

Supporting Information

Construction of polymeric carbon nitride and dibenzothiophene dioxide-Based intramolecular donor-acceptor conjugated copolymers for photocatalytic H₂ evolution

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Scheme S1. Possible thermal polymerization processes during the synthesis of CNSO-X.

Table S1. Elemental composition (atom ratios) of samples according to XPS analysis.

Sample	C/at %	N/at %	O/at %	S/at %	C/N
CN	42.7	56.2	1.1	0	0.76
CNSO-20	44.7	53.2	1.5	0.6	0.84

Table S2. Relative ratios of two carbon species determined by C 1s spectra for samples.

Sample	C=C			C-N ₃		
	Binding Energy(eV)	area	%	Binding Energy(eV)	area	%
CN	284.6	1333.1	4.8	288.1	26153.6	95.2
CNSO-20	284.6	2731.6	9.8	287.69	25053.1	90.2

Table S3. Relative ratios of four nitrogen species determined by N 1s spectra for samples.

Sample	C= N-C			N-C ₃			N-H			π excitation		
	Binding Energy (eV)	area	%	Binding Energy (eV)	area	%	Binding Energy (eV)	area	%	Binding Energy (eV)	area	%
CN	398.87	48018	72.5	400.59	14610.7	22.1	401.3	551.9	0.8	404.71	3060.4	4.6
CNSO-20	398.91	52367.2	77.9	400.87	9814.4	14.6	400.89	1737.6	2.6	404.75	3294.9	4.9

Table S4. Relative ratios of two oxygen species determined by O 1s spectra for samples.

Sample	S=O (C=O)			Adsorbed water		
	Binding Energy(eV)	area	%	Binding Energy(eV)	area	%
CN	532.04	548.2	24.1	532.4	1722.3	75.9
CNSO-20	532.04	2142.7	94.9	532.4	114.6	5.1

Table S5. PHE rate and specific test conditions for other reported g-C₃N₄-based D-A conjugated polymers under visible light. (‘/’ means the specific information was not provided).

Materials	Catalyst Dosage (mg)	Cocatalyst	Reactant solution and sacrificial reagents	HER ($\mu\text{mol h}^{-1}$)	AQY (%)	Refs.
g-C₃N₄-MF	50	Pt (3 wt%)	Water (80 mL) and TEOA (20 mL)	180.6	8.6 (420 nm)	[S1]
CNAL-X	100	Pt (3 wt%)	Water (90 mL) and TEOA (10 mL)	226	/	[S2]
CNQ-X	100	Pt (3 wt%)	Water (90 mL) and TEOA (10 mL)	436	3.8 (420 nm)	[S3]
UCN-BD	50	Pt (3 wt%)	Water (90 mL) and TEOA (10 mL)	171.4	12.3 (450 nm)	[S4]
BS-CN	100	Pt (3 wt%)	Water (90 mL) and TEOA (10 mL)	1233	17.7 (420 nm)	[S5]
BD-CN	50	Pt (3 wt%)	Water (90 mL) and TEOA (10 mL)	158.3	5.36 (400 nm)	[S6]
CNSO-20	50	Pt (3 wt%)	Water (50 mL) and TEOA (10 mL)	251	10.16 (420 nm)	This work

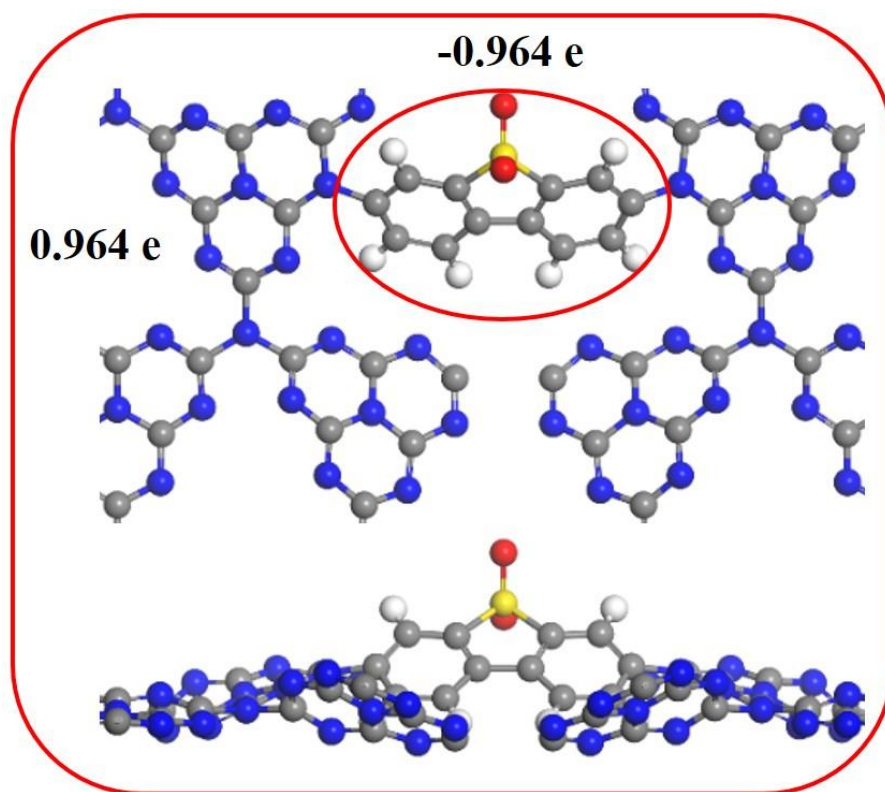


Fig. S1. The Bader charge analysis in the CNSO-X D-A conjugated polymers.

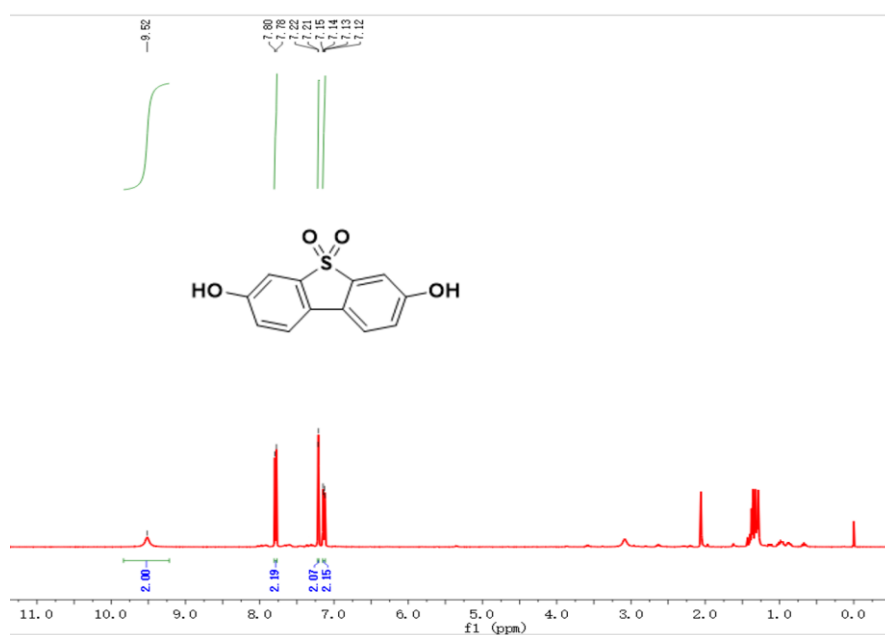


Fig. S2. ¹H NMR of 3,7-dihydroxydibenzo [b,d] thiophene 5,5-dioxide in deuterated acetone.

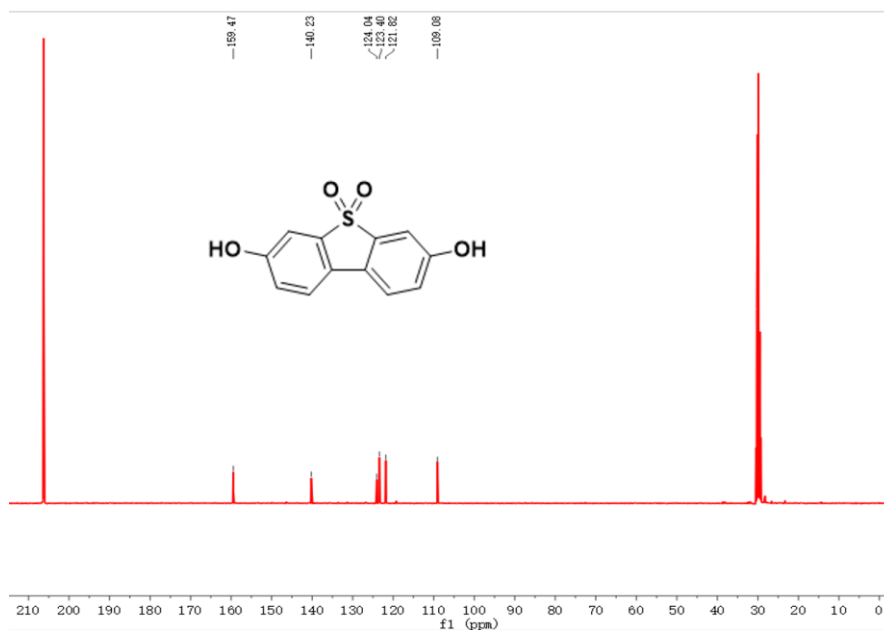


Fig. S3. ^{13}C NMR of 3,7-dihydroxydibenzo [b,d] thiophene 5,5-dioxide in deuterated acetone.

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

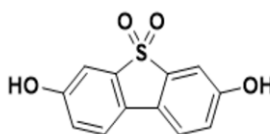
34 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-83 H: 0-87 O: 0-4 S: 0-1

JL-HUA

HL-YF-13 7 (0.065) Cm (7.8)



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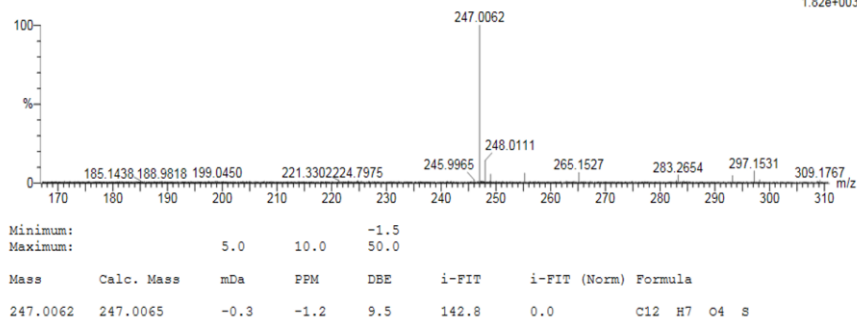


Fig. S4. HRMS spectrum of 3,7-dihydroxydibenzo [b,d] thiophene 5,5-dioxide.

References

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