Molecular Engineering of g-C$_3$N$_4$ with Dibenzothiophene Groups as Electron Donor for Enhanced Photocatalytic H$_2$-Production

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Characterization. X-ray diffraction (XRD) patterns were obtained by a diffractometer (Shimadzu XRD-6100) using a Cu Kα radiation with a range of 5~80°. UV-vis diffuse reflectance spectra (DRS) of the samples were obtained on a UV-vis spectrometer (UV-2600, Shimadzu, Japan). Morphological observations of the as-synthesized samples were observed by a field emission scanning electron microscope (FESEM, JSM 7500F) and a transmission electron microscope (TEM, Talos F200S). The Fourier transform infrared spectra (FTIR) of all samples were recorded on an IR Affinity-1 FTIR spectrometer. Photoluminescence (PL) emission spectra were observed on a Fluorescence Spectrophotometer (F-7000, Hitachi, Japan) with an excitation wavelength of 360 nm. Time-resolved photoluminescence (TRPL) measurements were performed through an Edinburgh FLS1000 fluorescence lifetime spectrophotometer with the excitation wavelength at 375 nm. Nitrogen adsorption-desorption isotherms were recorded by a Micromeritics ASAP 2020 nitrogen adsorption apparatus. All the samples were degassed before adsorption measurements. The Brunauer-Emmett-Teller (BET) specific surface area (S_{BET}) of all the samples was obtained by the multipoint BET method. The pore size distribution was evaluated using desorption data with the Barrett-Joyner-Halenda (BJH) method. The chemical compositions and states of the samples were confirmed by X-ray photoelectron spectroscopy (XPS), which was equipped with an ultrahigh vacuum VG EXCALAB 210 electron spectrometer by using Al Kα radiation as the X-ray source. All binding energies were referenced to the C 1s peak of adventitious carbon at 284.8 eV.

Photoelectrochemical Analysis. The photoelectrochemical measurements were performed on a CHI660C workstation using a standard three-compartment electrochemical cell with a platinum foil and a Ag/AgCl as counter and reference electrodes correspondingly. The samples were coated on an FTO glass serving as the working electrodes. The transient photocurrent-time (I-t) was measured using 500 W Xe lamp with lamp on and off at a time interval of 60 s with -0.2 V bias. The electrochemical impedance spectroscopy (EIS) measurements were carried out over the frequency range of 1 MHz to 0.01 Hz with 5 mV amplitude. The Mott-Schottky (MS) plots were measured at frequencies of 1000, 1500 and 2000 Hz.

The apparent quantum efficiency (AQE) was obtained under similar photocatalytic reaction conditions except that the Xe lamp was replaced by four 420 nm LEDs. AQE is calculated using following equation.

$$AQE~(\%)~=\frac{\text{number of reacted electrons}}{\text{number of incident photons}}\times 100\%$$

$$=\frac{\text{number of evolved hydrogen molecules} \times 2}{\text{number of incident photons}}\times 100\%$$

$$=\frac{2R \times N_A}{\frac{E \times S \times T \times \lambda}{hc}}\times 100\%$$

Where R is the hydrogen evolution amount per hour; N_A is the Avogadro constant (6.022×10^{23} mol^{-1}); S is the illumination area (16.83 cm^2); E is the light intensity; t is the illumination time (3600 s); λ is the wavelength of the monochromatic light; h is the Plank constant (6.626×10^{-34} J·s); c is the speed of light (3×10^8 m·s^{-1}), and E is 0.0044 W·cm^{-2} at 420 nm. Besides, the R is 2.69 μmol and 3.85 μmol of TCN and TCN-DBT$_4$, respectively.

Computational Details. The structural optimization of TCN and TCN-DBT$_4$ has been calculated using DMol3 code[1,2], where several different atomic structures have been tested. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) function[3] and all-electron double numerical basis set with polarized function (DNP) have been employed. The convergence tolerance of energy, maximum force and maximum displacement are 1.0×10^{-5} Ha, 1.0×10^{-3} Ha/Å and 5.0×10^{-3} Å for geometry optimization. The Grimme method for DFT-D dispersion correction is considered for all calculations. Each atom in the storage models is allowed to relax to the minimum in the enthalpy without any constraints. The electronic structures of the structures have been calculated. The H atom was adsorbed on the N or C atom of TCN and TCN-DBT D-A conjugated copolymer.

The adsorption free energy of a H atom on the sample was calculated based on model:

$$\Delta G_H = \Delta E_H + \Delta G_{total} = \Delta E_H + \Delta E_{ZPE} + \Delta H - T\Delta S \tag{1}$$

ΔH, ΔS and ΔG_{total} are corrected at 298 K, where ΔE_{ZPE} and ΔS are the changes of zero-point energy and entropy, T is the room temperature (298 K), ΔG_{total} is Gibbs free energy change of system, and ΔE_H denotes the adsorption energy of hydrogen atom on substrates and calculated by:

$$\Delta E_H = E(sub/H) - E(sub) - E(H_2)/2 \tag{2}$$

Where E(sub/H), E(sub) and E(H$_2$) are the total energies of a H atom on substrate, bare substrate and hydrogen gas, respectively.
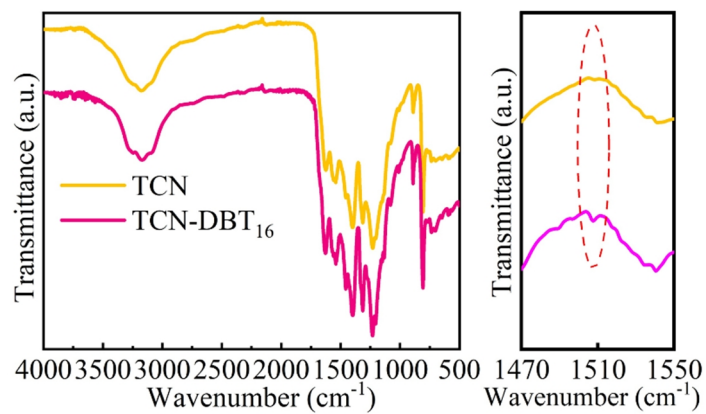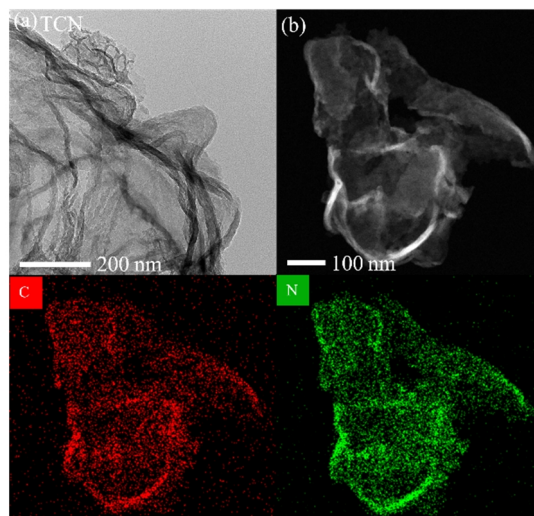
Figure S1. FTIR spectra of TCN and TCN-DBT$_{16}$.

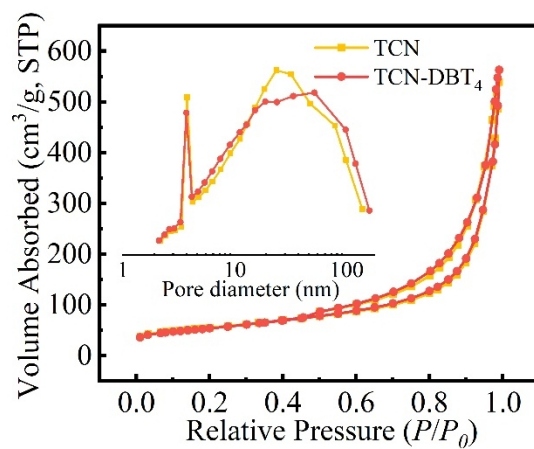**Figure S2.** (a) TEM image of TCN and (b) corresponding mapping of TCN.

Figure S3. N_2 adsorption-desorption isotherms and the corresponding pore size distribution (inset) of TCN and TCN-DBT$_4$.
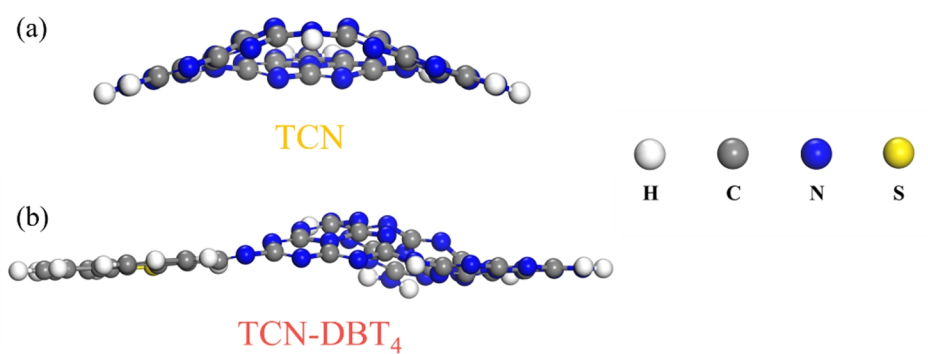
(a)

TCN

(b)

TCN-DBT$_4$

H   C   N   S

Figure S4. Side review of (a) TCN and (b) TCN-DBT$_4$.
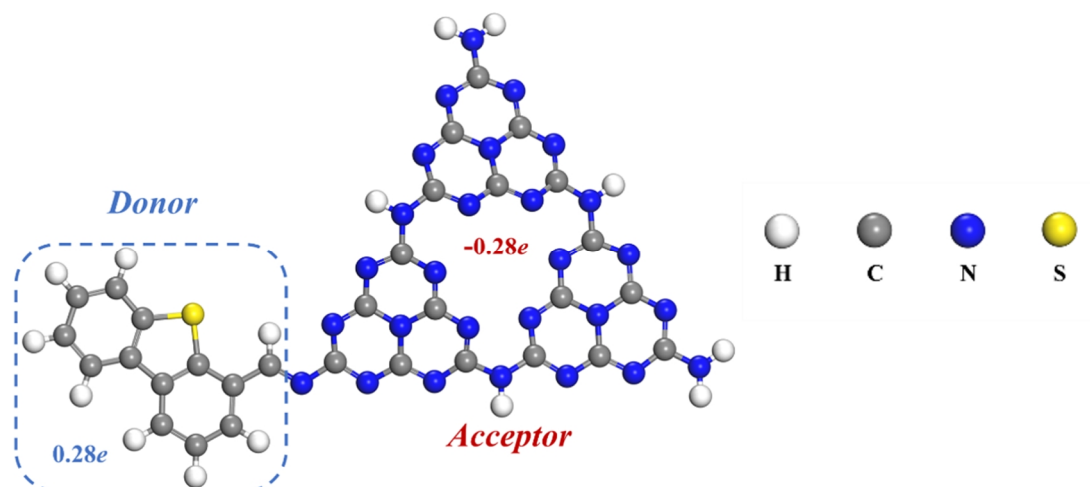
Figure S5. Mulliken charge distribution of TCN-DBT$_4$.

Table S1. The Atomic Percentage of the Elements Contained in TCN and TCN-DBT$_4$.

Samples		Atomic (%)
TCN	C 1s (284.8 eV)	7.61
	C 1s (288.1 eV)	33.91
	N	56.26
	C/N	0.74
	O	2.22
	S	0
	Total	100
TCN-DBT$_4$	C 1s (284.8 eV)	8.06
	C 1s (288.1 eV)	34.58
	N	52.39
	C/N	0.81
	O	3.93
	S	1.04
	Total	100

Table S2. The Specific Surface Area, Pore Size Data of TCN and TCN-DBT$_4$.

Samples	$S_{BET}/m^2 \cdot g^{-1}$	$V_{pore}/cm^3 \cdot g^{-1}$	d_{pore}/nm
TCN	193	0.58	12.0
TCN-DBT$_4$	189	0.59	12.5

Table S3. The Fitted Emission Decay Lifetime of TCN and TCN-DBT$_4$.

Samples	τ_1(ns)	A_1(%)	τ_2(ns)	A_2(%)	τ_3(ns)	A_3(%)	τ_{ave}(ns)
TCN	1.96	24.8	6.84	53.34	34.35	21.87	11.65
TCN-DBT$_4$	1.60	26.88	6.17	51.50	31.10	21.62	10.30

The average lifetime is calculated using the following formula:

$$\tau_{ave} = A_1\tau_1 + A_2\tau_2 + A_3\tau_3 \qquad\qquad (3)$$

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