Covalent organic frameworks as pH responsive signaling scaffolds†

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A β-ketoenamine based covalent organic framework, COF-JLU4, was synthesized by condensation of 2,5-dimethoxyterephthalohydrazide with triformylphloroglucinol under solvothermal conditions. This COF has strong crystallinity, good porosity, photoluminescence properties and wettability for water. It can serve as the first COF-based fluorescent pH sensor in aqueous solutions.

As a novel class of porous crystalline materials, covalent organic frameworks (COFs) are assembled from molecular building blocks using reticular chemistry via covalent bond formation, and exhibit periodic architectures, low densities and predesignable pore parameters. The rational construction in their skeleton structure promises that these porous materials can be tailored to specific functional applications, including gas storage and separation, catalysis, optoelectronics, energy storage, and proton conduction. However, these materials have only rarely been explored as chemosensors; in particular, pH dependent fluorescence properties of COFs are still unexplored. The weak stability and wettability of COF skeletons in aqueous solution are obvious bottlenecks, which restricted their potential for pH sensing.

In this contribution, a new two-dimensional (2D) COF with high crystallinity and large surface area, termed COF-JLU4, was designed and constructed through continuous reversible and irreversible reactions. Interestingly, the COF-JLU4 skeleton features a keto-enamine form, and it shows an outstanding hydrolytic stability and wettability. Furthermore, COF-JLU4 exhibits pH dependent fluorescence response in aqueous solutions with a wide pH range. To the best of our knowledge, this study is the first example of applying COF materials as fluorescent pH sensors.

COF-JLU4 was synthesized by condensation of 2,5-dimethoxyterephthalohydrazide with triformylphloroglucinol under solvothermal conditions (Scheme 1A). The resulting COF was unambiguously characterized by Fourier transform IR spectroscopy, 13C cross-polarization/magic-angle-spinning (CP/MAS) NMR spectroscopy, and elemental analysis. The FT-IR spectra of COF-JLU4 do not show the characteristic stretching vibration peaks of imine and hydroxyl groups (Fig. S1, ESI†). Compared with its monomer (1639 cm⁻¹), the carbonyl C=O peak of COF-JLU4 shifts to a lower energy characteristic of the β-ketoenamine carbonyl stretch (1619 cm⁻¹), becomes simultaneously broad and merges with the C≡C stretching vibration.

Scheme 1 (A) Schematic representation of the synthesis of COF-JLU4 and (B) top and side views of the AA stacking structure of COF-JLU4.
resolved by X-ray diffraction (XRD).

The elemental analysis of COF-JLU4 revealed that the C, H and N contents were 51.36, 4.08, and 13.77%, respectively, which were close to 53.63, 3.94, and 15.64% expected for an infinite 2D sheet. Field-emission scanning electron microscopy (HR-TEM) exhibited a porous texture (Fig. S3B, ESI†), which was close to the lattice resolved by X-ray diffraction (XRD).

The XRD measurement was performed on COF-JLU4 samples to determine their crystallinity. The experimental XRD pattern displayed a strong peak at 3.31° and relatively weak signals at 5.91, 6.76, and 9.26°, which were assigned to 100, 110, 200, and 210 facets, respectively. The slightly broad peak at higher 2θ (~26.9°) is mainly due to π–π stacking between the COF layers and corresponds to the 001 plane (Fig. 1A, red curve). The simulation of the XRD pattern of the AA stacking mode can reproduce the experimental data in the peak position and intensity (yellow curve), while the staggered AB mode produced a profile (green curve) that deviates from the experimental pattern. The Pawley refinement showed an XRD pattern (Fig. 1B, blue curve) that is in good agreement with the experimentally observed pattern, as evidenced by their negligible difference (black curve). The P3 space group with parameters \( a = b = 31.154 \text{ Å}, c = 3.4 \text{ Å}, \) and \( \alpha = \beta = 90°, \gamma = 120° \) was simulated.

The porous structure was investigated using nitrogen sorption measurements at 77 K. COF-JLU4 exhibited a typical type-IV isotherm, which indicated that the new COF was a mesoporous material (Fig. 2A). The Brunauer–Emmett–Teller (BET) surface area and pore volume were estimated to be 923 m² g⁻¹ and 0.573 cm³ g⁻¹, respectively. The \( \mathrm{SA}_{\text{BET}} \) value of COF-JLU4 is higher than those of the majority of the reported β-ketoamine-linked 2D-COFs,8 and is comparable to the highest value of 1120 m² g⁻¹ of DAAQ-TFP COF.5a The pore size distribution evaluated using nonlocal density functional theory was centered at 2.2 nm (Fig. 2B), which is reasonably close to the predicted pore size (2.3 nm). Carbon dioxide (CO₂) adsorption isotherms of COF-JLU4 were collected, showing that this material can store up to 128 mg g⁻¹ of CO₂ at 273 K and 1 bar, with an isosteric heat \( (Q_{\text{st}}) \) value of 33 kJ mol⁻¹ at low coverage (Fig. S4, ESI†).

Thermogravimetric analysis (TGA) was done for COF-JLU4 under a nitrogen atmosphere, which revealed that it was stable up to 305 °C (Fig. S5, ESI†). To evaluate the chemical stability of COF-JLU4, we dispersed the COF samples in different organic solvents such as tetrahydrofuran (THF), hexane, toluene, and CHCl₃ and aqueous solutions with different pH values at room temperature for 2 h. And then the samples were collected by filtration, washed with acetone, and dried under vacuum at 100 °C for 10 h. To our delight, all the samples display strong diffraction peaks in XRD patterns and the same network connection in FT-IR profiles (Fig. S6a and b, ESI†), implying that the good crystallinity is retained in the COF samples. The good chemical stability may be attributed to the hydrogen bond interactions on the skeleton of COF-JLU4.8

The luminescence properties of COF-JLU4 were investigated by UV/vis and fluorescence spectroscopy. The electronic absorption and fluorescence spectra of COF-JLU4 in water and the solid state are shown in Fig. 3A. COF-JLU4 displayed an absorption band at 380 nm in the solid state with a shoulder peak at 488 nm (red line in Fig. 3A). Compared with monomers and the model compound, the absorption band of COF-JLU4 has undergone an obvious red-shift, which implied an extended π-conjugation over a layer of network (Fig. S7, ESI†). The fluorescence spectrum of COF-JLU4 in the solid state displayed orange luminescence and an emission band observed at 568 nm with a quantum yield of 2.9% upon excitation at 380 nm (green line, Fig. 3A). However, the corresponding monomers exhibited

(1585 cm⁻¹), which is attributed to the strong intramolecular hydrogen bonding in the keto form of the 2D conjugated sheet (Fig. S1, ESI†).8 The atomic precision construction of COF-JLU4 was further verified by ¹³C CP/MAS NMR (Fig. S2, ESI†). The peaks at 182 and 161 ppm correspond to the carbon atoms of the carbonyl groups. The high-field peak at ~55 ppm can be assigned to the methoxy groups of the aromatic rings.

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almost no emission in the solid state upon excitation at 322 and 376 nm, respectively (Fig. S8, ESIF). The obvious difference in the fluorescence properties between COF-JLU4 and its monomers can be attributed to the extended π-conjugation skeleton of the COF and restriction of intramolecular rotation in the framework. Furthermore, this COF can be easily dispersed in water, owing to abundant heteroatoms in the skeleton. And a blue-shifted emission band with a peak at 475 nm was obtained upon excitation at 418 nm (blue line, Fig. 3A).

Compared with electrodes, fluorescent pH responsive sensors possess numerous advantages including facile pH detection, ease of device fabrication and flexibility of design and are of great importance in environmental and life sciences. Recently, some nanoscale fluorescent pH sensors such as metal–organic frameworks (MOFs) have been constructed successfully. Unfortunately, however, the use of luminescent COFs as fluorescent pH sensors has not been explored. COF-JLU4 exhibits good luminescence and wettability in aqueous solution, which provides a suitable platform and inspires us to explore its application as a nanoscale pH responsive sensor. Fig. 3B shows the emission spectra of COF-JLU4 in aqueous solution at various pH values. Interestingly, the fluorescence intensity and wavelength of COF are strongly correlated with the pH value of the dispersed solution in our experimental pH range (0.9–13.0). The most acidic solution displayed the strongest fluorescence, while the weakest intensity was obtained with a solution of pH = 13.0. The fluorescence enhancement and blue-shift in acidic solution are assumed to arise from the protonation of nitrogens. Furthermore, we investigated the fluorescence response of the model compound to the pH value, and found that the fluorescence intensity of the model compound also decreases gradually with increasing pH value of solutions (Fig. S9, ESIF).

We further explored the recyclability and reusability of COF-JLU4 as a fluorescent pH sensor. For example, when the pH value of the solution was 13.0, COF-JLU4 exhibited the same degree of fluorescence quenching after each cycle, and the fluorescence intensity recovered to a similar level when the pH value of the solution was changed to 7.0 (Fig. 4A). Moreover, COF-JLU4 exhibited an enhancement in fluorescence in acidic solution (pH = 1.0), even after reuse (Fig. 4B). To our delight, the crystallinity of the COF-JLU4 framework is still well maintained after multiple uses (Fig. S10, ESIF).

In conclusion, a β-ketoamine based 2D covalent organic framework (COF-JLU4) was successfully designed and synthesized under solvothermal conditions. The new COF has excellent porosity with a high BET surface area of over 900 m² g⁻¹, strong crystallinity, good stability and photoluminescence properties. Furthermore, we also highlight that the crystalline framework exhibits interesting fluorescence response to the pH value in aqueous solution, showing for the first time the utility of the crystalline COFs for developing pH-sensing systems. This research expands the scope of COFs and constitutes an important step toward porous crystalline organic architectures with designed functions.

This work was supported by the National Natural Science Foundation of China (No. 51473064, 61435005, 21274050 and U1462111).

Notes and references

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