# Journal of Materials Chemistry A

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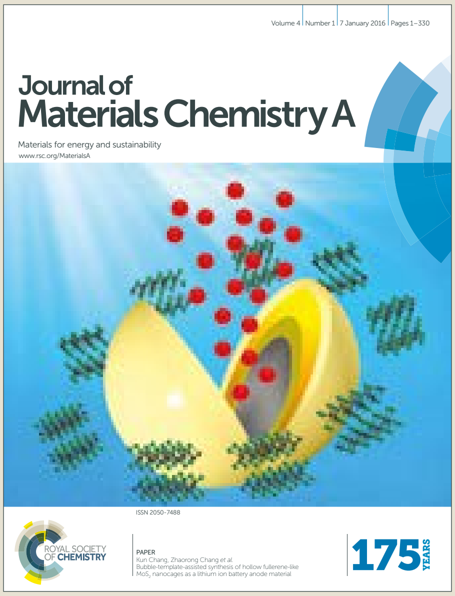

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PAPER
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ARTICLE

# Robust porous organic polymers as efficiently heterogeneous organo-photocatalysts for aerobic oxidation reactions

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Metal-free, visible-light active and heterogeneous organic photocatalysts offer a more sustainable and environmentally friendly alternative to traditional metal-based catalysts. Here a porous organic hyper-crosslinked polymer, CF-HCP was successfully synthesized through a facile and cost-effective process. The chemical and structural properties of CF-HCP were fully characterized by using powder X-ray diffraction analysis, Fourier transform infrared spectroscopy, $^{13}$C solid-state NMR spectroscopy, electron microscopy, thermogravimetric analysis, X-ray photoelectron spectroscopy and nitrogen adsorption. The new three-dimensional hyper-crosslinked network possesses a high Brunauer–Emmett–Teller (BET) specific surface area up to 1200 $m^2$ $g^{-1}$ with a pore volume of 0.92 $cm^3$ $g^{-1}$, and exhibits good thermal, chemical and photochemical stability. Importantly, CF-HCP was found to be a highly effective heterogeneous photocatalyst for a wide range of organic reactions, including the oxidative coupling of primary amines, dehydrogenation of nonactive secondary amine substrates, and selective oxidation of sulfide under visible-light irradiation and using molecular oxygen as a clean oxidant. In particular, mild reaction conditions, ease of product separation by simple filtration, significant recyclability and low cost make this network material an economical and eco-friendly catalyst for the preparation of versatile organic compounds.

## Introduction

Visible-light-driven organic transformation has recently attracted a great attention owing to the environmental friendship of visible light and mild reaction conditions.[1] For efficient transformation to desired products under light irradiation, the employ of photosensitizers is essential to provide the excitons transfer to reactants. To date, organometallic compounds[2] involving precious metals such as ruthenium or iridium and small-molecule organic dyes[3] have been widely explored as photosensitizers in photocatalysis due to their rich redox chemistry at the excited state. However, these homogeneous photocatalysts with some intrinsic drawbacks, like the weak stability of the organic dyes, high price and toxicity of precious metals, as well as limited availability and product purification steps for catalyst remove.[4] Recently, inorganic-organic hybrid porous materials through heterogenization of metal complexes onto metal-organic frameworks have been explored as highly efficient photocatalysts for organic reactions.[5] However, it only addresses partially the issue of reusability and the limited abundance of their constituent precious metals limit scale-up synthesis for industrial applications. Therefore, the development of efficient heterogeneous photocatalysts that combining the requirements of high cost-efficiency, good catalytic activity and excellent reusability is still an important challenge.

Over the past few years, covalently linked porous organic polymers (POPs) have attracted tremendous scientific attention owing to their large specific surface areas, excellent stability and functional designability.[6] Numerous efforts have been made to identify POPs that serve as platforms for integrating different molecular functional components to achieve efficient gas storage and separation,[7] chemical sensor,[8] and heterogeneous catalysis.[9] In particular, exploration of POPs as a new class of robust and efficient heterogeneous photocatalysts has recently emerged, which is attributed to their excellent absorption in the visible region and tunable band gap. A series of research results have demonstrated their potential applications in light-induced hydrogen evolution,[10] photocatalytic oxidative coupling of amines,[11] selective oxidation of organic sulfide,[12] molecular oxygen activation,[13] carbon-carbon bond formation,[14] and so on.[15] However, most of these POPs as heterogeneous catalysts have a relatively low surface area, and expensive metal catalyst and specific reaction groups in building blocks are needed for their preparation.[10-15] From the viewpoint of practical application, up to now, the efficient, recyclable, metal-free and cost-efficient heterogeneous photocatalysts based on POPs by facile preparation processes have rarely been explored.[16] Previously, Tan and co-workers have developed a facile and low-cost method for the preparation of

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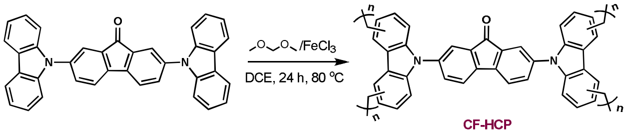
porous organic polymers through a one-pot Friedel-Crafts alkylation of aromatic monomers using a formaldehyde dimethyl acetal (FDA) as cross-linker in the presence of anhydrous $FeCl_3$.[17] Very recently, our group reported a series of homogeneous-like solid based catalysts, which demonstrate well the combination of advantages of both homogeneous and heterogeneous catalysts, using a intriguing strategy of hypercrosslinking homogeneous catalytic molecule.[18] In this context, 2,7-bis-(N-carbazolyl)-9-fluorenone (CF) is easily synthesized through commercial raw material, and allows large-scale preparation. And it has strongly absorption in the range of visible light and rich redox properties. With these considerations in mind, in this contribution, we report on the construction of a carbozole-fluorenone based porous hyper-crosslinked polymer (CF-HCP) utilizing CF as a single monomer by the strategy of hypercrosslinking homogeneous catalytic molecule. The obtained CF-HCP possesses high surface area, large pore volume, hierarchical porosity and superior stability, and can be a highly effective, visible-light-driven solid organo-photocatalyst for a wide range of organic transformations including the oxidative coupling of primary amines, aerobic dehydrogenation of secondary amine substrates and selective oxidation of sulfide under visible-light irradiation. As expected, the resultant polymer network also exhibits excellent reusability without the significant loss of photocatalytic activity in the visible light-driven oxidative reactions. In addition, the mechanism of the oxidative coupling reactions of amines that were effectively catalyzed by CF-HCP under light irradiation was also fully investigated.



**Scheme 1.** Schematic representation of the synthesis of CF-HCP.

## Results and discussion

The porous organic polymer CF-HCP was synthesized via one pot Friedel-Crafts alkylation reaction using a formaldehyde dimethyl acetal (FDA) as a external cross-linking agent promoted by anhydrous $FeCl_3$ under a nitrogen atmosphere (Scheme 1). We can find that the hypercrosslinking reaction occurs immediately in 1,2-dichloroethane (DCE) under high temperature, and the dark precipitation is obtained. The different ratio of monomer to cross-linking agent or catalyst was studied first, in order to achieve a high specific surface area for the resulting polymer networks (Fig. S1). After cross-linking reaction, the resulting solid was filtered and washed with various solvents to afford a red-brown powder with a low density in high yield, and is insoluble in water and common organic solvents. The chemical composition and connectivity of polymer CF-HCP were researched by spectral and analytical methods, which includes Fourier transform infrared spectroscopy (FT-IR), $^{13}C$ cross polarization magic angle spinning (CP/MAS) NMR, and elemental analysis. The success of the crosslinking was first confirmed by FT-IR measurement.

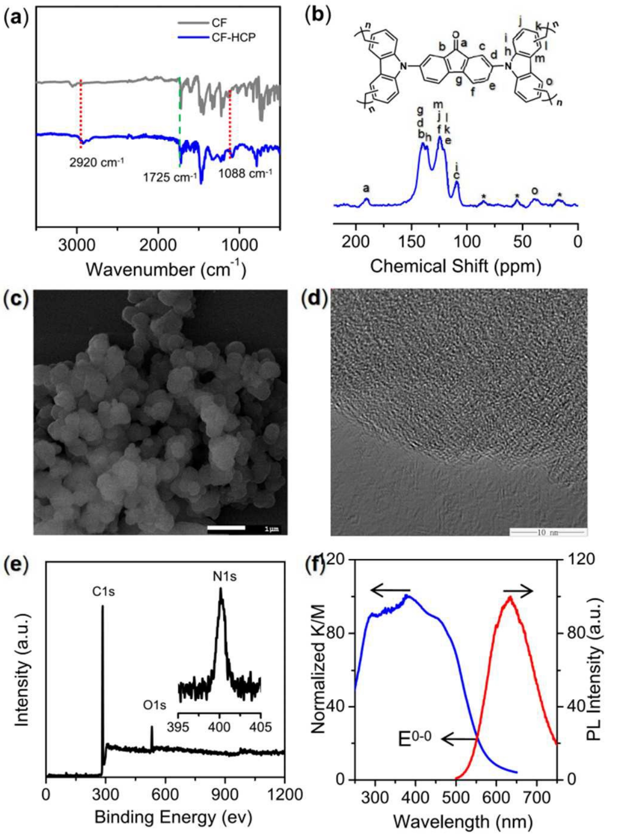


**Fig. 1** (a) FT-IR spectra; (b) $^{13}C$ CP/MAS NMR spectrum, the asterisks denote spinning sidebands; (c) SEM image; (d) TEM image; (e) XPS pattern; (f) Normalized UV-vis (blue line) and emission (red line) spectra of CF-HCP in the solid state.

The FT-IR spectra of CF-HCP and its monomer are displayed in Fig. 1a. We found that polymer CF-HCP also retains some feature peaks of the monomer. For example, the signals at 1604 and 1450 $cm^{-1}$ indicate the vibration of the aromatic rings in the polymer skeleton, and the band around 1725 $cm^{-1}$ is attributed to the stretching vibration of carbonyl C=O. In addition, the weak peaks at 2920 and 1088 $cm^{-1}$ could be attributed to C-H and C-O stretching vibrations, which could originate from the structure of $-CH_2-$ and a minor amount of unreacted $-CH_2OCH_3$ in the polymer network, respectively. The $^{13}C$ CP/MAS NMR spectroscopy (Fig. 1b and S2) of CF-HCP showed resonance peaks at about 39 ppm, which can be assigned to the carbon in the methylene linker formed from the Friedel-Crafts reaction. The characteristic signals from 108 to 140 ppm are assignable to substituted and nonsubstituted aromatic carbon in the polymer backbone. Additionally, the signals at ～190 ppm is attributed to the carbon of carbonyl C=O in the fluorenone unit. Powder X-ray diffraction measurements (PXRD) profiles did not show any strong signals, indicating that CF-HCP is an amorphous polymer (Fig. S3). Field-emission scanning electron microscopy (SEM) was performed to investigate the morphology of the polymer network. The SEM image displayed that the CF-HCP adopts a

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spherical shape with size of 500-600 nm (Fig. 1c). High-resolution transmission electron microscopy (HR-TEM) image revealed the presence of a porous texture (Fig. 1d). X-ray photoelectron spectroscopy (XPS) was conducted for CF-HCP to determine their chemical composition (Fig. 1e). Additionally, no catalyst residues in the polymer network could be detected by ICP measurement. The electronic absorption spectroscopy of CF-HCP showed an intense absorption band with the absorption maxima at 398 nm, and the absorption band edge extends to 600 nm (Fig. 1f, blue line). Under light irradiation, the CF-HCP exhibited an intense luminescence band at 632 nm in nitrogen atmosphere (Fig. 1f, red line). The luminescent lifetime curve of CF-HCP can be fitted well with a double exponential function and exhibit a relatively long decay lifetime (Fig. S4). In addition, cyclic voltammetric (CV) characterization of CF-HCP exhibits a reversible half wave potential ($E_{1/2}$) at −0.87 V (Fig. S5). On the basis of a free energy change ($E^{0\text{-}0}$) between the vibrationally related excited state and the group state of 2.25 eV (Fig. 1f), the potential of valence band was calculated as 1.38 eV (Table S2).

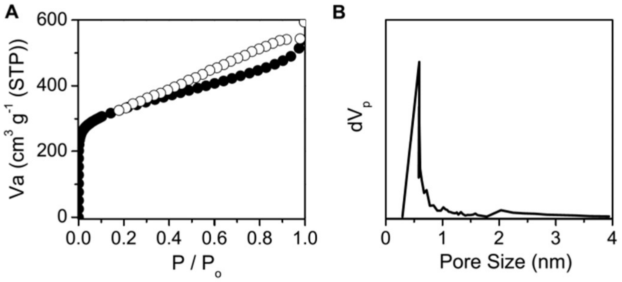

**Fig. 2** (a) Nitrogen adsorption-desorption isotherm (filled circles: adsorption; open circles: desorption) of CF-HCP at 77 K; (b) Pore size distribution of CF-HCP on the $N_2$ adsorption isotherms.

In order to characterize the porosity parameters of CF-HCP, the $N_2$ sorption isotherms were measured at 77 K. As shown in Fig. 2a, the CF-HCP displays a type I $N_2$ sorption isotherm features, according to the IUPAC classification, and shows a steep uptake of nitrogen gas at low relative pressures, thus reflecting the microporous nature of the network. The nitrogen sorption increases with increasing pressure, which indicates a large external surface area owing to the presence of small particles. Derived from the $N_2$ adsorption data, the Brunauer-Emmet-Teller (BET) specific surface area of CF-HCP evaluated from the $0.02 < P/P_0 < 0.1$ region is calculated to be 1217 $m^2$ $g^{-1}$, the Langmuir model gives a surface area of 1367 $m^2$ $g^{-1}$. The CF-HCP has a wide pore size distribution, with the pore widths centering around at 0.62, 0.85, 1.01 and 2.08 nm, respectively, as calculated by the Saito-Flory method (Fig. 2b). The total volume calculated with $N_2$ adsorbed at $P/P_0 = 0.99$ was 0.92 $cm^3$ $g^{-1}$.

Thermogravimetric analysis (TGA) was done on the dry CF-HCP under $N_2$ atmosphere, which revealed that it was stable to 300 °C, and the polymer retained more than 70% of the mass even at 800 °C (Fig. S6). In addition, we also investigated the chemical and photochemical stability of new polymer network. The CF-HCP samples were immersed in different organic solvents like N,N-dimethylformamide (DMF), dimethyl sulphoxide (DMSO), acetonitrile ($CH_3CN$), aqueous HCl (1 M) and NaOH (1 M) solutions and stirred at 25 °C for 24 h. Moreover, the dispersion solution of CF-HCP in $CH_3CN$ was irradiated by green light-emitting diode (LED) lamp (520 nm, 30 W) for 24 h at 25 °C. The all samples were collected by filtered, washed with water, THF, and dried under vacuum at 120 °C for 5 h. Pleasantly, these samples exhibit high surface areas and remain same network connection compared with that of the as-synthesized CF-HCP (Fig. S7 and S8). Therefore, controlled experimental results indicates that CF-HCP had sufficient thermal and chemical stability and as well as photochemical stability.

**Table 1**. Photocatalytic oxidative coupling reaction of benzylamine by CF-HCP[a]

| | entry | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5[c] | 6[d] | 7[e] | 8[f] |
| CF-HCP | + | + | - | + | + | + | + | + |
| *hv* | + | - | + | + | + | + | + | + |
| $O_2$ | + | + | + | $N_2$ | + | + | + | + |
| Yield (%)[b] | 91 | 2 | 3 | 8 | 14 | 46 | 10 | 23 |

[a] CF-HCP (5.0 mg), solvent (2.0 mL), benzylamine (0.2 mmol), green LED lamp (520 nm, 30 W). [b] Determined by $^1$H-NMR spectroscopic analysis. [c] KI as hole scavenger. [d] $NaN_3$ as single oxygen scavenger. [e] Benzoquinone (BQ) as superoxide scavenger. [f] Isopropanol as •OH scavenger.

The CF-HCP possesses remarkable stability, excellent porous character and strong absorption in visible-light range, and these features promoted us to examine its heterogeneous photocatalytic performances. We investigated the photocatalytic activity of CF-HCP in the oxidative coupling of various amine compounds. The oxidative coupling of benzylamine 1a as a model reaction was carried out in the presence of CF-HCP and molecular oxygen under irradiation by a green LED (520 nm, 30 W). The influence of different solvents on yield was firstly researched. As could be seen in Table S1, in toluene, methanol, DMF and dimethyl sulphoxide (DMSO), the conversions were relatively poor (7-28%, Table S1, entries 1-4). When selecting $CH_3CN$ as reaction medium, benzylamine was converted into the corresponding product with high yield (91%) under same condition (Table S1, entry 5). However, the low catalytic yield was obtained under blue or white light irradiation (Table S1, entries 8 and 9). The enhanced activity can be attributed to the effective overlap between the absorption band of CF-HCP and the emission wavelength of the green LED irradiation. In addition, the control experiments indicated that only traces of the target product were detected without light and without CF-HCP as a photocatalyst, respectively (Table 1, entries 2 and 3). In order to further explore the reaction mechanism and the assignments of the photogenerated electron/hole pairs in the photochemical conversion of benzylamine 1a to imine 2a, some control experiments were performed. When the

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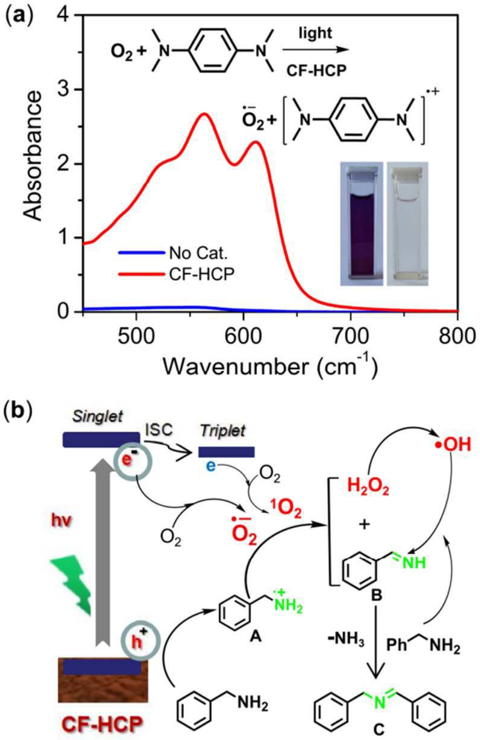
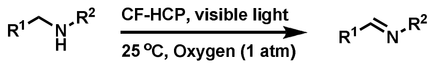
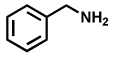
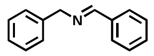
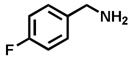
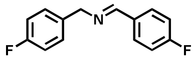
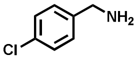
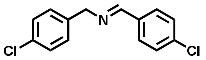
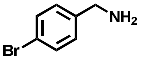
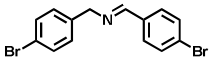
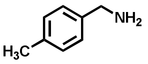
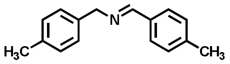
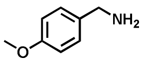
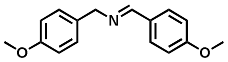
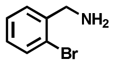
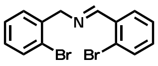
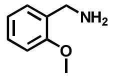
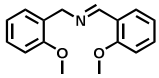
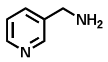
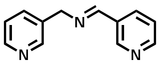
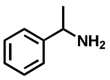
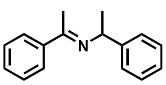


**Fig. 3** (a) UV-vis absorption spectra and photograph of the cationic radical of TMPD generated by CF-HCP in the presence of light and oxygen; (b) Proposed reaction mechanism for the oxidative coupling of benzylamine photocatalyzed by CF-HCP.

replacement of $O_2$ with $N_2$ gas, benzylamine was hardly converted into the corresponding product (Table 1, entry 4), indicating the vital role of oxygen in the reaction process. According to previously experimental results in the literature,[11] the molecular $O_2$ is converted into activated oxygen species (singlet oxygen $^1O_2$ and superoxide radical anion $O_2^{\bullet-}$) through energy transfer or electron transfer from the excited state of photosensitizers. By adding KI as hole scavenger, a low conversion of 14% was obtained (Table 1, entry 5). Sodium azide as a singlet oxygen $^1O_2$ scavenger was added to the reaction mixture, and a conversion of 46% was observed (Table 1, entry 6). P-benzoquinone (BQ), which is well-known as a superoxide radical anion $O_2^{\bullet-}$ scavenger, was added to the reaction mixture under standard conditions, and a low yield of product was determined (Table 1, entry 7). In addition, it is well known that the photoactive macromolecular systems could mediate the electron transfer from N,N,N`,N`-tetramethyl-phenylenediamine (TMPD) to molecular oxygen, thereby resulting in superoxide radical $O_2^{\bullet-}$ and blue-colored cationic radical species.[19] Under irradiation with a green LED, indeed, polymer CF-HCP with high photooxidative activity mediated the abstraction of an electron from TMPD to form blue-color species with strong absorption band at 563 nm and 612 nm (Fig. 3a). Furthermore, we also carried out the EPR experiments to study the activate oxygen species generated by using the CF-HCP. 5,5-dimethyl-1-pyrroline N-oxide (DMPO) and 2,2,6,6-tetramethylpiperiding (TEMP) were used as typical spin-trapping agents for $O_2^{\bullet-}$ and $^1O_2$, respectively. As shown in Fig. S9, both active oxygen species could be determined by CF-HCP as photocatalyst under light irradiation. These results displayed that both activated oxygen species ($^1O_2$ and $O_2^{\bullet-}$) were involved in the photooxidative coupling reaction of benzylamine. Furthermore, using isopropanol as a hydroxyl radical (·OH) scavenger, the product yield decreased importantly to 23% (Table 1, entry 8). Thus, we surmised that ·OH, which generated from $H_2O_2$ that as a side product in the oxidative coupling reaction, could show a certain role in the reaction process. Based on the results from the above control experiments, we propose a reaction mechanism responsible for the photooxidative coupling reaction of amine by CF-HCP, as shown in Fig. 3b. Under light irradiation, the polymer CF-HCP was excited, and its photogenerated holes are

**Table 2**. Photocatalytic oxidative conversion of primary amines into imines by CF-HCP[a]



| Entry | Substrate | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  | 91.0 |
| 2 |  |  | 72.7, 94.8[c] |
| 3 |  |  | 93.9, 96.2[c] |
| 4 |  |  | 97.5 |
| 5 |  |  | 97.6 |
| 6 |  |  | 98.0 |
| 7 |  |  | 76.0, 98.0[c] |
| 8 |  |  | 99.1 |
| 9 |  |  | 92.2 |
| 10 |  |  | 48.8, 74.1[c] |

[a] Reaction conditions: CF-HCP (5.0 mg), substrate (0.2 mmol), $CH_3CN$ (2.0 mL), green LED lamp (520 nm, 30 W), 6 h. [b] Determined by $^1H$-NMR spectroscopic analysis. [c] 10 h.

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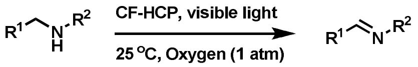
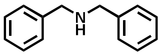
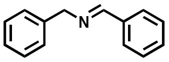
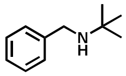
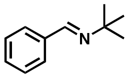
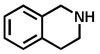
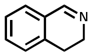
transferred to amine, producing an amine radical cations **A**. Simultaneously, the photogenerated electrons of CF-HCP can activate $O_2$ via an energy transfer or single electron transfer (SET) process, yielding both active oxygen species $^1O_2$ and $O_2^{\bullet-}$. A reaction between the amine radical cation and both active oxygen species $^1O_2$ and $O_2^{\bullet-}$ forms the intermediate imine **B** and $H_2O_2$. The imine further reacts with an additional amine molecular to produce the desired product **C** after removal of ammonia. In this process, the obtained ·OH could also abstract a proton from **A** to form the imine intermediate.

**Table 3**. Photocatalytic aerobic dehydrogenation of secondary amines by CF-HCP[a]



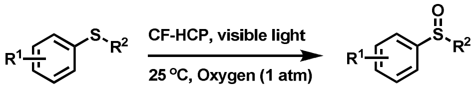
| Entry | Substrate | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  | 80.6 |
| 2 |  |  | 79.3, 93.0[c] |
| 3 |  |  | 90.1, >99.0[c] |

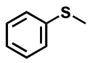
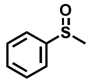
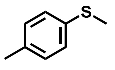
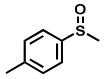
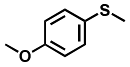
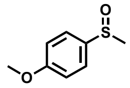
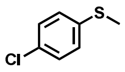
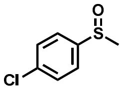
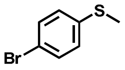
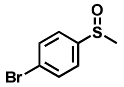
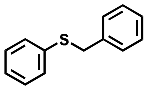
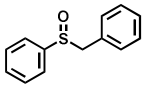
[a] Reaction conditions: CF-HCP (5.0 mg), substrate (0.2 mmol), $CH_3CN$ (2.0 mL), green LED lamp (520 nm, 30 W), 6 h. [b] Determined by $^1$H-NMR spectroscopic analysis. [c] 10 h.

Next, the oxidative coupling reactions of various primary amines photocatalyzed by CF-HCP were examined (Table 2). In general, benzylamines bearing electron-donating or electron-withdrawing substituents were converted into the corresponding target products with excellent yields. However, the electronic properties of the substituents on the phenyl ring have some effects on the efficiency of the reaction. The benzylamines with electron-donatng groups like -Me and -OMe reduce the reaction time (Table 2, entries 5 and 6) and undergo photocatalyzed oxidative coupling more efficiently than those with electron-withdrawing groups such as -F and-Cl (Table 2, entries 2 and 3). Moreover, the position of substituent group have impact on the coupling reaction, the benzylamine having a bromo at an ortho position decreases the rate of reaction and prolongs the reaction time in comparison to the para isomer (Table 2, entry 7). As a representative of the heterocyclic amine, 3-picolylamine could also be transformed into the corresponding imine with high yield (Table 2, entry 9). However, the methyl substituent at the methylene of benzylamine showed relatively poor yield because of steric effects (Table 2, entry 10).

Further, we investigated the efficiency of the photocatalytic aerobic dehydrogenation of secondary amines, the results are depicted in Table 3. For example, dibenzylamine is converted to the corresponding imine in 80.6 % yield (Table 3, entry 1). In the oxidation of N-tertbutylbenzylamine, the N-benzylidene is obtained with a good yield (Table 3, entry 2). Furthermore, the CF-HCP was still capable of selectively oxidizing 1,2,3,4-tetrahydroiso quinoline to the corresponding imine in high yield (Table 3, entry 3), which is an important precursor for the synthesis of isoquinoline alkaloids.

**Table 4**. Photocatalytic selective oxidation of sulfides by CF-HCP[a]



| Entry | Substrate | Product | Yield (%)[b] |
|---|---|---|---|
| 1 |  |  | >99 |
| 2 |  |  | >99 |
| 3 |  |  | 87.3, >99[c] |
| 4 |  |  | 26.1, 90[c] |
| 5 |  |  | 31.7, 99[d] |
| 6 |  |  | 70, 92[c] |

[a] Reaction conditions: CF-HCP (5.0 mg), substrate (0.2 mmol), $CH_3CN$ (2.0 mL), methanol (0.8 mL), green LED lamp (520 nm, 100 W), 6 h. [b] Determined by GC using n-undecane as internal standard. [c] 10 h. [d] 20 h.

Sulfoxides play an important role as intermediates in organic synthesis or as biologically active compounds in the pharmaceutical industry.[20] One of the efficient and atom-economic methods for the preparation of sulfoxides is through photocatalytic selective oxidation of sulfides.[21] To further evaluate the photocatalytic activity of CF-HCP, the photocatalytic selective oxidation of sulfides were performed at 25 °C under visible-light irradiation using $O_2$ as an oxidant. As summarized in Table 4, CF-HCP can promote the transformation of various sulfides into sulfoxides with high efficiency and excellent selectivity. These photocatalytic selective oxidation reactions are strongly affected by substituent groups on the sulfides. For instance, thioanisoles with electron-donating group on the phenyl ring were found to react faster than those with electron-withdrawing group such as -Br and -Cl (Table 4, entries 4 and 5). Such an electronic effect has also been observed in previous reports on light-induced sulfoxidation reactions.[21]

Besides the excellent photocatalytic activity and wide substrate adaptability, the recycling of the catalyst is the most

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important advantage in the heterogeneous reaction for commercial application. Thus we investigated the recyclability of CF-HCP in the photocatalytic selective oxidation of thioanisole under visible-light irradiation. The polymer network was separated from the reaction mixtures by centrifugation, washed and reused in the subsequent round of coupling reaction. It was found that the catalyst CF-HCP can be efficiently recycled and reused for five repeating cycles without significant loss of catalytic activity and the original structure (Fig. 4a and S10). In addition, we filtered the catalyst from the solution at 52% conversion, the isolated solution did not exhibit any further reactivity, which indicated clearly that the heterogeneous photocatalytic property of CF-HCP (Fig. 4b). In relation to this, we were curious if the catalyst is applicable to the scale-up synthesis. As shown in Scheme S1, we examined this possibility using thioanisole (1.0 g, 8.05 mmol) as substrate in 4.0 mL of solvent at 25 °C. An excellent yield (98%) was also afforded in the scaled-up reaction.

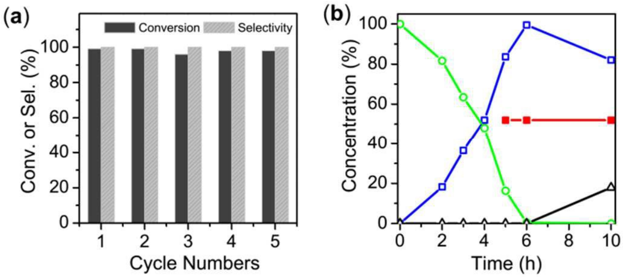

**Fig. 4** (a) Recyclibility of CF-HCP in thioanisole oxidation reaction under visible-light irradiation. Condition: 25 °C, oxygen (1 atm), green LED lamp (520 nm, 100 W), (b) Kinetic profiles of thioanisole conversion (green line), and corresponding sulfoxide (blue line), sulphone (black line) formation by CF-HCP under visible-light irradiation at 1 atm $O_2$. The concentration of sulfoxide after removing the CF-HCP at 52% thioanisole conversion (red line).

In particular, we are well known that the oxidative coupling reactions of monomer CF may still occur under Friedel-Crafts alkylation conditions (Table S3). In order to further investigate the influence of coupling fragment on photocatalytic properties, a new porous organic polymer (CF-CMP) was synthesized by oxidative coupling polymerization using CF as single monomer (Scheme S2). The BET surface area and pore volume of CF-CMP were calculated to be 1067 $m^2$ $g^{-1}$ and 0.88 $cm^3$ $g^{-1}$, respectively. In comparison with CF-HCP, the absorption spectrum of CF-CMP is obvious red-shifted (Fig. S11c). Surprisingly, CF-CMP has a three-dimensional conjugate structure like previously reported solid photocatalysts,[10-15] however it exhibited weaker photocatalytic properties than that of hyper-crosslinked polymer CF-HCP under same catalytic systems (Table S4), which may be due to the relatively low oxidation potential and short luminescence lifetime of CF-CMP (Fig. S11d-f and Table S2).

## Conclusions

In summary, a porous organic hyper-crosslinked polymer (CF-HCP) was successfully designed and constructed via one pot Friedel-Crafts alkylation reaction by anhydrous $FeCl_3$ under solvothermal conditions. The new polymer has an excellent light absorption property, good porosity with a high surface area, a large pore volume and an outstanding stability. And it can serve as a cost-efficient, metal-free heterogeneous photocatalyst with a highly catalytic efficiency for a wide range of organic transformations, including the oxidative coupling of primary amines, aerobic dehydrogenation of nonactive secondary amine substrates and selective oxidation of sulfide under visible-light irradiation. Furthermore, CF-HCP photocatalyst can be recycled and reused for multiruns without obvious decrease in catalytic efficiency. We also highlight that this work expands the known scope of porous organic polymers as heterogeneous photocatalysts and opens up new way for the design and construction of excellent solid catalysts at a molecular level. Currently, such researches are underway in our laboratory.

## Experimental section

**Instrumentations.** FT-IR spectra were recorded from 400 to 4000 $cm^{-1}$ on an Avatar FT-IR 360 spectrometer by using KBr pellets. UV/Vis spectra have been carried out on a Perkin Elmer Lambda 950 spectrophotometer. Solid-state $^{13}C$ CP/MAS NMR measurement was recorded using a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. Elemental analyses were carried out on an Elementar model vario EL cube analyzer. Field emission scanning electron microscopy was performed on a SU8020 model HITACHI microscope. Transmission electron microscopy was performed on a JEOL model JEM-2100 microscope. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 spectrometer. Powder X-ray diffraction data were recorded on a PANalytical B.V. Empyrean diffractometer diffractometer by depositing powder on glass substrate. Thermogravimetric analysis (TGA) was performed on a TGA Q500 thermogravimeter by measuring the weight loss under nitrogen. The EPR spectra were recorded on a JEOL JES-FA200 EPR spectrometer. Nitrogen sorption isotherms were measured at 77 K with a JW-BK 132F analyzer. Before measurement, the samples were degassed in vacuum at 120 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume, the Saito-Flory method was applied for the estimation of pore size distribution. The catalytic products were quantified by GC analysis (Shimadzu GC-2014C) using an SE-54 column (30 m × 0.25 mm × 0.25 μm). Electrochemical measurements were performed in a three-electrode system with a CHI660E electrochemical workstation (CH Instruments, USA). The glass carbon electrode (GCE) was used as working electrode, a platinum wire electrode, and a saturated calomel electrode (SCE) as counter and reference electrode, respectively. Luminescence decay experiments were carried out on an Edinburgh FLS920 spectrometer. To create measurable HCP films, the HCP was mixed and ground with 5 wt % Nafion, the mixture was dropped on top of a glassy carbon working electrode, and the solvents were evaporated in a vacuum oven for at least 30 min. The measurements were carried out in a 0.1 M solution of

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tetrabutylammonium phosphate in acetonitrile. A Pt counter electrode and a SCE reference electrode were used. Scan rate: 100 mV/s, T = 25 $^{o}$C.

**Synthesis of CF-HCP.** The monomer CF (100.0 mg, 0.196 mmol) and FDA (0.08 mL, 0.783 mmol), anhydrous $FeCl_3$ (0.127 g, 0.783 mmol) and 1,2-dichloroethane (4.0 mL) were added into a 10 mL Schlenk bottle at room temperature. Then the mixture was degassed via three freeze-pump-thaw cycles. The bottle was flame-sealed and heated at 80 $^{o}$C for 24 h under a nitrogen atmosphere. The mixture was then cooled to room temperature, the precipitated network was filtered and washed with water, methanol, dichloromethane and acetone, respectively. The further purification of the network was carried out by Soxhlet extraction from methanol for 24 h. The product was dried in vacuum for 10 h at 80 $^{o}$C to give CF-HCP as a deep-red powder (101.0 mg, 92% yield). Elemental analysis (%) calcd.: C 75.46, H 4.41, N 7.65; found: C 74.63, H 4.31, N 6.54; IR (KBr): 2925, 2812, 1724, 1605, 1562, 1479, 1448, 1323, 1227, 1191, 1083,1017, 885, 837, 789, 741, 699, 645 and 591 cm$^{-1}$. The surface area ($SA_{\mathrm{BET}}$) of CF-HCP (CF:$FeCl_3$:FDA = 1:4:4) is 1217 m$^2$ g$^{-1}$. The molar ratio of monomer CF:$FeCl_3$:FDA = 1:2:2 and 1:6:6 in the polymerization reaction were investigated, in order to achieve high surface areas for the resulting polymer networks. The isolation yields for obtained under various reaction conditions are 76.9% for CF-HCP (CF:$FeCl_3$:FDA = 1:2:2) and 99.5% for CF-HCP (CF:$FeCl_3$:FDA = 1:6:6), respectively. Then the molar ratio of FDA to the monomer CF was set at 4:1, the obtained polymer has the highest surface area. The nitrogen sorption isotherms of CF-HCPs under different reaction conditions are shown in Fig. S1.

**General Procedure for Photocatalytic Oxidative Coupling of Amines.** A 10 mL pyrex tube was charged with benzylamine or its derivatives (0.2 mmol), polymer network (5.0 mg), and acetonitrile (2.0 mL). The pyrex tube was sealed under oxygen atmosphere by equipping with an oxygen balloon. The reaction mixture was irradiated with a green LED lamp (520 nm, 30 W) at room temperature. After reaction for a certain period of time, the solvent was removed under vacuum. To determine the conversion, $^1$H NMR samples of the crude mixture were taken after the polymer was filtered off. For reuse studies, the catalyst CF-HCP was recovered by centrifugation and washed with methanol, $CH_2Cl_2$, THF and acetone. Before being reused in the next photocatalytic run, the catalyst should be dried under vacuum overnight.

**General Procedure for Photocatalytic Oxidation of Thioanisole.** A 10 mL pyrex tube was charged with thioanisole (0.2 mmol), polymer network (5 mg), and acetonitrile (2 mL) and methanol (0.8 mL). The pyrex tube was sealed under oxygen atmosphere by equipping with an oxygen balloon. The reaction mixture was irradiated with a green LED lamp (520 nm, 100 W) at room temperature. After reaction for a certain period of time, the conversion determined by GC using n-dodecane as internal standard. For reuse studies, the catalyst CF-HCP was recovered by centrifugation and washed with methanol, $CH_2Cl_2$, THF and acetone. Before being reused in the next photocatalytic run, the catalyst should be dried under vacuum overnight.

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## Notes and references

1 (a) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.,* 2013, **113**, 5322; (b) D. A. Nicewicz, D. W. C. MacMillan, *Science*, 2008, **322**, 77; (c) D. M. Schultz, T. P. Yoon, *Science*, 2014, **343**, 1239176; (d) J. M. Narayanam, J. W. Tucker, C. R. Stephenson, *J. Am. Chem. Soc.,* 2009, **131**, 8756; (e) K. Zeitler, *Angew. Chem., Int. Ed.,* 2009, **48**, 9785; (f) J. Long, S. Wang, Z. Ding, S. Wang, Y. Zhou, L. Huang, J. Zhang, X. Wang, *Chem. Commun.,* 2012, **48**, 11656.

2 (a) J. M. Narayanam, C. R. Stephenson, *Chem. Soc. Rev.,* 2011, **40**, 102; (b) L. Shi, W. Xia, *Chem. Soc. Rev.,* 2012, **41**, 7687; (c) M. Rueping, C. Vila, A. Szadkowska, R. M. Koenigs, J. Fronert, *ACS Catal.,* 2012, **2**, 2810; (d) J. Xuan, W. Xiao, *Angew. Chem., Int. Ed.,* 2012, **51**, 6828; (e) T. P. Yoon, *ACS Catal.,* 2013, **3**, 895; (f) D. P. Hari, B. König, *Angew. Chem., Int. Ed.,* 2013, **52**, 4734; (g) M. N. Hopkinson, B. Sahoo, J. L. Li, F. Glorius, *Chem.-Eur. J.,* 2014, **20**, 3874.

3 (a) T. P. Yoon, M. AIschay, J. Du, *Nature Chem.,* 2010, 2, 527; (b) L. Shi, W. Xiao, *Chem. Soc. Rev.,* 2012, **41**, 7687; (c) Y. Zou, J. Chen, W. Xiao, *Angew. Chem., Int. Ed.,* 2013, **52**, 11701; (d) X. Wang, Q. Meng, J. Zhong, X. Gao, T. Lei, L. Zhao, Z. Li, B. Chen, C. Tung, L. Wu, *Chem. Commun.,* 2015, **51**, 11256.

4 (a) S. Wang, W. Yao, J. Lin, Z. Ding, X. Wang, *Angew. Chem., Int. Ed.,* 2014, **53**, 1034; (b) S. Wang, Z. Ding, X. Wang, *Chem. Commun.,* 2015, **51**, 1517; (c) X. Wang, S. Blechert, M. Antonnietti, *ACS Catal.,* 2012, **2**, 1596.

5 (a) Z. Xie, C. Wang, K. E. deKrafft, W. Lin, *J. Am. Chem. Soc.,* 2011, **133**, 2056; (b) C. Wang, Z. Xie, K. E. deKrafft, W. *Lin, J. Am. Chem. Soc.,* 2011, **133**, 13445; (c) J.-L. Wang, C. Wang, W. Lin, *ACS Catal.,* 2012, **2**, 2630.

6 (a) A. Thomas, *Angew. Chem., Int. Ed.,* 2010, **49**, 8328; (b) Y. Xu, S. Jin, H. Xu, A. Nagai, D. Jiang, *Chem. Soc. Rev.,* 2013, **42**, 8012; (c) D. Wu, F. Xu, B. Sun, R. Fu, H. He, K. Matyjaszewski, *Chem. Rev.,* 2012, **112**, 3959; (d) S. Das, P. Heasman,; T. Ben, S. Qiu, *Chem. Rev.,* 2017, **117**, 1515; (e) L. Tan, B. Tan, *Chem. Soc. Rev.,* 2017, DOI: 10.1039/c6cs00851h.

7 (a) Q. Chen, M. Luo, P. Hammershoj, D. Zhou, Y. Han, B. Laursen, C. Yan, B. Han, *J. Am. Chem. Soc.,* 2012, **134**, 6084; (b) R. Dawson, A. I. Cooper, D. J. Adams, *Polym. Int.*, 2013, **62**, 345; (c) Z. Li, X. Feng, Y. Zou, Y. Zhang, H. Xia, X. Liu, Y. Mu, *Chem. Commun.,* 2014, **50**, 13825; (d) Z. Li, Y. Zhi, X. Feng, X. Ding, Y. Zou, X. Liu, Y. Mu, *Chem.-Eur. J.,* 2015, **21**, 12079; (e) X. Liu, Y. Xu, Z. Guo, A. Nagai, D. Jiang, *Chem. Commun.,* 2013, **49**, 3233; (f) X. Liu, H. Li, Y. Zhang, B. Xu, S. A, H. Xia, Y. Mu, *Polym. Chem.*, 2013, **4,** 2445; (g) X. Liu, Y. Zhang, H. Li, S. A, H. Xia, Y. Mu, *RSC Adv.,* 2013, **3**, 21267.

8 (a) S. Ding, M. Dong, Y. Wang, Y. Chen, H. Wang, C. Su and W. Wang, *J. Am. Chem. Soc.,* 2016, **138**, 3031; (b) X. Liu, Y. Xu, D. Jiang, *J. Am. Chem. Soc.,* 2012, **134**, 8738; (c) Z. Li, H. Li, H. Xia, X. Ding, X. Luo, X. Liu, Y. Mu, *Chem.-Eur. J.,* 2015, **21**, 17355; (d) Z. Li, Y. Zhang, H. Xia, Y. Mu, X. Liu, *Chem. Commun.,* 2016, **52**, 6613; (e) Y. Zhang, X. Shen, X. Feng, H. Xia, Y. Mu, X. Liu, *Chem. Commun.,* 2016, **52**, 11088.

9 (a) A. Thomas, *Angew. Chem., Int. Ed.,* 2010, **49**, 8328; (b) Q. Sun, Z. Dai, X. Meng, F. Xiao, *Chem. Soc. Rev.,* 2015, **44**, 6018; (c) P. Kaur, J. Hupp, S. Nguyen, *ACS Catal.,* 2011, **1**, 819; (d) H. Xu, J. Guo, D. Jiang, *Nature Chem.,* 2015, **7**, 905; (e) H. Li, B. Xu, X. Liu, S. A, C. He, H. Xia, Y. Mu, *J. Mater. Chem. A*, 2013, **1**, 14108; (f) Y. Zhang, S. A, Y. Zou, X. Luo, Z. Li, H. Xia, X. Liu, Y. Mu, *J. Mater. Chem. A,* 2014, **2**, 13422; (g) J. Schmidt, J. Weber, J. D. Epping, M. Antonietti A. Thomas, *Adv. Mater.,*

View Article Online
DOI: 10.1039/C7TA02205K

2009, **21**, 702; (h) D. S. Kundu, J. Schmidt, C. Bleschke, A. Thomas,S. Blechert, *Angew. Chem., Int. Ed.,* 2012, **51**, 5456; (i) L. Chen,Y. Yang, D. Jiang, *J. Am. Chem. Soc.,* 2010, **132**, 9138; (j) J.-X. Jiang, C. Wang, A. Laybourn, T. Hasell, R. Clowes, Y. Z. Khimyak, J. Xiao, S. J. Higgins, D. J. Adams, A. I. Copper, *Angew. Chem., Int. Ed.,* 2011, **50**, 1072; (k) C. Wang, Z. Zhang, T. Yue, Y. Sun, L. Wang, W. Wang, Y. Zhang, C. Liu, W. Wang, *Chem.-Eur. J.,* 2012, **18**, 6718; (l) X. Liu, S. A, Y. Zhang, X. Luo, H. Xia, H. Li, Y. Mu, *RSC Adv.,* 2014, **4**, 6447.

10 (a) R. S. Sprick, J.-X. Jiang, B. Bonillo, S. Ren, T. Ratvijitvech, P. Guiglion, M. A. Zwijnenburg, D. J. Adams, A. I. Cooper, *J. Am. Chem. Soc.,* 2015, **137**, 3265; (b) V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld, B. V. Lotsch, *Nature Commun.,* 2015, **6**, 8508.

11 (a) N. Kang, J. H. Park, K. C. Ko, J. Chun, E. Kim, H. W. Shim, S. M. Lee, H. J. Kim, T. K. Ahn, J. Y. Lee, S. K. Son, *Angew. Chem., Int. Ed.,* 2013, **52**, 6228; (b) Z. J. Wang, S. Ghasimi, K. Landfester, K. A. I. Zhang, *Adv. Mater.,* 2015, **17**, 6265.

12 M. Liras, M. Lglesias, F. Sánchez, *Macromolecules,* 2016, **49**, 1666.

13 (a) X. Ding, B. Han, *Angew. Chem., Int. Ed.,* 2015, **54**, 6536; (b) X. Ding, B. Han, *Chem. Commun.,* 2015, **51**, 12783; (c) X. Chen, M. Addicoat, E. Jin, L. Zhai, H. Xu, N. Huang, Z. Guo, L. Liu, S. Irle, D. Jiang, *J. Am. Chem. Soc.,* 2015, **137**, 3241.

14 (a) J.-X. Jiang, Y. Li, X. Wu, J. Xiao, D. J. Adams, A. I. Cooper, *Macromolecules,* 2013, **46**, 8779; (b) Z. J. Wang, S. Ghasimi, K. Landfester, K. A. I. Zhang, *Chem. Mater.,* 2015, **27**, 1921; (c) L. Pan, M. Xu, L. Feng, Q. Chen, Y. He, B. Han, *Polym. Chem.,* 2016, **7**, 2299; (d) W. Zhang, B. C. Ma, D. Wang, Z. J. Wang, R. Li, L. Wang, K. Landfester, K. A. I. Zhang, *J. Mater. Chem. A,* 2017, **5**, 3792.

15 Z. J. Wang, S. Ghasimi, K. Landfester, K. A. I. Zhang, *J. Mater. Chem. A,* 2014, **2**, 18720.

16 (a) J. Luo, X. Zhang, J. Zhang, *ACS Catal.,* 2015, **5**, 2250; (b) R. Li, Z. J. Wang, L. Wang, B. C. Ma, S. Ghasimi, H. Lu, K. Landfester, K. A. I. Zhang, *ACS Catal.*, 2016, **6**, 1113.

17 (a) B. Li, R. Gong, W. Wang, X. Huang, W. Zhang, H. Li, C. Hu, B. Tan, *Macromolecules,* 2011, **44**, 2410; (b) B. Li, Z. Guan, W. Wang, X. Yang, J. Hu, B. Tan, T. Li, *Adv. Mater.,* 2012, **24**, 3390.

18 Z. Dou, L. Xu, Y. Zhi, Y. Zhang, H. Xia, Y. Mu, X. Liu, *Chem.-Eur. J.,* 2016, **22**, 9919

19 C. Su, M. Acik, K. Takai, J. Lu, S. J. Hao, Y. Zheng, P. Wu, Q. T. Bao, T. Enoki, Y. J. Chabai, K. P. Loh, *Nature Commun.,* 2012, **3**, 1298.

20 (a) I. Fernández, N. Khiar, *Chem. Rev.,* 2003, **103**, 3651; (b) J. Legros, J. R. Dehli, C. Bolm, *Adv. Synth. Catal.,* 2005, **347**, 19.

21 (a) C. Shen, H. Yu, Z. Wang, *Chem. Commun.,* 2014, **50**, 11238; (b) Y. L. Zhu, H. Long, W. Zhang, *Chem. Mater.,* 2013, **25**, 1630.

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A novel nanoporous organic polymer (CF-HCP), which exhibits excellent heterogeneous catalytic performances for a wide range of organic reactions under visible-light irradiation, is reported.