Metal-Organi c Framework Nanoparticles with Universal Dispersibility through Crown Ether Surface Coordination for Phase-Transfer Catalysis and Separation Membranes

Xiaoxin Yang, Qiao Zhang, Yufeng Liu, Mengjie Nian, Min Xie, Shasha Xie, Qinglian Yang, Suna Wang, Hui Wei, Jingui Duan, Shengyi Dong, and Hang Xing*

In memory of Dr. Chia-Kuang “Frank” Tsung

Abstract: Dispersing metal-organic framework (MOF) solids in stable colloids is crucial for their availability and processibility. Herein, we report a crown ether surface coordination approach for functionalizing the surface-exposed metal sites of MOF particles with amphiphilic carboxylated crown ether (CE'). The surface-bound crown ethers significantly improve MOF solvation without compromising the accessible voids. We demonstrate that CE'-coated MOFs exhibit exceptional colloidal dispersibility and stability in 11 distinct solvents and six polymer matrices with a wide range of polarities. The MOF-CE' can be instantaneously suspended in immiscible two-phase solvents as an effective phase-transfer catalyst and can form various uniform membranes with enhanced adsorption and separation performance, which highlights the effectiveness of crown ether coating.

The stable dispersion of nanomaterials in various media is essential for their application. Thereby, surface chemistries that can enhance particle-solvent interactions are particularly important.[1] Metal-organic framework (MOF), an emerging class of crystalline porous materials,[2] have attracted significant interest in chemical sensing,[3] heterogeneous catalysis,[4] gas storage,[5] and chemical separation.[6] Typically, mass-synthesized MOFs are available as nano- to micro-meter scale crystalline powders and therefore need to be dispersed into stable colloids before usage.[7] Due to their surface-exposed metal sites, MOFs are mostly hydrophilic and tend to disperse well only in high-polarity solvents, limiting their potential applications in non-polar environments.

To improve the availability and processibility of MOFs, a common practice is to incorporate functions onto the external surface via post-synthetic modification.[8] Various hydrophobic molecules, including phospholipid,[9] octadecylphosphonic acid,[10] phenylsilane,[11] N-heterocyclic carbene,[12] calix[n]arenes,[13] and polymers,[14] have been employed as capping agents to improve MOF dispersibility in hydrophobic environments. Biomacromolecules like nucleic acids have also been introduced onto MOF to facilitate biological applications under physiological conditions.[15] Despite these efforts, no effective approach has been demonstrated so far that allows MOF particles to disperse simultaneously in immiscible polar and non-polar solvents.[16] In addition, the use of no-cavity capping agents may potentially affect the porosity of the host MOF structure.[9]

Herein, we report a crown ether surface coordination (CESC) approach to enable MOFs to achieve universal solubility in common solvents and polymers with a wide range of polarities. Crown ethers with cyclic cavities and balanced hydrophilic and hydrophobic microdomains have been previously reported as supramolecular chelators for ion sensing and catalysis,[17] and as dispersion matrices to prepare porous liquid with permanent cavities.[18] Thus, by incorporating bulky carboxylated crown ether (CE') onto the exterior surface of six MOFs via coordination, its amphiphilic nature significantly improves particle-solvent interactions, rendering MOFs with exceptional colloidal dispersibility in 11 distinct solvents while maintaining their adsorption capacity (Scheme 1). Furthermore, MOF-CE' has been demonstrated as an effective phase-transfer catalyst in an immiscible two-phase system, and to prepare...
a series of mixed-matrix membranes of high uniformity and enhanced performance.

First, we synthesized the 4-carboxybenzo-21-crown-7-ether (C\textsubscript{21}E\textsubscript{7}-COOH), featuring an amphiphilic 21-membered polyether ring and a benzene carboxylic group. The obtained C\textsubscript{21}E\textsubscript{7}-COOH was verified using \textsuperscript{1}H NMR spectroscopy (Figure S1).

\[1\]

UiO-66 was chosen for our initial study due to its high stability and appropriate pore openings, which are smaller than C\textsubscript{21}E\textsubscript{7}-COOH (Figure S2).

\[2\]

Octahedral UiO-66 with ca. 100–120 nm edge length was synthesized using a solvothermal process (Figure 1a).

\[3\]

The C\textsuperscript{E}-coated UiO-66 (UiO-66-C\textsuperscript{E}) was prepared by incubating C\textsubscript{21}E\textsubscript{7}-COOH with MOF suspension at 80°C for 6 hours, followed by ethanol washing and vacuum drying. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), dynamic light scattering (DLS), and powder X-ray diffraction (PXRD) revealed that the morphology, size, and crystallinity of UiO-66-C\textsuperscript{E} was well-preserved with a slightly increased surface potential (Figure 1b, c, d, S3, and S4). Fourier transform infrared spectroscopy (FT-IR) revealed the characteristic peaks of C=O stretching and C–O–C vibration in UiO-66-C\textsuperscript{E}, correlating well with the peaks of free C\textsuperscript{E} (Figure 1e).

\[4\]

The energy downshift of Zr 3d\textsubscript{3/2} and Zr 3d\textsubscript{5/2} was observed after crown ether modification in X-ray photoelectron spectroscopy (XPS) results (Figure S5), which could be attributed to the coordination to Zr sites. In addition, the C 1s energy peak and increased carbon content confirmed the successful C\textsuperscript{E}-coating on MOF (Figure S6 and Table S1).

The C\textsuperscript{E} coverage on the MOF surface was assessed quantitatively using \textsuperscript{1}H NMR spectroscopy and theoretical estimation. The number of Zr atoms, ligands, and surface area of a UiO-66 particle were determined based on a geometric approximation of the octahedral and crystal structure. After decomposing UiO-66-C\textsuperscript{E} in HF, H...
resonances from both ligand and $\text{C}_2\text{E}_7\text{-COOH}$ were recorded, revealing a $\text{CE}^\circ$-to-ligand molar ratio of ca. 0.072 (Figure S7 and S8). The $\text{CE}^\circ$ surface density was calculated to be ca. 0.41 nmol/cm$^2$, corresponding to ca. $8.6 \times 10^7$ molecules on one UiO-66-CE$^\circ$ particle, which was consistent with theoretical estimation (Table S2). Both UiO-66-CE$^\circ$ and pristine UiO-66 exhibited almost identical type-II $\text{N}_2$ adsorption isotherms before 0.9 $P/P_0$ with similar pore size distributions (Figure 1f and S9), indicating well-maintained porosity. The increase in $\text{N}_2$ uptake at high $P/P_0$ was likely due to the packing of MOF particles.$^{[9]}$ These data indicate that CE$^\circ$ molecules are mostly mounted onto the external surface without compromising the voids for adsorption.

We next studied the impact of crown ether modification on the dispersibility of MOFs. We gradually increased the CE$^\circ$ wt % during post-modification and redispersed the resulting UiO-66-CE$^\circ$ particles with different degrees of CE$^\circ$ coating in DCM. The Zr content in the DCM solution after 30 min settling was measured using inductively coupled plasma mass spectrometry (ICP-MS). We found that while Zr was scarcely detectable for pristine UiO-66, CE$^\circ$ coating greatly increased the dispersibility of MOF particles, with more than 81 % Zr in solution (Figure 1g and Table S3). Moreover, CE$^\circ$ coating also enhanced the chemical stability of UiO-66 under 1 M HCl treatment (Figure S10). Importantly, the UiO-66-CE$^\circ$ in DCM appeared stable colloidal suspension with characteristic

![Figure 2](image-url). a) Dispersion of five distinct MOF-CE$^\circ$ particles in 11 different solvents. b) The change of partition coefficient of MOF particles before and after CE$^\circ$ coating. The index of MOF concentration changes upon CE$^\circ$ coating c) in n-octanol and d) in water.

Tyndall effect, while the pristine MOF and mixtures of MOF and CE exhibited severe aggregation (Figure 1h and S11). The free Zr complexes in DCM appeared colorless and transparent solution with no observable light scattering (Figure S12). Notably, UiO-66-CE\textsuperscript{C} dry powders can be instantaneously dispersed in 11 common solvents of broad polarities with gentle sonication for only 30 seconds (Figure 1i and Table S4), showing clear Tyndall effect (Figure S13) and improved dye adsorption ability (Figure S14). All 11 solutions exhibited superior dispersibility and colloidal stability with minimal release of free Zr even after two-week settling (Figure S15). The dispersion of MOF-CE\textsuperscript{C} was fully reversible, allowing the UiO-66-CE\textsuperscript{C} colloids in one solvent to be easily dried and redispersed in another solvent of vastly different polarity for recyclable usages (Figure 1j).

To demonstrate the generality of the CESC approach, we extended this method to five additional MOFs, namely MIL-53-Fe, MIL-101-Cr, UiO-67, PCN-223, and HKUST-1, representing four distinct metal clusters and ligands. All MOFs were synthesized with particle sizes around 100–400 nm and were functionalized with CE\textsuperscript{C} (Figure 1j).

Figure 1. a) Scheme showing the different surface properties of HKUST-1 particles with different coatings. b) HKUST-1-CE\textsuperscript{C} formed homogeneous suspension in immiscible solvents. c) Scheme and photo showing the fluorogenic reaction in a two-phase system using HKUST-1-CE\textsuperscript{C} as the phase-transfer catalyst. d) The kinetics and e) the calculated reaction rate constant k values of the fluorogenic reaction catalyzed by different MOFs.

Finally, we investigated the potential of MOF-CE\textsuperscript{C} for the preparation of uniform mixed-matrix membranes (MMMs) using standard solution-processing (Figure 4a). UiO-66-CE\textsuperscript{C} was blended with polystyrene (PS) in DCM, and the miscible blend was drop-casted onto glass to form a continuous thin film. UiO-66-CE\textsuperscript{C}@PS formed uniform film with homogeneous Zr distribution, whereas unmodified MOF or MOF&CE mixture showed large agglomerations, as confirmed by photograph, SEM, and energy dispersive X-ray spectroscopy (EDX) point scanning (Figure 4b, c, S24, and S25). Importantly, the dispersibility of MOF-CE\textsuperscript{C} is universal for polymers of different polarities. PCN-223-CE\textsuperscript{C} particles were demonstrated to form highly uniform MMMs in six distinct polymer matrices, including polystyrene (PS), polysulfide (PSF), polycarbonate (PC), polyvinylidene fluoride (PVDF), polyimide (PI), and poly-
styrene sulfonic acid (PSS), as demonstrated by SEM and element cross-section analyses (Figure 4d and e). Compared with MMMs prepared from MOF&CE mixture or pristine MOF, UiO-66-CE@PI exhibited higher CO₂ and N₂ adsorption capacity with improved CO₂/N₂ selectivity than some reported UiO-66@PI MMMs (Figure 4f and S26).[20] The UiO-66-CE@PI also showed reasonable gas permeability with higher CO₂ retention, while control MMMs showed leakage because of large fractures (Figure S27). Additionally, UiO-66-CE@PSF MMM showed

![Image of Figure 4](https://onlinelibrary.wiley.com/doi/10.1002/anie.202303280)

**Figure 4.** a) Preparation of homogeneous MMM using MOF-CE particles. b) Photographic and SEM images, and c) the measured Zr compositions of MMMs prepared from 280k polystyrene and 20 wt% of UiO-66 or UiO-66-CE. d) Photograph of PCN-223-CE@PS MMM. e) SEM images and Zr element linear scanning of different MMMs prepared from PCN-223 and PCN-223-CE. f) UiO-66-CE@PI showed improved CO₂/N₂ selectivity. g) Dye removal study using UiO-66-CE@PSF MMM.
enhanced dye removal capabilities and recyclability under vacuum filtration (Figure 4g, S28, and S29). The improved performance of MOF-CE MMM could be attributed to its high uniformity, where CE coating improves MOF-polymer interaction without sacrificing porosity.

In conclusion, we report an effective strategy to achieve universal dispersion of MOFs in various chemical environments through crown ether surface coordination. This study presents the first demonstration of the instantaneous suspension of various MOF dry powders into immiscible polar and nonpolar solvents, exhibiting exceptional dispersibility and colloidal stability while retaining porosity. Furthermore, MOF-CE exhibits potential as an effective phase-transfer catalyst and can be recycled for use in different solvents. Most notably, MOF-CE is compatible with various polymer matrices, enabling the fabrication of uniform MMMs with improved performance. The CESC approach described herein has the potential to overcome processibility barriers, facilitating large-scale fabrication and practical application of MOF materials.

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Conflict of Interest
The authors declare no conflict of interest.

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

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A crown ether surface coordination (CESC) approach enables the preparation of metal-organic framework (MOF) particles with universal dispersibility, enhanced colloidal stability, recyclability, and preserved porosity. The MOF-CE\textsuperscript{c} particles can be instantaneously suspended in immiscible two-phase solvents as an effective phase-transfer catalyst and can be used to prepare various uniform membranes with enhanced adsorption and separation performance.