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A π -electronic covalent organic framework catalyst: π -walls as catalytic beds for Diels-Alder reactions under ambient conditions

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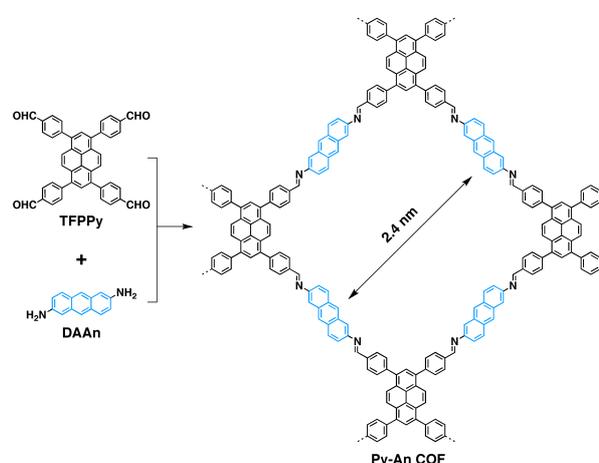
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We report a strategy for developing π -electronic covalent organic frameworks as heterogeneous catalysts that enable the use of columnar π -walls as catalytic beds to facilitate organic transformations in their one-dimensional open channels. The π -frameworks exhibit outstanding catalytic activity, promote Diels-Alder reactions under ambient conditions and are robust for cycle use.

Two-dimensional covalent organic frameworks (2D COFs) consist of polygon sheets that are layered via π - π stacking to form periodic columnar π -arrays and ordered one-dimensional (1D) channels in a predesignable manner.¹⁻⁴ The columnar π -wall architecture together with the open-accessible 1D channels render 2D COFs able to function as π -electronic beds that catalyse organic transformations. However, this potential has not been explored to date. Herein, we show the development of π -electronic walls of 2D electronic COFs as a catalytic bed to drive organic transformations.

The [4 + 2] cycloaddition reactions, known as Diels-Alder reactions, are a class of thermally allowed reactions that occur at elevated temperature. Diels-Alder reactions are one of the cornerstone transformations in modern organic chemistry and have been frequently used for the synthesis of biologically active compounds and natural products.⁵ The high temperature has thus far precluded any practical implementations. In this context, to develop a catalyst that can reduce the reaction temperature is highly desired. To the best of our knowledge, heterogeneous catalysts for the Diels-Alder reactions under ambient conditions are unprecedented.^{1a}

Here, we report a strategy for developing π -electronic COFs as a heterogeneous catalyst for the Diels-Alder



Scheme 1 Schematic Representation of Synthesis of Imine-Linked Pyrene-Anthracence COF (Py-An COF).

reactions under ambient conditions. We synthesised a new imine-linked COF with pyrene at the vertices and anthracene on the edges, via the condensation of 1,3,6,8-tetrakis(*p*-formylphenyl) pyrene (TFPPy) with 2,6-diaminoanthracene (DAAn) under solvothermal conditions (Scheme 1, Py-An COF). The resulting COF was unambiguously characterised by various spectroscopic and thermogravimetry analysis (Figs. S1-S4). The formation of the imine linkages was confirmed by the infrared spectroscopy, which exhibited a stretching vibration band at 1627.6 cm^{-1} assignable to the C=N bond (Fig. S1). Field emission scan electron microscopy revealed regular belt morphology (Fig. S2). High-resolution transmission electron microscopy revealed tetragonal porous texture (Fig. S3), which were close to the lattice resolved by X-ray diffraction (XRD).

The XRD patterns revealed that the Py-An COF was a crystalline material (Fig. 1A, red curve). The most intense peak at $2\theta = 3.14^\circ$ corresponds to the (110) facet of a square lattice. The other minor diffraction peaks at 4.67° , 6.38° , 9.66° , 12.89° and 25.1° are assigned to the (200), (220), (330), (440) and (001) facets, respectively. To

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clarify the lattice packing, we constructed and evaluated two typical modes of crystal lattices, *i.e.*, the eclipsed AA and staggered AB modes, using Materials Studio software package. The simulation of the XRD pattern of the AA stacking mode (green curve) matched the experimental data both in peak position and intensity, while the staggered AB-stacking mode produced a profile (orange curve) that was inconsistent with the experimental pattern.

We reconstructed the eclipsed AA mode by using an optimal monoclinic space group (C2/m), which gave rise to a more plausible layer morphology and higher correlation with the experimental XRD pattern (Fig. 1B, blue curve). The Pawley refinements were subsequently performed within the Materials Studio Reflex Plus Module to determine the unit cell parameters, producing the unit-cell parameters of $a = 38.4173 \text{ \AA}$, $b = 44.4373 \text{ \AA}$, $c = 3.9932 \text{ \AA}$, $\alpha = 66.75^\circ$, and $\beta = \gamma = 90^\circ$. The refined profile matched the experimental XRD pattern very well (Fig. 1B, blue curve) as evidenced by their negligible difference (black curve). The AA stacking mode constituted 1D channels with pore size of 2.4 nm (Fig. 1C), whereas the AB mode resulted in overlapped pores (Fig. 1D).

The Py-An COF exhibited typical type-IV nitrogen sorption isotherms collected at 77 K (Fig. 2A), which indicated that the Py-An COF was a mesoporous material. The Brunauer–Emmett–Teller (BET) surface area and pore volume were estimated as high as $1479 \text{ m}^2 \text{ g}^{-1}$ and $0.7 \text{ cm}^3 \text{ g}^{-1}$, respectively. The pore-size distribution profile (Fig. 2B) revealed that the Py-An COF contained only one type of mesopore with size of 2.4 nm.

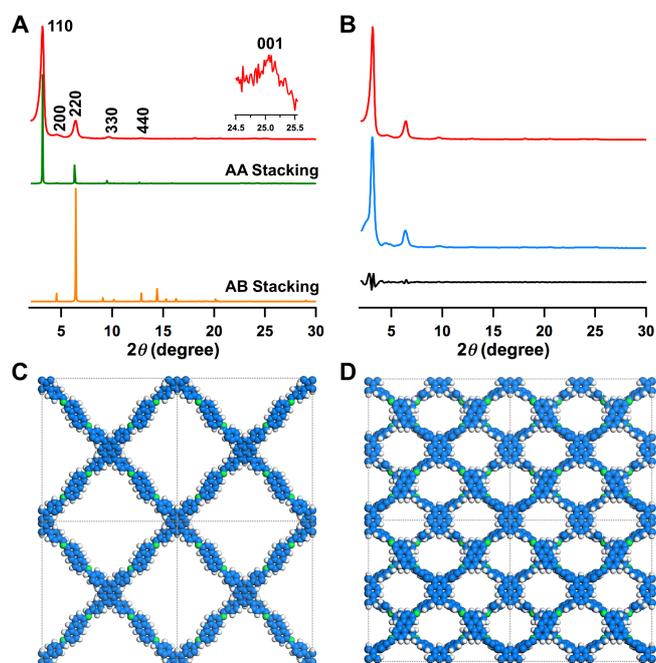


Fig. 1 (A) XRD profiles of Py-An-COF experimentally observed (red), Pawley refinement (blue), and their difference (black). (B) XRD profiles of Py-An-COF experimentally observed (red), simulated by using AA-stacking (green) and AB-stacking (orange) modes. Crystal structures of (C) the AA-stacking and (D) the AB-stacking modes.

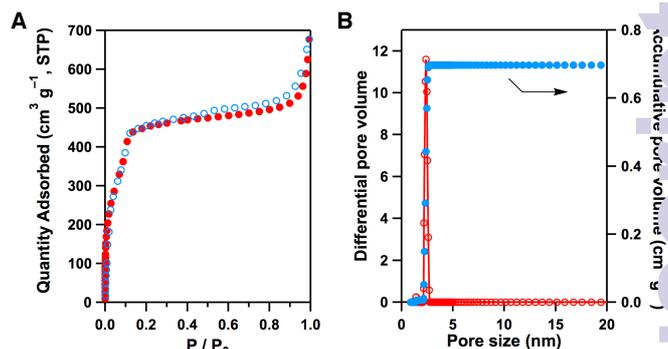


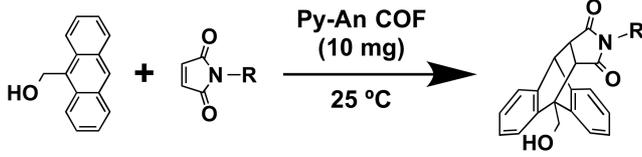
Fig. 2 (A) Nitrogen sorption isotherm curves measured at 77 K (red circle: desorption, blue circle: adsorption). (B) Pore size (red circle) and pore size distribution (blue circle) profiles.

The stability was investigated by dispersing the COF samples in different solvents, such as hexane, THF, acetone, methanol, ethanol, and water at 25 °C for 2 weeks (Fig. S5). XRD patterns of the samples exhibit similar XRD patterns, which indicated that the Py-An COF retained crystallinity in these solvents.

The ordered anthracene columnar π -walls and the open channels together with solvent stability make the Py-An COF an interesting material for heterogeneous catalysis. We chose the Diels-Alder reaction of 9-hydroxymethylanthracene (0.05 mmol) and *N*-substituted maleimide derivatives (0.05 mmol) in the presence of Py-An COF (10 mg) catalyst and observed that the Diels-Alder reaction proceeded smoothly and cleanly at room temperature and 1 bar. The Diels-Alder adduct formed quantitatively after 6-h reaction (Table 1, entry 1, > 99% yield based on ^1H NMR analysis, Fig. S6). By contrast, control experiments without Py-An COF under otherwise identical conditions resulted in only 24% yield. This result indicates that the Py-An COF facilitate the Diels-Alder reaction under ambient conditions. To investigate the reactant scope, a variety of maleimide derivatives with different *N*-substituents, including *N*-benzyl, *N*-(*p*-bromo)phenyl, *N*-(*p*-nitro)phenyl, *N*-ethyl, *N*-cyclohexyl (entries 2-6) were used for the reaction with 9-hydroxymethylanthracene. In all cases, the Py-An COF catalysts significantly enhanced the yields, compared to the controls without the COF catalyst. To the best of our knowledge, the Py-An COF exhibited the highest catalytic activities among the heterogeneous catalysts reported to date that work at elevated temperatures.⁵

The using of neat water as an environmentally benign solvent has received considerable attention with respect to green chemistry. We observed that the Py-An COF enabled the use of water as solvent for the Diels-Alder reactions. Dramatically, the Py-An COF enhanced the reaction yield by 6 fold (Table 1, entry 7, increased from 13% to 91%) compared to the control experiment.

A long catalyst lifetime and the capability of cycle use are highly desired for applications. The Py-An COF catalyst was easily separated from the reaction mixture and recovered; centrifuge and subsequent rinsing with solvents and water refreshed the catalyst for the next-

Table 1 Catalytic Diels-Alder reaction of 9-hydroxymethylanthracene and *N*-substituted maleimide using Py-An COF catalyst at 25 °C, 1 bar


Entry	R =	Solvent	Reaction Time (h)	Yield (%)	
				No COF	With COF
1	phenyl	EtOH	6	24	> 99
2	benzyl	EtOH	6	10	87
3	<i>p</i> -bromophenyl	EtOH	24	21	83
4	<i>p</i> -nitrophenyl	EtOH	24	5	50
5	cyclohexyl	EtOH	24	22	60
6	ethyl	EtOH	24	38	87
7	phenyl	Water	48	13	91

round reaction. Notably, the Py-An COF catalyst retained its high activities even after 4 cycles (Table S1), without the use of a prolonged reaction time or elevated reaction temperature (Fig. S7). The FE-SEM and HR TEM images of the COFs after catalytic use exhibited similar images as those of as-synthesized ones (Fig. S8). Nitrogen sorption isotherm measurements revealed that the COF samples retained their porosity (Fig. S9; BET surface area = 1149 m² g⁻¹).

The acceleration of the Diels-Alder reactions by the Py-An COF catalyst is likely related to the enhanced reactant concentration within the pores of the COFs and C–H⋯π interactions between the π-walls of COFs with 9-hydroxymethylanthracene. The reaction involves three steps. (1) Accumulation of reactants within the pores of the Py-An COF enhanced concentrations. (2) The C–H⋯π interactions between the pore walls and 9-hydroxymethylanthracene reduced the entropy loss and activation energy of the reactions.⁶ Anthracene has been reported to form C–H⋯π interactions as evident by single crystal structure.^{6b} In the Py-An COF, the anthracene units in the π-walls offer ordered, dense and open-accessible arene C–H protons.^{6b} These C–H units trigger the C–H⋯π interactions with 9-hydroxymethylanthracene; three intermolecular C–H⋯π bonds are possible between one anthracene unit in the π-walls of COF and one 9-hydroxymethylanthracene molecule. (3) Cycloaddition yielded the Diels-Alder adducts and the products were excluded from the pores. Compared to the planar 9-hydroxymethylanthracene, the product decreased in aromaticity and adopted a bent conformation. These structural features significantly weakened the C–H⋯π interactions between the products and π-walls. This

difference in interactions facilitates the mass transport through the pores. In this sense, the channels of the COF function as the pockets of enzymes in biological systems.

We conducted encapsulation experiments by adding the Py-An COF samples to the ethanol solution of 9-hydroxymethylanthracene (Fig. S10). We observed that the absorbance of the ethanol solution decreased, which indicated that 9-hydroxymethylanthracene was trapped within the pores of the COF. From the absorption spectra change, the concentration of 9-hydroxymethylanthracene in the Py-An COF is approximately 56 fold greater than that in the bulk solution.

In summary, we have developed π-electronic COFs as a new type of heterogeneous catalysts by exploring the π-walls of COFs as efficient catalytic beds. The π-electronic COFs enable the high-performance catalysis of Diels-Alder reactions in neat water and under ambient conditions. The results suggest a tremendous potential of COFs for achieving novel catalytic systems via π-arene structural design.

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