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A novel azobenzene covalent organic framework†

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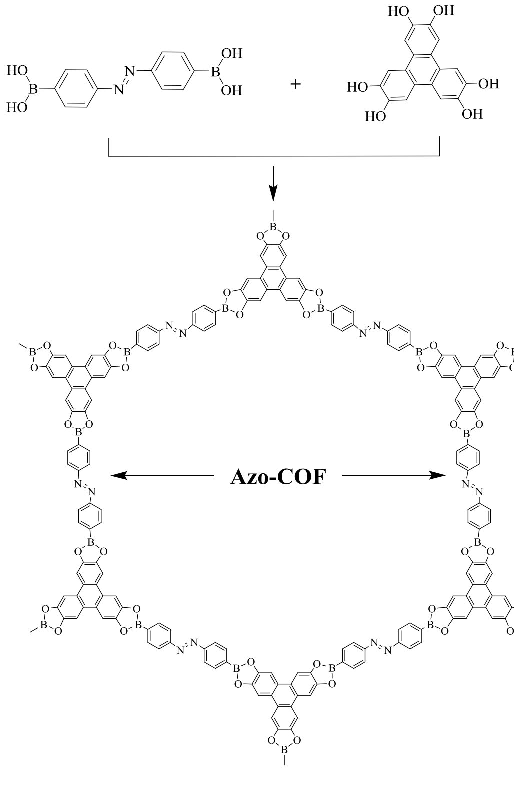
A novel azobenzene (Azo) monomer was synthesized and employed to produce Azo-containing covalent organic frameworks (Azo-COF) through the borate ester formation reaction. The *trans*-to-*cis* photoisomerization of Azo units in Azo-COF occurred under the radiation with 365 nm UV light. The phoisomerization of Azo units could decrease the crystallinity of Azo-COF, while could not change the pore size of Azo-COF.

Covalent organic frameworks (COFs),[1] as a new class of crystalline porous polymers, have received much attention in recent years, owing to their structural periodicity, permanent porosity and thermal stability. Various reversible condensation reactions, such as borate ester,[2] boroxine,[3] borosilicate,[4] imine,[5] triazine,[6] hydrazone,[7] azine[8] and squaraine[9] forming reactions promote the development of synthetic COFs. Due to high surface area, large pore volume and low density, COFs are intensively investigated for gas absorption and storage,[10] catalytic,[11] and optoelectronic[3b,12] applications. COFs are generated by atomically precise integration of building blocks. Thus, the diversity of functional building blocks will definitely bring about the variation of topological structures, pore sizes as well as functions of the resulting COFs.

Azobenzene (Azo) is capable of reversible change in shape between *trans*- and *cis*-isomer by irradiation of light with different wavelength, resulting in wide applications in optical switching,[13] optical data storage,[14] photo-robotics[15] and drug delivery system.[16] The *trans*-isomer of Azo has a thermally stable and planar rigid configuration, thus it can be as a C_2-symmetric building block to construct 2D COFs. We report herein a novel 2D COF, in which Azo and triphenylene linked alternatively in a mesoporous hexagonal skeleton. The unique *trans-cis* photoisomerization of Azo motivates us to figure out whether it will change the structures and pore sizes of 2D COFs.

The new C_2-symmetric building block, azobenzene-4,4'-diboronic acid (ABDA), was prepared in three steps from the precursor 4,4'-dihydroxyazobenzene (ESI†). Then, the condensation reaction of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and ABDA under solvothermal condition produces hexagonal azobenzene COF (Azo-COF), where HHTP occupies the vertices and ABDA acts as the edges (Scheme 1). The typical experimental procedure is as follows: A 1,4-dioxane/mesitylene mixture (20 mL, 1/1 in vol.) of ABDA (101 mg, 0.375 mmol) and HHTP (81 mg, 0.25 mmol) was placed in a 50 mL Pyrex tube. Then the tube was degassed via three freeze-pump-thaw cycles, sealed and heated at 85 °C for 3 days. The precipitate was collected by centrifugation, washed with anhydrous acetone and dried at 80 °C under vacuum to afford Azo-COF (100 mg) as a yellow powder in 64.5% yield. Fourier transform infrared (FI-TR) measurement was employed to verify the formation of boronate ester linkages. As shown in Fig. 1, the characteristic vibrational bands at 1352, 1241 and 1010 cm^{-1} are corresponding to



Scheme 1 Schematic representation of the synthesis of Azo-COF.

the B-O, C-O and B-C bonds of boronate ester unit, respectively.[12a] Meanwhile, compared with the HHTP and ABDA monomers, Azo-COF exhibited a strongly attenuated O-H band in the range of 3000-3600 cm^{-1}. Elemental analysis showed that the C, H, N contents were 64.10, 3.49 and 6.53%, respectively, which are close to the calculated values of 69.63, 2.92 and 6.77% speculated from an infinite 2D sheet ($C_{12}H_6BNO_2$). Azo-COF was thermally stable up to 490 °C (Fig. S1).

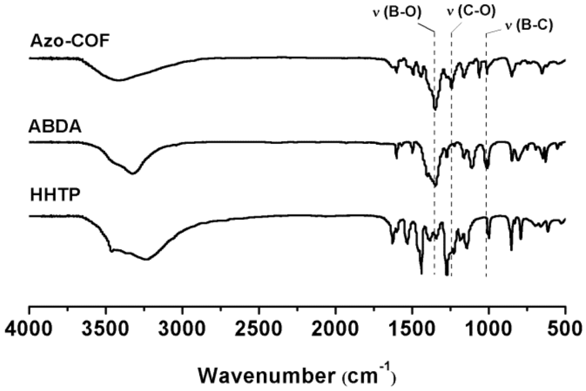


Fig. 1 FT-IR spectra of Azo-COF, ABDA and HHTP.

Field-emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM) were performed to investigate the morphology and inner structure of Azo-COF. As presented in Fig. 2, FE-SEM revealed that the Azo-COF was crystallized in multi-layered sheets. Furthermore, paralleled straight lines were clearly observed from HR-TEM image, which illustrated that Azo-COF consisted of parallel aligned 2D sheets.[12f] The crystallinity of Azo-COF was evaluated by powder X-ray diffraction (PXRD) measurement as given in Fig. 3 (black curve). The clear diffraction peaks located at 2θ of 2.60, 4.46, 5.20, 6.83, 9.07 and 26.2° were obtained, which are assigned to (100), (110), (200), (210), (310) and (001) facets, respectively. Based on the peaks of 2.60 and 26.2°, the center-to-center distance between neighboring pores and the inter-sheet interval were determined to be 3.39 nm and 3.3 Å, respectively. It is widely believed that a typical 2D COFs structure can stack in two potential forms: an eclipsed (AA, Space Group *P*6/m) form or a staggered (AB, Space Group *P*63/m) form. Thus, we built both two models and then compared their simulated PXRD patterns with the experiment data (Fig. 3). The simulation of the PXRD pattern of the AA structure (Fig 3, magenta curve) matched the experimental data decently both in peak position and intensity, while AB model (Fig. 3, cyan curve) produced an unnatural peak alignment that was inconsistent with the experimental pattern. Such a distinct contrast implies that the AA model would be an appropriate representative for the Azo-COF. The Pawley refinement was applied on the optimized AA stacking lattice, producing the refined PXRD profile with lattice parameters a = b = 39.2728 Å and c = 4.1653 Å, with the moderate R_{wp} and R_p values converged to 5.42% and 4.29%, respectively. The Pawley refined pattern (Fig. 3, red curve) was in accord with the experimental PXRD pattern (Fig. 3, black curve) and confirmed the assignment of the observed diffraction peaks.

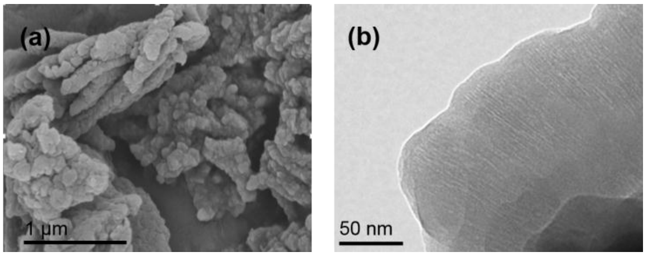


Fig. 2 a) FE-SEM and b) HR-TEM images of AZO-COF.

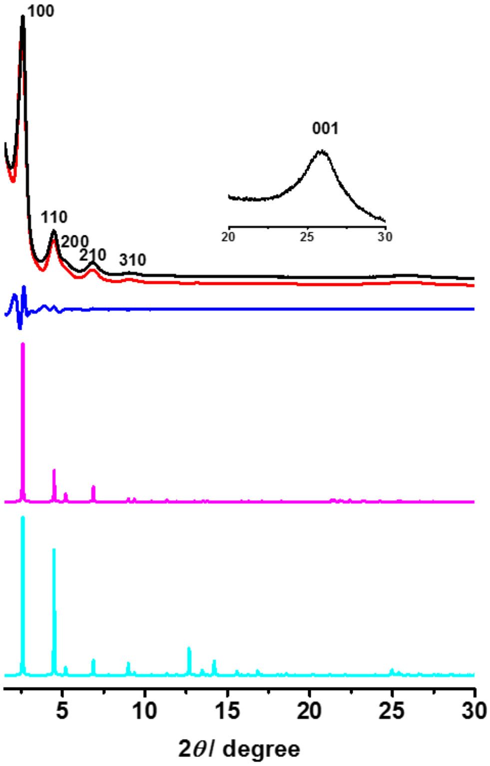


Fig. 3 Experimentally obtained PXRD pattern of Azo-COF (black), the Pawley refinement (red), their difference (blue), and simulated PXRD patterns with AA (magenta) and AB stacking (cyan).

Nitrogen sorption isotherm measurement at 77 K was carried out to study the porosity of Azo-COF. Fig. 4 exhibited a typical type IV nitrogen sorption curve, indicating that Azo-COF is a mesoporous material.[2b] The analysis of the sorption curve using the Brunauer-Emmett-Teller (BET) method demonstrated that the specific surface area and pore volume value as 810 m^{2}g^{-1} and 0.7279 cm^{3}g^{-1}, respectively. Moreover, the pore size calculated with the nonlocal density functional theory (NLDFT) method was nearly 3.04 nm. The pore size distribution curve confirmed that the surface areas of Azo-COF mainly derived from the mesopores.

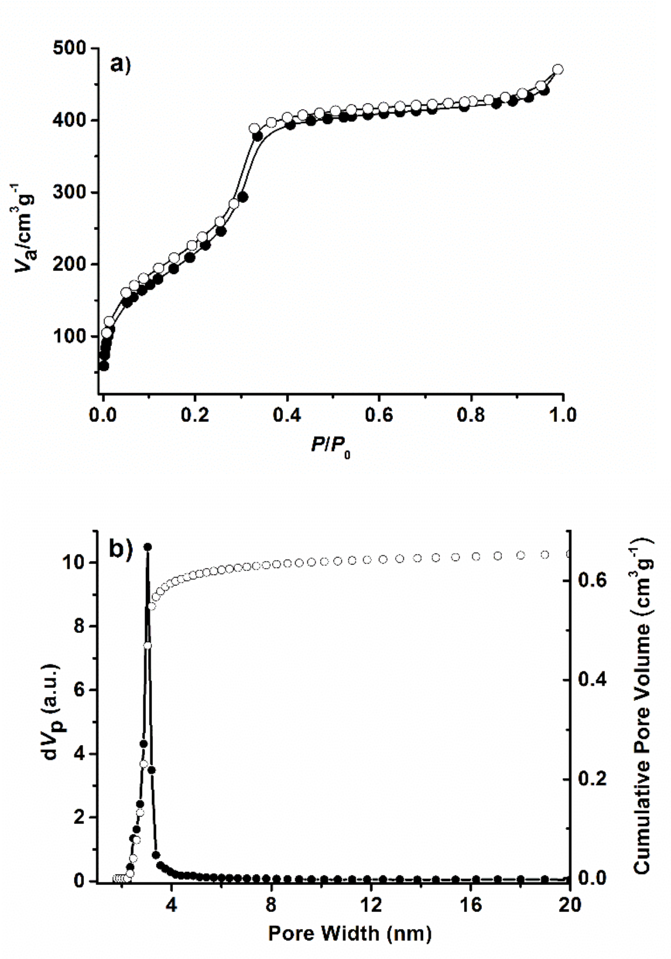


Fig. 4 a) Nitrogen sorption isotherm curve measured at 77 K. b) Pore-size (left axis) and pore-size distribution profiles (right axis).

Azo compounds show photoisomerization behavior and undergo isomerization from *trans*- to *cis*-forms under 365 nm UV light irradiation.[17] High density of Azo chromophores was achieved in obtained Azo-COF. The changes in UV-vis spectra of Azo-COF powder at different irradiation times by 365 nm light were recorded in Fig. 5. The absorption band at around 350 nm was assigned to the characteristic π-π^* transition of *trans*-isomer of Azo in Azo-COF. After irradiation with 365 nm UV light, the *trans*-isomer changed to the *cis*-isomer (n-π^* transition) as evidenced by a rapid decrease of the band at 350 nm as well as a slight increase of the band in the region of 500-650 nm. The contents of *trans*- and *cis*-form of Azo unit in Azo-COF was estimated using the method as reported.[17b] About 17.1% Azo units changed from *trans*-form to *cis*-form after irradiation with 365 light for 100 min. To our surprise, the back *cis*-to-*trans* photoisomerization could not be achieved under the irradiation of 546 nm light, and even after staying in the dark for 24 h (Fig. S2). The reason for the undetected *cis*-to-*trans* photoisomerization is not clear, and the further study is currently underway in our lab.

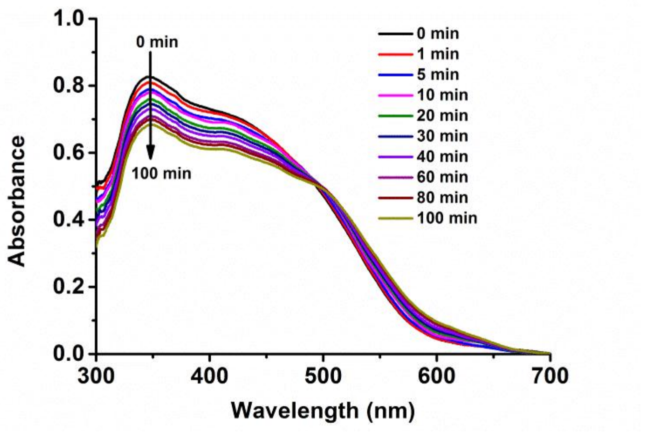


Fig. 5 UV-vis absorption changes of Azo-COF under different time interval during the irradiation with 365 nm UV light.

The influence of *trans*-to-*cis* photoisomerization on crystal structure and pore size of Azo-COF was further investigated by PXRD measurement. As shown in Fig. 6, the reflection intensities of PXRD patterns of Azo-COF decreased after irradiation with 365 nm UV light, which implied the decline of Azo-COF crystallinity. The *cis*-isomer of Azo is lack of planarity, that is not favorable for the construction of COFs.[1b] Hence, the *trans*-to-*cis* photoisomerization can induce the decrease of Azo-COF crystallinity. However, there were no obvious shifts of the reflection positions, meaning the pore size of Azo-COF was still the same after UV light irradiation. Furthermore, the change in pore size was also not detected from the BET measurement, which was still 3.04 nm after irradiation with 365 nm light for 12 h (Fig. S4). The unchanged pore size before and after UV light irradiation was in consistent with the previous results reported by Lyndon and his coworkers.[18] Hence we can draw a conclusion that the transition between *trans*- and *cis*-isomer of Azo was local and could not alter the original periodicity of Azo-COF.

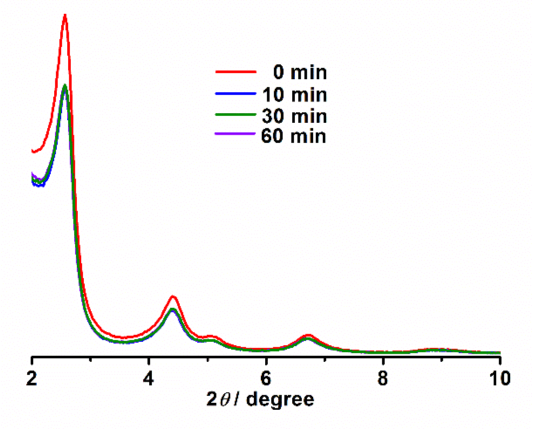


Fig. 6 Changes in PXRD patterns of Azo-COF under different radiation times with 365 nm UV light.

As far as we know, Azo-COF is the first example of Azo building block containing COFs, showing a *trans*-to-*cis* isomerization behavior of Azo unit under radiation with a UV light. In previous studies of metal-organic frameworks (MOFs), the photo-induced isomerizaion of Azo units only occurred when the Azo units were covalently attached to the inner pore wall of MOFs,[19] owing to the restricted Azo units in the rigid framework. Most recently, Lyndon and his coworkers[18] reported an Azo-containing MOF, Zn(AzDC)(4,4'-BPE)$_{0.5}$, which incorporating Azo units into the backbones of MOFs. They found that the transition of Azo *trans*- and *cis*-isomers occurred at vibration level on a short range scale and in a dynamic fashion, which brought about the remarkable property of low-energy CO_2 capture and release. As like as Zn(AzDC)(4,4'-BPE)$_{0.5}$, Azo-COF also showed unchanged reflection positions in PXRD patterns before and after UV light irradiation. The *trans*-to-*cis* isomerization of Azo units in Azo-COF may be also local and dynamic. However, the directly observed changes in UV-vis spectra and the decreased reflection intensities in PXRD patterns after UV light irradiation revealed that the transition of Azo *trans*- and *cis*-isomers was possible. Therefore, the photo-induced isomerizaion of Azo units in Azo-COF may be composed of dynamic and static processes: the surface of Azo-COF powder proceeded static *trans*-to-*cis* isomerization of Azo units, while the inner of Azo-COF powder underwent local and dynamic *trans*-to-*cis* isomerization of Azo units with the irradiation of UV light.

In summary, we reported the first example of a novel Azo-containing 2D COF with a hexagonal skeleton, high crystallinity and permanent porosity. The condensation reaction of triphenylene and Azo monomers gives Azo-COF, where triphenylene units occupy the vertices and Azo units act as the edges. The *trans*-to-*cis* photoisomerization of Azo units in Azo-COF takes place under irradiation with 365 nm light, while the back *cis*-to-*trans* photoisomerization is undetected. The *trans*-to-*cis* photoisomerization can lead to the decline of Azo-COF crystallinity, while cannot impact the pore size of Azo-COF. The current results will provide the strategy for designing smart COF materials.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Materials and characterizations, synthesis procedures, TGA analysis, the *cis*-to-*trans* photoisomerization and simulation of PXRD pattern and crystal packing of Azo-COF, and the N_2 adsorption isotherm and pore size distribution of Azo-COF after irradiation with 365 nm light results.

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Graphic Abstract

A novel azobenzene-linked covalent organic framework

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