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Sol-gel asynchronous crystallization of ultraselective metal-organic framework membranes for gas separation[†]

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Metal–organic framework (MOF) membranes possess superior separation performance, but their inferior processability is an intrinsic drawback. Herein, we report a scalable and versatile sol–gel transformation strategy to synthesize MOF membranes by two steps of precursor-coating for gel dispersion and thermal-treatment for membrane growth, similar to the processing of polymeric membranes. The asynchronous crystallization between the bottom and the top of gels found here is critical for the formation of defect-free MOF membranes. The prepared ZIF-8 membranes with a ligand/zinc ratio of 4 show impressive performance in hydrogen purification and hydrocarbon separation, with H_2/CH_4 , H_2/C_3H_8 and C_3H_6/C_3H_8 selectivities of up to 30, 9000 and 200, respectively. Moreover, sol–gel transformation can deposit MOF layers with controllable thickness, down to 130 nm, on both discs and hollow fibers without deterioration in performance in a solvent-/precursor-saving manner.

The purification of hydrogen and separation of light hydrocarbons have great significance in chemical, environmental and energy-related industries.¹⁻³ Membrane separation is a more energy-efficient technology for molecular purification than traditional thermodynamically driven processes. Molecular sieving membranes composed of microporous crystalline materials, such as zeolites and metal-organic frameworks (MOFs), have superior permeability and selectivity than broadly used polymeric membranes, because of their high porosities and tunable transport channels.4-13 MOFs, as new promising porous crystalline materials, show impressive performance in various applications, attributed to their high specific surface areas and tunable physico-chemical properties.14-20 MOFs are usually assembled into structural materials from preliminary crystal particles or fundamental metal salts and ligands for better applications.²¹ Amidst these materials, membranes formed with polycrystalline MOF layers on substrates have shown rapid development recently due to the outstanding capacity in hydrogen purification, hydrocarbon separation and carbon dioxide capture.²²⁻²⁴ Crystallization in precursor solutions, through hydro/solvothermal growth, interfacial synthesis and contra-diffusion synthesis, is a dominant formation mechanism for obtaining continuous MOF membranes.24-34 For hydro/solvothermal growth, homogeneous crystallization in solutions is adverse to the growth of continuous membranes and will reduce the utilization of expensive precursors. Consequently, despite running counter to the efficient and straightforward preparation, modifications of substrates by seeding and grafting are encouraged to enhance the heterogeneous nucleation of MOFs. Theoretically, interfacial synthesis can fabricate MOF membranes on a large scale, but a sharp interface of two immiscible precursor solutions is a prerequisite for providing the crystallization region. The solubility problems between solvents and MOF precursors may limit membrane synthesis.35 Furthermore, typical solution synthesis will cause massive consumption of organic solvents. Recently, we prepared MOF membranes by scalable gel-vapor deposition and demonstrated the feasibility of scale-up production.36 Nevertheless, the good flowability of the sol results in high requirements of substrate microstructures to form a continuous coating layer, as well as the evaporation of ligands may hinder the mild fabrication of MOF membranes that consist of ligands with high sublimation temperature. The above issues possibly hinder the further development of MOF membranes and their separation application in the future.

Herein, we report a novel sol–gel transformation methodology that can deposit continuous MOF layers with controllable thicknesses on various substrates for achieving precise synthesis of molecular sieving membranes, performed by two steps of gelation and crystallographic transformation, which is a sophisticated technique for the processing of nanoparticles, fibers, films and monoliths, with multifarious materials from pioneering inorganic oxides to polymers and burgeoning hybrid composites.^{37–42} As shown here, sol–gel synthesis is developed to

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fabricate MOF membranes for the first time. The proposed solgel transformation in this study is executed by gel coating for precursor dispersion followed by thermal-treatment for crystallization (Fig. 1a–c). These procedures are similar to those for the preparation of most broadly-applied gas separation membranes that are composed of highly processable polymers, which are usually fabricated by ink casting for polymer molding and subsequent heat-treatment for solvent evaporation.^{43–46} The MOF membranes thus prepared on discs and hollow fiber substrates with controllable thickness have precise molecular sieving properties.

To demonstrate the feasibility of the sol-gel transformation, ZIF-8, a sodalite-topological MOF with 2-methylimidazole (MeIM) ligands and zinc centers, was employed to obtain continuous membranes, due to its excellent chemical stability, moisture resistance and 0.34 nm ultra-micropore structure.47,48 Zinc salt and ethanolamine were mixed in ethanol under thermaltreatment to achieve the transparent sol. Ethanolamine served as a stabilizing and chelating agent to realize sol formation. After adding MeIM, the sol displayed great reduction in flowability and was converted to a nontransparent gel (Fig. 1a). X-ray diffraction (XRD) patterns with broad and relatively weak characteristic peaks confirmed the existence of ZIF-8 colloidal crystals (Fig. 1d), which reduced the gel transparency. With the increase of the MeIM/Zn ratio, the gel flowability decreased firstly and then increased (Fig. S1, ESI⁺). The increased viscosity was ascribed to the formation of ZIF-8 nanocrystals and the additional complexation between the metal salt and MeIM besides acetate and ethanolamine. The decline of viscosity for the gels with ratios over 4 was the result of the increased volumes, more free molecules and undissolved MeIM ligands. The strong characteristic

peaks in the XRD patterns and the white plaques in photographs verified the solid MeIM dispersion (Fig. 1d and S1, ESI[†]). The gels were deposited on anodic aluminum oxide (AAO) substrates by spin coating and subjected to thermal-treatment for membrane formation (Fig. 1b and c and S2, ESI[†]). The XRD patterns with greatly enhanced characteristic peaks proved the follow-up crystallization of ZIF-8 (Fig. S3, ESI⁺). The enhancement of peak intensity became larger with the increase of the MeIM amount (Fig. 1e). With the consumption of zinc cations for crystallization, the peak intensity reached the maximum when the MeIM/Zn ratio increased to 4. In fact, the MeIM/Zn ratio of ZIF-8 is 2 based on the stoichiometry, but experiments verified that the ratios over 2 were beneficial to fabricate continuous membranes. This was attributed to the balance between the evaporation of organic molecules and the competitive reactions of ethanolamine, acetate and MeIM with zinc cations. The excess MeIM could promote the reaction with ZIF-8. The Fourier transform infrared (FTIR) spectra of the different membranes were obtained (Fig. 1f and S4, ESI[†]). For the membranes with low MeIM/Zn ratios, the intensive peaks of the C=O bond at 1580 and 1401 cm^{-1} for acetate and of the bonds between 600–1300 cm^{-1} for MeIM were strengthened obviously. As the MeIM/Zn ratio increased, apart from the improved intensity, MeIM peaks showed an obvious blue shift, indicating the deprotonation of ligands. The FTIR results of the membranes with MeIM/Zn ratios equal to and over 4 showed no peaks for gels and showed the typical ZIF-8 spectra, verifying the pure chemical structure of the frameworks. In line with the observation in XRD characterization, the membrane with an MeIM/Zn ratio of 4 showed the strongest characteristic peaks, as a result of more pure chemical composition or higher loading.



Fig. 1 (a) Photograph of the gel with an MelM/Zn ratio of 4. (b) Schematic of membrane synthesis. (c) Photograph of the prepared ZIF-8 membrane with an MelM/Zn ratio of 4. (d) XRD patterns of the gels with MelM/Zn ratios from 0.5 to 12. (e) XRD patterns of the ZIF-8 membranes with MelM/Zn ratios from 0.5 to 12. (f) FTIR spectra of the ZIF-8 membranes with various MelM/Zn ratios.

Membrane continuity is vital for separation applications. The scanning electron microscopy (SEM) images of the obtained ZIF-8 membranes were captured and are presented in Fig. 2, S5 and S6, ESI.[†] The membranes with MeIM/Zn ratios of 0, 0.5 and 1 showed granular morphologies, while the membrane with an MeIM/Zn ratio of 2 comprised dense zinc complexes and mixed ZIF-8 nanoparticles. It should be noted that the coating of the sol with an MeIM/Zn ratio of 0 could not fabricate a continuous gel layer similar to a previous study.36 This was attributed to the fact that the relatively good flowability of the sol and slow evaporation of the solvent caused massive injection of the sol in substrates with vertical channels. The membranes with large MeIM/Zn ratios from 4 to 12 possessed well-intergrown and polyhedral morphologies. Because of the superfluous MeIM in gels, the membranes fabricated with high MeIM/Zn ratios had many wrinkles and void grain boundaries (Fig. S6, ESI[†]). The downward and then upward tendency of the membrane thickness was consistent with that of the viscosity. Compared to the membranes with higher MeIM/Zn ratios, which showed flat cross-sectional structures, the membrane with a ratio of 3 had a grainy sectional morphology. This should be ascribed to the fact that the residual zinc complexes existed at gaps between ZIF-8 crystals. As a result of gel injection, a portion of ZIF-8 was formed in the porous structures of the substrates, which would improve membrane compatibility significantly.^{34,36} In comparison with the MOF membranes prepared by traditional crystallization in precursor solutions with a volume of tens to hundreds of milliliters, 200 microliters of gels could reduce solvent consumption immensely. Certainly, the dosages of high-cost MOF precursors were cut down substantially as well.



Fig. 2 (a–f) Cross-sectional and (g–i) top view SEM images of the ZIF-8 membranes with MeIM/Zn ratios of (a, d and g) 2, (b, e and h) 3 and (c, f and i) 4. The schematics display the internal structure of the different membranes. The zinc complexes and ZIF-8 are depicted in blue and yellow, respectively.

It should be noted that there is an uncustomary phenomenon of membrane formation by using sol-gel transformation. Traditional sol-gel synthesis normally involves preparation of porous materials from stacked particles,37-41 but the ZIF-8 membranes in this study are dense. We attempt to describe the formation mechanism further. The initial solvent evaporation leads to a concentrated gel, thereby promoting crystal growth. Ligand volatilization results in a concentration gradient with increasing trend from top to bottom. Because a greater MeIM/Zn ratio enhances the formation of nanocrystals,49,50 faster crystallization to form smaller crystals occurs in the bottom region originating from higher nucleation density. Correspondingly, slower crystal growth from a smaller MeIM/Zn ratio in the region close to the membrane surface promotes the formation of ZIF-8 grains with larger size (Fig. 3a). By reason of the asynchronous crystallization, the membranes thus prepared are continuous. The validity of the assumed mechanism was investigated by experiments. The weight variation of the membrane with an MeIM/Zn ratio of 4 was monitored as a function of growth time (Fig. S7, ESI†). After thermaltreatment for 10 min, the weight of the gel decreased by 43.5%, which is approximately equivalent to the ethanol content. The progress of thermal-treatment contributed to the weight decrease. When the processing time was longer than 10 hours, the weight showed hardly any change with the extension of time. The residual 22.7% weight was similar to the theoretical value of 20.4% calculated using the gel composition and molecular formula of ZIF-8 (Zn(MeIM)₂). This revealed that the prepared membrane was composed of Zn bridged by two MeIM ligands. The transmission electron microscopy (TEM) images of the ZIF-8 colloidal crystals and cross-sectional SEM images, particle size distributions and XRD patterns of the ZIF-8 membranes with different durations of thermal-treatment are presented in Fig. 3b-d, S8 and S9 (ESI†). The ZIF-8 membrane after 1 h thermal-treatment showed more nanocrystals in the bottom region than in the region close to the membrane surface (Fig. 3c). With the extension of thermal-treatment, both the nanoparticle size shown in the SEM images and the peak intensity of the XRD patterns increased. These results confirmed the proceeding of crystallization. After reaction, the dense ZIF-8 layer was formed. Since the powerful crystal connection of the membrane with an MeIM/Zn ratio of 4 caused relatively flat fracture, the membrane with a ratio of 3 was employed to prove the asynchronous crystallization through intuitionistic SEM investigation. The top layer was excised to expose the bottom structure. The ZIF-8 membrane clearly showed hetero-structures with larger top crystals and smaller bottom ones (Fig. 3e and S10, ESI[†]). The result proved the asynchronous crystallization intuitively. The membrane with an MeIM/Zn ratio of 4 was purified by washing in methanol and characterized by X-ray photoelectron spectroscopy (XPS) and FTIR. As expected, the as-synthesized membrane had higher Zn element than the purified one (Fig. 3f and g). The change in high-resolution C 1s, N 1s and O 1s spectra also indicated the existence of amorphous Zn-based complexes by reason of the lowest MeIM/Zn ratio (Fig. S11, ESI†). However, the similar FTIR spectra of the as-synthesized and purified membranes



Fig. 3 (a) Schematic of the crystallization of the ZIF membrane fabricated by sol-gel transformation. (b) TEM image of the ZIF-8 nanocrystals in the gel with an MeIM/Zn ratio of 4. (c) Cross-sectional SEM images of the ZIF-8 membranes with thermal-treatment for 1 h. (d) Particle size distributions of the ZIF-8 membranes with thermal-treatment for 1 and 3 h. (e) SEM images of the surface and bottom fracture of the ZIF-8 membrane with an MeIM/Zn ratio of 3. (f) Element content of the as-synthesized and purified ZIF-8 membranes with an MeIM/Zn ratio of 4. (g) High-resolution Zn XPS spectra of the as-synthesized and purified ZIF-8 membranes.

demonstrated the consistent bulk structures (Fig. S12, ESI[†]). In consideration of XPS detecting depth of several nanometers, this result proved that the tiny residue of zinc complexes at the membrane surface was derived from MeIM evaporation. All the above results confirmed the proposed formation mechanism.

We investigated the N2 adsorption-desorption isotherms of the membrane with an MeIM/Zn ratio of 4. The large Brunauer-Emmett-Teller (BET) specific surface area of 198.4 m² g⁻¹ indicated its excellent porosity (Fig. S13, ESI[†]). Considering the micropore area of 150.9 $m^2~g^{-1}$ and the 7.3 \pm 0.6% content of the deposited layer in the whole membrane, the formed ZIF-8 possessed a remarkable micropore area of 1881–2232 m² g⁻¹, which was even higher than those of the previously solvothermally synthesized ZIF-8 materials.47-50 The pore width of approximately 1 nm proved the existence of the sodalite cage, in agreement with the theoretical topology of ZIF-8. The porosities of the ZIF-8 membranes with other MeIM/Zn ratios were also studied (Fig. S14, ESI[†]). The micropore area of the membranes increased first and then decreased (Table S1, ESI[†]). This result demonstrated that the other membranes had relatively poor microstructures compared to the ZIF-8 membrane with an MeIM/Zn ratio of 4. On account of the results of XRD, FTIR, stoichiometry, porosity and energy-dispersive X-ray mapping

(Fig. S15, ESI[†]), it was clear that almost all of the Zn element was transformed to ZIF-8 and the prepared framework layer with an MeIM/Zn ratio of 4 had excellent purity.

After demonstrating the feasibility and formation mechanism of sol-gel transformation, we investigated the separation performance of the prepared membranes. The permeances of various gases with different kinetic diameters (KDs) through the prepared ZIF-8 membranes were measured (Fig. 4a and S16, ESI[†]). With the increase of MeIM/Zn ratios from 0 to 12, the gas permeances displayed a trend of first decrease and then increase (Fig. S17, ESI[†]). The ZIF-8 membrane with an MeIM/Zn ratio of 2 was impermeable due to the large loading of amorphous zinc complexes (Fig. S18, ESI[†]). The gas permeances showed a decreasing trend as the kinetic diameters of the membranes with MeIM/Zn ratios increased from 3 to 12. These membranes exhibited excellent permselectivity for H₂ over other gases (Fig. 4b). For example, the H_2/CO_2 , H_2/O_2 , H_2/N_2 , H₂/CH₄, H₂/C₃H₆ and H₂/C₃H₈ ideal selectivities of the membrane with an MeIM/Zn ratio of 4 reached as high as 5.7, 15.1, 20.7, 26.3, 47.0 and 7733, respectively, with a large H_2 permeance of 31.5×10^{-8} mol m⁻² s⁻¹ Pa⁻¹ (about 941 gas permeation units-GPU, 1 GPU = 3.348×10^{-10} mol m⁻² s⁻¹ Pa⁻¹). The much higher ideal selectivities than Knudsen diffusion



Fig. 4 (a) Single-component permeances through the ZIF-8 membranes with MeIM/Zn ratios of 3, 4, 6, 8, and 12. (b) Ideal selectivities of the ZIF-8 membranes with various MeIM/Zn ratios. X_n represents the various gases. Separation performance of (c) H_2/C_3H_8 and (d) C_3H_6/C_3H_8 mixtures through the ZIF-8 membranes with various MeIM/Zn ratios. Comparison of the ZIF-8 membranes prepared by sol-gel transformation with the reported high-performance polymeric, carbon and MOF membranes for (e) H_2/C_3H_8 and (f) C_3H_6/C_3H_8 systems. The previously reported MOF membranes were prepared by a hydro/solvothermal method, contra-diffusion/interfacial synthesis, layer by layer growth and vapor-deposition. The separation data and synthesis methods of the ZIF-8 membranes here and the reported membranes are shown in Tables S2 and S3 (ESI†).

coefficients confirmed the precise molecular sieving properties. The theoretical pore size of ZIF-8 is 0.34 nm, which is larger than that of the H₂ (0.289 nm), similar to CO₂ (0.33 nm) and smaller than the other gases employed in this study. However, because the ligand rotation endows the framework with dynamic flexibility,⁵¹ the functional transport channel of ZIF-8 is larger than the kinetic diameter of C₃H₆ (0.40 nm) but smaller than that of C₃H₈ (0.43 nm).^{52,53} Therefore, the prepared membranes showed the largest sharp drop in C₃H₈ permeance rather than in O₂ permeance (0.346 nm). C₃H₆ could penetrate through the prepared ZIF-8 membranes and displayed a permeance of 0.6–24 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹. The C₃H₆/C₃H₈ ideal selectivity could be achieved as 164. Relatively, the as-synthesized membrane with an MeIM/Zn ratio of 4 exhibited lower permeances and ideal selectivities owing to rare residual zinc complexes (Fig. S19, ESI[†]).

Based on the investigation of single-component permeation, the separation performance of H_2/C_3H_8 and C_3H_6/C_3H_8 mixtures through the membranes with MeIM/Zn ratios of 3–12 was studied (Fig. 4c and d). Similar to the observation in singlecomponent permeation, the improvement of the MeIM/Zn ratio led to the enhanced H_2 and C_3H_6 permeances. The H_2/C_3H_8 and C_3H_6/C_3H_8 selectivities increased firstly and decreased subsequently. Among all the tested membranes, the membrane with an MeIM/Zn ratio of 4 exhibited the highest H_2/C_3H_8 and C_3H_6/C_3H_8 selectivities of 8674 and 191, respectively, which were calculated by averaging three values of different membrane samples with the largest ones up to 9999 and 203 (Table S2,

ESI[†]). The similar separation performance of the three membrane samples of the ZIF-8 membranes proved the good reproducibility of the membranes (Table S2, ESI⁺). Theoretically, because of the appropriate aperture, the ZIF-8 membrane should possess precise molecular sieving properties, with total exclusion for C₃H₈. However, since the poor microstructures, such as the unobservable nanometer-sized grain boundary, which generally exist in the membranes composed of crystalline materials, provide the by-pass transports, the reported MOF membranes usually show smaller selectivity than the theoretical one.^{34,54} For the ZIF-8 membranes prepared by sol-gel transformation, the high nucleation density improved the intergrowth of polycrystalline layers, and thus the membranes had an enhanced grain boundary structure and showed impressive performance.55 Comparatively, the lower permeances and selectivities of the membrane with an MeIM/Zn ratio of 3 were interpreted by the residual amorphous complexes at grain boundaries. The increased permeances and decreased selectivities of the membranes with MeIM/Zn ratios of 6-12 were explained by the fact that the excess MeIM disturbed the crystallization process and resulted in the formation of membranes with poor microstructures, wrinkles and void grain boundaries (Fig. S18, ESI^{\dagger}). The separation performance of H₂/CH₄ showed an analogous trend similar to those of H2/C3H8 and C3H6/C3H8 systems, with the largest selectivity of 30.3 among the tested membranes (Fig. S20, ESI[†]). The operational durability of the membranes is very important for practical application. The

small fluctuation of separation performance over five days indicated the long-term stability of the prepared ZIF-8 membranes (Fig. S21, ESI†). We studied the effect of the pressure on separation performance (Fig. S22, ESI†). Similar to the observations in previous studies,^{36,53} the C_3H_6/C_3H_8 selectivity decreased with increasing pressure, because of the competition of two feed gases through the membrane and the aggravating concentration polarization. Relative to the reported carbon and MOF membranes, the ZIF-8 membranes prepared by sol–gel transformation showed outstanding separation performance in H_2/C_3H_8 and C_3H_6/C_3H_8 separations (Fig. 4e and f, and Table S3, ESI†). The separation performance of the prepared membranes could surpass the upper bound of polymeric membranes easily.

Membrane thickness is crucial for permeation. The gels with an MeIM/Zn ratio of 4 but lower concentrations were employed to fabricate ZIF-8 membranes with small thickness. When the gel with a concentration of 0.5 times was used, an ultrathin membrane with a thickness of 130 nm was uniformly deposited on the substrates (Fig. 5a). This thickness was smaller than those of most reported MOF membranes.²²⁻²⁴ When the more dilute gel was employed, abundant ZIF-8 nanoplates with a size of several micrometers were formed on the substrates due to the small gel loading (Fig. S23, ESI[†]). This should be explained by the high viscosity and drying shrinkage of gels under thermaltreatment. If the affinity between the substrates and the gels is improved, a thinner membrane may be prepared. Similar to the previous demonstration,^{5,7,24,32,36,53,55} polymeric hollow fiber substrates are preferable for supporting MOF membranes in terms of cost, processability and membrane area per volume. We attempted to prepare ZIF-8 membranes on polyvinylidene fluoride (PVDF) hollow fibers by sol-gel transformation. After crystallization, a continuous and defect-free ZIF-8 layer was successfully deposited on the hollow fiber surface (Fig. 5b).



Fig. 5 SEM images of (a) the ultrathin ZIF-8 membrane and (b) the ZIF-8 hollow fiber membrane. (c) Separation performance of the ultrathin ZIF-8 membrane and the ZIF-8 hollow fiber membrane for H_2/CH_4 , H_2/C_3H_8 and C_3H_6/C_3H_8 systems.

We characterized the separation performance of the ultrathin membrane and the hollow fiber membrane. Gas permeation results revealed that both membranes exhibited precise molecular sieving properties (Fig. S24 and S25, ESI[†]). In H₂ purification and hydrocarbon separation (Fig. 5c), although the ultrathin membrane exhibited lower selectivities compared to the micrometer-sized membrane prepared in this study, good H₂/CH₄ (21.2), H₂/C₃H₈ (3482) and C₃H₆/C₃H₈ (115) selectivities were still achieved. Moreover, gas permeances as high as 206 (H₂, H₂/CH₄), 201 (H₂, H₂/C₃H₈) and 6.0 (C₃H₆, C₃H₆/C₃H₈) \times 10^{-8} mol m⁻² s⁻¹ Pa⁻¹ were achieved. The hollow fiber membrane exhibited similar performance as the micrometersized membrane prepared in this study, with selectivities of 28.6 (H₂/CH₄), 8397 (H₂/C₃H₈) and 170 (C₃H₆/C₃H₈), as well as gas permeances of 37.8 (H₂, H₂/CH₄), 35.4 (H₂, H₂/C₃H₈) and 0.8 $(C_3H_6, C_3H_6/C_3H_8) \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. These two kinds of ZIF-8 membranes also showed competitive separation performance, compared with the high-performance membranes in previous studies (Fig. 4e and f). These results revealed that solgel transformation synthesis had great controllability and wide applicability for diverse substrates.

Conclusions

We have reported a facile and scalable sol-gel transformation strategy for synthesizing MOF membranes in a solvent-/ precursor-saving manner. Similar to the fabrication of highly processable polymeric membranes, the sol-gel transformation reported here, performed by gel coating and thermal-treatment without the requirement of any special equipment, can deposit MOF layers with controllable thickness on various substrates with different constructions. As a result of asynchronous crystallization, the prepared MOF membranes are defect-free and show impressive performance in H_2 purification and hydrocarbon separation. Inspired by the development of the sol-gel method, further progresses may be achieved in the fabrication of MOF membranes with other features, such as orientation, hybridization and atomic level doping, for better gas separation and energy-related applications.

Conflicts of interest

There are no conflicts to declare.

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