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2D covalent organic frameworks with built-in amide active sites for efficient heterogeneous catalysis[†]

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Benzene-1,3,5-tricarboxamides (BTAs) are versatile building blocks for supramolecular assembly due to the strong intermolecular hydrogen bonding. Herein, a BTA based amine, N^1, N^3, N^5 -tris-(4-aminophenyl)benzene-1,3,5-tricarboxamide (TABTA), was successfully applied to construct two new amide functionalized covalent organic frameworks (COFs) with apparent crystallinity, which were further applied as efficient catalysts for Knoevenagel condensation.

Amide functionalized molecules with Lewis alkalinity are often used as building units for catalytic porous materials.^{1–3} For instance, many amide based ligands are utilized to construct metal–organic frameworks (MOFs).^{4–9} In addition, polyamides represent one of the high performance functional polymers featuring prominent thermal and mechanical properties¹⁰ and are widely used in proton exchange membranes.^{11*a*} Thus, it is intriguing to introduce amide linkages into functionalized porous organic polymers (POPs) by strong covalent bonds, which usually exhibit excellent physicochemical stabilities. For example, Woo and coworkers reported a series of nitrogen-rich microporous polymers with both imine and amide linkages.^{11*b*} Yavuz and co-workers developed ester- and amide-linker-based POPs and these were further used as efficient solid sorbent materials.^{12*a*}

Covalent organic frameworks (COFs), with designable topologies and permanent porosity, are a burgeoning kind of cystalline POPs, which have been extensively explored in electrochemical energy storage,¹³ catalysis,^{14,15} chemosensors,¹⁶ gas separation and storage,¹⁷ *etc.* The amide of COFs is generally present in polyimide COFs and amide functionalized COFs.¹⁸ As for amide functionalized COFs, amide is often incorporated into the framework by post-modification strategies. A post-synthetic oxidation strategy of transforming the imine COFs to amide linked COFs was recently developed by Yaghi and others using sodium chlorite as the oxidant.^{19,20} Nevertheless, this approach usually suffers from incomplete conversion and relatively poor adaptability compared with the bottom-up synthesis.

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Herein, amide functionalized COFs (i.e., TABTA-COF-1 and TABTA-COF-2, Scheme 1a) were designed and synthesized via a bottom-up synthesis strategy. N¹,N³,N⁵-Tris(4-aminophenyl)benzene-1,3,5-tricarboxamide (TABTA) comprising three amide bonds was selected as the building block. Notably, the benzene-1,3,5-tricarboxamide (BTA) core of TABTA is widely used for supramolecular assembly due to the strong intermolecular hydrogen bonding interactions.^{12b} The amide functionalized COFs were synthesized by the condensation of TABTA with benzene-1,4dicarboxaldehyde (BDA) or 1,3,5-tri(4-formylphenyl)benzene (TFPB) and were further characterized by FT-IR, ¹³C/CP-MAS NMR, FE-SEM, TEM and PXRD measurements. The as-prepared COFs possessed inherent porosity and built-in alkaline active sites rendering them with excellent catalytic activities for Knoevenagel condensation. Furthermore, the TABTA-COFs can be easily recycled with good retention of high stability and catalytic activity.

The synthetic conditions for TABTA-COFs were systematically screened and optimized including solvent combinations, temperature, reaction time, concentration and pressure etc. The crystalline and porous materials were obtained in a mixed solvent of mesitylene and *n*-butanol or tetrahydrofuran with acetic acid as the catalyst (Tables S1 and S2, ESI[†]). The crystallinities of TABTA-COF-1 and TABTA-COF-2 were confirmed by powder X-ray diffraction (PXRD) analysis (Fig. S4, ESI[†]). And the optimized parameters of simulated structures for the COFs were acquired by data processing using Materials Studio package. For example, the PXRD pattern of TABTA-COF-1 displayed a series of diffraction peaks at 2.35°, 4.05°, 6.95° and 24.40° which could be assigned to the (100), (200), (300) and (001) facets, respectively. The simulated eclipsed AA stacking of TABTA-COF-1 in the hexagonal P6/m was in good agreement with the experimental data. And the PXRD profile of TABTA-COF-2 exhibited different peaks at 3.50°, 6.10°, 7.05°, 9.35° and 24.75°, separately corresponding to the (100), (110), (200), (210) and (001) facets (Fig. 1a and d). The experimental data of TABTA-COF-2 also fit well with the AA stacking mode in the hexagonal $P\bar{6}$ space group. The unit cell parameters were further optimized by Pawley refinement

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Scheme 1 (a) Synthesis of TABTA-COF-1 and TABTA-COF-2; (b) top and (c) side views of TABTA-COF-1; (d) top and (e) side views of TABTA-COF-2.



Fig. 1 (a and d) The experimental PXRD patterns (blue: TABTA-COF-1; red: TABTA-COF-2), their difference (yellow) with corresponding Pawley refinement (black), simulated staggered AB (green) and eclipsed AA (magenta) modes. The extended structures of AA stacking modes for (b) TABTA-COF-1 and (e) TABTA-COF-2; the extended structures of AB stacking modes for (c) TABTA-COF-1 and (f) TABTA-COF-2.

 $(R_p = 3.04\% \text{ and } R_{wp} = 3.61\% \text{ for TABTA-COF-1}; R_p = 3.52\% \text{ and} R_{wp} = 4.92\% \text{ for TABTA-COF-2})$, (Tables S10 and S11, ESI†).

To verify the chemical structures of these TABTA-COFs, their Fourier transform infrared (FT-IR) spectra were compared with the corresponding building blocks (Fig. S5, ESI[†]). The signals at 3349 and 3263 cm⁻¹ ascribed to N-H of monomer TABTA nearly disappeared; meanwhile, a new peak of C=N at 1593 cm⁻¹ appeared, indicating highly efficient aldimine condensation between TABTA and the aldehydes. The N-H stretch vibrations of amide appeared at 3304 cm⁻¹ for TABTA-COF-1 and 3302 cm⁻¹ for TABTA-COF-2, respectively. The amide II band was observed at 1513 cm⁻¹ and 1509 cm⁻¹ for each TABTA-COF. The peaks of C=O for TABTA-COF-1 and for TABTA-COF-2 were clearly centered at 1667 cm⁻¹ and 1665 cm⁻¹, respectively. These results concomitantly suggest that the amide groups were retained in the framework. The FT-IR spectra of the molecular model compound (TABTA-BA) synthesized by full condensation of benzaldehyde and TABTA were measured for comparison and further verification (Fig. S8b, ESI⁺). The vibrations at 3269 cm⁻¹ (N–H stretch), 1653 cm⁻¹ (C=O stretch) and 1507 cm⁻¹ (amide II stretch) are unambiguously assigned to the amide group in the BTA core,²¹ which further illustrates the retention of amide groups in TABTA-COFs. More detailed chemical structure information was confirmed by solid-state nuclear magnetic resonance (NMR) spectroscopy (Fig. S7, ESI†). The chemical shifts at 165 ppm for TABTA-COF-1 and 164 ppm for TABTA-COF-2 further confirmed the existence of amide groups (Fig. S8a, ESI⁺). Meanwhile, the signals of imine C=N bond linkages for the TABTA-COF-1 and TABTA-COF-2 were located at 158 and 159 ppm, respectively.

Elemental analysis of TABTA-COFs revealed that the C, H, and N contents were well fitted with the theoretical values calculated based on an infinite network structure (Table S3, ESI⁺). The morphology



Fig. 2 Representative SEM images of (a) TABTA-COF-1 and (c) TABTA-COF-2; TEM images of (b) TABTA-COF-1 and (d) TABTA-COF-2.

of both TABTA-COFs displayed a laminar microstructure, which was recorded by field-emission scanning electron microscopy (FE-SEM, Fig. 2 and Fig. S9, ESI[†]). Interestingly, the transmission electron microscopy (TEM) images further indicated that both TABTA-COFs displayed fringes of periodicity corresponding to the stacked 2D layers which could be assigned to the (001) facet (Fig. 2).

The porosity of the TABTA-COFs was unveiled by Nitrogen adsorption/desorption measurements at 77 K. The Brunauer-Emmett-Teller (BET) specific surface areas of TABTA-COF-1 and TABTA-COF-2 were determined to be 246 m² g⁻¹ and 368 m² g⁻¹, respectively (Fig. 3). CO₂ sorption isotherms were further recorded at 195 K to evaluate the porosity of the TABTA-COFs. Similar BET surface areas were obtained as 264 $\ensuremath{m^2\ g^{-1}}$ for TABTA-COF-1 and 432 m² g⁻¹ for TABTA-COF-2 (Fig. S6, ESI[†]).²² The amide linked conjugated porous polymers were reported to exhibit low surface area because of the unfavorable interactions between the polymer skeleton and guest gas molecules.^{11b} This might also be the reason that causes the decrement in the specific surface areas for TABTA-COFs. And a similar phenomenon has also been reported by others.^{19,23} In addition, the pore size distribution simulated by the nonlocal density functional (NLDFT) method based on nitrogen adsorption suggested uniform mesopore distribution with a diameter of 3.68 nm for TABTA-COF-1 and 2.32 nm for



Fig. 3 (a) Nitrogen sorption isotherms of TABTA-COF-1 at 77 K (inset: photograph of the pore size distribution of TABTA-COF-1); (b) nitrogen sorption isotherms of TABTA-COF-2 at 77 K (inset: photograph of the pore size distribution of TABTA-COF-2).

TABTA-COF-2 (Fig. 3 inset). These results were in good agreement with the values of *d*-spacing that were recorded from the PXRD patterns for TABTA-COF-1 at $2\theta = 2.35^{\circ}$ (3.76 nm) and TABTA-COF-2 at $2\theta = 3.50^{\circ}$ (2.53 nm).

Physicochemical stabilities represent one of the paramount parameters for applications of COFs, especially in hetergeneous catalysis aspects. The thermostability of TABTA-COFs was checked by thermogravimetric analysis under nitrogen atmosphere, and the results indicated that TABTA-COF-1 and TABTA-COF-2 were thermally stable up to ca. 410 and 487 °C, respectively (Fig. S10, ESI[†]). The ordered framework structure of TABTA-COF-2 could be maintained at least at 400 °C (Fig. S11, ESI⁺). Although the crystallinity of TABTA-COF-1 decreases with increasing temperature, the IR spectrum of TABTA-COF-1 indicates that the chemical structure remains stable at elevated temperatures even up to 400 °C (Fig. S12, ESI[†]). In addition, both TABTA-COFs were insoluble and stable in conventional solvents (such as THF, toluene, and water) and strong acidic/basic conditions (Fig. S13 and S14, ESI†), etc. Moreover, the -NH moiety of amide is an appealing active site with Lewis alkalinity.²² Therefore, the amide functionalized TABTA-COFs are expected to be heterogeneous alkaline catalysts.^{22,24}

To verify the catalytic activity of the TABTA-COFs, Knoevenagel condensation reaction was selected.²⁵ Malonitrile was chosen as the typical nucleophilic reagent and various benzaldehydes were tested as substrates to evaluate the catalytic performance and generality of TABTA-COFs toward Knoevenagel condensation. The conversion efficiency was monitored by a gas chromatographymass spectrometer (GC-MS) analyzer at different intervals of reaction time (Fig. S17, ESI†). The products were further analyzed and validated by ¹H NMR measurements (Fig. S20–S24, ESI†). As shown in Fig. 4, almost all the benzaldehydes were converted to the corresponding products within a short time. The catalytic conversion efficiencies of different substrates are summarized in Tables S4 and S5 (ESI†). It can be concluded that the substrates with electron-withdrawing substituents showed higher yields than the counterparts bearing electron donating groups. And in



Fig. 4 Catalytic performance of TABTA-COFs toward Knoevenagel condensation of malonitrile with various aldehydes after one hour.

all cases, the TABTA-COFs exhibited great robustness with well retained crystallinity and chemical composition after treatments under catalytic Knoevenagel condensation conditions (magenta lines in Fig. S13 and S14, ESI†). To investigate the possible effect of the imine bonds of TABTA-COFs on the catalytic activity, a control experiment using TFPB-TAPB-COF²⁶ as the catalyst with a similar structure but without amides linkages was carried out (Fig. S15 and Table S7, ESI†). The low catalytic efficiency indicated that the amides play vital roles while the imines exert less effect on the catalysis.

The recyclability of the catalysts is another significant metric for practical applications. The reusability of TABTA-COF-2 with better stability for catalyzing Knoevenagel condensation was investigated in detail. Taking the Knoevenagel condensation between benzaldehyde and malonitrile as an example, TABTA-COF-2 can effectively catalyze the reaction after at least 5 recycling processes under identical experimental conditions (Table S9, ESI†). Meanwhile, both the crystallinity and chemical structure of the sample were also well retained after 5 cycles (Fig. S18 and S19, ESI†).

On the other hand, the condensation between malononitrile and benzaldehyde showed very low conversion (24%) even after 1 h in the absence of COF catalysts (Table S6, ESI†), suggesting a high catalytic activity of the TABTA-COFs. The reusability of TABTA-COF-1 is also summarized in Table S8 and Fig. S16 (ESI†). The mesopores facilitating the mass transfer of substrates along with the densely arranged amide functional groups are beneficial to the catalytic performance.

In summary, two new BTA-derived 2D COFs bearing amide built-in functional groups were synthesized *via* a bottom-up strategy. TABTA-COFs possessed crystallinity and exhibited high catalytic activity toward Knoevenagel condensation with a broad substrate scope and excellent recyclability. Further oxidation of the imine bond linkages in TABTA-COF-1 to amide groups resulting in a fully 2D polyamide network with complete amide linkages is currently underway in our laboratory. It could be envisioned that the introduction of amide groups into the scaffolds could expand the scope of functional COFs and the application of COF-based materials.

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Conflicts of interest

There are no conflicts to declare.

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