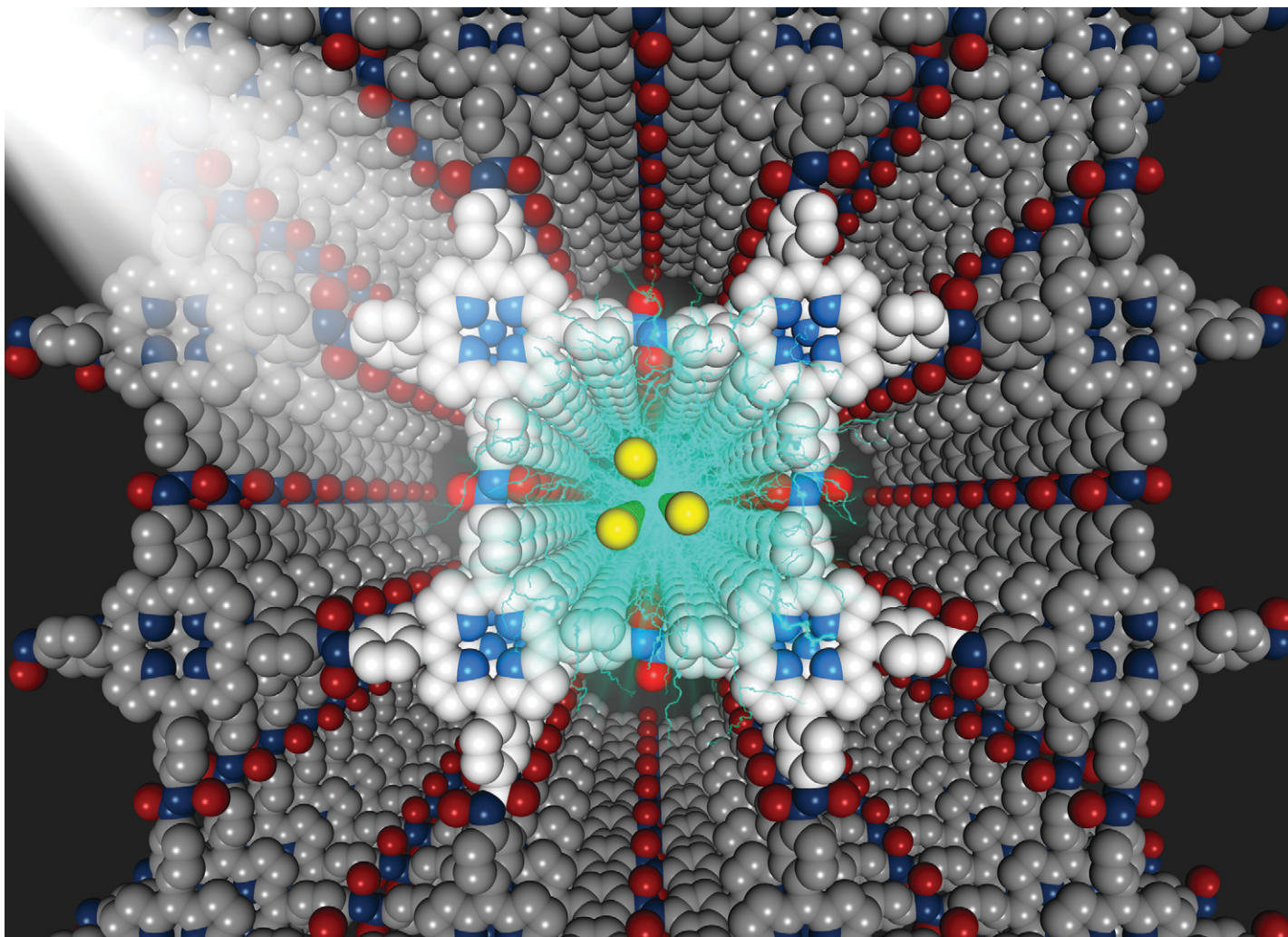




Showcasing research by Bhaskar Nath, Wen-Hua Li, Jia-Hong Huang, Guan-E. Wang, Zhi-hua Fu, Ming-Shui Yao and Gang Xu* from State Key Laboratory of Structural Chemistry (<http://www.fjirsm.cas.cn/yjxt/jgcyjs/xgktz/ktzjj/>) at Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (People's Republic of China).

A new azodioxy-linked porphyrin-based semiconductive covalent organic framework with I_2 doping-enhanced photoconductivity

A homogeneous solution phase reaction at ambient condition is employed to prepare a porphyrin based Covalent Organic Framework (COF). The electrical conductivity of the newly reported COF increases more than three orders on iodine doping and it shows doping induced photo-current generation.

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A new azodioxy-linked porphyrin-based semiconductive covalent organic framework with I₂ doping-enhanced photoconductivity†

Bhaskar Nath, Wen-Hua Li, Jia-Hong Huang, Guan-E. Wang, Zhi-hua Fu, Ming-Shui Yao and Gang Xu*

A room-temperature solution phase reaction was developed to synthesize a covalent organic framework (COF) for the first time. The synthesized azodioxy-linked porphyrin-based COF (POR-COF) possesses a 2D chess board-like structure in the *ab*-plane and a 1D channel with an open-window size of around 1.9 nm along the *c*-axis in the modeled crystal structure. The electrical conductivity of POR-COF increases by more than 3 orders of magnitude through I₂ doping. The photoconductivity of the I₂-doped COF material was also studied firstly. POR-COF shows interesting doping-enhanced photo-current generation.

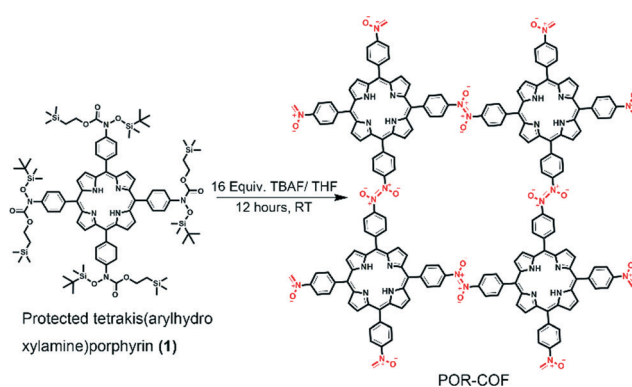
Organic conductive materials have attracted considerable attention for a long time, not only for their interesting electrical and optoelectronic properties but also for their low cost, low weight and easy process.¹ A large number of π -conjugated organic molecules were found to show semiconducting behaviours, where the charge transport originates from the $\pi \cdots \pi$ interaction between the molecules in the solid state.² On the other hand, $\pi \cdots \pi$ interaction is one of the foremost driving forces for assembling π -conjugated molecules to form crystalline states.

Covalent organic frameworks (COFs) are a class of crystalline organic polymers with well-defined porous structures.³ They have received considerable attention from materials chemists as they have appeared as promising materials for catalysis,⁴ drug delivery,⁵ gas storage/separation⁶ and electrical applications.⁷ For electrical applications, building blocks based on highly electron-rich systems such as pyrene, porphyrin and phthalocyanine have been involved in COF materials due to their intrinsic semiconductive and photoconductive properties. Moreover, the porous structure of COFs makes it very convenient to modulate their electrical proper-

ties by doping suitable dopants to form charge transfer complexes.

The key factor for the crystallization of COFs is to find a reaction which can slowly and reversibly form covalent bonds, for example, the formation of boronate esters from boronic acids,⁷ imines from the condensation of aldehydes and primary amines,⁸ *etc.* Most COFs reported to date were synthesized under special care, such as the use of harsh experimental conditions (*e.g.*, high temperature and high pressure), inert atmosphere, and heterogeneous reaction mixtures and long reaction time.^{4–8} The synthesis of COFs under ambient conditions using homogeneous solution phase reaction is still a big challenge. Thus, it is very important to find a rapid and mild synthetic approach for COF materials.

In this work, we report the room-temperature synthesis of a COF using a homogeneous solution phase reaction for the first time to the best of our knowledge. A π -conjugated semiconductive molecule, porphyrin, is connected by azodioxy (–ON=NO–) linkers to form a two-dimensional COF, namely POR-COF. The structure determination, the gas sorption properties and the electrical properties of POR-COF before and after I₂ doping were shown. Notably, it is also



Scheme 1 Synthesis of the azodioxy-linked porphyrin-based covalent organic framework (POR-COF).

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observed firstly that the photoconductivity of a COF material can be significantly enhanced by I_2 doping.

To synthesize POR-COF, a protected tetrakis(arylhydroxylamine)porphyrin (**1**) was synthesized as a precursor by following a reported procedure from tetra(*p*-bromophenyl)porphyrin.⁹ When this protected tetrakis(arylhydroxylamine)porphyrin (**1**) was treated with 16 equivalents of 1 M tetrabutylammonium fluoride (TBAF) in THF at room temperature, it formed tetrakis(arylhydroxylamine)porphyrin which is expected to transform into tetrakis(arylnitroso)porphyrin *in situ*, followed by polymerization to give POR-COF as shown in Scheme 1. Arylhydroxylamines are reactive compounds and have a tendency to be oxidized easily.¹⁰ Anderson *et al.* have reported the oxidation of *N*-hydroxyamphetamine by aerated toluene to give the corresponding nitroso dimer.^{10c} In this work, the *in situ* generated tetrakis(arylhydroxylamine)porphyrin has four arylhydroxylamine groups attached to an electron-rich porphyrin unit. The presence of electron-rich groups may further increase the reactivity of the arylhydroxylamine groups. Therefore, they are expected to be oxidized by the aerated solvent to form tetrakis(arylnitroso)porphyrin for further polymerization. The strong absorption peaks at 1735 cm^{-1} (C=O stretching) and $2950\text{--}2850\text{ cm}^{-1}$ (aliphatic C-H stretching) in the FT-IR spectra of **1** disappear in POR-COF, which indirectly demonstrates the complete de-protection of **1** by TBAF (Fig. S2a†). On the other hand, the peak at around 1283 cm^{-1} confirms the presence of the *trans*-azodioxy bond (dimeric nitroso group, $-\text{ON}=\text{NO}-$) in POR-COF (Fig. S2b†).^{11a} In general, the N=N bond length in the *trans*-azodioxy compound is virtually constant and its Raman-active stretching frequency lies in the range of $1436\text{--}1447\text{ cm}^{-1}$.^{11b} Therefore, the absorption band at 1447 cm^{-1} in the Raman spectra of POR-COF confirms the presence of the *trans*- N_2O_2 dimer (Fig. S3†).^{11c} Arylnitroso compounds are well known to form dimers through both *cis*- and *trans*-azodioxy bonds ($-\text{ON}=\text{NO}-$), and most of the organic nitroso compounds exist as dimers in the solid state.¹² Interestingly, in the present case, IR and Raman spectra suggest that there is only the *trans*-azodioxy bond in POR-COF. The ^{13}C cross-polarized magic angle spinning (CP-MAS) solid-state NMR spectrum (Fig. 2a) of POR-COF shows signals at 152.5, 142.0, 132.2 and 118.7 ppm. These chemical shifts are comparable with those of other porphyrin-based COFs.¹³ Moreover, there is no resonance in the region of 155–170 ppm in the ^{13}C CP-MAS spectrum which suggests the virtual absence of any monomeric nitroso groups and thus excludes the presence of any oligomeric unit. Therefore, from the above experimental evidence, it is reasonable to expect that the tetrakis(arylnitroso)porphyrin building blocks self-polymerize through the formation of azodioxy bonds which may result in the generation of a COF structure.

POR-COF has excellent thermal stability which remains stable up to $350\text{ }^\circ\text{C}$ as observed from the TG experiment (Fig. S5†). Therefore, it can be activated at $150\text{ }^\circ\text{C}$ to remove the lattice solvent molecules inside the framework for gas

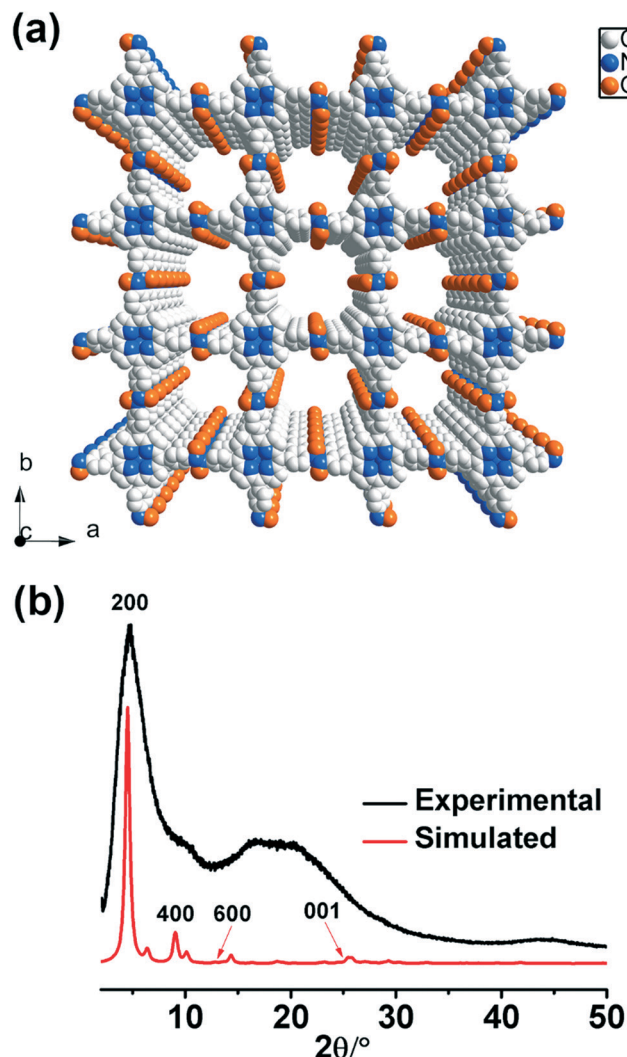


Fig. 1 (a) Modeled crystal structure of POR-COF; (b) simulated and experimental PXRD patterns of POR-COF.

sorption measurement. The N_2 adsorption-desorption experiment using POR-COF at 77 K (Fig. 2b) shows a type I isotherm which suggests its micro-porous nature. The BET surface area of POR-COF was found to be $447\text{ m}^2\text{ g}^{-1}$ which is similar to the reported values for other 2D COFs.¹⁴ The pore size distribution plot of POR-COF obtained using the BJH method (Barrett-Joyner-Halenda method) reveals a pore width of around 1.95 nm (Fig. S6†).

SEM (scanning electron microscopy) and TEM (tunneling electron microscopy) images show that POR-COF has a nanoparticle morphology with a size of around $150\text{--}200\text{ nm}$ which is too small to be used for determining the crystal structure (Fig. S7 and S8†). Powder X-ray diffraction (PXRD) measurement indicates that POR-COF is a crystalline material (Fig. 1b). Most of the peaks in its PXRD pattern are too broad to undergo Rietveld refinement. However, according to the describable peaks in the PXRD pattern, gas sorption analysis, IR, Raman as well as NMR spectra, a possible crystal structure model of POR-COF was simulated. The simulated structure has a *P4* space group with

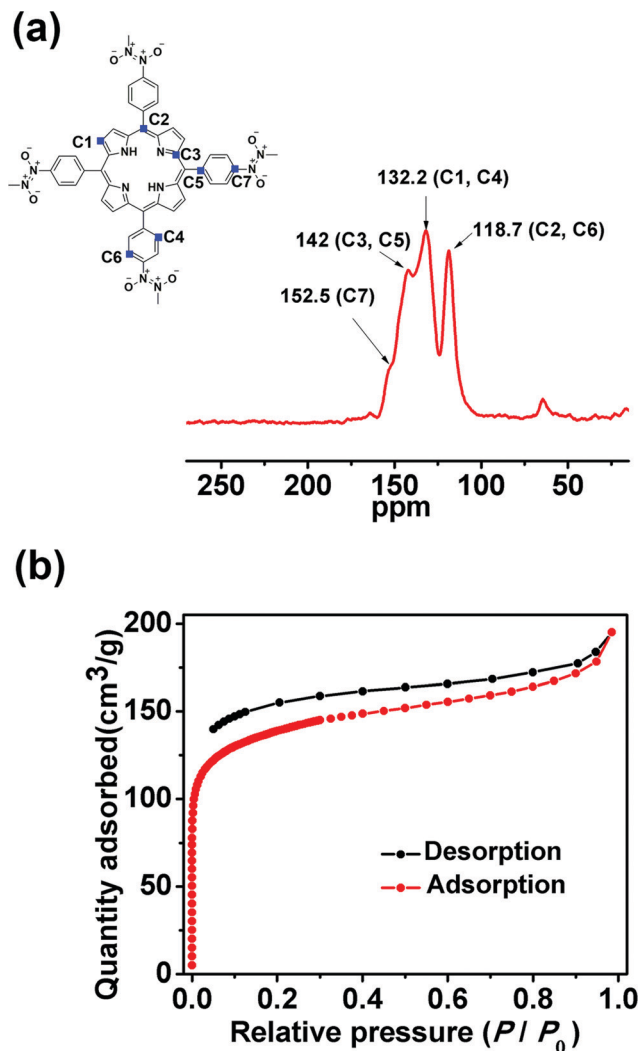


Fig. 2 (a) Solid-state cross-polarized magic angle spinning (CP-MAS) ^{13}C -NMR spectrum of POR-COF; (b) nitrogen adsorption-desorption curve of POR-COF.

$a = b = 39.0 \text{ \AA}$, $c = 3.5 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$ (Fig. 1a). In this modeled structure, one porphyrin unit is connected to four neighboring porphyrins through *trans*-azodioxy bonds to form a 2D chess board-like structure in the *ab*-plane. The 2D sheets of POR-COF are not perfectly planar; the connecting aryl rings lie in a different plane from the central porphyrin units. These 2D sheets further pack with each other through $\pi \cdots \pi$ interactions along the *c*-axis to produce a 1D channel with an open-window size of around 1.9 nm which agrees very well with the data analysis of N_2 sorption measurement.

A two-probe method was employed to investigate the conductive properties of POR-COF. A pressed pallet of POR-COF was prepared by mixing it with 20 wt% polymethyl methacrylate (PMMA), where both faces of the pallet were painted with silver paint and dried in air for a few hours before the measurement. As shown in Fig. 3a and S9†, the *I*-*V* curve of POR-COF shows almost a linear profile indicating an ohmic contact between the sample and electrodes. The electrical conductivity of POR-COF is $4.6 \times 10^{-11} \text{ S cm}^{-1}$ at room tempera-

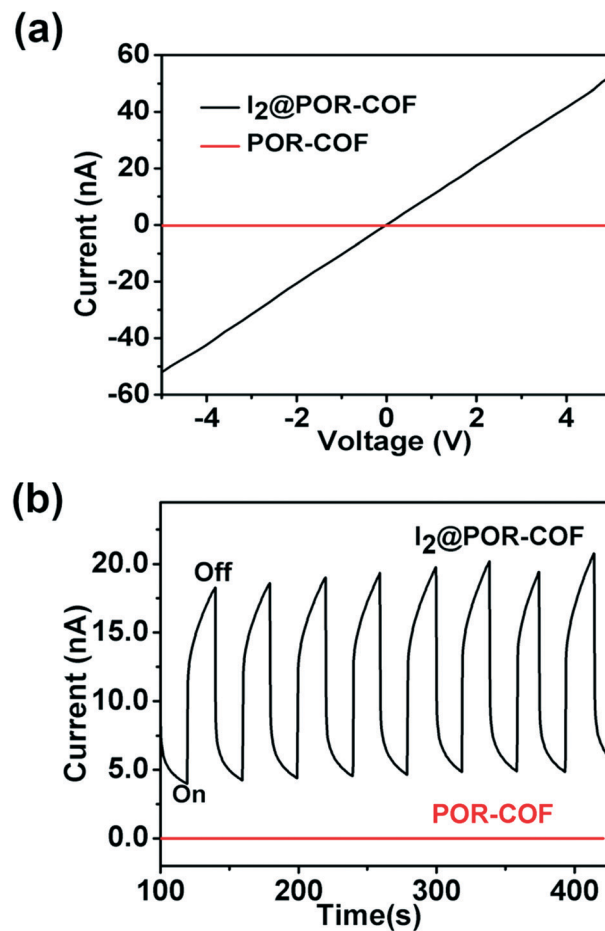


Fig. 3 (a) *I*-*V* profiles of POR-COF and I_2 -doped POR-COF; (b) photo-current of POR-COF with the light on and off from a 300 W xenon lamp.

ture in air. This value is comparable with the reported conductivity of other 2D COFs.¹⁵ The temperature-dependent electrical conductivity of POR-COF was also measured. The conductivity of POR-COF increases almost linearly with increasing temperature (Fig. S10†), which indicates its semiconductive nature. In general, COF materials exhibit lower intrinsic conductivity, and it can be enhanced through doping of appropriate guest molecules.¹⁶ Due to its porous structure, POR-COF can be easily doped with I_2 by using a simple solution method. The sample was prepared by immersing POR-COF in a solution of *n*-hexane containing I_2 for 30 hours, filtered and washed many times with *n*-hexane and then dried in an oven at 70°C overnight. After doping with I_2 , POR-COF shows its color change from purple to black indicating the formation of a charge transfer complex. The formation of the charge transfer complex is also evident in the electronic spectra as there are significant changes of the absorption in the region of 700–1200 nm when compared with that of pure POR-COF, which is typical for I_2 -doped 2D COF materials (Fig. S4†).¹⁷ The electronic conductivity of I_2 -doped POR-COF was measured exactly using the same method as that for pure POR-COF, which also shows a linear *I*-*V* plot

(Fig. 3a). Compared to that of pure POR-COF, the conductivity of I₂-doped POR-COF increases by more than 3 orders of magnitude and reaches $1.52 \times 10^{-7} \text{ S cm}^{-1}$. Tetraphenylporphyrin is a p-type semiconductor¹⁸ and iodine is an electron acceptor. Doping POR-COF with iodine results in charge transfer from the host to the dopant and creates free holes to migrate through the organic framework under irradiation. Therefore, this improvement in conductivity upon doping with I₂ indicates that there is a remarkable amount of holes generated and POR-COF is a p-type semiconductor.

As shown in Fig. 3b, the photoconductivity of both POR-COF and I₂-doped POR-COF was studied. The experiments were performed by sandwiching the film samples between two ITO glasses and irradiating with light generated from a xenon lamp. The POR-COF thin film shows a very low current and almost no response to light irradiation. Interestingly, it is observed for the first time that I₂ doping can significantly enhance the photoconductive response of a COF material. The current of I₂-doped POR-COF sharply rose upon irradiation by light with the on-off ratio greater than one order of magnitude. This photocurrent can be reversibly switched many times with almost no deterioration (Fig. 3b). Similar to other material systems, this I₂ doping-induced photoconductivity enhancement may also be attributed to the fact that the doped I₂ can make the host material more photosensitive, decrease the energy barrier for charge transport and improve the mobility of holes by trapping electrons.¹⁹

Conclusions

In conclusion, a homogeneous solution phase reaction under ambient conditions was developed to synthesize a COF material for the first time. The conductivity of the synthesized POR-COF can increase by more than three orders of magnitude through doping with iodine, indicating the hole-transport nature of this material. Moreover, I₂-doped POR-COF shows significantly enhanced photo-current generation when irradiated with light and it can be generated reversibly without any decline in the on-off ratio. This doping-induced enhancement in the photo-electrical properties of POR-COF may open up a new opportunity to tailor the semiconductive properties of COF materials for their future applications.

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