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Donor-acceptor type [4+3] covalent organic frameworks: sub-stoichiometric synthesis and photocatalytic application

Qiaobo Liao[†], Wentao Xu[†], Xin Huang, Can Ke, Qi Zhang, Kai Xi^{*} & Jin Xie^{*}

State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China

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Three unprecedented 2D [4+3] covalent organic frameworks (TTCOF-1, TTCOF-2, and TTCOF-3) have been prepared by substoichiometric condensation of tetratopic and tritopic monomers, overcoming the limitations of the design rules of conventional topologies. By reticulating the tetraphenylethylene (TPE)-based and triazine-based moieties into COF frameworks, novel electron donor-acceptor (D-A) type structures were obtained. These TTCOFs have good photocatalytic activity in aerobic $C(sp^3)$ –H bond functionalization and arylboronic acid oxidation driven by visible light, with yields up to 94%. This can expedite possibilities of COFs with new structural and topological complexities and can also expand the application of COF-based photocatalysis in synthetic chemistry.

COF, sub-stoichiometric synthesis, crystal engineering, photocatalysis, aerobic oxidation

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1 Introduction

Covalent organic frameworks (COFs), an intriguing class of crystalline porous organic materials, can be constructed by incorporating organic building blocks into extended periodic networks through strong covalent bonds [1–7]. Two-dimensional COFs have emerged in the past decade to be auspicious in photocatalysis due to their extended conjugation and periodic π - π arrays [8–15], in which the donoracceptor (D-A) structures are important to enhance their performances in optoelectronic devices and photocatalysis [11,16–21]. Generally, sophisticate monomers bearing specific moieties, such as triphenylene [16,18,20], pyrene [19,11,22], benzothiadiazole [18] are necessary for the synthesis of D-A COFs. However, the currently prevalent topologies usually lead to a very limited array of monomers

[†]These authors contributed equally to this work.

which can be used for the synthesis of D-A COFs [3,4,9,10]. For instance, tetraphenylethylene (TPE)-based units have previously been used as an electron donor [23-27] and the electron-deficient triazine ring has been esteemed as a good electron-acceptor [28-30]. Although they have been widely used to synthesize COFs [9,30-36], 2D COFs constructed with TPE-based and triazine-based monomers have not been reported previously. The key challenge stems from the undeveloped topology from tetratopic monomers with C_2 symmetry and tritopic monomers with C_3 symmetry. Therefore, it is still desired to broaden the topology diagram of 2D COFs to increase their diversity [37].

In the prevalent topology diagrams of COFs [32,37–40], the monomers are reacted stoichiometrically and the functional groups of the building blocks are completely consumed [33]. Accordingly, we rationalized that substoichiometric synthesis would be one feasible manner to diversify COF topologies. It is worth noting that very re-

^{*}Corresponding authors (email: xikai@nju.edu.cn; xie@nju.edu.cn)

cently Banerjee and Lotsch et al. [41] and Yaghi et al. [42] have reported several 2D COFs based on sub-stoichiometric condensation, opening a new door towards functionalized COFs. Since the symmetries of TPE-based monomers and triazine-based monomers are C_2 and C_3 , respectively, we envisioned that sub-stoichiometric [4+3]condensation of these monomers would be a good choice to fabricate D-A COFs. In this work, by linking tetratopic TPE-based monomers and the tritopic triazine-based monomers with π -conjugated spacers of the imine bonds, three novel D-A COFs (termed TTCOFs, tetratopic-tritopic covalent organic frameworks) with non-conventional topologies are constructed successfully in terms of [4+3] condensation, with potential application in photocatalysis (Figure 1). Importantly, TTCOF-2 is featured by its high crystallinity, and large porosity as well as the D-A structure, and shows outstanding performance for aerobic oxidation reactions under visible-light irradiation with high product vields up to 94%.

2 Experimental

2.1 Synthesis of TTCOFs

Synthesis of TTCOF-1. 20.0 mg (0.045 mmol) of (4,4',4",4"' (ethene-1,1,2,2-tetrayl) tetrabenzaldehyde (ETTB), 21.3 mg (0.06 mmol) of (2,4,6-tris(4-aminophenyl)-1,3,5-triazine (TAPT), 0.2 mL of 1,4-dioxane and 0.05 mL of 12 M aqueous acetic acid solution were charged into a 2 mL glass tube. The mixture was degassed by three freeze-pump-thaw cycles. The glass tube was flame-sealed under vacuum and then heated at 120 °C for 6 d. After cooling, the mixture was filtered through a 0.22 μ m PTFE membrane and washed with tetrahydrofuran (THF) several times to remove unreacted monomers, the catalyst and solvent. The filter cake was further purified by Soxhlet extraction using THF for 24 h, followed by drying under supercritical CO₂ flow. Yield: 86.3%.

Synthesis of TTCOF-2. 33.9 mg (0.045 mmol) of 4',4''',4''''', 4'''''''-(1,2-ethene-diylidene) tetrakis[1,1'-biphenyl]-4-carboxaldehyde (ETBC), 21.3 mg (0.06 mmol) of TAPT, 0.2 mL of *o*-DCB/*n*-butanol (v/v=7:3) and 0.05 mL of 12 M aqueous acetic acid solution were charged into a 2 mL glass tube. The mixture was degassed by three freeze-pump-thaw cycles. The glass tube was flame-sealed under vacuum and then heated at 120 °C for 5 d. After cooling, the mixture was filtered through a 0.22 µm PTFE membrane and washed with THF several times to remove unreacted monomers, the catalyst and solvent. The filter cake was further purified by Soxhlet extraction using THF for 24 h, followed by drying under supercritical CO₂ flow. Yield: 73.3%.

Synthesis of TTCOF-3. 23.6 mg (0.06 mmol) of 4,4',4", 4"'-(ethene-1,1,2,2-tetrayl)-tetraaniline (ETTA)), 31.5 mg (0.09 mmol) of 2,4,6-tris(4-formylphenyl)-1,3,5-triazine



Figure 1 Schematic representation of a donor-acceptor structure containing the electron donor tetraphenylethylene (TPE) and an acceptor, triazine (color online).

(TFPT), 0.2 mL of *o*-DCB/*n*-butanol ($\nu/\nu=7:3$) and 0.05 mL of 12 M aqueous acetic acid solution were charged into a 2 mL glass tube. The mixture was degassed by three freezepump-thaw cycles. The glass tube was flame-sealed under vacuum and then heated at 120 °C for 9 d. After cooling, the mixture was filtered through a 0.22 µm PTFE membrane and washed with THF several times to remove unreacted monomers, the catalyst and solvent. The filter cake was further purified by Soxhlet extraction using THF for 24 h, followed by drying under supercritical CO₂ flow for 3 h. Yield: 95.6%.

Synthesis of HCOF-1. 40.2 mg (0.30 mmol) of TA, 70.8 mg (0.20 mmol) of TAPT, 1.0 mL of *o*-DCB/*n*-butanol (v/v=7:3) and 0.1 mL of 6 M aqueous acetic acid solution were charged into a 5 mL glass tube. The mixture was degassed by three freeze-pump-thaw cycles. The glass tube was flame-sealed under vacuum and then heated at 120 °C for 3 d. After cooling, the mixture was filtered through a 0.22 µm PTFE membrane and washed with THF several times to remove unreacted monomers, the catalyst and solvent. The filter cake was further purified by Soxhlet extraction using anhydrous THF for 24 h, followed by drying under supercritical CO₂ flow. Yield: 41.8%.

2.2 Photochemistry part

1,2,3,4-tetrahydroisoquinoline derivatives **1** (0.2 mmol) and TTCOF-2 (6.0 mg, 0.0014 mmol) were placed in a transparent Schlenk tube equipped with a stirring bar. The solvents of MeNO₂ (2.0 mL) were added under air condition. The reaction mixture was stirred under the irradiation of two 45 W blue LEDs (distance app. 4.0 cm from the bulb) at room temperature for 18 h. When the reaction finished, the mixture was quenched with water and extracted with ethyl acetate (3×10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate).

3 Results and discussion

3.1 Characterizations of TTCOFs

In this work, three D-A type 2D COFs were prepared by [4+3] condensation of tetratopic TPE-based monomers with C_2 symmetry ETTB. ETBC and ETTA with tritopic triazinebased monomers with C_3 symmetry TAPT and TFPT (Figure 2). The resulting products are denoted as TTCOF-1 (from ETTB and TAPT), TTCOF-2 (from ETBC and TAPT) and TTCOF-3 (from ETTA and TFPT). By co-condensation of monomers in a flame-sealed glass tube at 120 °C, TTCOF-1 and TTCOF-2 were obtained as yellow powders and TTCOF-3 as a red powder, and all of them are insoluble in common organic solvents, such as acetone, dichloromethane, methanol, tetrahydrofuran, and N.N-dimethylformamide. The scanning electron microscopy (SEM) images (Figures S3-S5, Supporting Information online) reveal that these TTCOFs adopt irregular morphology with different dimensions which may be caused by polycrystalline nature of these COFs [43]. Thermogravimetric analysis (TGA) demonstrates that all three TTCOFs exhibit high thermal stability with the major derivative thermogravimetric (DTG) peaks over 500 °C under a N₂ atmosphere (Figures S6-S8). A decrease in the apparent mass of TTCOF-2 can be ascribed to water molecules absorbed into the channels. Elemental analysis of TTCOFs shows that C contents are below the theoretical values, while the H contents are larger than expected (Table S1, Supporting Information online). This result may stem from the absorbed water molecules, which is also consistent with TGA analysis.

3.2 Structural elucidation of TTCOFs

The powder X-ray diffraction (PXRD) patterns of all three TTCOFs show several strong diffraction peaks (Figure 3(a)). The main peaks of these TTCOFs possess small full-width at half-maximum (FWHM) values of 0.239, 0.214 and 0.229, respectively, confirming the crystalline nature of the



Figure 2 Schematic representation of the synthesis of TTCOFs by [4+3] condensation reactions (color online).



Figure 3 (a) PXRD patterns of TTCOFs. Insets: the corresponding stacking reflections. (b) The PXRD patterns of the as-prepared TTCOF-2 (blue curve), and TTCOF-2 after heating at 120 °C for 6 d (red curve). (c– e) HRTEM images of TTCOF-2 (scale bars: 5 and 10 nm). Insets: Fourier-filtered images of the selected regions in the red squares in the TTCOF-2 images (scale bars: 5 and 10 nm) (color online).

TTCOFs. Besides, the crystallite sizes estimated by Scherrer's equation using the Jade software (v. 6.5) [44] are 31.3, 65.5 and 46.6 nm, respectively. These results reflect highest crystallinity of TTCOF-2, which is further demonstrated by high-resolution transmission electron microscopy (HRTEM) (Figure 3(c-e)). Lattice fringes corresponding to main reflections (100), (120), (200) and (220) can be observed clearly from the images, agreeing well with PXRD results. Moreover, many smaller fringes with d-spacing distances less than 0.3 nm can also be found in Figure 3(e), which may attribute to the cutting effect [45]. Although a drop-off at around 100 °C is found in the TGA curve of TTCOF-2, its crystallinity remains almost intact when heated at 120 °C in air for 6 d (Figure 3(b)), revealing the excellent thermal stability of the crystalline structure. Considering that the planar triazine-cord monomers and the propeller-shaped TPE-based monomers afford highly crystalline 2D COFs [34,36,37], we envisioned that TTCOFs tend to adopt largely planar 2D structures. The insets of Figure 3(a) show stacking reflections of TTCOFs centered at 22.4°, 22.8° and 19.5°, respectively, suggesting the π - π stacking distances of 0.396 nm for TTCOF-1, 0.390 nm for TTCOF-2 and 0.455 nm for TTCOF-3. The stacking reflections provide proof toward our hypothesis for 2D structures of these TTCOFs.

Possible crystal models were therefore constructed based on the reasonable 2D tth and bex nets in the light of the reticular chemistry structure resource (RCSR) [46] using the Materials Studio software package. For both topologies, four possible stacking configurations, i.e., eclipsed (AA), staggered (AB) and two serrated stacking modes (a-AB and b-AB) were examined (Figure 4, Figures S9, S10). The calculated PXRD pattern of the unit cell with the b-AB stacking mode of bex net was found to match well with the experimental results from TTCOF-1 and TTCOF-2 (Figure 4(a), Figure S9(a), khaki curves), except for a weak reflection at 2.8° of TTCOF-1 which was not found in the simulated pattern. We posit that some of the ETTB linkers were absent, giving rise to the defective unit cell shown in Figure 4(f). One can clearly observe this peak accompanied with main reflections in the calculated pattern of the defective unit cell (Figure 4(a), light blue curve). In view of the relative intensities of peaks, the defective unit cell is speculated to be a fraction of the crystalline TTCOF-1. Conversely, the simulation results suggest that TTCOF-3, an isomer of TTCOF-1, adopts a **tth** net topology rather than a **bex** topology (Figure S10(a), red curve). Although Lan et al. [47] have reported two 3D COFs with ffc topology using a similar symmetrical combination of monomers, the simulated PXRD patterns of unit cells with this topology for TTCOFs fail to match the experimental patterns, ruling out this possibility in our case (Figure 4(a), Figures S9(a), S10(a)).

Nitrogen sorption analysis was carried out to determine the permanent porosity and pore size distributions of TTCOFs. For all samples, the N₂ isotherms measured at 77 K have a typical type I shape (Figure 5(a)) [9], suggesting that micropores exist in the TTCOFs. The Brunauer-Emmett-Teller (BET) surface area of TTCOF-2 is up to 1996 m² g⁻¹, calculated from the low-pressure region of the adsorption isotherm (Figure S12), and the total pore volume is $1.05 \text{ cm}^3 \text{ g}^{-1}$ $(P/P_0=0.99)$. The BET surface areas of TTCOF-1 and TTCOF-3 are calculated to be 978 and 740 m² g⁻¹ (Figures S11, S13), and their total pore volumes are 0.51 and $0.45 \text{ cm}^3 \text{g}^{-1}$, respectively. The porosity of TTCOF-2 is much higher than that of the other two TTCOFs, which may mainly originate from the higher crystallinity of TTCOF-2 [48]. To analyze the pore size distributions in TTCOFs, the adsorption isotherms were fitted using a nonlocal density functional theory (NLDFT) model (Figure 5(b)). The results reveal that TTCOF-1 has a microporous channel with average pore widths of 13.5 Å, which is in good agreement with the simulated structure with a b-AB stacking mode of bex



Figure 4 (a) Experimental and simulated PXRD patterns of TTCOF-1. The proposed unit cells of TTCOF-1 with **bex** topology: (b) the eclipsed (AA) mode, (c) the staggered (AB) mode, (d, e) the serrated stacking modes with adjacent sheets slipped by 1/2 of the unit cell distances along a axis (a-AB) and b axis (b-AB), respectively, (f) the defective unit cell based on **bex**-b-AB stacking mode. The proposed unit cells of TTCOF-1 with **tth** topology: (g) the eclipsed (AA) mode, (h) the staggered (AB) mode, (i, j) the serrated stacking mode with adjacent sheets slipped by 1/2 of the unit cell distances along a axis (a-AB) and b axis (b-AB). (k) The proposed 3D unit cell of TTCOF-1 with **ffc** topology. C: grey; H: white; O: red; N: blue (color online).

net. In terms of the preliminary analysis of TTCOFs, TTCOF-2 has a topologic structure with only one kind of micropore, which is similar to that of TTCOF-1. However, TTCOF-2 possesses two kinds of micropores with average pore widths of 13.5 and 17.2 Å. In addition, TTCOF-3 also has two main distributions at 5.0 and 14.4 Å, smaller than those of the predicted unit cell with the eclipsed mode of **tth** net (6.6 and 17.7 Å). It is noteworthy that the first pore is probably smaller than 5.0 Å, with the measuring range of 5–50 Å. These mismatches suggest that TTCOF-2 and TTCOF-3 possess the more complicated stacking modes than the eclipsed or staggered structures [49].

In the light of the dual-pore structures of TTCOF-2 and TTCOF-3, these TTCOFs were proposed to adopt slightly serrated stacking modes. According to the PSD results, either layers in the unit cells of TTCOF-2 and TTCOF-3 were displaced by 4.5 and 4 Å, respectively, to form serrated stacking modes (Figure 6(d, f)). All reasonable structures were geometry-optimized by the Forcite molecular dynamics module, giving rise to slightly inclined unit cells. The calculated PXRD patterns of the unit cells reproduce the experimental patterns well (Figure 6(a, c, e), black and green curves). Pawley refinement was carried out for the simulated structures of TTCOFs (Figure 6(a, c, e), red curves), and produced good agreement factors (TTCOF-1: R_{wp} =7.71%, $R_{\rm p}$ =4.28%, a=22.31 Å, b=44.77 Å, c=8.14 Å, a=94.16°, β =93.72° and γ =90.74°; TTCOF-2: R_{wp} =9.59%, R_{p} =7.03%, a=28.45 Å, b=61.98 Å, c=8.06 Å, $a=79.34^{\circ}$, $\beta=88.44^{\circ}$ and γ =87.39°; TTCOF-3: R_{wp} =3.71%, R_p =2.95%, a=49.20 Å, b=47.36 Å, c=9.25 Å, $\alpha=91.81^{\circ}$, $\beta=87.43^{\circ}$ and $\gamma=119.89^{\circ}$).



Figure 5 (a) Nitrogen sorption isotherms of TTCOFs at 77 K. (b) Pore size distribution (PSD) profile of TTCOFs, calculated from the nonlocal density theory model (color online).



Figure 6 Experimental PXRD patterns (black curve), Pawley-refined patterns (red curve) and simulated patterns (green curve) for (a) TTCOF-1, (c) TTCOF-2 and (e) TTCOF-3. (b) Top view and side view of the Pawley-refined unit cell of TTCOF-1 with b-AB stacking mode of **bex** net. (d) Top view and side view of the Pawley-refined unit cell of TTCOF-2 with 4.5 Å-serrated b-AB stacking mode of **bex** net. (f) Top view and side view of the Pawley-refined unit cell of TTCOF-3 with 4 Å-serrated AB mode for **tth** net. (g) The distances between uncondensed aldehyde groups and the nearest atoms on the frameworks (color online).

According to the Pawley-refined unit cell of TTCOF-3 with **tth** topology, the distances between the free aldehyde groups and the nearest atoms on the framework are \sim 3.0 Å away (Figure 6(g)). Due to the propeller shape of TPE-based moiety, the phenyl rings on the framework rotate to maximize the distances and so decrease the van der Waals interactions.

Abundant remnant aldehyde groups rather than amine groups are anchored on the backbones according to the predicted crystal results of TTCOFs. The FTIR spectra (Figure 7(a)) of all TTCOFs reveal the characteristic imine stretching mode at $\sim 1620 \text{ cm}^{-1}$, indicating the occurrence of imine condensation. Moreover, peaks at around 1700 cm⁻¹ arising from the stretching vibration band of C=O are much more intense than those of stoichiometric crystalline COFs such as HCOF-1 (synthesized using terephthalaldehyde and 2,4,6-tris(4-aminophenyl)-1,3,5-triazine, Figures S17, S18), indicating that there are free aldehvde groups remaining in the synthesized TTCOFs (Figure 7(a)). In contrast, the weak peaks at \sim 3300–3500 cm⁻¹ imply that the amine functionalities have been nearly exhausted during the condensation reaction (Figures S14-S16). Solid-state ¹³C cross-polarization magic angle spinning (CP-MAS) NMR spectroscopy further confirmed the presence of the unreacted aldehyde functionalities (Figure 7(b)). The characteristic signals at 159 and 190 ppm are assigned to the imine and the aldehvde groups, respectively. These intense signals of the aldehyde groups are comparable to those of the reported TPE-COF-II which has many remaining aldehyde groups [32], suggesting the signals arise not only from the edge groups [8] but also from those inside the lattice of the TTCOFs. Those results indicate that aldehyde groups are abundant in the frameworks, and further verify the unusual crystal structures of the TTCOFs. The foregoing results strongly suggest that



Figure 7 (a) FTIR spectra, (b) solid-state ¹³C CP-MAS NMR spectra, (c) UV-Vis spectra and (d) the estimated band gaps of TTCOFs (color online).

TTCOFs with sophisticated **bex** and **tth** topology were constructed successfully via sub-stoichiometric [4+3] condensation. By means of reversible coupling reactions and π - π stacking interactions [4], crystalline lattices stitched by TPE and triazine motifs are constructed, forming electron D-A structures in TTCOFs.

3.3 Photocatalysis

Recently, D-A type photocatalysts, such as organic types (carbazolyl dicyanobenzenes, acridiniums and pyryliums) [50-54] and MOFs [55,56], have been used widely in photoredox catalysis for organic synthesis. In view of the periodic D-A structures, the synthesized TTCOFs may have photochemical characteristics. Solid state diffuse reflectance UV/Vis spectra show that TTCOF-1 and TTCOF-2 possess similar absorptions with the strongest absorption peak at ~420 nm while TTCOF-3 has a red-shifted absorption peak at \sim 500 nm (Figure 7(c)), which is also shown by optical images (Figure S19). The optical band gaps of TTCOF-1, TTCOF-2 and TTCOF-3 calculated by the Kubelka-Munk function, are 2.04, 2.13 and 1.73 eV, respectively (Figure 7 (d)). The lower bandgap of TTCOF-3 may origin from the tth net which has a higher degree of conjugation. In comparison with the well-known C₃N₄ with a band gap of 2.78 eV [57], these TTCOFs show a narrower band gap and enhance the intensity of visible-light absorption, implying their potential as photocatalysts [58-61].

The $C(sp^3)$ -H bonds are ubiquitous in organic molecules. Visible-light-driven selective α -functionalization of tertiary amines affords a powerful platform with which to construct diverse amine derivatives under mild reaction conditions and thus has attracted significant attention in recent years [62– 67]. In our study, 2-phenyl-1,2,3,4-tetrahydroisoquinoline was selected as a substrate due to its appearance in a wide range of natural compounds [68] and its use in the aza-Henry reaction [69-73]. Based on the results from our UV/Vis absorption spectra, blue LEDs were used as visible light source. Screening of TTCOFs showed that TTCOF-2 was the most effective (entries 1-3, Table 1). Under irradiation by blue LEDs, the desired aerobic cross-dehydrogenative coupling between 2-phenyl-1,2,3,4-tetrahydroisoquinoline and nitromethane occurs smoothly with TTCOF-2 as a photocatalyst, furnishing a product (2a) in 89% yield (entry 2, Table 1). Since the use of blue LEDs, the model reaction can give the desired coupled product with and without TTCOF-2. In the presence of TTCOF-2, a slightly better result was obtained (entries 2 and 4, Table 1). The control experiments suggest that visible light and O₂ can promote aza-Henry reaction, which is consistent with König and Gschwind's work [71]. Accordingly, it is difficult to determine its catalytic reactivity. Much to our delight, under the irradiation with 23 W CFL, the use of TTCOF-2 as the heterogeneous

 Table 1
 Optimization of the reaction conditions^{a)}

	N _{Ph} MeNO ₂ , r	OF	Za NO ₂
Entry	Photocatalyst	Light source	Conversion (%) ^{b)}
1	TTCOF-1 ^{c)}	Blue LEDs	87
2	TTCOF-2 ^{d)}	Blue LEDs	99 (89)
3	TTCOF-3 ^{e)}	Blue LEDs	65
4	_	Blue LEDs	83
5	TTCOF-2	23 W CFL	70
6	_	23 W CFL	12
$7^{\rm f)}$	TTCOF-2	Blue LEDs	64
8 ^{g)}	TTCOF-2	Blue LEDs	10
9	Pd/Pt removed- TTCOF-2 ^{h)}	Blue LEDs	95

a) Reaction conditions: **1a** (0.2 mmol), TTCOF (6 mg), MeNO₂ (2 mL), air, blue LEDs, rt, 18 h. b) Determined by GC. The number in parentheses is the isolated yield. c) TTCOF-1 (6 mg, 0.002 mmol). d) TTCOF-2 (6 mg, 0.0014 mmol). e) TTCOF-3 (6 mg, 0.0008 mmol). f) argon atmosphere. g) Under dark conditions. h) Synthesized by monomers treated by a commercial scavenger agent to remove trace Pd and Pt.

photocatalyst can give a much better reuslt (70% versus 12%). In addition, we found that without the TTCOF-2, no reaction could occur for the reaction of oxidation of arylboronic acids to corresponding phenols (5c). Moreover, to exclude the possibility that cross coupling was catalyzed by residue Pd or Pt, Pd/Pt removed-TTCOF-2 was synthesized using monomer treated by a commercial scavenger agent to remove trace Pd and Pt (Table S2). The catalytic efficiency of this COF has almost not been changed, indicating that the residue of Pd and Pt catalytic role is less likely in these organic transformations (entries 9, Table 1). These control experiments may indicate the photocatalytic reactivity of prepared TTCOF-2.

As shown in Figure 8(A), direct aerobic cross-dehydrogenative coupling between 2-phenyl-1,2,3,4-tetrahydroisoquinoline and nitromethane or ketones is successful. Generally, TTCOF-2 shows a better photocatalytic activity for the electron-drawing substituents. A variety of N-aryltetrahydroisoquinolines can be employed to give the desired products (2a-2f and 3a-3f) in moderate to good yields. α aminonitriles are important building blocks for further subsequent transformations to α -amino acids [74]. With TTCOF-2 as a photocatalyst, selective α -cyanation can readily occur and the corresponding products (4a-4g) are produced in good to excellent yields. Recently, Wang et al. [75] acquired access to a series of ultrastable benzoxazolebased COFs, and showed that they can be successfully used in the photocatalytic transformation of arylboronic acids to phenols. In the light of Wang's work, we hypothesized that TTCOF-2 may catalyze the reaction for the synthesis of



Figure 8 The visible-light-mediated aerobic organic transformations catalyzed by TTCOF-2. (A) Selective $C(sp^3)$ –H bond functionalization: [a] 1 (0.2 mmol), TTCOF-2 (6.0 mg, 0.0014 mmol), MeNO₂(2 mL), air, blue LEDs, 18 h; [b] 1 (0.2 mmol), TTCOF-2 (6.0 mg, 0.0014 mmol), L-proline (20 mol%, 0.04 mmol), acetone (2 mL), air, blue LEDs, 24 h; [c] 1 (0.2 mmol), TTCOF-2 (6.0 mg, 0.0014 mmol), TMSCN (1.5 equiv., 0.3 mmol), MeCN (2 mL), air, blue LEDs, 24 h; (B) arylboronic acid (0.2 mmol), TTCOF-2 (4.0 mg, 0.00094 mmol), ⁱPr₂NEt (1.0 mmol), MeCN/H₂O (1.6/0.4 mL), air, blue LEDs, 24 h. [d] Without TTCOF-2 (color online).

phenols. When the reaction was carried out with 0.2 mmol scales, 4 mg TTCOF-2 showed an excellent catalytic activity and the corresponding phenol products were obtained in good yields (**5a–5d**). TTCOF-2 is easily recovered from the reaction mixture and excellent catalytic activity with 95% conversion was observed after 2 cycles (see Supporting Information online for details). Based on König's work [71], a possible reaction mechanism was proposed (Figure 9). Under irradiation, an electron in the unit of TTCOF-2 transfers to its electron acceptors. Thus this species absorbs an electron from tetrahydroisoquinolines (**1**) to generate radical cation, just like the excited [Ru(bpy)3]₂^{+*}. The following chemical bond formation steps are similar to the previous works [70,71].

4 Conclusions

In conclusion, we have prepared electron donor-acceptor 2D imine-linked TTCOFs via sub-stoichiometric [4+3] condensation. The TTCOFs obtained by the solvothermal condensation of an unconventional combination of C_2 symmetric and C_3 symmetric monomers, adopt unusual **tth** and **bex** net topologies. Evidence for this was obtained from various characterization methods including PXRD, N₂



Figure 9 The proposed mechanism (color online).

sorption, structural simulation and Pawley refinement. More interestingly, the TTCOFs adopt D-A structures with TPE moieties as donors and triazine moieties as acceptors, which enable the superior photoactivity of these COFs in the aerobic oxidation reaction. The TTCOFs bearing frustrated networks possess abundant unreacted aldehyde groups in the regular pores, allowing for downstream post-modification. Such TTCOFs have potential applications in gas separation, proton conduction and photo-catalyzed synthesis.

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