

# Unveiling Charge Dynamics in Acetylene-Bridged Donor $-\pi$ – Acceptor Covalent Triazine Framework for Enhanced Photoredox Catalysis

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**ABSTRACT:** Covalent triazine frameworks (CTFs) with donoracceptor motifs have been identified as prospective semiconducting materials for photocatalysis. Though donor-acceptor motifs can favor forward intramolecular charge separation, some cases still suffer from backward charge recombination, resulting in the decrease of the photocatalytic activity. Herein, acetylene-bridged CTFs bearing an extended donor- $\pi$ -acceptor motif was fabricated to prompt exciton dissociation. Experimental investigations and density functional theory calculations prove that the acetylene moiety can suppress backward charge recombination, minimize exciton binding energy, and enhance charge carrier lifetime, thereby prompting forward charge transfer/separation in comparison to the analogous one without acetylene. Thus, the acetylene-bridged CTFs showcased a higher photocatalytic activity for metal-free photocatalytic oxidative



amines coupling with oxygen under visible-light irradiation, and apparent quantum efficiency at 420 nm was achieved up to 32.3%, that is, twofold higher than the one without acetylene. Furthermore, the acetylene moieties can adsorb oxygen molecules and provide active sites to lower the energy barrier and thus significantly enable the photoredox catalysis. This work provides alternative insights into the design and construction of high-performance CTFs, with prospective applications in solar-to-chemical energy conversion. **KEYWORDS:** acetylene, covalent triazine frameworks, donor– $\pi$ –acceptor, charge transfer/separation, photocatalysis

# INTRODUCTION

Photoredox catalysis has become deemed as a promising alternative strategy in facilitating organic reactions to value-added products,<sup>1,2</sup> as it offers the possibility of using solar energy to enable numerous challenging chemical transformations,<sup>3-5</sup> even under mild conditions. Besides being thermodynamically allowed for photoredox catalysis, in general, an efficient photocatalyst also needs to possess enough advantages in kinetic aspects,<sup>6</sup> such as adsorption and activation for reactants, charge-separation/transfer efficiency, and subsequent charge utilization. Notwithstanding such guidance, attempting to precisely control these complicated kinetic behaviors is quite challenging. Tremendous efforts have been devoted on the pursuit of exploring some regulating strategies<sup>7-10</sup> and developing efficient photocatalysts in recent decades, especially for heterogeneous photocatalysis. However, to a certain degree, more or less restrictions, for example, tedious synthetic procedures, hampered redox ability, as well as limited charge utilization, are still involved in some cases. Consequently, constructing efficient heterogeneous photocatalysts with additional developments is urgently required.

Covalent triazine frameworks (CTFs),<sup>11–13</sup> emerging as a class of porous organic materials, have aroused extensive

interests in various fields because of their flexible structural designability, high chemical stability, and tunable functionality.<sup>14,15</sup> Their inherent semiconducting properties make them particularly attractive candidates for applications in photocatalysis.<sup>16</sup> CTFs, analogous to the chemical structure of g-C<sub>3</sub>N<sub>4</sub>, can be precisely fabricated using different nitrile precursors even at a low temperature.<sup>17,18</sup> By rationally choosing electron-donor building blocks connected to electron-acceptor triazine units, an intriguing donor–acceptor motif can be directionally constructed with modified band alignment and photoelectric property.<sup>19</sup> Along this line, recent years have also witnessed their promising potentials in photocatalysis, especially for photocatalytic H<sub>2</sub> evolution,<sup>20–27</sup> CO<sub>2</sub> reduction,<sup>28–33</sup> and organic transformations<sup>34–38</sup> under visible-light irradiation. Though donor–acceptor dyads enable

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**Figure 1.** (a) Schematic diagram of the photoexcited electron-transfer process in the D–A system and D– $\pi$ –A system. (b) Scheme of synthesis of CTF-1 and A-CTF-2 following acid-catalyzed trimerization.

to favor forward intramolecular charge separation, most examples still suffer from backward charge recombination simultaneously due to their charge attraction<sup>39</sup> as well as weak optical absorption in the visible-light region. Thus, it is essential to minimize the exciton binding energy and prompt charge separation in CTFs to attain a high quantum efficiency.<sup>40</sup> The unique  $\pi$ -conjugated structure with the donor-acceptor dyad endows them with a rather enhanced light-harvesting ability and mitigated charge recombination because of the larger delocalization and the extending migrating distance of charge carriers (Figure 1a).<sup>39,41,4</sup> Hence, we envisioned whether extending the conjugated structures or incorporating chromophores into the framework might modulate the electronic band structure and further promote charge transfer/separation in the skeleton by modulating the charge-transfer pathway.

In this work, two CTFs bearing donor– $\pi$ –acceptor (D– $\pi$ – A) motifs without or with acetylene as the bridge were fabricated by acid-catalyzed trimerization at a low temperature (Figure 1b). Their structures consisted of a central electronrich tertiary amine as the donor and electron-deficient triazine as the acceptor, which were linked by an extended  $\pi$ conjugation unit regardless of the acetylene  $(-C \equiv C -)$ moiety. Outcomes from comprehensive investigations and density functional theory (DFT) calculations reveal that the acetylene moiety in CTFs is crucial to modulate the electronic structure and photoelectric property of CTFs. In essence, the extended  $\pi$ -conjugation by the acetylene unit can not only inhibit backward charge recombination and thus energetically favor the separation and transfer of charge carriers but also boost the charge carrier migration lifetime from the donor to acceptor, giving rise to an enhanced photocatalytic activity. As suggested in these results, acetylene-bridged CTFs exhibited much enhanced photocatalytic performances for the metal-free photocatalytic oxidative homocoupling of primary amines using oxygen under visible-light irradiation, compared to that of CTFs without the acetylene linker. Last but not least, DFT calculations suggest that the acetylene moiety can also act as an adsorption site to facilitate oxygen adsorption and provide active sites to lower its energy barrier in the visible-light-driven oxidative coupling process. Consequently, it is believed that the strategy by integrating an alkyne moiety into the D- $\pi$ -A

motif can efficiently optimize the kinetics in electronic and adsorptive behaviors for enhanced photoredox catalysis.

### EXPERIMENTAL SECTION

Synthesis of CTF-1. A 50 mL Schlenk flask was charged with trifluoromethanesulfonic acid (TfOH) (400  $\mu$ L) in 2 mL of CHCl<sub>3</sub>, which was cooled to 0  $^{\circ}$ C. Compound 1 (109 mg) in 8 mL of chloroform (CHCl<sub>3</sub>) was added dropwise into the acid solution with stirring for 30 min at the temperature of 0 °C under an Ar atmosphere. The solution was stirred for another 1 h at 0 °C and then heated to 35 °C for 24 h to complete the trimerization of the terminal cyano groups. Once completed, a certain amount of NH<sub>3</sub>·H<sub>2</sub>O solution was added in the resulting solution until the reaction mixture became neutral or alkaline, and the mixture was subsequently stirred for another 2 h. The resultant solid precipitate was filtered; sequentially washed with excess water, acetone, tetrahydrofuran (THF), and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>); and dried at 70  $^{\circ}$ C under vacuum overnight, finally affording CTF-1 as a yellow powder (100 mg, 92%).

**Synthesis of A-CTF-2.** A 50 mL Schlenk flask was charged with TfOH (100  $\mu$ L) in 10 mL of CHCl<sub>3</sub>, which was cooled to 0 °C. Compound 2 (125 mg) in 8 mL of CHCl<sub>3</sub> was added dropwise into the acid solution with stirring for 40 min at the temperature of 0 °C under an Ar atmosphere. The solution was stirred for another 1 h at 0 °C and then heated to room temperature for 24 h to complete the trimerization of the terminal cyano groups. Once completed, a certain amount of NH<sub>3</sub>·H<sub>2</sub>O solution was added in the resulting solution until the reaction mixture became neutral or alkaline, and the mixture was subsequently stirred for another 2 h. The resultant solid precipitate was filtered; sequentially washed with excess water, acetone, THF, and CH<sub>2</sub>Cl<sub>2</sub>; and dried at 70 °C under vacuum overnight, finally affording A-CTF-2 as a dark yellow powder (104 mg, 83%).

General Procedure for the Photocatalytic Oxidative Coupling of Amines. The photocatalytic oxidative coupling of amines was conducted in a self-designed stainless steel reactor with a water bath for controlling the temperature, and a 300 W xenon lamp (15 A, PLS-SXE 300) with a 400 nm cut filter was used as a light source that illuminated the reaction mixture from the top of the reactor (the distance was approximate 8 cm). In a typical procedure, a photocatalyst

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Figure 2. (a)  ${}^{13}$ C CP/MAS NMR spectra of CTF-1 and A-CTF-2. (b) N<sub>2</sub> adsorption–desorption isotherms of CTF-1 and A-CTF-2. SEM images of (c) CTF-1 and (d) A-CTF-2. TEM images of (e) CTF-1 and (f) A-CTF-2.

(8 mg) and 0.2 mmol amines were first added into 2 mL of acetonitrile in a quartz glass vial, which was ultrasonically dispersed for 5 min. Three parallel vials were sealed in the reactor placed on a magnetic stirring apparatus, and five successive vacuum/oxygen cycles were conducted to remove air and charged with O<sub>2</sub> (99.99%) to 0.1 MPa. Prior to light illumination, the mixture was magnetically stirred for 30 min in darkness to reach an adsorption–desorption equilibrium and then irradiated by the 300 W Xe lamp for 4 h. For product analysis, the conversion and selectivity were quantified by an Agilent 7820A gas chromatography (GC) system with flame ionization detection using the area normalization method. All the products were identified by an Agilent 5975C gas chromatography–mass spectrometry (GC–MS) system.

**Characterization.** Fourier transform infrared spectra (FT-IR) in the 4000–400 cm<sup>-1</sup> regions were measured on a Nicolet iS10 spectrometer in transmission mode at room temperature. The solid-state <sup>13</sup>C cross-polarization magic-angle spinning nuclear magnetic resonance (CP/MAS NMR) spectroscopy was carried out on a Bruker AVANCE III model 600 MHz NMR spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo ESCALAB 250xi spectrometer. Powder X-ray diffraction (PXRD) patterns were obtained using a Bruker D8 AVANCE, with the Cu K $\alpha$  radiation source from 2 to 40° with a scanning rate of 1° min<sup>-1</sup>. Thermogravimetric analysis (TGA) was carried out on STA449C/QMS403C/ TENSOR27 from 30 to 800 °C under a nitrogen atmosphere with a heating rate of 10 °C min<sup>-1</sup>. Surface area and pore size distributions were measured by

nitrogen adsorption-desorption at 77 K on an Autosorb-iQ-MP analyzer . Surface area was obtained by the Brunauer-Emmett-Teller (BET) method, and pore size distribution was derived from the N<sub>2</sub> desorption branch using nonlocal DFT (NLDFT). Scanning electron microscopy (SEM) was recorded using a Hitachi SU8010 instrument. Transmission electron microscopy (TEM) was conducted using a JEOL JEM-2100F microscope. Photoluminescence (PL) spectra of the samples in solvents and solid powders were recorded at room temperature on a steady-state spectrofluorometer Edinburgh FS5. The ultraviolet-visible diffuse reflectance spectroscopy (UV/vis DRS) was performed on a Shimadzu UV-3600 spectrophotometer tested from 200 to 800 nm using  $BaSO_4$  as a reference. The electron spin resonance (ESR) measurements were analyzed by a Bruker A300 spectrometer at room temperature, with light irradiation using a 300 W Xe lamp. O<sub>2</sub> temperatureprogrammed desorption (TPD) with the TCD tests was conducted on an AutoChem II 2920 instrument from the temperature range of 50 to 500 °C.

Electrochemical and Photoelectrochemical Measurements. All the electrochemical and photoelectrochemical measurements were carried out on an electrochemical workstation (CHI 760E, CH Instruments Inc., Shanghai) *via* a standard three-electrode system. The working electrode was prepared as follows: 2 mg sample was dispersed in 500  $\mu$ L of dimethylformamide and then the mixture was ultrasonically dispersed for 30 min. Following that, 100  $\mu$ L of the slurry was taken out and dropped on 1 × 1 cm<sup>2</sup> indium tin oxide and dried at room temperature. Furthermore, Ag/AgCl electrode



Figure 3. Fluorescence spectra of (a) CTF-1 and (b) A-CTF-2 dispersed in various solvents (1.0 mg mL<sup>-1</sup>) under excitation at 365 nm.

(saturated KCl), platinum wire, and 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution were used as the reference electrode, auxiliary electrode, and electrolyte solution, respectively. Mott–Schottky (M–S) plots were recorded at a scan rate of 5 mV/s in the dark at different frequencies of 800, 1000, and 1500 Hz. The on–off transient photocurrent responses were recorded with a sampling interval of 20 s using a 500 W Xe lamp and a certain applied bias of 0.5 V. Electrochemical impedance measurements were recorded over a  $0.01-10^6$  Hz frequency range with a 5 mV amplitude.

DFT Calculation Methods. DFT calculations and the nonadiabatic molecular dynamics (NAMD) simulation were performed using a GPU-based code with a plane-wave basis, PWMAT.<sup>43</sup> Full structure relaxation was performed until the forces became lower than 0.01 eV/A. As a large vacuum spacing (20 Å) was used in our simulations, the planaraveraged electrostatic potential converged to a constant value far from the surface. The norm-conserving pseudopotentials and the generalized gradient approximation of the Perdew-Burke-Ernzerhof (PBE) functional were adopted.44 Meanwhile, we had employed the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional to obtain the accurate band structure.<sup>45</sup> The plane-wave cutoff energy was 50 Ry, and the k-point mesh is  $1 \times 1 \times 1$ . Test calculations showed that this cutoff and k-mesh were sufficient to obtain converged energies, nonadiabatic coupling coefficients, and force. Molecular dynamics (MD) simulations were performed at  $\sim$ 300 K under the NVE ensemble with the Verlet algorithm. The time step for MD simulations was 2.0 fs. About 50 states were used in the valence band to expand the hot-carrier wave function.46

### RESULTS AND DISCUSSION

**Synthesis and Characterization.** The two CTFs without acetylene (CTF-1) and with the acetylene unit (A-CTF-2) were synthesized by TfOH-catalyzed trimerization of tris-4,4',4"-(4-cyanophenyl)triphenylamine (1) and tris-4,4',4"-(4-cyanophenylethynyl) triphenylamine (2), respectively (Figure 1b). Various measurements were performed for their structural characterizations. The FT-IR spectra in Figure S1 show the characteristic signals of triazine ring at 1510 and 1358 cm<sup>-1</sup> for CTF-1 or 1502 and 1322 cm<sup>-1</sup> for A-CTF-2.<sup>18,47</sup> The concomitant attenuation in the intensity of the carbon–

nitrogen triple (C≡N) stretching vibration at 2221 or 2226 cm<sup>-1</sup> in comparison with their nitrile monomers also indicates the transformation of  $-C \equiv N$  into the triazine-conjugated structure. Solid-state <sup>13</sup>C CP/MAS NMR spectroscopy exhibits the characteristic signals of sp<sup>2</sup> carbon atoms in triazine rings at ~169 ppm (Figure 2a). Meanwhile, the sp<sup>2</sup> C–N at ~144 ppm for CTF-1 or A-CTF-2 and the sp carbon atom in acetylene for A-CTF-2 also apparently validate the integrity of their backbones, respectively.<sup>48,49</sup> These results were further confirmed by XPS analyses (Figure S2). High-resolution XPS spectra of C 1s and N 1s of CTF-1 and A-CTF-2 showcase the carbon (285.48 or 285.42 eV) and nitrogen (398.80 or 398.76 eV) of sp<sup>2</sup>-hybridized C=N bond, indicating the formation of the triazine ring.<sup>50-52</sup> Moreover, sp  $(C \equiv C)$ -hybridized carbons at 285.07 eV can be deconvoluted from the C 1s peak of A-CTF-2, further reflecting the presence of acetylene moiety in A-CTF-2.53 The PXRD patterns of CTF-1 and A-CTF-2 clearly suggest their amorphous nature with partial  $\pi - \pi$ stacked structures (Figure S3). TGA under N2 reveals that both CTF-1 and A-CTF-2 are chemically stable and possess good thermal stability up to 350 °C (Figure S4).

The porosities and specific surface areas of CTF-1 and A-CTF-2 were assessed by N<sub>2</sub> adsorption-desorption isotherms measured at 77 K, as shown in Figure 2b. CTF-1 displays a steep uptake in the low-pressure region  $(P/P_0 < 0.01)$  and a subsequent more gradual increase at high-pressure values, which is a typical type I isotherm with hysteresis. The hysteresis in the isotherm can be ascribed to the pores swelling with the increasing gas pressure. The curve of CTF-1 demonstrates the presence of micropores, and the pore size mainly distributed in 0.52 and 0.88 nm was calculated by NLDFT (Figure S5). The BET surface area was calculated to be 924 m<sup>2</sup> g<sup>-1</sup>. However, A-CTF-2 presents a type IV isotherm, suggesting the existence of mesopores and macropores, with the BET surface area being only 24 m<sup>2</sup> g<sup>-1</sup>. It is still unclear why the surface area of A-CTF-2 is so low, but similar observations are found for the CTFs prepared by acidcatalyzed strategy in previous works.<sup>25,48</sup> We suppose that the low surface area is probably caused by its rapid reaction and relatively low reaction temperature to avoid undesired side reactions; also, compound 2 is rather sensitive in the extremely acidic TfOH, leading to its carbonization, which can likely



**Figure 4.** Optical and electronic properties of CTF-1 and A-CTF-2. (a) UV/vis DRS spectra (the inset digital pictures show the color of CTF-1 (up) and A-CTF-2 (down)), (b) band gap determined from the Kubelka–Munk-transformed reflectance, (c,d) M–S plot measured in 0.2 M  $Na_2SO_4$ , with Ag/AgCl as the reference electrode in dark, (e) experimental estimated band structure diagrams, (f) steady-state PL emission spectra, (g) *I*–*t* curves, EIS Nyquist plots (h) in darkness and (i) under light illumination of CTF-1 and A-CTF-2.

cause the low surface area. The morphologies of CTF-1 and A-CTF-2 were then observed by SEM and TEM (Figures 2c–f and S6). CTF-1 presents the randomly stacked chunks with an angular shape in a wide range of sizes, whereas A-CTF-2 exhibits regular cluster-like nanospheres, with the dimensions in the ~460 nm range. By carefully observing the high-resolution TEM images in Figure S7, microporous channels can be clearly discerned in CTF-1; however, such channels are hardly seen in A-CTF-2, consistent with the N<sub>2</sub> sorption results.

**Photoelectric Properties.** The electronic properties of CTF-1 and A-CTF-2 were systematically investigated by photophysical and electrochemical analyses. Both CTFs contain a central tertiary amine donor with a  $\pi$ -cross-linker unit connected to the triazine acceptor. The chemical structure is favorable for electronic absorption and emission; thus, their optical properties were first investigated by fluorescence spectroscopy in solvents with various polarities. Compounds 1 and 2 were highly soluble in moderate polarity solvents and exhibited blue-green emissions under excitation at 365 nm (Figures S8 and S9). Upon dispersing the powder of CTF-1 in different solvents, orange or light green fluorescence was observed, and a distinct bathochromic shift of the emission

maxima was found with an increase in the polarity of the solvent (Figure 3a). In contrast, the suspensions of A-CTF-2 in the same solvents exhibited weak fluorescent colors, and varying the polarity of the solvents only resulted in a slight bathochromic shift (Figure 3b). Such a very weak solvato-chromic behavior of A-CTF-2 probably originates from the extended conjugated nature and periodical arrangement of the framework, which can stabilize well the excited-state intra-molecular charge transfer.<sup>54,55</sup> Additionally, the fluorescence intensity of A-CTF-2 is much weaker than that of CTF-1, likely arising from the greater  $\pi$ -stacking in the latter structure.<sup>56</sup>

Solid-state UV/vis DRS spectra exhibit an intrinsic absorption extending to the visible-light region, originating from their D–A interactions and  $\pi-\pi^*$  electron transition of the conjugated ring. Apparently, the absorption edge of A-CTF-2 is remarkably red-shifted in comparison with that of CTF-1 (Figure 4a), indicating that the extended  $\pi$ -conjugated structure along with the incorporation of the acetenyl group into the skeleton can enhance the light-harvesting ability in the visible region. The optical band gaps of CTF-1 and A-CTF-2 were calculated by the Kubelka–Munk function.<sup>57,58</sup> The band gaps were measured to be 2.46 eV for CTF-1 and 2.35 eV for A-CTF-2 (Figure 4b). To further determine the electronic





**Figure 5.** Energy band gap structures of (a) CTF-1 and (b) A-CTF-2 using DFT calculations. (c,d) Spatial distributions of VBM and CBM along with the projections of 3D band structures of (c) CTF-1 and (d) A-CTF-2 for the VBM and CBM in the  $K_x$ - $K_y$  plane, respectively. All energies were calculated with reference to the vacuum level. The brown, gray, and white balls represent C, N, and H atoms.

structures of CTFs, M–S measurements were conducted at three different frequencies to estimate their conduction band potentials ( $E_{\rm CB}$ ). The positive slopes regardless of the varied frequencies suggest the typical n-type semiconductor characteristic for CTFs. The derived flat band potentials ( $E_{\rm fb}$ ) of CTF-1 and A-CTF-2 were extrapolated to be about –0.88 and –0.71 V versus Ag/AgCl, respectively (Figure 4c,d). In general, it can be accepted that the  $E_{\rm CB}$  potential is approximately equal to the  $E_{\rm fb}$  potential in n-type semiconductors.<sup>59</sup> Thus,  $E_{\rm CB}$  of CTF-1 and A-CTF-2 are –0.88 and –0.71 V, respectively. Combined with the aforementioned optical band gap, the

valence band potentials ( $E_{\rm VB}$ ) of CTF-1 and A-CTF-2 can be calculated to be 1.58 and 1.64 V *versus* Ag/AgCl, respectively, according to the formula  $E_{\rm CB} = E_{\rm VB} - E_{\rm g}$ .<sup>60</sup> The corresponding band structure alignments of CTF-1 and A-CTF-2 are schematically illustrated in Figure 4e.

To reveal the kinetics of the photogenerated charge carriers, steady-state PL emission spectroscopy, transient photocurrent response (I-t) analysis, and electrochemical impedance spectroscopy (EIS) were comparatively conducted for CTF-1 and A-CTF-2. PL intensity in the solid state for A-CTF-2 is remarkably lower than that of CTF-1 (Figure 4f), which in

principle indicates the higher efficiency on the separation and transfer of photogenerated charge carriers for A-CTF-2.<sup>61</sup> The transient photocurrent responses in Figure 4g also exhibit a higher photocurrent density on A-CTF-2, which further illustrates the more efficient separation of photogenerated electron-hole pairs, indicating the promoted transfer kinetics of charge carriers.<sup>62</sup> The enhanced charge separation and transfer efficiency were also confirmed by EIS in the dark and under visible light. Obviously, A-CTF-2 presents a smaller arc radius and a lower resistance in charge transportation than that of CTF-1 (Figure 4h), and the arc radius is further decreased under visible light (Figure 4i), strongly suggesting that A-CTF-2 possesses superior charge-transfer efficiency,<sup>63</sup> in line with its efficient charge separation efficiency. These photoelectrochemical analyses provide solid proof that A-CTF-2 shows enhanced separation and migration of charge carriers, which can be attributed to the extended  $\pi$ -conjugated structure and migration distance of photogenerated charge carriers because of the incorporation of the acetenyl group into the skeleton.

**DFT Calculations.** For an in-depth understanding of the electronic structural features at the atomic level, the monolayers of CTF-1 and A-CTF-2 were investigated by DFT calculations. The light absorption and exciton formation processes from the electronic structure of the two CTFs were first simulated. The calculated band structures with an ideal infinite model shown in Figure 5a,b (upper panel) suggest the indirect band gaps of 2.55 and 2.36 eV for CTF-1 and A-CTF-2, respectively, which are in good agreement with the experimental values. In order to better understand the difference between the electronic structures of the two CTFs, we plot the total density of states (Figure S10). Compared with CTF-1, as the alkynyl group in A-CTF-2 reduces the energy of the conduction band minimum (CBM) state, electrons in the valence band maximum (VBM) state are more likely to be excited to form electron-hole pairs under light illumination. The reduction of the band gap can facilitate the utilization efficiency of the visible light. The simulated CBM and VBM (vs vacuum) of CTF-1 locate at -2.626 and -5.176 eV, and of A-CTF-2 at -2.828 and -5.233 eV, respectively (Figure S11).

Moreover, the VBM electron-state density distribution of CTF-1 spatially overlaps and is mainly distributed in the triphenylamine donor along with the benzene  $\pi$ -conjugation units. The CBM is only located over triazine acceptors (Figure 5c). This means that the charges can migrate from the tertiary amine and  $\pi$ -conjugation units to the triazine moiety under the light irradiation. A similar phenomenon can also be observed from A-CTF-2 (Figure 5d). Nevertheless, alkynyls also contribute some charges to the VBM; also, partial electrons can stay on the alkynyls in the CBM, which means that the alkynyl can disperse the charge concentration of the triazine unit. The donor part and acceptor part of the two CTFs are separated in space, so photogenerated electrons need to undergo a long-range charge transfer to recombine with holes. From the projections of the three-dimensional (3D) energy band structure of CTF-1 and A-CTF-2, the electronic structures of the VBM state of both are almost the same, but the compositions of the CBM state have distinct differences. Although the VBM and CBM of both COFs are composed of the p<sub>z</sub> orbitals of the C and N atoms, the energy band dispersion relationship of A-CTF-2 containing alkynyl groups is very different from that of CTF-1. The lowest point in the conduction bands of CTF-1 is at the edge of the first Brillouin

zone, while the lowest point in the conduction bands of A-CTF-2 is close to the  $\gamma$  point, as shown in Figure 5. The indirect band gap structures of both CTFs in Figure 5a,b suggest that the electronic transition process requires phonons to participate in changing the electron momentum and thus inhibit the recombination of electrons and holes. Such energy band structure significantly affects the migration of carriers. The effective carrier masses for the edge states of CTF-1 samples are  $m_{\rm h}^* = 1.71 m_0$  and  $m_{\rm e}^* = 0.844 m_0$ , while those for A-CTF-2 samples are  $m_{\rm h}^* = 1.45 m_0$  and  $m_{\rm e}^* = 0.352 m_0 (m_0$ denotes the electron rest mass). These results suggest that the incorporation of alkynyl groups causes a faster migration of the A-CTF-2 band-edge carriers, resulting in their easier transfer to the molecules from its framework. Furthermore, the larger relative effective mass  $(m_h^*/m_e^*)$  of A-CTF-2 also reflects its lower carrier recombination efficiency,<sup>64</sup> which strongly indicates a superior photocatalytic activity for A-CTF-2.

Additionally, in order to evaluate the lifetimes of the photoexcited carriers, we thus calculated the transition dipole moments  $(P_{a\rightarrow b} = \varphi_i | -\hat{r} | \varphi_i)^{65}$  between the ground state and first excited state of the two COFs. As shown in Figure 5a,b (lower panel), it is obvious that the electrons on the VBM of A-CTF-2 have greater transition probability and oscillator strength. The fluorescence lifetimes of COFs are simulated via  $au = \frac{3}{2*f^*\Delta E^2}$ , where the oscillator strength  $f = \frac{2}{3}\Delta E |\varphi_i| - \hat{r} |\varphi_i|^2$  and  $\Delta E$  is the energy difference between state  $i(\varphi_i)$  and state  $j(\varphi_i)$ , only considering the first excited state,<sup>66</sup> suggesting the fluorescence lifetimes of 11.2 and 13.5 ns for CTF-1 and A-CTF-2. The prolonged lifetime for A-CTF-2 further demonstrates the higher stabilization of carriers because of the existence of alkynyls. Furthermore, the charge separation and mobility were simulated by NAMD, with a hot hole distribution in VBM and a hot electron distribution in CBM (Figures S12 and S13). The results reveal that charge carriers directly migrate from the donor to acceptor along with the skeleton (Figure 6a,b), resulting in the construction of an internal electric field; also, the time of charge carrier mobility in A-CTF-2 is distinctly prolonged compared with that of CTF-1 due to the extended  $\pi$ -conjugation. For both the COFs, the hot hole relaxation time is much longer than the hot electron relaxation time, which proves that the relaxation process of the holes is the rate-determining step of electronhole pair recombination.<sup>46</sup> Correspondingly, the lifetime of the generated hot electrons and holes in A-CTF-2 is also longer than that of CTF-1. From the perspective of the hot carrier dynamic process, the hot carriers of A-CTF-2 have a thermal equilibrium time. The hot carriers would not immediately cool from the excited state to the ground state, as shown in Figure 6c,d. The alkynyl group of A-CTF-2 not only acts as a bridge for carrier transfer but also becomes a stable group for hot carriers. The incorporation of the alkynyl group in A-CTF-2 leads to a longer carrier migration distance, implying a better stabilization of electrons and holes in the excited state. The above discussion on the nonequilibrium kinetics of excitons provides us with a clear theoretical picture, which proves that the alkynyl group of A-CTF-2 is an important reason for its excellent photocatalytic performance.

**Photocatalytic Activities.** With the experimental and theoretical investigations on the photoelectric properties of CTF-1 and A-CTF-2, a visible-light-driven oxidative coupling reaction of primary amines was also conducted to evaluate



Figure 6. (a,b) Isosurface of the electron orbitals of magenta VBM and blue CBM (upper panel) and the charge transport processes (lower panel) for (a) CTF-1 and (b) A-CTF-2. (c) Hot electron and (d) hole carrier cooling time of CTF-1 and A-CTF-2 estimated by NAMD calculations.

their photocatalytic activities. Photocatalytic selective aerobic oxidation of primary amines to imines is a more fascinating alternative for oxidative coupling because of its environmentally benign process and mild conditions.<sup>67-69</sup> We first selected the conversion of benzylamine (BAN) into Nbenzylidenebenzylamine as a model reaction (Figure 7a). Either CTF-1 or A-CTF-2 could proceed smoothly and afford good conversions of BAN. The apparent quantum efficiency at 420 nm was estimated to be about 16.9% for CTF-1 and 32.3% for A-CTF-2. Apparently, A-CTF-2 showed a higher catalytic efficiency than the former. Control experiments revealed that the photocatalyst, visible light, and oxygen were all indispensable for this oxidation; otherwise, only little conversions were observed. The initial O<sub>2</sub> pressure was further investigated for the oxidation of benzylamine, and a slackened change was found with a gradually increasing O2 pressure, suggesting that the O2 pressure is not the key factor for this oxidation (Figure S14). In sharp contrast,  $g-C_3N_4$  only gave a 28.7% conversion under identical conditions. In addition, the photocatalyst concentration and different solvents were also investigated in detail. These results suggested the optimal concentration as 4.0 g/L (Table S1) and CH<sub>3</sub>CN as the optimal solvent (Table S2).

Apart from the excellent activities, catalyst recycling is also significant for heterogeneous catalysis; thus, the recyclability of our superior photocatalyst A-CTF-2 was examined for the model reaction after it was separated by simple filtration from the reaction mixture. A-CTF-2 remained highly active for at least five cycles (Figure 7b), and the FT-IR spectrum of the used A-CTF-2 was almost consistent with that of the fresh one (Figure S15), suggesting its excellent photochemical stability. Next, various substituted amines were tested for photocatalytic oxidative coupling with CTF-1 and A-CTF-2 under the



**Figure 7.** (a) Visible-light-driven oxidative coupling of benzylamine. (b) Stability of the A-CTF-2 photocatalyst. (c) Visible-light-driven oxidative coupling of various primary amines over CTF-1 and A-CTF-2. Reaction conditions: 0.2 mmol amines, 8 mg catalyst, 2 mL of CH<sub>3</sub>CN, 0.1 MPa O<sub>2</sub>, 4.0 h, room temperature, visible light ( $\lambda > 400$  nm); conversion and selectivity are determined by GC and GC–MS.



**Figure 8.** (a) Proposed mechanism for the photocatalytic oxidative coupling of benzylamine. (b) Adsorption energy barriers of  $O_2$  in different sites for CTF-1 and A-CTF-2. (c) Adsorption model of  $O_2$  in the acetylene unit of A-CTF-2. The brown, gray, pink, and red balls represent C, N, H, and O atoms, respectively.

optimal conditions, respectively (Figure 7c). Interestingly, all the amines bearing electron-donating or electron-withdrawing groups as substrates could furnish the corresponding imines in high conversions over A-CTF-2, whereas CTF-1 exhibited an obviously lower photocatalytic activity for these substrates. Furthermore, time-dependent experiments on the oxidative coupling of para-substituted BAN, including H, OCH<sub>3</sub>, CH<sub>3</sub>, F, Cl, and CF<sub>3</sub> groups, were conducted using A-CTF-2 to investigate the reaction kinetics (Figure S16a). Kinetic experiments showed a zero-order rate equation for the oxidative coupling of amines. Their Hammett plots have no reasonable linear relationship between  $log(k_X/k_H)$  and the Brown–Okamoto constant  $\sigma^+$  (Figure S16b), which can be attributed to the negligible influence of the substituent at the oxidation potential of amines, that is, all the benzylic amines have relatively low oxidation potentials.<sup>70</sup> These results also indicate that the steric effect is the main influencing factor for the reaction rate rather than the electronic effect.

To gain insights into the key active species involved in the photocatalytic oxidation, a series of trapping experiments using different scavengers were conducted, as shown in Table S3. After adding KI as a hole scavenger, the BAN conversion was drastically decreased, suggesting that the photogenerated holes were vital for the coupling reaction. With AgNO<sub>3</sub> as the electron scavenger, the reaction was also inhibited. Furthermore, evident decreases in BAN conversions were observed in the presence of *p*-benzoquinone as a superoxide radical anion  $(O_2^{\bullet-})$  scavenger and 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a singlet oxygen  $({}^{1}O_2)$  scavenger, indicating

that both  $O_2^{\bullet-}$  and  ${}^1O_2$  as reactive oxygen species (ROS) participated in this photocatalysis. The addition of t-BuOH and catalase exhibited a negligible decrease in the conversion, which might rule out the existence of the hydroxyl free radical ( $^{\circ}$ OH) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) during the photocatalytic process. To further verify the ROS  $O_2^{\bullet-}$  and  ${}^1O_2$ , the ESR measurement was exploited with 5,5-dimethyl-pyridine-Noxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidone (TEMP) as trapping agents<sup>72</sup> (Figure S17). ESR signals for  $O_2^{\bullet}$ captured by DMPO obviously increased under light illumination for 3 min, and the signals were decreased after adding BAN into the mixtures; also, the characteristic ESR signals of the TEMPO radical, a stable nitroxide that was produced by the reaction between TEMP and <sup>1</sup>O<sub>2</sub>, also showed similar results. These observations collectively corroborate that  $O_2^{\bullet-}$ and <sup>1</sup>O<sub>2</sub> synergistically serve as the main ROS for the photocatalytic oxidation reaction.

Based on the experimental and computational results, a tentative mechanism for the photocatalytic oxidative coupling of benzylamine with different CTFs is illustrated in Figure 8a. Both CTFs are first photoexcited to produce excitons, bound electron-hole pairs, that further dissociated into free charge carriers under visible-light irradiation. In CH<sub>3</sub>CN, O<sub>2</sub> is reduced to  $O_2^{\bullet-}$  with photogenerated electrons, which is followed by the oxidation of the latter with the remaining hole to  ${}^{1}O_2$  on the surface of CTFs,<sup>73</sup> whereas the photogenerated holes mainly participate in the oxidization of BAN into its cationic radical form. Both CTF-1 and A-CTF-2 possess sufficiently reductive and oxidative potentials to support the

redox process.<sup>67</sup> In this photoredox process, the adsorption of O2 and benzylamine on CTFs is a crucial step to reduce or oxidize them into active species; thus, DFT calculation was performed to examine their adsorption energies  $(E_{abs})$ . The  $E_{\rm abc}$  values of A-CTF-2 for O<sub>2</sub> molecules in the tertiary N and triazine N active sites are slightly lower than that of CTF-1 (Figure 8b). Notably, the calculation results reveal that the acetylene moieties in A-CTF-2 can adsorb O2 molecules and provide active sites to lower the energy barrier of  $O_2$  (-0.958) eV), which is much lower than that of the N active sites (Figure 8b), thus indicating that acetylene moieties are more active for adsorbing O2 molecules and promoting the ROS formation by the reduction of electrons (Figure 8c). The adsorption of O<sub>2</sub> on these CTFs can also be confirmed by O<sub>2</sub>-TPD (Figure S18). This peak at about 400 °C corresponding to the chemisorption of O<sub>2</sub> species in A-CTF-2 is much stronger than that of CTF-1, further indicating that the alkynyl group can provide additional adsorbtion sites for oxygen species. Furthermore, the  $E_{abs}$  value of A-CTF-2 for benzylamine (-0.765 eV) is also lower than that of CTF-1 (-0.368)eV). As a consequence, incorporating alkynyl groups can simultaneously promote the adsorption of O<sub>2</sub> and benzylamine on A-CTF-2, which is favorable for enhancing the photocatalytic efficiency. The resulting  $O_2^{\bullet-}$  and  ${}^1O_2$  reacted with the formed cationic BAN with the generation of hydroperoxy (phenyl)methanamine intermediate with  $H_2O_2$ . The trapping experiment using N,N-diethyl-1,4-phenylenediamine without or with A-CTF-2, and for the model reaction, was then conducted to verify this process, which was monitored by an UV/vis spectrometer (Figure S19).<sup>74</sup> The gradually increasing intensity of the absorption peak at 500 nm was observed; also, the signal intensity with A-CTF-2 was obviously higher than that without A-CTF-2, suggesting that A-CTF-2 can assist the formation of  $H_2O_2$ . The resulting benzylimine then reacts with another BAN to give N-benzyl-1-phenylmethanediamine as the intermediate. After this, the final coupled product is generated through the elimination of ammonia.

# CONCLUSIONS

In summary, two new CTFs containing  $D-\pi-A$  motifs without or with acetylene cross-linkers were successfully synthesized via the trimerization of nitrile monomers. Their chemical structures consisted of a central electron-rich tertiary amine as the donor and electron-deficient triazine as the acceptor, which were connected by an extended  $\pi$ -conjugation. The comprehensive investigations based on photoelectric properties and DFT calculations suggest that the acetylene moiety as a  $\pi$ -cross-linker unit incorporated into the CTF skeleton is crucial to modulate the electronic band structures and photoelectric properties of CTFs and prompt exciton dissociation, which in essence inhibits backward charge recombination and minimizes exciton binding energy, thereby improving the separation and transfer of charge carriers, thus giving rise to the improvement of the photocatalytic activity. Photocatalysis experiments for the metal-free photocatalytic oxidative coupling of primary amines using oxygen show significantly enhanced photocatalytic performances for acetylene-bridged CTFs in comparison to that of CTFs without the acetylene linker. DFT calculations reveal that the acetylene moiety can not only improve the photoelectric property but also facilitate oxygen adsorption in the visible-light-driven oxidative coupling reaction. These present results further provide important insights into the design and construction of high-performance CTFs, with prospective applications in solarto-chemical energy conversion.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.1c01794.

Materials and experiment methods, structural analyses of compounds 1 and 2, and additional results and discussion (PDF)

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#### Notes

The authors declare no competing financial interest.

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