

# A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

# **Accepted Article**

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202006618

Link to VoR: https://doi.org/10.1002/anie.202006618

# WILEY-VCH

# Metal-Free Photocatalytic Hydrogenation Using Covalent Triazine Polymers

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Abstract: Photocatalytic hydrogenation of biomass-derived organic molecules transforms solar energy to high-energy-density chemical bonds, and may enable the production of industrial building-block chemicals with great economical values. Despite its great potential, photocatalytic hydrogenation remains poorly explored up to now. Existing researches are mostly based on broad bandgap inorganic semiconductors and require the assistance of noble metal based cocatalysts. Herein, we report the preparation of thiophene-containing covalent triazine polymer as the photocatalyst with unique donoracceptor units, and for the first time demonstrate the metal-free photocatalytic hydrogenation of unsaturated organic molecules exemplified by maleic acid and furfural. Under the visible light illumination, our polymeric photocatalyst enables the transformation of maleic acid to succinic acid with an incredible production rate of ~2 mmol g<sup>-1</sup>h<sup>-1</sup>, and furfural to furfuryl alcohol with a production rate of ~0.5 mmol g<sup>-1</sup>h<sup>-1</sup>. Great catalyst stability and recyclability are also measured. Given the structural diversity of polymeric photocatalysts and their readily tunable optical and electronic properties, metal-free photocatalytic hydrogenation represents a highly promising approach for solar energy conversion.

Tremendous efforts have been invested on the pursuit of artificial photosynthesis for the direct conversion of solar energy to chemical energy.<sup>[1-5]</sup> Most of them have focused on photocatalytic water splitting that produces molecular hydrogen with the solar-to-hydrogen conversion efficiency up to ~1%.<sup>[6-8]</sup> Unfortunately, hydrogen as the energy carrier intrinsically suffers from low volumetric density under the ambient condition. This poses a severe challenge to its storage and transportation.<sup>[9-10]</sup> More recently, solar-driven organic transformation emerges as a possible alternative and attracts increasing attention.<sup>[11-13]</sup> It may give rise to higher-density products that can be more readily stored and transported and with have greater economical values, thereby opening a new avenue toward the effective utilization of solar energy.

In industry, catalytic hydrogenation holds an essential key to the synthesis of a variety of fine chemicals and bulk commodities. The reaction usually proceeds under an elevated temperature (>400°C) and pressure (up to 150 atm) using molecular hydrogen as the reductant, and therefore is energy-intensive and potentially hazardous.<sup>[14]</sup> It is highly desirable to develop alternative hydrogenation strategies that operate under milder conditions. Photocatalytic hydrogenation offers an ideal solution. It is

<sup>+</sup> The two authors contribute equally. Institute of Functional Nano & Soft Materials (FUNSOM), Jiangsu Key Laboratory for Carbon-Based Functional Materials and Devices, Soochow University, Suzhou 215123, China E-mail: <u>yanguang@suda.edu.cn</u> generally performed under room temperature and ambient pressure, using protic solvents like H<sub>2</sub>O or alcohols as the hydrogen source instead of molecular hydrogen. Moreover, it allows for the on-site decentralized production of chemicals that can take place close to the location of consumption. Despite its great potential, studies about photocatalytic hydrogenation are very scarce. Among a handful of demonstrations, Guo and coworkers showed that Au-SiC could be used for the selective hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes to their corresponding unsaturated alcohols with high turnover frequency (487 h<sup>-1</sup>) and selectivity (100%) under visible light irradiation.<sup>[15]</sup> Priti Sharma and coworkers reported that Pd-g-C<sub>3</sub>N<sub>4</sub> was efficient for the selective reduction of a wide range of unsaturated derivatives and nitro compounds with great yields (>99%).[16] However, the use of broad bandgap inorganic semiconductors (>2.5 eV) limited the available solar spectrum that they could absorb. Most of them also required the assistance of noble metal (Au or Pd) cocatalysts, which considerably compromised their potential applications.

Compared to those well-studied inorganic semiconductor materials, photoactive conjugated polymers are famed for their structural diversity as well as tunable optical and electronic properties.[17-24] In particular, covalent triazine polymers (CTPs) which earn the name with their characteristic triazine nodes in the formation of two-dimensional or three-dimensional frameworks attract rapidly growing attention, and have been investigated for photocatalytic hydrogen generation and CO2 reduction.[25-30] Herein, we for the first time report photocatalytic hydrogenation, exemplified by the hydrogenation of maleic acid to succinic acid (hydrogenation of C=C bonds) and furfural to furfuryl alcohol (hydrogenation of C=O bonds) on a metal-free thiophenecontaining CTP. Both succinic acid and furfuryl alcohol are topvalued chemicals and have an annual market size of \$100-1000 million.<sup>[31-33]</sup> Remarkably, we demonstrate an incredible production rate of ~2 mmol g<sup>-1</sup>h<sup>-1</sup> for succinic acid, and ~0.5 mmol g<sup>-1</sup>h<sup>-1</sup> for furfuryl alcohol as well as great stability under visible light illumination ( $\lambda > 420$  nm).

A thiophene-containing covalent triazine polymer (denoted as CTP-Th) was prepared by the superacid-catalyzed trimerization reaction of its corresponding aromatic nitrile precursor to yield yellow powders at the gram scale (Figure 1a,b). The synthetic details are described in the Supporting Information. Thiophene and triazine moieties are designed and incorporated here as the electron donor (D) and acceptor (A) units respectively in the conjugated skeleton of CTP-Th (Figure 1a). They are expected to promote the  $\pi$ -electron delocalization over the molecular backbones, and enhance the light absorption and charge separation.<sup>[34-35]</sup> The final product was first characterized by a range of spectroscopic techniques to probe its molecular structure. X-ray diffraction (XRD) analysis of CTP-Th indicates its amorphous nature like many other CTPs (Figure S1). Solid-state

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<sup>13</sup>C cross-polarization magic-angle-spinning nuclear magnetic resonance (CP-MAS NMR) spectrum confirms the presence of sp<sup>2</sup>-hybridized carbons in triazine with its peak at 169.7 ppm, thereby providing definitive evidence for the successful polymerization of monomers.<sup>[36-37]</sup> The signals at 143 ppm and 125 ppm are contributed from the thiophene units in the conjugated skeleton (Figure 1c).<sup>[38]</sup> Fourier transform infrared (FT-IR) spectrum of CTP-Th displays two signature bands of triazine units at 1506 cm<sup>-1</sup> and 1364 cm<sup>-1</sup>, assignable to the aromatic C-N stretching and breathing vibrations respectively (Figure 1d).<sup>[39]</sup> The absence of the vibrational band from the terminal cvano group at 2221 cm<sup>-1</sup> corroborates that the polymerization is complete.<sup>[40]</sup> Elemental analysis result also agrees with the expectation (Table S1). In addition, the microstructure of CTP-Th was imaged under transmission electron microscopy (TEM) and is shown to consist of aggregated nanoparticles of 20-50 nm in size and with abundant porosity (Figure 1e). Its N<sub>2</sub> adsorption and desorption isotherm reveals the presence of mesopores and macropores with Brunauer-Emmett-Teller (BET) surface areas measured to be 72 m<sup>2</sup> g<sup>-1</sup> (Figure S2). Importantly, CTP-Th is chemically stable, and exhibits thermal stability up to 400°C under N<sub>2</sub> from thermogravimetric analysis (TGA) (Figure S3).



**Figure 1**. Preparation and characterization of CTP-Th. (a) Schematic illustration of the synthesis of CTP-Th from the monomer (Th); (b) photograph of asprepared CTP-Th powders; (c) solid-state <sup>13</sup>C NMR spectrum of CTP-Th; (d) FT-IR spectra of CTP-Th and Th; (e) TEM image of CTP-Th.

We next interrogated the optical property and electronic structure of CTP-Th, and compared them with those of the thiophene monomer (denoted as Th). Figure 2a depicts the ultraviolet-visible diffuse reflection (UV-vis DR) spectra of CTP-Th

and Th. Compared to the latter, CTP-Th exhibits a slightly redshifted absorption edge at ~530 nm and an extended tail up to ~700 nm. Their optical band gaps are estimated to be 2.26 eV and 2.38 eV for CTP-Th and Th respectively based on the Kubelka-Munk equation (Figure 2b). The enhanced light absorption and reduced band gap of CTP-Th is believed to result from the increased electron delocalization within its conjugated framework. In order to accurately determine the electronic band structure of CTP-Th. electrochemical Mott-Schottky analysis was performed by casting its thin film on fluorine-doped tin oxide (FTO) conductive glass as the working electrode. As shown in Figure S4 (Supporting Information), the inverse of its square capacitance (C-<sup>2</sup>) is found to linearly correlate with the working potential between 0.2 V and 0.5 V (versus saturated calomel electrode or SCE) in 0.2 M Na<sub>2</sub>SO<sub>4</sub>. The extrapolation of this linear region to the potential axis is derived to be -1.36 eV, corresponding to the flat band potential or lowest unoccupied molecular orbital (LUMO) level. The highest occupied molecular orbital (HOMO) level of CTP-Th is accordingly determined to be +0.9 eV. Furthermore, performed steady-state photoluminescence (PL) we spectroscopy analysis with an excitation wavelength of 450 nm in order to probe the electron transfer dynamics. Th exhibits a pronounced PL emission peak centered at 521 nm. When polymerized, the PL intensity of CTP-Th becomes red-shifted to 536 nm and significantly quenched by more than five times (Figure 2c). Time-resolved PL spectroscopy reveals a photoexcited carrier lifetime ( $\tau$ ) of 0.35 and 0.77 ns for Th and CTP-Th, respectively (Figure 2d). The attenuated PL emission and prolonged carrier lifetime of CTP-Th in comparison with those of Th unambiguously support that the radiative recombination of photoexcitons is effectively retarded upon polymerization, due to the enhanced photoexciton dissociation as facilitated by the D-A structure. The enhanced charge separation within CTP-Th was also confirmed using the density functional theory (DFT) simulations. As shown in Figure S5 (Supporting Information), the HOMO and LUMO electron-state-density distribution of Th spatially overlap and evenly distribute throughout the molecule. As for CTP-Th (here modelled using a trimer), its HOMO is mainly located on the electron-donating thiophene struts, while the LUMO is more delocalized over the conjugated framework owing to the presence of the electron-withdrawing triazine ring. The spatial asymmetric distributions of HOMO and LUMO evidence facile photoexciton dissociation (Figure 2e). Such advantageous optical property and charge dynamics render CTP-Th an ideal metal-free candidate for photocatalytic applications as would be discussed below.

The photocatalytic performance of CTP-Th for the selective hydrogenation of unsaturated C=C and C=O double bonds (exemplified using the reduction of maleic acid and furfural respectively) were carried out by dispersing the photocatalyst powder in corresponding aqueous solution under the irradiation of a 300 W Xe lamp equipped with a 420 nm cutoff filter (see Supporting Information for details). Additionally, ascorbic acid was added to the reaction solution here as the sacrificial electron donor in order to unveil the intrinsic activity and full potential of CTP-Th for photocatalytic hydrogenation. Of note, it should be highlighted that no cocatalyst was introduced so the entire photocatalytic system was essentially metal-free. Since the measured LUMO level of CTP-Th is higher than the theoretical

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reduction potential of maleic acid (-0.03 V at pH = 7 solution) and furfural (-0.34 V at pH = 7 solution), photogenerated electrons on CTP-Th are sufficiently energetic to drive their reductive transformation (Figure 2f).



**Figure 2.** Optical property and charge dynamics analysis of CTP-Th. (a) UV-Vis DR spectra of CTP-Th and Th; (b) band gap determination of CTP-Th and Th according to the Kubelka–Munk equation; (c) steady-state PL emission spectra of CTP-Th and Th excited at 450 nn; (d) time-resolved PL spectra of CTP-Th and Th; (e) simulated HOMO and LUMO electron-state-density distributions on CTP-Th; (f) HOMO and LUMO levels of CTP-Th plotted together with the theoretical reduction potentials of maleic acid and furfural.

We first explored the photocatalytic hydrogenation of maleic acid to succinic acid (Figure 3a). The reaction product was analyzed and quantified using <sup>1</sup>H NMR (Figure 3b and Figure S6). It is found that in the presence of maleic acid, the hydrogen production rate is suppressed from 6.61 mmol g<sup>-1</sup>h<sup>-1</sup> (normalized to the mass of CTP-Th) to 0.18 mmol g<sup>-1</sup>h<sup>-1</sup> (Figure S7a,b). By contrast, 2.05 mmol g<sup>-1</sup> of succinic acid is yielded in the first hour under the visible light illumination. The product linearly accumulates with the irradiation time, and at the end of 30 h, reaches a great amount of 56.5 mmol g<sup>-1</sup> (or a total of 0.28 mmol of succinic acid). This translates to a remarkable average production rate of 1.88 mmol g<sup>-1</sup>h<sup>-1</sup>. We demonstrate that this reaction is completely light-controlled. Under the alternating lightdark period, the amount of succinic acid correspondingly increases at the rate of ~2 mmol g-1h-1 when irradiated, and remains unchanged when not (Figure 3c), ultimately leading to the accumulation of ~0.058 mmol of succinic acid after 12 h reaction. Worth noting is that no hydrogenation product is measured in the absence of CTP-Th, light or ascorbic acid within the instrumental detection limit under otherwise identical conditions, suggesting their indispensable roles in photocatalysis (Figure S8). The Th monomer is also not photocatalytic active. Replacing ascorbic acid with methanol or lactic acid as the sacrificial electron donor quenches the photocatalytic activity. Moreover, our control experiments show that the photocatalytic hydrogenation of maleic acid could not proceed on TiO<sub>2</sub> P25 or  $C_3N_4$  free of any noble metal cocatalyst.

Photocatalytic hydrogenation may involve H<sup>+</sup> or water molecule as the hydrogen source. Even though a detailed mechanistic study is beyond the scope of this work, we are interested at the pH-dependence of the photocatalytic activity in order to shed light on the possible reaction pathway. To this end, experiments were conducted in solution with pH adjusted from ~1.6 (the standard condition) to >12 under otherwise identical conditions. We find that the photocatalytic activity (measured by the accumulated amount of succinic acid after 6 h irradiation) monotonically declines with the increase of solution pH, and become completely suppressed at pH > 7 (Figure 3d). This trend leads us to conclude that H<sup>+</sup> directly participates in the rate-determining step while H<sub>2</sub>O is not an effective proton donor. Interestingly, when H<sub>2</sub>O is replaced with dimethyl sulfoxide (DMSO) as the solvent, the production rate of succinic acid is lowered to 0.92 mmol g<sup>-1</sup>h<sup>-1</sup>. It suggests that H<sub>2</sub>O promotes hydrogenation presumably by facilitating the proton dissociation of ascorbic acid (Figure S9).



**Figure 3.** Photocatalytic hydrogenation on CTP-Th. (a) Schematic showing the photocatalytic hydrogenation of maleic acid and furfural to corresponding products on CTP-Th; (b) photocatalytic production rates of succinic acid and furfuryl alcohol over the reaction time; (c) photocatalytic hydrogenation of maleic acid under the alternating light-dark period; (d) pH-dependent photocatalytic activities in the hydrogenation of maleic acid; (e,f) recyclability of CTP-Th for the photocatalytic hydrogenation of (e) maleic acid and (f) furfural.

Following the successful demonstration about the photocatalytic transformation of maleic acid, we went on to study the photocatalytic hydrogenation of furfural to furfuryl alcohol. The resultant liquid product was quantitatively analyzed by high

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performance liquid chromatography (HPLC) (Figure S10). Its amount is also observed to follow a linear dependence on the irradiation time with an average production rate of 0.5 mmol g<sup>-1</sup>h<sup>-1</sup> in 18 h (Figure 3b). The competing hydrogen production rate is measured to be only ~0.09 mmol g<sup>-1</sup>h<sup>-1</sup> (Figure S7c). The photocatalytic activity for the hydrogenation of furfural is still significant, but admittedly lower than that of maleic acid probably owing to its smaller thermodynamical driving force as indicated in Figure 2f.

In addition to excellent activities, catalyst recycling is important in heterogeneous catalysis as this would greatly reduce the material cost. We here examined the recyclability of our polymeric photocatalyst for both reactions. This was done by filtrating the catalyst out from the solution after 6 h light experiment (defined as one cycle), carefully rinsing it with distilled water and then redispersing it in fresh solution for the subsequent cycle. When comparing the product amount accumulated within the 6 h period for each cycle, we find that CTP-Th can maintain ~80% of the original activity for the hydrogenation of succinic acid after 4 cycles (Figure 3e), and 92% of the original activity for the hydrogenation of furfural after 3 cycles (Figure 3f). The slight activity decay doesn't reflect the intrinsic activity loss, but is more likely caused by the unavoidable material loss during the transfer and re-dispersion of our polymeric photocatalyst. CTP-Th collected after the recycling experiments exhibits no apparent change in its molecular structure as revealed from UV-vis DR, FT-IR and TEM image (Figure S11).

In summary, we reported a thiophene-containing covalent triazine polymer as a visible-light photocatalyst for the metal-free photocatalytic hydrogenation of maleic acid and furfural. The incorporation of alternating thiophene and triazine units in the conjugated skeleton of CTP-Th results in a unique D-A structure that promoted the  $\pi$ -electron delocalization and enhanced the charge separation, as evidenced by our charge dynamics study and DFT calculations. Photocatalytic experiments showed that under visible light illumination ( $\lambda$  > 420 nm), CTP-Th could enable the selective hydrogenation of maleic acid to succinic acid with an incredible production rate of ~2 mmol g-1h-1 as well as the hydrogenation of furfural to furfuryl alcohol with a production rate of ~0.5 mmol g<sup>-1</sup>h<sup>-1</sup>. Great catalyst stability and recyclability were also observed for both reactions. Even though our study here was centered on two specific organic molecules as the examples, the demonstrated principle of metal-free photocatalytic hydrogenation on CTPs can be readily extended to other organic molecules containing unsaturated C=C or C=O bonds. Compared to photocatalytic hydrogen generation, photocatalytic hydrogenation adds hydrogen to unsaturated chemical bonds, and yields products with higher energy storage density and greater economical values. At last, the structural and functional diversity of CTPs may allow us to precisely tune their optical and electronic properties for optimal photocatalytic performances.

#### Acknowledgements

We acknowledge the support from the Ministry of Science and Technology of China (2017YFA0204800), the Priority Academic Program Development of Jiangsu Higher Education Institutions, and Collaborative Innovation Center of Suzhou Nano Science and Technology. W. Huang thanks the support from China Postdoctoral Science Foundation (2018M640518).

**Keywords:** metal-free photocatalytic hydrogenation • covalent triazine polymers • donor-acceptor units • maleic acid • furfural

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# Metal-Free Photocatalytic Hydrogenation Using Covalent Triazine Polymers

Covalent triazine polymeric photocatalyst with unique donoracceptor units could enable the metal-free photocatalytic hydrogenation of maleic acid to succinic acid as well as furfural to furfuryl alcohol with an incredible production rate, great stability and recyclability.