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An Upgraded “Two-in-one” Strategy Toward Highly Crystalline Covalent Organic Frameworks

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Abstract: A highly crystalline bicarbazole-based covalent organic framework (BCzP-COF) was synthesized *via* an upgraded “two-in-one” strategy by the self-polycondensation of A_2B_2 monomer with two neopentyl acetal and two amine groups. Such strategy is propitious to afford higher crystallinity, larger special surface areas and better morphology than that of using unprotected monomer with free aldehydes and amines. Additionally, the off-white powder of BCzP-COF could serve as acidichromism sensor with a significant color change. Intriguingly, the conductivity of the protonated BCzP-COF can improve six orders of magnitude compared to that of the pristine samples. This work opens new potentials for bicarbazole-functional materials toward chemosensors and electronic devices.

Covalent organic frameworks (COFs) have attracted increasing interest because multifarious tailor-made building blocks can be reticulated into extended crystalline and porous networks *via* fascinating dynamic covalent chemistry.^[1] It has been demonstrated in many cases that the functions and performance of COF are highly related to their inherent metrics such as crystallinity, specific surface areas and stability, etc.^[2] Substantial efforts have been devoted for improving COF synthesis,^[3] which endow COFs with promising application potentials in high gas sorption/separation,^[4] energy storage,^[5] optoelectronics,^[6] sensing,^[7] catalysis^[8] and environmental remediation,^[9] etc. Recently, we developed a “two-in-one” strategy toward convenient synthesis of high quality COFs with good solvent adaptability and reproducibility.^[10-12] Different from the conventional co-condensation method using two or more monomers, the “two-in-one” strategy applies self-polycondensation of elaborately designed single monomers with two reactive groups integrated into the same molecules (e.g. aldehyde and amino groups). However, we found that it is challenging to isolate pure two-in-one monomers in some cases because of the easy self-polymerization of such bifunctional monomers during the work-up process.

To address this issue, we herein upgrade this “two-in-one” strategy *via* selective introduction of protected groups (i.e. neopentyl acetals labile groups) and the other unprotected groups (i.e. free amines). Previous reports indicate that condensation of a protected monomer with another unprotected monomer usually afford COFs with better crystallinity than using two unprotected monomers. For example, as for the imine COF synthesis, either

the amines^[13,14] or aldehydes protection^[15,16] method was developed and demonstrated to be conducive to the improvement of crystallinity and porosity. *N*-aryl benzophenone imines (**1**, Figure 1a) were directly applied as monomers for synthesizing imine- and β -ketoenamine-linked COFs with various aldehydes. In addition, tert-butyloxycarbonyl (Boc) group protected amine (**2**, Figure 1a) could also serve as the building blocks to synthesize a 3D woven imine COF-112^[14] with 2,6 pyridinedicarboxaldehyde. On the other hand, direct condensation of protected aldehydes (e.g. dimethyl acetals **3**^[15] or methylene diacetate **4**,^[16] Figure 1b) and free amines can afford highly crystalline imine COFs as well. In the above-mentioned cases, the compatible conditions of acid-promoted imine condensation and acid induced deprotection of the precursors enable easy synthesis of crystalline COFs in one-pot manner. Inspired by these pioneering works, we herein designed an aldehyde protected bifunctional A_2B_2 monomer (4,4'-(6,6'-bis(4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)-[9,9'-bicarbazole]-3,3'-diyl)dianiline, BCzP) based on a rigid *N,N'*-bicarbazole^[17,18] aromatic core with two neopentyl acetal and two amine groups. The synthetic routes were summarized in Scheme S3. For maintaining good solubility of the monomer, we adopt a bulky neopentyl group to protect the aldehyde groups. The new bifunctional monomer was synthesized by stepwise bromination and Suzuki coupling (Scheme S3). To shed more insights into the current “two-in-one” strategy using protected monomers, another “two-in-one” monomer counterpart (4,4'-(6,6'-bis(4-aminophenyl)-[9,9'-bicarbazole]-3,3'-diyl)dibenzaldehyde, BCz) was also synthesized for comparison. To our delight, BCzP could not only be purified and obtained more easily, but also form the same bicarbazole based COFs featuring better crystallinity and higher porosity. This improved “two-in-one” strategy would provide a universal method for new COF synthesis.

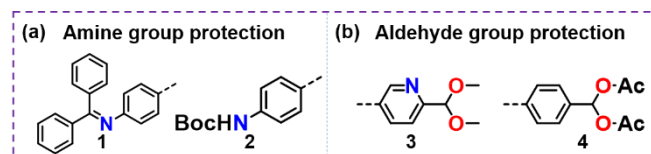
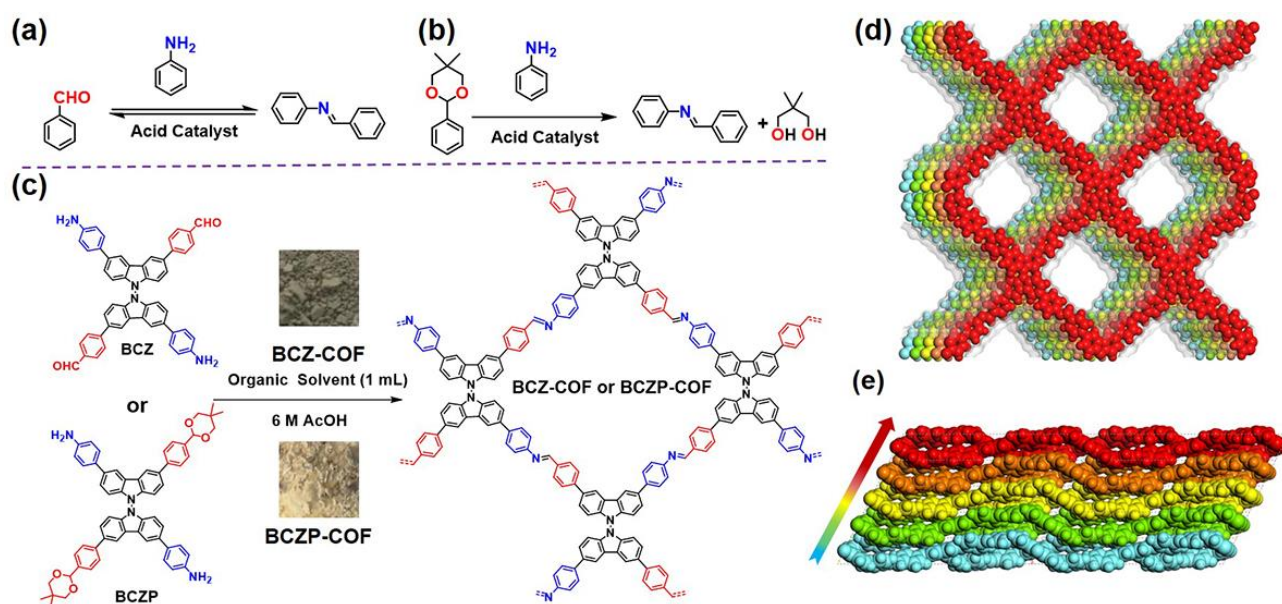


Figure 1. The survey of (a) amine group protection and (b) aldehyde group protection for imine-based COF synthesis.

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Scheme 1. The model reaction of (a) aldehyde and amine and (b) neopentyl acetals and amine; (c) the synthetic routes of the same BC-based COFs using two different monomers (BCz and BCzP), respectively; (d) top view and (e) side view of the simulated AA-stacking model.

All the new intermediates and target molecules BCz and BCzP were readily synthesized and unambiguously characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and high-resolution mass spectra (see ESI). The neopentyl acetals monomer BCzP is highly soluble in common organic solvents like CHCl_3 , THF, DMF etc. In contrast, there are always some insoluble precipitates in CHCl_3 solution of BCz (Figure S17b), which might be ascribed to the oligomers formed by self-polymerization between the highly active aldehyde and amine during the work up process. The bicarbazole based COFs were synthesized by the self-polycondensation of either BCz or BCzP in several single solvent systems. Considering the good solubility of free amines in alcohols, six different alcohols were applied as the reaction media. In a typical synthetic protocol, the “two-in-one” monomer was suspended in the mixture of alcoholic solvent (1 mL) with 6 M acetic acid at 120°C for 3 days to afford the corresponding crystalline powder (denoted as BCz-COF_{solvents} and BCzP-COF_{solvents}). BCz-COF was obtained as grey solid, while BCzP-COF was afforded as off-white powder (Scheme 1c). Fourier transform infrared (FT-IR) spectra of BCzP-COF was nearly identical with that of BCz-COF (Figure S15). The free-amine vibration band around 3364 cm^{-1} of the monomer BCzP disappeared for BCzP-COF while the aliphatic stretch at $2952\text{--}2865\text{ cm}^{-1}$ significantly decreased (Figure S14). As for BCz-COF, the -N-H stretching (3370 cm^{-1}) and for the vibration of carbonyl groups (1694 cm^{-1}) of BCz were almost vanished (Figure S13). Furthermore, the appearance of new vibration band of -C=N imine linkages at 1622 cm^{-1} was confirmed by comparison with that of the module compound BCz-4CHN (Figure S16). In addition, the ^{13}C cross-polarization magic-angle spinning (CP MAS) NMR spectra of both COFs displayed a signal of imine at 158 ppm (Figures S9 and S10). For BCzP-COF, the weak signals at the high magnetic field around 20–30 ppm could be attributed to the residual neopentyl groups. The other aromatic carbon signals could be reasonably assigned as well. The contents of C, H in BCzP-COF from the elemental analysis are higher than those in

BCz-COF, further indicating the residual neopentyl groups (Table S1).

The crystallinity of both COFs was confirmed by the powder X-ray diffraction (PXRD) measurements (Figure 2a). The two bicarbazole based COFs exhibited nearly same diffraction patterns with identical peak positions at about 4.5° , 9.1° , 13.7° and 21.9° , corresponding to the 110, 220, 330 and 001 reflections, respectively. To resolve the two COF framework structures, the experimental data were compared with the simulated results using Material Studio software packages. The calculated AA-stacking model with space group $P1$ match well with the experimental PXRD patterns of both COFs due to lower total energy for optimal geometry (Figure 31, Table S3). Furthermore, the profile of Pawley refinement (Figure 2a, blue lines) reproduce the experimental diffractions with negligible difference (black line). In contrast, the theoretical PXRD pattern based on the AB-stacking mode largely deviated from the experimental results (Scheme 1d–1e, Figure 2a and S30). The lattice parameters of Pawley refinement were $a = 28.4435\text{ \AA}$, $b = 31.0504\text{ \AA}$, $c = 4.4461\text{ \AA}$, $\alpha = 87.0530^\circ$, $\beta = 60.8278^\circ$, $\gamma = 89.8602^\circ$ with the final R_{wp} and R_p values converged to 4.74% and 3.05%. Based on the FT-IR, NMR and PXRD analysis, both COFs feature same framework structures, but in the different quality. As shown in Figure 2b, both the PXRD peak intensity and the FWHM of both COFs suggest that the crystallinity of BCzP-COF (FWHM: 0.35°) is much better than that of BCz-COF (FWHM: 0.4°). Furthermore, as proved by the diverse condition screening process, the solvent adaptability and reproducibility of BCzP-COF are more prominent than BCz-COF (Figure S11). The morphologies of BCzP-COF and BCz-COF were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (Figure 2c–2d, S26 and S27). Both COFs appeared as rod-like microcrystals. However, the surface of BCzP-COF is smoother with clear and sharp edges. In contrast, BCz-COF is composed of rough and uneven particles (Figure 2c–2d). In addition, the length of the microcrystallite for

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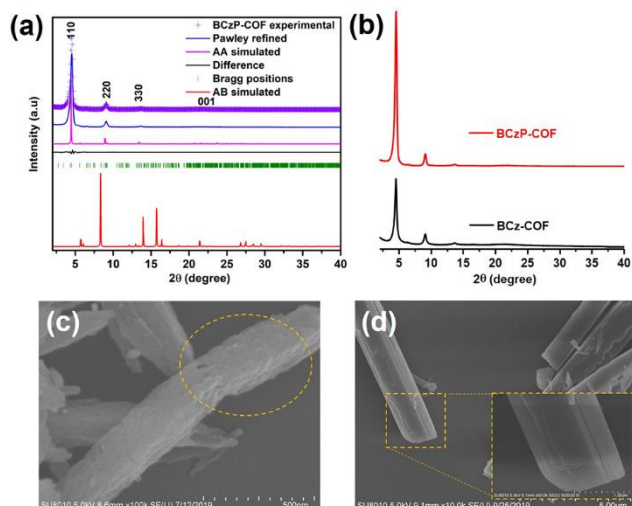


Figure 2. (a) PXRD patterns of the BC-based COFs: experimental (purple), Pawley refined (blue), Difference (black), AA-stacking (magenta), and AB-stacking (red); (b) PXRD comparison of BCzP-COF and BCz-COF; (c) SEM patterns of BCz-COF and (d) BCzP-COF.

BCzP-COF is much longer (up to 20 μm) than that of BCz-COF. These results reflect that neopentyl acetals were propitious to reducing reaction kinetics of imine self-condensation and thus enhancing the crystallinity of the resulted COFs.^[19]

The permanent porosity of both bicarbazole based COFs was evaluated by the N_2 sorption measurements at 77 K. Both COFs exhibited sharp N_2 uptake under $P/P_0 < 0.05$ indicative of microporous characteristics.^[20] The Brunauer-Emmett-Teller (BET) surface areas of BCzP-COF_{solvents} synthesized from different solvents were nearly identical (ca. 2200 $\text{m}^2 \text{g}^{-1}$, Figure 3), which were much larger than the specific surface areas of BCz-COF_{solvents} under the same corresponding solvent (1005 $\text{m}^2 \text{g}^{-1}$ or even smaller, Figures S11c and S12). The pore size distribution

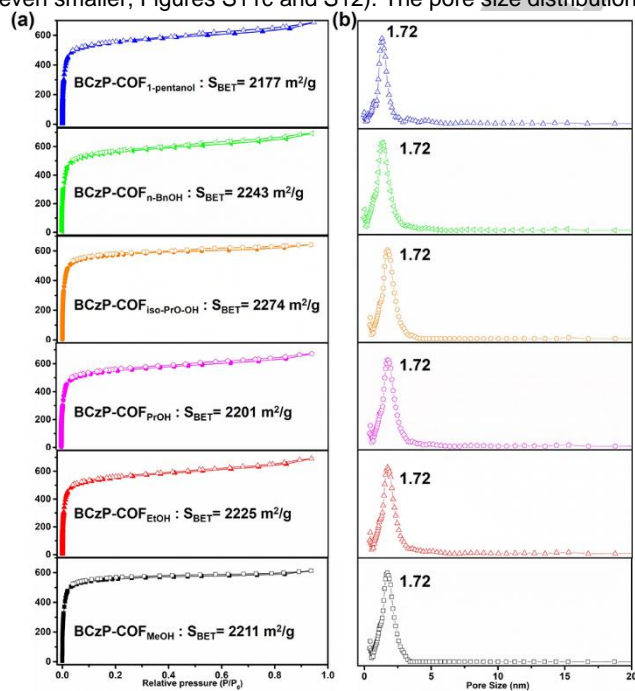


Figure 3. (a) Nitrogen sorption isotherms and (b) Pore size distribution curves of BCZP-COF synthesized from different solvent systems.

of both COFs calculated by nonlocal density functional theory (NLDFT) method also suggested microporous with approximately 1.72 nm, which agrees well with their theoretical values (1.76 nm).

Similar to the reported COFs synthesized by self-condensation of two-in-one monomers,^[10-12] BCzP-COF exhibited excellent stability and good tolerance against the boiling water, strong base (12 M NaOH) and acid (12 M HCl) (Figure S21c). As revealed by the PXRD, BET and FT-IR measurements (Figures S21 and S24), both the crystallinity, porosity and chemical structures were retained after treatments in these harsh conditions. But BCz-COF showed low stability under these harsh conditions probably due to the relatively lower crystallinity than that of BCzP-COF (Figure S22 and S23). On the other hand, thermogravimetric (TGA) analysis illustrated that BCzP-COF and BCz-COF were thermally stable up to about 450 $^{\circ}\text{C}$ under N_2 atmosphere (Figure S25).

Intriguingly, during the chemical stability tests, we observed that the off-white powder of BCzP-COF rapidly changed to deep red upon soaking in HCl aqueous solution. UV-vis diffuse reflectance spectroscopy of BCzP-COF showed a distinct red-shift (201 nm, from 476 nm to 677 nm) for the absorption edge after acidic treatment, corresponding to a reduced optical band gap by ~ 0.8 eV (Figure S17a). Unlike the neutral state, the protonated BCzP-COF exhibited intensive NIR fluorescence emission at 672 and 757 nm (Figure S19a). The acidochromism behavior^[21,22] of the BCzP-COF was proved to be highly reversible when it was repeatedly washed with aqueous ammonia solution, water, alcohol and ethyl acetate (Figure S17a). Such phenomenon triggered us to further investigate the detailed color change of BCzP-COF upon treatments in different concentrations of CF_3COOH in THF solution (Figure 4 and S20). As shown in Figure 4c, the color turned from white to orange, and further changed to red or even deep red upon gradually increasing the acid concentrations. No obvious color change was observed until the CF_3COOH concentration is up to 0.1 M (Figure 4c). As shown in the absorption difference spectrum between the protonated and the non-protonated BCzP-COF (Figure 4b), the bleach bands were observed below 400 nm. Meanwhile, the protonation-induced absorption bands at ca. 487 nm appeared under low concentration and the new absorption bands further appeared at ca. 550 nm above 0.1 M. Such stepwise protonation is similar to the recently reported perylene-based COFs.^[22]

To shed more light into the sensing mechanism (i.e. active sites) of BCzP-COF toward acids, the UV-visible absorption spectra of the two model compounds (bicarbazole core and BCz-4CHN with four imine branches) were measured in CHCl_3 solution before and after adding trifluoroacetic acid (TFA, Figure S18a). The absorption spectra of the base bicarbazole core molecules suggested no obvious change even after adding excess amount of TFA. In sharp contrast, the absorption maximum at 339 nm of BCz-4CHN was distinctively attenuated and a new absorption band appeared at 426 nm (Figure S18b). Clear color change from colorless to yellow was observed for the BCz-4CHN solution upon addition of TFA (Figure S18b inset). In addition, the maximum emission of the BCz-4CHN also shifted from 476 nm to 633 nm upon acid treatment with much amplified intensity (Figure S19b). The FT-IR spectra of protonated COFs showcased the disappearance of vibration band at 1622 cm^{-1} for -C=N and a novel peak at 1651 cm^{-1} was observed (Figure S28), which indicate that the imine linkages were much easier to be protonated than the N-N bond of the central BC motifs. Compared

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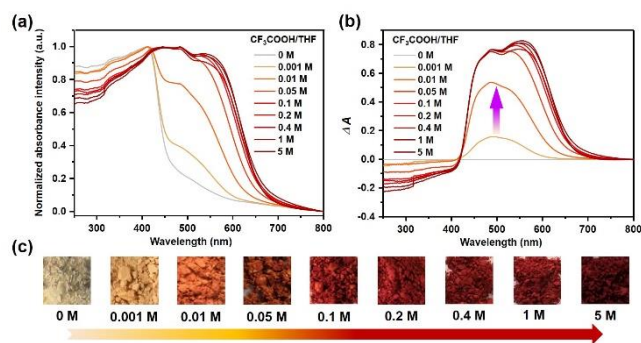


Figure 4. (a) UV-vis diffuse reflectance spectroscopy and (b) Plot of the absorption difference between the protonated and the non-protonated for the bulk BCzP-COF powders in different concentrations of CF_3COOH in THF; (c) the photography of colour change for the BCzP-COF powders.

to their neutral form, the protonated imine counterparts exhibited strong electrophilic property which resulting in the bathochromically shifted absorption and emission band (Figure S17 and S19).^[22] Interestingly, the protonated ^[23] BCzP-COF exhibited six orders of magnitude higher conductivity ($1.71 \times 10^{-4} \text{ S m}^{-1}$) than that of the pristine COFs ($5.31 \times 10^{-10} \text{ S m}^{-1}$, Figure S29, Table S2).

In summary, we report a novel bicarbazole-based COF (BCzP-COF) based on upgraded “two-in-one” strategy through self-condensation of bifunctional monomer with two protected aldehyde (i.e. neopentyl acetals) and two amine groups, which exhibited higher crystallinity, larger porosity and more regular morphology than its counterpart BCz-COF obtained by the unprotected monomer. The current work provides an easier and better way for preparation COFs utilizing “two-in-one” strategy. Furthermore, BCzP-COF exhibited obvious acidochromism sensing behavior and much improved conductivity, which show potential applications in chemosensors and electronic devices.

Acknowledgements

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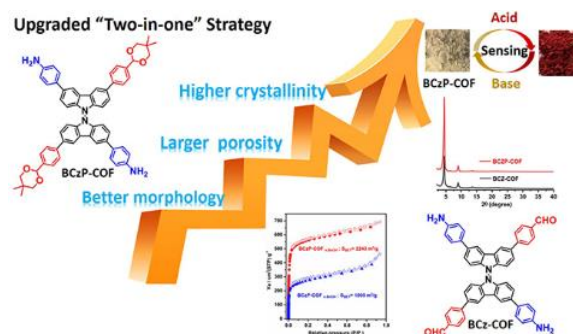
Keywords: bicarbazole • covalent organic framework • two-in-one • aldehyde protection

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An upgraded "two-in-one" strategy is developed by the self-polycondensation of A_2B_2 monomer (BCzP) with two neopentyl acetal and two amine groups, which exhibited higher crystallinity, larger porosity and better morphology than that of using unprotected monomer (BCz).