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# Facile synthesis of 3D covalent organic frameworks *via* a two-in-one strategy<sup>†</sup>

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A "two-in-one" strategy was employed to construct 3D-COFs for the first time. Based on this strategy, a 3D-Flu-COF could be readily synthesized in various simplex organic solvents. Benefitting from the non-conjugated structure, the 3D-Flu-COF showcased excellent acidichromic sensing performance with good sensitivity, reversibility and naked eye visibility.

Covalent organic frameworks (COFs) represent a new class of polymers composed of light elements (such as C, H, O, N, and B) featuring high crystallinity and permanent porosity, which are solely connected by covalent linkages.<sup>1</sup> Since the first example reported by Yaghi in 2005,1a COFs have received considerable research interests due to their prominent application potential in gas storage and separation,<sup>2</sup> energy storage,<sup>3</sup> heterogeneous catalysis,<sup>4</sup> drug delivery,<sup>5</sup> and sensors,<sup>6</sup> among others. Generally, COFs can be categorized into twodimensional (2D) COFs and three-dimensional (3D) COFs according to their structural dimensionality. 2D COFs are mainly synthesized from relatively planar building blocks, which are beneficial to form layered eclipsed (AA) stacking structures. In contrast, 3D COFs are constructed from nonplanar (typically tetrahedral) building blocks that tend to form highly porous networks.<sup>7a</sup> However, compared to the large family of 2D COFs, only about 40 examples of 3D COFs have been reported to date,<sup>7c</sup> although their intrinsic characteristics of higher surface area and lower density make them ideal candidates for gas storage, gas separation and catalysis.<sup>7</sup> The possible reasons and remaining challenges that cause the development of 3D COFs to persistently lagbehind 2D COFs might be the poor synthetic accessibility<sup>7a,8</sup> and difficulties in

structural illustration.9 In contrast to the strong intra-layer covalent bonds and interlayer interactions existing in 2D COFs, only covalent bonds direct the formation of 3D COFs, which make them more inclined to afford amorphous frameworks.7a,8,9 To address these challenges, great efforts have been devoted to optimize the synthesis of 3D COFs, and significant progress has been recently made. For example, a facile synthetic method towards 3D COFs under ambient conditions has been reported by Fang et al. using the ionothermal method, which could generate high crystallinity COFs in minutes.12 Despite the great advantages of this approach, there are several open questions that remain to be addressed. For example, the residual ionic liquid in the pores of the as-prepared COFs may reduce the internal surface areas and make the structure-property relationships elusive. Therefore, it is still highly desired to develop simple yet effective approaches for 3D COF synthesis for further advancing this promising research field.

Recently, our group developed a "two-in-one" strategy that directly uses bifunctional monomers to construct 2D COFs *via* self-polycondensation. Thanks to the stoichiometry of the two functional groups which is kept identically equal irrespective of synthetic conditions, such a "two-in-one" strategy avoids the tedious screening process of solvents compared to the conventional co-condensation and thus reduces the difficulties in obtaining highly crystalline 2D COFs. Accordingly, a series of 2D COFs with good solvent adaptability, high crystallinity and excellent repeatability were obtained by using this "two-in-one" strategy.<sup>4c,10,11d</sup> However, this strategy has not yet been explored in 3D COF synthesis. We envision that the "two-inone" strategy is also adapted for the synthesis of 3D COFs (Scheme 1).

To verify our hypothesis, we designed a new tetrahedral  $A_2B_2$  type monomer through the "two-in-one" strategy. 4,4'-(3,6-bis(4-(5,5-dimethyl-1,3-dioxan-2-yl)phenyl)-9*H*-fluorene-9,9-diyl)dianiline (Fig. 1a,  $A_2B_2$ -Flu) with two neopentyl acetal and two amine groups in one fluorene core was synthesized (Scheme S1, ESI†) and further applied to construct a fluorene-based imine 3D COF (defined as 3D-Flu-COF<sub>solvent</sub>). Notably, to avoid auto-polymerization of the  $A_2B_2$ -monomer during the synthesis and workup process,

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Scheme 1 Schematic diagrams for 3D COFs constructed using (a) the conventional co-condensation method and (b) the "two-in one" strategy.



Fig. 1 (a) Schematic illustration of the molecular design and synthesis of a 3D-Flu-COF, (b) PXRD patterns, and (c) solid-state  $^{13}$ C NMR (75 MHz) spectrum of 3D-Flu-COF<sub>benzylalcohol</sub>.

neopentyl glycol groups were introduced to protect the aldehydes, which could be *in situ* deprotected by acetic acid during COF synthesis (Scheme S1, ESI†).<sup>11d,13</sup> As expected, 3D-Flu-COFs can not only be readily synthesized in various simplex organic solvents, such as benzyl alcohol, dioxane, mesitylene, *n*-BuOH *etc.*, but also exhibit high crystallinity and large surface areas.

As shown in Scheme S1, ESI,<sup>†</sup>  $A_2B_2$ -Flu was prepared through a facile three-step synthetic route in high yield, and was unambiguously characterized by nuclear magnetic resonance (NMR) and high-resolution mass spectroscopy (HR MS). 3D-Flu-COFs were synthesized as off-white powders in 90–97% yields (Table S1, ESI<sup>†</sup>) upon self-condensation of  $A_2B_2$ -Flu under solvothermal conditions in different simplex organic solvents. The chemical structures of 3D-Flu-COFs were characterized by Fourier transform infrared (FT-IR) spectroscopy and solid-state <sup>13</sup>C cross-polarization magic-angle-spinning (<sup>13</sup>C CP/MAS NMR spectra). FT-IR spectra of 3D-Flu-COFs prepared in different solvents were nearly identical. The stretching bands of free amine (N–H,  $\sim$  3300 cm<sup>-1</sup>) and methyl (-CH<sub>3</sub>,  $\sim 2900 \text{ cm}^{-1}$ ) ascribed to the monomer nearly disappeared, and a new C=N stretching vibration band appeared at 1629 cm<sup>-1</sup>, indicating the formation of imine linkages in 3D-Flu-COFs (Fig. S4, ESI<sup>+</sup>). The existence of imine bonds was further verified by <sup>13</sup>C solid-state NMR spectroscopy with a clear characteristic peak at 153 ppm (Fig. 1c). In addition, a residual weak peak of the neopentyl acetal group was observed at 68 ppm, which indicates that the deprotection and condensation of the neopentyl acetal group may occur simultaneously.<sup>13</sup> Although with identical structures, 3D-Flu-COFs prepared in different solvents showcased different morphologies, as observed from scanning electron microscopy (SEM) images, 3D-Flu-COF<sub>benzyl alcohol</sub>, 3D-Flu-COF<sub>dioxane</sub> and 3D-Flu-COF<sub>mesitylene</sub> exhibited a uniform "coral rod"-like morphology, while 3D-Flu- $COF_{n-BuOH}$  exhibited plate-like aggregates (Fig. S7, ESI<sup>+</sup>). It has also been previously reported that the differences in the morphology of COFs caused by solvents may be due to changes in the polarity of the solvents.<sup>10a,14</sup>

The structures of 3D-Flu-COFs were resolved by powder X-ray diffraction (PXRD) analysis combined with structural simulations (Fig. 1b). After minimizing geometric energy using the Materials Studio software package based on a 7-fold interpenetrating **dia** network, a fitted unit cell parameter of a = b = 27.3960 Å, c = 7.1325 Å,  $\alpha = \beta = \gamma = 90^{\circ}$  was obtained. The powder samples of 3D-Flu-COFs obtained in different solvents exhibited exactly the same patterns with an intense peak at 6.45° and other five distinct diffractions at 4.60°, 10.25°, 13.05°, 16.70°, and 19.85° corresponding to the (200), (110), (310), (400), (141), and (431) facets of the space group *P*43, which were in good agreement with the simulated PXRD patterns. The refinement result was nearly overlapped with the observed ones with reasonable  $R_{wp} = 4.32\%$  and  $R_p = 2.94\%$ . Based on the



**Fig. 2** (a) Nitrogen adsorption (solid) and desorption (open) isotherms at 77 K, and (b) pore size distribution of 3D-Flu-COFs prepared in benzyl alcohol (green), *n*-BuOH (pink), dioxane (orange), and mesitylene (violet).



above results, the 3D-Flu-COFs most probably adopt a 7-fold

interpenetrated structure with **dia** topology, showing a microporous cavity of about ~1.16 nm (Fig. 3). The porosity and surface areas of 3D-Flu-COFs prepared in different solvents were measured by  $N_2$  adsorption and

alfierent solvents were measured by N<sub>2</sub> adsorption and desorption measurements at 77 K. All these 3D-Flu-COFs displayed the typical type I isotherms with a sharp N<sub>2</sub> uptake under low relative pressures ( $P/P_0 < 0.05$ ), which is the typical characteristic of microporous materials (Fig. 2a). The BET surface areas for these 3D-Flu-COFs were determined to be 1270–1590 m<sup>2</sup> g<sup>-1</sup> from the N<sub>2</sub> adsorption isotherms under the low pressure region (Fig. S6, ESI†). All of the 3D-Flu-COFs showed a narrow pore size distribution in the range of 1.15–1.20 nm as simulated on the basis of nonlocal density functional theory (NLDFT) (Fig. 2b), which was in good agreement with the theoretical value from the crystal structures (1.16 nm) (Fig. 3).

Taking 3D-Flu-COF<sub>benzyl alcohol</sub> as an example, the thermal stability as well as chemical stability of 3D-Flu-COFs were investigated in detail. Thermogravimetric analysis (TGA) suggested that 3D-Flu-COF<sub>benzyl alcohol</sub> exhibited a high thermal stability with only 5% weight loss of its initial mass at 561 °C under a nitrogen atmosphere (Fig. S9, ESI†). Moreover, the chemical stability of 3D-Flu-COF<sub>benzyl alcohol</sub> was explored upon treatments in boiling water, 12 M HCl, and 12 M NaOH, respectively, for 3 days, and these samples maintained their chemical constitution, crystallinity and porosity upon treatments under the above conditions (Fig. S10–S14, ESI†). All these experiments confirmed that 3D-Flu-COFs feature excellent stability.

Consistent with the off-white colour appearance, the UV-vis spectrum of 3D-Flu-COFs displayed a dominant absorption peak centred at 390 nm, which can be attributed to the 3D non-conjugated structure (green line in Fig. 4a and the solid line in Fig. S15, ESI†). Inspired by the application of imine-linked 2D COFs as acidichromic sensors,  $^{11a-c}$  we speculated that both the responsivity and sensitivity would be improved if a 3D-Flu-COF was applied to acid sensing due to the highly accessible porosity of such 3D open frameworks. As expected, all 3D-Flu-COFs prepared in different solvents undergo a rapid and distinctive colour change from off-white to yellow when exposed to trifluoroacetic acid (TFA) vapor, corresponding to the red-shifted absorption band in UV-vis spectra from 390 nm to 470 nm (Fig. S15, ESI†). The UV-Vis absorption spectra of 3D-Flu-COFs prepared in different solvents differ slightly, probably



**Fig. 4** (a) UV/Vis absorption spectra of 3D-Flu-COF<sub>benzyLalcohol</sub> powder before and after treatment of TFA vapor (inset: Optical photographs of 3D-Flu-COF<sub>benzyLalcohol</sub> powder before (off-white) and after (yellow) treatment of TFA vapor); (b) absorption spectra of 3D-Flu-COF<sub>benzyLalcohol</sub> powder upon treatment with different concentrations of TFA in 1,4-dioxane; (c) plot of the absorption difference between the protonated and the non-protonated 3D-Flu-COF<sub>benzyLalcohol</sub> upon treatment with different concentrations of TFA in 1,4-dioxane; and (d) optical photographs of colour change for the 3D-Flu-COF<sub>benzyLalcohol</sub> powders upon treatment with different concentrations of TFA in 1,4-dioxane.

due to their different porosity morphology. For convenience, 3D-Flu-COF<sub>benzyl alcohol</sub> was used to investigate the details of the responsive behaviour unless otherwise stated. Then, the responsive behaviour of the 3D-Flu-COF powder was further investigated in detail. As shown in Fig. 4b-d, the 3D-Flu-COF is still sensitive to a trace amount of TFA with a low concentration of 0.0002 mol  $L^{-1}$ (22.8 ppm) as the new peak at 470 nm still appeared in the UV-vis spectra. With the increase of the TFA concentration, the absorption intensity at 470 nm gradually increased without any saturation effects until the concentration of TFA reached 5 mol  $L^{-1}$ . Besides, the colour of the acid-treated 3D-Flu-COF (defined as 3D-Flu-COF-TFA) could be recovered to the original white upon exposure to trimethylamine (TEA) vapor (Fig. 4d). Notably, the crystallinity, porosity as well as morphology of the 3D-Flu-COF after the sensing performance are still maintained and comparable with those of the pristine samples, except for a slight decrease in PXRD peak intensity (Fig. S16-S20, ESI<sup>+</sup>). As already discussed above, 3D-Flu-COFs applied as acidichromic sensors toward trifluoroacetic acid not only feature a detection limit as low as 22.8 ppm, but also exhibit a wide response range of 4 orders of magnitude, which outperform most reported COFs (Table S2, ESI<sup>+</sup>).<sup>11b-d</sup> Similar to previous reports,<sup>11</sup> the colour change of the 3D-Flu-COF can be attributed to the protonation of the imine linkages under acidic conditions (Fig. S21, ESI<sup>+</sup>), which was verified by the FI-IR spectra. With the increase of TFA concentration, a new band at 1668 cm<sup>-1</sup> ascribed to the C=NH<sup>+</sup> stretching vibration gradually appeared, accompanied by the attenuation of the imine C=N band around 1629  $cm^{-1}$  in the FT-IR spectra. Furthermore, the FT-IR spectrum of 3D-Flu-COF-TFA could be recovered to the original mode upon exposure to the TEA vapour (Fig. S22, ESI<sup>+</sup>).

In summary, we have successfully constructed a new iminelinked three-dimensional COF (3D-Flu-COF) *via* a "two-in-one" molecular design strategy for the first time. This approach greatly simplified the synthetic procedure of 3D COFs, and a 3D-Flu-COF with high crystallinity could be obtained in various simplex solvents. Benefiting from the non-conjugated structure as well as the imine linkages, the 3D-Flu-COF exhibits excellent acidichromic sensing performance with high sensitivity and good reversibility. This "two-in-one" strategy would open new opportunities for the facile construction of novel 3D COFs, and we envision that more functional 3D COFs will be developed in the near future.

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### Conflicts of interest

There are no conflicts to declare.

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