Polymer modification

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Coumarin linkages for robust frameworks

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Post-synthetic modification of olefin moieties to form coumarin linkages within covalent organic frameworks enhances their stability.

Covalent organic frameworks (COFs) are a class of crystalline porous polymers that allow the atomically precise integration of π units to create predesigned skeletons and nanopores in bulky solids and thin films[1]. The unique features of COFs such as their well-defined crystalline porous structure, high stability and tunable functionality make them excellent platforms for a diverse range of applications, such as gas storage and separation, catalysis, sensing, and optoelectronics[2]. Typically, the synthesis of COFs uses the formation of reversible bonds, such as boroxines, boronate esters, imines, and hydrazones, which can result in high crystallinity[2]. However, to some extent, the reversibility of the linking bonds sacrifices the stability of COF materials. To overcome this shortcoming, substantial efforts to develop new polymerization reactions and connection bonds to strike a balance between the crystallinity and stability of the COF materials have been made. Notably, post-synthetic modification is an effective and commonly used strategy to form a diverse range of COF-based materials based on existing COFs[3,4]. For instance, COFs with imine linkages can be transformed into COFs bearing stable heteroaromatic structures such as quinoline, benzoxazole, benzothiazole, and benzimidazole by post-synthetic modification[3,4] (Fig.1a). This approach not only enhances the structural stability but also enables the introduction of tailored functional moieties. However, to date, this strategy has not been widely applied to COFs beyond imine-linked frameworks[5].

Now writing in *Nature Synthesis*, Omar M. Yaghi and co-workers report a two-step strategy to convert cyano–olefin-linked COFs into highly crystalline coumarin-linked COFs[6]. Over the past decade, cyano–olefin-linked COFs, constructed via stable –C=C(CN)– bonds, have been developed, and these COFs exhibit excellent chemical stability in acids, bases, and most common organic solvents. Their exceptional stability and highly conjugated skeleton confer advantages such as high conductivity and excellent catalytic activity[7,8]. In previous studies, the –C=C– bond primarily served as a connector for building a conjugated skeleton, however, modification and functionalization of olefin linkages in COFs are limited. Coumarin, a naturally occurring molecular moiety known for its chemical stability and photoluminescence, is ubiquitous in natural products. Interestingly, this work provides a synthetic route to form coumarin-linked COFs.

In this study, a methoxymethoxy (MOM)-protected salicylaldehyde monomer, 3,3′-bis(methoxymethoxy)-[1,1′-biphenyl]-4,4′-dicarbaldehyde (DHBD-MOM), is reacted with 1,3,5-tris(4-cyanomethylphenyl)benzene (TCPB) to prepare a coumarin-linked COF, via a two-step strategy. Specifically, the highly crystalline COF (COF-991-CN), connected by the –C=C(CN)– bond, is synthesized through a Knoevenagel condensation, under alkaline conditions. Subsequently, exposure of COF-991-CN to acidic conditions, through a Pinner reaction, forms the coumarin-linked COF (COF-991) in high yield (Fig. 1b). In contrast, using unprotected salicylaldehyde as the monomer yielded no target product, owing to its low solubility in organic solutions under basic conditions, which reduces the reversibility of the condensation reaction. Using this process, four other coumarin-linked COFs with different chemical compositions and pore sizes have been successfully synthesized using consecutive Knoevenagel condensation and Pinner reaction process, demonstrating the broad applicability of this strategy for constructing diverse stable coumarin-linked COFs from different monomers.

The coumarin ring does not immediately form during the initial crystallization process because the MOM group remains stable under alkaline conditions (Fig. 1b). However, the MOM group can be feasibly removed under acidic conditions, releasing free hydroxyl groups to attack the cyano group to form lactone units, thereby leading to the formation of coumarin linkage (Fig. 1b). Notably, converting ^{13}C-labelled COF-991-CN (COF-991-^{13}CN) into the corresponding product (^{13}C-enriched COF-991), provides evidence for formation of coumarin linkages, as revealed by ^{13}C cross-polarization magic-angle spinning solid-state nuclear magnetic resonance spectroscopic analysis. Specifically, the resonance peak of the ^{13}C label shifts from 117.9 to 159.4 parts per million for COF-991-^{13}CN and ^{13}C-enriched COF-991, respectively, confirming the conversion of cyano–olefin linkages into lactone carbonyl units. Overall, this approach combines reversible covalent bond-forming reactions to confer crystallinity with irreversible steps that confer stability.

The five coumarin-linked COFs exhibit high compositional purity, crystallinity, and porosity as shown by ^{13}C cross-polarization magic-angle spinning solid-state nuclear magnetic resonance spectroscopy, powder X-ray diffraction, and nitrogen sorption isotherm measurements. Additionally, the five coumarin-linked COFs exhibit high chemical stability in strong acids and bases, and thermal stability with a decomposition temperature of ~600 °C.

Coumarin moieties typically exhibit unique fluorescence properties. Unlike commercial coumarin-based fluorescent dyes, which show characteristic blue-to-purple emission of (410–490 nm), COF-991 exhibits a broad emission spectrum with a maximum emission wavelength of 542 nm (green light) upon 400 nm excitation. This red-shifted maximum emission stems from the highly planar and conjugated nature of the COF, which narrows the energy gap between excited and ground states.

The preparation of coumarin-linked COFs further enriches the structural diversity of COFs. This method reported by Yaghi and co-workers serves as one of the first examples of post-synthetically modifying olefin-linked COFs to form COFs with a new linkage and high porosity. Crucially, considering that the introduction of methoxymethoxy groups is straightforward for many monomers, this strategy provides a potential modification approach for various robust COFs with similar structures. Furthermore, it establishes an iterative strategy for the use of existing materials, guiding researchers toward developing more diverse post-synthetic conversions and application-oriented functionalization of various types of COFs.

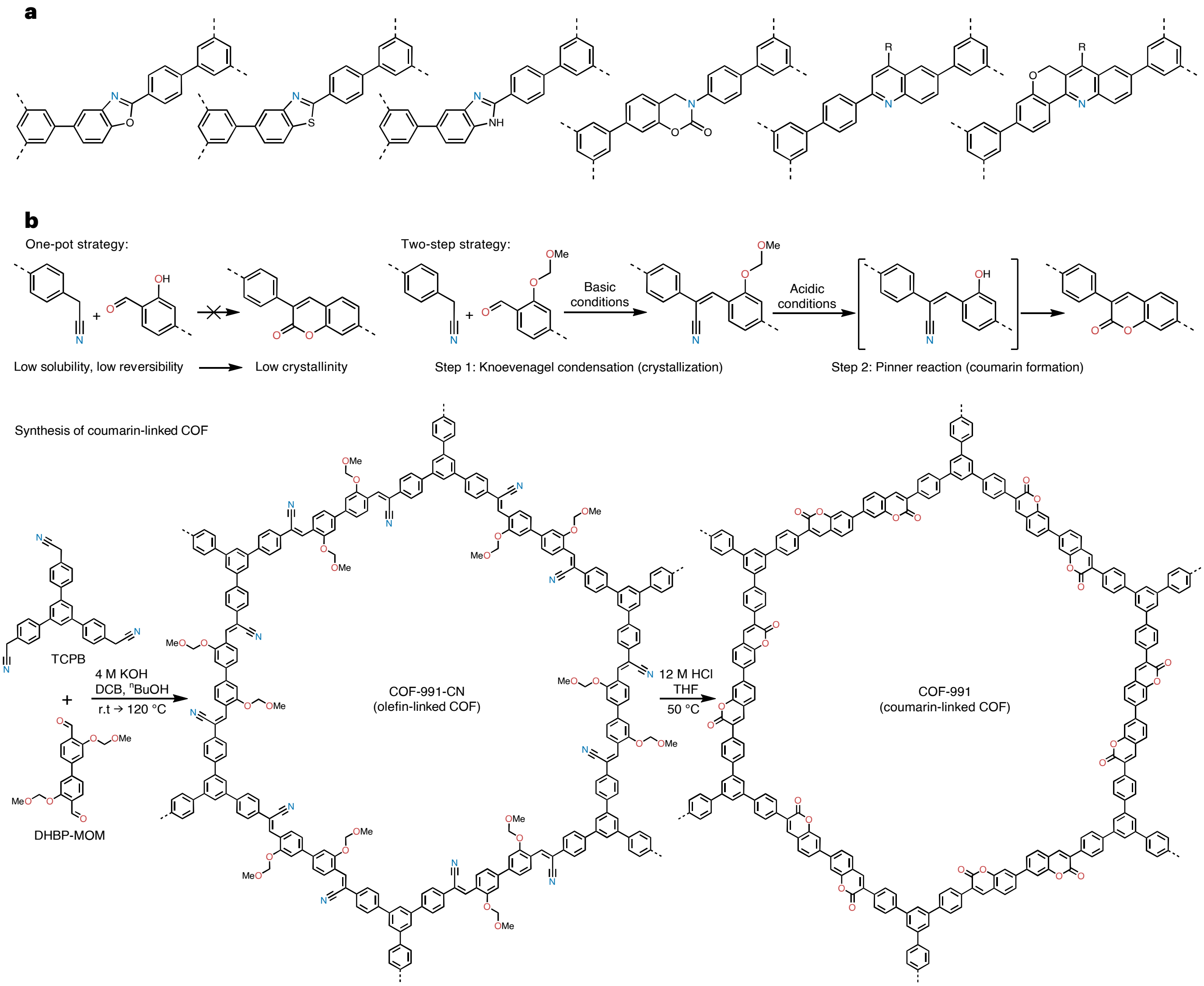

Fig. 1 | Schematics of heteroaryl-linkages in modified imine-linked COFs and synthesis of coumarin-linked COF-991. a, Heteroaryl-linked COFs formed through post-synthetic modifications of imine-linked COFs. **b**, Attempted one-step strategy and successful two-step strategy towards the synthesis of coumarin-linked COF-991. The two-step strategy comprises a Knoevenagel condensation between MOM-protected salicylaldehyde and benzyl cyanide functionalized monomers to yield a highly crystalline olefin-linked COF, COF-991-CN, followed by a Pinner reaction to form the crystalline coumarin-linked COF, COF-991. r.t., room temperature; DCB, 1,2-dichlorobenzene; THF, tetrahydrofuran.

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Competing interests

The authors declare no competing interests.