Supplementary Information (SI) for ChemComm.

# Supporting Information

## Regulating the substituent of electron-acceptor in D-A system for boosting $H_2O_2$ photosynthesis from air and water

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## EXPERIMENTAL SECTION

### 1. Materials and general methods

The raw materials for synthesizing DCTP-Cl, DPTP-H, and DHTP-OH, along with organic solvents of 99% purity, were procured from Aladdin Biochemical Technology Co., Ltd. All reagents were used as received without further purification. Fourier transform infrared (FT-IR) spectra were acquired using a Bruker VERTEX 70 spectrometer within the wavenumber range of 700–3600cm$^{-1}$. Nitrogen adsorption-desorption isotherms were measured on a Belsorp-max instrument using ultrahigh-purity (purity:>99.999%) nitrogen. X-ray photoelectron spectroscopy (XPS) data were collected using a Thermo Scientific ESCALAB 250 Xi spectrometer, while scanning electron microscopy (SEM) images were captured using a Hitachi SU 8100 Scanning Electron Microscope. Photoelectrochemical experiments were conducted on a CHI760 workstation. Ultraviolet-visible (UV-vis) spectroscopy results were recorded in diffuse reflectance (DR) mode at room temperature using a SHIMADZU UV-2700 spectrophotometer equipped with an integrating sphere attachment. Solid-state nuclear magnetic resonance (NMR) experiments were performed on a Varian Infinityplus 300 solid-state NMR spectrometer (300 MHz). Photoluminescence decay profiles were measured using the time-correlated single photon counting (TCSPC) mode on a Picosecond Lifetime Fluorescence Spectrometer (QUANTAURUS-TAU C11367-11). Temperature-dependent photoluminescence spectra were recorded using a HORIBA Fluorolog-3 modular fluorescence spectrometer.

### 2. Synthesis of DCTP-Cl

2,4-Diamino-6-chloropyrimidine (DC, 24.5 mg, 0.15 mmol) and 1,3,5-triformylphloroglucinol (TP, 21.0 mg, 0.1 mmol) were charged into a glass ampoule containing 1-butanol (1 mL) and 1,2-dichlorobenzene (1 mL). The mixture was sonicated for 10 min, followed by the addition of aqueous acetic acid (6 mol L$^{-1}$, 0.2 mL) as a catalyst, and sonicated for another 5 min. After degassing via three freeze-pump-thaw cycles, the glass ampoule was sealed under vacuum, and the condensation reaction was conducted at 120 °C for 72h. Upon cooling to room temperature, the resulting solid was washed with N,N-dimethylformamide (DMF), yielding yellow powdery DCTP-Cl with a yield of approximately 87%.

### 3. Synthesis of DPTP-H

2,4-Diaminopyrimidine (DP, 16.52 mg, 0.15 mmol) and 1,3,5-triformylphloroglucinol (TP, 21.014 mg, 0.1 mmol) were charged into a glass ampoule containing 1-butanol (1 mL) and 1,2-dichlorobenzene (1 mL). The solution was sonicated for 10 min, followed by the addition of aqueous acetic acid (6 mol $L^{-1}$, 0.2 mL) as a catalyst, and sonicated for an additional 5 min. After degassing via three freeze-pump-thaw cycles, the glass ampoule was sealed under vacuum, and the condensation reaction was conducted at 120 °C for 72h. Upon cooling to room temperature, the resulting solid was washed with N,N-dimethylformamide (DMF), yielding orange powdery DPTP-H with a yield of approximately 83%.

### 4. Synthesis of DHTP-OH

2,4-Diamino-6-hydroxypyrimidine (DH, 19.065 mg, 0.15 mmol) and 1,3,5-triformylphloroglucinol (TP, 21.014 mg, 0.1 mmol) were charged into a glass ampoule containing 1-butanol (1 mL) and 1,2-dichlorobenzene (1 mL). The solution was sonicated for 10 min, followed by the addition of aqueous acetic acid (6 mol $L^{-1}$, 0.2 mL) as a catalyst, and further sonicated for 5 min. After degassing via three freeze-pump-thaw cycles, the glass ampoule was sealed under vacuum, and the condensation reaction was performed at 120 °C for 72h. Upon cooling to room temperature, the resulting solid was washed with N,N-dimethylformamide (DMF), yielding red powdery DHTP-OH with a yield of approximately 72%.

### 5. Photosynthesis of $H_2O_2$

5 mg of catalyst and 50 mL of deionized water (or 48 mL of water and 2 mL of active species trapping agent) were used. The mixture was continuously stirred under a xenon lamp for different time periods. After filtration through an organic membrane, the content of $H_2O_2$ was determined by UV-visable (UV-vis) spectrophotometry. Typically, 1 mL of the test solution, 1 mL of potassium hydrogen phthalate (0.1 mol/L), and 1 mL of potassium iodide (0.4 mol/L) were mixed and added to a 10 mL

volumetric flask, followed by standing for 1h. The concentration of hydrogen peroxide was determined at the maximum absorption wavelength of 350 nm.

## 6. Apparent quantum yield (AQE)

The apparent quantum efficiency (AQE) is similarly conducted according to references [28]. The apparent quantum efficiency (AQE) is calculated by measuring the photocatalytic synthesis of hydrogen peroxide ($H_2O_2$) over these materials under irradiation of 400 nm monochromatic light. The light intensity is measured using a PROVA-1010 digital optical power and energy meter. The photocatalytic reaction is performed in a system containing 50 mL of deionized water and 5 mg of photocatalyst. The AQE is then calculated by the following formula:

$$AQE(\%) = \frac{[GH_2O_2\,[produced(mol)] \times 2}{photons\ entered\ the\ reactor(mol)} \times 100\%$$

$$= \frac{[N_a \times h \times c][GH_2O_2\, produced(mol)] \times 2}{t \times S \times I \times \lambda}$$

Where $N_a$ is the Avogadro's constant ($6.022\times10^{23}$), h is the Planck constant ($6.626\times10^{-34}$), c is the speed of light ($3\times10^{8}$), S is the irradiation area ($cm^2$), I is the intensity of light irradiation ($W/m^2$), t is the irradiation time (3600 s) and $\lambda$ is the irradiation wavelength ($4\times10^{-7}$ m).

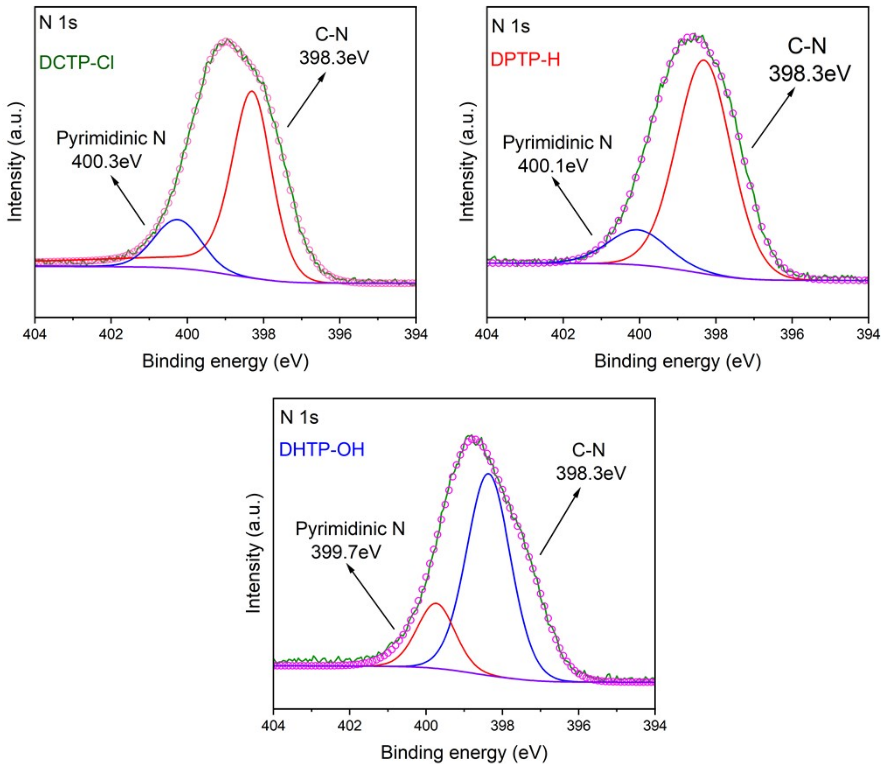

**Fig. S1** XPS N element of DCTP-Cl, DPTP-H and DHTP-OH.

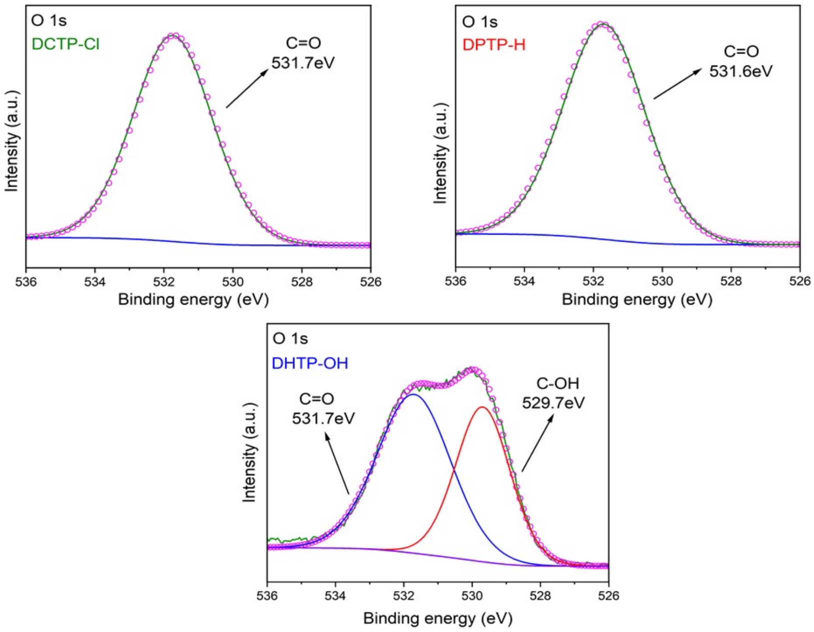

**Fig. S2** XPS O element of DCTP-Cl, DPTP-H and DHTP-OH.

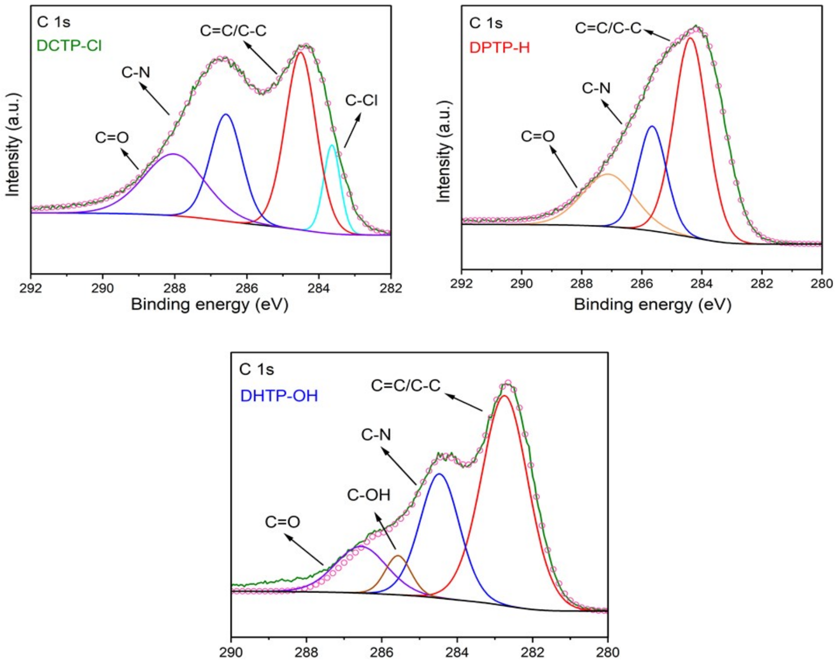

**Fig. S3** XPS C element of DCTP-Cl, DPTP-H and DHTP-OH.

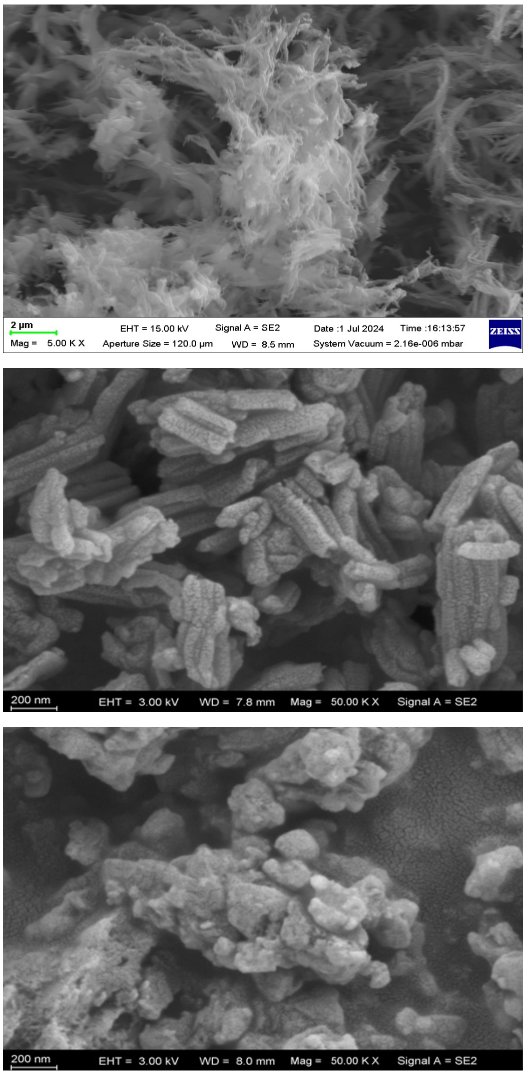

**Fig. S4** SEM image of DCTP-Cl(above), DPTP-H (middle) and DHTP-OH (below).

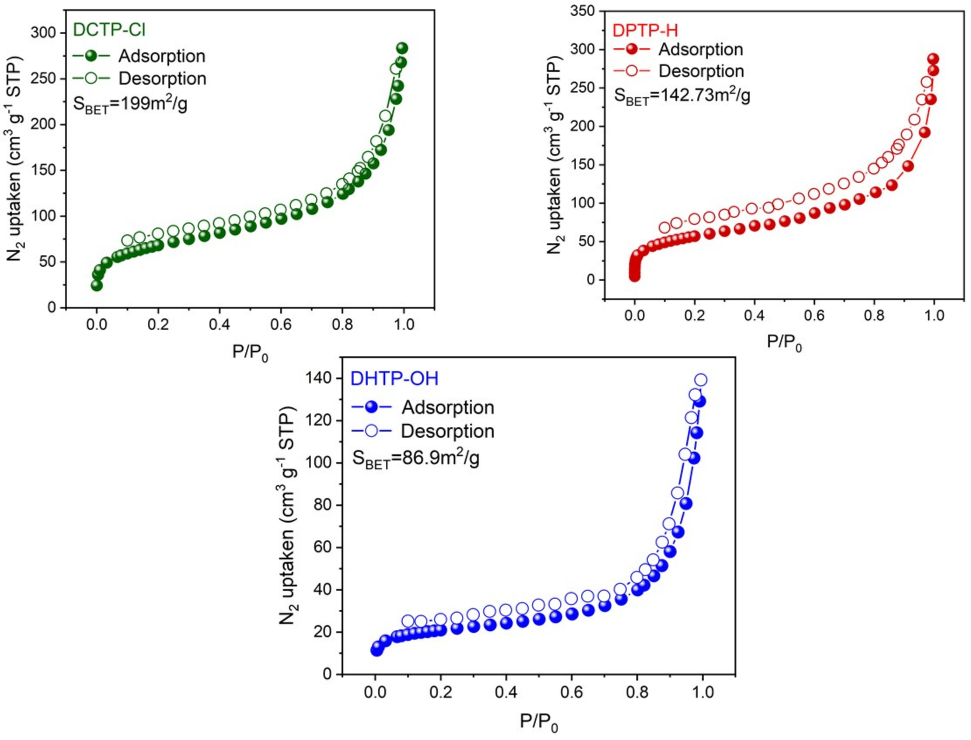

**Fig. S5** $N_2$ adsorption-desorption isotherms of DCTP-Cl、DPTP-H and DHTP-OH.

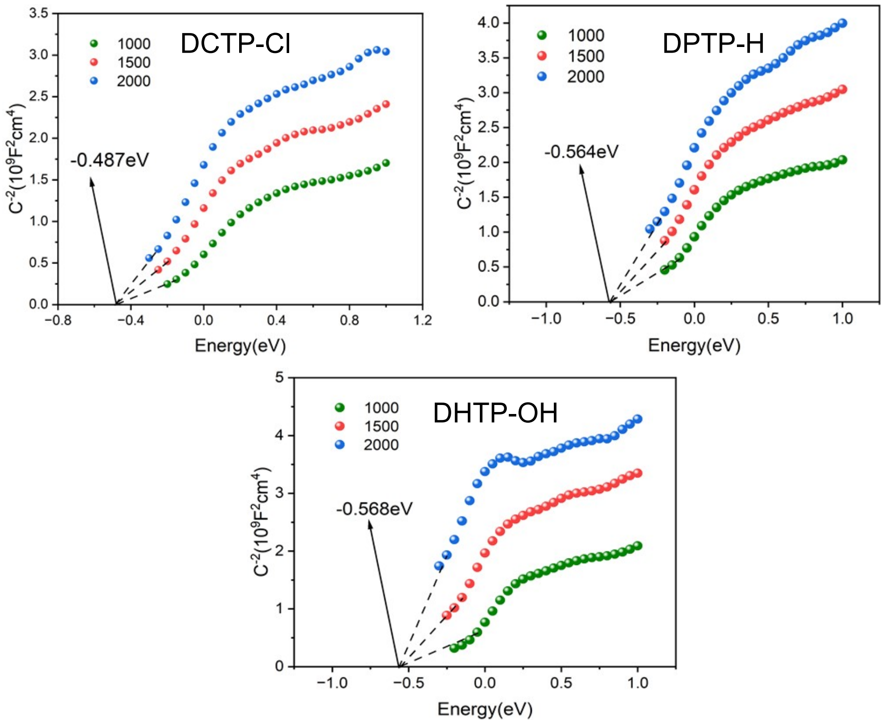

**Fig. S6** Mott-Schottky (MS) analysis of DCTP-Cl, DPTP-H and DHTP-OH.

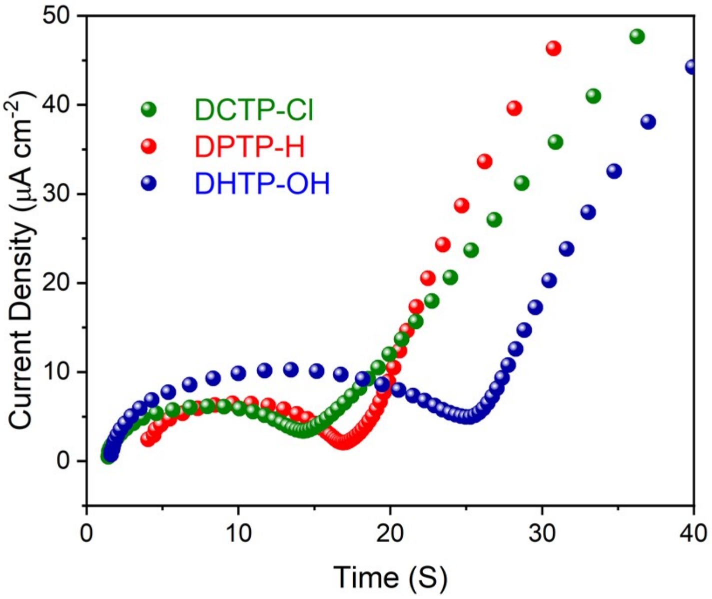

**Fig. S7** EIS of DCTP-Cl, DPTP-H and DHTP-OH.

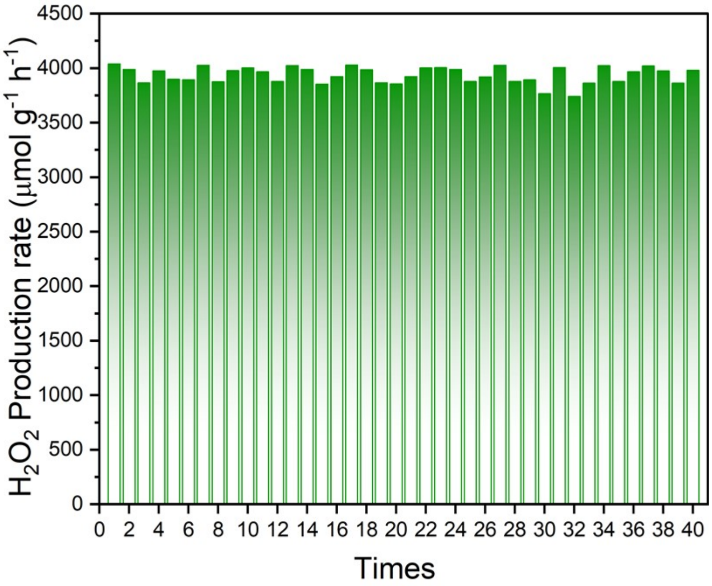

**Fig. S8** The stability of $H_2O_2$ photosynthesis upon DCTP-Cl in open air and pure water.

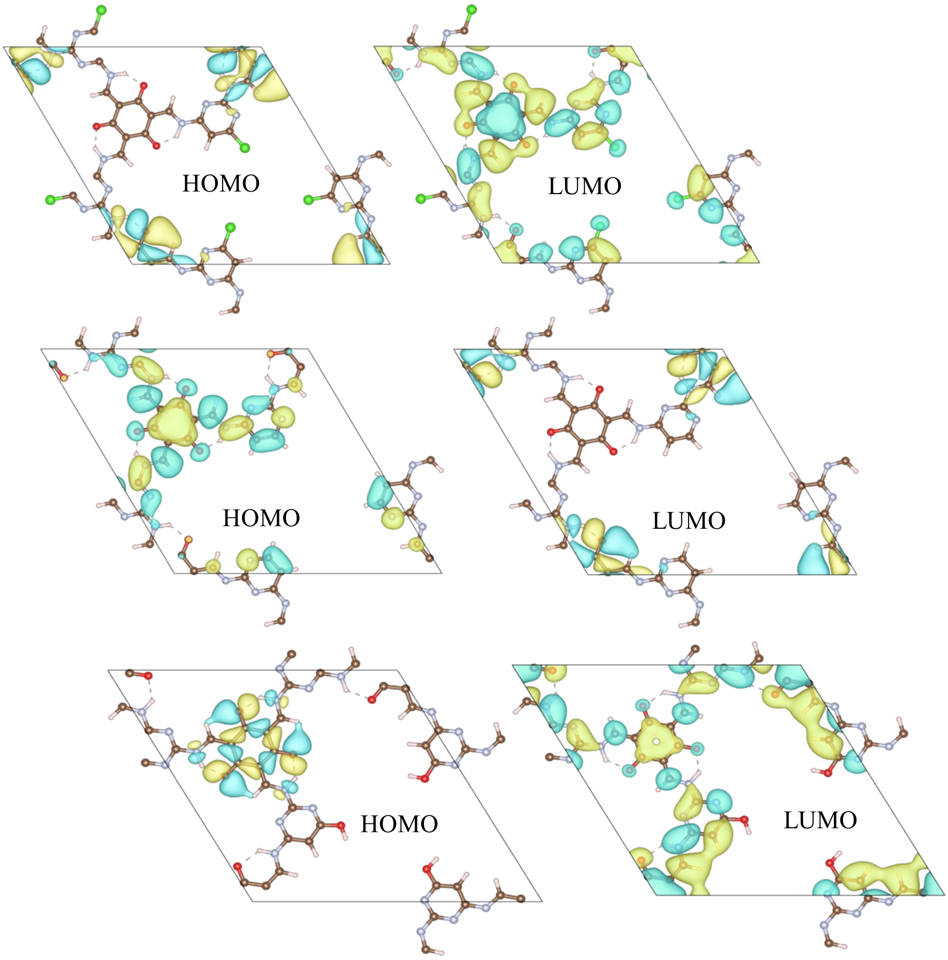

**Fig. S9** View of HOMO and LUMO of these materials in this work.