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Research Article

Trifluoromethyl-Functionalized 2D Covalent Organic Framework for High-Resolution Separation of Isomers

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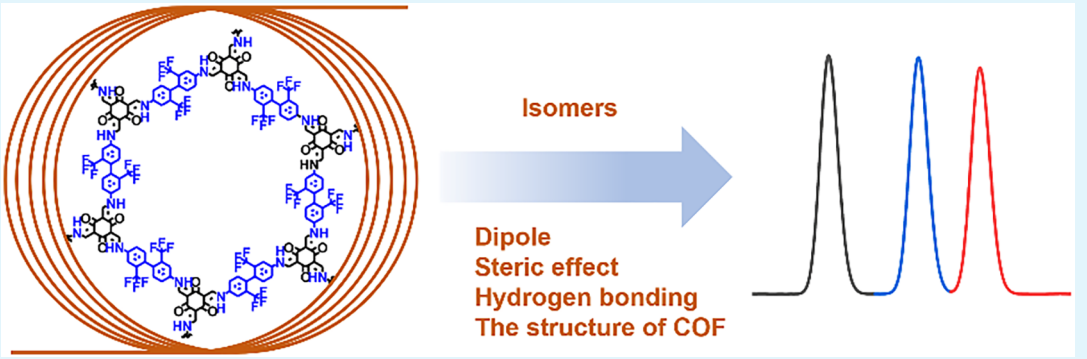

ABSTRACT: Development of novel functional materials for effective isomer separation is of great significance in environmental science, chemical industry, and life science due to the different functions of isomers. However, the similar physicochemical properties of isomers make their separation greatly challenging. Here, we report the fabrication of trifluoromethyl-functionalized 2D covalent organic framework (COF) TpTFMB with 2,2′-bis(trifluoromethyl)benzidine (TFMB) and 1,3,5-triformylphloroglucinol (Tp) for the separation of isomers. TpTFMB was in situ-grown on the inner surface of a capillary for the high-resolution separation of isomers. The introduction of hydroxyl and trifluoromethyl functional groups with uniform distribution in 2D COFs is a powerful tactic to endow TpTFMB with various functions such as hydrogen bonding, dipole interaction, and steric effect. The prepared TpTFMB capillary column enabled the baseline separation of positional isomers such as ethylbenzene and xylene, chlorotoluene, carbon chain isomers such as butylbenzene and ethyl butanoate, and cis−trans isomers 1,3-dichloropropene. The hydrogen-bonding, dipole, and $\pi-\pi$ interactions as well as the structure of COF significantly contribute to the isomer separation. This work provides a new strategy for designing functional 2D COFs for the efficient separation of isomers.

KEYWORDS: *2D covalent organic framework, trifluoromethyl, isomers, separation, gas chromatography*

INTRODUCTION

Gas chromatography (GC) has drawn great attention owing to its powerful separation capability. Chromatographic column is the core component of GC, and introduction of novel stationary phases is vital for chromatographic separation.[1,2] Covalent organic frameworks (COFs), composed of light elements such as C, O, N, H, and B, are a class of porous materials connected by dynamic covalent bonding. COFs have drawn widespread attention for various applications in adsorption,[3−5] catalysis,[6,7] sensing,[8−11] and separation[12−15] due to their excellent features such as high stability, abundant pore channels, and large surface area.[16] The designability of COFs endows them the potential to introduce various forces to improve selectivity as the stationary phase.[17−19] Functional groups such as hydroxyl and amino groups are usually introduced to COFs to improve the separation performance.[20] However, quite limited functional groups have been introduced to COFs for chromatography so far. In addition, conventional post-modification suffers from the nonuniform distribution of the introduced functional groups in COFs. Rational screening of ligands for the homogeneous distribution of functional groups on the COF backbone makes the combination of multiple physicochemical interactions easy for the high recognition of the target.[13]

Fluorine is a nonmetallic element with unique chemical properties due to its small atomic radius and large electronegativity.[21] The physical, chemical, and pharmacological properties of organic molecules can significantly change by the introduction of fluorine. Fluorination has emerged as a potent strategy for creating pharmaceuticals and novel

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materials.[22−24] Fluorine is frequently introduced to structures through trifluoromethylation.[25,26] Trifluoromethyl groups have unique potential for structural recognition and selection because they can produce steric effects and strong polarization ability to induce dipoles with unsaturated compounds.[27,28] Thus, trifluoromethyl-functionalized COFs are expected to introduce abundant noncovalent forces as promising stationary phases. Fluorine-containing monomers were used to synthesize COFs for liquid chromatography and electrochromatography separation of organic halides and fluoroquinolones, respectively.[29,30] However, to our knowledge, the trifluoromethyl-functionalized COFs have not been explored for GC separation so far.

Exploration of novel functional materials for isomer separation is important in environmental science, chemical industry, and life science due to the different functions of isomers.[14,31,32] However, the similar physicochemical properties of isomers make their separation greatly challenging.[33−36] Cryogenic distillation[37] and crystallization[38] are traditional techniques for the separation of isomers, but they are typically accompanied by high energy consumption. Compared to liquid chromatography, GC has the advantage of high sensitivity and excellent separation capacity, although it is suitable for a smaller number of analytes. Recently, COFs were employed as the stationary phase for the GC separation of isomers. Cai et al.[39] synthesized a hydrazone-linked chiral 2D COF as the GC stationary phase for the separation of nitrotoluene, chloronitrobenzene, benzenediol, naphthol, and xylene isomers. Although the isomers of nitrotoluene, benzenediol, and naphthol were baseline-separated, those of chloronitrobenzene and xylene were not completely resolved, possibly owing to the simple forces provided by the 2-methylbutoxy-functionalized COF. Ma et al.[40] fabricated [(1-phenylethyl)amino]acetic acid-functionalized 2D COF via a postmodification method and achieved the baseline separation of fluoroaniline, chloroaniline, nitrotoluene, pinene, ionone, and 1,3-dichloropropene isomers. However, weakly polar isomers such as xylene and chlorotoluene were not separated for the low content or uneven distribution of the functional groups introduced by postmodification. Qian et al.[20] synthesized 3D COF-NH_2 via the building block exchange strategy for GC separation of the isomers of xylene, propylbenzene, and dichlorobenzene. The hydrogen-bonding force provided by the amino group enhanced the separation ability of the stationary phase.

Based on previous publications, 3D COFs seem better than 2D COFs for isomer separation. However, the availability of 3D COFs is very limited due to the difficulty in their synthesis. Compared to 3D COFs, 2D COFs are much easier to synthesize with abundant monomers. Nevertheless, it is difficult to achieve good separation of isomers with unmodified 2D COFs as the stationary phases for GC. Rational introduction of specific functional groups with uniform distribution in the 2D COFs may provide a promising way to enhance the performance of 2D COFs for isomer separation. Since trifluoromethyl groups can provide abundant noncovalent interactions and steric effects, we expect that trifluoromethyl-functionalized 2D COF is a good choice for isomer separation.

Herein, we show the design and preparation of trifluoromethyl-functionalized 2D COF as the stationary phase for the high-resolution separation of isomers. 1,3,5-Triformylphloroglucinol (Tp) with the hydroxyl group and 2,2′-bis-(trifluoromethyl)benzidine (TFMB) with the trifluoromethyl group are selected as ligands for the synthesis of trifluoromethyl-functionalized 2D COF TpTFMB. The prepared TpTFMB gives high thermal stability and large surface area. The TpTFMB-bonded capillary column is fabricated by the in situ growth of TpTFMB on the inner walls of a silica capillary. Positional isomers like ethylbenzene and xylene, carbon chain isomers like butylbenzene, and cis−trans isomers like 1,3-dichloropropene are baseline-separated on the fabricated TpTFMB-bonded capillary column with good resolution and precision. The dipole and hydrogen-bonding forces provided by the introduced trifluoromethyl and hydroxyl groups, combined with the structure of COF, greatly enhance the performance of the TpTFMB-bonded capillary column for isomer separation. This work provides a new idea for the design of 2D COFs for isomer separation.

EXPERIMENTAL SECTION

Chemicals and Materials. Tp and 1,3,5-benzenetricarboxaldehyde (Tb) were provided by Jilin Chinese Academy of Science-Yanshen Technology Co. (Jilin, China). Benzidine (BD), isobutylbenzene, 3,3,3-trifluoropropionic acid, TFMB, ethyl isovalerate, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl), 3-aminopropyltriethoxysilane (APTES), ethyl butanoate, 2,5-diaminobenzo-trifluoride (Pa-CF_3), *n*-butanol (*n*-BuOH), *n*-propylbenzene, cumene, ethyl isobutyrate, isoamyl formate, ethyl 2-methylbutanoate, isoamyl acetate, ethylbenzene, xylene isomers, nitrotoluene isomers, chlorotoluene isomers, *n*-butylbenzene, *n*-hydroxy succinimide (NHS), and sec-butylbenzene isomers were provided by Aladdin Chemical Co. (Shanghai, China). Dichlorobenzene isomers were obtained from TCI Chemical Industry Development Co. (Shanghai, China). Ethanol (EtOH), dichloromethane (DCM), methanol (MeOH), tetrahydrofuran (THF), acetonitrile (ACN), 1,4-dioxane, HCl, NaOH, and acetic acid (HAc) were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Mesitylene, *o*-dichlorobenzene (*o*-DCB) and 1,3-dichloropropene isomers were provided by Maclean Biochemical Technology Co. (Shanghai, China). Fused silica capillary (0.32 mm i.d.) was provided by Yongnian Optic Fiber Plant (Hebei, China). Ultrapure water (Wahaha Foods Co., Hangzhou, China) was used throughout. All used chemicals were of analytical grade.

Materials Characterization and GC Separation. The instruments used for materials characterization are described in the Supporting Information. A 2030 Plus system (Shimadzu, Japan) with a flame ionization detector was used for GC separation with a split ratio of 80:1. High-purity N_2 (99.999%) was employed as the carrier gas. Isomer separation was evaluated on the TpTFMB-bonded capillary column (15 m × 0.32 mm).

Synthesis of TpTFMB and Polymer TpTFMB (P-TpTFMB). Tp (5.3 mg) and TFMB (12 mg) were added to a Schlenk flask (O.D. 26 × L. 125 mm, 35 mL) with 1 mL of *n*-BuOH/*o*-DCB (1:1, v/v). 300 μL of HAc solution (6 mol L^{-1}) was then added as the catalyst, and the mixture was sonicated, freeze-degassed three times and heated at 120 °C for 3 days. The resulting yellow powder was washed with THF triplicate and dried in a vacuum oven at 60 °C for 12 h. Details for the synthesis of P-TpTFMB are described in the Supporting Information.

Preparation of TbTFMB. Tb (0.05 mmol, 8.1 mg) and TFMB (0.075 mmol, 24 mg) were dispersed in ACN/EtOH (7:3, v/v, 1 mL), while HAc (6 mol L^{-1}, 300 μL) was added as a catalyst under sonication. The mixture was kept at room temperature for 3 days. The white material was washed with THF three times, collected by centrifugation, and dried in a vacuum oven at 60 °C overnight.

Synthesis of TpBD and TpPa-CF_3. TpBD was prepared according to the method of Banerjee et al.[41] with minor modifications (see the Supporting Information). Tp (0.05 mmol, 10.5 mg) and Pa-CF_3 (0.075 mmol, 13.2 mg) were dispersed in 1.65 mL of a mixture of mesitylene/1,4-dioxane/6 mol L^{-1} of HAc solution (5:5:1, v/v/v) in a 35 mL Schlenk flask (O.D. 26 × L. 125 mm); the mixture was

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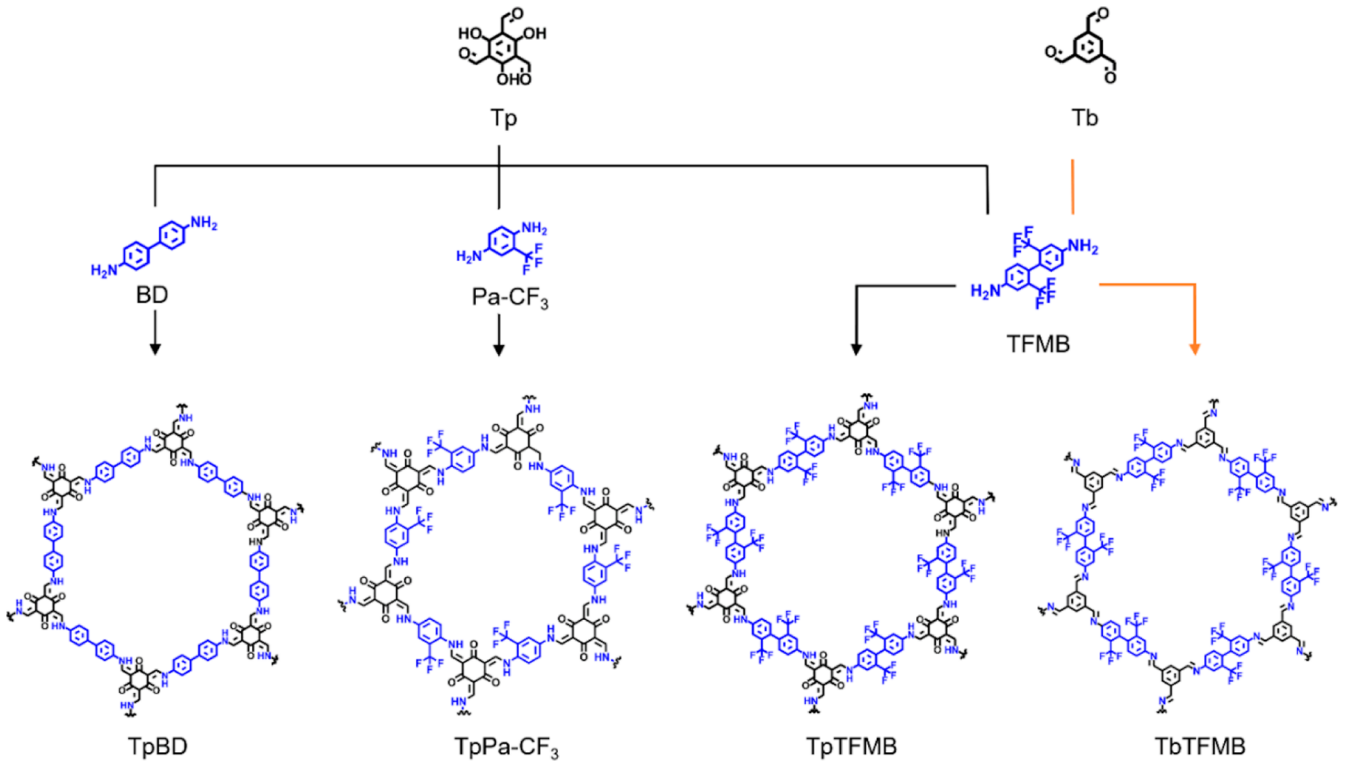

Figure 1. Illustration for the synthesis of COF TpTFMB and the design of other COFs for comparison.

sonicated, freeze-degassed for three cycles, and maintained at 120 °C for 48 h. The reddish-brown powder was washed with THF, collected by centrifugation, and dried in a vacuum oven at 60 °C for 12 h.

Preparation of TpTFMB and P-TpTFMB-Bonded Capillary Columns. All fused silica capillaries were pretreated with 1 mol L^{-1} NaOH solution.[12] Then, a mixture of MeOH/APTES (1:1, v/v) solvent was filled into the pretreated capillary and a plunger was used to block both ends of the capillary. The mixture in the cappilary was then incubated at 70 °C for 24 h and rinsed with EtOH and blown dry with N_2 at 120 °C to obtain an amino-functionalized capillary.

Tp (5.3 mg) and TFMB (12 mg) were dispersed in 1.5 mL of ACN, and the mixture was sonicated and injected into the amino-functionalized capillary using a syringe and held at 120 °C for 5 h. Afterward, the capillary column was washed with EtOH and dried with N_2 at 120 °C. Then, a mixture of 1.5 mL of *n*-BuOH/*o*-DCB (1:1, v/v) and 6 mol L^{-1} HAc solution (300 μL) was injected into the capillary, and the reaction was performed at 120 °C for 72 h. All the above reactions were performed after the two ends of the capillary were blocked. Finally, the TpTFMB-bonded capillary column was rinsed with EtOH and blown dry with N_2. Before use, a GC oven was aged according to the following procedure: 35−190 °C at a ramp rate of 3 °C min^{-1} and maintained at 190 °C for 2 h at a flow rate of 1 mL min^{-1}. Details for the fabrication of the P-TpTFMB-bonded capillary column are given in the Supporting Information.

Preparation of TbTFMB-Bonded Capillary Column. Tb (6.4 mg) and TFMB (18 mg) were added to 1 mL of the solvent mixture of ACN/EtOH (7:3, v/v), and 300 μL of 6 mol L^{-1} HAc solution was added as the catalyst. The mixture was sonicated for 1 min, injected into the amino-functionalized capillary column, and reacted at room temperature for 72 h after the two ends of the capillary were blocked. Then, the TbTFMB-bonded capillary column was washed with EtOH and aged in the same way as that of the TpTFMB-bonded capillary column.

Preparation of TpPa-CF_3-Bonded Capillary Column. Tp (5.3 mg) and Pa-CF_3 (6.6 mg) were added to 1.5 mL of ACN and dispersed under sonication. The mixture was injected into the amino-functionalized capillary column and kept at 120 °C for 5 h for polymerization. Then, the capillary column was rinsed using EtOH and dried at 120 °C under a stream of N_2. Afterward, 1.5 mL of the reaction solution (mesitylene/1,4-dioxane/6 mol L^{-1} of HAc solution, 5:5:1, v/v/v) was injected into the capillary column and incubated at 120 °C for 48 h after the ends of the column were blocked. Then, the capillary column was rinsed with EtOH and dried under N_2. The TpPa-CF_3-bonded capillary column was aged in the same way as that of the TpTFMB-bonded capillary column.

Preparation of TpBD-Bonded Capillary Column. 4 mg of Tp and 5 mg of BD were dispersed in 1.5 mL of mesitylene/1,4-dioxane (1:1, v/v) solvent, and 300 μL of 6 mol L^{-1} HAc solution was added. The solution was sonicated for 5 min and injected into the amino-functionalized capillary column by a syringe. The column was kept at 120 °C for 72 h after the ends of the capillary column were closed. Finally, the column was washed with EtOH and aged as that of the TpTFMB-bonded capillary column.

Preparation of Trifluoroethyl-Bonded Capillary Column. A trifluoroethyl-bonded capillary column was prepared for comparison to show the significance of COF materials in the separation of isomers. 50 mg of 3,3,3-trifluoropropionic acid, 112 mg of EDC·HCl, and 67 mg of NHS were dissolved in 1.5 mL of DCM, sonicated, and stirred for 30 min. The mixture was injected into the amino-functionalized capillary column by a syringe and maintained at room temperature for 24 h. After that, the capillary column was rinsed with EtOH, dried with N_2, and aged as other columns.

RESULTS AND DISCUSSION

Design of COFs and Capillary Columns. TFMB and Tp ligands were chosen for the synthesis of trifluoromethyl-functionalized COF TpTFMB via a Schiff base reaction as the stationary phase for isomer separation. The large polarization ability of the trifluoromethyl group provided by the TFMB ligand easily induces dipoles to unsaturated compounds, increasing the selectivity of the stationary phase. The structure of Tp was converted from the enol form to the irreversible keto form after the reaction to enhance the stability of COF while retaining the hydrogen-bonding forces. Moreover, TbTFMB without hydroxyl groups, TpBD without trifluoromethyl

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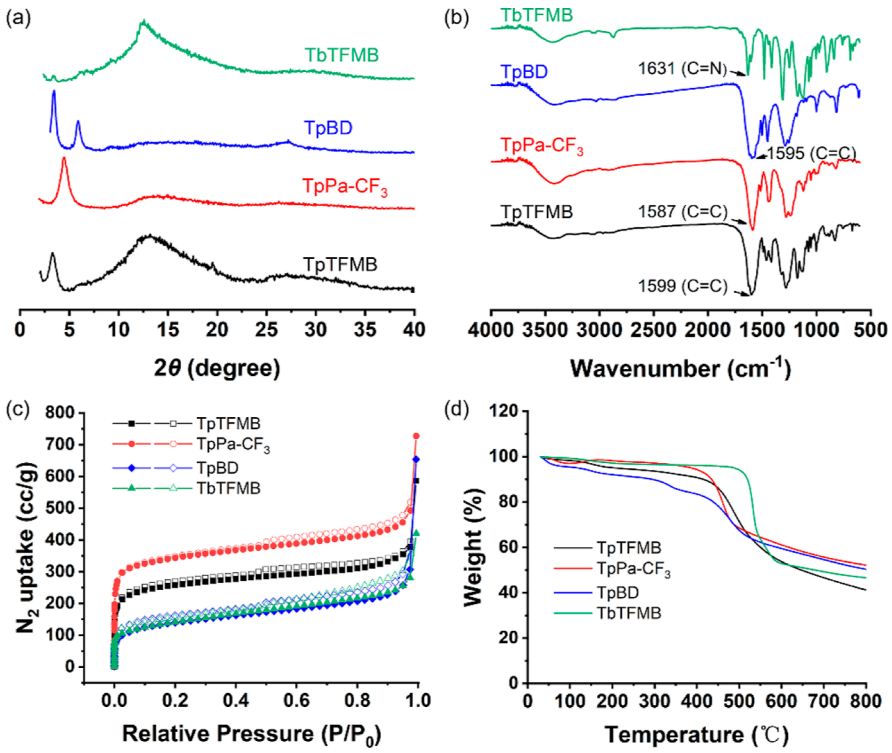

Figure 2. Characterization of TbTFMB, TpBD, TpPa-CF_3, and TpTFMB. (a) XRD patterns; (b) FT-IR spectra; (c) nitrogen adsorption−desorption isotherms; and (d) TGA curves.

groups, TpPa-CF_3 with fewer trifluoromethyl active sites, and trifluoroethyl-bonded capillary columns were designed to explore the role of hydrogen bonding, dipole interaction, and the structure of COF in the isomer separation of the TpTFMB-bonded capillary column (Figure 1).

Fabrication and Characterization of COFs. The synthesis conditions of COFs (solvent type, solvent ratio, reaction temperature, and time) were optimized since they affect the solubility of monomers, reactivity, and reversibility. As a result, TpTFMB with a yield of 65% was prepared in *o*-DCB/*n*-BuOH/6 mol L^{-1} HAc (5:5:3, v/v/v, 1.3 mL) at 120 °C for 72 h (Figure S1), while TbTFMB with a yield of 70% was synthesized in ACN/EtOH/6 mol L^{-1} HAc (7:3:3, v/v/v, 1.3 mL) at RT for 72 h (Figure S2). Meanwhile, TpPa-CF_3 was synthesized at a mixed solution (mesitylene/1,4-dioxane/6 mol L^{-1} of HAc, 5:5:1, v/v/v, 1.65 mL) at 120 °C for 48 h with a yield of 83% (Figure S3 and Table S1).

The crystalline structure of the prepared COFs was characterized by X-ray diffraction. The XRD patterns of TpTFMB, TbTFMB, and TpPa-CF_3 showed characteristic diffraction peaks at 3.4, 3.3, and 4.5° respectively, indicating that COFs formed an ordered crystalline structure. The characteristic diffraction peak of TpBD at 3.3° was consistent with that reported in the literature (Figure 2a).[41] Structural simulation and Pawley refinement of the synthesized COFs were performed using Material Studio to further understand the crystal structures of COFs TpTFMB, TbTFMB, and TpPa-CF_3. Optimal cell parameters were obtained as follows: space group of *P6/m*, $a = b = 30.1128$ Å, $c = 5.6492$ Å, $\alpha = \beta = 90°$, and $\gamma = 120°$ for TpTFMB; space group of *P6/m*, $a = b = 30.0468$ Å, $c = 5.6340$ Å, $\alpha = \beta = 90°$, and $\gamma = 120°$ for TbTFMB, and space group of P-6, $a = b = 22.0085$ Å, $c = 4.2319$ Å, $\alpha = \beta = 90°$, and $\gamma = 120°$ for TpPa-CF_3. The AA stacking and AB staggered models of the COFs were constructed (Figures S4−S6), and the XRD diffraction patterns of the COFs were simulated by the powder diffraction module. The AA stacking model is more suitable to describe the structures of TpTFMB, TbTFMB, and TpPa-CF_3 than the AB staggered model, indicating that the prepared COFs TpTFMB, TbTFMB, and TpPa-CF_3 are all AA stacking 2D materials (Figures S7−S9). Finally, the cell parameters of the COFs were refined by the Pawley refinement module, and the Rwp and Rp values of the prepared COFs with the AA stacking model were as follows: Rwp, 7.13% and Rp, 5.00% for TpTFMB; Rwp, 5.41% and Rp, 3.48% for TpPa-CF_3; Rwp, 6.81% and Rp, 4.85% for TbTFMB (Figures S10−S12). The corresponding main atomic coordinates after refinement are shown in Tables S2−S4.

FT-IR spectroscopy was applied to characterize the chemical structure of the monomers and COFs (Figure 2b). The characteristic peaks of C═O of Tp (1643 cm^{-1}) and−NH_2 of TFMB (3443 and 3340 cm^{-1}) disappeared after the reaction, whereas those of C═C (1599 cm^{-1}) and C−N (1281 cm^{-1}) appeared in TpTFMB, demonstrating the successful synthesis of the ketone form of TpTFMB (Figure S13). Similarly, the disappearance of the characteristic peak of C═O of Tp (1643 cm^{-1}) and the presence of the C═O peak (1617 cm^{-1}) and C═C peak (1595 cm^{-1}) reveal the successful synthesis of TpBD (Figure S14). Meanwhile, the successful synthesis of TpPa-CF_3 was confirmed by the absence of the $-NH_2$ characteristic peak (3450 and 3419 cm^{-1}) and the appearance of the C═C (1587 cm^{-1}) and C−N (1279 cm^{-1}) characteristic peaks (Figure S15). The loss of the C═O characteristic peak (1696 cm^{-1}) of Tb and the emergence of the C═N peak (1631 cm^{-1}) indicate the successful formation of an imine bond between the building blocks via Schiff base condensation, demonstrating the successful synthesis of TbTFMB (Figure S16).

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Nitrogen adsorption−desorption experiments were performed to characterize the surface area, pore size, and pore volume of COFs at 77 K (Figure 2c). The Brunauer−Emmett−Teller surface areas of TpTFMB, TpBD, TpPa-CF_3 and TbTFMB were 964, 504, 1306, and 500 $m^2\ g^{-1}$, respectively. The pore sizes of TpTFMB, TpBD, TpPa-CF_3, and TbTFMB were 15.5, 17.2, 14.5, and 17.8 Å, respectively (Figures S17−S20), with the pore volumes of 0.555, 0.435, 0.702, and 0.491 $cm^3\ g^{-1}$, respectively. TpTFMB has a slightly larger pore size and a smaller pore volume than TpPa-CF_3 due to the occupation of more trifluoromethyl active sites. The lack of hydroxyl groups or trifluoromethyl groups is responsible for the larger pore size of TbTFMB and TpBD than TpTFMB, respectively. The weaker crystallinity may cause the smaller pore volume of TbTFMB. Compared with TpBD, TpTFMB showed worse crystallinity, likely due to the steric effect from the large group of $-CF_3$, but larger specific surface area and pore volume, probably owing to the self-complementary π-electronic interaction provided by the introduction of fluorine.[42−44]

SEM was utilized to characterize the morphology of COFs. TpTFMB, TpBD, TpPa-CF_3, and TbTFMB exhibited poorly regular spherical, lamellar, spherical/fibrous, and spherical morphology, respectively (Figure S21). The thermal stability of the COFs was assessed by thermogravimetric analysis. TpTFMB, TpBD, TpPa-CF_3, and TbTFMB were stable at 400, 320, 400, and 500 °C (Figure 2d), respectively, demonstrating the potential of the COFs as stationary phases for GC. TpTFMB, TpBD, TbTFMB, and TpPa-CF_3 are stable in EtOH, MeOH, THF, H_2O, and ACN, as no obvious change of the XRD patterns and FT-IR spectra was observed in these solvents (Figures S22−25).

Characterization of Bonded Capillary Columns. SEM images show that TpTFMB, TpBD, TpPa-CF_3, and TbTFMB were uniformly and densely covered on the inner wall of the capillary columns, proving the successful fabrication of the COF-bonded capillary columns (Figures 3a−e, S26). Further element mapping for the bare column and trifluoroethyl-bonded capillary column reveals the uniform coverage of the fluorine element, demonstrating the introduction of the trifluoroethyl group on the inner surface of the capillary column (Figures S27 and 3f). FT-IR spectra of the prepared TpTFMB, TpBD, TpPa-CF_3, and TbTFMB bonded capillary columns gave the characteristic peaks of C═C and C═N at 1599, 1595, 1587, and 1631 cm^{-1}, respectively, further supporting the successful preparation of the COF-bonded capillary columns (Figure S28). In addition, the consistency between the XRD patterns confirms that the synthesized TpTFMB and TpPa-CF_3 powders are the same as TpTFMB and TpPa-CF_3 bonded on the inner walls of the capillary (Figure 2a, cf. Figure S29).

McReynolds Constants for the Bonded Capillary Columns. The McReynolds constant is commonly employed to describe the polarity of the stationary phase. The probes containing 1-nitropropane (U), 2-pentanone (Z), benzene (X), pyridine (S), and *n*-butanol (Y) were selected to determine the average polarity of the capillary column. The obtained McReynolds constants are summarized in Table 1. Details for the calculation are given in the Supporting Information.

According to the three-stage division of the McReynolds constant, average values less than 100, 100−400, and more than 400 indicate weak, moderate, and strong polarity of the stationary phase, respectively. As shown in the Table 1, TpBD was a weakly polar stationary phase, and TpTFMB, TpPa-CF_3, and TbTFMB were moderately polar stationary phases, while the trifluoroethyl-bonded capillary column was a strongly polar stationary phase. The larger values of Y, Z, and U for the TpTFMB-bonded capillary column reveal that the stationary phase has strong proton−donor and proton−acceptor abilities as well as dipole forces due to the introduction of the hydroxyl and trifluoromethyl groups. The larger values of Y and Z but slightly smaller value of U for the TpPa-CF_3 stationary phase may be attributed to the lower dipole force due to the reduced content of the trifluoromethyl active sites. Moreover, the absence of the hydroxyl group reduced the hydrogen-bonding force, resulting in a slightly smaller Y value of the TbTFMB stationary phase. The strong electronegativity and polarization ability of the C−F bond led to a strongly polar trifluoroethyl stationary phase. Similarly, the absence of trifluoromethyl groups resulted in a weakly polar stationary phase of TpBD.

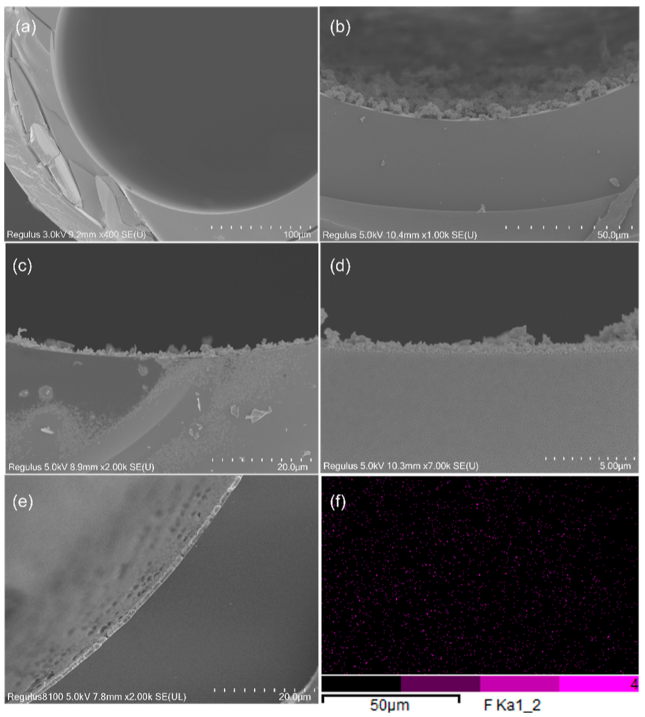

Figure 3. SEM images of the edge of the dissected capillary columns: (a) bare column; (b) TpTFMB-bonded; (c) TpBD-bonded, (d) TpPa-CF_3-bonded; and (e) TbTFMB-bonded. (f) Elemental mapping of the trifluoroethyl-bonded capillary column.

Table 1. McReynolds Constants of Trifluoroethyl-, TpBD-, TpTFMB-, TpPa-CF_3-, and TbTFMB-Bonded Capillary Columns

stationary phase	X	Y	Z	U	S	Av.
trifluoroethyl	373	713	597	401	714	560
TpBD	3	62	84	64	41	51
TpTFMB	47	230	198	185	112	155
TpPa-CF_3	14	248	208	178	60	142
TbTFMB	13	101	207	199	70	118

Separation of Isomers. We then investigated the performance of our TpTFMB-bonded capillary column for isomer separation. Various isomers with different substituents (C8 alkyl aromatic isomers, propylbenzene, butylbenzene,

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chlorotoluene, and nitrotoluene) were selected to investigate the effect of the functional groups of the prepared capillary column on the separation ability of substances with different polarities. In addition, various kinds of isomers (positional isomers like dichlorobenzene; carbon chain isomers like isoamyl acetate and ethyl butanoate; and cis−trans isomers like 1,3-dichloropropene) were chosen to explore the versatility of the prepared column for isomer separation.

The TpTFMB-bonded capillary column was first applied for the separation of C8 alkyl aromatic isomers (*o*-, *m*-, *p*-xylene, and ethylbenzene). These four isomers are important not only for the chemical industry but also for environmental chemistry.[45] However, the comparable structures, polarizabilities, kinetic diameters, and boiling points of these isomers make their separation very challenging.[31] Even so, our TpTFMB-bonded capillary column gave the baseline separation of ethylbenzene and xylene isomers with a high column efficiency (33,255 plates m^{-1} for ethylbenzene, 24,852 plates m^{-1} for *o*-xylene, 30,488 plates m^{-1} for *m*-xylene, and 31,722 plates m^{-1} for *p*-xylene (Figure 4a).

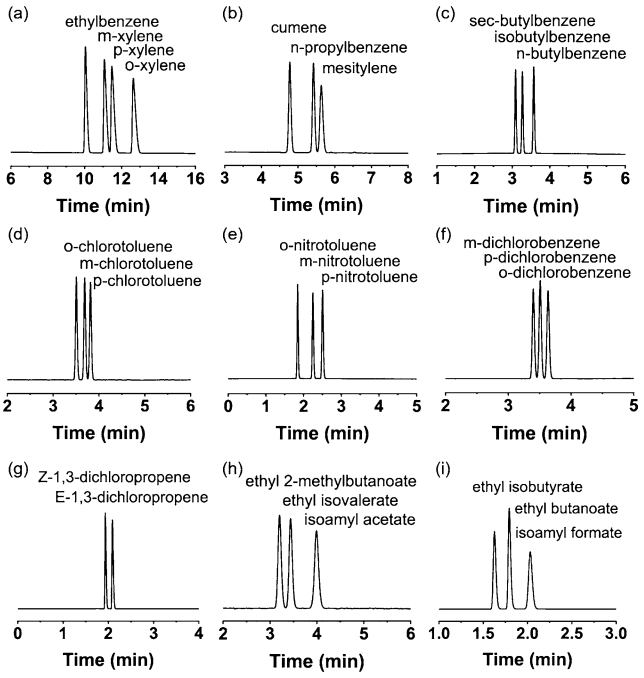

Figure 4. Chromatograms on the TpTFMB-bonded capillary column: (a) ethylbenzene and xylene isomers at 180 °C (1 mL min^{-1} N_2); (b) propylbenzene isomers at 220 °C (1 mL min^{-1} N_2); (c) butylbenzene isomers at 260 °C (1 mL min^{-1} N_2); (d) chlorotoluene isomers at 230 °C (1 mL min^{-1} N_2); (e) nitrotoluene isomers at 270 °C (2.5 mL min^{-1} N_2); (f) dichlorobenzene isomers at 240 °C (1 mL min^{-1} N_2); (g) 1,3-dichlorobenzene isomers at 210 °C (1.5 mL min^{-1} N_2); (h) isoamyl acetate isomers at 220 °C (1.5 mL min^{-1} N_2); and (i) ethyl butanoate isomers at 230 °C (1.5 mL min^{-1} N_2).

In addition, the TpTFMB-bonded capillary column enabled a highly selective separation of various isomers with different polarities (C8 alkyl aromatic isomers, propylbenzene, butylbenzene, chlorotoluene, and nitrotoluene isomers) (Figure 4b−e). Moreover, dichlorobenzene positional isomers, isoamyl acetate and ethyl butanoate carbon chain isomers, and 1,3-dichloropropene cis−trans isomers were baseline-separated on the TpTFMB-bonded capillary column. All the above separations were completed within 4 min, except for the C8 alkyl aromatic isomers and propylbenzene isomers (Figure 4 and Table S5). The above results demonstrate the great potential of the prepared TpTFMB-bonded capillary column for the high-resolution separation of various kinds of isomers.

The repeatability of the prepared TpTFMB-bonded capillary column was assessed for isomer separation. The relative standard deviations (RSDs, %) for intraday (n = 5), interday (n = 3), and column-to-column (n = 3) were <0.39, 1.37, and 1.41% for retention time, respectively, and <5.70, 6.81, and 7.69% for peak area, respectively, demonstrating the good precision of the TpTFMB-bonded capillary column (Table S6).

Separation Mechanism. To further understand the interaction between the TpTFMB stationary phase and the targets, TbTFMB-, TpBD-, TpPa-CF_3-, P-TpTFMB-, and trifluoroethyl-bonded capillary columns were prepared for comparison. TbTFMB (without hydroxyl groups) was fabricated for comparison with TpTFMB to reveal the role of hydrogen-bonding interaction in separation. The baseline separation of dichlorobenzene, nitrotoluene, propylbenzene, 1,3-dichloropropene, isoamyl acetate, and ethyl butanoate isomers was achieved on the prepared TbTFMB-bonded capillary column, except for ethylbenzene and xylene isomers, chlorotoluene, and butylbenzene isomers (Figure S30). The relatively poor separation ability of the TbTFMB-bonded capillary column for weakly polar isomers demonstrates the importance of hydrogen bonding in the separation of isomers.

In contrast to TpTFMB, TpBD was designed with BD monomers but without the trifluoromethyl functional group to show the role of the dipole force and steric effect in the separation of isomers. Thus, the only structural difference between the COFs TpTFMB and TpBD is that the former contains the trifluoromethyl group, while the later does not have the trifluoromethyl group. The constructed TpBD-bonded capillary column had poor separation performance and failed to achieve baseline separation of all the studied isomers (Figure S31), indicating that the dipole force and steric effect provided by the trifluoromethyl groups are essential for isomer separation.

TpPa-CF_3 was designed with fewer trifluoromethyl active sites than TpTFMB. The prepared TpPa-CF_3-bonded capillary column achieved the baseline separation of dichlorobenzene, chlorotoluene, nitrotoluene, 1,3-dichloropropene, butylbenzene, isoamyl acetate, and ethyl butanoate isomers but did not provide the baseline separation of ethylbenzene and xylene isomers and propylbenzene isomers (Figure S32). The separation ability of the TpPa-CF_3 stationary phase for the weakly polar isomers reduced as the content of trifluoromethyl groups decreased. The results show that the dipole force interaction and the steric effect of trifluoromethyl groups play an important role in the isomer separation, especially for weakly polar isomers.

To further study the significance of the crystallinity of COF for the separation, the P-TpTFMB-bonded capillary column was fabricated for comparison. The prepared P-TpTFMB did not have a crystalline structure (Figure S33) and gave a smaller Brunauer−Emmett−Teller surface area (459 m^2 g^{-1}) than TpTFMB (964 m^2 g^{-1}) (Figure S34a,b). Meanwhile, the pore distribution of P-TpTFMB was irregular (Figure S34c). Although P-TpTFMB was uniformly bonded on the inner walls of the capillary column (Figure S35), only 1,3-dichloropropene isomers were baseline-separated, indicating

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that the crystalline structure of COF played an important role in the separation (Figure S36).

Meanwhile, a trifluoroethyl-bonded capillary column was prepared for comparison to reveal the role of the COF structure in the separation. The results show that only ethyl butanoate isomers among the abovementioned isomers were baseline-separated with tailing and poor peak shape on the prepared trifluoroethyl-bonded capillary column (Figure S37). The poor isomer separation performance of the trifluoroethyl-bonded capillary column suggests that the structure of COF significantly contributes to the separation of isomers.

The TpTFMB-bonded capillary column gave a higher column efficiency for most of the abovementioned isomers separated than the other capillary columns studied in this work (Table S7). In addition, the separation performance of the TpTFMB-bonded capillary column was also compared with the other reported capillary columns for the GC separation of xylene (Table S8). TpTFMB gave a better resolution and faster separation of isomers than lots of other reported stationary phases, such as UiO-66,[46] 2D COF BtaMth,[39] MOF-CJ3,[47] ZIF-8@PDMS,[48] graphene quantum dots,[49] and zeolitic metal azolate framework MAF-6,[50] but a little worse separation performance than 3D COF JNU-5.[20] The outcomes show obvious advantages of the TpTFMB-bonded capillary column in the separation isomers. Meanwhile, the hydrogen bonding provided by the hydroxyl groups, the dipole force and spatial effects provided by the trifluoromethyl groups, and the crystallinity and the structure of COF play significant roles in the separation of isomers.

To further understand the retention behavior of the isomers on the TpTFMB-bonded capillary column, the thermodynamic parameters for the separation of the studied isomers were measured (Table S9). The negative values of Gibbs free energy (ΔG) indicate that the separation of the isomers occurred spontaneously, and the elution sequence of the analytes followed the descending order of ΔG. The negative values of enthalpy change (ΔH) and entropy change (ΔS) for all analytes imply that the isomer separation is an enthalpy-driven process on the TpTFMB-bonded capillary column. The good linearity of the Van't Hoff plots for all the isomers suggests that the interaction mechanism does not change in the temperature range studied (Figure S38).

CONCLUSIONS

We have reported the design and fabrication of trifluoromethyl-functionalized 2D COF TpTFMB for high-resolution separation of isomers. The rational introduction of hydroxyl and trifluoromethyl functional groups with a uniform distribution in the 2D COFs provides abundant noncovalent interactions and steric effects for the effective separation of isomers. The prepared 2D COF of TpTFMB-bonded capillary column enables the baseline separation of various isomers including ethylbenzene, xylene, propylbenzene, butylbenzene, chlorotoluene, nitrotoluene, dichlorobenzene, 1,3-dichloropropene, ethyl butanoate, and isoamyl acetate with good precision. The hydrogen bonding, dipole interaction, steric effect, crystallinity, and the structure of 2D COFs play important roles in the separation of isomers. This work provides a new method for the design of 2D COFs as stationary phases for the separation of isomers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.3c05369.

Additional information including instruments for material characterization; synthesis of TpBD and P-TpTFMB; preparation of P-TpTFMB-bonded capillary column; calculation of McReynolds constant and thermodynamic parameters; XRD and FT-IR images; Pawley refinement; morphology, porosity, and structure of the prepared TpTFMB, TbTFMB, TpPa-CF_3, and TpBD; morphology and FT-IR spectra of the prepared TpTFMB-, TbTFMB-, TpPa-CF_3-, and TpBD-bonded capillary columns; XRD patterns of TpTFMB and TpPa-CF_3 bonded on the inner walls of capillary columns; XRD pattern and porosity of P-TpTFMB; morphology of the prepared P-TpTFMB-bonded capillary column; chromatograms for the separation of isomers on the TbTFMB-, TpPa-CF_3-, TpBD-, P-TpTFMB-, and trifluoroethyl-bonded capillary columns; Van't Hoff plots for isomers on the TpTFMB-bonded capillary column; yield of TpPa-CF_3 synthesized for different reaction times; fractional atomic coordinates for the unit cell of TpTFMB, TbTFMB, and TpPa-CF_3 after Pawley refinement; column efficiency, resolution, precision, and thermodynamic parameters for the isomer separation on the TpTFMB-bonded capillary column; column efficiency of the isomer separation on the TbTFMB-, TpPa-CF_3-, TpBD-, and trifluoroethyl-bonded capillary columns; and comparison of the separation performance of xylene isomers on the TpTFMB-bonded capillary column with other reported capillary columns (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Chen, J.; Huang, Y. N.; Wei, X.; Lei, X. Q.; Zhao, L.; Guan, M.; Qiu, H. D. Covalent Organic Nanospheres: Facile Preparation and Application in High-Resolution Gas Chromatographic Separation. *Chem. Commun.* **2019**, *55*, 10908−10911.

(2) Wang, Z.; Zhang, S.; Chen, Y.; Zhang, Z.; Ma, S. Covalent Organic Frameworks for Separation Applications. *Chem. Soc. Rev.* **2020**, *49*, 708−735.

(3) Li, H. Z.; Yang, C.; Qian, H. L.; Yan, X. P. Room-Temperature Synthesis of Ionic Covalent Organic Frameworks for Efficient Removal of Diclofenac Sodium from Aqueous Solution. *Sep. Purif. Technol.* **2023**, *306*, 122704.

(4) Da, H. J.; Yang, C. X.; Yan, X. P. Cationic Covalent Organic Nanosheets for Rapid and Selective Capture of Perrhenate: An Analogue of Radioactive Pertechnetate from Aqueous Solution. *Environ. Sci. Technol.* **2019**, *53*, 5212−5220.

(5) Wang, X. M.; Ji, W. H.; Chen, L. Z.; Lin, J. M.; Wang, X.; Zhao, R. S. Nitrogen-Rich Covalent Organic Frameworks as Solid-Phase Extraction Adsorbents for Separation and Enrichment of Four Disinfection by-Products in Drinking Water. *J. Chromatogr. A* **2020**, *1619*, 460916.

(6) Kundu, T.; Wang, J.; Cheng, Y. D.; Du, Y. H.; Qian, Y. H.; Liu, G. L.; Zhao, D. Hydrazone-Based Covalent Organic Frameworks for Lewis Acid Catalysis. *Dalton Trans.* **2018**, *47*, 13824−13829.

(7) Li, F.; Kan, J.-L.; Yao, B.-J.; Dong, Y.-B. Synthesis of Chiral Covalent Organic Frameworks via Asymmetric Organocatalysis for Heterogeneous Asymmetric Catalysis. *Angew. Chem. Int. Ed.* **2022**, *134*, No. e202115044.

(8) Jhulki, S.; Evans, A. M.; Hao, X. L.; Cooper, M. W.; Feriante, C. H.; Leisen, J.; Li, H.; Lam, D.; Hersam, M. C.; Barlow, S.; et al. Humidity Sensing through Reversible Isomerization of a Covalent Organic Framework. *J. Am. Chem. Soc.* **2020**, *142*, 783−791.

(9) Zhang, Y. W.; Shen, X. C.; Feng, X.; Xia, H.; Mu, Y.; Liu, X. M. Covalent Organic Frameworks as pH Responsive Signaling Scaffolds. *Chem. Commun.* **2016**, *52*, 11088−11091.

(10) Wu, X. W.; Han, X.; Xu, Q. S.; Liu, Y. H.; Yuan, C.; Yang, S.; Liu, Y.; Jiang, J. W.; Cui, Y. Chiral BINOL-Based Covalent Organic Frameworks for Enantioselective Sensing. *J. Am. Chem. Soc.* **2019**, *141*, 7081−7089.

(11) Yue, J. Y.; Song, L. P.; Ding, X. L.; Wang, Y. T.; Yang, P.; Ma, Y.; Tang, B. Ratiometric Fluorescent pH Sensor Based on a Tunable Multivariate Covalent Organic Framework. *Anal. Chem.* **2022**, *94*, 11062−11069.

(12) Guo, J. X.; Yang, C.; Yan, X. P. Thiol-ene Click Synthesis of Chiral Covalent Organic Frameworks for Gas Chromatography. *J. Mater. Chem. A* **2021**, *9*, 21151−21157.

(13) Wang, H. J.; Zhai, Y. M.; Li, Y.; Cao, Y.; Shi, B. B.; Li, R. L.; Zhu, Z. T.; Jiang, H. F.; Guo, Z. Y.; Wang, M. D.; et al. Covalent Organic Framework Membranes for Efficient Separation of Monovalent Cations. *Nat. Commun.* **2022**, *13*, 7123.

(14) Zheng, Q.; Huang, J.; He, Y.; Huang, H.; Ji, Y.; Zhang, Y.; Lin, Z. Single-Crystalline Covalent Organic Frameworks as High-Performance Liquid Chromatographic Stationary Phases for Positional Isomer Separation. *ACS Appl. Mater. Interfaces* **2022**, *14*, 9754−9762.

(15) Zheng, Q.; He, Y.; Ma, W.; Wu, Y.; Chen, Z.; Wang, R.; Tong, W.; Lin, Z. Facile Synthesis of Spherical Covalent Organic Frameworks as Stationary Phases for Short-Column Liquid Chromatography. *Chem. Commun.* **2021**, *57*, 7501−7504.

(16) Liu, R. Y.; Tan, K. T.; Gong, Y. F.; Chen, Y. Z.; Li, Z. E.; Xie, S. L.; He, T.; Lu, Z.; Yang, H.; Jiang, D. L. Covalent Organic Frameworks: An Ideal Platform for Designing Ordered Materials and Advanced Applications. *Chem. Soc. Rev.* **2021**, *50*, 120−242.

(17) Li, Z.; Liu, Z. W.; Li, Z. Y.; Wang, T. X.; Zhao, F. L.; Ding, X. S.; Feng, W.; Han, B. H. Defective 2D Covalent Organic Frameworks for Postfunctionalization. *Adv. Funct. Mater.* **2020**, *30*, 1909267.

(18) Merí-Bofí, L.; Royuela, S.; Zamora, F.; Ruiz-González, M. L.; Segura, J. L.; Muñoz-Olivas, R.; Mancheño, M. J. Thiol Grafted Imine-Based Covalent Organic Frameworks for Water Remediation through Selective Removal of Hg(II). *J. Mater. Chem. A* **2017**, *5*, 17973−17981.

(19) Tang, B.; Wang, W.; Hou, H.; Liu, Y.; Liu, Z.; Geng, L.; Sun, L.; Luo, A. A β-cyclodextrin Covalent Organic Framework Used as a Chiral Stationary Phase for Chiral Separation in Gas Chromatography. *Chin. Chem. Lett.* **2022**, *33*, 898−902.

(20) Qian, H.-L.; Wang, Z.-H.; Yang, J.; Yan, X.-P. Building-Block Exchange Synthesis of Amino-Based Three-Dimensional Covalent Organic Frameworks for Gas Chromatographic Separation of Isomers. *Chem. Commun.* **2022**, *58*, 8133−8136.

(21) Berger, R.; Resnati, G.; Metrangolo, P.; Weber, E.; Hulliger, J. Organic Fluorine Compounds: A Great Opportunity for Enhanced Materials Properties. *Chem. Soc. Rev.* **2011**, *40*, 3496−3508.

(22) Sun, X. W.; Ji, W. H.; Hou, S. H.; Wang, X. Facile Synthesis of Trifluoromethyl Covalent Organic Framework for the Efficient Microextraction of Per-and Polyfluorinated Alkyl Substances from Milk Products. *J. Chromatogr. A* **2020**, *1623*, 461197.

(23) Mellah, A.; Fernandes, S. P. S.; Rodriguez, R.; Otero, J.; Paz, J.; Cruces, J.; Medina, D. D.; Djamila, H.; Espina, B.; Salonen, L. M. Adsorption of Pharmaceutical Pollutants from Water Using Covalent Organic Frameworks. *Chem.—Eur. J.* **2018**, *24*, 10601−10605.

(24) Yin, D. H.; Su, D. Q.; Jin, J. Photoredox Catalytic Trifluoromethylation and Perfluoroalkylation of Arenes Using Trifluoroacetic and Related Carboxylic Acids. *Cell Rep. Phys. Sci.* **2020**, *1*, 100141.

(25) Xu, X.-H.; Matsuzaki, K.; Shibata, N. Synthetic Methods for Compounds having CF_3-S Units on Carbon by Trifluoromethylation, Trifluoromethylthiolation, Triflylation, and Related Reactions. *Chem. Rev.* **2015**, *115*, 731−764.

(26) Morstein, J.; Hou, H. Y.; Cheng, C.; Hartwig, J. F. Trifluoromethylation of Arylsilanes with [(phen)$CuCF_3$]. *Angew. Chem. Int. Ed.* **2016**, *55*, 8054−8057.

(27) Nie, J.; Guo, H. C.; Cahard, D.; Ma, J. A. Asymmetric Construction of Stereogenic Carbon Centers Featuring a Trifluoromethyl Group from Prochiral Trifluoromethylated Substrates. *Chem. Rev.* **2011**, *111*, 455−529.

(28) Rabasa-Alcaniz, F.; Asensio, A.; Sanchez-Rosello, M.; Escolano, M.; Del Pozo, C.; Fustero, S. Intramolecular Nitrone Cycloaddition of

alpha-(Trifluoromethyl)styrenes. Role of the CF_3 Group in the Regioselectivity. *J. Org. Chem.* **2017**, *82*, 2505−2514.
(29) Zheng, Q.; Liu, J.; Wu, Y.; Ji, Y.; Lin, Z. Fluoro-Functionalized Spherical Covalent Organic Frameworks as a Liquid Chromatographic Stationary Phase for the High-Resolution Separation of Organic Halides. *Anal. Chem.* **2022**, *94*, 18067−18073.
(30) Zong, R.; Yin, H.; Xiang, Y. H.; Zhang, L.; Ye, N. S. Fluorinated Covalent Organic Frameworks as a Stationary Phase for Separation of Fluoroquinolones by Capillary Electrochromatography. *Microchim. Acta* **2022**, *189*, 237.
(31) Yang, Y. X.; Bai, P.; Guo, X. H. Separation of Xylene Isomers: A Review of Recent Advances in Materials. *Ind. Eng. Chem. Res.* **2017**, *56*, 14725−14753.
(32) Wang, T.; Lee, H. G. Advances in Research on cis-9, trans-11 Conjugated Linoleic Acid: A Major Functional Conjugated Linoleic Acid Isomer. *Crit. Rev. Food Sci.* **2015**, *55*, 720−731.
(33) Barcia, P. S.; Guimaraes, D.; Mendes, P. A. P.; Silva, J. A. C.; Guillerm, V.; Chevreau, H.; Serre, C.; Rodrigues, A. E. Reverse Shape Selectivity in the Adsorption of Hexane and Xylene Isomers in MOF UiO-66. *Microporous Mesoporous Mater.* **2011**, *139*, 67−73.
(34) Peralta, D.; Chaplais, G.; Paillaud, J. L.; Simon-Masseron, A.; Barthelet, K.; Pirngruber, G. D. The Separation of Xylene Isomers by ZIF-8: A Demonstration of the Extraordinary Flexibility of the ZIF-8 Framework. *Microporous Mesoporous Mater.* **2013**, *173*, 1−5.
(35) Krishna, R. Separating Mixtures by Exploiting Molecular Packing Effects in Microporous Materials. *Phys. Chem. Chem. Phys.* **2015**, *17*, 39−59.
(36) Tan, H. L.; Chen, Q. B.; Chen, T. T.; Liu, H. L. Selective Adsorption and Separation of Xylene Isomers and Benzene/Cyclohexane with Microporous Organic Polymers POP-1. *ACS Appl. Mater. Interfaces* **2018**, *10*, 32717−32725.
(37) Minceva, M.; Rodrigues, A. E. Understanding and Revamping of Industrial Scale SMB Units for p-Xylene Separation. *AIChE J.* **2007**, *53*, 138−149.
(38) Lima, R. M.; Grossmann, I. E. Optimal Synthesis of p-Xylene Separation Processes Based on Crystallization Technology. *AIChE J.* **2009**, *55*, 354−373.
(39) Huang, X. L.; Lan, H. H.; Yan, Y. L.; Chen, G.; He, Z. H.; Zhang, K.; Cai, S. L.; Zheng, S. R.; Fan, J.; Zhang, W. G. Fabrication of a Hydrazone-Linked Covalent Organic Framework-Bound Capillary Column for Gas Chromatography Separation. *Sep. Sci. Plus* **2019**, *2*, 120−128.
(40) Ma, T. T.; Yang, C.; Qian, H. L.; Yan, X. P. Post-Modification of Covalent Organic Framework for Gas Chromatographic Separation of Isomers. *J. Chromatogr. A* **2022**, *1673*, 463085.
(41) Biswal, B. P.; Chandra, S.; Kandambeth, S.; Lukose, B.; Heine, T.; Banerjee, R. Mechanochemical Synthesis of Chemically Stable Isoreticular Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2013**, *135*, 5328−5331.
(42) Li, W. B.; Cheng, Y. Z.; Yang, D. H.; Liu, Y. W.; Han, B. H. Fluorine-Containing Covalent Organic Frameworks: Synthesis and Application. *Macromol. Rapid Commun.* **2022**, *44*, 2200778.
(43) Chu, J. Q.; Lu, Y.; Gan, S. X.; Qi, Q. Y.; Jia, C.; Yao, J.; Zhao, X. A Superhydrophobic Trifluoromethyl-Containing Covalent Organic Framework Membrane for Efficient Oil/Water Separation. *Macromol. Rapid Commun.* **2022**, *44*, 2200641.
(44) Alahakoon, S. B.; McCandless, G. T.; Karunathilake, A. A. K.; Thompson, C. M.; Smaldone, R. A. Enhanced Structural Organization in Covalent Organic Frameworks Through Fluorination. *Chem.—Eur. J.* **2017**, *23*, 4255−4259.
(45) Gu, Z. Y.; Yan, X. P. Metal-Organic Framework MIL-101 for High-Resolution Gas-Chromatographic Separation of Xylene Isomers and Ethylbenzene. *Angew. Chem. Int. Ed.* **2010**, *49*, 1477−1480.
(46) Chang, N.; Yan, X. P. Exploring Reverse Shape Selectivity and Molecular Sieving Effect of Metal-organic Framework UIO-66 Coated Capillary Column for Gas Chromatographic Separation. *J. Chromatogr. A* **2012**, *1257*, 116−124.
(47) Fang, Z. L.; Zheng, S. R.; Tan, J. B.; Cai, S. L.; Fan, J.; Yan, X.; Zhang, W. G. Tubular Metal-organic Framework-Based Capillary Gas Chromatography Column for Separation of Alkanes and Aromatic Positional Isomers. *J. Chromatogr. A* **2013**, *1285*, 132−138.
(48) Srivastava, M.; Roy, P. K.; Ramanan, A. Hydrolytically Stable ZIF-8@PDMS Core-shell Microspheres for Gas-Solid Chromatographic Separation. *RSC Adv.* **2016**, *6*, 13426−13432.
(49) Zhang, X.; Ji, H.; Zhang, X.; Wang, Z.; Xiao, D. Capillary Column Coated with Graphene Quantum Dots for Gas Chromatographic Separation of Alkanes and Aromatic Isomers. *Anal. Methods* **2015**, *7*, 3229−3237.
(50) He, C. T.; Jiang, L.; Ye, Z. M.; Krishna, R.; Zhong, Z. S.; Liao, P. Q.; Xu, J. Q.; Ouyang, G. F.; Zhang, J. P.; Chen, X. M. Exceptional Hydrophobicity of a Large-Pore Metal-Organic Zeolite. *J. Am. Chem. Soc.* **2015**, *137*, 7217−7223.

https://doi.org/10.1021/acsami.3c05369
ACS Appl. Mater. Interfaces 2023, 15, 32926−32934