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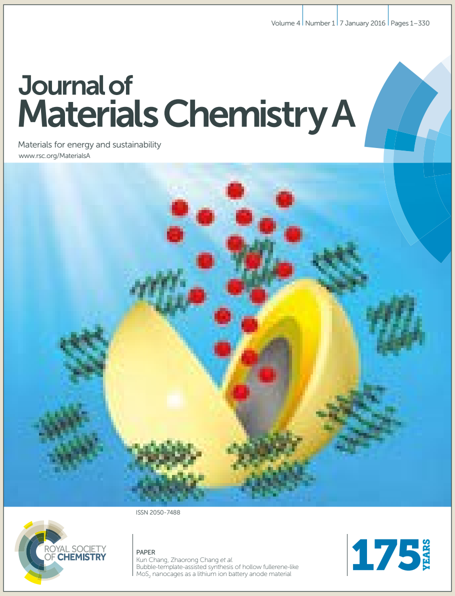

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Covalent organic frameworks as metal-free heterogeneous photocatalysts for organic tranformations

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Two-dimensional covalent organic frameworks (2D-COFs) are excellent candidates for photocatalytic organic transformations arise from their periodic columnar π-arrays and ordered nanochannels. Here, we present a novel 2D-COF that features a permanent porosity with high surface area and large pore volume, and exhibits a high crystllinity, an excellent stability. Indeed, the new 2D-COF was found to be a highly efficient, metal-free, recyclable heterogeneous photocatalyst for oxidative C-H functionalizations under visible-light irradiation using O_2 as a green oxygen source.

As a new generation of crystalline porous polymer materials, covalent organic frameworks (COFs) are two-dimensional (2D) or three-dimensional (3D) periodic architectures with permanent porosity.[1] Owing to their low density, large specific surface area and high thermal stability, COFs have recently attracted huge attention for promising applications in gas adsorption,[2] catalysis,[3] sensing,[4] proton conduction,[5] drug delivery,[6] and energy storage.[7] In particular, the most remarkable feature for 2D-COFs is periodic columnar π-arrays arise from layered stacking of 2D polymer sheets. The ordered columns are ideal channels for exciton diffusion, migration and separation,[8] and 2D-COFs has proven as a powerful platform for designing functional materials in optoelectronic devices.[9] Surprisingly, however, the field of 2D-COFs as heterogeneous photocatalysts for organic transformations remains largely untrapped up to now.[10]

The use of visible-light to drive organic transformations offers a green and sustainable way for efficient synthesis of fine chemicals. Over the last decades, various kinds of dye molecule such as transition metal complexes, organic dyes and inorganic semiconductors have been proved to be highly efficient photocatalysts in photoredox reactions via signal electron transfer process.[11] In order to overcome the important shortcomings of the homogeneous photocatalysts including high price, tedious separation and low recyclability, some photoactive solid catalysts like graphitic carbon nitride, metal-organic frameworks and mesoporous silica have also been explored for a serious of photocatalytic organic reactions.[12] From a standpoint of principle, however, an ideal photocatalyst should have an excellent porosity, columnar π-arrays, a strong crystallinity. On the other hand, the low cost, metal-free, good recyclability and scale-up synthesis are still important for industrial applications. In this context, predesignable 2D-COF can be an excellent scaffold for heterogeneous photocatalysis of organic transformations. Herein, we report a novel 2D-COF with high surface area, strong srystallinity and robust stability (Scheme 1, COF-JLU5), and that exhibit excellent heterogeneous photocatalytic performances for oxidative C-H functionalizations under visible-light irradiation.

In order to obtain an excellent COF-based heterogeneous photocatalyst for organic transformations, a suitable structure was rationally designed. First, select triazine based tri-amines as a knot, because its plane structure can increase π-π interaction between the layers to improve the crystallinity of the COF, but also it possesses a good electron-deficient property. Second, introduction an -OMe with electron-rich group adjacent to Schiff-base centers to enhance the chemical stability of skeleton by integrating resonance effect.[3b] Third, the construction of the electronic donor-acceptor structure in the layer can adjust the photoelectric properties to increase the photocatalytic efficiency of the COF. Therefore, a new COF-JLU5 was synthesized under solvothermal conditions by condensation of 1,3,5-tris-(4-aminophenyl)triazine (56.6 mg, 0.16 mmol) and 2,5-dimethoxyterephthaldehyde (46.6 mg, 0.24 mmol), in the presence of 6 M aqueous acetic acid (0.2 mL) using mesitylene/1,4-dioxane (2.0 mL, 4:1 by vol.) as the solvent at 120 °C for 3 days, which afforded a yellow-green microcrystalline solid in 88% yield (Scheme 1). Fourier transform infrared (FT-IR) spectrum

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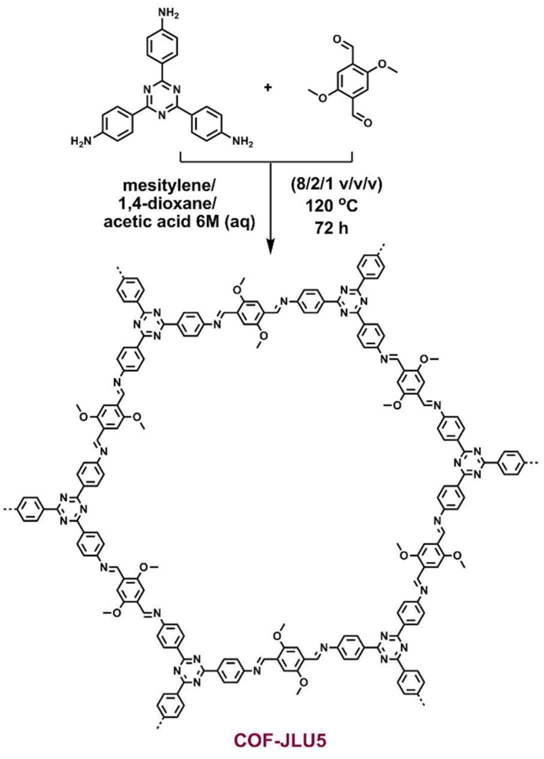
of COF-JLU5 exhibited a strong vibration band at 1584 cm^{-1}, indicating the formation of C=N linkages (Fig. S1). The precise connections were assessed by solid state ^{13}C CP/MAS NMR analysis. The peak at about 151 ppm is assigned to the carbon atoms of imine groups, and the high-field peak at about 53 ppm can be attributed to the methoxy groups (Fig. S2). Elemental analysis of the COF-JLU5 confirmed that the C, H, N contents were 71.53, 4.94, and 14.15, which were in good agreement with the calculated values of 73.08, 4.60, and 14.20 expected for an infinite 2D sheet.



Scheme 1. Synthesis of COF-JLU5 by imine condensation reaction.

The crystalline structure of COF-JLU5 was determined by powder X-ray diffraction (PXRD) analysis in connection with structural simulations (Fig. 1). The experimental PXRD pattern exhibits a strong diffraction peak at 2.76°, and relatively weak signals at 5.84°, 7.61°, 9.71°, and 24.9°, which can be assigned to the (100), (200), (210), (220) and (001) reflections, respectively (black curve). The *d* spacing was found to be 3.57 Å, which implied the exitence of π-π interaction of the adjacent layers. The structural simulation of PXRD pattern suggests that COF-JLU5 possesses preferably the AA stacking mode (blue curve). In this model, the Pawley refined profile (red curve) is in good agreement with observed pattern, as evidenced by their negligible difference (green curve, R_{wp} = 5.40% and R_p = 3.92%, respectively). The expected crystalline morphology of the COF was evidenced by field-emission scanning electron microscopy (FE-SEM). The SEM image revealed that COF-JLU5 with a flowerlike morphology (Fig. S3a and b), and each independent flower can be deemed as the result of aggregation of abundant petals with lengths in the nanometer size (200-300 nm) (Fig. S3c). In addition, high-resolution transmission electron microscopy (HR-TEM) image showed the direct visualization of the layered nanomorphology and hexagonal pore texture (Fig. S3d and e).

The permanent porosity of COF-JLU5 was evaluated by measuring nitrogen gas adsorption isotherm of the activated samples at 77 K. As shown in Fig. 2A, the sorption profile was classified as typical type IV isotherm with a rapid uptake under at a low relative pressure of $p/p_0 < 0.1$ and a step in rang of p/p_0 = 0.05-0.20, indicating that COF-JLU5 is a mesoporous material. The Brunauer-Emmett-Teller (BET) surface area of COF-JLU5 was evaluated to be 1632 m^2 g^{-1}. Based on the non-local density functional theory method, the average pore size was calculated to be 2.7 nm (Fig. 2B), which is reasonably close to the theoretical value form the crystal simulation. The total pore volume of COF-JLU5 was still estimated to be 1.59 cm^3 g^{-1} at p/p_0 = 0.99.

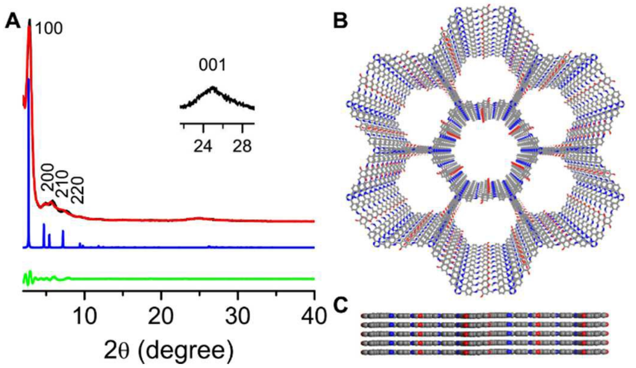


Fig. 1 (A) Observed PXRD pattern (black line), the Pawley refined pattern (red line), the difference plot (green line) and the simulated pattern (blue) for AA-stacking model of COF-JLU5. Space filling models showing AA stacking: top view (B) and side view (C); Carbon (grey), Nitrogen (blue), Oxygen (red), hydrogen is omitted for clarity.

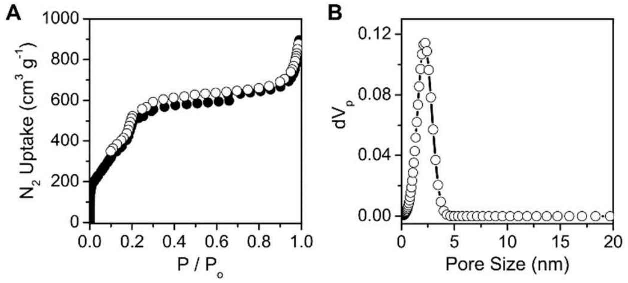


Fig. 2 (A) Nitrogen adsorption (point) and desorption (circle) isotherm of COF-JLU5 at 77 K, (B) Pore size distribution of COF-JLU5 on the N_2 adsorption isotherm.

The stability of material is an important parameter for practical applications. Such, we tested the stability of COF-JLU5 under various conditions. Thermogravimetric analysis (TGA) displayed that the COF has an excellent thermal stability up to 450 °C under nitrogen atmosphere (Fig. S4). To research the chemical stability of COF-JLU5, we dispersed the pristine samples in different organic solvents, aqueous HCl (12 M) and NaOH (14 M) solutions at 25 °C for three days. Then the samples were collected by filtration, washed with methanol, and dried under vacuum. To our delight, all the samples also show strong peaks in XRD patterns, and the similar skeleton connection in FT-IR profiles and almost no wight loss (Fig.

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S5). Even under the additional visible-light irradiation (blue LED: 460 nm, 30 W) for methanol suspension of COF-JLU5, the strong crystallinity is still retained in the COF sample after treatment (Fig. S6). Therefore, the experimental results indicated unambiguously that the new COF possesses an excellent thermal, chemical and photochemical stability.

Electron absorption spectrum of the COF-JLU5 in the solid state exhibited an absorption band at 470 nm (Fig. 3A, blue line), which is red-shifted from that its monomers (Fig. S7). Upon excitation at 470 nm, COF-JLU5 displayed an intense orange-red luminescence band at about 580 nm (Fig. 3A, red line). Cyclic voltammetry measurements revealed an onset potential at 0.90 V (vs SCE), attributable to the redox potential of the COF-JLU5$^+$/COF$^-$JLU5 couple (Fig. 3B). On the basis of a free energy change (E^{0-0}) between the ground state and the vibrationally related excited state of 2.40 eV (516 nm, Fig. 3A), the redox potential of the excited state COF-JLU5$^+$/COF-JLU5* couple was calculated as -1.50 V. The potentials are comparable to that of the excited state of classical transition metal complexes,[11] as a result COF-JLU5 was expected to be a candidate in photoredox catalytic organic transformations.

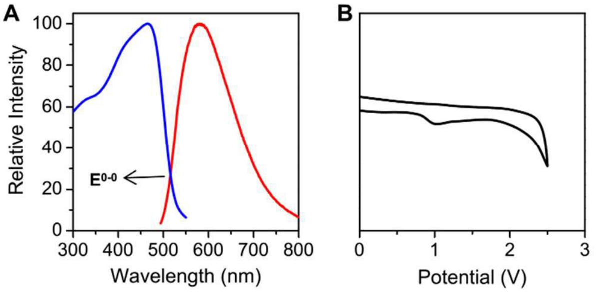
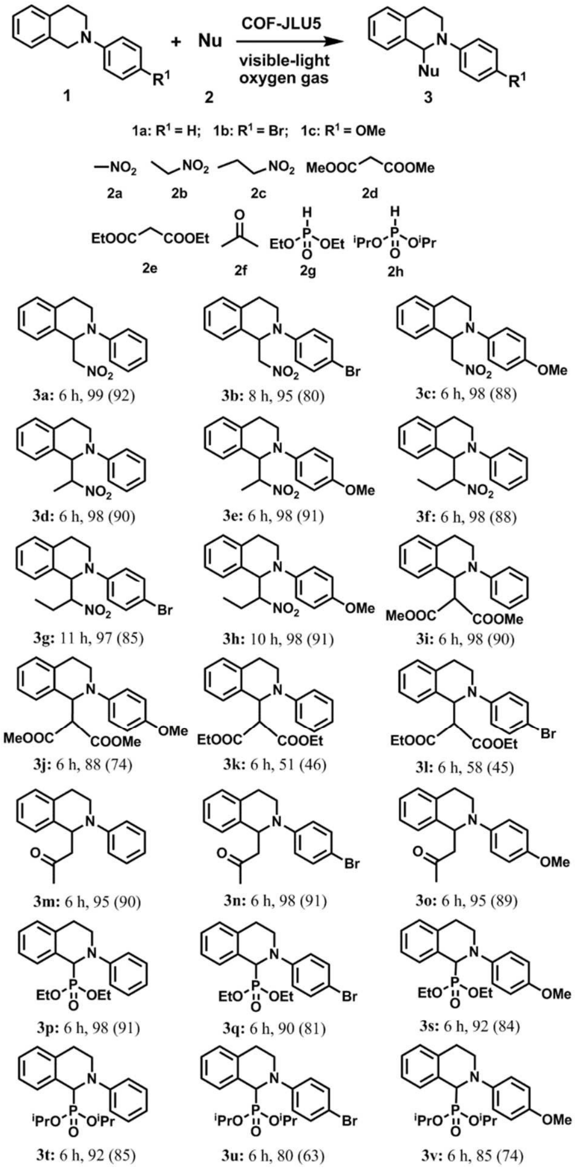


Fig. 3 (A) Normalized absorption (blue line) and emission spectra (red line) of COF-JLU5 excited at 470 nm. (B) Solid-state cyclic voltammetry of COF-JLU5 with a scan rate of 100 mV s^{-1}.

The COF-JLU5 offers an excellent porosity, a high crystallinity, an exceptional stability, and the columnar π-arrays, as well as the promising photoredox properties, and serves as a unique heterogeneous photocatalyst for organic transformations. In order to validate our hypothesis, we conducted the aerobic cross-dehydrogenative coupling (CDC) reaction of N-aryltetrahydroisoquinolines, which is one of the most classical photocatalytic transformation.[13] We first examined the reaction of N-phenyl-1,2,3,4-tetrahydroisoquinoline (THIQ, **1a**) with nitromethane (**2a**) containing a catalytic amount of COF-JLU5 under irradiation of blue LEDs at 25 °C in the presence of O_2 as green oxygen source. Compared with toluene and cyclohexane, the rapid conversion rate and high yield (99%) were obtained in methanol solvent (Fig. S8). The results of control experiments revealed that the light, oxygen gas and photocatalyst COF-JLU5 are all essential for this reaction (Table S1). However, the TPB-DMTP COF without the triazine core only achieved low yield (42 %, Table S1, entry 8) under the optimized conditions, which implying the rationality of the structural design for COF-JLU5. Besides catalytic activity, the recyclibity of catalyst is the most crucial advantage in the heterogeneous reaction for commercial use. The photocatalyst COF-JLU5 was easily isolated from the reaction mixtures by centrifugation, washed, dried and reused at least ten cycles without any obvious loss of catalytic activity and the original structure (Fig. S9). It is mainly attributed to the outstanding stability of the COF. Furthermore, we separated COF-JLU5 form the reaction solution at 68% conversion, the filtrate did not display further reactivity, which indicate unambiguously the heterogeneous photocatalytic feature of the new COF photocatalyst. We also examined the possibility of a larger scale synthetic using **1a** (0.5 g, 2.39 mmol) as a substrate in 30 mL of methanol at 25 °C for 10 h. An excellent yield (95 %) was afforded in the scaled-up reaction (Scheme S1).

Scheme 1. Photocatalytic C-C/C-P coupling reaction of N-phenyltetrahydroisoquinonlines with various nucleophiles using COF-JLU5 as photocatalyst[a]



[a] Reaction conditions: COF-JLU5 (4.0 mg), **1** (0.2 mmol), **2** (0.6 mmol), methanol (2.0 mL), O_2 (1 bar), 30 W blue LEDs with 460 nm, 25 °C, the yields

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detected by NMR spectroscopy and the isolated yields are given are in parentheses.

Further, we explored the substrate scope of the visible-light mediated COF catalyzed aerobic CDC reaction. As shown in Scheme 1, in general, different THIQ derivatives **1a-c** with nitroalkanes were subjected to the aerobic aza-Henry reaction, giving the desired reaction products **3a-h** in excellent yields. The presence of electronic properties for the substituent group in the phenyl ring and alkyl attached on nitroalkanes had little influence on the yields. Then we researched the applicability of other nucleophiles. To our delight, higher substituted dialkyl malonates were still able to perform this coupling reaction showing slightly reduced activities. Subsequently, utilizing acetone as nucleophile, we investigated the oxidative Mannich reaction, which offers a powerful way to valuable β-amino-ketones. In the presence of proline as Lewis base to activate the ketone, the reaction also proceeded smoothly by COF-JLU5 to prove the desired products **3m-o** in high yield. In addition to the C-C bond formation, notably, the COF heterogeneous photocatalytic system could also directly accelerate the C-P bond crossing reaction. And good yields of α-amino dialkyl phosphonates **3p-v** were obtained. Indeed, COF-JLU5 is an outstanding photocatalyst for the aerobic CDC reaction, and its photocatalytic activity is better than that of the reported solid photocatalyst, comparing the best results of the homogeneous photocatalysts (Table S2 and S3).

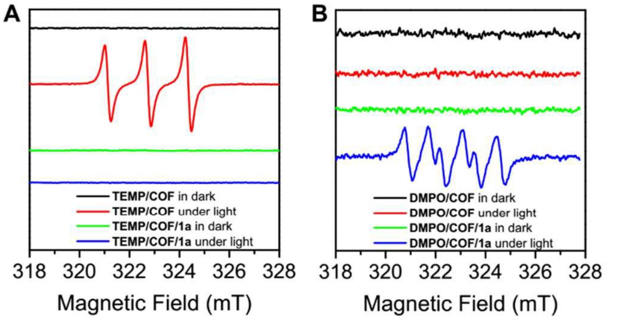

Fig. 4 (A) ESR spectra of the mixture COF-JLU5 (1.0 mg mL^{-1}) and TEMP (0.1 M) in air-saturated CH_3CN in dark (black line) and upon light irradiation (red line); ESR spectra of the mixture COF-JLU5 (1.0 mg mL^{-1}), **1a** (1.0×10^{-2} M) and TEMP (0.1 M) in air-saturated CH_3CN in dark (green line) and upon light irradiation (blue line); (B) ESR spectra of the mixture COF-JLU5 (1.0 mg mL^{-1}) and DMPO (0.1 M) in air-saturated CH_3CN in dark (black line) and upon light irradiation (red line); ESR spectra of the mixture COF-JLU5 (1.0 mg mL^{-1}), **1a** (1.0×10^{-2} M) and DMPO (0.1 M) in air-saturated CH_3CN in dark (green line) and upon light irradiation (blue line).

According to previous results in the literature,[14] molecular O_2 is converted into active oxygen species (single oxygen $^1O_2$ and superoxide radical anion $O_2^{\bullet-}$) through energy or electron transfer from the excited state of macromolecular photosensitizers. To study the active oxygen species generated by COF-JLU5, electron spin resonance (ESR) measurements were performed in which 2,2,6,6-tetramethylpiperiding (TEMP) and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) were employed as singlet oxygen $^1O_2$ and superoxide radical anion $O_2^{\bullet-}$ scavengers, respectively. As shown in Fig. 4 , the typical characteristic of $^1O_2$ (Fig. 4A, red line) was observed upon irradiation of the air-saturated CH_3CN mixture of COF-JLU5 and TEMP. However, the $^1O_2$ signal disappeared upon the addition of the substrate **1a** to the mixture of TEMP and COF-JLU5 (Fig. 4A, blue line). By contrast, when DMPO, an $O_2^{\bullet-}$ scavenger, was used instead of TEMP in the same air-saturated solution, a clear characteristic signal of $O_2^{\bullet-}$ was detected (Fig. 4B, blue line). These results suggest that the effective electron transfer between excited COF-JLU5 and **1a** can be effectively suppressed the production of $^1O_2$.[15]

Accordingly, a plausible reaction mechanism for the aerobic photocatalytic C-H functionalizations by COF-JLU5 is proposed (Fig. 5). Under visible-light irradiation, the COF-JLU5 generates the excited species COF-JLU5*, which is reductively quenched by **1a** via a single electron transfer (SET) process to form an radical cation **A** and radical anion COF-JLU5$^{\bullet-}$. Then generated radical anion COF-JLU5$^{\bullet-}$ delivered an electron to molecular O_2 to form the superoxide anion $O_2^{\bullet-}$ and simultaneously to regenerate COF-JLU5 to its ground state. The active oxygen species $O_2^{\bullet-}$ subsequently abstracts a proton from **A** to produce the the hydroperoxide radical and the intermediate **B**. Further, the obtained hydroperoxide radical can abstract a hydrogen atom from **1a** to afford intermediate **B** alone with the formation of H_2O_2. The **B** lose one electron to afford the iminium ion **C**. Finally, the **C** undergoes nucliophilic addition to give the desired product **D**.[15]

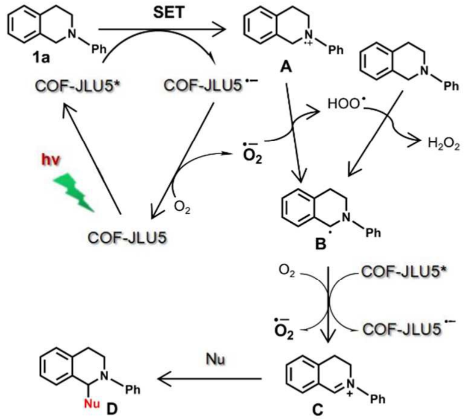

Fig. 5 Proposed reaction mechanism for the aerobic photocatalytic C-H functionalizations by COF-JLU5.

Conclusions

In summary, we have developed a photoactive 2D-COF for photocatalytic organic transformations. The COF-JLU5 can catalyze oxidative C-H functionalizations under visible-light, and exhibit high catalytic activity, broad substrate adaptability and outstanding recyclability, owing to combining some key features such as permanent porosity, high crystallinity and columnar π-arrays as well as an outstanding stability. The new COF as a heterogeneous photocatalyst possesses some distinct advantages over other known catalytic materials that its inherent pores provide space for the transport and transformation of matter, columnar π-arrays offer ideal channels for charge conduction and separation, the strong crystallinity presents a possibility for structural tailoring and performance adjustments. Considering the inherent advantages of

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the 2D-COF and the sustainability for photocatalytic organic reactions, the present work not only demonstrates the possibility of 2D-COF as outstanding heterogeneous photocatalytic platforms for organic transformations, but also expands the application scope of COFs and will promote greatly the development of the photocatalytic field.

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