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EosinY-Functionalized Conjugated Organic Polymers for Visible-Light Driven CO₂ Reduction with H₂O to CO with High Efficiency

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Abstract: Visible-light driven photoreduction of CO₂ to energyrich chemicals in the presence of H₂O without any sacrifice reagent is of significance, but challenging. Herein, we report EosinY-functionalized porous polymers (PEosinY-N, N=1~3) with high surface areas up to 610 m² g⁻¹, which exhibit high activity for photocatalytic reduction of CO₂ to CO in the presence of gaseous H₂O without any photosensitizer or sacrifice reagent under visible light irradiation. Especially, PEosinY-1 derived from coupling of EosinY with 1,4-diethynylbenzene shows the best performance for the CO₂ photoreduction, affording CO as the sole carbonaceous product with a production rate of 33 µmol g⁻¹ h⁻¹ and a selectivity of 92%. It is indicated that the EosinY sites and conjugated structure of PEosinY-N could realize the light absorption and efficient separation of photo-generated electron/hole, as well as the adsorption and activation of CO2 and H₂O. This work provides new insight for designing and fabricating photocatalytically active polymers with high efficiency for solar-energy conversion.

The visible-light driven CO₂ photoreduction into energy-rich chemicals, such as CO, HCOOH, CH₃OH and CH₄, has attracted tremendous attention, considering its double benefits for utilization of CO₂ as a renewable and green C1 building block and conversion of solar energy.^[1] In this research area, various photocatalysts such as transition-metal complexes,^[2] metal oxides/sulfides^[3] and metal-organic frameworks^[4] have been developed for the photocatalytic reduction of CO₂. However, in most cases sacrifice reagents rather than H₂O are required to realize the photoreduction of CO₂. Inspired by the natural photosynthesis that realizes the transformation of CO₂ and H₂O simultaneously under ambient conditions, the photoreduction of CO₂ combined with H₂O oxidation has been paid much attention, however, still remained a significant challenge due to the lack of efficient photocatalysts.^[5]

In recent years, conjugated organic polymers (COPs) have emerged as a kind of materials with promising application potentials because they can be designed with specific properties

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by varying the organic precursors and synthetic methods.^[6] For example, COPs with CO₂-philic groups have been reported for efficient capture and further conversion of CO₂.^[7] Due to their tunable optical and electronic properties, 1,3-diyne-linked COP nanosheets and diacetylene-functionalized ketoenamine COPs have been applied in photocatalytic water splitting, showing higher or comparable activities compared to the most of inorganic photocatalysts.^[6b, 8] Nonetheless, COPs have been rarely reported for photocatalytic reduction of CO₂.



Figure 1. Synthetic procedure for PEosinY-N (N=1~3).

Herein, we present a kind of EosinY-functionalized COPs (PEosinY-N, N=1~3) prepared via direct Sonogashira-Hagihara cross-coupling of Eosin Y with aromatic alkynes (Figure 1, A1, A2 and A3). The resultant materials possessed porous structures with Brunauer-Emmett-Teller (BET) surface areas up to 610 m^2g^{-1} , and could adsorb and activate CO₂ and H₂O simultaneously, confirmed by in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analysis and density functional theory (DFT) calculations. Moreover, PEosinY-N could absorb visible light with suitable band structures (Eg=2.42~2.53 eV), which makes them be capable of catalysing the photoreduction of CO₂ with gaseous H₂O without using sacrifice reagent under visible light irradiation. Especially, PEosinY-1 showed the best performance, affording CO as the sole carbonaceous product with a production rate of 33 µmol g⁻¹ h⁻¹ and a selectivity of 92%. It was indicated that the EosinY sites and conjugated structure of **PEosinY-N** were responsible for the light absorption as well as efficient electron/hole separation.

As shown in Figure 1, **PEosinY-N** were dark red powders, which were insoluble in common solvents (e.g. H_2O , ethanol, CH_2Cl_2 and tetrahydrofuran). Their formation was verified by Fourier transform infrared spectroscopy (FTIR), cross-polarization magic-angle spinning (CP/MAS) ¹³C NMR and X-ray photoelectron spectroscopy (XPS) (Figure S1, S2 and S3, SI).

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FTIR analysis showed that PEosinY-1 had the least unreacted C≡CH (3296 cm⁻¹) groups, suggesting that it had the highest polymerization degree and the best conjugated structure, while PEosinY-3 was contrary, probably due to the difference in chemical structures of their monomers. The powder X-ray diffraction analysis indicated that PEosinY-N was amorphous (Figure S4, SI), which was composed of tiny particles with irregular shapes and sizes confirmed by field-emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observation (Figure S5, SI). The thermogravimetric analysis indicated that PEosinY-N was stable in air up to 300 °C (Figure S6, SI).

The N₂ sorption analysis indicated that each PEosinY-N displayed type I sorption isotherm (Figure S7A, SI), indicating the presence of micropores in the polymeric matrices, as shown by the curves of the pore size distribution (Figure S7B, SI). Based on the sorption isotherms, the BET surface areas of PEosinY-1. PEosinY-2 and PEosinY-3 were estimated to be 445, 131, 610 $m^2{\cdot}g^{\text{-}1},$ respectively (Figure S8, SI). The differences in their BET surface areas resulted from the chemical structure and activity of their monomers. The CO₂ adsorption capacity of PEosinY-N was measured at 273 K and pressure range of 0.002~1 bar (Figure S9, SI). It was demonstrated that their CO₂ adsorption capacities were related to their BET surface areas and reached 39. 24 and 62 mg g⁻¹ at 1.0 bar for PEosinY-1, PEosinY-2 and PEosinY-3, respectively. The porous structures and high surface areas of these polymers may be favorable to the capture and activation of CO₂ or H₂O molecules at the active sites of the polymers.^[9]

The optical and electronic properties of PEosinY-N were examined to evaluate their potential application in photocatalytic CO₂ reduction and H₂O oxidation. **EosinY** as one of the building monomer of the polymers showed absorption in the range of 220~640 nm (Figure 2A), while PEosinY-N displayed obviously red-shifted absorption edges with enhanced intensity over a wide range of 250~750 nm, possibly ascribed to the formation of conjugated structures in the polymers. In comparason with metal oxide semiconductors $^{[10]}\!\!, \ g\text{-}C_3N_4{}^{[11]}$ and some organic polymer photocatalysts^[6a] with the light absorption edges up to 380, 400 and 450 nm, respectively, PEosinY-N had stronger capability to absorb visible light. The optical bandgaps of PEosinY-N were estimated from Tauc plots, which were 2.45, 2.53 and 2.42 eV for PEosinY-1, PEosinY-2 and PEosinY-3, respectively (Figure S10, SI). The bandgap of PEosinY-3 was the smallest, while DFT calculations indicated that PEosinY-3 should have the largest bandgap (Figure S11 and S12, SI). This discrepancy may result from the low polymerization degree of PEosinY-3, and DFT result could not give the actual information. Mott-Schottky plots analysis was carried out to estimate the relative conduction band (CB) positions of PEosinY-N, and the positive slopes of the plots for PEosinY-N (Figure S13) demonstrated their typical characters of n-type semiconductors.^[12] The valence band (VB) positions of PEosinY-N were obtained by combining the acquired bandgaps from Taus plots with the relative CB positions, and their relative electronic band structures are shown in Figure 2B. Obviously, the CB and VB energies of each PEosinY-N straddle the potentials of CO2 reduction to CO (-0.69 eV vs. Ag/AgCl, pH=6.8) and H₂O oxidation to O₂ (0.64 eV vs. Ag/AgCl, pH=6.8). This suggests that PEosinY-N is likely to be appropriate for photocatalytic reduction of CO $_2$ to CO and oxidation of H_2O to $O_2.$

The charge-transfer ability of PEosinY-N was examined by electrochemical impedance spectroscopy (EIS), photo-current spectra, and time-resolved fluorescent decay spectroscopy (TRFDS). The EIS spectrum of each PEosinY-N (Figure S14 and Table S1, SI) showed that the radius of semicircular Nyquist plot obtained under visible light irradiation was much smaller than that obtained in dark, elucidating that the visible light illumination on PEosinY-N induced the generation of electronhole pairs that separated rapidly, and PEosinY-1 had the best charge transfer efficiency. As shown in Figure 2C, each PEosinY-N exhibited fast, uniform and repeatable photo-current responses upon cycling the light on and off, and PEosinY-1 displayed the highest photocurrent of 0.401 µA/cm⁻². The TRFDS spectra were collected to illustrate the interfacial transition of the photogenerated charge carriers. The average photoluminescence lifetime was 254 ps for **PEosinY-1**, which was the longest (Figure 2D), indicating that PEosinY-1 could offer more opportunities for free charges to participate in the surface photoreaction, thereby enhancing its photocatalytic activity.



Figure 2. (A) UV–Vis light absorption spectra of EosinY and **PEosinY-N** (N=1~3). (B) CB and VB positions of **PEosinY-N**. (C) Transient photocurrent responses of **PEosinY**-N (λ >420). (D) TRFDS spectra of **PEosinY-N**, which were recorded at 640 nm under excitation of 405 nm. (E) Average production rates of CO from CO₂ photoreduction over **PEosinY-N** (λ >420) for 50h. (F) DRIFT spectra of **PEosinY-1** for CO₂ and H₂O adsorption and their photoreaction under visible light irradiation. The bands with apparent changes are marked with full and imaginary lines, in which the full lines refer to the decreased or the gradually disappeared bands, and the imaginary lines denote the new appeared or increased bands.

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With good CO₂ uptake, visible-light absorption, and high separation and transfer efficiency of photoinduced charge carries, PEosinY-N were tested for the photoreduction of CO2 with gaseous H₂O under visible light (>420 nm) irradiation at ambient conditions. It was indicated that each PEosinY-N was effective for the photoreduction of CO₂ with H₂O, producing CO as the sole carbonaceous product together with H_2 (Figure 2E). As expected, PEosinY-1 showed the best performance, affording CO with a production rate of 33 $\mu mol~g^{\text{-1}}~h^{\text{-1}}$ and selectivity of 92%, even superior to some metal oxides/sulfides $^{[13]}$ or ${\rm MOF}^{[14]}$ photocatalysts in the presence of sacrifice reagents. For comparison, EosinY was tried to catalyze the CO₂ photoreduction under the otherwise identical conditions, and only H_2 was obtained with a production rate of 5 µmol g⁻¹ h⁻¹ without any carbonaceous product detectable. The coupling of EosinY with aryl alkynes made the resultant polymer be capable of catalyzing CO₂ photoreduction, which suggestes that the combination of the EosinY sites with C=C and the conjugated structure in the polymers jointly contribute to the photocatalytic activity of the polymers. The cyclic runs of CO₂ photoreduction over PEosinY-1 indicated that the CO productivity and selectivity slightly decreased to 25 µmol g⁻¹ h⁻¹ and 73.5%, respectively, after 5 runs (Figure S15, SI). However, comparing the TEM, SEM images and FTIR, UV-Vis light absorption spectra of **PEosinY-1** before and after the cycle (Figure S16, SI), no obvious changes were observed in the morphology, and the FTIR, UV–Vis absorption spectra changes little.

To gain insight into the CO₂ reduction with H₂O over **PEosinY-1**, control experiments were performed under Ar atmosphere or in dark, and no carbonaceous species were detected in these two cases. In the isotope-labeling experiment using ¹³CO₂ instead of CO₂, ¹³CO was obtained confirmed by the GC-MS spectrum with a peak at m/z =29 (Figure S17, SI) and GC spectrum (Figure S18, SI). These results indicate that **PEosinY-N** catalysed the photoreduction of CO₂ to CO under visible-light irradiation.

To further reveal the reaction mechanism, in-situ DRIFTS of PEosinY-1 under experimental conditions were performed, and the DRIFTS spectra are shown in Figure 2F. The DRIFTS spectrum of **PEosinY-1** under N₂ atmosphere (Figure S19, SI) was taken as the background, and the other DRIFTS spectra were collected after CO2 and gaseous H2O was injected. After adsorption for 15 min, the DRIFTS spectrum was collected, in which the bands at 3729-3597 and 1643 cm⁻¹ were assigned to the isolated or physically adsorbed H₂O on the surface of PEosinY-1, while the wide and strong bands at 3427 and 3237 cm⁻¹ were ascribed to the hydrogen bonding of the surface OH on **PEosinY-1** with H₂O. The bands at 1789, 1763 cm⁻¹ were the characteristic signals of C=O on PEosinY-1 interacting with CO2. These results indicate that the EosinY-functionalized polymers can capture CO₂ and H₂O by the C=O and -OH groups, which is beneficial to the activation of CO₂ and H₂O. After visible light irradiation, in the DRIFT spectra of PEosinY-1 collected at different time, new bands appeared at 1606, 1405 and 1294 cm⁻ ¹, ascribing to CO_2 , which indicates that the CO_2 might be the intermediate in the process of CO₂ photoreduction.^[15] Notably, a new band appeared at 1719cm⁻¹, which may be attributed to the bending vibration of C=O derived from CO.^[16] The intensity of this band increased with time, suggesting the accumulation of CO on the surface of PEosinY-1. The strong adsorption of CO on the surface of **PEosinY-1** might be resposible for the slight

decrease in the catalytic efficiency of $\ensuremath{\text{PEosinY-1}}$ as it was reused .

In-situ electron paramagnetic resonance (EPR) analysis was carried out to detect the spin reactive species dissolved in water or adsorbed on PEosinY-1 using 5,5-dimethyl-1-pyrroline Noxide (DMPO) as a free radical trap. As shown in Figure S20, no obvious signals of radicals were observed in the case of performing the reaction in dark, while characteristic signals of •OH with relative intensities of 1:2:2:1 were clearly observed under light illumination. Radical signals with six characteristic peaks of equal intensities were also detected, which might be attributed to the [PEosinY]' radicals originated from the EosinY active sites in **PEosinY-1**.^[17] These results indicate that visible light irradiation resulted in the formation of reactive •OH and [PEosinY]' radicals. Moreover, H2O2 was also detected by FeCl₂/KSCN and UV-vis spectrophotometry (Figure S21, SI). Considering that the VB position of **PEosinY-1** is higher than the redox potential of H_2O oxidation to H_2O_2 , it is thermodynamically unfavorable for **PEosinY-1** to catalyzing H_2O oxidation to H_2O_2 . We performed cyclic voltammetry (CV) detection on PEosinY-1 in 0.2 M Na₂SO₄ aqueous solutions saturated with O₂ or CO₂. respectively. An O2 reduction peak was observed at -0.52 V in the collected CV curve under CO₂ atmosphere though it was very weak compared to that observed in the case of O₂ atmosphere (Figure S22, SI). After potentiostatic reduction at -0.52 V for 1 h, H₂O₂ was detected in the electrolyte. Therefore, we speculated that the formation of H_2O_2 in the CO_2 photoreduction may undergo the following processes. Under the visible light irradiation, H₂O was oxidized to O₂, which was further reduced to H_2O_2 on the surface of the catalyst. $\ensuremath{^{[18]}}$ This could also explain why no O_2 was detected in the CO_2 photoredution process over PEosinY-N.

To understand the mechanism of photogenerated electron transport during the CO₂ photoreduction, DFT calculations were performed taking M-1 (as shown in Figure S23A and S23B, SI), the typical structure unit of **PEosinY-1**, as a module compound. The highest occupied molecular orbital (HOMO) (Figure S23C, SI) and the lowest unoccupied molecular orbital (LUMO) (Figure S23D, SI) were used to elucidate the transfer of photoexcited charge carrier in M-1. It was indicated that the HOMO of M-1 mainly consisted of 2pz orbitals of O and C (center 27, 62, 63) as shown in Table S2, which could serve as the light-absorption sites and the electron donors. The LUMO of M-1 mainly composed of the 2pz orbitals of C (center 1, 5, 15) as shown in Table S3, suggesting that the photogenerated electrons could transfer to or through these atoms to realize the photoreduction of CO2. Hence, it can be deduced that during the CO2 photoreduction process over PEosinY-N, EosinY building block and C=C within the polymer backbone serve as light-absorption sites for generation of electrons and holes, as well as for the subsequent electron transfer.

The interaction sites for CO₂ and H₂O on **M-1** were explored as well. The coordination of -OH and -COO- of **M-1** with CO₂ were taken into consideration (Figures 3A and 3B). After optimization, the binding energies of -OH, and -COO- with CO₂ were calculated to be -3.99 and -4.50 Kcal/mol, respectively, suggesting that both -OH and -COO- could adsorb CO₂, and -COO- had better capability. Likewise, -OH and -COO- could also adsorb H₂O, with binding energies of -9.22, and -5.99

Kcal/mol, respectively, and –OH showed the better ability to interact with H_2O (Figures 3C and 3D). The adsorbed CO_2 and H_2O may be activated by the interaction sites to some extent. Hence, it can be deduced that CO_2 is mainly adsorbed and activated at –COO– sites, getting electrons from LUMO of **PEosinY-N** and further being reduced to CO, while H_2O can be mainly adsorbed and activated at –OH sites, getting holes from HOMO and further being oxidized to oxygen.



Figure 3. The binding distance and binding energy between –OH or –COO- in M-1 and CO₂ (A) (B) and H₂O (C) (D).

Based on the above experimental and calculation results, the mechanism for photocatalytic CO₂ reduction over **PEosinY-N** was proposed as shown in Scheme S1. Upon visible light irradiation, the photo-generated electrons (e⁻) migrate from VB to CB of the catalyst, leaving holes (h⁺) at VB. The absorbed H₂O on the catalyst surface captures h⁺, generating H⁺ and O₂. Subsequently, O₂ captures e⁻ and H⁺, forming •OH, which further converts to H₂O₂. The adsorbed CO₂ accepts electron to form CO₂⁻⁻ intermediate, which further combines with H⁺ to form [COOH]_{ads}. After accepting another pair of H⁺/e⁻, [COOH]_{ads} undergoes dehydration, generating adsorbed CO, which then disengages from the catalyst surface into free CO.

In summary, the EosinY-functionalized porous polymers with high surface areas were designed, which achieved the photocatalytic reduction of CO₂ with gaseous H₂O under visible light irradiation, affording CO as the sole carbonaceous product with a production rate up to 33 µmol g⁻¹ h⁻¹ and a selectivity of 92%. DFT calculations indicate that the EosinY sites could adsorb and activate the CO₂ and H₂O molecules, and the EosinY sites and C=C bonds together with the conjugated structure of **PEosinY-N** could realize light absorption and efficient separation of electron/hole, as well as the adsorption and activation of CO₂ and H₂O. This work provides new insight for designing and fabricating photocatalytically active polymers with high efficiency for solar-energy conversion.

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Keywords: porous organic polymer \cdot photocatalysis \cdot CO₂ reduction \cdot H₂O oxidation \cdot CO

- [1] J. L. White, M. F. Baruch, J. E. Pander Iii, Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abelev, A. B. Bocarsly, *Chem. Rev.* **2015**, *115*, 12888-12935.
- [2] a) J. Bonin, M. Robert, M. Routier, *J. Am. Chem. Soc.* 2014, *136*, 16768-16771; b) D. Hong, Y. Tsukakoshi, H. Kotani, T. Ishizuka, T. Kojima, *J. Am. Chem. Soc.* 2017, *139*, 6538-6541; c) H. Rao, L. C. Schmidt, J. Bonin, M. Robert, *Nature*. 2017, *548*, 74-77.
- [3] a) A. Bhardwaj, J. Kaur, M. Wuest, F. Wuest, *Nat. Commun.* 2017, 8, 1; b) H. Li, Y. Gao, Y. Zhou, F. Fan, Q. Han, Q. Xu, X. Wang, M. Xiao, C. Li, Z. Zou, *Nano. Lett.* 2016, 16, 5547-5552; c) S. C. Yan, S. X. Ouyang, J. Gao, M. Yang, J. Y. Feng, X. X. Fan, L. J. Wan, Z. S. Li, J. H. Ye, Y. Zhou, Z. G. Zou, *Angew. Chem. Int. Ed.* 2010, 49, 6400-6404; *Angew. Chem.* 2010, 122, 6544-6548.
- [4]a) Y. Fu, D. Sun, Y. Chen, R. Huang, Z. Ding, X. Fu, Z. Li, Angew. Chem. Int. Ed. 2012, 51, 3364-3367; Angew. Chem. 2012, 124, 3420-3423; b) L. Zeng, X. Guo, C. He, C. Duan, ACS. Catal. 2016, 6, 7935-7947
- [5] a) J. Zhang, X. Chen, K. Takanabe, K. Maeda, K. Domen, J. D. Epping, X. Fu, M. Antonietti, X. Wang, *Angew. Chem. Int. Ed.* 2010, 49, 441-444; *Angew. Chem.* 2010, 122, 451-454;
- [6] a) Z. A. Lan, Y. Fang, Y. Zhang, X. Wang, *Angew. Chem. Int. Ed.* **2018**, 57, 470-474; *Angew. Chem.* **2018**, *130*, 479-483; b) P.
 Pachfule, A. Acharjya, J. Roeser, T. Langenhahn, M. Schwarze, R. Schomacker, A. Thomas, J. Schmidt, *J. Am. Chem. Soc.* **2018**, *140*, 1423-1427.
- [7] a) Z. Yang, B. Yu, H. Zhang, Y. Zhao, Y. Chen, Z. Ma, G. Ji, X. Gao, B. Han, Z. Liu, *ACS. Catal.* **2016**, *6*, 1268-1273; b) Z. Z. Yang, Y. Zhao, H. Zhang, B. Yu, Z. Ma, G. Ji, Z. Liu, *Chem. Commun.* **2014**, *50*, 13910-13913.
- [8] a) R. S. Sprick, J. X. Jiang, B. Bonillo, S. Ren, T. Ratvijitvech, P. Guiglion, M. A. Zwijnenburg, D. J. Adams, A. I. Cooper, *J. Am. Chem. Soc.* 2015, *137*, 3265-3270;b) L. Wang, Y. Wan, Y. Ding, S. Wu, Y. Zhang, X. Zhang, G. Zhang, Y. Xiong, X. Wu, J. Yang, H. Xu, *Adv. Mater.* 2017, *29*, *1702428*.
- [9] X. Chang, T. Wang, J. Gong, Energ. Environ. Sci. 2016, 9, 2177-2196.
- [10] K. L. Bae, J. Kim, C. K. Lim, K. M. Nam, H. Song, Nat. Commun. 2017, 8, 1156.
- [11] J. Li, B. Shen, Z. Hong, B. Lin, B. Gao, Y. Chen, Chem. Commun. 2012, 48, 12017-12019.
- [12] a) Y. Chen, C. Zhang, C. Yang, J. Zhang, K. Zheng, Q. Fang, G. Li, *Nanoscale.* 2017, 9, 15332-15339; b) Z. Vlčková Živcová, O. Frank, S. Drijkoningen, K. Haenen, V. Mortet, L. Kavan, *RSC. Adv.* 2016, *6*, 51387-51393.
- [13] L. B. Hoch, L. He, Q. Qiao, K. Liao, L. M. Reyes, Y. Zhu, G. A. Ozin, *Chem. Mater.* **2016**, *28*, 4160-4168.
- [14] E. X. Chen, M. Qiu, Y. F. Zhang, Y. S. Zhu, L. Y. Liu, Y. Y. Sun, X. Bu, J. Zhang, Q. Lin, *Adv. Mater.* **2018**, *30*, *1704388*.
- [15] Y. L. Men, Y. You, Y. X. Pan, H. Gao, Y. Xia, D. G. Cheng J. Song, D. X. Cui, N. Wu, Y. Li, S. Xin, J. B. Goodenough, *J. Am. Chem. Soc* **2018**, *140*, 13071-13077.
- [16] R. Zhang, H. Wang, S. Tang, C. Liu, F. Dong, H. Yue, B. Liang, ACS. Catal. 2018, 8, 9280-9286
- [17] X. Z. Fan, J. W. Rong, H. L. Wu, Q. Zhou, H. P. Deng, J. D. Tan, C. W. Xue, L. Z. Wu, H. R. Tao, J. Wu, *Angew. Chem. Int. Ed* . 2018, *57*, 8514-8518; *Angew. Chem.* 2018, *130*, 8650-8654
- [18] R. Shi, H. F. Ye, F. Liang, Z. Wang, K. Li, Y. Weng, Z. Lin, W. F. Fu, C. M. Che, Y. Chen, *Adv. Mater.* **2017**, *30*, *1705941*.

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EosinY-functionalized organic polymers exhibit high catalytic efficiency for CO_2 photoreduction in the presence of H_2O under visible light irradiation, affording CO as the sole carbonaceous product with a rate of 33 µmol g⁻¹h⁻¹ and a selectivity of 92%.



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Organic Polymers for Visible-Light

Driven CO_2 Reduction with H_2O to CO

with High Efficiency