve membranes fabricated from porous organic cage molecules. The solution processability of POCs allows coating and modification of various membranes to form composite membranes for separation of industrially and environmentally important gas molecules. Although these first-generation molecular cage films tend to densify over time, as reflected by loss in gas permeability under vacuum, they are chemically robust as shown by stable selectivity even after 30 d. Our work suggests a simple and generic approach that facilitates the fabrication of cage thin films and membranes, for example in applications such as functional coatings, composites, sensing, catalysis, separation membranes, and energy storage.

**Experimental Section**

**Synthesis of Porous Organic Cages:** All the cages, CC3, CC13, ASPOC, RCC3, and FT-RCC3 were synthesized following previous work. CC3 was synthesized from reaction between 1,3,5-triformylbenzene (TFB) and (1R,2R)-1,2-cyclohexanediamine (CHDA) in dichloromethane at room temperature.[18] The crystals were recovered by filtration, and washed with 95% ethanol/5% dichloromethane, and finally dried under vacuum. CC13 was synthesized by reactions between 2-methyl-1,2-propanediamine and TFB, followed by precipitation in petroleum ether, and further vacuum dried.[5b] Amorphous scrambled porous organic cages (ASPOC) were synthesized by co-reaction of TFB with a mixture of both 1,2-ethylenediamine (EDA) and CHDA in dichloromethane at 70 °C.[19] The reaction was cooled to room temperature and the FT-RCC3 was prepared by reacting the RCC3 cages with paraformaldehyde in methanol at 70 °C.[23] The reaction was cooled to room temperature and the FT-RCC3 was obtained after filtration and washing with methanol and further dried under vacuum.

**Fabrication of Cage Thin Films:** The cage solids were dissolved in solvents to give cage solution with a certain concentration. In some cases, co-solvents of methanol (MeOH) and dichloromethane (DCM) or chloroform was used with mass ratios changed. The cage solution was then purified by syringe filters (PTFE, 0.2 μm). Afterward, cage thin films were prepared by spin coating the cage solution on different substrates. A drop of cage solution is applied on the substrate which is not spinning initially. Then the substrate is rotated at high speed (500–4000 rpm, typically at 2000 rpm) with an acceleration speed of 1500 rpm.

**Characterization Techniques:** Scanning electron microscopy (SEM) analyses were performed using a Hitachi S5500 microscope. The films were fractured in air and coated with a 2-nm-thick layer of gold using...
an Emitech sputter coater. Wide-angle X-ray diffraction (XRD) was performed with a Bruker D8 machine operated at 40 mA and 40 kV using Cu Kα radiation with a step of 0.02° per second. Cage films for XRD analysis were prepared with various substrates, particularly cages were coated directly on low-background Si sample holders. Fourier transform infrared (FTIR) spectra were collected on a Nicolet spectrometer. Cage films were coated on CaF2 disks and analyzed in transmission mode. UV–vis absorption spectra were measured using a spectrometer, with an operating spectral range of 190–1000 nm.

**Gas Adsorption Measurements:** N2 adsorption and desorption isotherms were measured at 77.3 K using Micromeritics 2020, or 2024 volumetric adsorption analyser. Powder samples were degassed offline at 110 °C for 15 h under dynamic vacuum (10−7 bar) before analysis. Gas sorption isotherms of CO2, CH4, N2, and H2 were also measured at 295 K with pressure up to 1 bar.

**Iodine Adsorption and Sensing:** The cage solution (1 wt%) was spin-coated on quartz substrate at a speed of 2000 rpm. Prior to spin coating, quartz plates were cleaned with acetone and isopropyl alcohol in ultrasonic bath for 10 min, respectively. The thin films coated on quartz plates were exposed to iodine solids to allow the adsorption of iodine in the films. The UV–vis absorption spectra were tracked as a function of sorption time.

**Fabrication of Thin-Film Composite Membranes:** Thin-film composite membranes based on POCs were prepared by simply spin-coating cage solutions on porous support. Anodized aluminium oxide (AAO) membrane (Anodisc, Whatman) with a surface layer of 20 nm nanopores was fixed on a PTFE substrate for spin-coating. The inorganic membrane support is quite brittle, so care was taken to fix and transfer the support from spin-coating to gas permeation tests.

**Gas Permeation Tests:** Pure gas permeation tests were carried out at temperatures of 22 °C and feed pressure of 1 bar, using a constant-volume pressure-increase apparatus described in detail elsewhere.[15,25] The membrane was loaded in the apparatus and thoroughly evacuated with a vacuum pump (Edwards RV3) prior to gas permeation measurements. The gas permeance (J, mol m−2 s−1 Pa−1) was measured directly. The ideal selectivity for a gas pair (A/B) is calculated from the ratio of their permeance. The uncertainties of the as-measured permeance at the moment of test are within 10%, and selectivity within 5%. The uncertainties of the as-measured permeance were propagated to as-measured permeance measurements up to 1 bar at 295 K. The diffusion coefficient (D) (at 1 bar) is calculated from the permeability (D = P/S).

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

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