Supplementary Information

N…Br Halogen Bond Broadened Visible-Light Degradation of Decabromodiphenyl Ether on Organic Amine Intercalated Zinc Sulfide

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Experimental section

Materials

Diethylenetriamine ($C_4H_{13}N_3$) (AR, 99.0%), thioacetamide (C_2H_5NS) (AR, 98.0%), tetraethylenepentamine ($C_8H_{23}N_5$) (AR, 99.0%), methanol (AR, 99.5%), and Ethylenediamine ($C_2H_8N_2$) (AR, 99.0%) were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). $Zn(NO_3)_2{\cdot}6H_2O$ (AR, 95%) was purchased from Sinopharm Chemical Reagent Co. Ltd (China). Decabromodiphenyl ether (BDE209) was obtained from Aldrich Chemical Company (USA). All chemicals were used without further purification.

Preparation of ZD photocatalysts

The photocatalysts were prepared according to literature methods by a simply solvothermal approach.[1] Typically, 1.5 mmol of $Zn(NO_3)_2{\cdot}6H_2O$ and 1.5 mmol of C_2H_5NS were added into a 15 mL aqueous solution of diethylenetriamine (DETA). The volume ratios of H_2O to DETA were chosen as 1:0, 1:2, 1:4, 1:9, and 0:1, respectively. After achieving a homogeneous solution through vigorous stirring, the solution was transferred into 25 mL high-pressure reactor with polytetrafluoroethylene linings and placed into an oven set at 180 °C for 10 hours. Following a natural cooling period, the samples were washed three times with ethanol and deionized water, respectively. Finally, the obtained white powders were dried in an oven at 60 °C overnight and were labeled as ZD-0, ZD-2, ZD-4, ZD-9, and ZD-p, respectively. Finally, to explore the role of DETA, the ZD-4 was calcined at 350 °C with a rate of 2.5 °C/min in O_2 atmosphere for 4 hours to eliminate the DETA, labeled as ZD-Calcination.

To explore the universality of the organic amine intercalated catalysts in the degradation of BDE209, tetraethylenepentamine (TEPA) and ethylenediamine (EDA) were selected as substitutes for DETA, and other hydrothermal conditions were consistent with the preparation of ZD-4. The obtained products were labeled as ZT-4 and ZE-4, respectively.

Characterization

X-ray diffraction (XRD) patterns were measured using a Regaku D/Max-2500 diffractometer equipped with a Cu-Kα radiation source. The diffraction angle ranged (2θ) from 4° to 70° with a scanning speed of 5°/min. The morphologies of samples were characterized on a high-resolution transmission electron microscope (HRTEM, JEOL JSM-2011) and a scanning electron microscope (SEM, JEOL, JSM-6360LV). The elemental composition of the samples was analyzed using an energy - dispersive X-ray spectrometer (EDS, OXFORD, x-act). To optimize the analysis conditions, all samples were subjected to a pre - spraying treatment with gold (Au) before being placed in the EDS instrument. The Au coating effectively improved the surface conductivity of the samples, which is essential for obtaining high-quality EDS spectra and clear elemental distribution maps, reducing the interference caused by electrostatic charging and improving the precision of elemental identification and quantification.The sputter-coating process was carried out under a specific set of parameters. The chamber was first evacuated to a low pressure (around 10^{-2} - 10^{-3} mbar) to create an appropriate environment for sputtering. Then, a current was applied to the gold target, causing gold atoms to be ejected and deposited uniformly on the sample surface. The X-ray photoelectron spectroscopy (XPS) data were acquired using an X-ray photoelectron spectrometer (Thermo Scientific, K-Alpha+) equipped with an Al-Kα X-ray source. And the binding energies of all elements were calibrated relative to the C 1s peak at 284.80 eV using a Shirley background. Fourier transform infrared spectroscopy (FTIR, Nicolet-6700) was conducted to analysis the functional groups on the catalyst's surface. The specific surface areas of the samples were examined by Brunauer-Emmett-Teller (BET) on a Micromeritics ASAP 2020 plus. This instrument provides a resolution of up to 0.0005 m^2/g, ensuring precise quantification of the surface area. All samples underwent degassing at 150 ℃ for 3 hours to remove any adsorbed impurities. Subsequently, nitrogen physical adsorption was carried out at a temperature of 77 K to obtain the adsorption-desorption isotherms, from which the specific surface area was calculated based on the BET theory. The solid-state ultraviolet-visible (UV-vis) diffuse reflectance spectrum of the samples was collected on a Shimadzu UV-3600, with the wavenumber ranging

from 200 to 800 nm. The thermogravimetric analysis (TGA) was performed on a Henjiu HCT-3 TG/DTA thermal analyzer, from room temperature to 500 ℃ with a heating rate of 10 °C/min in nitrogen.

The photoelectrochemical performance test was conducted on a VSP300 electrochemical station (Bio-Logic) in 0.1 mol/L Na_2SO_4 solution. A three-electrode configuration was used, with a glassy carbon electrode coated with the catalyst as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum (Pt) electrode as the counter electrode. To prepare the working electrode, 5 mg of catalyst was dispersed into 1 mL of isopropanol and sonicated for 20 min to ensure a homogeneous mixture. Subsequently, 50 μL of DuPont Nafion solution was added and the mixture was sonicated for an additional 10 min. Finally, a total of 20 μL of the resultant mixture was deposited onto the surface of the clean glassy carbon electrode. The photocurrent density was recorded at the open circuit potential vs SCE under discontinuous irradiation of Xenon lamp (CEL-HXUV300, λ>300 nm).

Photocatalytic degradation of BDE209

The photocatalytic degradation of BDE209 were conducted in a homemade reaction vessel using 5 mg of catalyst dispersed in 5 mL of methanol solution containing 1×10^{-5} mol L^{-1} BDE209 under visible light irradiation (Xe lamp, CEL-HXUV300, with a 420 nm cutoff filter). Before photocatalytic degradation, the vessel was purged with high-purity argon (99.999%) for 10 minutes to establish an oxygen-free environment conducive to the photo-reduction reaction. The N_2-protected solution was stirred in darkness for 30 minutes to ensure adsorption equilibrium of BDE209 on catalyst's surface. During the photodegradation, 0.5 mL of the suspension was taken out every 1 h and filtered through a 0.22 μm membrane to eliminate catalyst particles. The filtered solution was then subjected to analysis on high-performance liquid chromatography (HPLC, Shimadzu, LC-20AT). Meanwhile, with other experimental conditions remaining unchanged, oxygen, hydrogen peroxide, and *p*-benzoquinone were introduced as electron trapping agents, to gain a more in-depth understanding of the debromination active species.

For the repeated experiments, the following operational steps were carried out: After the completion of one reaction, the reaction flask was left stationary for 10 minutes. Then, the supernatant was removed, and the remaining substance containing the catalyst was washed with methanol and centrifuged three times. Subsequently, the catalyst was placed in an oven and dried at 60 °C. After recovery, the catalyst was further added into a methanol solution containing 1×10^{-5} mol L^{-1} BDE209 to complete subsequent degradation cycle tests.

The degradation products were analyzed using gas chromatography equipped with a microcell electron capture detector (GC-μECD, Agilent 7890A, Agilent Technologies Co., U.S.A.). The GC-μECD system was outfitted with a programmable pressure on-column injection port and a DB-5 capillary column (30 m × 50 μm inner diameter × 0.1 μm film thickness). A 10-μL splitless injection was manually performed at 300 °C. Helium was employed as the carrier gas with a constant flow rate of 1.0 mL min^{-1}. The oven temperature program was set as follows: initially held at 100 °C for 2 minutes, then increased to 230 °C at a rate of 15 °C min^{-1}, subsequently raised to 270 °C at 5 °C min^{-1}, and finally increased to 320 °C at 10 °C min^{-1} and maintained for 10 minutes. The standard samples of nona-, octa-, hepta- and hexa-BDEs were used to identify the degradation products.

DFT calculation

Theoretical calculations concerning geometrical optimization were carried out with the Gaussian 16 software package. The electrostatic potential and optimization of BDE209 and DETA were conducted using the Becke three parameters and Lee-Yang-Parr nonlocal correlation functional (B3LYP). The basis set for C, N, H, O, and Br was 6-31G(d). To better describe the molecular dispersion effect, D3(BJ) is used for dispersion correction. The solvent effect was considered by the conductor-like polarized continuum model (CPCM).[2]

Supplementary Figures

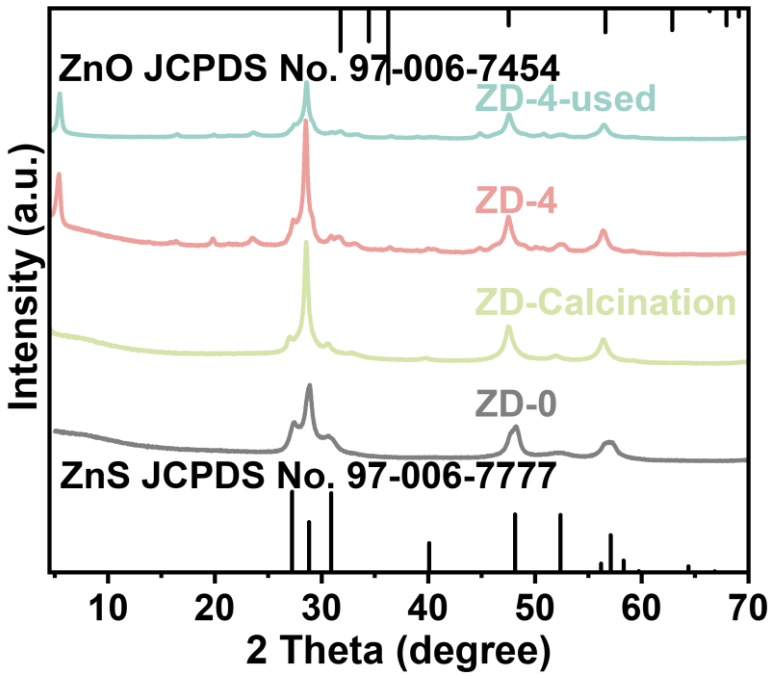


Fig. S1. XRD patterns of fresh ZD-0, ZD-4, ZD-4-used, and ZD-Calcination.

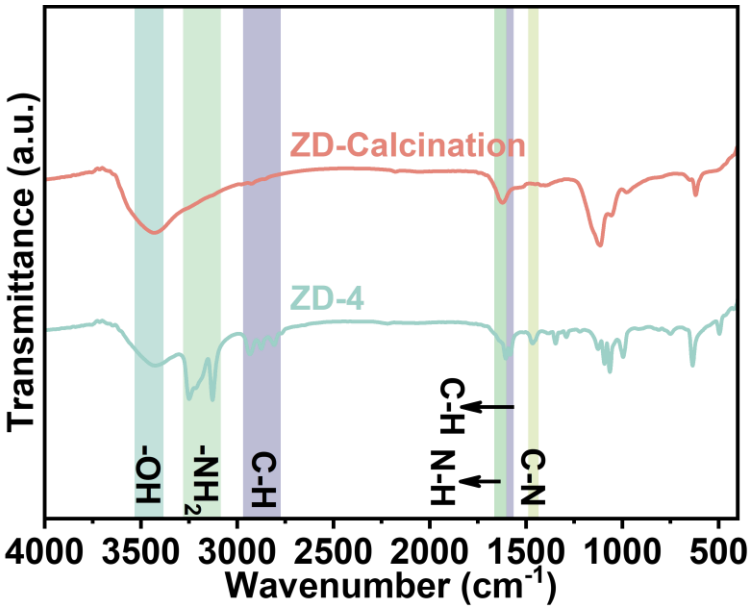


Fig. S2. FT-IR spectra of ZD-4 and ZD-Calcination.

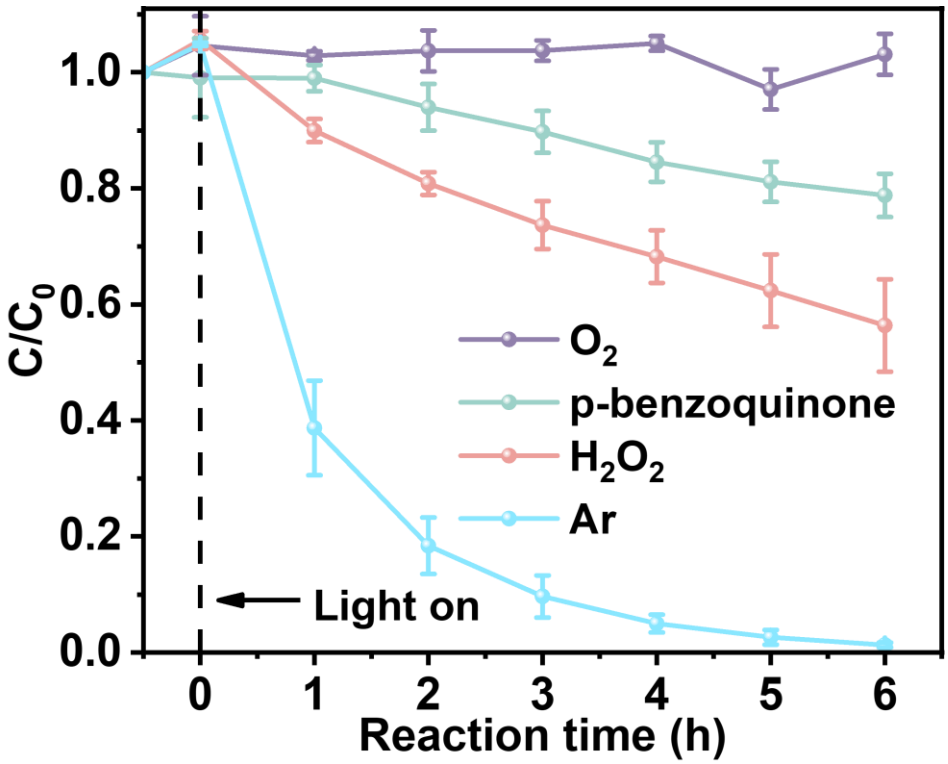


Figure S3 Effects of photoelectron scavengers (O_2, H_2O_2 and *p*-benzoquinone) on the degradation of BDE209 overZD-4

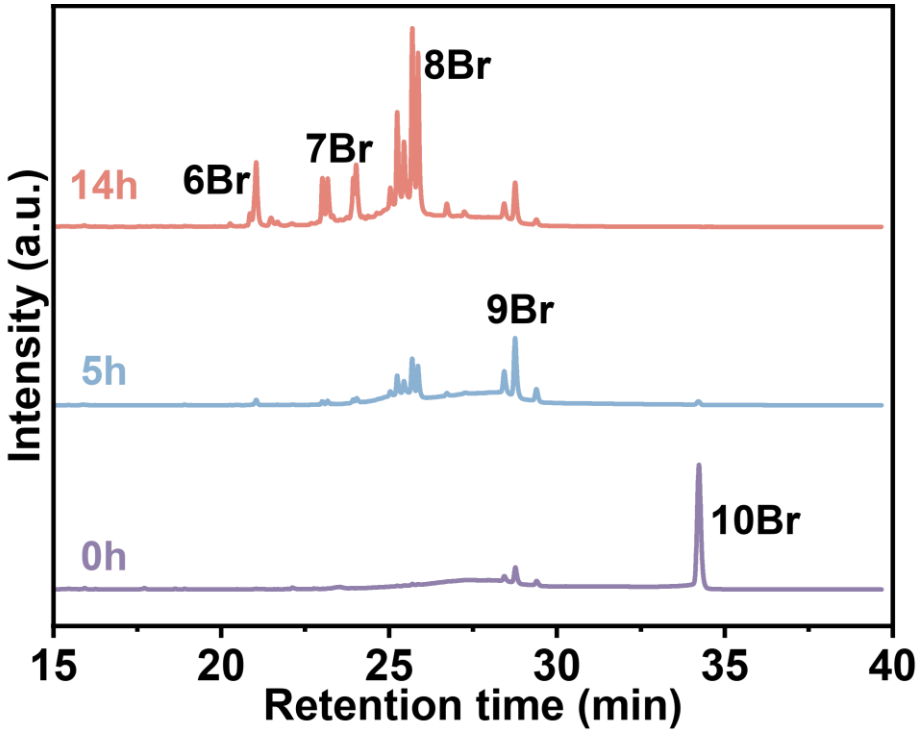
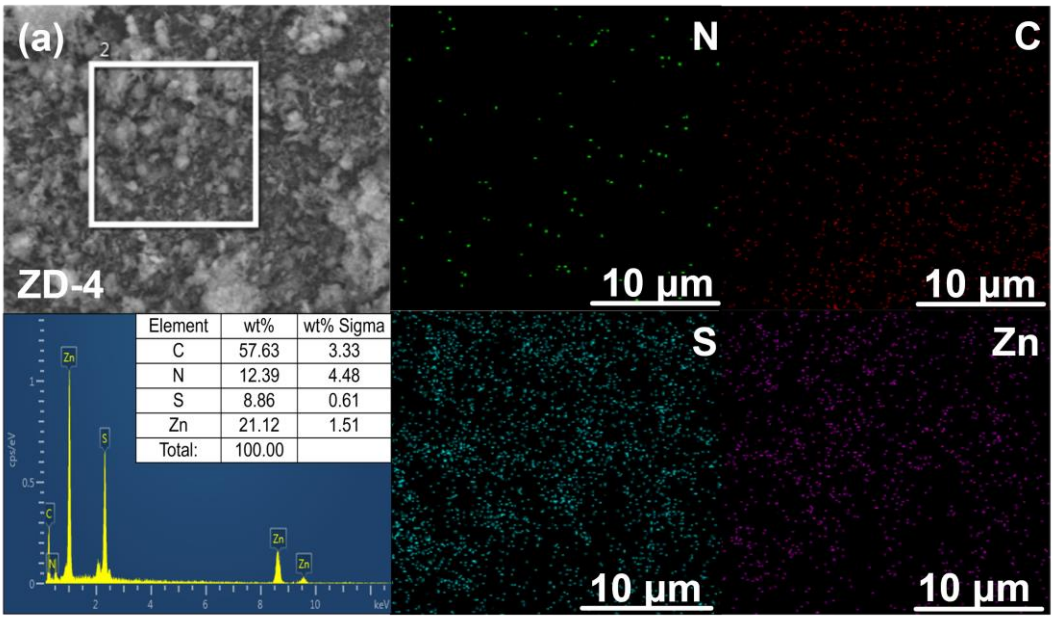


Fig. S4 GC-μECD chromatograms of degradation products of BDE209 under different irradiation times.



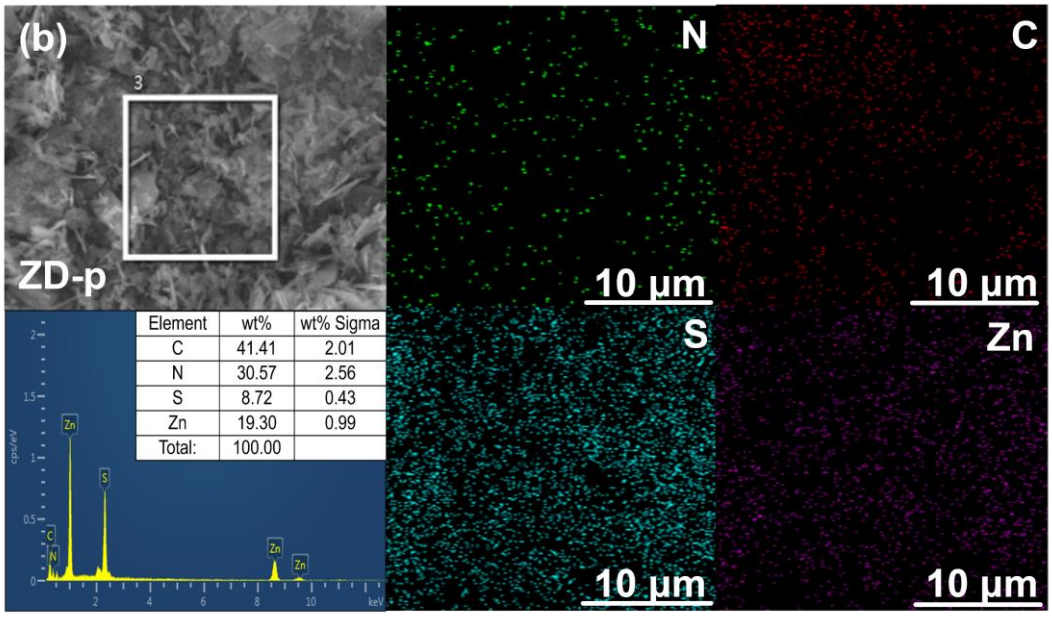


Fig. S5. Elemental content and mapping images of (a) ZD-4 and (b) ZD-p.

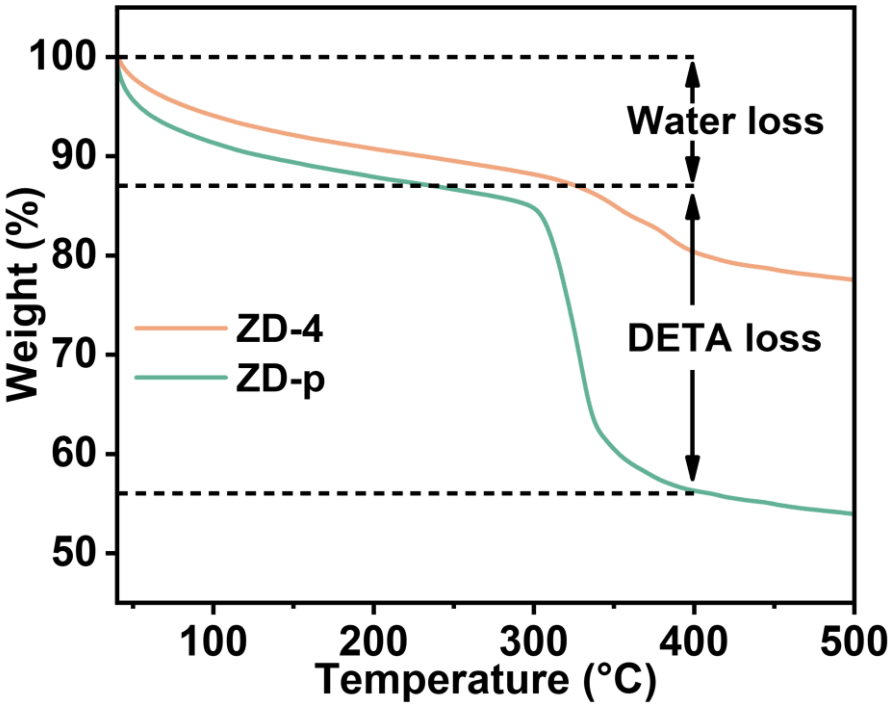


Fig. S6. TG curves of ZD-4 and ZD-p.

The former loss (<120 °C) was assigned to water evaporation.[3]

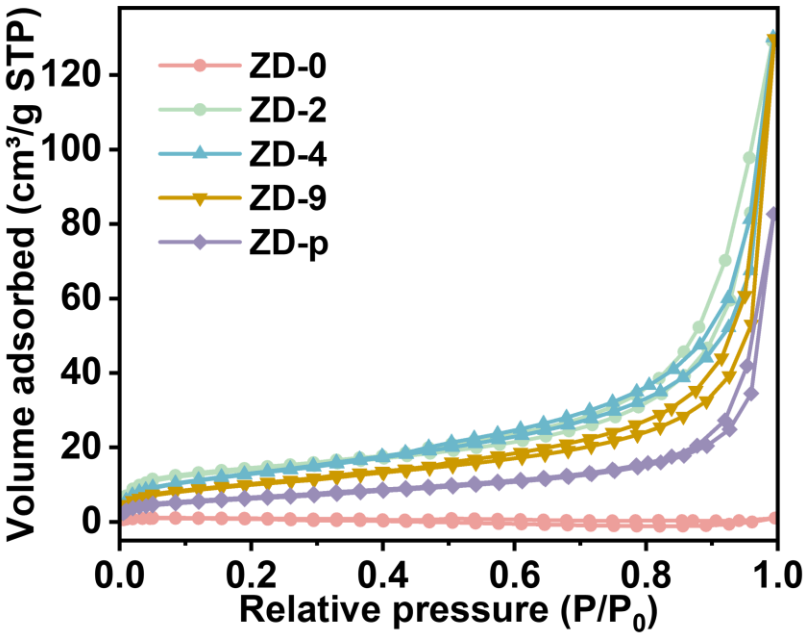


Fig. S7. N_2 adsorption-desorption isotherms of ZD-0, ZD-2, ZD-4, ZD-9, and ZD-p.

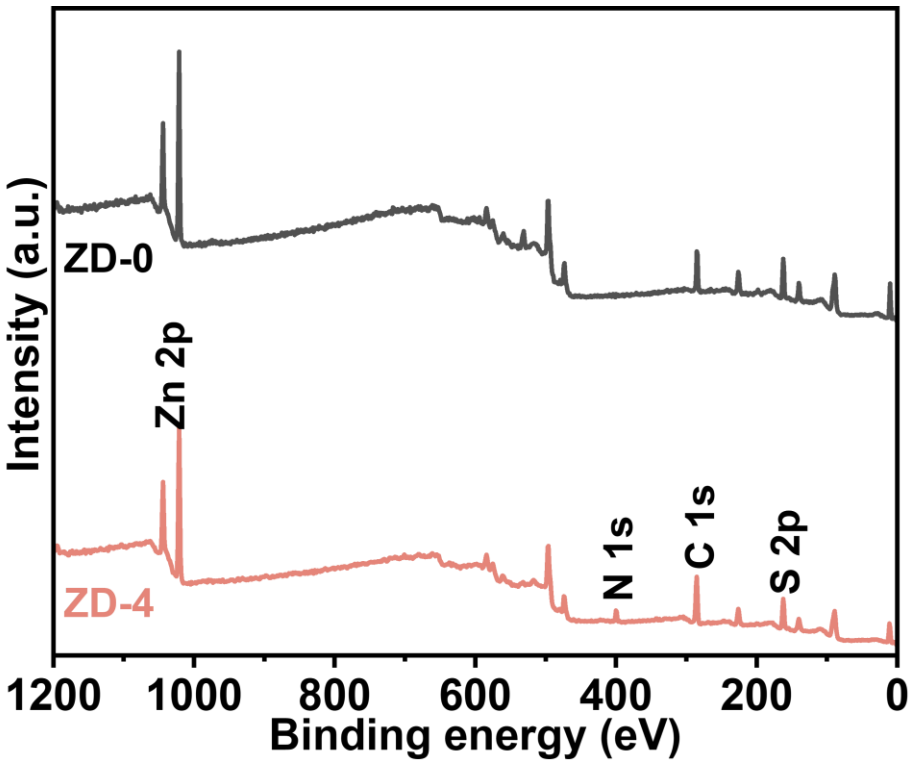


Fig. S8. XPS spectra of ZD-0 and ZD-4.

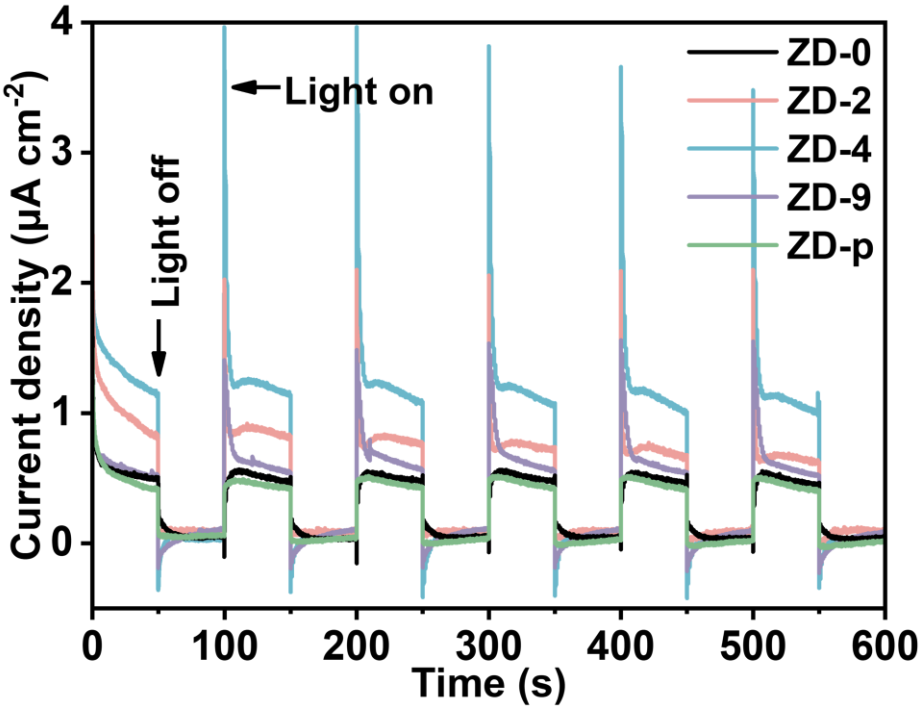


Fig. S9. Transient photocurrent responses spectra of ZD-0, ZD-2, ZD-4, ZD-9, and ZD-p under open circuit voltage.

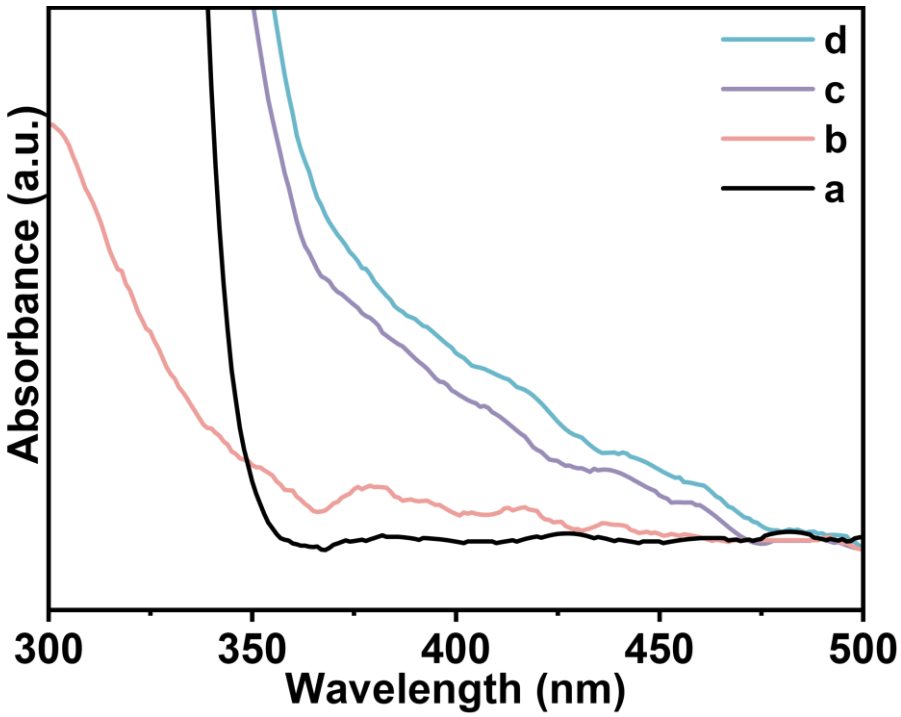


Fig. S10. UV-vis absorption spectra of DETA and BDE209 in DMSO solution. (a) 1 mM BDE209, (b) 100mM DETA, (c) 100mM DETA and 0.5 mM BDE209, (d) 100mM DETA and 1 mM BDE209.

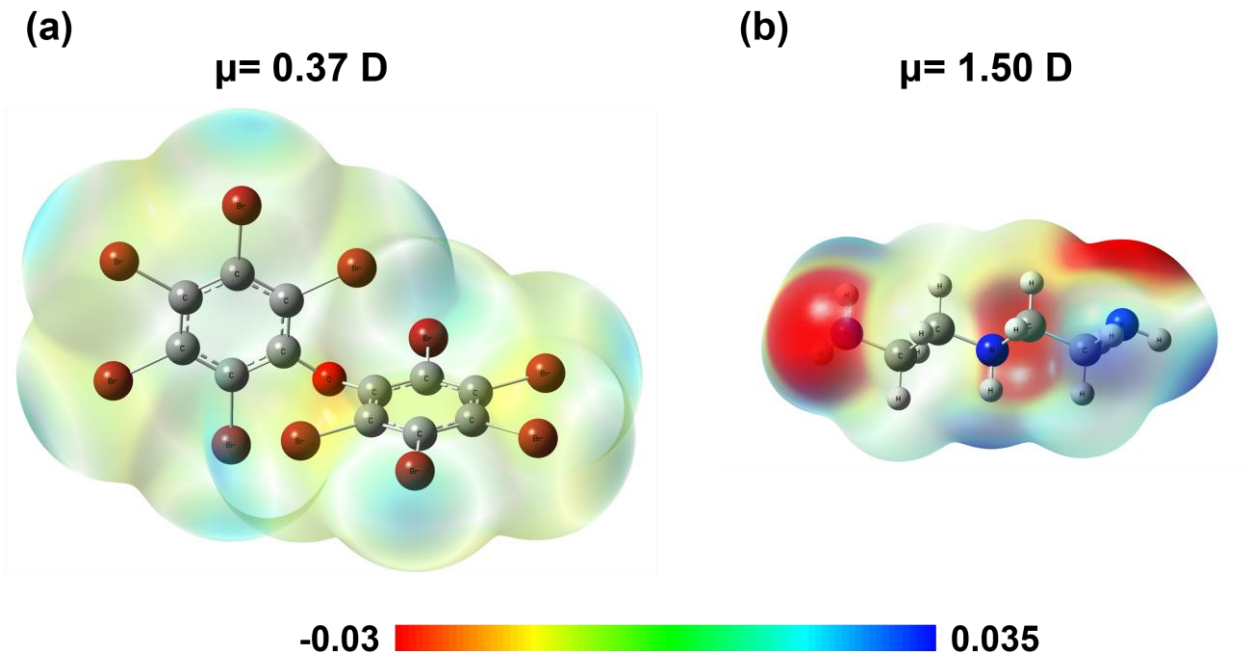


Fig. S11. The electrostatic potential mapped on the surface of molecular electron density of (a) BDE209 and (b) DETA.

Supplementary Table

Table S1. The distance of N···Br and the length of C-Br bonds were obtained by DFT calculation.

	Bond length (Å)			
/	*ortho*-Br-C	*meta*-Br-C	*para*-Br-C	N···Br
Original	1.8882(2)	1.8911(0)	1.8936(2)	/
N···*ortho*-Br	1.9104(6)	/	/	2.7755(4)
N···*meta*-Br	/	1.9140(1)	/	2.7589(8)
N···*para*-Br	/	/	1.9170(6)	2.7548(5)
Δ Å	0.0222(4)	0.0229(1)	0.0234(4)	/

Notes and references

1 Y. Yu, J. Zhang, X. Wu, W. Zhao and B. Zhang, Nanoporous Single-Crystal-Like $Cd_xZn_{1-x}S$ Nanosheets Fabricated by the Cation-Exchange Reaction of Inorganic–Organic Hybrid ZnS–Amine with Cadmium Ions, *Angew. Chem. Int. Ed.*, 2012, **51**, 897–900.

2 M. Lei, S. Guo, Z. Wang, L. Zhu and H. Tang, Ultrarapid and Deep Debromination of Tetrabromodiphenyl Ether over Noble-Metal-Free Cu/TiO_2 Nanocomposites under Mild Conditions, *Environ. Sci. Technol.*, 2018, **52**, 11743–11751.

3 N. Meng, C. Liu, Y. Liu, Y. Yu and B. Zhang, Efficient Electrosynthesis of Syngas with Tunable CO/H_2 Ratios over $Zn_xCd_{1-x}S$-Amine Inorganic–Organic Hybrids, *Angew. Chem. Int. Ed.*, 2019, **58**, 18908–18912.