

# Direct Electron Transfer in Covalent Triazine Framework for Enhanced Photocatalytic Hydrogen Evolution

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## 1. Experiment Details

### 1.1 Materials

Terephthalonitrile (98%), 4,7-dibromo-2,1,3-benzothiadiazole (98%), copper cyanide (99%), tetraethylorthosilicate (TEOS, 98%), trifluoromethanesulfonic acid (TfOH, 98%) and triethanolamine (TEOA, 98%) were purchased from Aladdin. All solvents were purchased from Aladdin and were used directly without further purification.

### 1.2 Methods

#### 1.2.1 Characterization

**Solution NMR.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker (Rheinstetten, Germany) Avance 500 instrument at room temperature in chloroform-d ( $\text{CDCl}_3$ ,  $\delta = 7.26$ ). The chemical shifts ( $\delta$ ) were reported in ppm referenced to tetramethylsilane (TMS). Coupling constant values (J) were given in hertz (Hz), the multiplicity was abbreviated in the following way: s (singlet), d (doublet), triplet (t), and m (multiplet).

**Fourier-transform infrared (FT-IR) spectroscopy.** FT-IR spectra were recorded on a VARIAN 1000 FT-IR spectrometer in the region of  $400\text{-}4000\text{ cm}^{-1}$  at a resolution of  $4\text{ cm}^{-1}$ . The vibrational transition frequencies are reported in wavenumbers ( $\text{cm}^{-1}$ ). Band intensities are assigned as weak (w), medium (m), and strong (s).

**Solid-state  $^{13}\text{C}$  cross-polarization magic-angle-spinning ( $^{13}\text{C}$  CP-MAS) NMR.**  $^{13}\text{C}$

CP-MAS NMR experiments were conducted on a Bruker ADVANCE III 500M spectrometer at  $^{13}\text{C}$  resonance frequency of 500 MHz at ambient pressure using a standard cross-polarization total sideband suppression (CP-TOSS) pulse sequence probe with 4 mm (outside diameter) zirconia rotors. The  $^{13}\text{C}$  ninety-degree pulse widths were 4  $\mu\text{s}$ . The decoupling frequency corresponded to 72 kHz. The TOSS sample-spinning rate was 5 kHz.

**Ultraviolet-visible (UV-vis) absorption.** Solid-state UV-vis absorption spectra were collected at room temperature on a Shimadzu UV-vis NIR diffuse reflectance spectrophotometer (referenced to barium sulfate as the optical standard) at a photometric range of 300–800 nm. Band gap values were calculated from the reflectance data using the Kubelka–Munk equation.

**Field Emission scanning electron microscopy (FE-SEM).** SEM SE (secondary electron) detector images were obtained on either a Zeiss Merlin or a VEGA TS 5130MM (TESCAN) with a SEMEDX using a Si/Li detector (10 kV acceleration voltage, Oxford). Samples were prepared by dispersing on mica substrate. The sample was then carbon coated using a Leica EM SCD 500 Sputter at 10–4 mbar of pressure in an argon atmosphere for 45 s while maintaining 15 mA of current. Sample was analyzed on a scanning electron microscope with accelerating voltages ranging from 1 to 15 kV. All the SEM images were taken from the same sample.

**High-resolution Transmission electron microscopy (HRTEM).** HRTEM was performed with a Philips CM30 ST (300kV, LaB6 cathode) at an accelerating voltage of 200 kV. To record the HRTEM images, dilute CMPs suspensions in ethanol were sonicated for 5 min, followed by drop-casting the sample on carbon-coated copper TEM grids (TED PELLA, INC. 200 line/inch Hexagonal mesh).

**Nitrogen sorption isotherm, pore size, and surface area measurements.** Low-pressure N<sub>2</sub> adsorption measurements were performed on the Micromeritics ASAP2460 volumetric analyzer. Before measurement, the samples were degassed in vacuum at 100 °C for 12 h. The amount of inert gas adsorbed to the surface of the sample was measured at varying relative pressures by this technique. As relative pressure increased to near saturation pressure (adsorption), accessible pores of increasing size filled with condensed gas. Once the pressure was reduced incrementally (desorption), the condensed gas evaporates from the pores. From the resulting isotherm, the Barrett-Joyner-Halenda (BJH) theory was used to determine the cylindrical equivalent pore volumes and pore areas from the amount of gas absorbed and desorbed. The surface area can also be determined using the Bruner-Emmet-Teller (BET) theory. The surface area calculated based on the BET model was normalized by the sample mass.

**Electrochemical measurements:** For PC and EIS measurements were conducted under a 300 W Xe lamp irradiation (wavelength: 200-1000 nm). CHI-610E electrochemical workstation was employed to record electrochemical experiments. To conduct electrochemical measurements, a three-electrode system was used. The

working electrode was made of indium tin oxide (ITO) glass plate coated with catalyst slurry with a diameter of 3 mm, the counter electrode was made of platinum wire, and the reference electrode was Hg/HgCl<sub>2</sub>. To prepare working electrode, the ITO glasses were first cleaned by being sonicated in acetone for 30 minutes and then dried under nitrogen flow. A slurry was then created by mixing 5 mg of CMP powder with 1 mL of ethanol and 10 μL 10 wt.% Nafion perfluorinated resin powder, which was ultrasonicated for 30 minutes. Next, 200 μL of the slurry was spread onto the ITO glass (1 × 2 cm<sup>2</sup>), and the uncoated area of the electrode was isolated using epoxy resin, forming a film that was allowed to dry under ambient temperature and pressure for 12 h. A 0.2 M aqueous solution of Na<sub>2</sub>SO<sub>4</sub> (pH 6.8) was utilized as the electrolyte, which was purged with argon gas for 1 h before the measurements. The working electrode was then allowed to immerse in the electrolyte for a period of 60 seconds before any measurement was conducted.

**Cyclic voltammetry (CV) measurements:** CV measurements were performed on a CHI 660E electrochemical working station using a three-electrode system: glassy carbon working electrode, Hg/HgCl<sub>2</sub> reference electrode and platinum wire counter electrode. The samples were grounded into fine powder and then dispersed in 5 wt% Nafion IPA solution, the mixture was dropped cast on top surface of a glassy carbon electrode and dried under a NIR lamp. The degassed 0.1 M tetrabutylammonium hexafluorophosphate acetonitrile solution as used as electrolyte. The anodic regions were carried out in the range of 0 V to 3 V with a scan rate of 10 mV s<sup>-1</sup> and the cathodic regions were carried out in the range of -1.2 V to 0 V with a scan rate of 10 mV s<sup>-1</sup>. The

equation  $E_{\text{NHE}} = E_{\text{SCE}} - 0.24 \text{ V}$  was applied to convert Hg/HgCl<sub>2</sub> redox couple to the Normal Hydrogen Electrode (NHE).

**Electron paramagnetic resonance (ESR):** EPR was performed using a Jeol/JES-FA200 to study the mechanism of the photocatalysts using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trap.

**Transient-state surface photovoltage (TPV):** TPV was obtained through the TPV system. The TPV system consisted of a YAG laser (Q-smart 450, Quantel), Preamplifier (5003, Brookdeal Electronics), and 500 MHz oscilloscopes.

**Computational Details:** Density function theory (DFT) calculations were performed by using the CP2K package. All of the geometry optimizations were performed using the Gaussian 16 suite of program at the B3LYP [S1-S3] density functional powered by Grimme's empirical dispersion-correction (D3BJ) [S4] with 6-311G(d,p) basis sets for all atoms. For ESP (Electrical Surface Potential) and MOs (Molecular Orbits), the Multiwfn 3.8 program is used for post-processing [S5].

### **1.2.2 Photocatalytic performance test.**

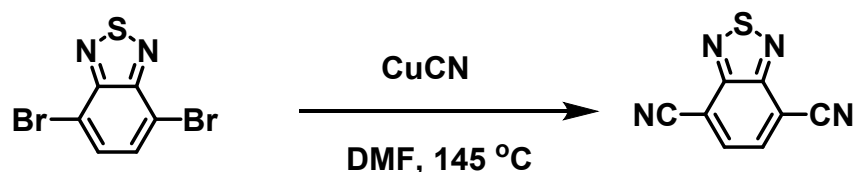
For photocatalytic hydrogen production test, 20 mg of photocatalyst was first dispersed to 100 mL MilliQ water under ultrasonication and then 10 mL TEOA as hole sacrificial agent was added. The reaction aqueous solution was evacuated to remove the air and then 3 wt% Pt was photo deposited onto the surface of photocatalysts under 300 W Xe lamp irradiation. Long-pass cut-off filters were used to achieve excitation light with

designed wavelength. The amount of generated H<sub>2</sub> was determined by a gas chromatography.

**Apparent Quantum Yield measurements:** The apparent quantum yield (AQY) was measured under the illumination of a 300 W Xe lamp with different band pass filters ( $\lambda_0 \pm 20$  nm) for 1 h. The reported AQY values here are maximum attainable results after varying the amounts of photocatalysts, the light intensities, and the light absorption areas.

## 1.3 Synthetic Procedures

### 1.3.1 Synthesis of monomers



**4,7-dicarbonitrile-2,1,3-benzothiadiazole:** To a solution of 4,7-dibromo-2,1,3-benzothiadiazole (2.0 g, 6.8 mmol) in DMF (10 ml), CuCN (1.8 g, 20.4 mmol) was added. The suspension was degassed with nitrogen for 10 min followed by heating to 145 °C for 20 h. The mixture was allowed to cool to room temperature. Then FeCl<sub>3</sub>·6H<sub>2</sub>O (14 g) in 2M HCl (32 ml) was added into the reaction solution. The resulting suspension was stirred for an hour. The mixture was extracted with DCM (100 mL × 3). The combined organic phase was washed with Milli Q water, dried with anhydrous MgSO<sub>4</sub>. The filtrate was concentrated under vacuum and purified through a silica column eluting with hexane/ dichloromethane (1:1) to give the titled product as pale yellow powder (52%).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.14 (s, 1H) ppm.

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 152.56, 134.58, 113.97 and 110.83 ppm.

### 1.3.2 Synthesis of silica nanoparticles

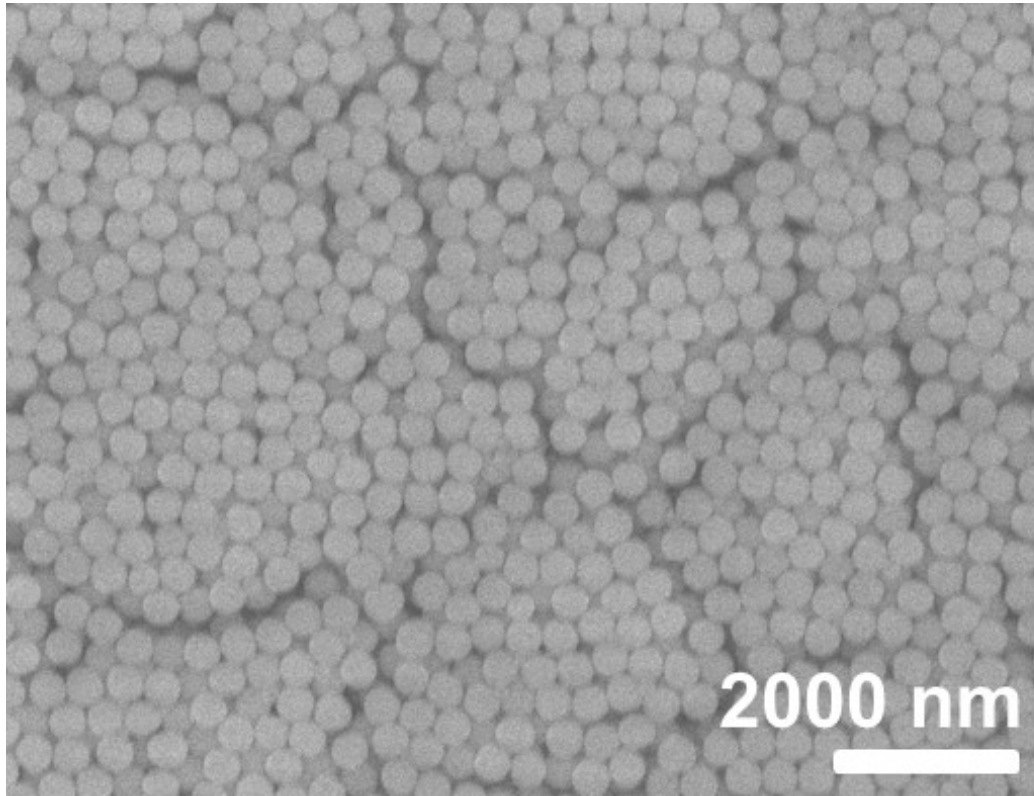
The silica nanoparticles were synthesized according to the Stöber method. TEOS (6.21 mL) was slowly added to a stirring mixture of ethanol (75.6 mL), H<sub>2</sub>O (16.2 mL) and 28 wt% ammonia aqueous solution (2 mL,) under vigorous stirring. Then, the mixture was then left stationary for 2 h at room temperature. The precipitated silica was separated by centrifugation and washed with water and ethanol. The silica spheres were



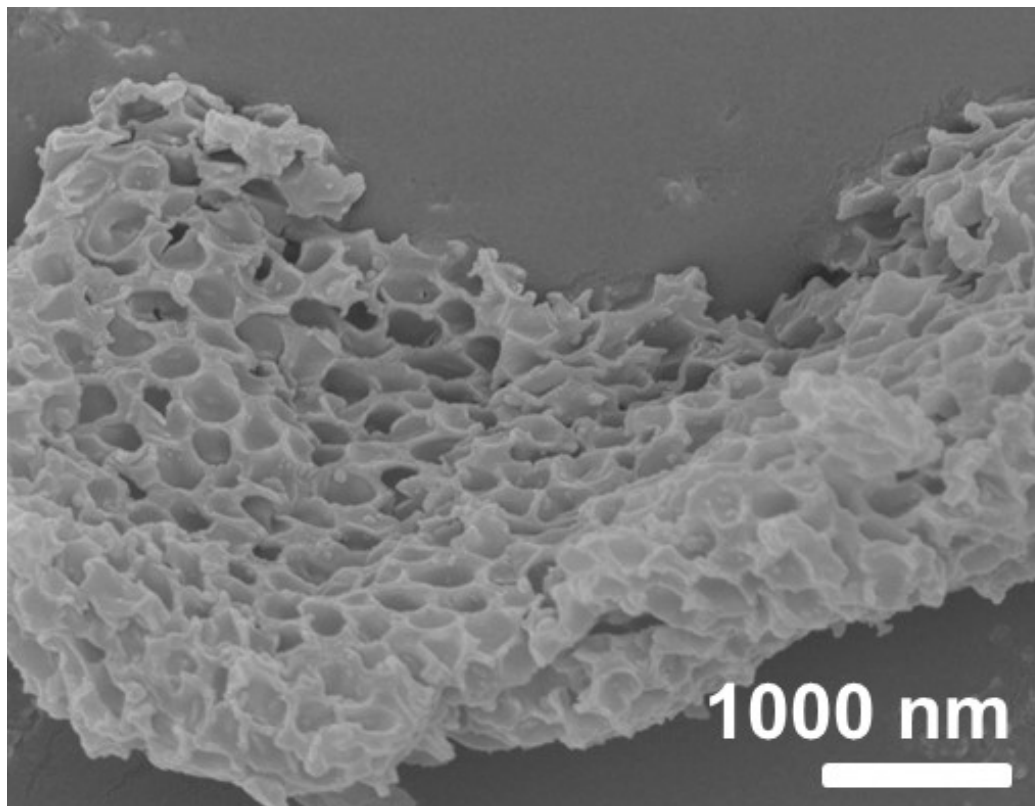
dried under high vacuum at room temperature overnight.

### **1.3.3 Synthesis of CTF materials**

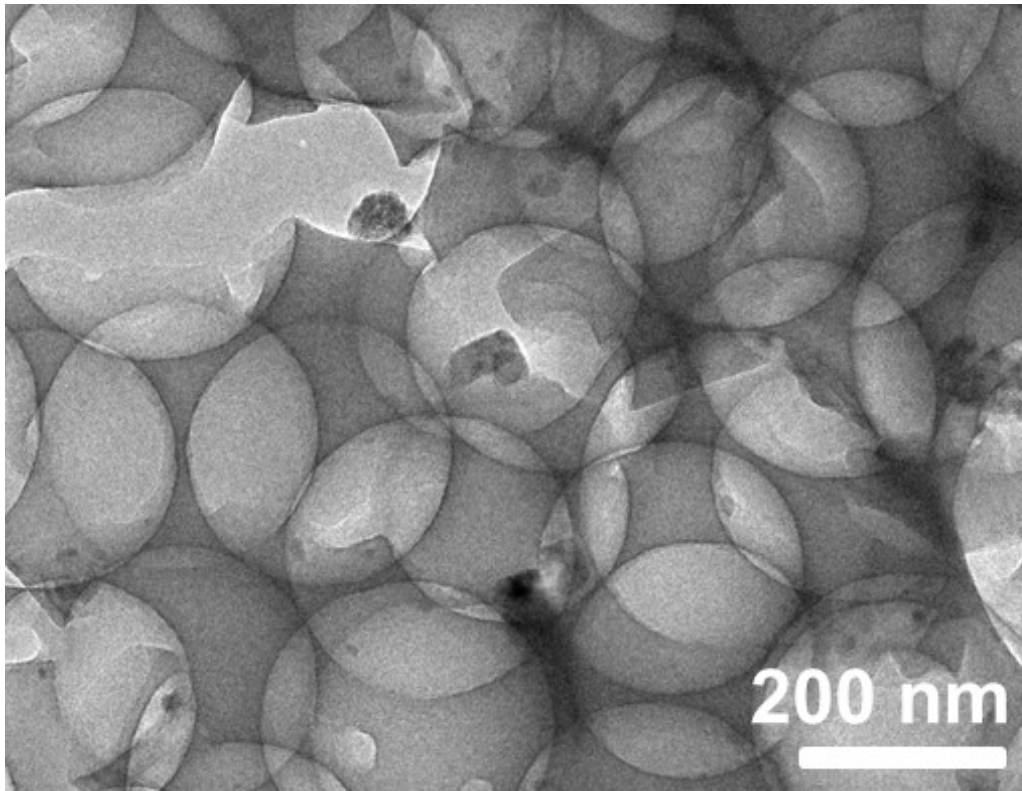
Nanoporous CTF-1 and CTF-BT-x were prepared according to the same procedure. Generally, 100 mg of monomer and 300 mg silica template were well dispersed in 5 ml of tetrahydrofuran in an ultrasonic bath for 30 min. Then the solvent was removed using rotary evaporator. During this process of solvent evaporation, the silica microspheres reorganized into a 3D close-stacked structure, simultaneously, the monomer precipitated out and filled the gaps between the silica spheres to form the initial monomer/silica precursor. The formed precursor was further annealed at 80 °C for 30 min under vacuum then was carefully transferred into a small glass vial. The vial with monomer/silica precursor was placed into a conical flask, in which there was another vial with 0.3 ml TfOH. The conical flask was degassed with nitrogen and sealed followed by heated up to 100 °C in a sand bath for 24 hours. After cooled down to room temperature, the product was immersed in water and washed well with ammonia solution and Milli Q water to remove the residual TfOH. The silica templates were etched by 20 ml of 4 M  $\text{NH}_4\text{HF}_2$ . The resultant products were washed with Milli Q water, ethanol and acetone followed by further purified with Soxlet extraction with  $\text{CH}_2\text{Cl}_2$ . After dried under vacuum at 80 °C, the products were obtained with a yield of 85-93%.



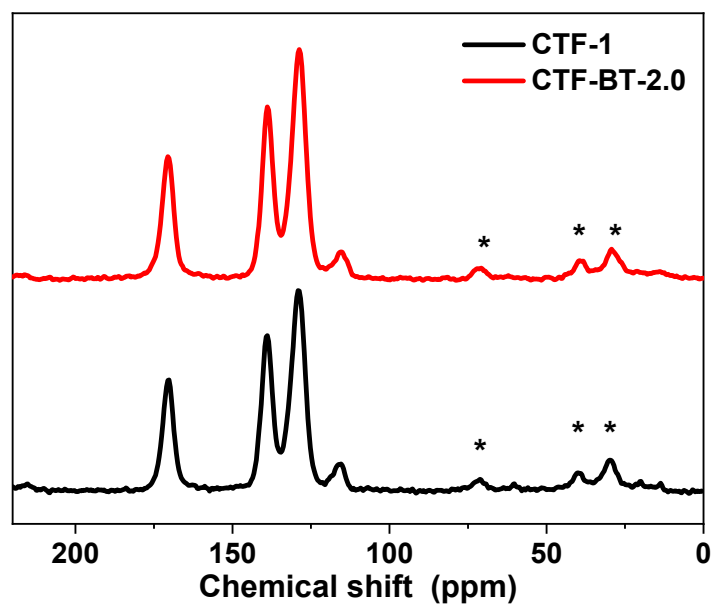
**Fig. S1** SEM image of SiO<sub>2</sub> spheres.



**Fig. S2** SEM image of CTF-BT-2.



**Fig. S3** TEM image of CTF-BT-2.



**Fig. S4** Solid-state  $^{13}\text{C}$  NMR spectra of CTF-1 and CTF-BT-2.0.

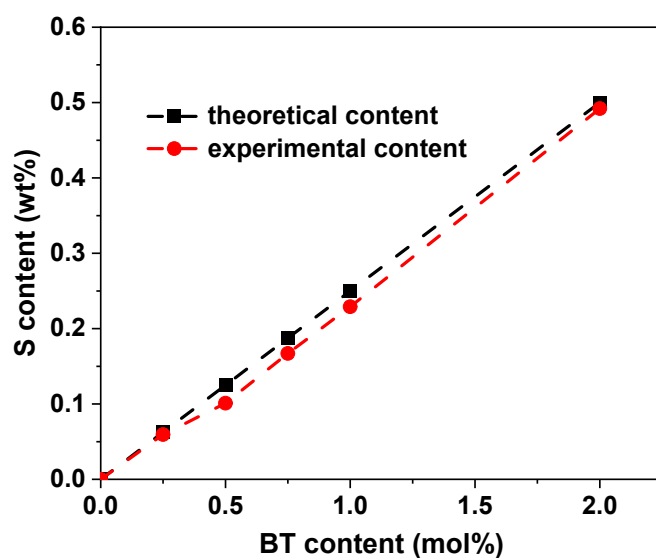


Fig. S5 Theoretical and experimental S content of CTF-1 and CTF-BT-x.

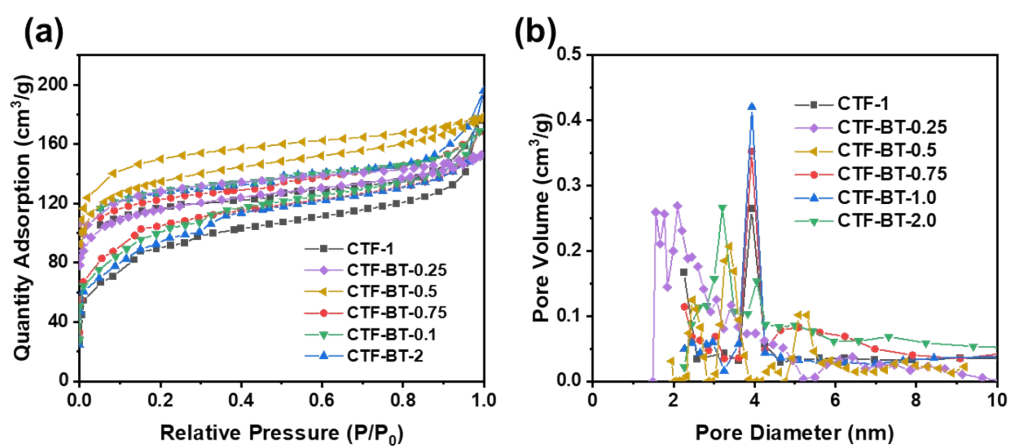
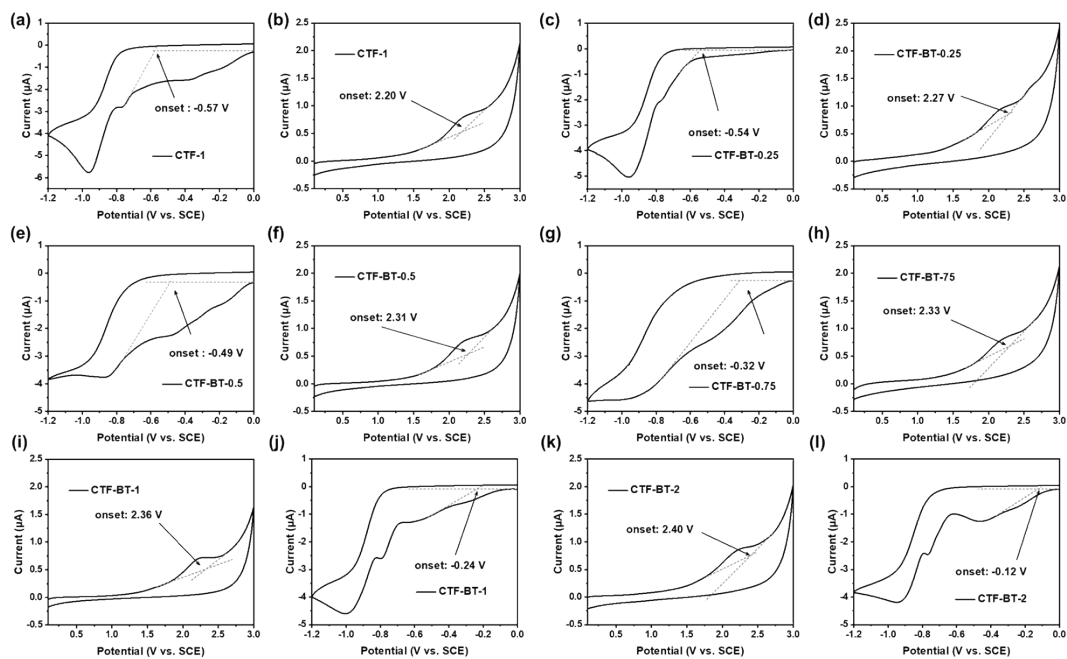
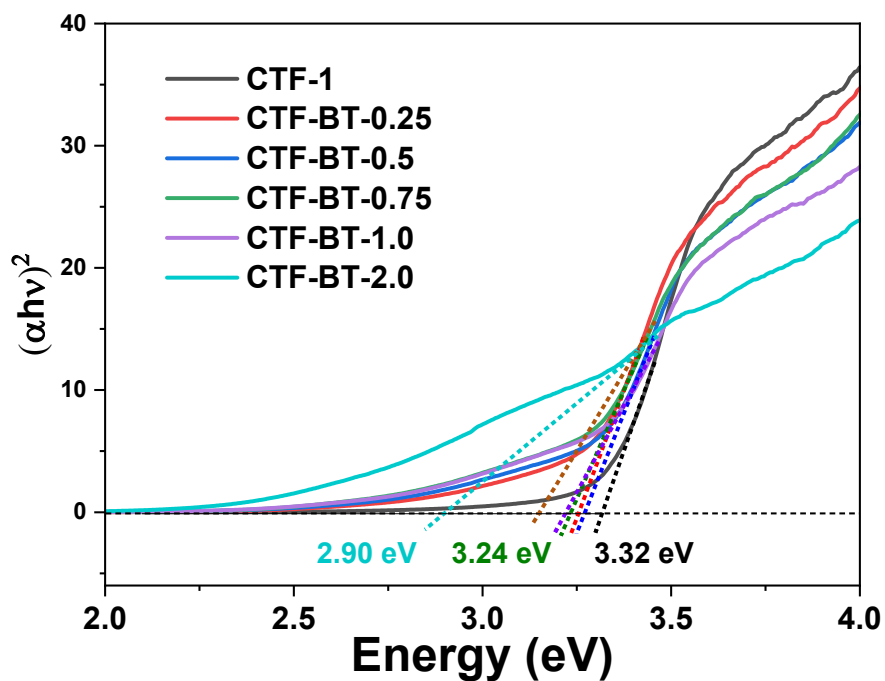


Fig. S6 (a) N<sub>2</sub> adsorption/desorption isotherm of CTFs and (b) corresponding pore distribution.



**Fig. S7** Cyclic voltammetry measurement for CTF-1 and CTF-BT-x (performed in dry  $\text{CH}_3\text{CN}$  by using 0.1 M tetra-n-butylammonium hexafluorophosphate as the electrolyte).



**Fig. S8** Tauc spectrum of CTF-1 and CTF-BT-x according to the UV-Vis measurement.

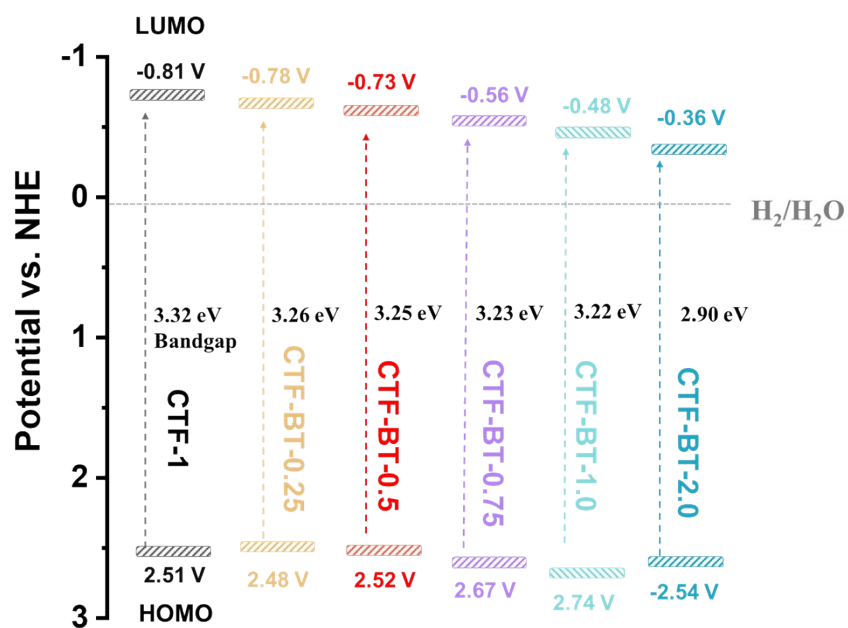


Fig. S9 Energy band positions of CTF-1 and CTF-BT-x.

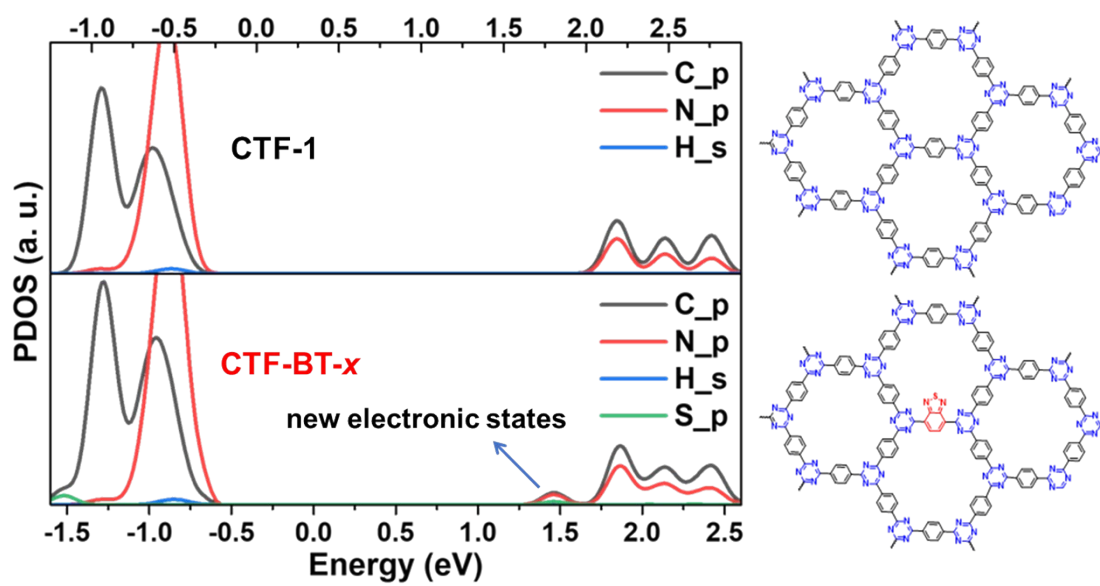
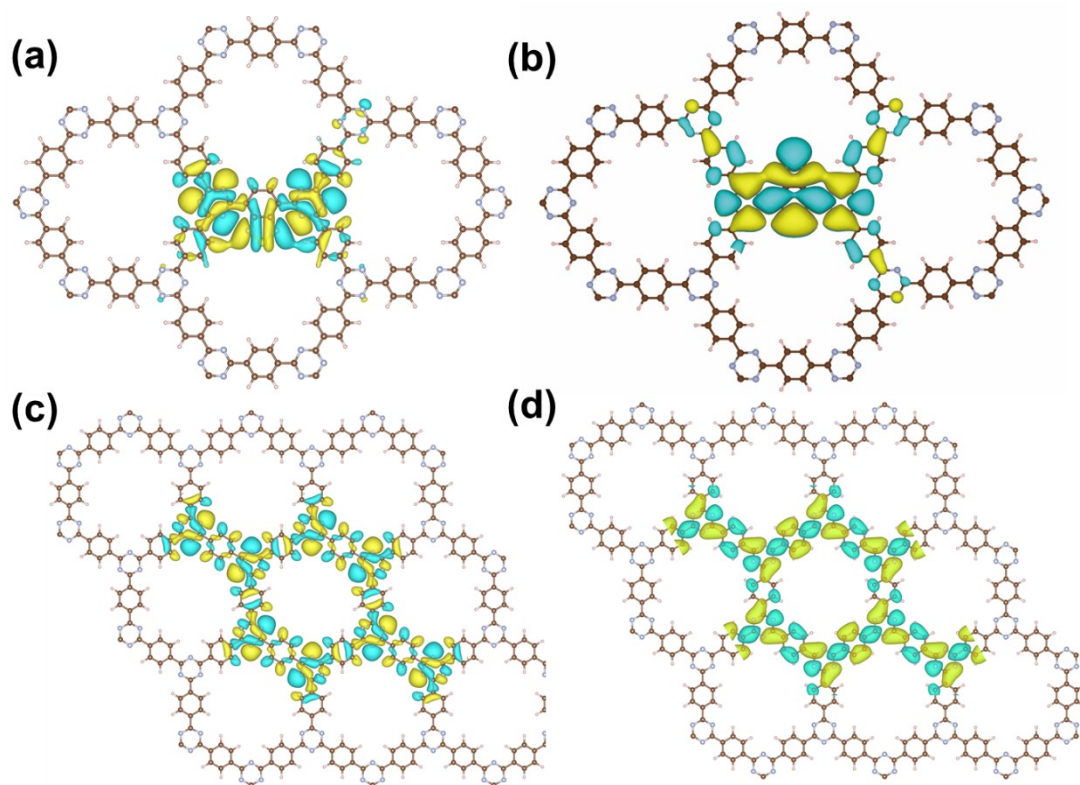
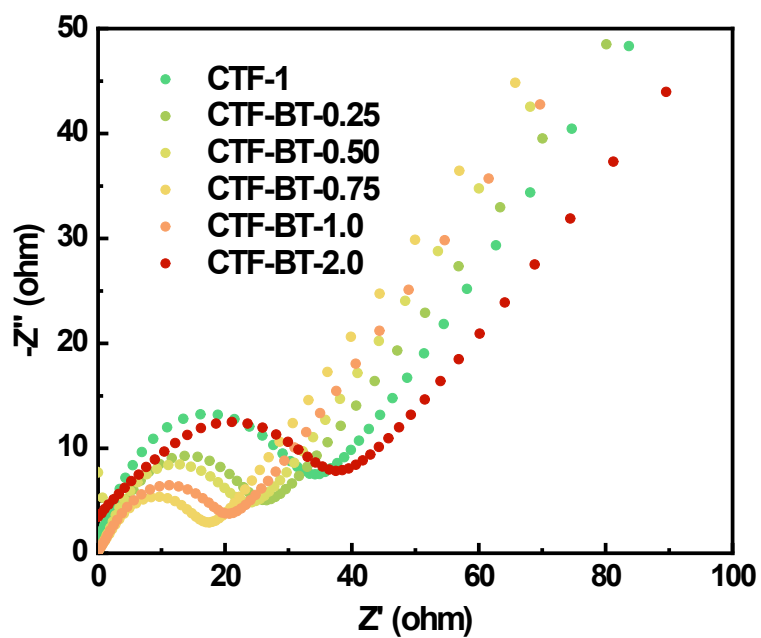


Fig. S10 PDOS of CTF-1 and CTF-BT-x.



**Fig. S11** Calculated HOMO (left) and LUMO (right) for the model molecule for the CTF-BT-5 (up) and CTF-1 (down).



**Fig. S12** EIS spectra of the CTFs.

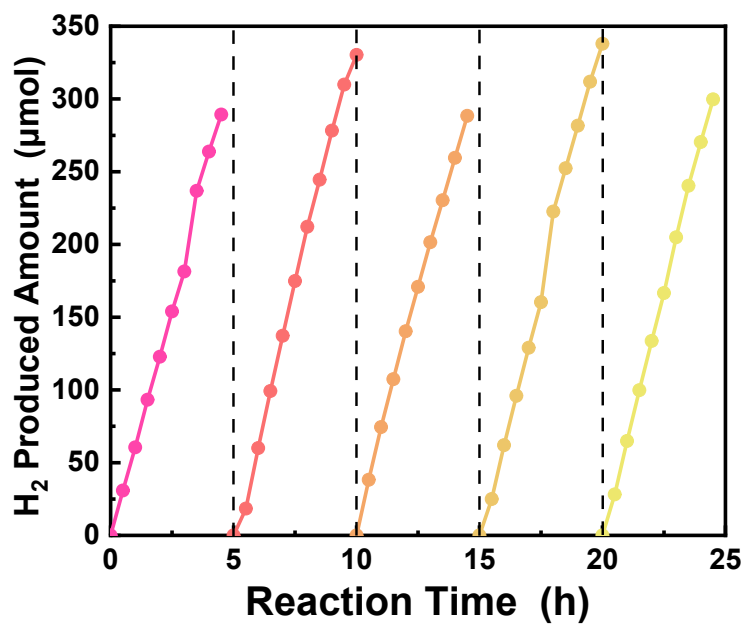


Fig. S13 Recycle photocatalytic hydrogen evolution test of CTF-BT-0.75.

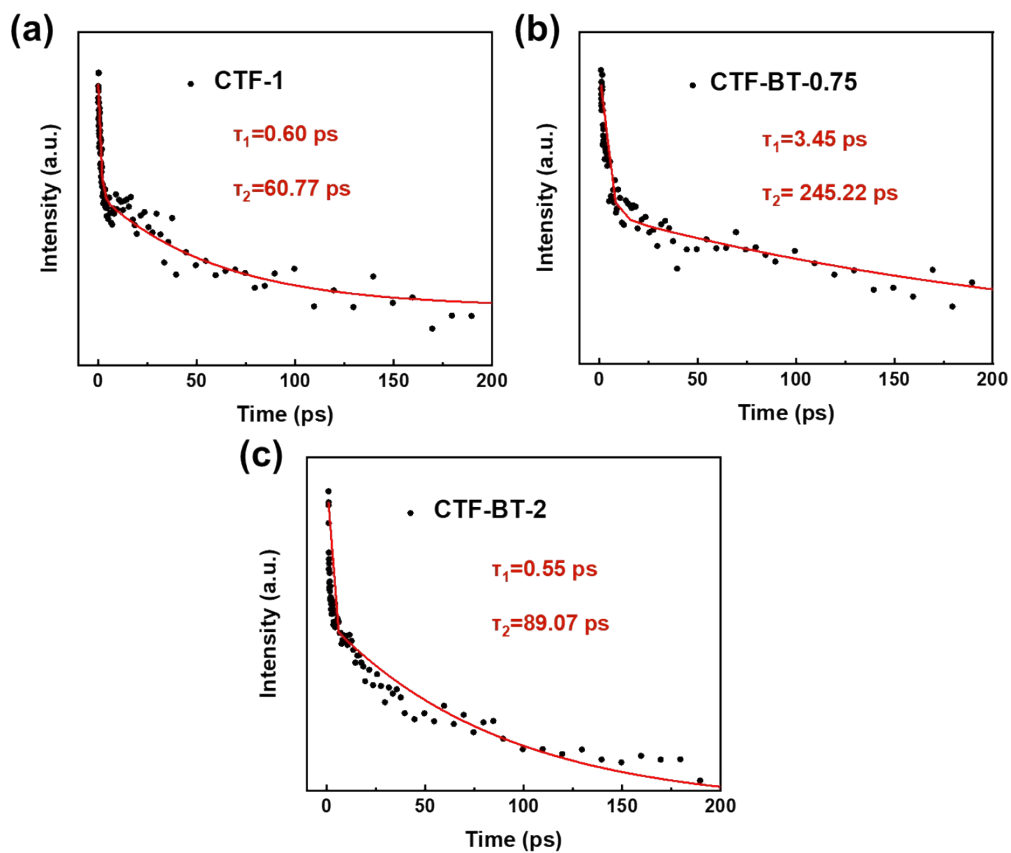
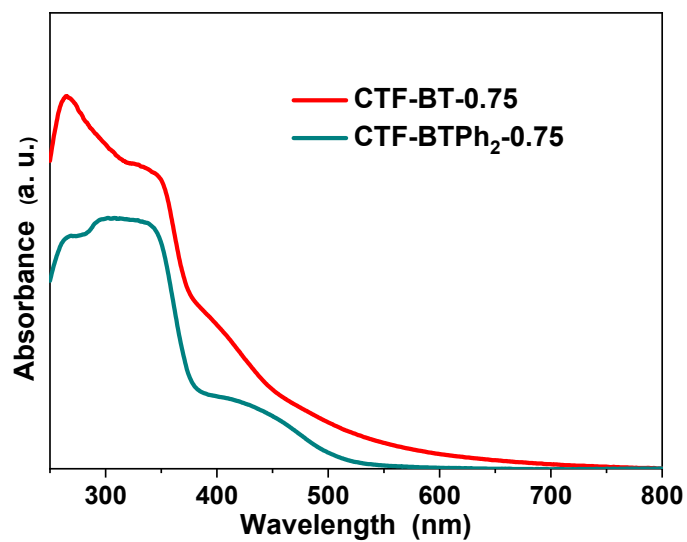
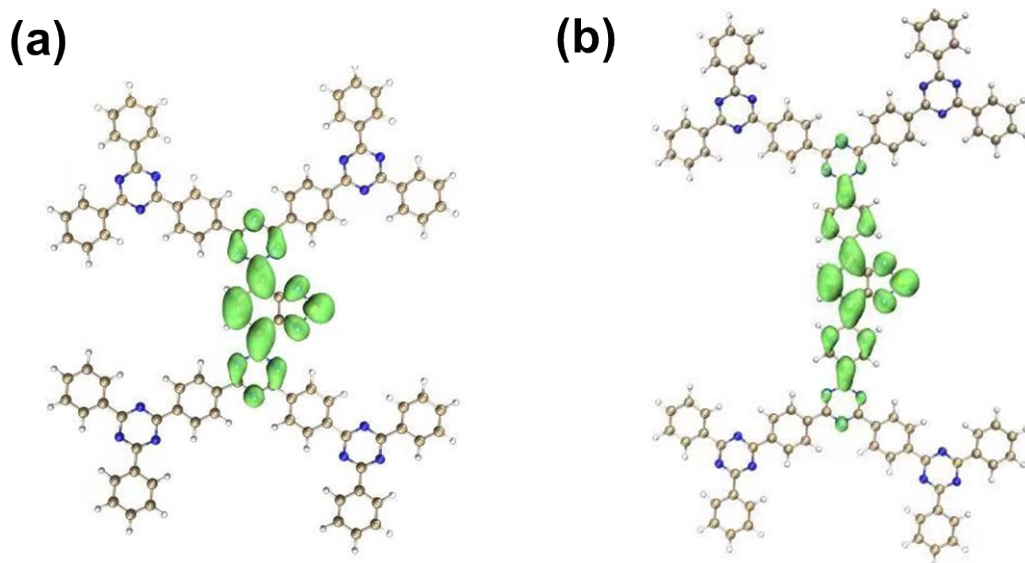


Fig. S14 Time profiles and fitted decay kinetics at 500 nm of transient absorption of (a) CTF-1, (b) CTF-BT-0.75 and (c) CTF-BT-2.





**Fig. S15** UV-Vis spectra of CTF-BT-0.75 and CTF-BTPH<sub>2</sub>-0.75.



**Fig. S16** Calculated LUMO for the model molecule of the direct connected A<sup>1</sup>-A<sup>2</sup> units (left) and indirect connected A<sup>1</sup>-A<sup>2</sup> units (right).

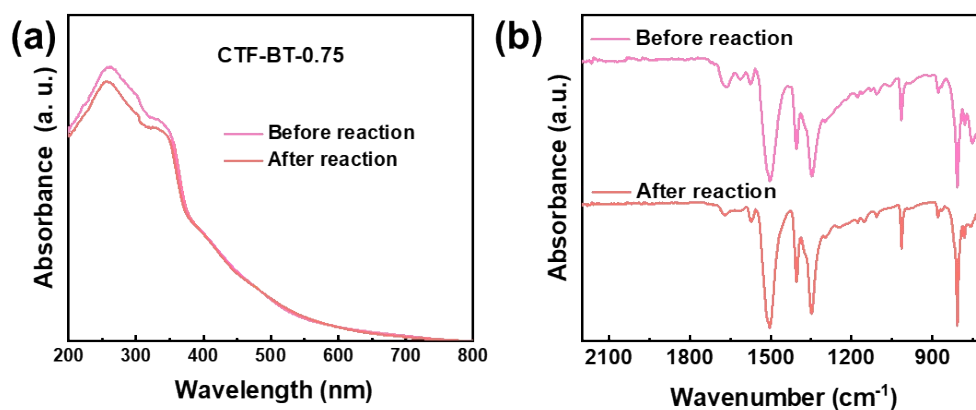


Fig. S17 UV-Vis and FT-IR spectra of CTF-BT-0.75 before and after reaction.

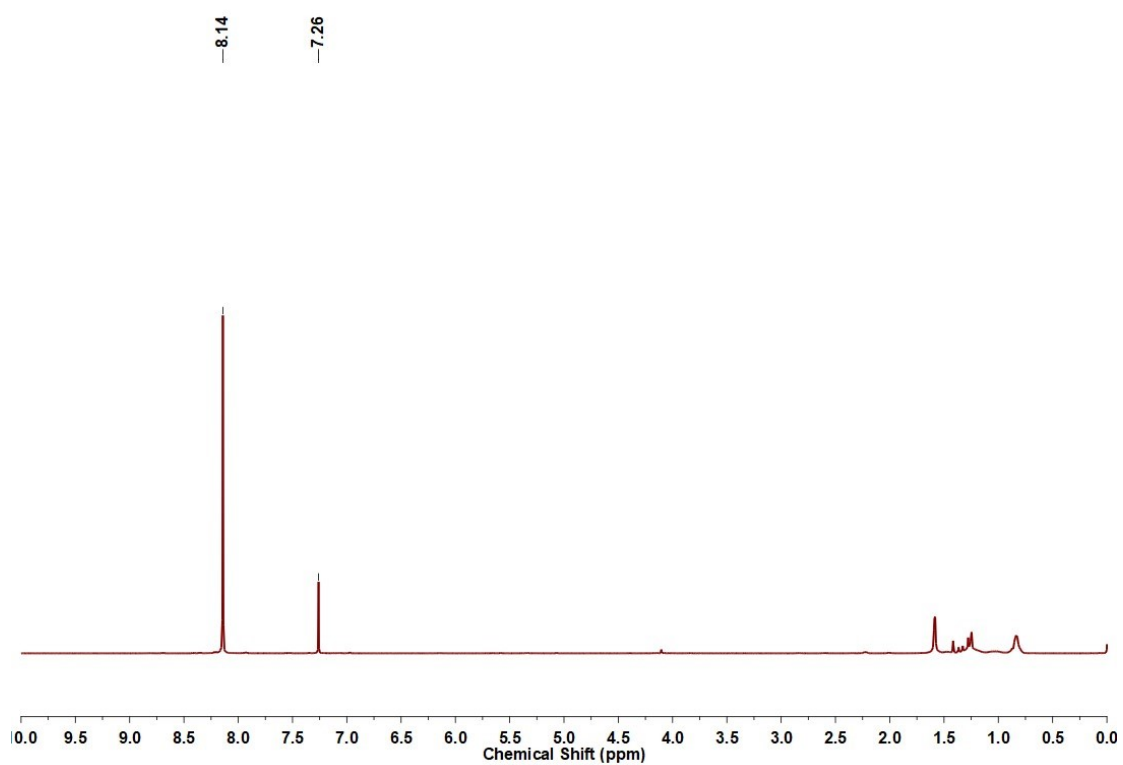


Fig. S18 <sup>1</sup>H NMR spectrum of BT-CN<sub>2</sub>

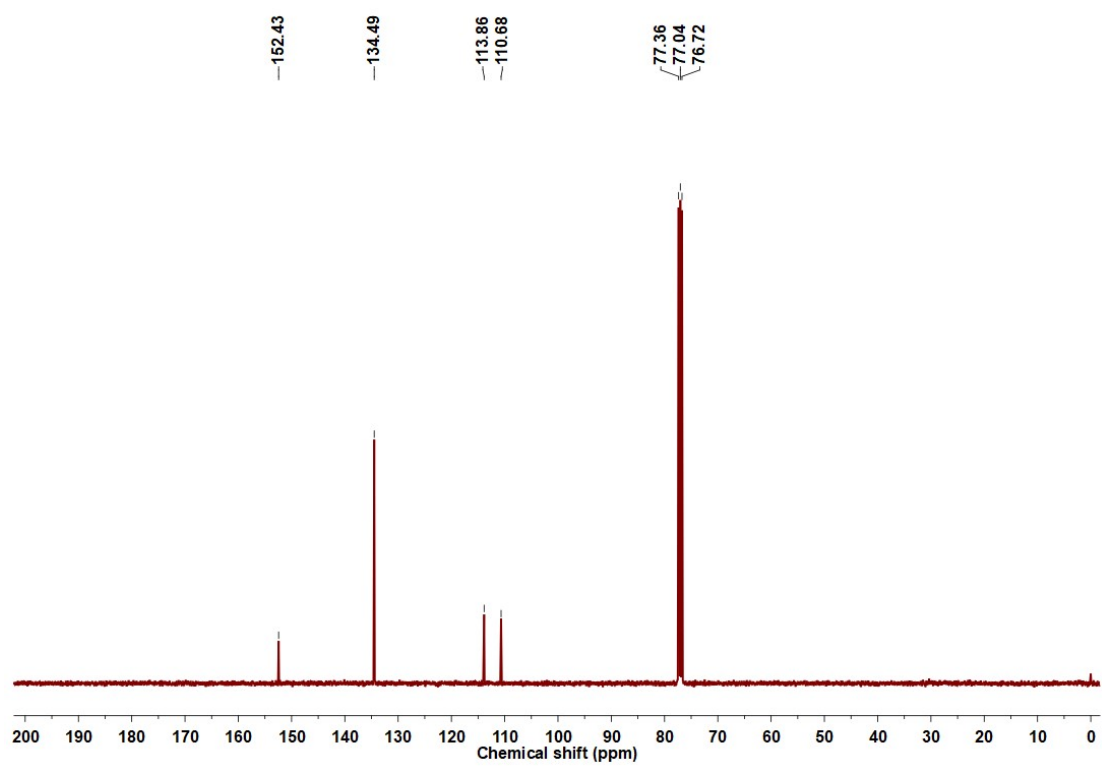


Fig. S19  $^{13}\text{C}$  NMR spectrum of BT-CN<sub>2</sub>

**Table S1.** Overview of molar ratios and weights of the polymer series 1 with increasing BT content.

Sample	BTCN <sub>2</sub> (mg)	BTCN <sub>2</sub> ( $\mu$ mol)	DCB (mg)	DCB (mmol)	BT (mol%)
CTF-1	0	0			0
CTF-BT-0.25	0.363	1.95			0.25
CTF-BT-0.50	0.726	3.905			0.5
CTF-BT-0.75	1.089	5.857	100	0.781	0.75
CTF-BT-1.0	1.452	7.810			1
CTF-BT-2.0	2.905	15.620			2

**Table S2.**  $\tau_1$  and  $\tau_2$  lifetime of the CTFs

Sample	$\tau_1$ lifetime (ns)	$\tau_1$ intensity	$\tau_2$ lifetime (ns)	$\tau_2$ intensity
CTF-1	0.99	5624	4.55	4134
CTF-BT-0.25	0.95	5571	4.18	4108
CTF-BT-0.50	0.97	6818	4.08	3576
CTF-BT-0.75	0.99	8077	4.14	3334
CTF-BT-1.0	1.01	8312	3.98	2457
CTF-BT-2.0	0.85	9264	3.39	1581

## Reference:

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