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Crystalline Porous Organic Frameworks Hot Paper

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Crystalline Porous Organic Frameworks Based on Multiple Dynamic Linkages

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Abstract: A novel class of crystalline porous materials has been developed utilizing multilevel dynamic linkages, including covalent B–O, dative B←N and hydrogen bonds. Typically, boronic acids undergo in situ condensation to afford B₃O₃-based units, which further extend to molecular complexes or chains via $B \leftarrow N$ bonds. The obtained superstructures are subsequently interconnected via hydrogen bonds and π - π interactions, producing crystalline porous organic frameworks (CPOFs). The CPOFs display excellent solution processability, allowing dissolution and subsequent crystallization to their original structures, independent of recrystallization conditions, possibly due to the diverse bond energies of the involved interactions. Significantly, the CPOFs can be synthesized on a gram-scale using costeffective monomers. In addition, the numerous acidic sites endow the CPOFs with high NH₃ capacity, surpassing most porous organic materials and commercial materials.

Introduction

Crystalline porous materials (CPMs), distinguished by their permanent porosity and well-ordered skeletons, have garnered considerable attention owing to their well-defined and precisely tailorable structures, as well as their customizable properties.^[1] Among these materials, metal–organic frameworks (MOFs)^[2] and covalent organic frameworks (COFs)^[3] stand out as prominent examples, renowned for their excep-

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tional material characteristics. However, these materials often demonstrate strong intrinsic bonding interactions, such as coordination bonds (typically in the range of 90-350 kJ mol⁻¹) in MOFs and covalent bonds (typically in the range of 300-600 kJ mol⁻¹) in COFs, which typically render these materials insoluble and challenging to process.^[1,4] In contrast, materials with relatively labile intermolecular interactions, such as hydrogen bonds (typically in the range of 10-40 kJ mol⁻¹) found in hydrogen-bonded organic frameworks (HOFs), display some degree of processability, allowing them to be soluable and recrystallizable in solution.^[5] Unfortunately, the suitable building blocks for constructing HOFs are limited, which stems from the specific requirements of HOF monomers, including rigid backbones, multiple hydrogen-bonding sites, and appropriate hydrogen-bond extension directions.^[6] Moreover, different crystalline phases have been found upon recrystallization of HOFs from various solution conditions, which poses an additional obstacle to their processability and recovery.^[7] Consequently, achieving processable and regenerable CPMs is highly desired yet remains a significant challenge.

To address this challenge, one potential solution might involve the integration of multiple dynamic linkages, encompassing both weak interactions to facilitate the dissolution process and relatively stronger bonds to aid in structure preservation. Recently, crystalline organic frameworks based on B–O and B←N bonds (BNOFs) provide a good opportunity.^[8] All connections in BNOFs, namely covalent B−O and dative B←N coordination bonds, are highly dynamic, but the B←N coordination can effectively protect sensitive boron centers from nucleophilic agents, providing BNOFs with satisfactory stability.^[9] Nonetheless, the development of BNOFs is significantly hampered by the difficulty in creating permanent porosity, attributed to the lack of additional interactions to stabilize their skeletons.^[8] It is hypothesized that, the integration of B–O/B–N bonds structural maintenance, together for with extra supramolecular interactions, such as hydrogen bonds, would be beneficial for achieving solution-processable crystalline porous organic frameworks (CPOFs). In this context, the CPOFs can be dissolved due to the facile disruption of weak hydrogen bonds (typically, $<40 \text{ kJ mol}^{-1}$), while their original crystal structures will be maintained after recrystallization on account of partially preserved superstructures in solution through relatively stronger covalent B-O (560 kJ mol⁻¹) and dative B \leftarrow N bonds (100 kJ mol⁻¹).^[4,8e] More importantly, the molecular complexes connected by $B-O/B \leftarrow N$ bonds demonstrate a well-defined tetrahedral

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topology with appropriate extending directions, facilitating their further assembly.^[9a,c] However, although this approach holds the potential to expand the range of reticular chemistry and simplify the fabrication of CPMs with permanent porosity and excellent solution processability, related results have not yet been reported so far.

Herein, a serial of novel CPOFs with multiple dynamic linkages, named CPOF-1 to CPOF-4, have been designed and synthesized (Scheme 1). Typically, low-cost and readily available building blocks, including carboxyphenylboronic acids and bipyridine or bifunctional pyridylboronic acid organic monomers, are connected by covalent B-O and dative B←N bonds, affording 0D organic assemblers or 1D chains, which serve as secondary building units (SBUs) to construct 3D frameworks via multiple hydrogen bonds and π - π interactions (Scheme 1). Remarkably, the resulting CPOFs exhibit excellent solution processability, allowing for easy dissolution and regeneration through simple recrystallization. Furthermore, the low-cost and commercially available monomers for the CPOFs enable scalable synthesis and potential practical applications. Motivated by the abundant acidic sites, such as boroxine (B₃O₃) and carboxylic acids, the CPOFs display outstanding performance in the capture of NH₃ gas. In particular, CPOF-3 exhibits intriguing NH₃ adsorption with high uptake $(11.69 \text{ mmol g}^{-1})$, which can be maintained for at least three cycles without any observable deterioration.

Results and Discussion

The CPOFs have been successfully synthesized via a one-pot solvothermal route (Figure S1, see Supporting Information, Experimental Section), while the synthetic conditions have been throughly investigated (Table S1 and Figure S2–5). Typically, there are two distinct kinds of SBUs in CPOFs, i.e., 0D organic assemblers in CPOF-1, -2, and 1D chains in CPOF-3, -4. Specifically, CPOF-1 and CPOF-2 based on 0D SBUs are generated by the polycondensation of 4-carbox-



Scheme 1. Schematic illustration showing the stepwise assembly of the resulting CPOFs by multiple dynamic linkages of covalent B–O, dative $B \leftarrow N$ and hydrogen bonds.

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yphenylboronic acid (CPBA) with 4,4'-bipyridine (BPY) or 1,2-bis(4-pyridyl)ethylene (BPE) in a molar ratio of 6:1 (Figure 1a and 1b). Initially, three CPBA molecules undergo dehydration and condensation via B-O bonds, forming a B₃O₃ ring with three benzoic acid groups (Figure S6a and S7a). Two such B₃O₃-connected moieties are bridged by BPY or BPE via B←N bonds, affording larger molecular complexes with six benzoic acid groups (Figure 1a and 1b). These organic assemblers can serve as SBUs and readily interact with each other through COOH wdrogen bonds, yielding the target 3D frameworks CPOF-1 and CPOF-2 (Figure 1c and 1d). On the other hand, CPOF-3 and CPOF-4 are constructed based on dynamic 1D chains as the SBUs (Figure 1e and 1f), utilizing CPBA and bifunctional pyrimidinylboronic acid (PMBA) or 4-(4pyridinyl)phenylboronic acid (PYBA) as organic monomers in a molar ratio of 1:2. Similarly, B₃O₃ rings are in situ generated from the dehydration of boronic acid groups in CPBA and PMBA/PYBA (Figure S8a and S9a), and $B \leftarrow N$ bonds are formed with nitrogen atoms from pyrimidinyl or pyridinyl moieties. Interestingly, dynamic 1D chains are generated in these structures (Figure 1e and 1f), which can be further fabricated into porous frameworks with the aid of COOH ... N hydrogen bonds, affording CPOF-3 and CPOF-4



Figure 1. The structures of hexacarboxylic molecular complexes (serving as SBUs) in (a) CPOF-1 and (b) CPOF-2. The crystal structures of (c) CPOF-1 and (d) CPOF-2. The structures of 1D chains (serving as SBUs) in (e) CPOF-3 and (f) CPOF-4. The crystal structures of (g) CPOF-3 and (h) CPOF-4. The gray, red, blue and pink spheres represent C, O, N and B atoms, respectively.

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(Figure 1g and 1h). To the best of our knowledge, this is the first attempt to integrate reversible B–O, B \leftarrow N and hydrogen bonds in CPMs.

The crystal structures of all the CPOFs have been resolved by single crystal X-ray diffraction (XRD) (Table S2), and the solvents incorporated into the structures were confirmed by analysis of the ¹H nuclear magnetic resonance (NMR) spectra (Figure S10-S13) and elemental analysis (Table S3). The CPOF-1 crystallizes in the triclinic space group P-1, where the asymmetric unit comprises one B₃O₃ ring with three benzoic acid groups and a half BPY molecule (Figure S6b). The assembly process generates a hexacarboxylic adduct with terminal benzoic acid groups in an anti-conformation state (Figure 1a). Then, the hexacarboxylic SBUs are connected head-to-head with six neighboring ones via intermolecular H-bonds to construct a 3D framework with the dia network (Figure 1c). The presence of large void spaces allows four equivalent nets to interpenetrate each other, leaving a channel (15.1 Å×17.1 Å) along the b axis (Figure S6c). The CPOF-2 also crystallizes in the triclinic space group P-1, where the asymmetric unit consists of one B₃O₃ ring with three benzoic acid groups, a half BPE, and one HCOOH molecule (Figure S7b). In contrast to those in CPOF-1, two types of hydrogen bonds can be found in CPOF-2, one formed head-to-head between two COOH groups and the other formed by one HCOOH and two COOH groups (Figure S7d). The involvement of HCOOH molecules alters the extension direction of the hexacarboxylic SBUs, resulting in each SBU connecting with four neighboring SBUs through hydrogen bonds, forming a 2D layer (Figure 1d). Interestingly, these layers further extend into a 3D polycatenated framework via an interlocking pattern with the aid of strong interlayer π - π interactions (Figure S7e).

CPOF-3 crystallizes in the monoclinic space group $P2_1/n$, with the asymmetric unit comprising a B₃O₃ unit with one benzoic acid and two pyrimidine groups (Figure S8a). Adjacent asymmetric units are connected to each other via dative $B \leftarrow N$ bonds to form infinite 1D chains (Figure 1e), which interlink with two adjacent chains via hydrogen bonds (Figure S8b) to form a layer extending along the ab plane (Figure 1g). These layers are arranged through strong $\pi - \pi$ interactions between pyrimidine and phenyl groups into a 3D porous framework with narrow channels measuring 3.5 Å×5.1 Å (Figure S8c). CPOF-4 crystallizes in the orthorhombic space group Pbca, and the asymmetric unit consists of the B₃O₃ unit with one benzoic acid and two 4-phenylpyridine groups (Figure S9a). Similar to CPOF-3, 1D chains are formed via dative $B \leftarrow N$ bonds (Figure 1f), which further interlink with four adjacent chains via COOH-N hydrogen bonds to form a 3D porous framework with a dia network (Figure 1h). Due to the large void spaces, six equivalent nets interpenetrate via π - π interactions between the phenyl rings, leaving a rectangular channel (5.1 Å×11.1 Å) along the baxis (Figure S9c).

The phase purity of the CPOFs is confirmed by powder XRD, wherein the experimental diffraction peaks closely match those predicted based on the crystal structures (Figure 2a, 2b and S14). Notably, all CPOFs demonstrate good



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Figure 2. Powder XRD patterns for (a) CPOF-3 and (b) CPOF-4. (c) Schematic representation of the large-scale synthesis, recrystallization and regeneration of the CPOFs.

stability in certain organic solvents, such as dichloromethane, acetonitrile, *n*-hexane, and acetone (Figure S15). Moreover, CPOF-2 exhibits excellent stability in aqueous solutions with pH values ranging from 1 to 13 for at least 24 h, surpassing that of the other CPOFs (Figure S16). The high hydrolytic stability of CPOF-2 can be attributed to its interlocking networks with the presence of strong π - π stacking. Additionally, the thermal stability of CPOFs has been characterized by thermogravimetric analysis (TGA), indicating the stability of the CPOFs up to temperatures ranging from 493 to 558 K under a nitrogen atmosphere (Figure S17).

The porosity of the CPOFs has been investigated through gas adsorption isotherms on activated samples, including nitrogen (N_2) adsorption at 77 K and carbon dioxide adsorption (CO₂) at 195 K (Figure S18 and S19). The N₂ adsorption at 77 K displays a typical type I isotherm for CPOF-1 (Figure S19a), with the surface area calculated to be 202 m²g⁻¹ using the Brunauer–Emmett–Teller (BET) equation. However, minimal N₂ adsorption capacities have been observed for the other CPOFs (Figure S19b-d), a phenomenon commonly reported in HOFs,^[5b,6b] though the exact reasons remain unclear. As a result, CO₂ sorption isotherms at 195 K have been employed to assess the pore feature. Interestingly, significant gate-opening effects can be observed in the CO₂ adsorption isotherms for both CPOF-2 and CPOF-4 (Figure S19b and S19d). The CO₂ adsorption capacity of CPOF-4 reaches 20.87 cm³g⁻¹ at 0.05 bar followed by another sharp increase observed between 0.25 to 0.4 bar (from 42.66 cm^3g^{-1} to 130.12 cm^3g^{-1}). These stepwise adsorption isotherms may arise from the framework flexibility, allowing for the provision of additional pore volumes for CO₂ adsorption.^[7,10] This flexibility can be further evidenced by a shift towards higher angles observed in the powder XRD patterns of CPOF-4 upon solvent removal GDCh

(Figure S18d). The BET surface areas are calculated to be 90, 207, and 212 m^2g^{-1} for CPOF-2 to CPOF-4, respectively, which are moderate compared with HOFs with permanent porosity.^[6b] These findings underscore the permanent porosity of CPOFs.

Moreover, the CPOFs can be readily recrystallized from organic solvents, such as dimethylformamide (DMF), Nmethylformamide (NMF), methanol (MeOH), and ethanol (EtOH). Typically, clear solutions can be easily obtained by dissolving CPOFs in these solvents, and high-quality single crystals of the corresponding CPOFs can be easily havested through a gradual solvent evaporation process. These crystals exhibit powder XRD patterns similar to those of the as-synthesized samples, regardless of the recrystallization solvent employed (Figure 2 and S20). For conventional CPMs, such as COFs and MOFs, they are usually challenging to be dissolved in most common solvents. Even for typical HOFs, they tend to disassemble into monomers in solution, resulting in the potential formation of diverse crystalline phases depending on the crystallization conditions,^[7] which is unpredictable and generally undesired. In contrast, given the variations in bond energies (e.g., 560 kJ mol⁻¹ for B–O and 100 kJ mol⁻¹ for B–N as well as 10-40 kJ mol⁻¹ for hydrogen bonds) in the obtained CPOFs,^[4,8e] it is assumed that the partially preserved covalent/coordinate bond-connected SBUs in solution would gurantees their unaltered overall structures in the recrystallization process, conferring a distinctive advantage in terms of superior solution processability.^[9c]

To further elucidate the state of CPOFs in organic solvent, complementary characterizations have been conducted for the dissolved CPOFs. The gel permeation chromatography (GPC) analysis in DMF solution has revealed high molecular weights ranging from 19 to 447 kDa for the dissolved CPOFs, indicating the partial preservation of oligomers rather than complete depolymerization into monomers (less than 1 kDa) (Figure S21). The presence of preserved large fragments in solution is further evidenced by the particle size distributions (2.0 to 50.7 nm) determined by dynamic light scattering (Figure S22). In addition, ¹¹B NMR spectroscopy has been employed to probe the bonding of boron atoms in solution. Two distinct signals have been observed at approximately 27.4-28.3 and 18.5-18.6 ppm (Figure S23-S26), corresponding to boron atoms with trigonal and tetrahedral geometries, respectively,^[11] evidencing the existence of the dative $B \leftarrow N$ bonds in solution. Furthermore, the presence of both the B₃O₃-connected moieties and their adducts with pyridinyl/pyrimidinyl units are also detected in the mass spectrum (Figure S27). Collectively, these results suggest that CPOFs do not completely depolymerize into monomers in solution but instead partially preserve the fragments connected by covalent B–O and coordinate $B \leftarrow N$ bonds.

Fuethermore, the scale-up synthesis of CPOFs has been investigated, suggesting that CPOF samples can be readily prepared on a gram-scale with high yields (see SI, Experimental Section S2.2). This accomplishment is crucial for potential industrial applications. More importantly, all the monomers required for CPOF synthesis are readily available

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from commercial sources at a relatively low cost. Coupled with the facile scale-up synthesis, CPOFs can be obtained at an exceptionally low production price on a large scale, compared to other solution-processable CPMs (Table S5). These characteristics position CPOFs as promising candidates for applications in interfacial coatings and processing, opening up a broad spectrum of potential uses. In addition, the facile dissolution and crystallization process also presents an opportunity to repair structural damage to the network, further reducing the cost associated with their utilization. For example, after losing their crystallinity in water, CPOFs can be regenerated under synthetic conditions, as demonstrated by powder XRD (Figure 2 and S28). In brief, the facile scale-up synthesis, promising solution processability and regenerability of CPOFs render them highly valued CPMs.

As a crucial chemical and unique carbon-free fuel with high energy density, the capture, storage, and desorption of NH₃ are highly important.^[12] Adsorbents with acidic sites can strongly interact with NH₃, making them ideal for its storage.^[13] For instance, Yaghi et al. first reported the utilization of the boronate ester COF (COF-10) as an NH₃ adsorbent in 2010.^[14] Subsequently, Long et al. demonstrated that introducing multiple acidic sites in porous materials can effectively enhance NH₃ capture.^[15] Inspired by these findings, we identified populated acidic sites, namely threecoordinate boron and carboxylic acid sites, within CPOFs, implying their potential for NH₃ capture. Significantly, CPOF-1 to CPOF-3 exhibit noteworthy NH₃ adsorption capabilities, with uptake amounts of 13.79, 10.80, and 11.69 mmol g^{-1} at 298 K and 1 bar (Figure 3a), respectively, which are much higher than that of CPOF-4 (5.43 mmol g^{-1}), possibly due to the different density of acidic sites (Table S6). For comparison, the NH₃ adsorption isotherms for the acidic monomers (CPBA, PMBA, and PYBA) have



Figure 3. (a) The NH₃ sorption isotherms measured at 298 K for CPOF-1 to -4. (b) Schematic diagram of the NH₃ adsorption capacity and price of adsorbents. (c) Three cycles of NH₃ adsorption isotherms at 298 K for CPOF-3. (d) Comparison of NH₃ adsorption capacities at 298 K for different samples of CPOF-3.

also been recorded at 298 K. These monomers exhibit much smaller NH₃ uptake capacities (less than 1 mmol g⁻¹), ruling out the possibility of monomer adsorption (Figure S29). Additionally, a comprehensive assessment of NH₃ capture capacities has been conducted by comparing CPOFs with other known porous organic materials, including COFs, HOFs and porous organic polymers (POPs) (Table S7). Encouragingly, although exhibiting slightly lower NH₃ uptake than that of COF-10 $(15.0 \text{ mmol g}^{-1})$,^[14] CPOF-1 and -3 surpass most metal-free porous organic materials $(TpBD-(SO_3H)_2,^{[16]} 11.5 \text{ mmol g}^{-1}; TpPa-1,^{[17]} 6.9 \text{ mmol g}^{-1};$ KUF-1a,^[18] 6.67 mmolg⁻¹; PHOF-1,^[19] 4.2 mmolg⁻¹; HOF-101,^[20] 8.44 mmol g⁻¹; FDU-HOF-3,^[20] 9.34 mmol g⁻¹, etc.) and commercially available materials (Amberlyst, [21] 11.34 mmol g^{-1} and 13X zeolites,^[21] 9.3 mmol g^{-1}). Particularly noteworthy is the excellent capacity-to-price ratio of CPOFs (up to 26.12 mmol USD⁻¹), outperforming reported porous organic materials in terms of NH₃ adsorption (Figure 3b and Table S8). Such exceptional cost-effectiveness of CPOFs is rare in the domain of organic porous materials, suggesting their potential for high-density NH₃ storage at room temperature.

Subsequently, the crystal structures of the CPOFs are monitored during the adsorption and desorption of NH₃. Notably, the diffraction peaks disappear or shift after NH₃ adsorption for all CPOFs (Figure S30), indicating the transformation from CPOFs into amorphous states or other crystalline phases, possibly associated with the disruption of hydrogen bonds after NH₃ binding.^[20] The original structures can be recovered upon NH₃ removal by heating under vacuum (Figure S30). The degassing at elevated temperatures (100 °C for CPOF-1 and -2; 80 °C for CPOF-3 and -4) is necessary in this process, possibly due to the relative strong interactions between the basic NH3 molecules and acidic binding sites (Figure S31), as also can be found for other porous framework materials (for examples, 90°C for HOF-101,^[20] 200°C for COF-10,^[14] and 130°C for P2- $CO_2H^{[22]}$). These findings imply the potential reusability of CPOF-3 and CPOF-4. Considering both the outstanding NH₃ uptake capacity and facile reactivation process, CPOF-3 has been selected for further in-depth study. Firstly, to verify the reusability, a temperature-dependent adsorptiondesorption process has been carried out using NH₃ isotherms. The adsorption occurs at 298 K and 1 bar NH₃, with reactivation at 80°C under vacuum for 4 h (Figure S32). Excitingly, the adsorption capacity can be maintained after three cycles without visible decay (Figure 3c and S32a). Subsequently, the CPOF-3 samples prepared on a large scale have been subjected to NH₃ adsorption, exhibiting almost identical NH₃ uptake capacity (11.67 mmol g^{-1}), indicating the promising potential for widespread utilization of these materials on a large scale (Figure 3d and S32b). Additionally, this uptake capacity remains unaltered (11.83 mmolg⁻¹) after the regeneration of hydrolysed samples, demonstrating the usability of the recovered framework (Figure 3d and S32b). In brief, the combination of large-scale synthesis, facile regeneration and excellent reusability will position CPOFs for great potential in industrial production and applications.

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To further establish the feasibility for CPOF-3 in NH₃ capture, dynamic NH₃ breakthrough tests are carried out. These tests involve passing a mixture of 5000 ppm NH₃ in N₂ through a fixed bed packed with CPOF-3 at 298 K, in which strong retention of NH₃ has been observed (Figure 4a). The breakthrough time of NH_3 is measured to be 172 min g⁻¹ for CPOF-3, and the saturation NH₃ uptake amount is found to be 1.13 mmol g^{-1} , which is consistent with the capacity of 0.89 mmolg⁻¹ obtained from NH₃ adsorption isotherm at 298 K under the same pressure of 5.0 mbar (Figure S33). To estimate the performance of CPOF-3 under realistic NH₃ conditions, a gravimetric NH3 vapor adsorption test has been conducted over time (Figure 4b, see SI, Experimental Section S2.7). Based on the NH₃ vapor adsorption curve, CPOF-3 exhibits rapid NH₃ adsorption with a saturated uptake of up to 25.3 g/g% after 48 h, confirming the high NH₃ capture capacity of CPOF-3.

To better understand the interaction between NH₃ and the framework, the FTIR spectroscopy has also been conducted (Figure 4c and S34). The FTIR analysis reveals the emergence of the characteristic N-H peak at approximately 3000 cm^{-1} along with blue-shifts in the peaks corresponding to C=O bonds (at approximately 1700 cm⁻¹) in COOH and B–O bonds (at approximately 1358 cm⁻¹) in B₃O₃ rings upon the introduction of NH₃ molecules.^[20] These spectral changes indicate interactions of NH₃ with COOH and B₃O₃ units within the framework. Additionally, based on isotherms measured at 273 and 298 K, the heat of adsorption (Q_{st}) of NH₃ on CPOF-3 is calculated to be 55 kJ mol⁻¹ (Figure S35 and S36), demonstrating the strong interactions between NH₃ molecules and the framework. Furthermore, TGA has also been performed on CPOF-3 after NH₃ adsorption (named CPOF-3@NH₃) and reactivation at 80 °C for 4 h (named CPOF-3@NH₃-reactivated) (Figure 4d). Notably, a weight difference of ~18% has been



Figure 4. (a) The NH₃ breakthrough curve of CPOF-3 at 298 K and 5000 ppm (0.5%) NH₃ concentration under N₂ flow. (b) The vapor adsorption curves for CPOF-3 as a function of time. (c) The FT-IR spectra of CPOF-3 before and after the adsorption of NH₃. (d) The TGA curves of CPOF-3@NH₃ and CPOF-3@NH₃-reactivated.

observed between the two TGA curves at 220 °C, which might be attributed to the loss of NH_3 from CPOF-3@ NH_3 , indicating the storage of NH_3 in the CPOFs.^[20] These results collectively indicate the strong interaction between NH_3 and CPOF-3, with potential binding sites including the acidic COOH and B_3O_3 rings.

Inspired by the excellent solution processability and NH₃ adsorption performance, a composite functional textile based on CPOF-3 has been fabricated for NH₃ capture. Typically, the as-synthesized CPOF-3 is dissolved in MeOH, and the resulting clear solution is evenly dropped onto nonwoven fabric. The gradual volatilization of MeOH facilitates the regeneration of crystalline CPOF-3, resulting in the formation of CPOF-3@fabric. Scanning electron microscope (SEM) images demonstrate that CPOF-3 coatings are covered on the fibers as a thin film, with some crystalline particles observed (Figure 5a). Powder XRD patterns (Figure 5b) and thermogravimetric analysis (Figure S37b) further confirm the composition of CPOF-3 in this coating process. The integration of porous CPOF-3 onto the fibers endows high porosity to the composite fabric, as revealed by CO₂ sorption isotherms at 195 K (Figure S37c). Importantly, CPOF-3@fabric exhibits notable NH₃ uptake of 4.05 mmol g^{-1} at 1 bar (Figure 5c), indicating its potential as a promising composite membrane for NH₃ capture.

Conclusion

In summary, a series of CPOFs have been successfully synthesized through the integration of dynamic bonds, including B-O, $B \leftarrow N$ and hydrogen bonds. These materials exhibit high crystallinity, permanent porosity, and low cost. Leveraging the cooperation of various dynamic bonds, CPOFs can be facilely prepared from small building blocks, which are easily available from commercial sources at extremely low prices. In addition, the CPOFs display excellent solution processability, allowing dissolution and subsequent crystallization with undisturbed structures, in-



Figure 5. (a) Schematic illustration of the coating process on fabrics with SEM images. (b) The powder XRD patterns and (c) NH_3 sorption isotherms of CPOF-3@fabric at 298 K.

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dependent of the recrystallization conditions. With abundant acidic sites in the frameworks, CPOFs demonstrate impressive NH₃ uptake performance, surpassing that of most organic porous materials. Coupled with their impressive reusability, exceptional cost-effectiveness, and facile scale-up synthesis, CPOFs have emerged as promising candidates for high-density NH₃ storage. Given the diversity of organic molecules bearing carboxylic acid, boronic acid and nitrogen heterocycles, it is anticipated that more innovative CPOFs based on B–O, B \leftarrow N, and hydrogen bonds will be developed for various applications in the future.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords: crystalline porous materials \cdot microporous materials \cdot solution processability \cdot dynamic bonds \cdot gas adsorption

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