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Conjugated microporous polymers as a visible light driven platform for photo-redox conversion of biomass derived chemicals[†]

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Photocatalytic conversion of biomass derived chemicals to valuable products is a highly sustainable process. Herein we report the photocatalytic hydrogenation of maleic acid to succinic acid and oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran using the same conjugated porous polymers (CMPs). The CMPs were constructed from 2,4,6-(tri-2-thienyl)-1,3,5-triazine as the knots and different benzene derivatives as linkers, and their morphologies, redox potentials, charge separation efficiency, and the consequent photocatalytic performance have been controlled. As a result, the CMP with benzene as the linker features the highest photocatalytic activities with production rates of 4.66 mmol g⁻¹ h^{-1} for succinic acid and 0.53 mmol q^{-1} h^{-1} for 2,5-diformylfuran, respectively. Most importantly, high photocatalytic activity has also been achieved under natural sunlight irradiation, implying its feasibility as an efficient photocatalytic platform for solar-tochemical energy conversion.

In the past century, the fossil-based industry has drastically promoted economic growth and greatly changed the face of the Earth. However, global overexploitation of fossil fuels has also caused ever increasing concern about serious environmental pollution and climate warming problems.¹⁻³ As a sustainable alternative, biomass, by appropriate upgrading processes, could be converted into a wide range of high-valued chemicals. Biomass refinery has mainly focused on catalytic reductive and oxidative upgrading of furan-based platform molecules, such as furfural and 5-hydroxymethylfurfural (HMF).⁴⁻⁶ In most catalytic research studies, the extensive use of noble metal catalysts, and high temperature and pressure substantially increase energy consumption and costs.7-9 In contrast, photocatalysis is known for its mild reaction conditions under ambient temperature and atmospheric pressure, and direct conversion of solar energy into chemical

energy.^{10,11} During a photocatalytic process, a photocatalyst absorbs light and generates photoexcited electrons and holes, which could drive reductive and oxidative reactions, respectively. Therefore, using carefully designed photocatalysts, many current catalytic redox processes involving harsh reaction conditions and high costs could be replaced by photocatalysis, with sunlight as the energy source.¹²

The last decade has witnessed tremendous efforts in the pursuit of novel heterogeneous photocatalysts with excellent activities. Among them, organic semiconductors, such as g-C₃N₄, CTFs, CMPs, and COFs, have gained considerable attention due to their advantages of lower price and less toxicity compared to their inorganic counterparts.¹³⁻¹⁸ In particular, conjugated microporous polymers (CMPs) are attracting rapidly growing attention due to their extended π -conjugation, high designability, large specific surface area, excellent thermal stability and tunable band structure, making them ideal for the development of efficient porous materials for photocatalysis, energy storage, energy conversion and photothermal therapy.^{19–22} A lot of research studies have demonstrated their outstanding activities on photocatalytic hydrogen evolution and CO₂ reduction.^{23,24} More recently, CMPs were also used in the photocatalytic transformation of biomass derived chemicals. For instance, CTP-Th could be used for efficient photocatalytic hydrogenation of maleic acid and furfural under visible light.²⁵ Using CTF-Th@SBA-15, HMF could be selectively oxidized to 2,5-diformylfuran (DFF).²⁶ However, apart from the relatively low photocatalytic rates, their sole use in reduction or oxidation limits the practical applications of these CMPs in the upgrading of biomass derived chemicals.

Herein, we report novel CMPs prepared by coupling 2,4,6-(tri-2-thienyl)-1,3,5-triazine (TTT) and different benzene derivative linkers for photocatalytic reductive and oxidative conversions of biomass-derived chemicals. The linkers in the CMPs play an important role in affecting their morphologies, and optical and electrical properties, as well as photocatalytic performance. The photocatalytic hydrogenation of maleic acid to succinic acid and oxidation of HMF to DFF were realized by

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the same CMP with remarkable high production rates of 4.66 mmol $g^{-1} h^{-1}$ for succinic acid and 0.53 mmol $g^{-1} h^{-1}$ for DFF. Most importantly, high photocatalytic activity has also been achieved under natural sunlight irradiation, implying its feasibility as an efficient photocatalytic platform for solar-to-chemical energy conversion.

To build our CMPs, we chose TTT as the knots because its inherent donor (three thiophene rings) and acceptor (triazine ring) extend the visible light absorption of all the corresponding CMPs. TTT was linked with three isomorphic linkers, benzothiadiazole (BTD), benzene (Ben) and dimethoxybenzene (DMOB), to form three CMPs (labeled as pTTT-BTD, pTTT-Ben and pTTT-DMOB, respectively) with adjusted optical and electrical properties. As illustrated in Fig. 1a, all the CMPs were synthesized by a C–H direct arylation reaction. Three CMPs were obtained as colored powders, which did not dissolve in water and general organic solvents.

Firstly, we applied elemental analysis, Fourier transform infrared (FT-IR) spectroscopy, and solid-state ¹³C CP/MAS NMR to confirm the chemical structures of the obtained CMPs. Elemental analysis results revealed that the carbon, hydrogen, nitrogen and sulfur contents are close to their calculated values (Table S1†). As shown in Fig. S2,† the intense peaks at 1500 and 1370 cm⁻¹ in the infrared spectra could be ascribed to the C–N stretching and breathing mode in the triazine ring, respectively. The characteristic bands of thiophene



Fig. 1 Synthetic routes (a) of CMPs and (b) 13 C solid state NMR spectra of TTT-based CMPs, spinning side bands are marked with an asterisk (*). (c) SEM and (d) TEM images of pTTT-Ben.

could also be found at 1030 and 720 cm⁻¹. The attenuation of the C-Br band around 1070 cm⁻¹ of CMPs clearly illustrates the high degree of polymerization.^{24,27} In addition, more detailed connection of these CMPs was obtained *via* solid-state ¹³C CP/MAS NMR. The low-field signals at δ = 167 ppm in the spectra of all CMPs are attributed to the carbon atoms in the triazine rings. All the remaining peaks could also be ascribed to specific carbons in the three CMPs. For example, the highfield peak at 55 ppm of pTTT-DMOB is derived from the carbon atom of the methoxy group, while the peak at 140 ppm is assigned to the carbon in the thiadiazole ring (Fig. 1b and Fig. S3†).^{28,29}

The surface morphologies of the three CMPs were observed by SEM and TEM (Fig. S6[†]). Both pTTT-BTD and pTTT-DMOB exhibited nonuniform bulk particles. However, pTTT-Ben presented a nanofiber morphology, which intertwined to further form a reticular structure (Fig. 1c). TEM images (Fig. 1d) showed that the diameter of the nanofibers ranged from 20 to 40 nm. It is believed that this 1D nanofiber structure enables better exposure of active sites, which leads to more efficient charge transfer compared to 3D bulk particles.³⁰ The different morphologies may be caused by the negative effect of side groups in benzothiadiazole and dimethoxybenzene on π - π stacking interaction, which made pTTT-Ben grow faster along the Z direction rather than X and Y directions.^{31–33} According to the N_2 sorption experiment at 77 K, the Brunauer-Emmett-Teller (BET) specific surface areas of pTTT-BTD, pTTT-Ben and pTTT-DMOB were found to be 66, 307 and 39 m² g⁻¹, respectively (Fig. S4[†]). As known, a high surface area plays a propitious role for catalysts in heterogeneous catalysis.34 Thermogravimetric analysis was conducted to study thermal stability (Fig. S10[†]). Thanks to the fully conjugated aromatic backbones, these CMPs are chemically stable and exhibit high thermal stability.^{35–37} Especially, pTTT-Ben has an excellent thermal stability of up to 600 °C.

The UV-Vis diffuse reflectance spectra (DRS) and solid-state fluorescence spectra of the CMPs are displayed in Fig. 2a and Fig. S11,† respectively. These CMPs exhibited different visiblelight absorption properties. Compared with pTTT-Ben, both pTTT-DMOB and pTTT-BTD have red-shifted absorption and emission, but the reasons are very different. For pTTT-DMOB, it can be explained by the more electron-rich linker of dimethylbenzene than benzene, while for pTTT-BTD, it is mainly the influence of the D-A structure consisting of benzothiadiazole and adjacent thiophenes. Calculated from the corresponding Tauc plot (Fig. 2b), their optical band gaps were determined to be 2.01 eV for pTTT-BTD, 2.50 eV for pTTT-Ben and 2.23 eV for pTTT-DMOB, which are in good agreement with their colors (insets of Fig. 2c). To further investigate the relative band structures, the electrochemical Mott-Schottky analysis was performed (Fig. S12[†]). The flat band potentials, or conduction bands (CB), were approximately -0.39, -0.48and -0.44 V (vs. SCE), with corresponding valence band (VB) positions at +1.62, +2.02 and +1.79 V for pTTT-BTD, pTTT-Ben, and pTTT-DMOB, respectively (Fig. 2c).

It is known that organic semiconductors have a high exciton binding energy, which makes charge separation a key



Fig. 2 Optical properties and band structure analysis. (a) UV/Vis DR spectra of three CMPs. (b) Tauc plot and their optical band gaps. (c) Calculated CB and VB positions. (d) Time-resolved photoluminescence spectroscopy.

factor influencing the photocatalytic efficiency of organic semiconductors.^{38,39} The carrier lifetime (τ) in time-resolved photoluminescence spectroscopy can evaluate the separation of the photogenerated electrons and holes. As shown in Fig. 2d and Table 1, pTTT-Ben has the longest carrier lifetime (τ = 0.36 ns), implying that it possesses the highest charge separation efficiency among the three CMPs. The highest photocurrent response of pTTT-Ben also shows its high production of photogenerated carriers (Fig. S13†).^{40,41}

Subsequently, the CMPs were applied to the photocatalytic transformation of organic chemicals. In order to study the application potential of these CMPs in biomass refinery, maleic acid and HMF were chosen as model molecules, because they are both important biomass derivatives. More importantly, their reduction/oxidation products, succinic acid and DFF, are also value-added chemicals. Succinic acid is widely used in food, pharmaceutical and plastic industries, while DFF can be used as a furan-based chemical for polymer materials, drug intermediates, antifungal agents and fluorescent agents.^{42,43} To our delight, the measured CB/VB levels of TTT-based CMPs match redox potentials of maleic acid

Table 1	Porous and	optical	properties	of three	CMPs
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CMPs	$S_{\rm BET}^{\ \ a} \left[{\rm m}^2 \; {\rm g}^{-1} \right]$	$E_{\mathrm{g}}^{\ b}\left[\mathrm{eV} ight]$	$CB^{c}\left[V\right]$	$VB^{c}\left[V\right]$	$\tau^d [\mathrm{ns}]$
pTTT-Ben	307	2.50	-0.48	+2.02	0.36
pTTT-DMOB	39	2.23	-0.44	+1.79	0.30
pTTT-BTD	66	2.01	-0.39	-1.62	0.30

^{*a*} Surface area calculated from the N₂ adsorption isotherm using the BET equation. ^{*b*} Optical band gaps calculated using the Kubelka–Munk function. ^{*c*} Conduction band valence band positions calculated from band gaps and flat band potentials *vs.* SCE. ^{*d*} Fluorescence lifetime calculated from the equation $\tau = t(I_0/e) - t(I_0)$.

 $(-0.03 \text{ V} vs. \text{ SCE})^{25}$ and HMF (+0.89 V vs. SCE),²⁶ indicating that photogenerated electrons/holes in TTT-based CMPs can kinetically drive these redox transformations.

Firstly, we explored the photocatalytic hydrogenation of maleic acid to succinic acid over the obtained CMPs using ascorbic acid as the sacrificial agent and a LED (40 W, 460 nm) lamp as the light source. The yields of succinic acid were determined by ¹H-NMR spectroscopy. As depicted in Fig. 3b, the succinic acid production rates were 0.16 mmol g^{-1} h⁻¹ for pTTT-BTD, 2.44 mmol g^{-1} h⁻¹ for pTTT-DMOB and 4.66 mmol g^{-1} h⁻¹ for pTTT-Ben. Among the three CMPs, pTTT-Ben exhibited the best photocatalytic performance. A time-dependent experiment demonstrated that the production of succinic acid correlates approximately linearly with the irradiation time in the initial stage and finally the yield reached 40% at 20 h (Fig. S15 and S16[†]). It is important to note that without light, photocatalyst or ascorbic acid, no hydrogenation product was detected, demonstrating the nature of the photocatalytic process (Fig. S18[†]).



Fig. 3 Photocatalytic activities of the CMPs. (a) and (b) show the photocatalytic production rates of succinic acid and DFF with different catalysts, respectively.

Communication

Encouraged by the excellent photocatalytic hydrogenation activity of these CMPs, we further tested their photocatalytic oxidation of HMF. Atmospheric air was used as the oxidant because it is cheaper, safer and more convenient than pure oxygen.⁴⁴ ¹H-NMR spectroscopy revealed that DFF was the sole product, with formation rates of 0.06, 0.04 and 0.53 mmol g⁻¹ h⁻¹ for pTTT-BTD, pTTT-DMOB and pTTT-Ben, respectively (Fig. 3c). The time-dependent experiment showed that the production yield of DFF was linearly correlated with irradiation time and the yield reached 25% at 60 h (Fig. S20 and S21†). Control experiments also confirmed that no production of DFF occurred in the dark, under a nitrogen atmosphere or in the absence of a photocatalyst (Fig. S23†). A pH-dependent experiment demonstrated that DFF production was totally inhibited when the reaction system was strongly basic (pH = 12, Fig. S22†).

Notably, using pTTT-Ben, both the photocatalytic rates of hydrogenation of maleic acid and oxidation of HMF are much higher than most reported works including some inorganic semiconductors (Table S5[†]).^{25,26,45,46} It is known that a photocatalytic reaction is controlled by three key factors, namely, light absorption, charge separation and surface reaction.¹³ From Fig. 2a, we find that pTTT-Ben absorbs less or similar light than the other two CMPs at 460 nm, while pTTT-Ben is quite different from them in surface properties and charge separation (Table 1 and Fig. S6[†]). So, we suspect that surface reaction and charge separation are indispensable reasons for the best photocatalytic performance of pTTT-Ben among the three CMPs. Since the CMPs were synthesized by the Pd catalyzed reaction, the residual Pd was detected by inductively coupled plasma atomic emission spectrometry (ICP-AES), which showed that Pd contents in all three CMPs were lower than 0.02% (Table S3[†]). Such low values were below the detection limit of energy-dispersive X-ray spectroscopy (EDX) (Table S2[†]). These contents are much lower than most other CMPs prepared by Pd catalyzed reactions.^{23,28} Several studies also show that there is no clear correlation between residual Pd and photocatalytic activity.47,48 Therefore, it is unlikely that the Pd contributes significantly to the observed high photocatalytic rates.

Considering that sunlight is free, ubiquitous and inexhaustible and one of the goals of photocatalysis is to directly convert solar energy to chemical energy,^{49,50} we conducted the two reactions with pTTT-Ben under natural sunlight irradiation. The reactions were carried out with test tubes half submerged in a water bath (Fig. S24†). The sunlight intensity was detected at every half-hour interval and is shown in Table S4.† As expected, pTTT-Ben also exhibited good photocatalytic ability. The average production rates of succinic acid and DFF were 0.57 and 0.28 mmol g^{-1} h⁻¹, respectively, lower than those under LED light irradiation. However, even under low solar irradiation and dense cloud in winter, the results are still impressive and demonstrate its high portability to other seasons and districts.

Besides the excellent activities, the recycling performance is an important virtue of heterogeneous catalysts for practical application. Thus, we examined the reusability and stability of the best catalyst pTTT-Ben in the photocatalytic conversion of maleic acid. The photocatalyst maintained over 85% of its original activity after 5 cycles, with its structure unaltered (Fig. S25 and S26†). The slight decay of activity is more likely due to photocatalyst mass loss during each solid–liquid separation process.

In summary, three CMPs with different isomorphic linkers were successively synthesized by C-H direct arylation polymerization. The linkers in the CMPs have huge multiple impacts on their morphologies, redox potentials and charge separation efficiency. The photocatalytic hydrogenation of maleic acid to succinic acid and oxidation of HMF to DFF were realized by using these CMPs as photocatalysts. The benzene linked pTTT-Ben has the highest surface area, nanofiber morphology, high thermal stability, relatively wide band gap, and strong charge separation effect, and therefore show the best photocatalytic properties in both reductive and oxidative reactions. In addition, high photocatalytic activity under natural sunlight irradiation has also been achieved. Our results showed that, according to rational design, CMPs could act as a promising sunlight-driven photocatalytic platform for efficient transformation of biomass derived chemicals.

Author contributions

Bo Chen: conceptualization, methodology, resources, investigation, writing – original draft, visualization. Lang Chen, Zijun Yan, Jinyang Kang, Shanyong Chen, Yongdong Jin and Lijian Ma: validation, resources. Hongjian Yan and Chuanqin Xia: project administration, supervision, funding acquisition, visualization, writing – review & editing.

Conflicts of interest

The authors claim no conflicts of interest.

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Green Chemistry

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