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## Triphenylamine based conjugated microporous polymers for selective photoreduction of CO<sub>2</sub> to CO under visible light†

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Organic  $\pi$ -conjugated polymers (CPs) have been intensively explored for a variety of critical photocatalytic applications in the past few years. Nevertheless, CPs for efficient CO<sub>2</sub> photoreduction have been rarely reported, which is mainly due to the lack of suitable polymers with sufficient solar light harvesting ability, appropriate energy level alignment and good activity and selectivity in multi-electron-transfer photoreduction of CO<sub>2</sub> reaction. We report here the rational design and synthesis of two novel triphenylamine (TPA) based conjugated microporous polymers (CMPs), which can efficiently catalyze the reduction of CO<sub>2</sub> to CO using water vapor as an electron donor under ambient conditions without adding any co-catalyst. Nearly 100% selectivity and a high CO production rate of 37.15  $\mu\text{mol h}^{-1} \text{g}^{-1}$  are obtained for OXD-TPA, which is significantly better than that for BP-TPA (0.9  $\mu\text{mol h}^{-1} \text{g}^{-1}$ ) as a result of co-monomer change from biphenyl to 2,5-diphenyl-1,3,4-oxadiazole. This difference could be mainly ascribed to the synergistic effect of a decreased optical band gap, improved interface charge transfer and increased CO<sub>2</sub> uptake for OXD-TPA. This contribution is expected to spur further interest in the rational design of porous conjugated polymers for CO<sub>2</sub> photoreduction.

For the past few decades, artificial photocatalysis has been well established as a sustainable technology for CO<sub>2</sub> conversion into carbonaceous chemical fuels such as CO, CH<sub>3</sub>OH, CH<sub>4</sub>, *etc.*<sup>1–6</sup> The technology is particularly appealing as it not only holds great promise to handle environmental issue caused by excess CO<sub>2</sub> release, but also provides fuels for energy supply. However, high energy input is required for CO<sub>2</sub> transformation owing to its remarkable stability with the dissociation energy of C=O bond up to 750 kJ mol<sup>−1</sup>,<sup>6</sup> which

makes it difficult to develop efficient photocatalysts. Since the pioneering report of heterogeneous CO<sub>2</sub> photoreduction using TiO<sub>2</sub> as the catalyst,<sup>7</sup> numerous inorganic semiconductors have been under active exploration. However, most inorganic photocatalysts suffer from limited tunability, potential heavy metal toxicity and wide band gap,<sup>7–10</sup> which hinder their practical applications and thus require the exploration of alternatives.

Conjugated microporous polymers (CMPs), a subclass of structurally diverse polymeric materials, have many advantages such as permanent porosity, large surface area, strong visible light activity, facile synthesis, tunable optoelectronic properties, and high chemical and thermal stability, making them attractive candidates for a range of applications, such as gas sequestration and separation,<sup>11–15</sup> heterogeneous catalytic reaction,<sup>16–20</sup> sensing,<sup>21,22</sup> and energy storage and conversion.<sup>23–27</sup> Recent studies have revealed that porous conjugated polymers (CPs) are promising photocatalysts for CO<sub>2</sub> reduction and their photocatalytic activities could be effectively enhanced by rational molecular design. For instance, Liu *et al.* reported photocatalytic CO<sub>2</sub> reduction using a series of pyrene-based porous CPs in a CO<sub>2</sub>-saturated ionic liquid, which yielded CO with a rate of 47.37  $\mu\text{mol h}^{-1} \text{g}^{-1}$  and reaction selectivity reached 98.3% (>420 nm).<sup>28</sup> By copolymerization between 2,4,6-triphenyl-1,3,5-triazine and different comonomers, the charge separation of the resulting polymers could be improved to give a maximum CO production rate of 18.2  $\mu\text{mol h}^{-1} \text{g}^{-1}$  with 81.6% selectivity in the presence of CoCl<sub>2</sub> and dipyrindyl as the co-catalysts.<sup>29</sup> Crystalline covalent organic framework (COF) based CO<sub>2</sub>-reduction photocatalysts were reported by Huang *et al.*, in which Re(bpy)(CO)<sub>3</sub>Cl was incorporated into the 2D COF to reduce CO<sub>2</sub> using triethanolamine as a sacrificial agent and 98% selectivity was obtained.<sup>30</sup> Despite this exciting progress, these CO<sub>2</sub> reduction reactions were carried out in CO<sub>2</sub>-saturated liquid media, which required the use of organic electron donors, co-catalysts or ionic liquids, adding cost and complexity. Moreover, the limited solubility of CO<sub>2</sub> in liquid media is unfavorable for

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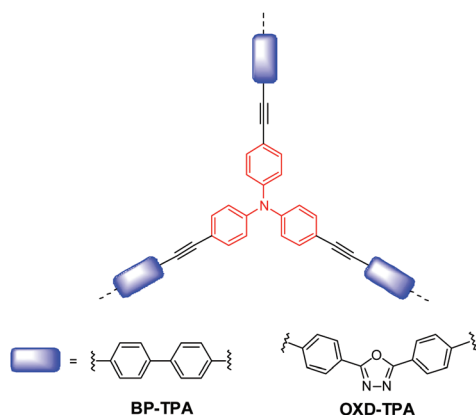
achieving high reaction efficiency. By contrast, the reduction reaction performed on a gas–solid interface relies on CO<sub>2</sub> chemisorption and activation by the photocatalysts, which eliminates the need for liquid media. This simple and environmentally-friendly approach uses only a trace amount of water vapor as the electron donor, which significantly inhibits the competing process of water reduction and favors the selectivity of CO<sub>2</sub> reduction.<sup>1,3</sup> However, to the best of our knowledge, the exploration of efficient polymers for CO<sub>2</sub> reduction on a gas–solid system remains a great challenge.<sup>31</sup> Very recently, Eosin Y-based conjugated porous polymers were developed for CO<sub>2</sub> photoreduction, which resulted in a CO production rate of 33  $\mu\text{mol h}^{-1} \text{g}^{-1}$  with 92% selectivity.<sup>31</sup> To achieve better photocatalytic performance, new polymers and useful molecular design strategies to reveal the critical parameters that control their photoactivities are highly desirable.

In this study, we present two specially designed CMPs as visible-light-active photocatalysts for the reduction of CO<sub>2</sub> to CO only in the presence of water vapor under ambient conditions. The polymer structures are shown in Scheme 1. Triphenylamine (TPA) based CMPs were developed owing to their inherent advantages of high surface area for effective CO<sub>2</sub> absorption, facile preparation, and fine optimization of energy levels.<sup>32,33</sup> The optical band gaps of the as-prepared CMPs could be tuned from 2.38 to 2.22 eV by replacing biphenyl (BP) with 2,5-diphenyl-1,3,4-oxadiazole (OXD). More importantly, the CO production rate could be enhanced to 37.15  $\mu\text{mol h}^{-1} \text{g}^{-1}$  with  $\sim 100\%$  selectivity under visible light irradiation ( $>420 \text{ nm}$ ). In addition, we provide a comprehensive understanding of the photocatalytic activity of polymers by complementary experimental and computational studies, which is critical for future development of conjugated polymers for CO<sub>2</sub> photoreduction.

The synthetic details and characterization of the monomers and conjugated microporous polymers are given in the ESI.† Tris(4-ethynylphenyl)amine was prepared by the Pd(II)-catalyzed coupling of tris(4-bromophenyl)amine and ethynyltrimethylsilane and subsequent deprotection promoted by K<sub>2</sub>CO<sub>3</sub>.<sup>34</sup> Starting from 4-bromobenzoyl chloride, 2,5-bis(4-bro-

mophenyl)-1,3,4-oxadiazole was obtained in three high yielding steps as depicted in Scheme S1.† A condensation reaction between 4-bromobenzoyl chloride and hydrazine hydrate afforded 1,2-bis(4-bromobenzoyl)hydrazide, followed by cyclodehydration to give 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole in 71% yield.<sup>35</sup> BP-TPA and OXD-TPA were synthesized from tris(4-ethynylphenyl)amine with 4,4'-dibromodiphenyl and 2,5-diphenyl-1,3,4-oxadiazole, respectively, by the Sonogashira coupling reaction in an Et<sub>3</sub>N/DMF (1:1, v/v) mixture with Pd(PPh<sub>3</sub>)<sub>4</sub> and CuI as catalysts. The resulting product was successively washed with water, acetone and methanol followed by Soxhlet extraction (THF and then CH<sub>2</sub>Cl<sub>2</sub>). BP-TPA and OXD-TPA are insoluble in all common solvents such as DMF, THF and CH<sub>2</sub>Cl<sub>2</sub>. The structural characterization of the two polymers was studied by solid-state <sup>13</sup>C NMR spectroscopy, FT-IR spectroscopy, and elemental analysis. Both polymers show aromatic peaks at 120–150 ppm and peaks at  $\sim 91 \text{ ppm}$  for quaternary alkynes (Fig. S1 and S2†), consistent with the CMPs synthesized by the Sonogashira polymerization.<sup>34</sup> In addition, the peak at 163 ppm in the NMR spectrum of OXD-TPA is ascribed to the carbon atom of oxadiazole. Fourier-transform infrared (FT-IR) spectra analysis confirmed the alkynyl linker of the two polymers by the evidence of stretching vibrations of triple bonds appearing around 2200  $\text{cm}^{-1}$  (Fig. S3†). BP-TPA and OXD-TPA show similarly spherical morphologies revealed by scanning electron microscopy (SEM) measurement (Fig. S4†). Negligible Pd residual was detected in both polymer networks and the content is 0.34% for BP-TPA and 0.54% for OXD-TPA, respectively. The powder X-ray diffraction (PXRD) patterns demonstrated that both polymers exhibited broad diffraction peaks with low intensities in the wide region, indicative of their amorphous nature (Fig. S6†). Thermal gravimetric analysis (TGA) demonstrated their excellent thermostability with 5% weight loss for BP-TPA and OXD-TPA observed at 463 °C and 412 °C, respectively (Fig. S7†).

The porosity of BP-TPA and OXD-TPA was evaluated by N<sub>2</sub> sorption isotherm measurements at 77 K. As shown in Fig. 1a, both polymer networks give rise to type I isotherms and exhibit a steep increase in the low relative pressure regions ( $<0.01$ ) due to their microporosity. The apparent BET surface area of BP-TPA is 512  $\text{m}^2 \text{g}^{-1}$ , which is lower than that of OXD-TPA (686  $\text{m}^2 \text{g}^{-1}$ ).



**Scheme 1** Chemical structures of the conjugated microporous polymers for CO<sub>2</sub> photoreduction in this study.



**Fig. 1** (a) N<sub>2</sub> sorption isotherm curves of the polymers obtained at 77 K. (b) CO<sub>2</sub> adsorption isotherm curves of the polymers at 298 K.

Both polymers have similar pore size distributions with pore widths at about 1.1, 1.5 and 2.7 nm, respectively (Fig. S5†). The CO<sub>2</sub> uptake capacities of the two polymers at 298 K were evaluated by CO<sub>2</sub> adsorption isotherms. OXD-TPA exhibited a higher volumetric CO<sub>2</sub> uptake than BP-TPA (Fig. 1b). In particular, the difference of CO<sub>2</sub> uptake became more distinct with increasing pressure. At *P* = 100 kPa, the CO<sub>2</sub> uptake capacities of BP-TPA and OXD-TPA were 24.1 and 30.3 cm<sup>3</sup> g<sup>−1</sup>, respectively. The enhanced CO<sub>2</sub> absorbing ability of OXD-TPA compared to BP-TPA is attributed to its higher BET surface area and the dipole-induced electrostatic interactions between the N or O atoms of the oxadiazole unit and the C atoms of CO<sub>2</sub>.<sup>36–38</sup>

The UV/vis diffuse reflectance spectra (DRS) and photoluminescence spectra of BP-TPA and OXD-TPA are displayed in Fig. 2a. OXD-TPA with extended  $\pi$ -conjugation shows broader absorption than BP-TPA. Accordingly, the optical band gaps estimated from the absorption onset of the DRS spectra are 2.38 eV for BP-TPA and 2.22 eV for OXD-TPA. Upon excitation at 380 nm, BP-TPA exhibits emission centered at 562 nm, which is slightly blue-shifted to 557 nm for OXD-TPA. Notably, the emission of OXD-TPA is significantly stronger than that of BP-TPA. This is largely due to the twisted conformation between phenyl and oxadiazole in 2,5-diphenyl-1,3,4-oxadiazole, which interrupts the  $\pi$ -conjugation and molecular stacking, thus blue-shifts the emission and enhances the fluorescence intensity.<sup>39,40</sup> In addition, time-resolved photoluminescence decay spectra demonstrated a slightly longer fluorescence lifetime of 0.82 ns for OXD-TPA than that of BP-TPA (0.61 ns) (Fig. S8†). The LUMO levels of polymers were evaluated using cyclic voltammetry (Fig. S9†). Both exhibited well-defined reversible reduction waves with the LUMO levels of −0.41 V (vs. NHE) for BP-TPA and −0.44 V (vs. NHE) for

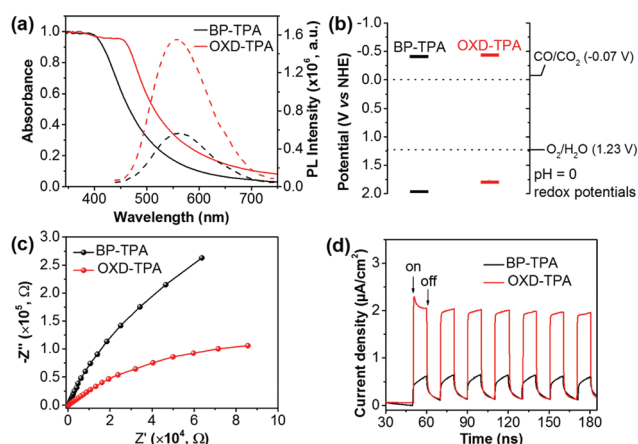
**Table 1** Optical and electrochemical properties, BET surface area and CO<sub>2</sub> uptake data of the polymers

Polymers	$E_g^a$ (eV)	$E_{\text{red, onset}}^b$ (V)	LUMO/ HOMO <sup>c</sup> (V, vs. NHE)	$S_{\text{BET}}$ (m <sup>2</sup> g <sup>−1</sup> )	CO <sub>2</sub> uptake <sup>d</sup> (cm <sup>3</sup> g <sup>−1</sup> )
BP-TPA	2.38	−1.04	−0.41/1.97	2.38	24.1
OXD-TPA	2.22	−1.07	−0.44/1.78	2.22	30.3

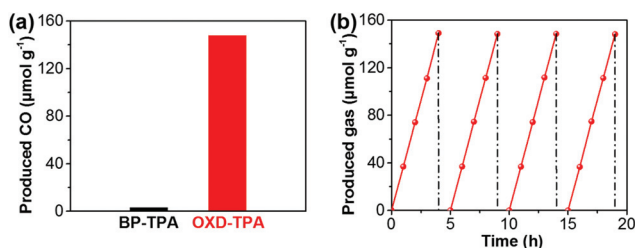
<sup>a</sup> Estimated from the UV/vis diffuse reflectance spectra onset ( $E_g = 1240/\lambda_{\text{onset}}$ ). <sup>b</sup> Versus Fc/Fc<sup>+</sup> in acetonitrile solution, 50 mV s<sup>−1</sup> scan rate. <sup>c</sup>  $E_{\text{NHE}} = E_{\text{Fc/Fc}^+} + 0.63$  V,  $E_{\text{HOMO}} = E_{\text{LUMO}} - E_g$ , opt. <sup>d</sup> At *P* = 100 kPa.

OXD-TPA (Table 1). Accordingly, the HOMO levels of BP-TPA and OXD-TPA were calculated to be 1.97 V and 1.78 V, respectively. The energy band structures of both polymers are well positioned for the reduction of CO<sub>2</sub> to CO, indicating that they are thermodynamically capable of generating CO from CO<sub>2</sub> photoreduction under light irradiation (Fig. 2b).<sup>41</sup> Photoelectrochemical measurements were conducted to compare the photogenerated charge carrier transport of the two polymers. As shown in Fig. 2c, the Nyquist plot of OXD-TPA exhibits a smaller diameter of the semicircular than that of BP-TPA, revealing a decrease of the charge-transfer resistance by replacing biphenyl with 2,5-diphenyl-1,3,4-oxadiazole. The improved photoinduced charge transport can be further supported by an increased transit photocurrent response of OXD-TPA as shown in Fig. 2d, which reveals a visible-light photocurrent of  $\sim 2 \mu\text{A cm}^{-2}$  for OXD-TPA and  $\sim 0.5 \mu\text{A cm}^{-2}$  for BP-TPA.

The CO<sub>2</sub> photoreduction reactions over the as-synthesized polymers were carried out in the presence of CO<sub>2</sub> and water vapor under ambient conditions. Interestingly, CO was detected as the only reductive product in the photocatalytic system (Fig. S10b†). As shown in Fig. 3a, after the four-hour irradiation of visible light (>420 nm), OXD-TPA produced 148.6  $\mu\text{mol g}^{-1}$  CO, which is much more than that by BP-TPA (3.6  $\mu\text{mol g}^{-1}$ ). At 420 nm, the quantum efficiencies are about 0% and 0.19% for BP-TPA and OXD-TPA (Fig. S19†), respectively. To the best of our knowledge, the photocatalytic activity of OXD-TPA (37.15  $\mu\text{mol h}^{-1} \text{g}^{-1}$ ) is much better than that of commonly used g-C<sub>3</sub>N<sub>4</sub> and many newly reported CPs under similar conditions (Table S1†).



**Fig. 2** (a) UV/vis diffuse reflectance spectra (solid line) and photoluminescence (PL) spectra (dashed lines;  $\lambda_{\text{ex}} = 380$  nm) of BP-TPA and OXD-TPA in the solid state. (b) Energy levels of BP-TPA and OXD-TPA relative to the potentials of CO<sub>2</sub> reduction to CO and water oxidation, respectively, vs. the NHE at pH = 0. (c) EIS Nyquist plots and (d) periodic transient photocurrent response of polymer electrodes in 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution.



**Fig. 3** (a) CO production from the photocatalytic CO<sub>2</sub> reduction over BP-TPA and OXD-TPA after 4 h irradiation (>420 nm). Reaction conditions: 15 mg polymer, CO<sub>2</sub> (1.0 atm), water vapor, room temperature. (b) Time course of photocatalytic CO<sub>2</sub> reduction over OXD-TPA.



To confirm the photocatalytic process, we have performed a series of control experiments. No reductive products were detected under dark conditions. Upon replacing  $\text{CO}_2$  with  $\text{N}_2$ , only a trace amount of CO could be detected, indicating that  $\text{CO}_2$  is the reductive agent in the system. When no  $\text{H}_2\text{O}$  is added to the reaction system, negligible CO could be measured, which suggests that  $\text{H}_2\text{O}$  plays an important role as an electron donor. Notably,  $\text{H}_2$  and other carbonaceous products, such as  $\text{CH}_4$ ,  $\text{HCHO}$ ,  $\text{HCOOH}$ , and  $\text{CH}_3\text{OH}$  were not found in our tests, demonstrating that the separated electrons on the surface of the polymer network are almost exclusively used for  $\text{CO}_2$  reduction to CO and  $\sim 100\%$  selectivity was obtained for OXD-TPA in the photocatalytic reaction.

To study the source of generated CO during the photocatalytic process, an isotopic experiment with  $^{13}\text{CO}_2$  (Fig. S11†) was conducted under the same reaction conditions ( $>420$  nm). When  $^{12}\text{CO}_2$  was replaced by  $^{13}\text{CO}_2$  in the reactor, a gas product with a retention time of 4.026 min was detected, which was different from that of  $^{12}\text{CO}$  at 3.958 min (Fig. S10b and c†). In addition, after adding concentrated NaOH aqueous solution into the reactor to remove unreacted  $^{13}\text{CO}_2$ , the gas sample was subsequently analyzed by MS spectrometry and a peak at  $m/z = 29$  was found (Fig. S12†), which was assigned to  $^{13}\text{CO}$ . This peak was not due to the fragmentation of  $^{13}\text{CO}_2$  during the MS analysis as the unreacted  $^{13}\text{CO}_2$  was completely removed prior to the analysis. Based on all these results, it could be concluded that CO originated from the reduction of  $\text{CO}_2$  on OXD-TPA.

The photocatalytic  $\text{CO}_2$  reduction stability and recyclability of OXD-TPA was evaluated by four cyclic testing (4 h-irradiation in each run). The photocatalytic reactor was treated under vacuum and then refilled with the mixture of  $\text{CO}_2$  and water vapor after each run. Steady CO production is observed over four runs (Fig. 3b). After the photocatalysis experiments, the recycled polymer did not show any significant structural changes (Fig. S13–S15†), indicating that OXD-TPA is highly stable during the photocatalytic process.

DFT calculations were performed to understand the electronic properties of both polymers. The optimized structures are shown in Fig. S16.† The excited electrons for both BP-TPA and OXD-TPA are distributed all over the backbone, whereas the excited holes are mainly localized in TPA due to its strong electron-donating feature (Fig. S17a and S17b†). Moreover, compared to the BP moiety, the more electronegative OXD moiety impairs the density of excited electrons within the TPA part, which decreases the overlap between the excited electrons and holes in OXD-TPA as compared to that of BP-TPA, indicating less recombination of photogenerated charges in OXD-TPA.

We further studied the adsorption energy of  $\text{COOH}^*$ , which is proposed to be the intermediate for  $\text{CO}_2$  reduction to CO, on different positions of BP-TPA and OXD-TPA (Fig. 4a and b), and the corresponding adsorption energies are shown in Fig. 4c. The most stable configurations of  $\text{COOH}^*$  are shown in the insert of Fig. 4c and Fig. S17c.† The most stable adsorbed  $\text{COOH}^*$  has similar configurations but the adsorp-

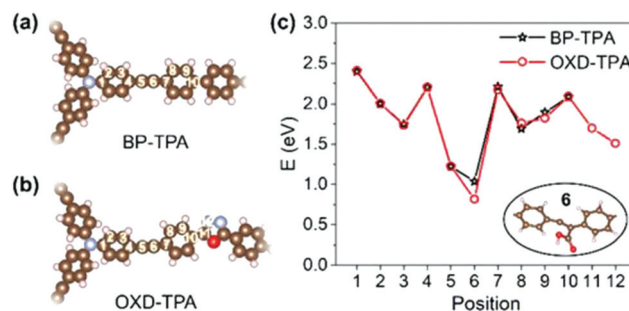


Fig. 4 Different adsorption sites on (a) BP-TPA and (b) OXD-TPA, and (c) the corresponding adsorption energies for  $\text{COOH}^*$ .

tion is  $\sim 0.2$  eV more stable on OXD-TPA, which facilitates the reduction of  $\text{CO}_2$ .

DFT calculations revealed that the band gaps for BP-TPA and OXD-TPA are 2.47 and 2.38 eV, respectively, which are in agreement with the optical bandgaps obtained in our experiments (2.38 eV for BP-TPA and 2.22 eV for OXD-TPA as shown in Table 1). Notably, the theoretically predicted HOMOs and LUMOs for BP-TPA and OXD-TPA are depicted in Fig. S18a.† The HOMO potential of BP-TPA (0.79 V) is approximate to the one required for water oxidation (0.82 V, neutral conditions), while it is 0.27 V more positive for OXD-TPA. The LUMO potentials of both BP-TPA ( $-1.68$  V) and OXD-TPA ( $-1.31$  V) are much more negative than the reduction potential of  $\text{CO}_2$  to CO ( $-0.53$  V). The results reinforced the sufficient redox ability of the two polymers to trigger the photocatalytic reactions in our system. The possible  $\text{CO}_2$  photoreduction process for the polymers is described as follows: the  $\text{CO}_2$  gas can be absorbed and activated by the porous polymers. Upon the illumination of visible light, the photogenerated electrons ( $e^-$ ) could migrate from the LUMO levels to the HOMO levels of the polymer. Subsequently, the absorbed  $\text{CO}_2$  captures electrons on the polymer surface, forming CO and  $\text{H}_2\text{O}$  ( $\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O}$ ), while the photoinduced holes were utilized for oxidizing water to generate oxygen and hydrogen ions *via* the half-reaction ( $2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow \text{O}_2 + 4\text{H}^+$ ) (Fig. S18b†). The low water concentration in the reaction system could efficiently inhibit the competitive reaction to give  $\text{H}_2$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_4$ , *etc.* This is beneficial for the high selectivity of polymers. The much better photocatalytic performance of OXD-TPA could be attributed to its smaller band gap, increased dissociation of photogenerated excitons, and more stable  $\text{COOH}^*$ .

## Conclusions

In conclusion, we present the rational design of two novel tri-phenylamine based CMPs for  $\text{CO}_2$  photoreduction to CO under visible light irradiation. The CO production rate could be significantly enhanced from 0.9 to  $37.15 \mu\text{mol h}^{-1} \text{g}^{-1}$  ( $>420$  nm) with  $\sim 100\%$  selectivity, which is much better than the newly reported CPs in similar photocatalytic systems (Table S1†). The enhancement in the photocatalytic activity of

polymers resulting from molecular tuning was fully investigated by experiments and theoretical calculations. Accordingly, we expect that this study will stimulate research interest in designing stable and highly efficient conjugated polymers for CO<sub>2</sub> photoreduction.

## Conflicts of interest

There are no conflicts to declare.

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