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Editorial

Linker-activated covalent organic frameworks with azo bridges



As an important functional group, azo derivatives ($-N=N-$) have attracted wide attention due to their excellent properties, for their narrow bandgap, Lewis base property, photo-isomerization and redox activity, in chemistry and materials science fields [1]. Among them, azo-benzene is one of the most popular candidates of optical molecular devices including easy synthesis, high quantum yields and fast switching. Generally, azo-benzene exists in two conformations, *i.e.* *trans*-state and *cis*-state, which are reversibly converted *via* $-N=N-$ bond transformation in the presence of appropriate stimuli including temperature, mechanical stress, electric field, and especially photoirradiation [2]. In addition, the azo group can not only endow the derivatives with narrow bandgap properties, but also permit the lone pair electrons on the nitrogen atom to accept protons, as well as it coordinates with a variety of metals to avoid encountering aggregation of bimetallic ions, suitable for multiple catalytic reactions, such as photodegradation, hydrogen evolution reaction [3].

On the other hand, covalent organic frameworks (COFs) are a new class of crystalline organic porous two-dimensional or three-dimensional extended network materials that are periodically connected by appropriate linkages through covalent bonds [3,4]. They are known for their widely potential applications in chemical sensing [5], catalysis [6] and separation [7], *etc.* Tang's group designed and constructed a COF with peroxidase activity through the condensation of benzene-1,3,5-tricarbohydrazide and 2,2'-bipyridine-5,5'-diformaldehyde followed by Cu^{2+} functionalization for detecting dopamine with high sensitivity and selectivity *via* fluorescence, colorimetric and smartphone methods. Hyperconjugated COFs containing porphyrin and triazine block structural units were constructed based on the self-polymerization of C_2 symmetry cyanoporphyrins which showed high photocatalytic performance in organic reactions such as benzylamine coupling due to the ability to produce extremely high singlet oxygen, superoxide radical and other reactive oxygen species under photo-excitation. Zhang *et al.* synthesized a new macrocyclic COF by using pillar [5] arene diamine and 1,3,5-triformylbenzene, which could selectively adsorb C_2H_2 and paraquat through the host-guest interaction of the macrocyclic part. The structure of COFs could be designed bottom-up through topological strategies, and their properties and functions can be adjusted through various building blocks and linkages. Therefore, it is believed that the combination of the vital multi-functional $-N=N-$ derivatives with COFs not only makes the material an ordered porous conjugated structure, but also endows the material with excellent performance. Although there have been some reports on the azo-functionalized COFs, most of them are based on COFs of azo fragments in which azo is only a part of

constituent elements but not a linkage, and the construction of the azo-linked COF has been rarely realized.

Recently, Zhao and coworkers [3] from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences reported a novel strategy for the synthesis of azo-bonded COFs by linker exchange based on the previously established "COF-to-COF" transformation strategy [8], which guided the formation of product COFs structure *via* the template effect of precursor COFs. Owing to the feasibility of connection bond transformation through model reaction (Fig. 1a), the author used imine-linked COFs (Im-COF-1 and Im-COF-2) as precursors to react with 1,4-dinitrosobenzene and replaced the units from terephthalaldehyde in the structure of imine COFs *in situ*, thus realizing the transformation of $-C=N-$ bond to $-N=N-$ bond and obtaining the corresponding azo-linked COFs (Azo-COF-1 and Azo-COF-2) (Fig. 1b).

To demonstrate the successful transformation of Im-COFs to Azo-COFs, a series of structural characterizations were performed. In the Fourier transform infrared spectroscopy, with the disappearance of the vibration peak of $-C=N-$ (1620 cm^{-1}), the vibration peaks of $-N=N-$ (1404 and 1452 cm^{-1}) appeared. Meanwhile, the ^{13}C solid-state cross-polarization magic angle spinning spectra results showed the disappearance of the signal peak of the imine bond at 157 ppm. The ^{13}C isotope labeling experiment also proved that the $^{13}C=N$ peak completely disappeared. In addition, in the Raman contrast spectra, the transformation of the imine bond (1628 cm^{-1} and 1631 cm^{-1}) to the azo bond (1441 cm^{-1} and 1443 cm^{-1}) was shown. X-ray photoelectron spectroscopy revealed that the binding energy of N 1s changed from 398.6 eV to 399.7 eV. These experimental results all prove that the imine bond is converted into an azo bond, corresponding to the conversion of Im-COFs to Azo-COFs. Powder X-ray diffraction results showed that the crystallinity of COFs remained intact before and after conversion, and the unit cell was very similar. Nitrogen adsorption-desorption experiments, scanning electron microscopy tests and hydrolysis experiments also provide favorable evidences for the conversion of Im-COFs into Azo-COFs.

Furthermore, the photophysical and photocatalytic properties of the transformed Azo-COFs were investigated. Compared with Im-COFs, the absorption range of Azo-COFs in the UV-vis-NIR diffuse reflectance spectra is from visible to near-infrared region, and the absorption spectrum is red-shifted. It has a narrower optical band gap by Tauc analysis, which is suitable for photocatalytic applications. Subsequently, Azo-COF-1 showed a more efficient catalytic effect in the photodegradation of organic dye rhodamine B (RhB). By means of photoluminescence spectrum measurement, fluorescence lifetime measurement, photocurrent test, catalytic ac-

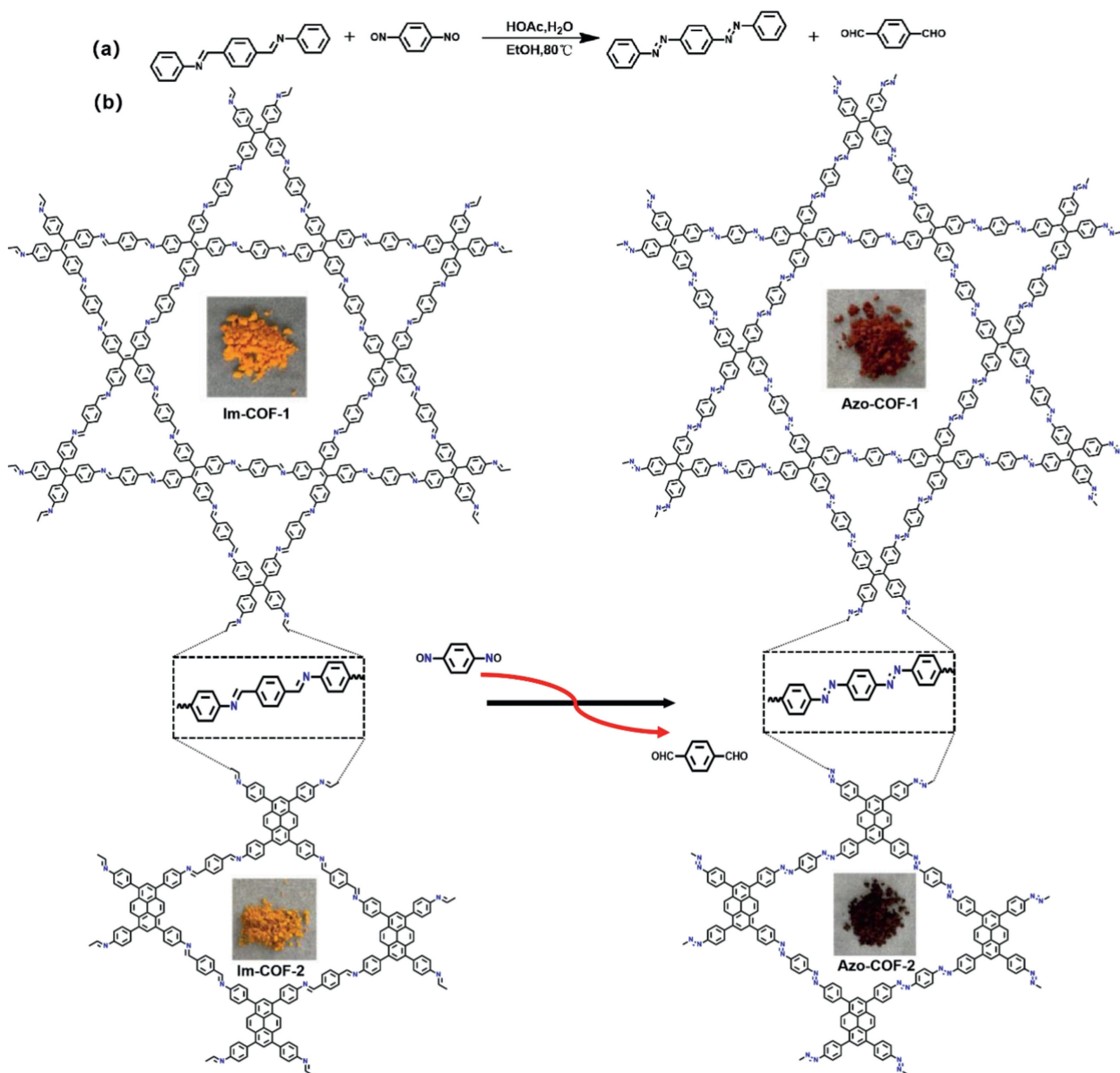


Fig. 1. Scheme illustration of (a) model reaction and (b) fabrication of azo-linked COFs via linker exchange.

tive species capture experiment and DFT theoretical calculations, the author confirmed that when the imine bond is converted into an azo bond, the energy level structure of COFs changes, and it is easier to produce reactive oxygen species ($O_2^{\cdot-}$) to participate in the photocatalytic reaction. After the separation of photo-excited charge, the photo-generated electrons become easier to transfer, thus avoiding recombination with holes.

In summary, in the development history of COFs, although a variety of linkages have been developed, including -B-O-, -C=N-, -B-N-, -C=C-, -C-N-, -C-O-, -Si-O- and -C-C-, the development of new linkage and further exploration of new functions are still a great challenge. Zhao and coworkers established a new method for the synthesis of Azo-COFs, in which azo-linked COFs was realized for the first time by the transformation from the -C=N- into -N=N- of COFs via a new linker exchange and exhibited efficient photo-catalytic properties for organic dyes. We believe that this linker exchange method can be applied to many other COFs that are difficult to construct by monomer polymer-

ization, including three-dimensional COFs with a specific recognition ability and high surface area. Moreover, these azo-based COFs could also be further modulated by light or enzymes as intelligent and controllable nano-reactors for *in situ* imaging and *in situ* drug release. This study not only enriches the linkage library of COFs but also provides a platform for the development of structure, property and application of new conjugated crystalline polymers.

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