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Proline Functionalization of the Mesoporous Metal–Organic Framework DUT-32

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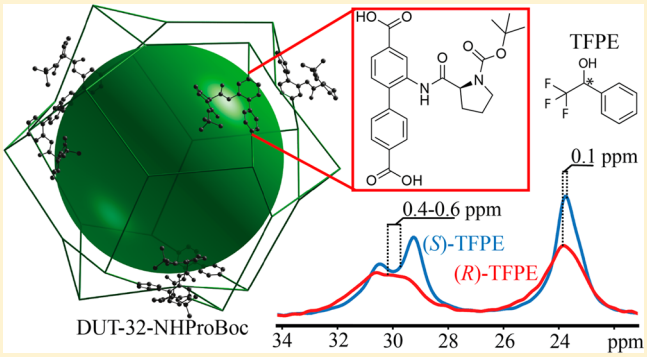
Supporting Information

ABSTRACT: The linker functionalization strategy was applied to incorporate proline moieties into a metal–organic framework (MOF). When 4,4′-biphenyldicarboxylic acid was replaced with a Boc-protected proline-functionalized linker (H_2**L**) in the synthesis of DUT-32 (DUT = Dresden University of Technology), a highly porous enantiomerically pure MOF (DUT-32-NHProBoc) was obtained, as could be confirmed by enantioselective high-performance liquid chromatography (HPLC) measurements and solid-state NMR experiments. Isotope labeling of the chiral side group proline enabled highly sensitive one- and two-dimensional solid-state ^{13}C NMR experiments. For samples loaded with (*S*)-1-phenyl-2,2,2-trifluoroethanol [(*S*)-TFPE], the proline groups are shown to exhibit a lower mobility than that for (*R*)-TFPE-loaded samples. This indicates a preferred interaction of the shift agent (*S*)-TFPE with the chiral moieties. The high porosity of the compound is reflected by an exceptionally high ethyl cinnamate adsorption capacity. However, postsynthetic thermal deprotection of Boc–proline in the MOF leads to racemization of the chiral center, which was verified by stereoselective HPLC experiments and asymmetric catalysis of aldol addition.



INTRODUCTION

It has been widely accepted that enantiomers of the same chiral compound may show quite different bioactivities, as well as different physical, chemical, pharmacological, and toxicological properties. Therefore, their preparation and especially analysis are important in many fields of science. To obtain a chiral heterogeneous selector/catalyst, usually the porous substrates are coated or immobilized with proteins, enzymes, oligosaccharides, or polysaccharides. Because important progress has been made in the field of porous materials through the development of metal–organic frameworks (MOFs), this material class is also considered to be very promising for the design and development of a new generation of chiral porous materials. The incorporation of chiral groups by ligand or cluster functionalization or the synthesis of chiral MOFs from achiral building blocks generates homochiral materials. Inspired by homogeneous chiral catalysis, the implementation of well-established chiral catalytically active groups as linkers or as side groups of the framework backbone has been reported for a variety of MOFs.[1−5] One common organocatalytic group for a wide range of asymmetric reactions is proline. Up to now, there are only a few homochiral MOFs with proline functionalities reported. So far, the incorporation of proline could be performed by coordination on open metal sites in MIL-101,[6] postsynthetic click reaction,[7] or postsynthetic amide coupling.[8] Furthermore, the incorporation of proline by chiral functionalization of the linker before MOF synthesis was carried out by Telfer et al.[9] The reported homochiral material could be used as heterogeneous chiral catalysts in asymmetric aldol reactions. The important point in the synthesis of enantiopure (proline-containing) MOFs is to avoid the racemization that can occur particularly under thermal conditions. Therefore, stereochemical investigation of the MOFs after synthesis plays an important role in characterization of the materials with respect to the desired applications.

In this work, we present the synthesis of the proline-functionalized homochiral MOF DUT-32-NHProBoc (DUT - Dresden University of Technology) by the incorporation of a chiral proline side group into the ligand. Because the direct MOF synthesis using a proline-substituted linker was not successful, the *N*-(*tert*-butoxycarbonyl) (Boc) protective group was introduced to prevent side reactions during the MOF formation. The enantiomeric excess (*ee*) of DUT-32-NHProBoc, as well as deprotection conditions, was studied by enantioselective high-performance liquid chromatography (HPLC) measurements, X-ray diffraction (XRD), and liquid- and solid-state NMR spectroscopy. Selective ^{15}N- and ^{13}C-

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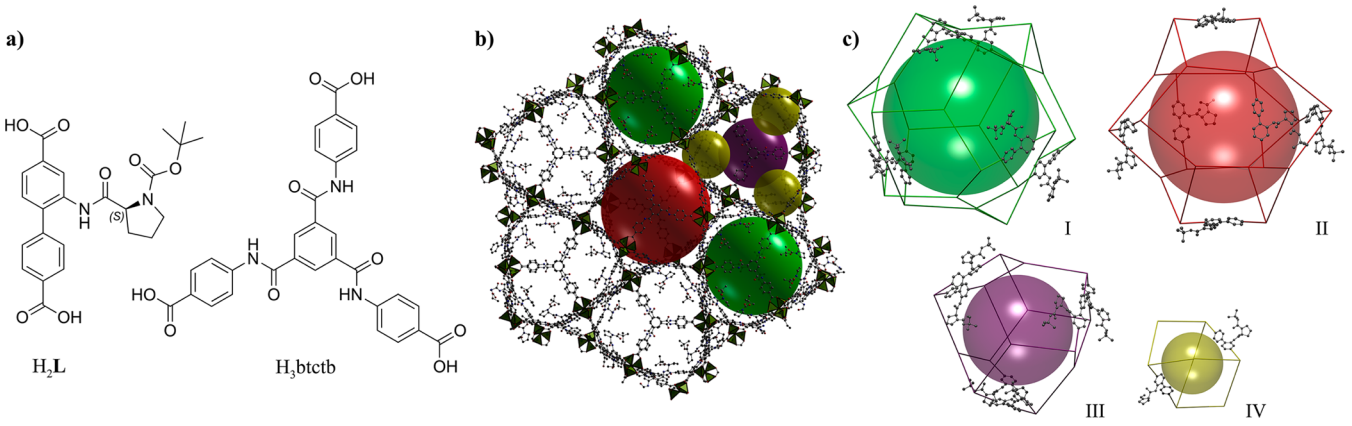


Figure 1. (a) Linker used for the synthesis of DUT-32-NHProBoc. (b) Crystal structure of DUT-32-NHProBoc. (c) Simplified representation of four pore types, highlighting bordering chiral ligand L^{2-}.

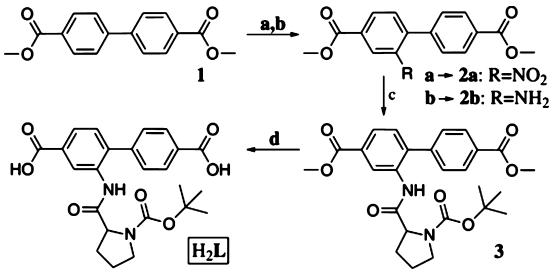
isotope labeling of the chiral side group of DUT-32-NHProBoc allows for comprehensive solid-state NMR spectroscopic investigations. An enantioselective interaction between the chiral MOF and the chiral guest molecule 1-phenyl-2,2,2-trifluoroethanol (TFPE) could be detected, which results, for example, in different mobilities for the two TFPE enantiomers. In order to load DUT-32-NHProBoc with TFPE, an elaborate exchange method was developed that enables fast and accurate monitoring of the solvent exchange in order to ensure complete replacement of *N*,*N*-dimethylformamide (DMF) by TFPE.

RESULTS AND DISCUSSION

DUT-32-NHProBoc Synthesis and Characterization. The highly porous MOF compound denoted as DUT-32 exhibits four different pores, including mesopores and micropores with dimensions of 30 × 40, 28 × 32, 20 × 26, and 14 × 18 Å (considering van der Waals radii of the atoms; Figure 1b).[11] The high porosity and open character of the framework are beneficial for the desired catalytic application. The structure contains Zn_4O clusters as well as two types of linkers: tritopic 4,4′,4′-[benzene-1,3,5-triyltris(carbonylimino)]trisbenzoate ($btctb^{3-}$) and ditopic 4,4′-biphenyldicarboxylate ($bpdc^{2-}$). The overall framework composition is given by the formula $Zn_4O(btctb)_{4/3}(bpdc)$.

Functionalization of the ditopic linker with a chiral NHProBoc group (synthesis of H_2L) was performed in three steps starting from dimethyl biphenyl-4,4′-dicarboxylate in analogy to the procedure described by Telfer et al.[9] (Scheme 1). First, the amino group was introduced following the method of Petushok et al.[10] with slight modifications. The introduction of the chiral group was performed by an amide coupling reaction with the reagents *N*,*N*′-dicyclohexylcarbodiimide (DCC) and hydroxybenzotriazole (HOBt). The proline derivative *N*-(*tert*-butoxycarbonyl)-L-proline (Boc-Pro-OH) was used as an enantiopure compound obtained from a commercial source. Furthermore, the insertion of isotope-labeled L-proline was carried out by the synthesis of the Boc-Pro*-OH compound using L-proline-$^{13}C_5$,^{15}N, giving H_2L*.

Scheme 1. Synthesis of Ligand H_2L in Three Steps: (a) HNO_3, H_2SO_4, 0 °C, 30 min; (b) Fe, HOAc, 50 °C, 12 h; (c) Boc-Pro-OH or Boc-Pro*-OH, HOBt, DCC, DCM, rt, 4 days; (d) aqueous KOH, THF, 50 °C, 19 h



The chiral MOF (further denoted as DUT-32-NHProBoc) was synthesized using reaction conditions similar to those applied by Grünker et al.[11] for the synthesis of DUT-32. A mixture of the trigonal ligand H_3btctb and the linear ligand H_2L or H_2L* in *N*,*N*-diethylformamide (DEF) was heated up to 100 °C for 48 h, giving rod-shaped crystals.

Analysis of the product by single-crystal and powder XRD confirmed the formation of a structure with a network isoreticular to DUT-32. The crystal structure of DUT-32-NHProBoc was determined using a combination of single-crystal XRD and modeling. The unit cell parameters as well as the space group were determined from the single-crystal XRD data. Because of the homochirality of the framework, the $P6_3$ space group was chosen for the structure solution. Unfortunately, only the atoms belonging to the DUT-32 backbone could be localized from the diffraction data; therefore, the NHProBoc groups in the *S* configuration were modeled on each $bpdc^{2-}$ linker in the structure using *Material Studio 5.0* because ^{1}H NMR studies of the material after mild decomposition in DCl demonstrated preservation of the side group of the linker H_2L during MOF synthesis.

In order to investigate preservation of the enantiomeric purity of proline during linker and MOF synthesis, an HPLC method with a stereoselective column was established [see the Supporting Information (SI), section 8]. The *ee*-value of H_2L after three steps of linker synthesis was determined as 99%. To examine the influence of thermal treatment on the *ee*-value of the linker during MOF synthesis, the supernatant solution after MOF synthesis was investigated. The measurements gave an *ee*-value beyond 90% for H_2L, indicating little influence of the synthetic conditions on the stereogenic center of the linker itself.

To identify the temperature range, where racemization can by induced thermally, further experiments were carried out. A solution of the linker H_2L in DMF (c = 0.013 mol L^{-1}) was heated at 100, 120, and 140 °C, and the enantiomeric purity

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was monitored by HPLC. The measurements of the solutions at 100 and 120 °C after defined treatment times show only low variations in the *ee*-value. Temperatures of 140 °C cause a distinctive decrease of the *ee*-value after 1 day or longer (Figure 2). These results confirm the assumption that the *ee*-value of

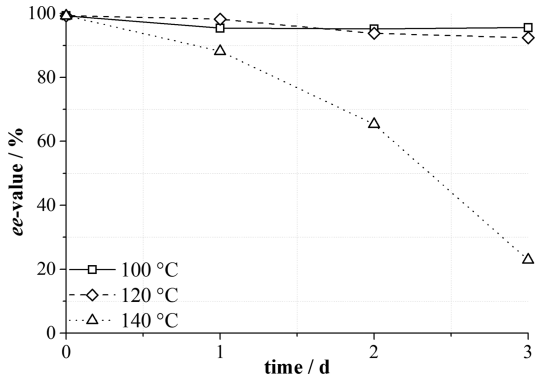

Figure 2. *ee*-value evolution of H_2**L** determined by enantioselective HPLC measurements after heating in DMF at 100, 120, and 140 °C.

the incorporated H_2**L** linker should be unchanged under the synthesis conditions chosen for DUT-32-NHProBoc (c = 0.013 mol L^{-1}, 100 °C, DEF).

Recently, a novel method for investigations of chirality in MOFs by solid-state NMR spectroscopy was developed, based on sample loading with chiral shift agents.[12] Interactions of enantiomerically pure shift agents with substrate isomers may induce nonequivalent diastereomeric complexes depending on the chirality of the substrates.[13−19] The new method was applied to DUT-32-NHProBoc, and the chiral solvating agent TFPE was used. The ^{13}C cross-polarization magic-angle-spinning (CP MAS) NMR spectra of DUT-32-NH($^{13}C_5$,^{15}N)ProBoc loaded with (*S*)- and (*R*)-TFPE (Figure 3) exhibit two characteristic differences: (i) In analogy to previous observations made on chirally modified UMCM-1,[12] enantioselectively induced ^{13}C chemical shifts are observable. The chemical shift differences induced by the two different enantiomers of TFPE are on the order of 0.1−0.6 ppm. The most pronounced differences are detected at the chiral center of L^{2-} and at its α position (C atom positions 4 and 2). The differences are less pronounced for the C atom positions 1 and 3.

This demonstrates the local and regioselective character of the host−guest interactions present between DUT-32-NH-($^{13}C_5$,^{15}N)ProBoc and TFPE. (ii) Remarkably, the line widths also exhibit pronounced differences for the samples loaded with the two different enantiomers, (*S*)- and (*R*)-TFPE. All signals are considerably narrower for the (*S*)-TFPE-loaded sample than the (*R*)-TFPE-loaded sample. This effect indicates a more defined state and/or lower mobility (stronger interaction) for the chiral proline side groups with (*S*)-TFPE-loaded DUT-32-NH($^{13}C_5$,^{15}N)ProBoc.

To substantiate the latter conclusion further, CP built-up curves were measured (see Figure 4). CP is sensitive to the presence of motional processes.[20] Indeed, a slightly faster CP built-up curve and a slower CP decay curve are observed for all ^{13}C CP MAS NMR signals of DUT-32-NH($^{13}C_5$,^{15}N)ProBoc loaded with (*S*)-TFPE. This behavior also points toward a less mobile state of the chiral side groups in the presence of (*S*)-TFPE compared with their state in (*R*)-TFPE-loaded samples. However, the observed differences are relatively small. Therefore, a further experiment was performed. ^{1}H-driven $^{13}C-^{13}C$ spin-diffusion (PDSD) spectra could be measured because the ^{13}C-labeled proline side groups provide sufficient signal intensity (see Figure 5). For a mixing time of 10 ms, a significant difference between the (*S*)- and (*R*)-TFPE-loaded samples occurs: Detectable cross peaks between atom positions 4 and 5 (chiral center and C═O group) appear for the (*S*)-TFPE-loaded sample. In contrast, no such cross peaks occur for the (*R*)-TFPE-loaded sample. This difference is an additional indication for a less mobile chiral L-proline side group in the (*S*)-TFPE-loaded DUT-32-NH($^{13}C_5$,^{15}N)ProBoc. The lower degree of mobility gives rise to stronger magnetic dipole−dipole interactions in the case of DUT-32-NH($^{13}C_5$,^{15}N)-ProBoc + (*S*)-TFPE, resulting in observable cross peaks in the $^{13}C-^{13}C$ PDSD spectrum.

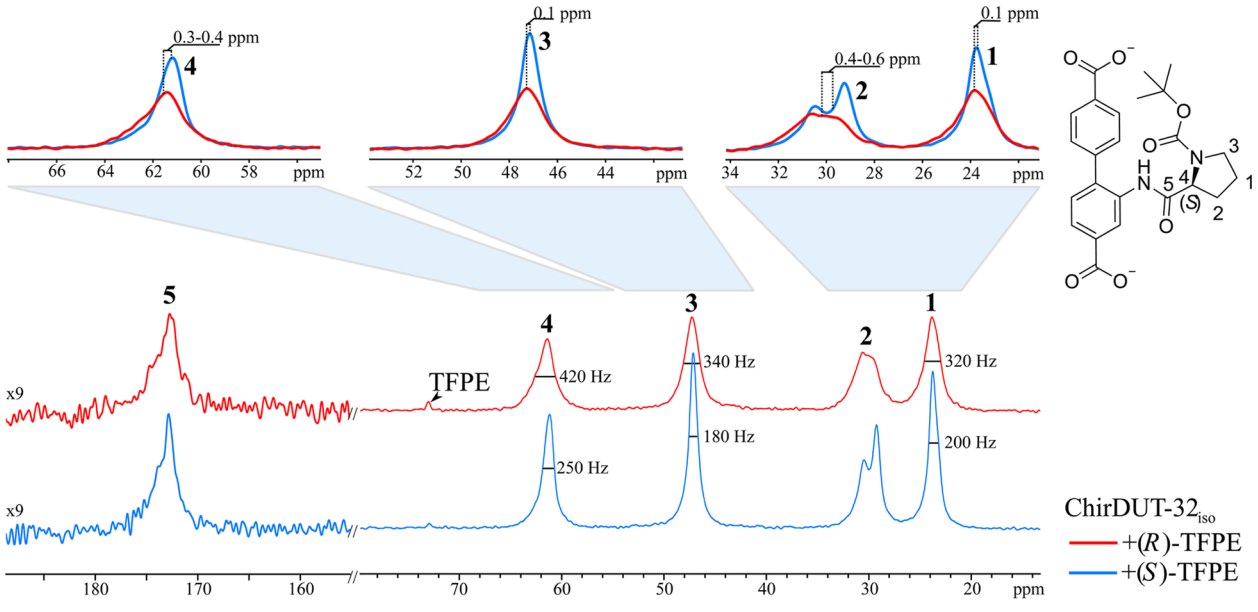

Figure 3. ^{13}C CP MAS NMR spectra of DUT-32-NH($^{13}C_5$,^{15}N)ProBoc loaded with (*S*)- and (*R*)-TFPE.

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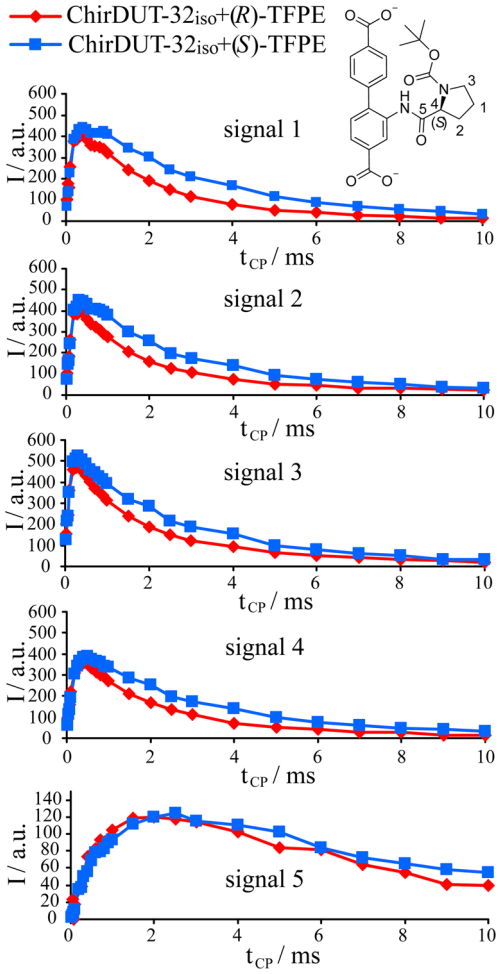

Figure 4. $^{1}H-^{13}C$ CP built-up curves of DUT-32-NH($^{13}C_5$,^{15}N)-ProBoc loaded with (*S*)- and (*R*)-TFPE. t_{CP} denotes the CP contact time.

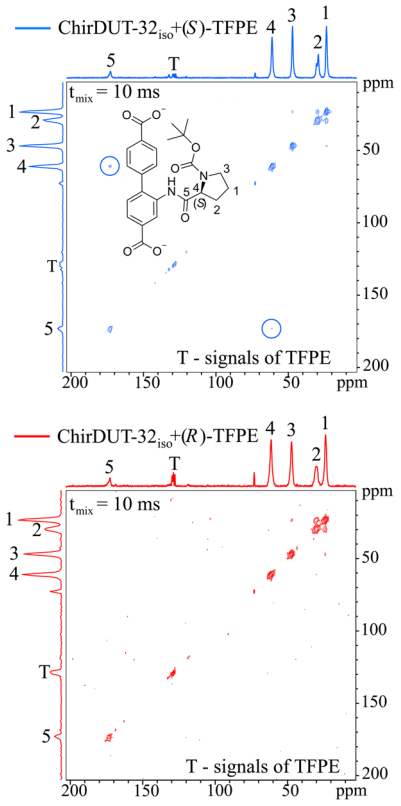

Figure 5. ^{1}H-driven $^{13}C-^{13}C$ PDSD spectra of DUT-32-NH-($^{13}C_5$,^{15}N)ProBoc loaded with (*S*)- and (*R*)-TFPE.

Porosity and Catalytic Activity. The pore sizes in the DUT-32-NHProBoc framework in comparison to those of DUT-32 are considerably influenced by the flexible proline groups of the $\mathbf{L}^{2-}$ because these groups protrude into the pores of the structure. The amount of chiral groups per pore can vary because of the flexibility of the side groups. Actually, each pore (except for the smallest micropore) can comprise the chiral group (Figure 1c). This ensures interaction of the side groups with potential substrates in the pores, which is necessary for the stereoselective properties of the material.

To measure the porosity of DUT-32-NHProBoc using N_2 gas as the probe, the activation procedure optimized for DUT-32 reported by Grünker et al.[11] was applied to the chiral-functionalized material DUT-32-NHProBoc. The synthesis solvent was exchanged to acetone or amyl acetate prior to supercritical drying. The samples were soaked in liquid CO_2 over 7 days (see the SI). Unfortunately, drying led to a loss of crystallinity and low nitrogen uptake of about 150 $cm^3\ g^{-1}$ for the acetone-exchanged sample and 190 $cm^3\ g^{-1}$ for the amyl acetate exchanged sample at 77 K (see the SI, Figure S3). Theoretical calculations show that the introduction of chiral groups into DUT-32 should not lead to a significant decrease of the porosity (ca. 14%). The theoretical pore volume of DUT-32-NHProBoc is 2.76 $cm^3\ g^{-1}$.

Because the porosity and accessibility of the pores for substrates in solution is of great importance for envisioned applications, liquid-phase adsorption experiments were performed. To probe the accessibility of the network for large substrates, the dye adsorption experiments were carried out using Nile Blue and Reichardt's dye as probe molecules in dichloromethane (DCM) as the solvent. Both compounds can be adsorbed on DUT-32-NHProBoc (see the SI, section 2). To quantify the specific pore volume, the procedure of Henschel et al.[21] determining the adsorption capacity of ethyl cinnamate in *n*-heptane was applied to the DUT-32 and DUT-32-NHProBoc materials and the adsorbed amounts were compared to the uptake published for other MOFs. DUT-32-NHProBoc is able to adsorb 610 mg g^{-1} ethyl cinnamate. This is comparable with the uptake measured for DUT-32 of 447 mg g^{-1} (Figure 6). Despite the lower pore volume, the chiral framework shows a higher adsorption capacity than DUT-32, indicating additional interactions of the chiral side groups of $\mathbf{L}^{2-}$ with ethyl cinnamate molecules. The effect is comparable to the effect arising from additional interactions of the substrate with open metal sites of the cluster in MIL-101 or Pd@MIL-101.

For catalytic applications, it is necessary to remove the protecting Boc group from DUT-32-NHProBoc. Usually deprotection can be performed acidolytically or thermally. Because the Zn-based MOFs are not acid-tolerant, thermal treatment was chosen as the deprotection method. Thermogravimetric analysis of $H_2\mathbf{L}$ indicates decomposition of the Boc group at about 120 °C and decomposition of the DUT-32-NHProBoc framework at temperatures beyond 300 °C (see the SI). Therefore, a temperature range of 120−170 °C was tested for deprotection of the material (see the SI, Table S1). Similar to the method of Telfer et al.[9] used for deprotection of

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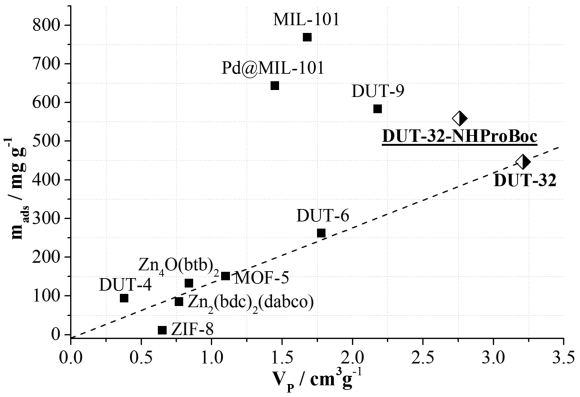
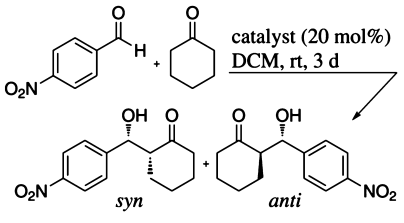


Figure 6. Adsorption of ethyl cinnamate in *n*-heptane on selected MOFs (reported by Henschel et al.[21]) and on DUT-32 and DUT-32-NHProBoc. [The total pore volume V_p for both DUT-32 systems was calculated theoretically (see the SI).]

IRMOF-ProBoc, the Boc group of DUT-32-NHProBoc was tested to be removed by microwave heating in DMF without acidic or basic additives (see the SI, Table S1, trial 2). However, the ^{1}H NMR studies show just a low degree of deprotection (about 30%), and structural changes caused by this treatment were observed by powder XRD. Further deprotection investigations were performed using conventional thermal treatment. An increasing deprotection degree of chiral linker $\mathbf{L}^{2-}$ was found by increasing the temperature or thermal treatment time in DMF and also by changing the structure of the crystalline phase. Therefore, mesitylene was tested as an alternative solvent. Using mesitylene, no change in the structure was observed. Furthermore, an increasing degree of deprotection with increasing temperature could be achieved. The optimum deprotection conditions to obtain pure DUT-32-NHPro are heating at 170 °C for 72 h in mesitylene, which was confirmed by ^{1}H NMR studies and powder XRD measurement (see the SI, Figures S6 and S7). Keeping in mind that racemization of the protected linker $H_2\mathbf{L}$ occurs at temperatures higher than 140 °C (see Figure 2), it is evident that the enantiomeric purity of the MOF might be affected under such deprotection conditions.

To test the enantioselectivity and catalytic activity of deprotected DUT-32-NHPro, asymmetric aldol addition between 4-nitrobenzaldehyde and cyclohexanone was performed as a test reaction (Scheme 2). The reaction process was monitored by qualitative chiral HPLC measurement (see the SI). A filtration test (after 48 h of reaction time) suggests that DUT-32-NHPro is a true heterogeneous catalyst for aldol addition. Unfortunately, the material catalyzed the aldol reaction with no specific stereoselectivity between *syn* and *anti* adducts. These results additionally indicate that racemization occurs during the deprotection process of DUT-32-NHProBoc.

Scheme 2. Asymmetric Aldol Addition between Cyclohexanone and 4-Nitrobenzaldehyde Catalyzed by DUT-32-NHPro with 20 mol % Active Proline Side Groups



CONCLUSIONS

A chiral MOF DUT-32NHProBoc could be synthesized using a Boc-proline-functionalized linker. The structure shows a high capacity in liquid-phase adsorption with ethyl cinnamate, confirming the high porosity of the framework comparable to that of achiral DUT-32. Stereoselective HPLC experiments confirmed the linker and MOF synthesis while the chirality was retained at the stereogenic center. Investigations on deprotection of the Boc group showed racemization effects due to high temperatures during the reaction. An asymmetric aldol reaction was used to verify these assumptions. Modification of the linker synthesis using isotope-labeled Boc−proline gave a $^{13}C_5$,^{15}N-marked linker for MOF synthesis. In order to investigate the interaction of chiral-isotope-labeled functional groups in DUT-32-NHProBoc with chiral guest molecules, the enantiomers of the chiral shift reagent TFPE were separately infiltrated and examined by solid-state NMR methods, using ^{13}C CP MAS NMR, CP built-up curves, and spin-diffusion experiments. In summary, these solid-state NMR studies are pointing toward a low degree of mobility of the chiral side groups in (*S*)-TFPE-loaded samples, i.e., a preferred interaction of (*S*)-TFPE with the functional groups of the MOF inner surface, demonstrating the value and variable applicability of this monitoring technique.

EXPERIMENTAL SECTION

General Remarks. If not stated else, the reactions were carried out under air. Chemicals were used as received without further preparation.

Synthesis of Dimethyl-2-nitro-1,1′-biphenyl-4,4′-dicarboxylate (2a). To a solution of concentrated sulfuric acid (820 mL) was added slowly dimethyl-1,1′-biphenyl-4,4′-dicarboxylate (76 g, 0.28 mol). Under stirring, the solution was cooled to −20 °C. Separately nitration acid was prepared by mixing a nitric acid solution (26.9 g, 65 wt %) with concentrated sulfuric acid (120 mL) at 0 °C. The cooled nitration acid was added to a precursor solution with a dropping funnel in a time range of 3 h. The reaction temperature was kept under −10 °C and stirred for 1 h after the complete addition of nitration acid. The reaction was interrupted by mixing of the solution with 1 L of ice water. The resulting white solid was dissolved in DCM, and the aqueous phase was extracted by DCM several times. Washing of the combined organic layers with saturated aqueous sodium hydrogen carbonate, drying over magnesium carbonate, and evaporation under reduced pressure gave a red solid. Purification by recrystallization in a 1:1 mixture of ethyl acetate and *n*-hexane completed the synthesis of a white solid. Yield: 65 g (0.2 mol, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 3.88 (s, 3H), 3.94 (s, 3H), 7.55 (dd, $^3J_1$ = 1.89 Hz, $^3J_2$ = 8.51 Hz, 2H), 7.76 (d, $^3J_1$ = 7.88 Hz, 1H), 8.05 (dd, $^3J_1$ = 1.89 Hz, $^3J_2$ = 8.51 Hz, 2H), 8.30 (dd, $^3J_1$ = 1.57 Hz, $^3J_2$ = 9.77 Hz, 1H), 8.50 (d, $^3J_1$ = 1.57 Hz, 1H).

Synthesis of Dimethyl-2-amino-1,1′-biphenyl-4,4′-dicarboxylate (2b). **2a** (10.3 g, 0.03 mol) was dissolved in 300 mL of acetic acid (HOAc). To the solution was added iron powder (18.2 g, 0.32 mol, 11 equiv), and the mixture was stirred at 50 °C for 14 h. The suspension was filtered, and the filtrate was partly dried in vacuum. After washing with saturated aqueous sodium hydrogen carbonate, the solution was extracted with DCM. The combined organic layers were dried under vacuum and recrystallized in DCM for purification. Yield: 8.48 g (29.7 mmol, 91%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 3.83 (s, 3H), 3.87 (s, 3H), 5.25 (s, 2H), 7.13 (d, $^3J_1$ = 7.88 Hz, 1H), 7.21 (dd, $^3J_1$ = 1.89 Hz, $^3J_2$ = 9.77 Hz, 1H), 7.44 (d, $^3J_1$ = 1.89 Hz, 1H), 7.60 (dd, $^3J_1$ = 1.89 Hz, $^3J_2$ = 8.51 Hz, 4H).

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Synthesis of (*S*)-Me$_2$L (3). **2b** (542 mg, 1.90 mmol), HOBt (282 mg, 2.09 mmol, 1.1 equiv), and Boc-Pro-OH (465 mg, 2.16 mmol, 1.1 equiv) were suspended in 14 mL of anhydrous DCM and stirred at room temperature in an argon flow. Afterward, the suspension was cooled to 0 °C. Separately a solution of DCC (431 mg, 2.09 mmol, 1.1 equiv) in 5 mL of anhydrous DCM was prepared and added slowly to the cooled reaction in a time range of 1 h. The reaction was heated to room temperature and stirred for 4 days under an argon atmosphere. The resulting suspension was filtered to remove a white solid. The solvent was removed by evaporation under reduced pressure. Flash chromatography of the raw product in ethyl acetate and hexane (1:1) and drying under high vacuum afforded a pale-yellow solid. Yield: 825 mg (1.71 mmol, 90%). ^{1}H NMR (500 MHz, CDCl3): δ (ppm) = 1.35 (s, 9H), 1.87−2.04 (m, 2H), 2.07−2.49 (m, 2H), 3.11−3.61 (m, 2H), 3.95 (s, 3H), 3.97 (s, 3H), 4.23−4.41 (m, 1H), 7.33 (d, $^3J_1$ = 7.9 Hz, 1H), 7.44 (d, $^3J_1$ = 7.9 Hz, 2H), 7.89 (d, $^3J_1$ = 7.9 Hz, 1H), 8.17 (d, $^3J_1$ = 78.2 Hz, 2H), 8.92 (s, 1H).

Synthesis of (*S*)-H$_2$L. (*S*)-Me$_2$**L** (825 mg, 1.71 mmol) was dissolved in 19 mL of tetrahydrofuran (THF), and a 1 M aqueous solution of KOH was added under stirring. The emulsion was stirred at 50 °C overnight. The organic solvent was removed under reduced pressure, and the resulting aqueous solution was cooled to 0 °C. The addition of aqueous 1 M HCl to set a pH value of 4 afforded a white precipitate, which was filtered and washed with water and ethanol. The product was isolated by drying in high vacuum. Yield: 684 mg (1.50 mmol, 88%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 1.30−1.40 (m, 9H), 1.62−1.80 (m, 3H), 1.97−2.11 (m, 1H), 3.20−3.32 (m, 2H), 4.09−4.18 (m, 1H), 7.47−7.53 (m, 2H), 7.53−7.60 (m, 1H), 7.82−7.89 (m, 1H), 7.98−8.04 (m, 2H), 8.14 (br d, ^3J = 37.2 Hz, 1H), 9.47 (br d, ^3J = 74.4 Hz, 1H), 13.08 (br s, 2H). For HPLC, separation and evaluation of the chiral ligand H$_2$**L** was carried out with the following parameters: mobile phase, 4:1 methanol/water (+0.05% trifluoroacetic acid); flow, 0.2 mL min^{-1} [t_R(*S* enantiomer) = 23.3 min; t_R(*R* enantiomer) = 21.6 min].

Synthesis of H$_3$btctb. In an argon atmosphere, a solution of 4-aminobenzoic acid (49.4 g, 0.36 mol, 3.8 equiv in 600 mL of anhydrous acetone) was prepared. Dried potassium carbonate (45.4 g, 0.33 mol, 3.5 equiv) was suspended in the educt solution and rinsed with 50 mL of anhydrous acetone. Separately, 1,3,5-benzenetricarbonyl trichloride (25.0 g, 0.09 mol) was dissolved in 45 mL of anhydrous acetone and added slowly to the educt suspension. Afterward, the suspension was stirred at 80 °C under reflux conditions for 16 h. The resulting yellow solid was filtered, washed with acetone, and stirred in 1 L of a 1 M aqueous HCl solution for 2 h. The solid was filtered and washed with water and acetone. For further purification, the solid was recrystallized in THF and dried in high vacuum. Yield: 49.5 g (0.09 mol, 93%). ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 7.96−8.04 (m, 12H), 8.79 (s, 3H), 11.0 (s, 3H).

Synthesis of DUT-32-NHProBoc. $Zn(NO_3)_2{\cdot}4H_2O$ (119 mg, 0.46 mmol, 4.6 equiv), H$_3$btctb (49 mg, 0.09 mmol), and (*S*)-H$_2$**L** (58 mg, 0.13 mmol, 1.5 equiv) were dissolved in 9.5 mL of DEF. The mixture was thermally treated at 100 °C for 48 h, affording large transparent rod-shaped crystals. These crystals were washed with DMF (3 × 10 mL). To activate DUT-32-NHProBoc solvent exchange from DMF in acetone or amyl acetate and additionally, exchange with CO_2 was performed, followed by supercritical drying. For liquid-phase adsorption experiments, the solvent DMF was exchanged by EtOH (5 × 10 mL), followed by *n*-heptane (5 × 10 mL) exchange. Mass determinations of the samples for liquid-phase adsorption were carried out by the pycnometer method using the crystallographic density of the crystals and solvents (see the SI). Yield: 82.4 mg (78% referred to the amount of H$_3$btctb). Elem anal. Calcd for $\{Zn_4O[(\mathbf{L})(btctb)_{4/3}]\}[(C_{64}H_{48}N_6O_{20}Zn_4){\cdot}5H_2O]$: C, 48.88; H, 3.72; N, 5.34. Found: C, 48.43; H, 3.82; N, 5.03. IR (cm^{-1}): 3311 (br), 3071 (br), 2976 (br), 1932 (w), 1675 (m), 1605 (s), 1524 (s), 1401 (s), 1312 (m), 1248 (m), 1177 (w), 1157 (w), 1121 (w), 1089 (w), 1015 (w), 1007 (w), 955 (w), 913 (w), 859 (m), 780 (m), 729 (w), 698 (w), 633 (w), 531 (w), 504 (w), 446 (w).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional X-ray data, HPLC spectra, physisorption isotherm, thermal analysis, NMR details, and general procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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