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An ultrastable olefin-linked covalent organic framework for photocatalytic decarboxylative alkylations under highly acidic conditions

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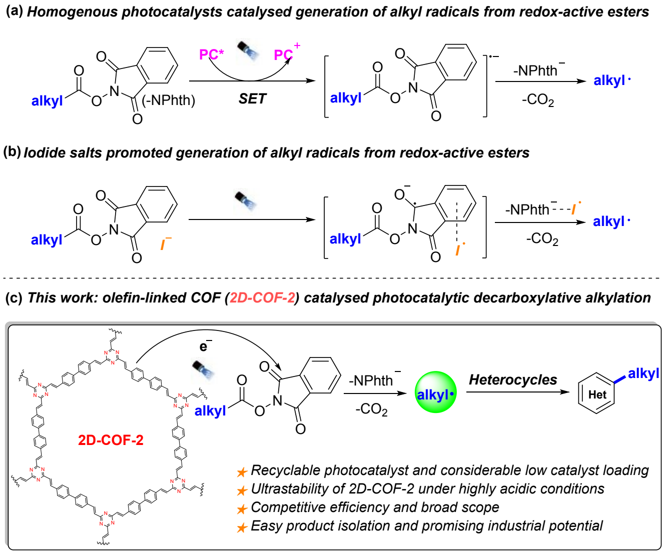
The application of two-dimensional covalent organic frameworks (2D-COFs) as photoredox catalysts offers a sustainable alternative for visible-light-driven organic transformations. However, under highly complicated organic reaction conditions, maintaining their basic structure and photoactivity is always neglected, which impedes their potential in more organic reaction types and industrial use. Herein, we describe a visible-light-driven decarboxylative alkylations of heterocycles catalysed by an olefin-linked covalent organic framework (2D-COF-2) instead of commonly used precious metal complexes and organic dyes. A wide range of alkylated heterocycles were selectively and efficiently synthesized under heterogenous reaction conditions. Relying on the ultrastability of olefin linkage, 2D-COF-2 maintained its basic structure and photoactivity under highly acidic conditions. Moreover, its streamlining industrial potential was demonstrated in recycle experiments, functionalization of bioactive molecules and scale-up reactions.

Introduction

Two-dimensional covalent organic frameworks (2D-COFs), featuring high surface areas, ordered layer structures, and extended π-conjugated frameworks, are becoming powerful heterogeneous photocatalysts.[1] For visible-light-driven organic transformations, their great potential has been demonstrated by the recent related pioneering works such as oxidation,[2] reduction,[3] C-H functionalization,[4] cyclization,[2d, 5] and *E-Z* isomerization.[6] Adjustable photoactivity and excellent recyclability are their two key advantages over homogenous photocatalysts and other inorganic photoactive semiconductors.[7] These two properties are intricately linked with the stability of 2D-COFs for holding the frameworks and maintaining the crystalline state.[8] In the past few years, massive efforts have been made for obtaining the robust linkages to keep the superior chemical and thermal stability.[9] Among them, olefin linkage, providing carbon-carbon double bonds and fully conjugated skeletons, represents the most attractive one.[10] Meanwhile, in most of previous reports,[9, 10] the stability of newly synthesized 2D-COFs was commonly verified by the simulations of strong base or alkali environment, and related catalytic applications were always performed under neutral or alkaline conditions. However, in the face of more complicated organic reaction conditions, especially under highly acidic conditions combining with long-term visible light irradiation, the real stability performances were always neglected, which could be a challenge for the future application of photoactive 2D-COFs.[11]

Photocatalytic decarboxylative alkylation of heteroarenes with redox-active esters[12] offers a fascinating strategy for the rapid synthesis and targeted modification of bioactive organic molecules,[13] which is vital for the development of new drugs and the study of structure-activity relationship. Over the past decade, a serial of ingenious works on it have been reported, and diverse photocatalysts, decarboxylative precursors and reaction conditions were employed to match the photoredox catalytic systems.[14] While significant improvements and high efficiency were achieved, the photocatalysts for delivering alkyl radicals *via* visible-light-induced single electron transfer (SET)


(a) *Homogenous photocatalysts catalysed generation of alkyl radicals from redox-active esters*

(b) *Iodide salts promoted generation of alkyl radicals from redox-active esters*

(c) *This work: olefin-linked COF (2D-COF-2) catalysed photocatalytic decarboxylative alkylation*

Scheme 1 Strategies for the generation of alkyl radicals from redox-active esters

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were always limited in precious metal complexes and organic dyes,[15] the reuse and recycle of which in the reprocessing posed a great challenge from green and sustainable chemistry point of view (Scheme 1a). To address this issue, in 2019, Fu and Shang group reported a novel photocatalytic decarboxylative system.[16] In this protocol, sodium iodide and triphenylphosphine served as the photoinitiator to accomplish the visible-light-driven alkylations *via* intermolecular electron transfer from the sodium iodide to redox-active ester, avoiding the addition of traditional dye- or metal complex-based photoredox catalysts. Very recently, Shang and co-workers described another iodide salt promoted photocatalytic decarboxylative alkylation,[17] in which the combination of ammonium iodide and amide solvent replaced the NaI/PPh_3, playing the key role in generating alkyl radicals from redox-active esters (Scheme 1b).

In this context, inspired by these elegant works, as our continuous goal of green and sustainable synthesis,[4f, 4g, 5, 18] herein, we would like to report an ultrastable olefin-linked COF (2D-COF-2) catalysed photocatalytic decarboxylative alkylation of heterocycles with *N*-hydroxyphthalimide (NHPI) esters (Scheme 1c). In our approach, the following features are exhibited: (i) reusable and readily available olefin-linked COF (2D-COF-2) as the heterogenous photocatalyst. (ii) prominent stability and persistent photoactivity of 2D-COF-2 under highly acidic conditions and long-term blue LED irradiation. (iii) considerable low catalyst loading. (iv) competitive efficiency and broad scope over homogenous photocatalysis. (v) easy product isolation and promising industrial potential.

Results and discussion

Preparation and photocatalytic performance verification of 2D-COFs

To verify the suitability, photoactivity and real stability for the visible-light-driven organic transformations, we commenced our study from the preparation of different 2D-COFs. With proper adjustments of previous reported synthetic procedures,[4a, 9f, 2b, 19, 20] four imine-linked 2D-COFs (2D-COF-1, 2D-COF-3, 2D-COF-4 and 2D-COF-5) and one olefin-linked COF (2D-COF-2) were successfully synthesized (section II, see details in ESI). The structures, porosity, and crystallinity of them were confirmed by ^{13}C solid-state NMR spectra, Fourier-transform infrared (FT-IR) spectra, N_2 sorption measurements and Powder X-ray diffraction (PXRD) analyses, respectively (section III, see details in ESI). Then, as key parameters for photoredox catalysis, the redox potentials, band gaps (Figure 1a) and UV/Vis absorption (Figure 1b, 1c) for these five 2D-COFs were measured and estimated (section III, see details in ESI). From the comparison with traditional Ru or Ir complex and organic dye, they all possessed suitable band gaps and excellent visible light absorption. Particularly, their considerable high reductive potentials implied the promising possibility to serve as strong reductants in visible-light-driven catalytic cycle. Moreover, comparisons of electrochemical impedance spectra (EIS) and photocurrent responses (Figure 1d, 1e) among these five prepared 2D-COFs were conducted, further revealing that they are all eligible for heterogenous photocatalysis. Notably, 2D-COF-2 possessed the highest transient photocurrent responses among all of five, implying the best efficient photoexcited electron-hole separation.

Subsequently, to examine the photocatalytic activity of these five 2D-COFs, the visible-light-driven decarboxylative alkylation of isoquinoline **1** with cyclohexyl *N*-hydroxyphthalimide (NHPI) ester **2a** in DMA was introduced, using stoichiometric trifluoroacetic acid (TFA) as the additive. To our delight, under the blue LED (2*40 W blue LED, 456 nm) irradiation for 24 hours, they were all capable to trigger this transformation and deliver the corresponding alkylated isoquinoline **3** smoothly (Figure 1f, Table S1, see details in ESI). And the olefin-linked 2D-COF-2 ranked among the most efficient one. When we checked the reaction tube, an interesting reaction phenomenon was observed. As heterogenous photocatalysts, at the beginning of the reaction, all of five were insoluble and suspended in the solvents. Along with the reaction proceeding, four imine-linked 2D-COFs dissolved and disappeared slowly in the reaction systems. By contrast, only olefin-linked 2D-COF-2 maintained the heterogenous state in the whole process under highly acidic organic reaction conditions (Figure 1g). Additionally, to verify the stability of all five COFs, PXRD analyses under different reaction conditions were conducted with increased COF loading. Both highly acidic conditions and long-term light irradiation could result in the decline of crystallinity, but 2D-COF-2 delivered the minimum weight loss under the standard reaction conditions (Figure S18, S19, see details in ESI). Based on this observation, we rationalized that the robust olefin linkage resulting ultrastability could be the key contributor to the superior photocatalytic performance and inbuilt heterogenous advantage. Consequently, we chose the ultrastable olefin-linked 2D-COF-2 as the preferred heterogenous photocatalyst for the photocatalytic decarboxylative alkylation of heterocycles with *N*-hydroxyphthalimide (NHPI) esters.

Reaction conditions screening and reaction scope

Next, to improve our heterogenous photocatalytic system, a serial of reaction conditions such as additive, solvent, light source and atmosphere were screened (Table S2, S3, see details in ESI). Importantly, in accordance with most of previous reports,[15] highly acidic additives were indispensable to get the better efficiency for this alkylation, further indicating that the maintaining of ultrastability for COFs under real highly acidic organic reactions and long-term visible-light-irradiation is essential (Table S3). Notably, different from the alkylations *via* photoactivation of transiently assembled chromophore,[16,17] amide solvents were not exclusive, and some readily available alcohols with low boiling points also delivered good, isolated yields of desired product **3** (Entries 5 and 10, Table S3). The comparison towards reaction sensitivity revealed that good output of **3** was closely correlated with the proper light wavelength (Entries 4-6, Table S2), and the transformation could be totally suppressed in the presence of oxygen (Entries 1-3, Table S2).

Having identified the optimized reaction conditions, the substrate scope of this heterogenous visible-light-driven

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reaction was investigated by using different NHPI esters and isoquinolines (Figure 2). As alkyl radical precursors, primary (**8**), secondary (**3**, **4**), and tertiary (**9**) alkyl NHPI esters were all well compatible in this heterogenous photocatalytic system, installing the corresponding alkyl groups onto isoquinolines at C2 position selectively and efficiently. Bromo (**5**, **7**) and methyl (**6**) substituents on the isoquinoline ring were also tolerated, and their position variations did not show conspicuous impact on the product yields. Notably, the current protocol was also amenable to NHPI ester derived from *L*-proline (**10**), providing a chance for the further modification of biomolecules.

Then the substrate scope was expanded into other heterocycles. For quinolines, no diminishing reactivity of the alkylation was observed under our standard reaction conditions (**11**-**19**). However, in consistent with previous homogenous approaches, quinolines, without substituents at C2 or C4 positions, resulted in almost no regioselectivity, affording inseparable isomers with corresponding ratios determined by ^{1}H NMR analyses (**11**-**15**). With respect to quinoxalin-2(1*H*)-ones, to gain the best conversion, in some cases, triethylamine (TEA) was employed to promote the radical addition step instead of TFA. All halogens (**20**, **40**-**42**) and methyl (**38**) groups, regardless of different positions on the heterocyclics, were successfully attacked by alkyl radicals to give the target products in good to excellent yields. Diverse *N*-protected (**25**-**32**) or *N*-free quinoxalin-2(1*H*)-ones (**38**) also underwent the alkylation smoothly, giving the selective alkylated product in high yield. Notably, NHPI esters derived from more sophisticated carboxylic acids such as tetrahydrofuranic acid (**36**), cyclohexenoic acid (**37**), and amantadanoic acid (**45**) all proved effective, and no obvious side reactions were observed.

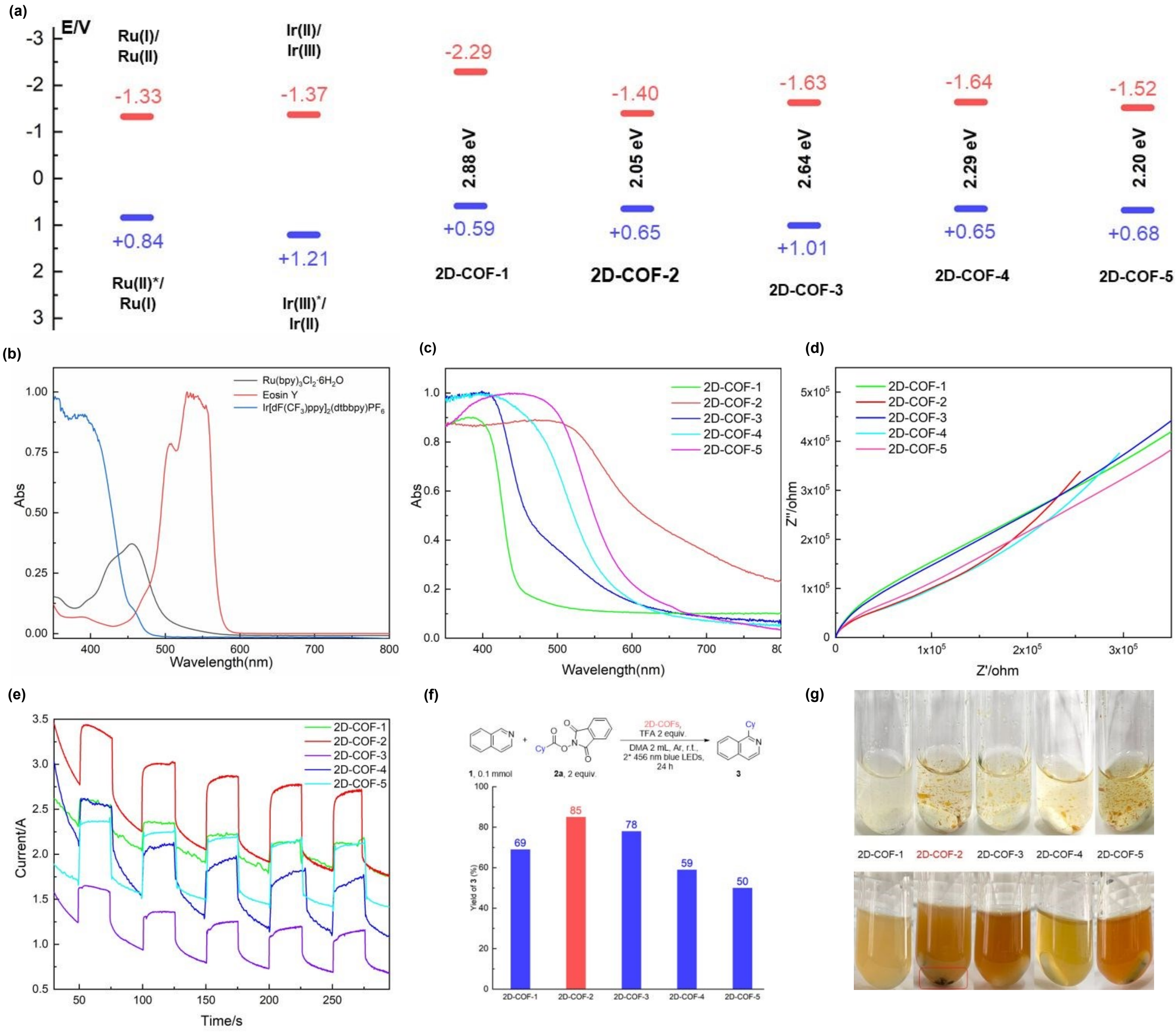
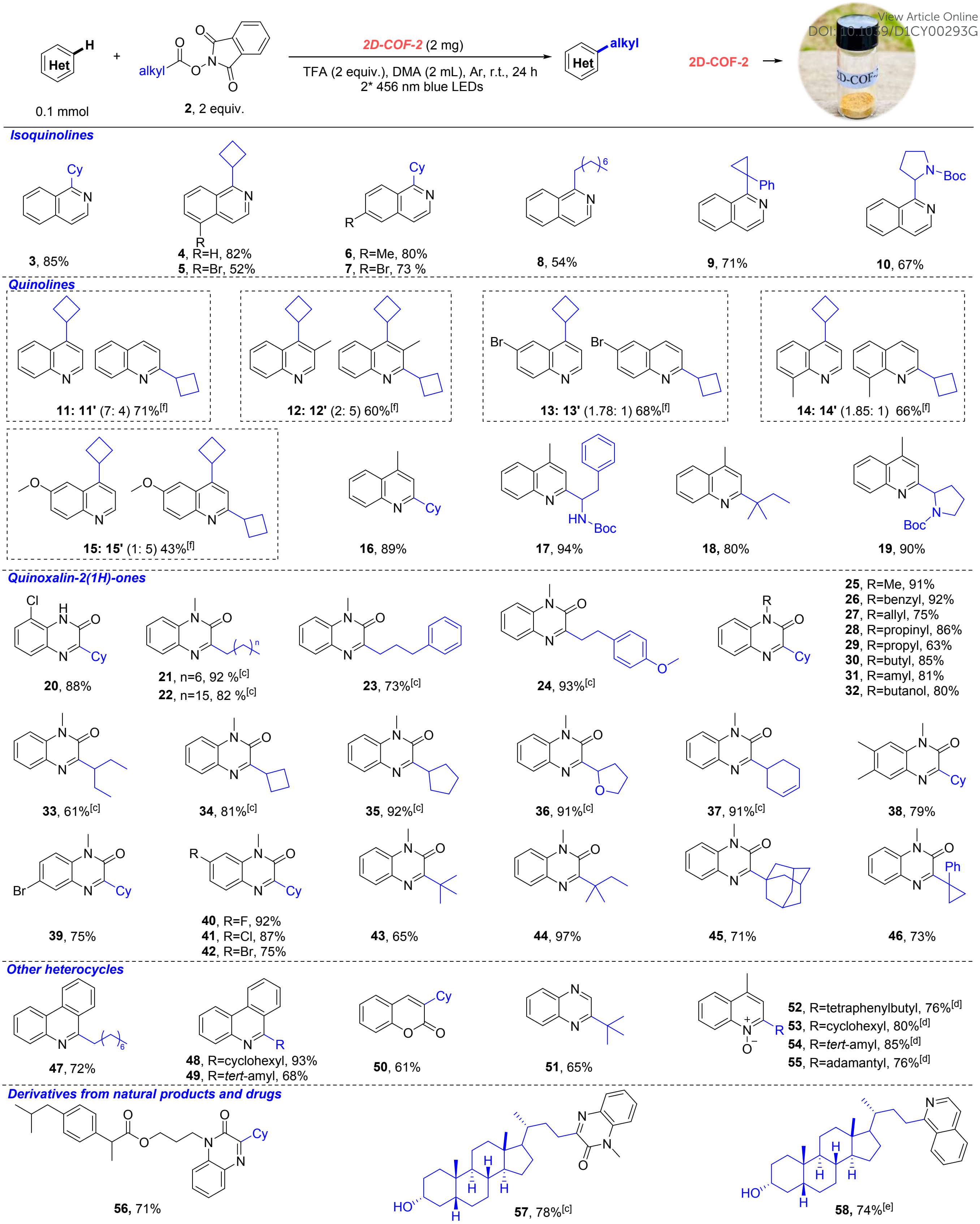


Figure 1 (a) Redox potentials (in V vs. SCE) of the 2D-COFs and some reported homogeneous photocatalysts. (b) Normalized UV/Vis absorption spectra of Ru(bpy)$_3$Cl$_2$·6H$_2$O, Eosin Y and Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$. (c) Normalized UV/Vis diffuse reflection spectra of 2D-COFs. (d) Electrochemical impedance spectra of 2D-COFs. (e) Photocurrent responses of different 2D-COFs. (f) Model reaction efficiency comparison with different 2D-COFs. (g) Model reaction phenomena comparison with different 2D-COFs



[a] Reaction conditions: Heteroarenes (0.1 mmol, 1.0 equiv.), alkyl NHPI esters (0.2 mmol, 2 equiv.), 2D-COF-2 (2 mg), TFA (0.2 mmol, 2 equiv.), DMA (2 mL), Ar, r.t., 24 h, 2* 40 W blue LED (456 nm). [b] Isolated yields. [c] Quinoxalin-2(1*H*)-ones (0.1 mmol, 1.0 equiv.), alkyl NHPI esters (0.2 mmol, 2 equiv.), 2D-COF-2 (2 mg), Et_3N (0.3 mmol, 3 equiv.), DMA (2 mL), Ar, r.t., 24 h, 2* 40 W blue LED (456 nm). [d] N-oxides (0.1 mmol, 1.0 equiv.), alkyl NHPI esters (0.15 mmol, 1.5 equiv.), 2D-COF-2 (2 mg), Cs_2CO_3 (2.5 mol%), DMF 2 mL, Ar, r.t., 12 h, 2* 40 W blue LED (456 nm). [e] Isoquinolines (0.1 mmol, 1.0 equiv.), alkyl NHPI esters (0.2 mmol, 2 equiv.), 2D-COF-2 (2 mg), TFA (0.2 mmol, 2 equiv.), EtOH (2 mL), Ar, r.t., 24 h, 2* 40 W blue LED (456 nm). [f] Isomer ratios determined by ^1H NMR analyses.

Figure 2 Substrate scope of 2D-COF-2 catalysed heterogeneous photocatalytic decarboxylative alkylation.[a, b]

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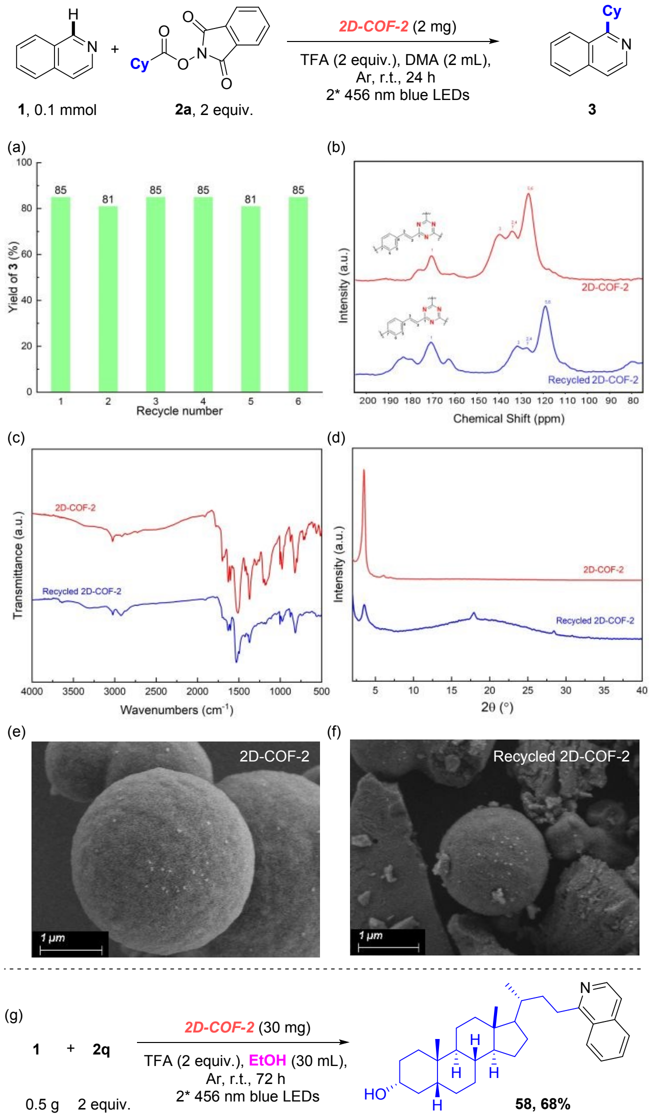

Figure 3 (a) Recycling experiments for 2D-COF-2. (b) ^{13}C solid-state NMR spectra of 2D-COF-2 before and after recycling. (c) FT-IR spectra of 2D-COF-2 before and after recycling. (d) PXRD spectra of 2D-COF-2 before and after recycling. (e) SEM image of newly synthesized 2D-COF-2. (f) SEM image for 2D-COF-2 after recycling. (g) Scale-up experiment (**2q**= NHPI ester derived from lithocholic acid).

In adddition, phenanthridines (**47**-**49**), coumarins (**50**), quinoxalines (**51**), and *N*-oxides (**52**-**55**), were also found to be suitable radical acceptors with the proper modification of reaction conditions, and the corresponding alkylated products were obtained in satisfying yields. Delightfully, this newly heterogenous photocatalytic system was also extended to derivatives from natural product or drug molecule such as lithocholic acid and Ibuprofen, producing the desired products in good yields (**56**-**58**), respectively.

Recyclability and synthetic utility

The most significant benefit of heterogenous catalytic system is the easy catalyst recyclability. To prove this, recycle experiments using **1** and **2a** as the substrates and relative comparisons for stability performance under our standard reaction conditions were carried out. Impressively, 2D-COF-2 was simply reused with rapid centrifugation in each run. Relying on the superior stability and excellent photoactivity of it, even under the highly acidic organic reaction conditions and long-term blue LED irradiation, it maintained unbated catalytic efficiency (Figure 3a), basic structures (Figure 3b and 3c) and BET surface aera (Figure S20-S22, see details in ESI) after six cycles despite decreased crystallinity (Figure 3d) and changed surface morphology (Figure 3e and 3f). Moreover, the industrial potential and practicality of our protocol were demonstrated in a scale-up reaction. With a green, cheap, and safe solvent-ethanol, isoquinoline derived from lithocholic acid **58** was smoothly and easily prepared in 68% yield on a gram scale (Figure 3g).

Mechanistic insights

To determine the real role of the heterogenous photocatalyst 2D-COF-2 for this alkylation, some mechanistic investigations were conducted. Firstly, as illustrated above, control reactions indicated that visible-light-irradiation and the 2D-COF-2 were essential for the favourable transformation of the substrates. With the standard reaction conditions, the formation of desired product **3** was drastically inhibited in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) as the radical scavenger (Figure 4a). Meanwhile, the cyclohexyl radical was captured by the detection of TEMPO adduct in GC-MS analysis (section VIII, see details in ESI). Both indicate the involvement of radical process in the catalytic cycle. Radical chain process is ruled out based on the low apparent quantum efficiency for the reaction of **1** and **2a** (Figure 4b). Additionally, *in situ* ESR spectra analysis with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) for the simulation of real photocatalytic enviroment was performed (Figure 4c). Along with the addition sequence of photocatalyst and substrates under the light irradiation, a sextet signal with a g-value = 2.0035, AN = 1.451 mT, AH = 2.124 mT was recorded, which was referred to be a carbon-centered radical. A triplet signal was also recorded, meanwhile, with a g-value = 2.0031,

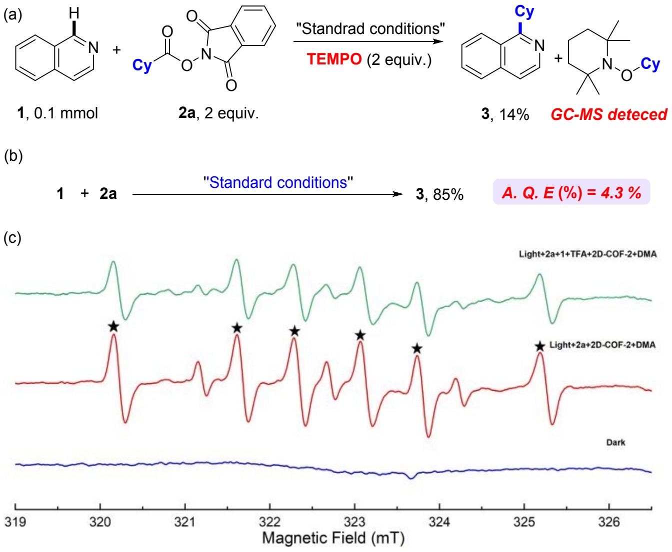

Figure 4 (a) Radical trapping experiment. (b) Apparent quantum efficiency for the preparation of **3**. (c) *In situ* ESR spectra for the 2D-COF-2 catalysed reaction of **1** and **2a** with DMPO under Ar atomosphere.

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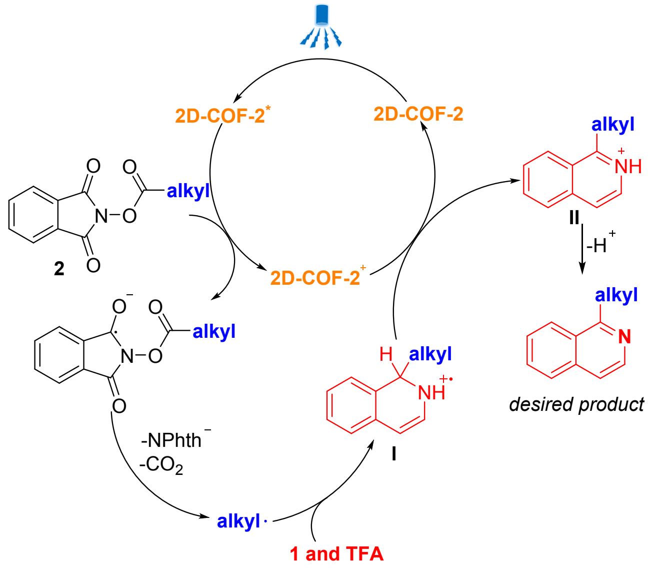

Figure 5 Proposed reaction mechanism

AN = 1.519 mT, which came from the broken up of the DMPO under light irradiation (section X, see details in ESI), suggesting that 2D-COF-2 played the crucial role in the generation of alkyl radical assisted by the visible-light-illumination.

Combining these findings with the inherent optical-electrical properties, a tentative mechanism was proposed as follows (Figure 5). Upon visible-light-irradiation, the exited 2D-COF-2, as a qualified reductant (reductive potential= -1.40 V vs SCE in CH$_3$CN, Figure 1b), can reduce the NHPI ester **2** (E$_{1/2}$ = –1.20 V vs SCE in CH$_3$CN-H$_2$O, 1:1 [15j]) directly *via* single electron transfer, affording an alkyl radical with the loss of carbon dioxide. Then the alkyl radical attacks the low electron density site on isoquinoline **1** which is activated by the TFA, accompanying with the formation of radical cation intermediate **I**. Subsequently, the intermediate **I** is oxidized by the 2D-COF-2$^+$ (oxidative potential= 0.65 V vs SCE in CH$_3$CN, Figure 1b), giving the alkylated isoquinoline cation **II** with the photocatalyst regeneration. Finally, the desired product is obtained *via* deprotonation.

Conclusions

In summary, an ultrastable olefin-linked two-dimensional covalent organic framework 2D-COF-2 was smoothly applied into the photocatalytic decarboxylative alkylations of heterocycles with NHPI esters. It offers an attractive alternative to commonly used homogenous photocatalysts and provides a greener and more rapid route towards precise synthesis of privileged alkylated heterocyclics. With the remarkable and persistent photoactivity, ultrastability under highly organic acidic conditions and excellent recyclability of 2D-COF-2, we expect that this successful application will stimulate more new usages for 2D-COFs catalysed photocatalytic organic transformations.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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