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A Strategy for Trapping Molecular Guests in MOF-5 Utilizing Surface-Capping Groups

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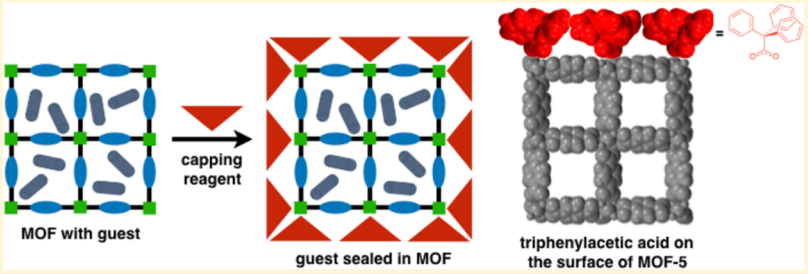

ABSTRACT: We have developed a simple strategy allowing molecular guests to be trapped within MOF-5 using carboxylic acids bearing sterically demanding substituents as capping reagents. We demonstrate that introducing triphenylacetic acid or diphenylacetic acid onto the surface of crystals of MOF-5 loaded with crystal violet (CV) prevents CV from escaping by blocking the openings of pores. In this study, MOF-5 was capped with four carboxylic acids and two 3° amines, and diffusion of CV out of capped MOFs was monitored using UV−vis spectroscopy to assess how variation in the steric demand of substituents affected retention of CV.

INTRODUCTION

Here we describe a method to seal molecular guests within MOF-5 by introducing sterically demanding capping groups to block the openings of pores exposed on the surface of crystals, as illustrated in Scheme 1. This work is part of a larger effort to develop strategies to regulate diffusion of molecular guests into and out of metal−organic frameworks (MOFs) by modifying the dimensions of the openings of pores, and to capture and release guests on demand.[1] To date, prevalent strategies for modifying the porous properties of MOFs rely on adjusting the dimensions of organic ligands to expand or contract the openings of pores,[2−6] post-synthetically modifying the internal surfaces of channels,[7−9] or altering the topology of frameworks.[6] The ability to control sorption and desorption of guests through modification at the surface of MOF crystals is attractive because it should allow the openings of pores of a given MOF to be tailored without amending the internal components or the underlying architecture of the framework. One advantage of this approach is the potential for MOF systems with desirable properties such as thermal or chemical stability to be adapted for applications involving storage or separation of molecules by tailoring the apertures of pores specifically at the surface of crystalline particles rather than throughout the entire internal structure of the framework.

Development of a reliable method to modify the aperture of pores on the surface MOF crystals as a means to control diffusion of molecular guests has yet to be realized. Toward that goal, our efforts have focused initially on demonstrating the feasibility of trapping guests within crystals of MOF-5 with surface-bound capping reagents, and assessing the limitations of that approach. MOF-5 was chosen deliberately as a representative MOF to test in this study for the following reasons. The framework features channels large enough to accommodate a range of organic guests. Large crystals of MOF-5 exhibiting well-developed faces and edges and low aspect ratio can be obtained under hydrothermal conditions. The high symmetry of the MOF creates an ordered array of pores with uniform square openings exposed on the surface of all crystalline facets. Most importantly, the octahedral arrangement of benzene-1,4-dicarboxylic acid (BDC) ligands bound to the tetrahedral zinc metal centers provides a template for anchoring capping reagents with substituents oriented orthogonal to the square openings of pores. We expected that orthogonal binding was necessary to saturate metal centers on the surface with capping groups in order to block all pores.

Sealing MOF-5 using this approach requires capping reagents bearing functional groups capable of coordinating to zinc metal ions as well as substituents large enough to fully or partially cover the openings of pores, yet compact enough to permit commensurate binding at all coordination sites to ensure full coverage on the surfaces of crystals. Accordingly, triphenylacetic acid (TPAA), diphenylacetic acid (DPAA),

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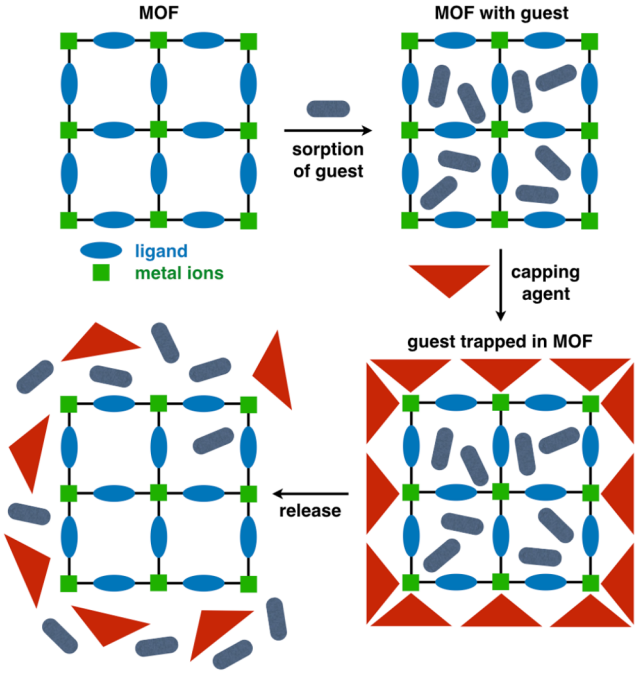
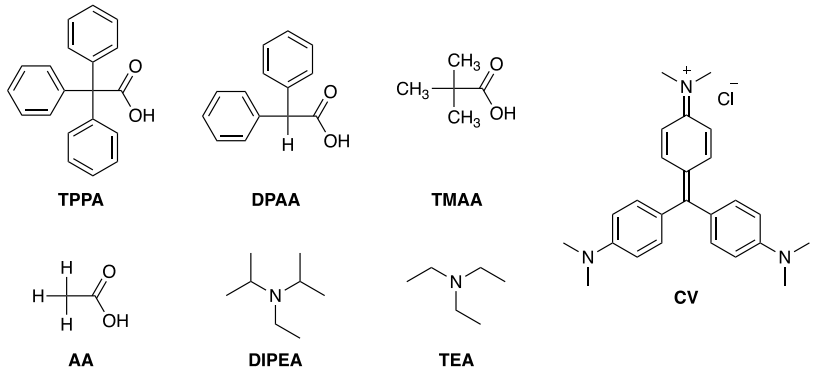
Scheme 1. Trapping of Molecular Guests in a MOF by Coordinating SterricallyDemanding Capping Groups on the Surface



trimethylacetic acid (TMAA), acetic acid (AA), diisopropylethylamine (DIPEA), and triethylamine (TEA) were used as capping reagents (Chart 1) to treat crystals of MOF-5 loaded with crystal violet (CV) as the guest. Carboxylic acids were chosen to anchor capping reagents due to compatibility with the existing modes of binding and coordination geometry of the framework. As shown in Figure 1A, the exterior of MOF-5 features zinc ions bonded to carboxylate groups of BDC, forming a reactive surface capable of coordinating carboxylic acids other than BDC. Studies of core−shell MOFs, or MOF-on-MOF systems, have established that seed crystals of MOF-5 readily template epitaxial growth of an outer shell of different carboxylate-based MOFs from solutions under hydrothermal and RT growth conditions.[5,10−12] Selective nucleation and growth of crystals of MOF-5 also has been demonstrated on the surface of self-assembled monolayers terminated with carboxylic acids that promote adhesion and subsequent nucleation by coordinating zinc ions.[13−15] Sealing with TEA and DIPEA also was examined to assess the effectiveness of monodentate Zn−N coordination toward capping and to determine whether 3° amines used as organic bases to promote coordination of carboxylic acids would compete in binding to MOF-5. We reasoned that a suitable guest for encapsulation should be aromatic, have high surface area to promote interaction with the aromatic surfaces on the interior of MOF-5, and have molecular dimensions small enough to diffuse within uncapped MOF-5 yet large enough for capping groups to prevent the guest from escaping the openings of pores. CV was selected as the guest accordingly because the aromatic structure features a large surface area and trigonal geometry that is relatively rigid with dimensions that allow diffusion of CV through the 10 Å openings of pores in MOF-5. In addition, the high extinction coefficient of CV permits release of CV from crystals of MOF-5 into solution to be observed visually and quantified spectroscopically. CV also exhibits relatively high solubility in the solvents diethylformamide and ethanol that were utilized for trapping and to quantify release of the guest.

It stands to reason that blocking of pores should be most effective for capping groups that occupy volumes closely matching the 12.9 Å spacing between the zinc clusters at the openings of pores in MOF-5. Shown in Figure 1, the trigonal triphenylmethyl headgroup of TPAA has an effective VDW rotational diameter of 12.4 Å that is compact enough to permit commensurate binding at metal centers, yet sterically demanding enough to reduce the aperture of pores significantly (Figure 1B,C). DPAA, TMAA, AA, DIPEA, and TEA have VDW rotational diameters varying from a maximum of 12.4 Å to a minimum of 4.9 Å (Figure 1D). Crystals of MOF-5 loaded with CV as guest were treated with those capping reagents to assess how decreasing the size of the substituents would impact coverage of pores and retention of CV. Considering that the MOF framework is 8.2 Å in width at the nodes of the metal centers, we expected that capping with TMAA, AA, DIPEA, and TEA would be ineffective at retaining CV within MOF-5 because substituents on those capping reagents are not sufficiently bulky to project outward over the backbone of the framework and reduce the aperture of pores. Although the steric demand of DPAA in principle should be similar to that of TPAA due to rotation of the diphenylmethyl group, it was unclear whether DPAA would be effective as a capping reagent with MOF-5 given that simultaneous alignment of the methine hydrogen atoms over pores should leave some pores open and not hinder diffusion of CV.

Chart 1. Capping Reagents and Crystal Violet (Guest)



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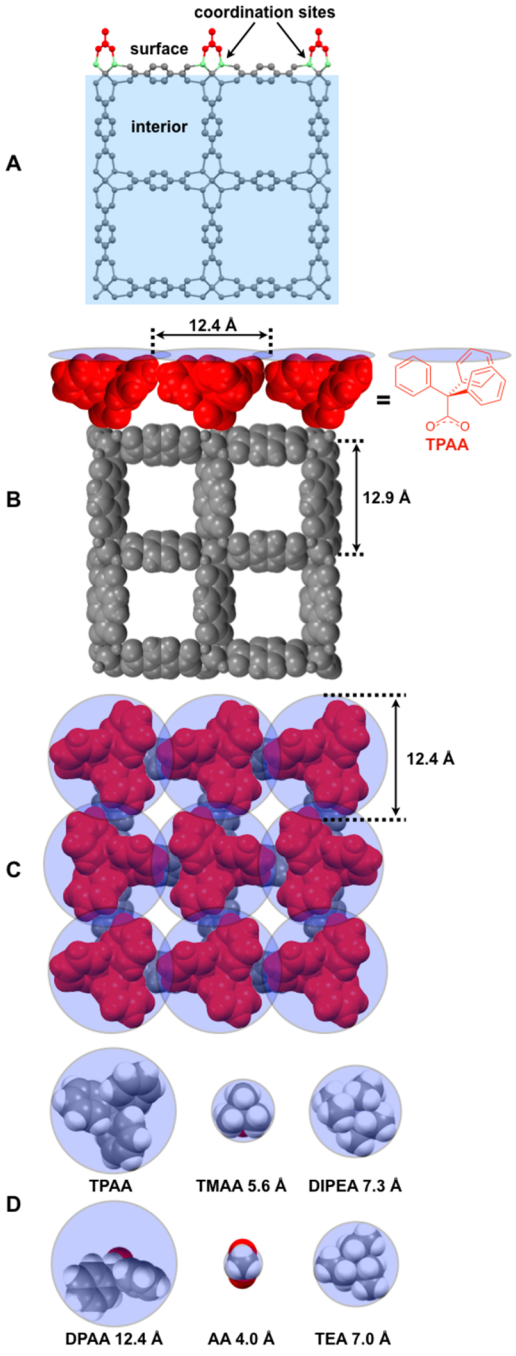

Figure 1. (A) Carboxylate groups (red) coordinated to Zn(II) ions (green) on the surface of MOF-5 (gray). Space-filling model of TPAA (red) docked on the surface of MOF-5 viewed from the side (B) and above (C). Blue circles represent the VDW rotational diameter of capping reagents (D).

EXPERIMENTAL SECTION

General Procedures. All reagents and solvents were purchased from Acros, Sigma-Aldrich, or TCI and used without further purification. Dimethylformamide (DMF) was dried over molecular sieves prior to use.

Synthesis of MOF-5. Two methods were used to prepare MOF-5.

Method 1. MOF-5 was prepared hydrothermally and handled according to established procedures with minor modifications.[16] Zinc nitrate hexahydrate (1.53 g, 5.2 mmol), benzene-1,4-dicarboxylic acid (0.70 g, 4.2 mmol), and 100 mL diethylformamide (DEF) were sealed in a 150 mL thick-walled glass pressure flask, heated in an oven at 100 °C for 48 h, and then cooled slowly over 6 h to room temperature to yield clear, colorless, cubic crystals. The DEF mother liquor was decanted and 50 mL of dry dimethylformamide (DMF) added to displace DEF and residual unreacted starting reagents and to ensure crystals of MOF-5 remained solvated prior to use.

Method 2. Attempts to prepare MOF-5 at room temperature were carried out following established procedures.[17] Zinc nitrate hexahydrate (1.52 g, 5.2 mmol), benzene-1,4-dicarboxylic acid (0.71 g, 4.2 mmol), triethylamine (0.47 g, 4.2 mmol), and 50 mL dry dimethylformamide (DMF) were stirred at room temperature for 30 min, during which a white precipitate formed. The fine white solid was isolated by vacuum filtration, washed with dry DMF, and stored in dry DMF prior to use. Unsuccessful attempts to prepare MOF-5 at room temperature by method 2 using wet DMF (not dried over molecular sieves) as the solvent for synthesis and washing also produced a white solid.

Characterization of Crystals of MOF-5. Samples of crystals of MOF-5 were characterized using a combination of optical microscopy, thermogravimetric analysis (TGA), and powder X-ray diffraction (PXRD). Bulk samples of crystals were isolated and examined under a low-power optical polarizing microscope to determine the morphology of crystals and to verify the homogeneity of samples. Samples of crystals of MOF-5 were analyzed by TGA to assess the porous behavior and thermal stability of MOF-5 using a TA Instruments 2950 Thermogravimetric Analyzer. Solvated crystals were removed from dry DMF, placed on filter paper, washed with several drops of ethanol, and quickly blotted dry. Solvated crystals of MOF-5 (12 mg) were loaded immediately to minimize the loss of guest solvent by evaporation, and heated from room temperature to 600 °C at a rate of 10 °C/min. PXRD data were collected on a Bruker-AXS D8-Advance diffractometer using Cu K_α radiation with X-rays generated at 40 kV and 40 mA. Bulk samples of solvated crystals were removed from the dry DMF solvent, ground wet in a mortar and pestle, placed into a sample holder, covered with parafilm, and then scanned at room temperature from 3° to 50° (2θ) in 0.05° steps at a scan rate of 2°/min. The experimental PXRD trace was compared to a simulated PXRD trace generated from the reported crystal structure of MOF-5 and previously reported PXRD traces of MOF-5 to confirm crystals contained MOF-5 and to assess homogeneity.[17,18]

Preparing CVMOF. Crystals of MOF-5 (75.0 mg, 97.4 μmol) stored in clean dry DMF were placed on filter paper and washed with several drops of ethanol, quickly blotted dry with filter paper, and transferred to a solution of crystal violet (CV) in ethanol (3 mL, 0.066 M, 90% saturated) that was covered and stored for 24 h at room temperature. Crystals of CVMOF were placed on filter paper, washed with several drops of ethanol, and blotted dry with filter paper prior to use.

Trapping CV in MOF-5 with Capping Reagents. Samples of crystals of CVMOF@TPAA, CVMOF@DPAA, CVMOF@TMAA, CVMOF@AA, CVMOF@TEA, and CVMOF@DIPEA were prepared using the following general procedure. Crystals of CVMOF (75.0 mg, 97.4 μmol), $Zn(NO_3)_2{\cdot}6H_2O$ (0.020 g, 0.67 mmol, 2 equiv), capping reagent (0.033 mmol, 1 equiv), and crystal violet (135 mg, 0.33 mmol) were added to diethylformamide (5 mL) to form a purple solution (0.066 M in CV) that was sealed in a 10 mL glass microwave vial, heated to 100 °C for 48 h, and then cooled to room temperature over 6 h. Capped crystals were washed with ethanol to remove external CV prior to analysis. Addition of zinc nitrate was necessary to promote coordination of capping reagents and prevent leakage of CV due to incomplete coverage.

General Spectroscopic Methods. UV−vis data were recorded on a Thermo Scientific Evolution 300 UV−vis spectrometer with Cary winUV software. Solutions were prepared using spectroscopic grade ethanol. UV−vis absorption spectra were obtained at room temperature using 1 cm quartz cuvettes containing 3 mL of solution.

Determination of CV Loading in CVMOF. The amount of CV contained in MOF-5 was quantified by digesting 2.0 mg of CVMOF in 20 mL of ethanol with 10 μL concentrated HCl. Absorbance at 580 nm of CV released was measured, and the concentration of CV was

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calculated with a calibration curve. Three trials showed an average loading capacity of 100 mg/g MOF-5, or 10 wt %.[1]

Release of CV from Capped MOFs. Capped crystals (7.0 mg) of CVMOF@TPAA, CVMOF@DPAA, CVMOF@TMAA, CVMOF@AA, CVMOF@TEA, and CVMOF@DIPEA were washed with ethanol to remove CV from the exterior, then dispersed in 3.0 mL ethanol, and the absorbance (450−650 nm) was recorded at 10 min intervals for 60 min.

RESULTS AND DISCUSSION

Growth and Analysis of MOF-5. Two methods to prepare MOF-5 were examined to confirm that crystals could be obtained under hydrothermal conditions (method 1) and under milder conditions at room temperature (method 2). Prior to carrying out capping experiments, it was important to determine which method produced homogeneous samples of MOF-5 reliably, to confirm whether using triethylamine (TEA) as the base at room temperature would promote coordination of carboxylic acid groups on benzene-1,4-dicarboxylic acid (BDC) to zinc ions consistent with MOF-5, and to establish a method for subsequently coordinating capping reagents to coordination sites on the surface of crystals of MOF-5. Crystals generated by both methods were stored in dry DMF prior to use to displace DEF and residual unreacted BDC and $Zn(NO_3)_2$ and to prevent desolvation of samples. Partially or fully desolvated MOF-5 left standing in air is known to react with water vapor and transform to a different porous phase with higher internal surface area and lower void volume due to partial hydrolysis of Zn−O bonds in the framework.[17]

PXRD traces for solids prepared under hydrothermal conditions (method 1) and at room temperature with TEA as base (method 2) are shown in Figure 2 with a simulated PXRD trace generated from the crystal structure of MOF-5.[18] The positions of peaks (2θ values) for solids prepared hydrothermally (Figure 2B) match those in the simulated trace (Figure 2A) and experimental PXRD traces for MOF-5 reported previously.[17,19] The positions of peaks in the PXRD trace for the solid prepared at room temperature using dry DMF match those in Figure 2A,B with the exception of two moderately intense peaks at 21.9° and 24.3°, indicating that MOF-5 formed as a mixture contaminated with a different crystalline phase in each of three different trials. Varying the amount of TEA systematically from 1 to 5 mol equiv relative to BDC using method 2 similarly produced contaminated mixtures containing some MOF-5 by PXRD analysis. The positions of peaks in the PXRD trace for the solid prepared by method 2 using wet DMF (Figure 2G) do not correspond to MOF-5, and are consistent with a different crystalline phase with higher surface area and lower void volume reported previously by Yan.[17] Shown in Figure 2F, the PXRD trace for crystals of MOF-5 grown hydrothermally using method 1 and then stored in wet DMF similarly matches the higher-surface-area phase. The latter two traces (Figure 2F,G) confirm that water present in untreated DMF is detrimental both to formation of MOF-5 via method 2 and to the stability of crystals of MOF-5 generated by method 1 when stored in DMF from which water has not been removed. Trace amounts of water introduced by addition of zinc nitrate hexahydrate do not appear to inhibit formation of MOF-5 or affect the stability of crystals of MOF-5. A stoichiometric amount of water (0.25 mol equiv relative to zinc) is necessary to promote coordination of zinc ions to oxygen during synthesis. On the basis of those findings, crystals of MOF-5 prepared hydrothermally and stored in dry DMF were used for capping experiments to ensure homogeneity. Coordination of capping reagents to the surface of crystals of MOF-5 also was carried out under hydrothermal conditions.

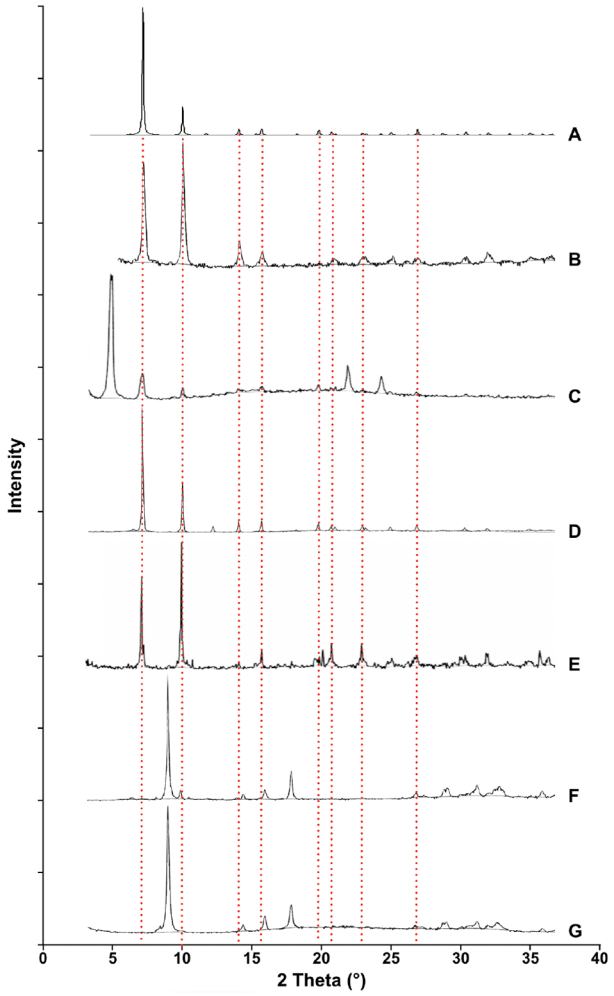

Figure 2. PXRD traces of crystals: (A) simulated from the crystal structure of MOF-5, (B) MOF-5 prepared hydrothermally at 100 °C (method 1), (C) solid prepared at room temperature with dry DMF (method 2), (D) CVMOF subjected to hydrothermal conditions for trapping CV in the absence of a capping reagent, (E) CVMOF@TPAA, (F) MOF-5 stored in wet DMF; (G) solid prepared at room temperature with wet DMF (method 2).

Thermal analysis was performed to confirm the porous behavior and stability of MOF-5 and to quantify the amount of guest solvent contained in the pores of MOF-5. Shown in Figure 3 is the TGA trace for solvated crystals of MOF-5 grown hydrothermally in DEF and then stored in dry DMF at room temperature. The reduction of 56 wt % by 270 °C corresponds to the loss of guest DMF and/or water contained within the MOF, followed by loss of 23 wt % above 450 °C, signifying decomposition of the MOF. That behavior is consistent with reported thermal properties for MOF-5.[17] To quantify the mass of guest solvent present in MOF-5 reproducibly, it was necessary to leave crystals in dry DMF prior to analysis to prevent loss of solvent from within the MOF. It also was important to minimize the amount of time crystals were in contact with filter paper to prevent wicking of

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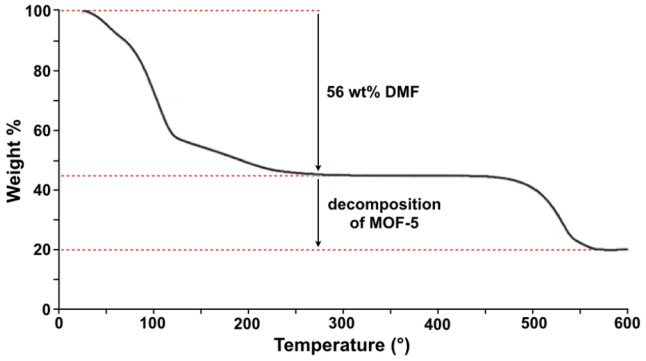

Figure 3. TGA trace of MOF-5 solvated with DMF.

the included solvent out of MOF-5. Crystals left on filter paper for 1 min after washing lost only 36 wt % of DMF by TGA, a reduction by 20 wt % compared to samples left in contact with filter paper for 10 s. The propensity of solvated MOF-5 to lose included guests rapidly via wicking is expected given the large 10 Å openings of pores exposed on the surface of crystals of MOF-5. Care must be taken when handling samples of MOF-5, particularly when quantifying loading or release of guests. For example, rapid leeching of crystal violet (CV) from uncapped crystals of MOF-5 loaded with CV (CVMOF) was observed visually on contact with filter paper and during subsequent washing of crystals. Consequently, the percent mass released of CV from uncapped CVMOF presented later (Figure 4) likely is conservative because it was necessary to remove dye from the exterior of samples by washing prior to spectral analysis.

Trapping of CV in MOF-5 with Capping Reagents. Shown in Figure 4 are profiles for the release of CV from

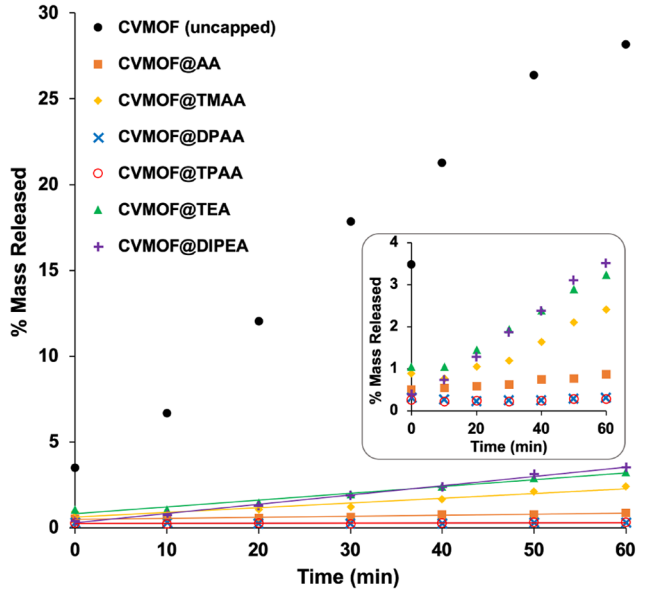

Figure 4. Profiles for release of crystal violet (CV) from uncapped CVMOF (black), CVMOF@AA (orange), CVMOF@TMAA (yellow), CVMOF@DPAA (blue), CVMOF@TPAA (red), CVMOF@TEA (green), and CVMOF@DIPEA (purple). Samples of capped crystals were dispersed in EtOH and changes in the absorbance at 580 nm were monitored over 60 min at room temperature. Inset: Profiles expanded between 0% and 4% mass released.

loaded samples of uncapped MOF-5 and MOF-5 capped with carboxylic acids and tertiary amines. Release of CV from uncapped CVMOF (Figure 4, black curve) is immediate, causing a perceptible change in hue from colorless to purple indicating that CV diffuses rapidly out of MOF-5 into ethanol with the release of 28% of CV after 60 min. Continued monitoring revealed that equilibrium in ethanol was established after 120 min with 45% of CV released.[1] These findings are consistent with the release of 52% of CV by CuBTC MOF reported previously,[20] and can be ascribed to comparable void volumes and surface areas in the two structures.[21] Retention of 55 wt % CV in MOF-5 at equilibrium suggests strong van der Waals and $\pi-\pi$ stacking interactions between the large aromatic surface area of CV and benzene rings in the framework, in addition to electrostatic attraction between the CV cations and carboxylate groups of BDC. Partial retention of CV by MOF-5 almost certainly is influenced by steric hindrance toward the diffusion of CV through channels. The VDW surface of channels undulates and narrows to 10 Å diagonally across the square pore opening of each unit cell as shown in Figure 5. Considering that the symmetric arms of CV

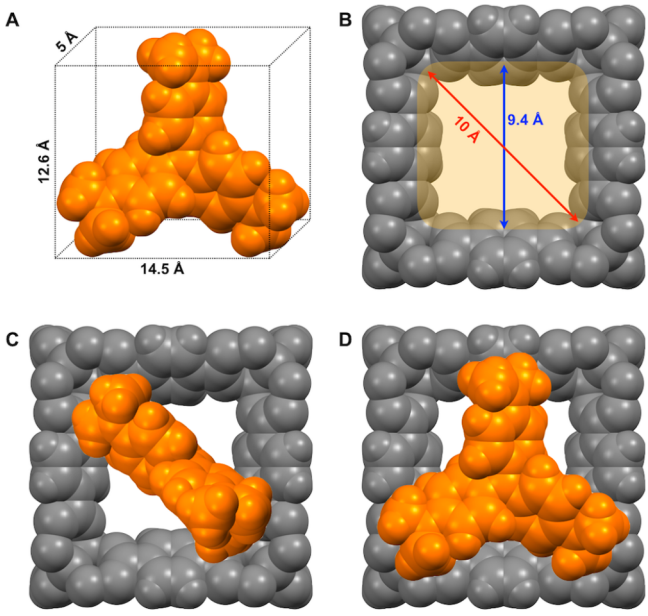

Figure 5. Space-filling models from the crystal structures of CV[22] (orange) and MOF-5[18] (gray) showing the dimensions of CV (A), the VDW surface and void space (yellow) of a channel (B), and CV docked at the pore opening of a channel in two different orientations (C and D).

are 8.5 Å in length and that a molecule of CV fits into a rectangular box with minimum dimensions of 5 Å × 12.6 Å × 14.5 Å (VDW contacts), molecules of CV are too large to diffuse through channels unimpeded (Figure 5C,D) without undergoing collision and reorientation at every unit cell.

In contrast to CVMOF, the profiles for release of CV from MOF-5 capped with carboxylic acids show that TPAA and DPAA both are highly effective at trapping CV within crystals of the MOF. After treating CVMOF with the capping procedure, crystals of CVMOF@TPAA and CVMOF@DPAA (Figure 4, red and blue curves) released no CV over 60 min. The initial value of 0.3% mass released for both CVMOF@TPAA and CVMOF@DPAA did not change over time (see inset) and is due to residual CV sorbed on the

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exterior of capped crystals that was not removed by washing with ethanol. Continued monitoring of CVMOF@TPAA showed no loss of CV after 5 h.[1] Total retention of CV by CVMOF@DPAA shows that the DPAA is as effective as TPAA at blocking diffusion of CV despite having just two phenyl groups. As shown in Figure 1D, the triphenylmethyl groups of TPAA have an effective VDW diameter of 12.4 Å due to rotation, yet do not cover the openings of pores completely. DPAA should provide lower coverage of pores relative to TPAA with some pores potentially remaining unblocked if the methine hydrogen on the head groups simultaneously rotate and align over pores. The ability of CVMOF@DPAA to retain CV completely suggests that free rotation of diphenylmethyl substituents on the surface is hindered sterically with an energetic barrier that favors conformations of DPAA at equilibrium that block all pores. The profiles for release of CV from MOF-5 treated with TMAA and AA show that trapping is not as effective with carboxylic acids featuring less sterically demanding *t*-butyl and methyl substituents as expected. CVMOF@TMAA and CVMOF@AA show net release of 1.5% and 0.4% of encapsulated CV after 60 min (Figure 4, yellow and orange curves), indicating that TMAA and AA were introduced during the capping procedure, but that coverage of pore openings on the surface of crystals was insufficient to prevent CV from slowly escaping. Similarly, the profiles for release of CV from CVMOF@TEA and CVMOF@DIPEA show a net release of 2.2% and 2.4% of encapsulated CV after 60 min, revealing that TEA and DIPEA introduced during the capping procedure only partially obstructed the openings of pores, allowing CV to diffuse slowly out of MOF-5 at rates only slightly faster than CVMOF@TMAA and CVMOF@AA.

Total inhibition of release of CV by TPAA and DPAA confirms that diffusion of guests out of MOF-5 can be prevented using carboxylic acids with substituents large enough to block the openings of pores exposed on the surface of crystals. These results support our hypothesis that effective capping requires a functional group capable of binding to zinc ions and a substituent small enough to permit commensurate binding at all coordination sites, but large enough to inhibit diffusion of guests. Retention of all CV indicates that coverage of crystals by TPAA and DPAA is complete, which supports commensurate binding of capping groups (Figure 1A−C), although the stoichiometry and geometry of coordination of carboxylic acids to zinc ions (e.g., monodentate, bidentate, etc.) at the surface of CVMOF@TPAA and CVMOF@DPAA is not known. Blocking of pores in MOF-5 could be explained by a different mechanism involving the formation of discrete coordination complexes within the channels of MOF-5 during the capping procedure. The ability of monocarboxylic acids to coordinate to zinc ions and form discrete structures such as paddlewheels is well established.[23] Blocking of pores in MOF-5 by discrete complexes containing TPAA or DPAA is unlikely considering the steric demand of the substituents and the lack of space within channels necessary to permit formation and to accommodate such large structures. It also is possible that blocking of pores could result from coordination of discrete complexes on the surface of MOF-5 instead of direct binding of molecules of TPAA or DPAA. Effective capping by such a mechanism necessarily would require coordination to BDC on the surface of MOF-5 to anchor discrete complexes over the openings of pores. Given the expected large dimensions of complexes containing TPAA or DPAA, commensurate 1:1 binding to BDC on the surface is unlikely and should leave the openings of some pores unblocked. Although this type of mechanism for capping cannot be completely ruled out for CVMOF@TPAA and CVMOF@DPAA, commensurate binding of TPAA or DPAA to coordination sites on the surface of MOF-5 more reasonably explains complete retention of CV.

Nonetheless, partial blocking of pores by direct coordination of molecules of TMAA and AA to the surface MOF-5 cannot explain the relatively slow rates at which CV diffuses out of CVMOF@TMAA, CVMOF@AA, CVMOF@TEA, and CVMOF@DIPEA compared to uncapped CVMOF. The rotational VDW diameters of *t*-butyl, methyl, triethylamine, and diisopropylamine substituents vary in diameter from 4.0 to 7.3 Å (Figure 1D). The backbone of the MOF is 8.2 Å in width at the nodes where carboxylate groups of benzene-1,4-dicarboxylic acid (BDC) coordinate to zinc ions. Accordingly, molecules of TMAA, AA, TEA, and DIPEA bonded to coordination sites on the surface of the crystals do not have enough steric bulk to project outward over the openings of pores and retard diffusion of CV out of pores. The observed slow leakage of CV from those capped MOFs likely can be explained by the presence of discrete coordination complexes either lodged within channels or coordinated to the surface that are of sufficient size to significantly reduce the aperture of pores. Formation of discrete complexes during the capping procedure can be expected considering that zinc ions and capping reagents are present in considerable excess relative to the available surface area of crystals of MOF-5 in order to promote capping, and that some free zinc ions and capping reagents are present within channels since coordination is reversible at equilibrium under hydrothermal conditions. In contrast to TPAA and DPAA capping reagents, TMAA, AA, TEA, and DIPEA are relatively compact with dimensions small enough to coordinate to free zinc ions and form discrete complexes within channels in MOF-5. Shown in Figure 6A,B as illustrative examples are paddlewheels of Zn_2AA_4[24] and Zn_2TMAA_4[25] docked over the pores of MOF-5, illustrating that such complexes can fit within the larger general void space in the interior of the unit cell but contact the framework at the smaller openings of pores. Similarly, discrete complexes that form in solution could coordinate to BDC projecting from the surface of the MOF, thereby partially blocking the openings of pores, as shown illustratively in Figure 6C,D. Although both of these mechanisms would account for the significantly reduced rate for leaking of CV from CVMOF@TMAA, CVMOF@AA, CVMOF@TEA, and CVMOF@DIPEA compared to uncapped CVMOF, the specific mechanism for the partial blocking of pores in those capped systems currently is not known.

It should be noted that attempts to introduce capping reagents without also adding zinc nitrate were unsuccessful. Leaking of CV was immediately evident visually when crystals of CVMOF were treated with capping reagents, but no zinc were placed into ethanol. That finding indicates that the carboxylic acids used as capping reagents do not appear to protonate BCD appreciably, leading to exchange with capping reagents on the surface. The lack of exchange is not surprising considering that the acidity of BDC (pK_a 3.5) exceeds that of TPAA (pK_a 4), which has the greatest acidity of the capping reagents (pK_as 4.0−5.0). Accordingly, we found that addition of free zinc nitrate is necessary to promote coordination of capping reagents and ensure maximum coverage on the surface of crystals of CVMOF during the capping procedure.

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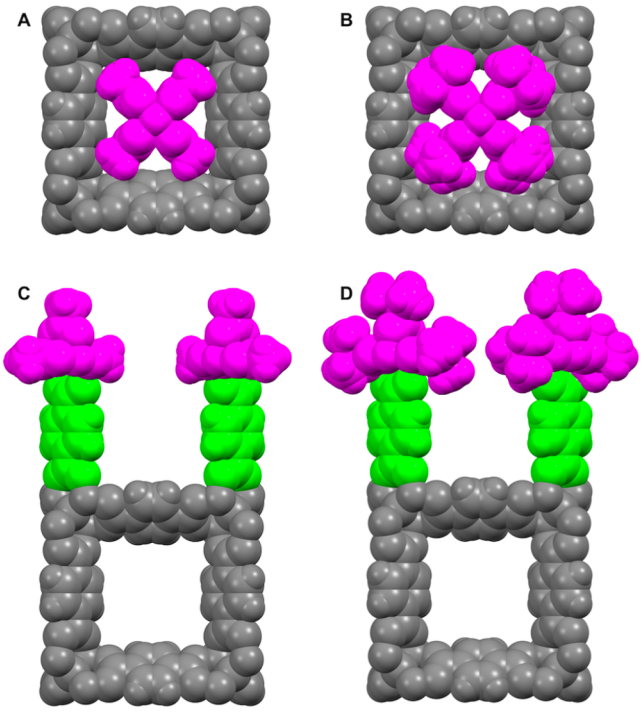

Figure 6. Space-filling models showing paddlewheels from crystal structures of Zn_2AA_4[24] (A) and Zn_2TMAA_4[25] (B) docked at the pore opening of MOF-5. Paddlewheels of Zn_2AA_3BDC (C) and Zn_2TMAA_3BDC (D) docked on BDC on the surface of MOF-5. Colors: Paddlewheels (magenta), BDC (green), and MOF-5 (gray).

Crystals of CVMOF and CVMOF@TPAA were examined by PXRD to ensure that the crystalline structure of MOF-5 was not affected by the capping procedure or addition of acidic trapping reagents such as TPAA. As shown in Figure 2D, the positions of peaks in the PXRD trace for CVMOF match those in the simulated and experimental traces for MOF-5 (Figure 2A,B) with no evidence of spurious peaks or broadening of peaks signifying phase changes or loss of crystallinity caused by storage of crystals in dry DMF prior to use, sorption of CV guest, or re-exposure of crystals to hydrothermal conditions. The PXRD trace for CVMOF@TPAA (Figure 2E) similarly matches the experimental trace for MOF-5 prior to capping indicating that the crystalline structure and phase were not affected by exposure to the acidic carboxylic acid group of TPAA under hydrothermal conditions. As mentioned previously, epitaxial growth of different carboxylate-based MOFs on the surface of MOF-5 has been demonstrated by others under hydrothermal and RT conditions without altering the structure of MOF-5.[5,10−12]

CONCLUSIONS

Use of carboxylic acids as capping reagents provides a convenient means to retain guests within MOF-5 by blocking the openings of pores on the surface of crystals. Complete retention of CV by CVMOF@TPAA and CVMOF@DPAA demonstrating this approach can be quite effective, provided that the steric demand of substituents is tailored to allow saturation of coordination sites on the surface of crystals and maximize coverage of underlying pore openings. These findings demonstrate the proof-of-concept that molecular trapping and storage in other MOFs should be possible, provided that the openings of pores are not overly large and appropriate capping reagents are utilized. Although the structural mechanism responsible for partial blocking of pores in CVMOF@TMAA, CVMOF@AA, CVMOF@TEA, and CVMOF@DIPEA remains uncertain, the observed reduction in the rate at which CV escapes after introducing TMAA, AA, TEA, and DIPEA suggests that treatment with smaller capping reagents may prove useful as a way to reduce the openings of pores post-synthetically without inhibiting diffusion altogether. We presently are expanding on this work by investigating other MOF systems with noncubic architectures, coordination geometries, and pore structures to assess the generality of surface capping and refine our understanding of the requirements, mechanisms, and limitations of this method. Ultimately, we expect to move beyond simple trapping and storage of guests by establishing that the aperture of pores can be contracted predictably as a means to gate and regulate molecular diffusion on the surfaces of MOF particles.

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Notes

The authors declare no competing financial interest.

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