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## A Covalent Triazine-based Framework Consisting of Donor-Acceptor Dyads for Visible-Light-Driven Photocatalytic CO<sub>2</sub> Reduction

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Abstract: Photocatalytic conversion of CO2 into value-added chemical fuels is a promising approach to address the depletion of fossil energy and environment-related concerns. Tailor-making electronic properties and band structures of photocatalysts are pivotal to improve their efficiency and selectivity in photocatalytic CO2 reduction. Herein, we report a covalent triazine-based framework containing electron-donor triphenylamine and electronacceptor triazine components (DA-CTF). The engineered mconjugated electron donor-acceptor dyads in DA-CTF not only optimize the optical band gap, but also contribute to visible light harvesting and migration of photoexcited charge carriers. The activity of photocatalytic CO2 reduction under visible light is significantly promoted when compared with those in traditional g-C<sub>3</sub>N<sub>4</sub> and reported covalent triazine-based frameworks. This study provides molecular-level insights into mechanistic understanding for photocatalytic CO<sub>2</sub> reduction.

#### Introduction

To address ever-increasing energy demands and environmentrelated concerns, the utilization of clean and renewable solar energy for the production of chemical fuels has attracted widespread attentions.<sup>[1]</sup> Photocatalytic reduction of CO<sub>2</sub> into value-added chemicals is of particular interests owing to its double benefits for enriching energy supply and mitigating CO<sub>2</sub> pollution.<sup>[2]</sup> A variety of semiconductor-based photocatalysts with suitable band gaps for CO<sub>2</sub> reduction have been reported,<sup>[3]</sup> but most of them have been focused on inorganic semiconductors,<sup>[3b,d]</sup> the limited variability in these inorganic

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photocatalytic materials is disfavorable for the modulation of electronic properties and band structures. Moreover, rapid recombination of photogenerated electrons and holes as well as low adsorption ability of CO<sub>2</sub> molecules on the semiconductor surface have inhibited the conversion efficiency and selectivity.<sup>[4]</sup> Hence, the design and development of one type of new photocatalytic systems that enable the efficient fixation/reduction of CO<sub>2</sub> are highly desirable to realize efficient photochemical transformation of CO<sub>2</sub>.

The conjugated microporous polymers with semiconductor properties have been extensively employed in photocatalytic organic reactions to complement inorganic counterparts.<sup>[5]</sup> They possess tremendous advantages in terms of processability, sustainability and tunable properties.[5b] Most attractively, their synthetic modularity provides rich options for modulating their porosities, band structures and interfacial properties at molecular level for photochemical applications.<sup>[6]</sup> These unique properties have endowed them promising applications in phototransistors,<sup>[7]</sup> photovoltaic devices<sup>[8]</sup> and photocatalysis.<sup>[5a]</sup> Recently, highly efficient photocatalytic hydrogen evolution reaction<sup>[9]</sup> and oxygen evolution reaction<sup>[10]</sup> based on conjugated microporous polymers have been demonstrated, some of them have exhibited comparable even superior photocatalytic activities over inorganic semiconductors in the water splitting reactions. However, their use in photocatalytic CO<sub>2</sub> conversion is still rare<sup>[11]</sup> because of the mismatched band position to satisfy high overpotential. It is a daunting challenge to seek for a facile approach to tailor-make suitable energy levels and improve the charge/electron mobility, and thus enhancing the photocatalytic efficiency. One of feasible methods is the rational design of the conjugated microporous polymers with alternate electron donoracceptor dyads in the backbone based on molecular design strategy.

Covalent triazine-based frameworks (CTFs) could be a promising candidate for this purpose because of their high chemical stability, large surface area, favorable semiconductor behavior and facile synthetic process.<sup>[12-14]</sup> By carefully choosing the electron-donor building units connected to the electronacceptor triazine units, the energy band structure and photoconductive properties of CTFs could be modified. The extended  $\pi$ -conjugated structure in CTFs with donor-acceptor dyads could maintain the maximum range of visible light absorption and simultaneously permit high degree of intramolecular electron transfer in photocatalytic reactions. [12c,13] Recent studies have revealed that triazine rings in CTFs could accelerate the adsorption and activation of CO2, and great achievements have been achieved in CO2 storage and separation using CTFs.<sup>[14]</sup> It could be anticipated that CTFs with narrow band gap and extended π-conjugated systems will be

ideal photocatalysts for CO<sub>2</sub> reduction. As a proof-of-concept study, herein, we report a covalent triazine-based framework consisting of electron-donor triphenylamine and electron-acceptor triazine components (DA-CTF) for photocatalytic CO<sub>2</sub> reduction under visible light irradiation. High photocatalytic performance has been validated to originate from alternate electron donor-acceptor dyads in DA-CTF. The well-defined structure in DA-CTF enables to better understand photocatalytic processes and redox mechanism in CO<sub>2</sub> photoreduction.

#### **Results and Discussion**



Figure 1. (a) Schematic illustration for the synthesis of DA-CTF. (b)  $N_2$  (Inset is pore size distribution) and (c) CO\_2 sorption isotherms for DA-CTF.

DA-CTF was readily prepared through cyclotrimerization of cyano groups in 4,4',4"-nitrilotribenzonitrile in the presence of trifluoromethanesulfonic acid (Figure 1a). The formation of DA-CTF was confirmed by Fourier Transform Infrared (FTIR) spectroscopy, solid state <sup>13</sup>C NMR spectrum and X-ray photoelectron spectroscopy (XPS) analysis. In the FTIR spectrum of DA-CTF, the emergence of the peaks at 1362 and 815 cm<sup>-1</sup> suggests the formation of triazine rings.<sup>[14d]</sup> The characteristic peak of the cyano group at 2220 cm<sup>-1</sup> is significantly attenuated, which indicates that 4,4',4"nitrilotribenzonitrile is highly polymerized (Figure S1). In solid state <sup>13</sup>C NMR spectrum of DA-CTF, the peak at 171 ppm is attributed to the carbon atoms of triazine ring, other peaks at 150 and 128 ppm are assigned to phenyl carbon atoms (Figure S2). X-ray photoelectron spectroscopy (XPS) survey spectrum of DA-CTF provides three types of signals at 285, 399 and 532 eV, which correspond to carbon, nitrogen and oxygen, respectively (Figure S3a). The high-resolution N 1s XPS spectrum shows two dominant binding energy peaks, the peak at 398.5 eV is assigned to nitrogen atoms of triazine ring, while the peak at 399.8 eV corresponds to the overlapped nitrogen atoms in triphenylamine moiety and the unreacted cyano group

(Figure S3b), which is consistent with FTIR results. Fieldemission scanning electron microscopy (SEM) images show that DA-CTF is mainly composed of nanosheets (Figure S4). Thermogravimetric analysis (TGA) indicates that DA-CTF is stable before 350  $^{\circ}$ C (Figure S5).

The porosities of DA-CTF were investigated by N<sub>2</sub> sorption experiment at 77 K (Figure 1b). The BET surface area and pore volume of DA-CTF are 715  $m^2~g^{\text{-1}}$  and 0.35 cm  $^3~g^{\text{-1}},$  respectively. The pore size of DA-CTP is mainly centered at 1.2 nm as determined by nonlocal density functional theory.<sup>[15]</sup> The CO<sub>2</sub> uptake amount of DA-CTF at 273 K and 1 atm is up to 2.5 mmol g<sup>-1</sup> (Figure 1c). The absorption selectivity of CO<sub>2</sub>/N<sub>2</sub> at 273 and 295 K are 24.51 and 20.46, respectively (Figure S6).The appreciable amounts of CO2 adsorption are ascribed to the combination of microporous character and nitrogen-rich framework.<sup>[16]</sup> The isosteric heat of adsorption (Qst) at zero coverage of DA-CTF is 17.8 kJ mol<sup>-1</sup> (Figure S7), which indicates CO<sub>2</sub> sorption is mainly physisorption (< 40 kJ mol<sup>-1</sup>) other than chemisorption.<sup>[16b]</sup> The reversibility of the isotherms suggests that the interaction between CO<sub>2</sub> and DA-CTF is weak enough for regeneration without introducing any external thermal energy.<sup>[16b]</sup> These results have demonstrated that DA-CTF holds great promises for the application in CO<sub>2</sub> catalytic conversion.



Figure 2. (a) UV-vis DRS spectra of DA-CTF and CTF-T1 (Inset is the picture of DA-CTF), (b) Band gap of DA-CTF obtained from UV-vis DRS. (c) The energy band gap structure and (d) the total and partial density of states of DA-CTF.

Different from black CTFs prepared by ZnCl<sub>2</sub>-catalyzed cyclotrimerization of cyano-containing aromatic building blocks,<sup>[17]</sup> DA-CTF prepared by acid-catalyzed reaction is yellow (inset in Figure 2a). UV-visible diffuse-reflectance spectrum (UV-Vis DRS) of DA-CTF shows a broad absorption band up to 700 nm, the addition of 2,2'-bipyridine and Co<sup>2+</sup> has no obvious effect on the absorption of DA-CTF (Figure 2a). A maximum absorption peak at 400-550 nm is assigned to the  $\pi$ - $\pi$ \* transitions of the conjugated aromatic frameworks. Compared with light-harvesting efficiency of CTF-T1 prepared from 1,4-dicyanobenzene,<sup>[18]</sup> the enhanced light absorption of DA-CTF is

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most likely attributed to the introduction of electron-donor triphenylamine group. The band gap of DA-CTF from UV-Vis DRS is 2.35 eV (Figure 2b), which is narrower than that of CTF-T1 (2.94 eV)<sup>[18]</sup> and reported covalent organic frameworks.<sup>[10a,19]</sup> The Mott-Schottky curves indicate a typical n-type plot for DA-CTF (Figure S8). The flatband potential of DA-CTF is determined to be -0.92 eV vs. NHE. Combined with the UV-vis DRS results, the corresponding valence band of DA-CTF is estimated to be 1.43 eV vs. NHE (Figure S9). To further analyze the electronic structure, the density of states and band-gap energy of DA-CTF were calculated using density functional theory.<sup>[20]</sup> The calculated band gap energy for DA-CTF is 1.86 eV (Figure 2c), where the valence band maximum (VBM) below the Fermi level mainly consists of the states of carbon and nitrogen atoms (Figure 2d), while the conduction band minimum (CBM) is dominantly composed of the states of carbon and a small contribution from nitrogen atoms. The states of hydrogen atoms are not involved in VBM or CBM around the EF level. The band gap energy of DA-CTF is slightly lower than the calculated value of CTF-1 (Eg = 2.56 eV) (Figure S10), which is in good agreement with the optical measurements. The introduction of triphenylamine group into the framework results in narrow band gap, a negative shift for the conduction band level is about 0.73 eV, while the valence bands are still retained (Figure S11). Notably, the edge of the conduction band of DA-CTF is more negative than E<sup>0</sup>(CO<sub>2</sub>/CO) (-0.53 V vs. NHE),<sup>[21]</sup> which indicates that photogenerated electrons and holes in the irradiated DA-CTF can react with adsorbed CO<sub>2</sub> to generate CO.



**Figure 3.** (a) Photoluminescence spectrum of DA-CTF (Inset pictures show sample with and without UV-light irradiation at 365 nm). (b) Room-temperature EPR spectra measured with and without light irradiation. (c) Photocurrent response and (d) EIS Nyquist plots for DA-CTF and CTF-T1.

DA-CTF emits green light centered at 520 nm upon excitation at 365 nm (Figure 3a). The room-temperature electron paramagnetic resonance (EPR) spectrum of DA-CTF exhibits paramagnetic absorption signals with the g value of 2.0038 and 2.0015 (Figure 3b). In sharp contrast, no apparent EPR signal is observed for CTF-T1 either in the dark or upon visible light irradiation. The EPR comparison suggests that the introduction of electron-donor triphenylamine components extends the  $\pi$ -conjugated system of the material, which could efficiently improve the photoinduced production of radical pairs.<sup>[22]</sup> DA-CTF presents a reproducible photocurrent response under visible light irradiation (Figure 3c). The photocurrent of the DA-CTF electrode is much larger than that of the CTF-T1 electrode. The electrochemical impedance spectroscopy (EIS) measurements show that the semicycle arc radius of Nyquist plot in DA-CTF is remarkably smaller than that of CTF-T1 (Figure 3d), which suggesting that fast interfacial charge transfer in DA-CTF,<sup>[23]</sup> thus improving separation efficiency of photoinduced electrons and holes.



**Figure 4.** (a) Kinetic profile for the production of CO and H<sub>2</sub>. (b) Effects of the Co<sup>2+</sup> content on CO and H<sub>2</sub> production in the initial 1 h. (c) Wavelength-dependent CO production in photocatalytic CO<sub>2</sub> reduction. (d) Recyclability of DA-CTF in the photocatalytic CO<sub>2</sub> reduction. Reaction conditions: DA-CTF (30 mg), CoCl<sub>2</sub>·6H<sub>2</sub>O (3.0  $\mu$ mol), 2,2'-bipyridine (0.1 mmol), CO<sub>2</sub> (1 atm), solvent (2 mL), TEOA (1 mL), visible light irradiation ( $\lambda \ge$ 420 nm).

Photocatalytic CO<sub>2</sub> reduction was initially performed in acetonitrile solution containing Co(bpy)<sub>3</sub><sup>2+</sup> (bpy is 2,2'-bipyridine) as a cocatalyst and triethanolamine (TEOA) as a sacrificial electron donor. CO (9.3 umol), H<sub>2</sub> (4.2 umol) and trace amount of CH<sub>4</sub> were evolved under visible light irradiation ( $\lambda \ge 420$  nm) for 2 h (Figure 4a). Prolonged reaction time increased the evolution amount of both CO and H<sub>2</sub>. The ion chromatograph analysis shows that formate amount in liquid phase is only 6.21 ppm, which is negligible in this reaction system. To validate the source of CO and CH4, an isotopic labeling experiment was performed in the presence of <sup>13</sup>CO<sub>2</sub> under idential photocatalytic conditions, and the products were analyzed by gas chromatography and mass spectra. As shown in Figure S12, the peaks at m/z = 29 and m/z = 17 correspond to <sup>13</sup>CO and <sup>13</sup>CH<sub>4</sub>, respectively, indicating that the carbon source of CO and CH<sub>4</sub> originate from CO2, not DA-CTF. The evolution of the trace amount of CH<sub>4</sub> is probably attributed that the eight-electron transfer process, which unfavorable in kinetics when compared with two-electron process for the evolution of CO.<sup>[24]</sup>

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The effects of Co<sup>2+</sup> and 2,2'-bipyridine conents on photocatalytic activity were also studied. With increasing amounts of  $Co^{2+}$  from 1 to 3  $\mu$ mol, CO production increased and reached a maximum value of 4  $\mu$ mol in 1 h. Excessive Co<sup>2+</sup> (5  $\mu$ mol) led to decreased photocatalytic activity in the production of both CO and H<sub>2</sub> (Figure 4b). The content of 2,2'-bipyridine shows a similar influence trend on the evolution of CO and H<sub>2</sub> (Figure S13). Upon fixing Co<sup>2+</sup> content at 3 umol, the evolution of both CO and H<sub>2</sub> was accelerated before the contents of 2,2'bipyridine rise to 100 and 150 µmol, which suggests that excess 2,2'-bipyridine is required in this catalytic system because the photocatalytic reaction was performed in acetonitrile, there is a competition coordination between 2,2'-bipyridine and acetonitrile with Co<sup>2+,[25]</sup> However, when 200 µmol of 2,2'-bipyridine was used in the catalytic system, both CO and H<sub>2</sub> production decreased, which is probably attributed that overmuch 2,2'bipyridine suppresses the formation of [Co(bpy)<sub>2</sub>(MeCN)-CO<sub>2</sub>]<sup>1+</sup> intermediates.<sup>[25]</sup> The photoreduction activity of DA-CTF containing as-synthesized Co(bpy)32+ was also investigated, 0.39 umol CO and 0.28 umol H<sub>2</sub> were generated. Notably, when the mixture of DA-CTF (30 mg), Co(bpy)<sub>3</sub>Cl<sub>2</sub> (3.0 µmol) and 2,2'bipyridine (91 µmol) was used, the evolution amount of CO and H<sub>2</sub> is very close to that in the optimized catalytic system consisting of DA-CTF (30 mg), CoCl<sub>2</sub>·6H<sub>2</sub>O (3.0 µmol) and 2,2'bipyridine (100  $\mu$ mol). The investigation of a variety of solvents revealed that MeCN was superior to DMF and THF (Figure S14). However, only trace amount of CO was detected when the reaction was performed in neat water. Interestingly, when the catalytic reaction was carried out in DEF, a large amount of H<sub>2</sub> with a small amount of CO was generated. Among the transition metal salts tested, CoCl<sub>2</sub> was found to be more effective than FeCl<sub>3</sub>, NiCl<sub>2</sub> and MnCl<sub>2</sub> (Figure S15). The dependence of CO production on irradiation wavelength showed that the trend of CO generation matched well with the photon absorption characteristics of DA-CTF (Figure 4c), confirming that the reaction was indeed induced by light excitation of DA-CTF.<sup>[12c]</sup> The apparent quantum yield of photocatalytic CO<sub>2</sub> reduction is estimated to be 0.62% upon monochromatic irradiation at 420 nm. For comparison,  $g-C_3N_4$  and CTF-T1 were employed as photocatalysts under the identical conditions, both samples showed negligible catalytic activity, indicating the cooperative interactions between triphenylamine donor and triazine acceptor in DA-CTF are responsible for photocatalytic CO2 reduction. The catalytic system possesses excellent recyclability, no apparent deactivation was observed after consecutive photocatalytic CO2 reduction under visible light irradiation for five runs (Figure 4d). The FTIR spectrum of recovered DA-CTF is identical with that of as-prepared DA-CTF, suggesting excellent stability and durability of DA-CTF in photocatalytic CO2 reduction (Figure S16).

Control experiments of photocatalytic  $CO_2$  reduction were also carried out under the same conditions. No appreciable  $CO_2$ reduction was detected in the absence of either cobalt ion or 2,2'-bipyridine or both of them, suggesting the cooperative effect of cobalt ion and 2,2'-bipyridine in the photocatalytic system. Notably, this catalytic system is also effective for low concentration of  $CO_2$ . When the reaction was performed using

the mixture gas of 10% CO2 and 90% N2, 3.26 umol CO was generated. To further understand the role of Co(bpy)32+ in photocatalytic  $CO_2$ reduction, the photoluminescence measurement of the catalytic system was performed (Figure S17). DA-CTF presents obvious photoluminescence signals at 422 and 496 nm. After the addition of Co<sup>2+</sup> or 2,2'-bipyridine, there is only a slight attenuation of the photoluminescence signals. However, the intensity of the emission band at 496 nm drops significantly after simultaneous addition of 2,2'-bipyridine and Co2+, indicating that the integration of cobalt redox mediators with DA-CTF could effectively inhibit the recombination of photogenerated charge carriers and accelerate the electron transfer/migration.[4c]

The electron spin resonance (ESR) measurements exhibit that strong absorption signals of DA-CTF are greatly attenuated after the addition of 2,2'-bipyridine and  $\text{Co}^{2+}$  (Figure S18a, b), which probably originates from the electron delocalization between DA-CTF and *in situ* formed  $[\text{Co}(\text{bpy})_3]^{2+}$ .<sup>[26a]</sup> Simultaneously, a new ESR signal with the g value of 2.2270 is observed (Figure S18c), which is assigned to Co(II) species.<sup>[26]</sup> Upon visible-light irradiation, the ESR peak of the Co(II) species almost disappears, which indicates a light-induced valence transformation from high-spin state Co(II) to low-spin state Co(I) species. However, when CO<sub>2</sub> is introduced into the irradiated system, the intensity of the Co(II) signal is enhanced, suggesting that some of Co(I) is oxidized back to Co(II) species owing to synchronous reduction of CO<sub>2</sub>.<sup>[27]</sup>



**Figure 5.** Photographs for (a) suspension of DA-CTF, CoCl<sub>2</sub>, 2,2'-bipyridine and TEOA in acetonitrile; (b) upon visible light irradiation under nitrogen atmosphere; (c) and (d) after turning off light and introducing  $CO_2$  or  $O_2$ . (e) Plausible mechanism of photocatalytic  $CO_2$  reduction under visible light irradiation.

A photochromic phenomenon is observed in this catalytic system. When the suspension of DA-CTF containing 2,2'-bipyridine,  $Co^{2+}$  and TEOA in MeCN was irradiated by visible light under nitrogen atmosphere, the color of the suspension changed from original yellow to green. However, when  $CO_2$  or  $O_2$  was introduced after turning off light, the green suspension

gradually restored to original yellow (Figure 5a-d). The photochromic phenomenon is reversible, which further validates the intervalence electron transfer between Co(II) and Co(I) species.<sup>[27a,28]</sup> *in situ* FTIR spectra have validated the interaction between CO<sub>2</sub> and Co(bpy)<sub>3</sub><sup>2+</sup>. As shown in Figure S19, molecular CO<sub>2</sub> exhibits a typical asymmetric stretching mode at 2335 cm<sup>-1</sup>, successive addition of Co(bpy)<sub>3</sub><sup>2+</sup> and DA-CTF results in obvious red shift of the adsorption peak.<sup>[27]</sup> After the release of CO<sub>2</sub>, the vibration peaks are greatly attenuated, the very weak signals are attributed to the adsorbed CO<sub>2</sub>.

Based on the aforementioned results and literature reports,  $^{\left[25,29\right]}$  a plausible mechanism for photocatalytic CO\_2 reduction has been proposed (Figure 5e). Under visible-light irradiation, the excited DA-CTF liberates the electrons from valence band to conduction band.  $[Co(bpy)_3]^{2+}$  acts as an electron mediator<sup>[25a]</sup> and accepts the electrons from the conduction band of DA-CTF, [Co(bpy)<sub>2</sub>(MeCN)<sub>2</sub>]<sup>1</sup> is simultaneously formed through a solvent exchange process.<sup>[29e]</sup> It should be mentioned that the cobalt species are located at the external surface of DA-CTF (Figure S20), the physisorbed CO<sub>2</sub> in DA-CTF is easily released and then replaces MeCN molecule to produce the CO<sub>2</sub> adduct [Co(bpy)<sub>2</sub>(MeCN)-CO<sub>2</sub>]<sup>1+</sup>, which further accepts the secend electron and protonatation to form [Co(bpy)<sub>2</sub>(MeCN)(CO<sub>2</sub>H)]<sup>1+</sup>. After the intermediate undergoes protonation and loses one water moleucle, CO is released and  $[Co(bpy)_3]^{2+}$  is regenarated for the next cycle.

#### Conclusions

we have developed an effective protocol for photocatalytic CO<sub>2</sub> reduction based on a covalent triazine-based framework consisting of triphenylamine and triazine units. The electron donor-acceptor dyads with an extended π-conjugated framework provide a highway to the transfer and separation of photoexcited charge carriers, which endows the photocatalytic system with high activity and durability in photocatalytic CO<sub>2</sub> reduction upon visible light irradiation. The self-functionalization approach of DA-CTF not only presents one promising strategy for precise engineering of organic semiconductors consisting of donoracceptor dyads, but also provides new insight into the fabrication of photocatalysts for efficient solar energy conversions. It can be expected that deliberate integration of various electron-donor building units and electron-withdrawing triazine rings can be extended to other versatile photocatalytic reactions, further investigation for photocatalytic application of CTFs with other donor-acceptor dyads is on progress.

#### **Experimental Section**

**Materials:** 4,4',4"-nitrilotribenzonitrile,<sup>[30]</sup> g-C<sub>3</sub>N<sub>4</sub><sup>[31]</sup> and CTF-T1<sup>[18]</sup> were prepared according to the modified literature methods. Other chemicals were commercially available and used without further purification.

Synthesis of DA-CTF: To a solution of 4,4',4''-nitrilotribenzonitrile (1.0 g, 3.2 mmol) in CHCl<sub>3</sub> (50 mL), trifluoromethanesulfonic acid (10 mL) was

added dropwise at 0 °C and then kept at 30 °C for 3 days. The mixture was neutralized with LiOH and stirred at room temperature for 12 h. The yellow precipitate was collected by filtration, washed with excess H<sub>2</sub>O, and then dried under vacuum at 80 °C for 12 h to afford DA-CTF. Yield: 0.91 g (91%). FTIR (KBr, cm<sup>-1</sup>): 2220 (w), 1597 (s), 1500 (s), 1362 (s), 1271 (m), 1177 (m), 1098 (w), 815 (m). Anal. Calcd for  $C_{21}H_{12}N_4$ : C, 78.73; H, 3.78; N, 17.49. Found: C, 63.80; H, 4.81; N, 13.55.

The synthesis of Co(bpy)<sub>3</sub>Cl<sub>2</sub>: A mixture of CoCl<sub>2</sub>·6H<sub>2</sub>O (71.4 mg, 0.3 mmol) and 2,2'-bipyridine (1560 mg, 10 mmol) in acetonitrile (300 mL) was stirred for 1 h, the resultant solution was kept in air for 3 day to afford brown-yellow crystals of Co(bpy)<sub>3</sub>Cl<sub>2</sub>.

**Photocatalytic test:** DA-CTF (30 mg) was dispersed in a solution of triethanolamine (1 mL), CoCl<sub>2</sub>·6H<sub>2</sub>O (3.0 µmol) and 2,2'-bipyridine (15.6 mg, 0.1 mmol) in acetonitrile (2 mL) in a Schlenk flask. The Schlenk flask was degassed with a vacuum pump and then backfilled with pure CO<sub>2</sub> gas. This process was repeated three times. After the last cycle, the flask was backfilled with CO<sub>2</sub> (1.0 bar). The temperature of the reaction solution maintained at 30 °C. Then the reaction mixture was irradiated under Xe lamp with  $\lambda$  > 420 nm cutoff filter under vigorous stirring. After reaction, the gases were analyzed by Agilent 7820B.

**Recyclability test:** The photocatalytic reactions were carried out as described above upon visible light illumination ( $\lambda > 420$  nm) for 2 h. After the reaction was completed, DA-CTF was separated by centrifugation, washed with acetonitrile (3 x 10 mL) and dried under vacuum at 80 °C. The recovered DA-CTF was used for the next catalytic cycle with the addition of fresh triethanolamine, CoCl<sub>2</sub> ·6H<sub>2</sub>O, 2,2'-bipyridine and CO<sub>2</sub>.

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**Keywords:** Covalent triazine framework • Donor-acceptor dyads • Visible light • CO<sub>2</sub> reduction • Porous organic polymers.

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### CO<sub>2</sub> reduction

### FULL PAPER

A covalent triazine-based framework consisting of triphenylamine and triazine (DA-CTF) shows high catalytic activity, selectivity and stability in visible-light-driven CO<sub>2</sub> reduction. The superior photocatalytic performance is mainly attributed to unique structure of DA-CTF. The  $\pi$ -conjugated electron donor-acceptor dyads contribute to visible light harvesting and migration of photoexcited charge carriers, while the porosities are favorable for CO<sub>2</sub> capture and the accommodation of electron mediators.



**Covalent Triazine-based Framework** 

Hong Zhong, Can Yang, Liuyi Li, Dongxu Tian, Xinchen Wang and Ruihu Wang\*



A Covalent Triazine-based Framework Consisting of Donor-Acceptor Dyads for Visible-Light-Driven Photocatalytic CO<sub>2</sub> Reduction

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