SUPPORTING INFORMATION

Rational Design of BODIPY Functionalized MOF Photocatalysts for Highly Efficient Hydrogen Production

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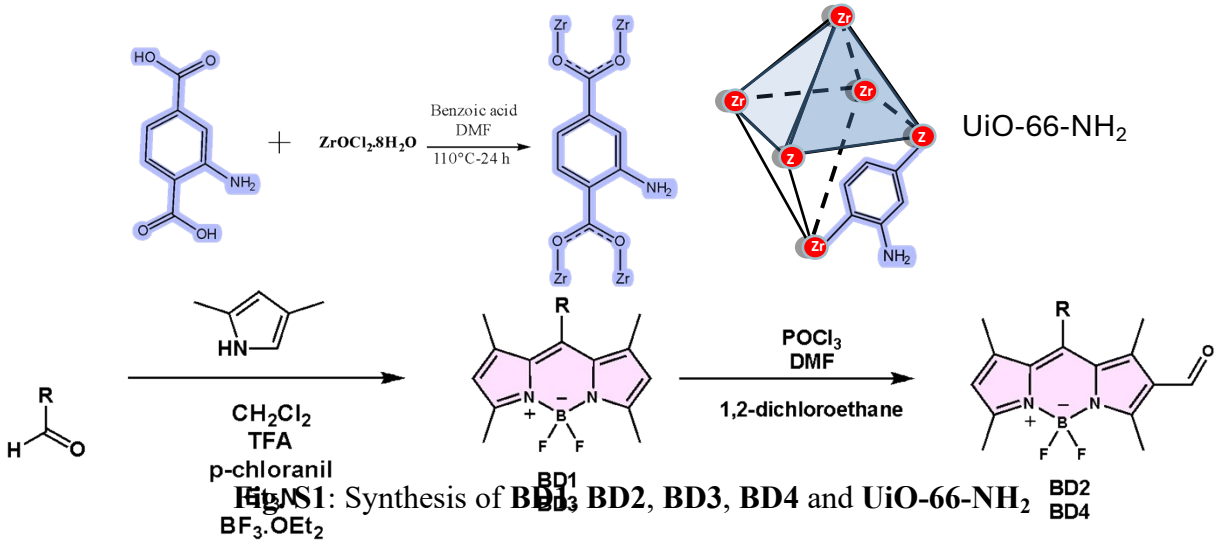
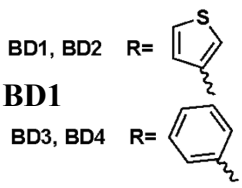


Fig. S1: Synthesis of **BD1**, **BD2**, **BD3**, **BD4** and **UiO-66-NH_2**

Synthesis of BD1



BD1 was synthesized according to the literature (38). 2,4-dimethylpyrrole (1 mL, 9.7 mmol) was added in the reaction flask after 200 mL of CH_2Cl_2 was purged with Ar for 30 min. Then, the reaction medium was purged with Ar for additional 10 min. 3-thiophenecarboxaldehyde (0.40 mL, 4.6 mmol) was added to the reaction medium. A few drops of trifluoroacetic acid was added later. The mixture was allowed to stir under Ar atm at room temperature for 3 hours. p-chloranil (1.13 g, 4.6 mmol) was added and the reaction mixture was stirred for 2 hours. 5 mL of Et_3N and 5 mL $BF_3.OEt_2$ was added to the reaction mixture dropwise, respectively. The reaction mixture was allowed to stir at room temperature for 3 hours and was extracted with water and organic layer was dried using Na_2SO_4. The crude product was purified by silica gel column chromatography using n-hexane:CH_2Cl_2 (3:1) as eluent to give **BD1** (orange solid, 200 mg, 13%) (Fig. S1). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm): 7.41 (m,1H, Ar-H), 7.11 (m, 1H, Ar-H), 6.89 (m, 1H, Ar-H), 5.91 (s, 2H, Ar-H), 2.47 (s, 6H, -CH_3), 1.42 (s, 6H, -CH_3) (Fig. S2). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C (ppm): 155.53, 143.14, 137.00, 134.50, 131.76, 127.48, 127.39, 123.78, 121.19, 14.61, 13.70 (Fig. S3).

Synthesis of BD3

BD3 was synthesized according to the literature (39). 2,4-dimethylpyrrole (1 mL, 9.7 mmol) was added in the reaction flask after 200 mL of CH_2Cl_2 was purged with Ar for 30 min. Then, the reaction medium was purged with Ar for an additional 10 min. Benzaldehyde (0.45 mL, 4.4 mmol) was added to the reaction medium. A few drops of trifluoroacetic acid were added later. The mixture was allowed to stir under Ar atm at room temperature for 3 hours. p-chloranil (1.08 g, 4.4 mmol) was added and the reaction mixture was stirred for 2 hours. 5 mL of Et_3N and 5 mL $BF_3.OEt_2$ was added to the reaction mixture dropwise respectively. The reaction mixture was allowed to stir at room temperature for 3 hours and was extracted with water and organic layer was dried using Na_2SO_4. The crude product was purified by silica gel column chromatography using n-

hexane:CH_2Cl_2 (3:1) as eluent to **BD3** (orange solid, 200 mg, 13%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm): 7.51 (m,3H) (Ar-H), 7.30 (m, 2H) (Ar-H), 6.00 (s, 2H) (Ar-H), 2.58 (s, 6H) (-CH_3), 1.39 (s, 6H) (-CH_3) (Fig. S4). ^{13}C NMR (101 MHz, $CDCl_3$) δ_C (ppm): 155.42, 143.17, 141.74, 134.99, 131.43, 129.14, 128.95, 127.93, 121.22, 14.60, 14.36 (Fig. S5).

Synthesis of UiO-66-NH_2

UiO-66-NH_2 was synthesized according to the literature with some modifications (40). Initially, 1.5 g (4.65 mmol) of $ZrOCl_2 \cdot 8H_2O$, 1.0 g (5.52 mmol) of NH_2-BDC, and 25.0 g (204.7 mmol) of benzoic acid were placed into a 250 mL glass bottle. Subsequently, 100 mL of DMF was added, and the mixture was sonicated in an ultrasonic bath until the solid components had completely dissolved, yielding a homogeneous solution. The reaction mixture was then placed in an oven and kept at 110°C for 24 hours. Upon completion of the reaction, the product was collected by centrifugation and thoroughly washed with DMF and acetone to remove unreacted residues and by-products. Finally, the material was dried overnight in an oven at 60°C, followed by additional drying under vacuum at 100°C. The resulting product was then subjected to characterization analyses.

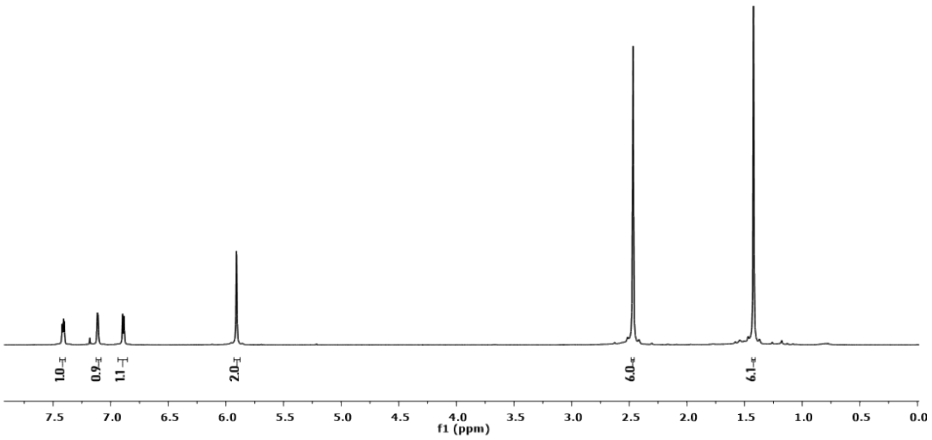


Fig. S2: The ^{1}H NMR spectrum of **BD1**

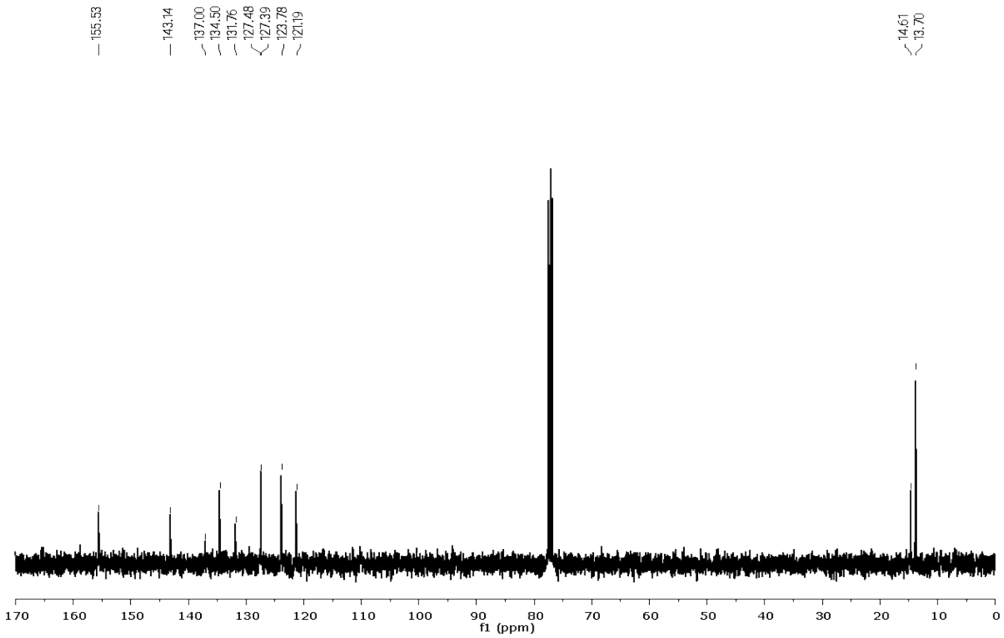


Fig. S3: The ^{13}C NMR spectrum of **BD1**

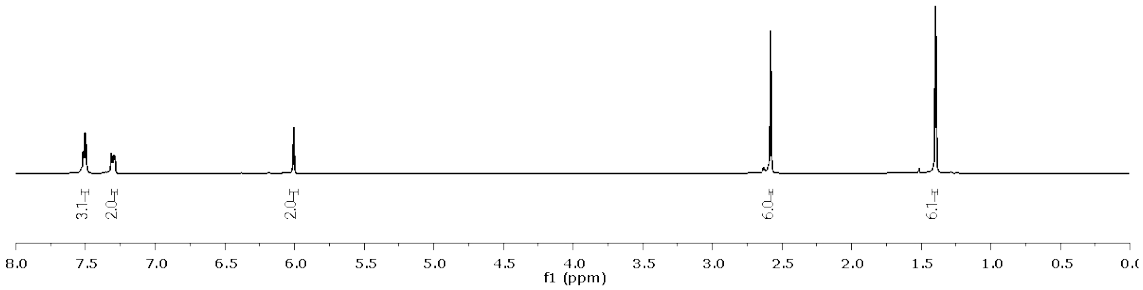


Fig. S4: The ^{1}H NMR spectrum of **BD3**

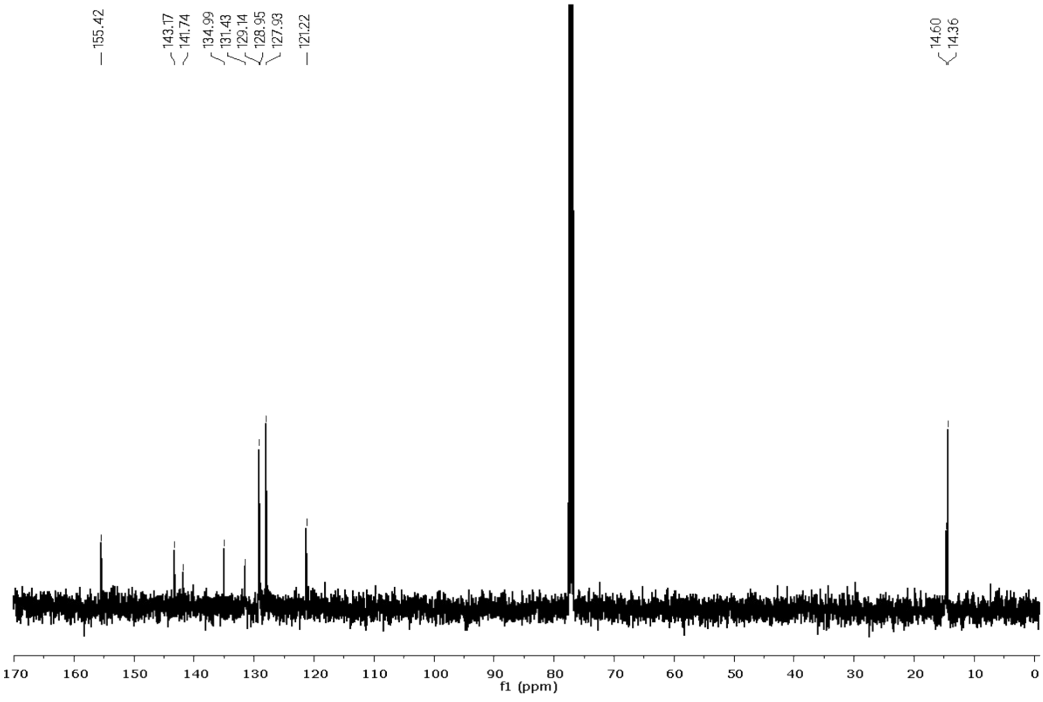


Fig. S5: The ^{13}C NMR spectrum of **BD3**

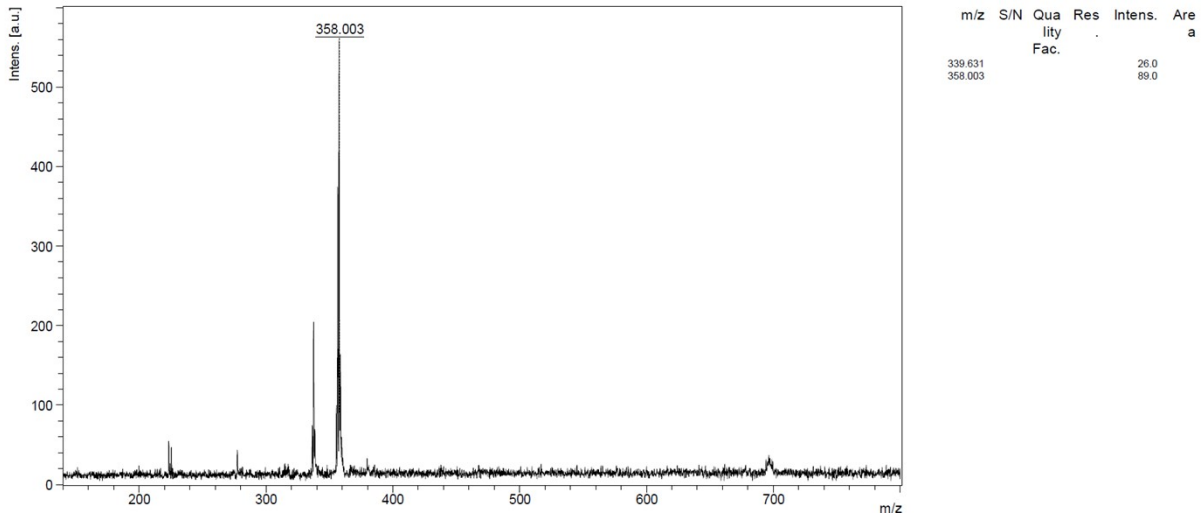


Fig. S6: The MALDI TOF mass spectrum of **BD2**

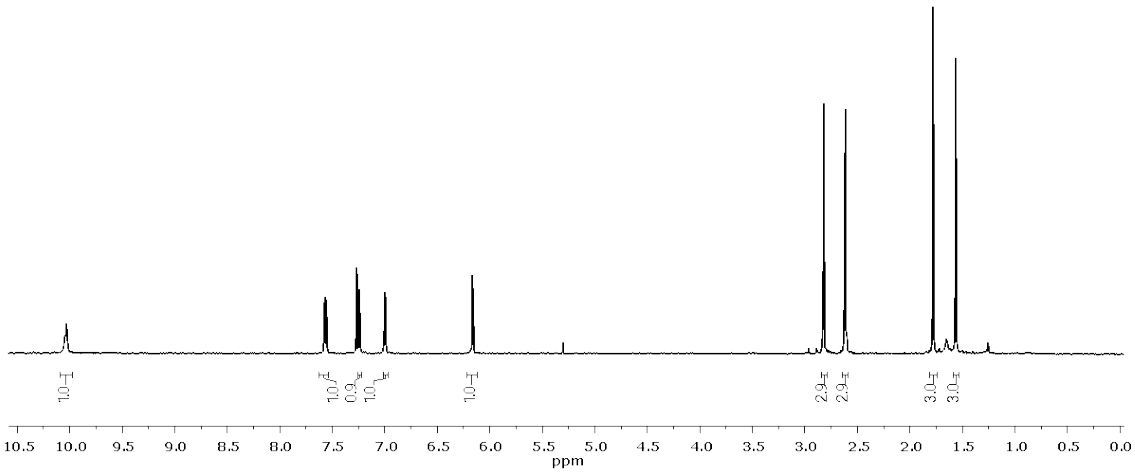


Fig. S7: The ^{1}H NMR spectrum of **BD2**

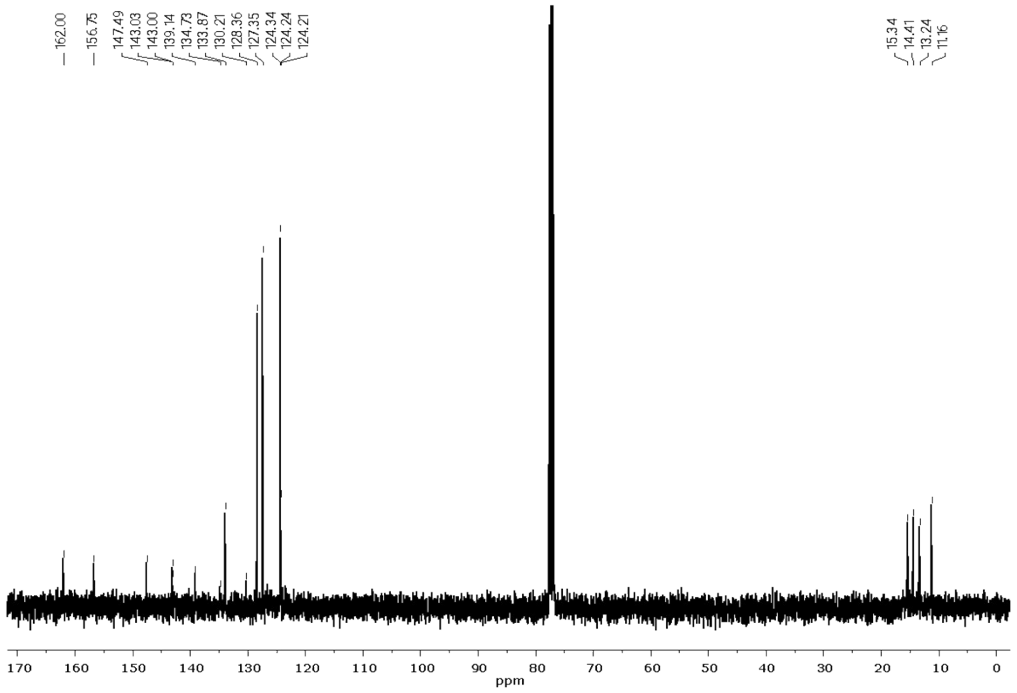


Fig. S8: The ^{13}C NMR spectrum of **BD2**

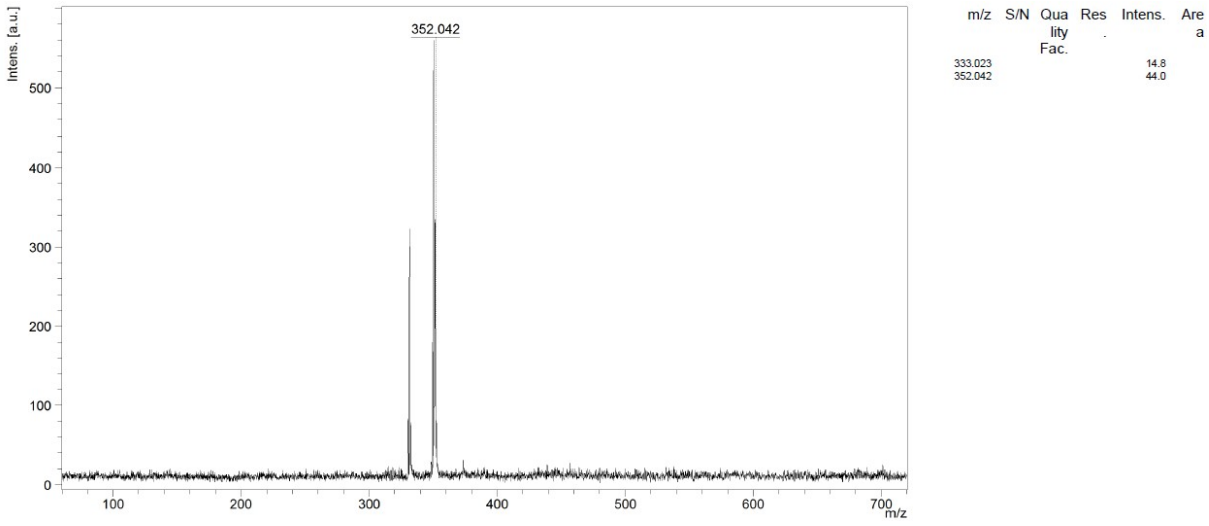


Fig. S9: The MALDI TOF mass spectrum of **BD4**

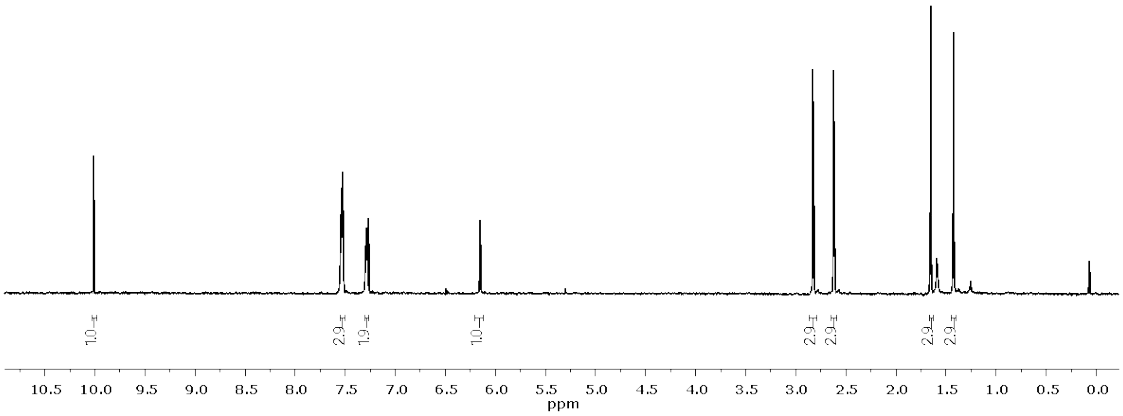
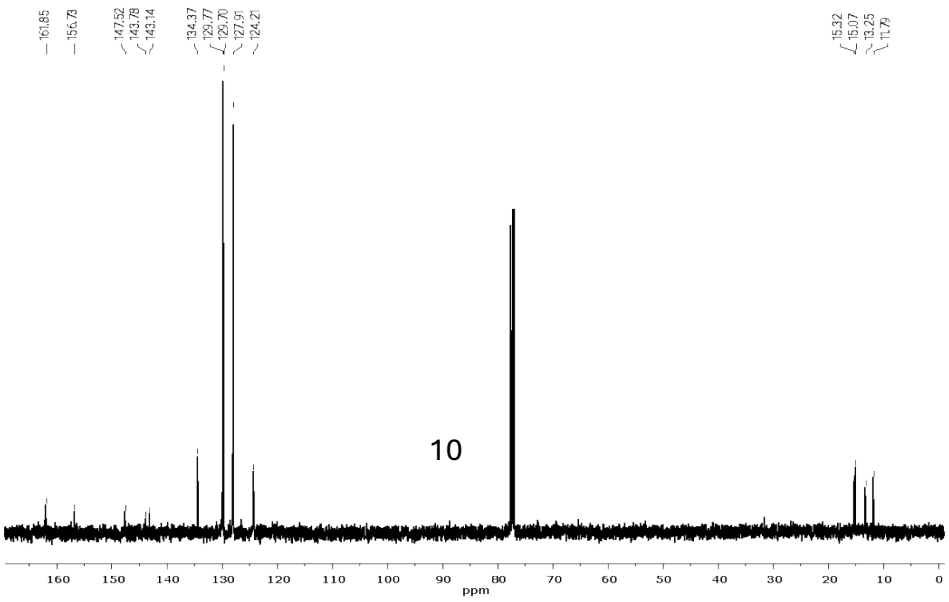


Fig. S10: The ^{1}H NMR spectrum of **BD4**

Fig. S11: The ^{13}C NMR spectrum of **BD4**



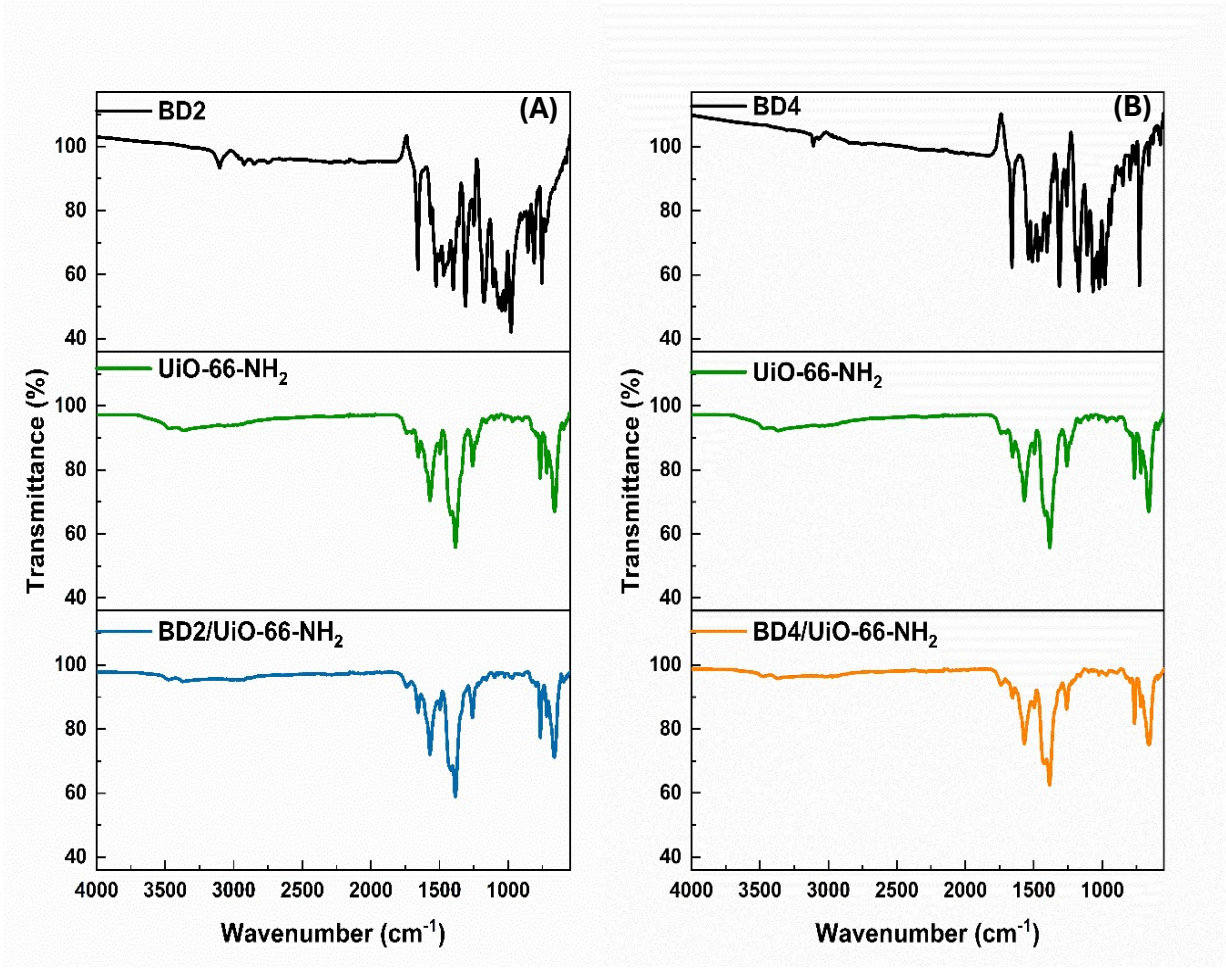


Fig. S12: FT-IR spectrums of (A) BD2/UiO-66-NH_2, (B) BD4/UiO-66-NH_2

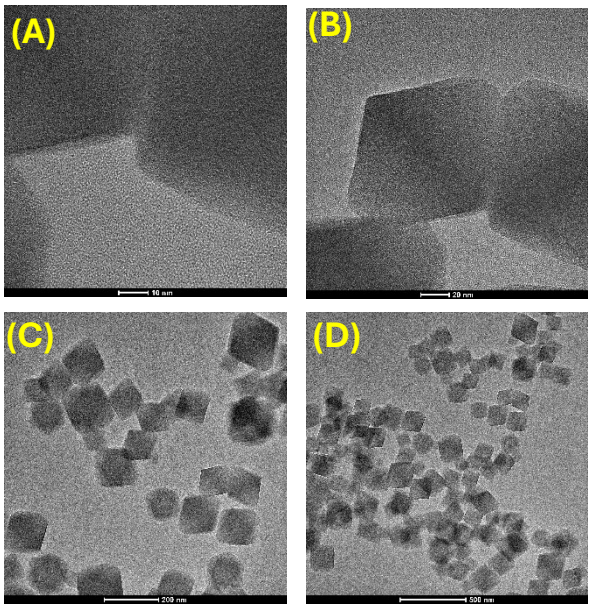


Fig. S13: HRTEM images of UiO-66-NH_2 (A) 10 nm, (B) 20 nm, (C) 200 nm, (D) 500 nm.

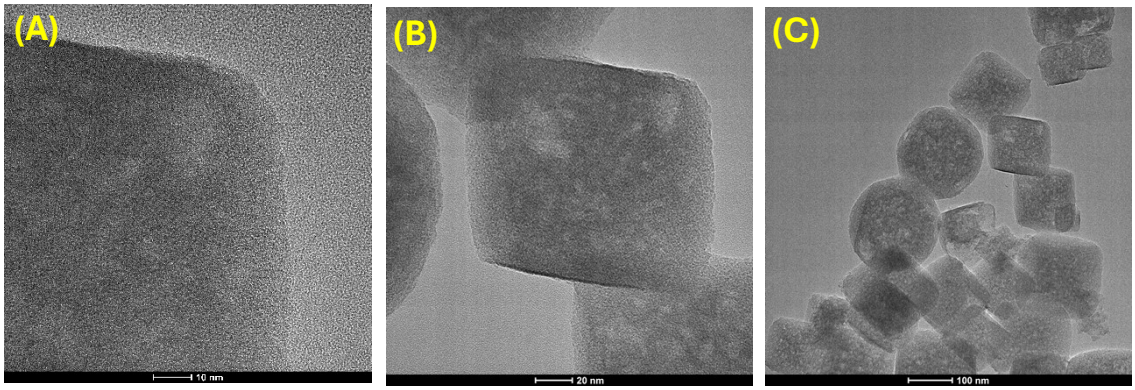


Fig. S14: HRTEM images of BD4/UiO-66-NH_2 (A) 10 nm, (B) 20 nm, (C) 100 nm.

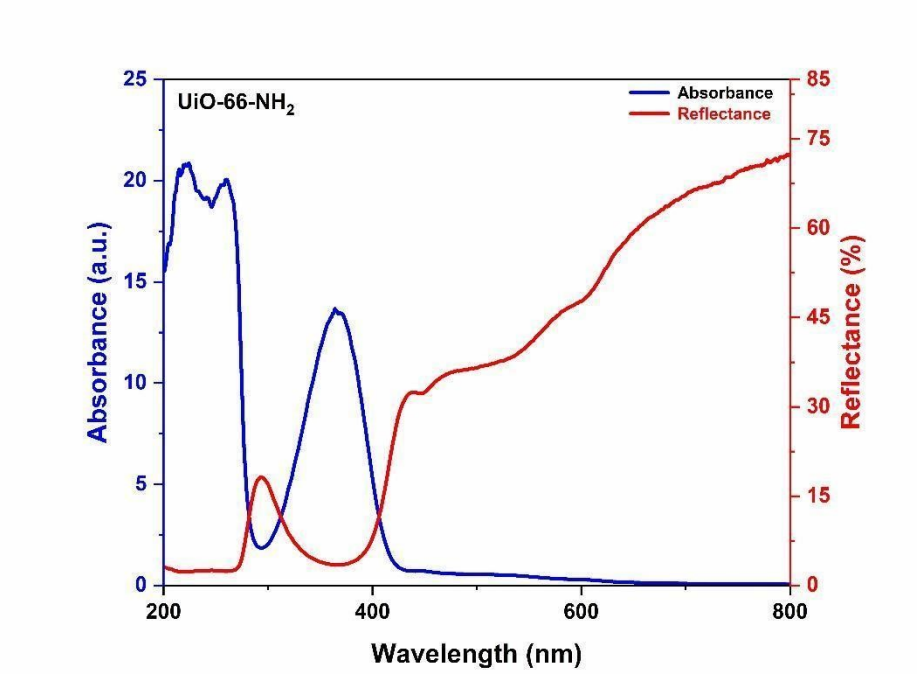


Fig. S15: Absorbance and reflectance spectrums of UiO-66-NH_2.

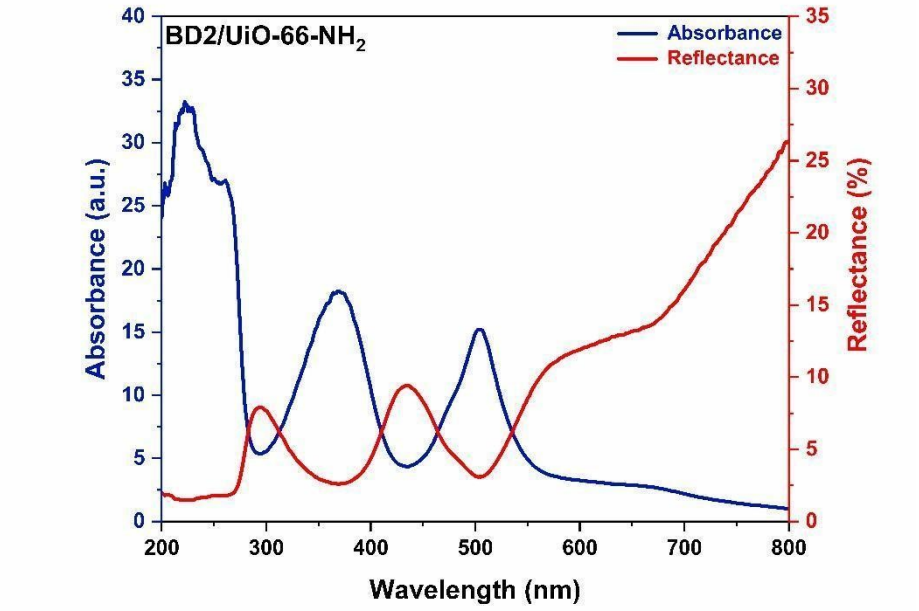


Fig. S16: Absorbance and reflectance spectrums of BD2/UiO-66-NH_2.

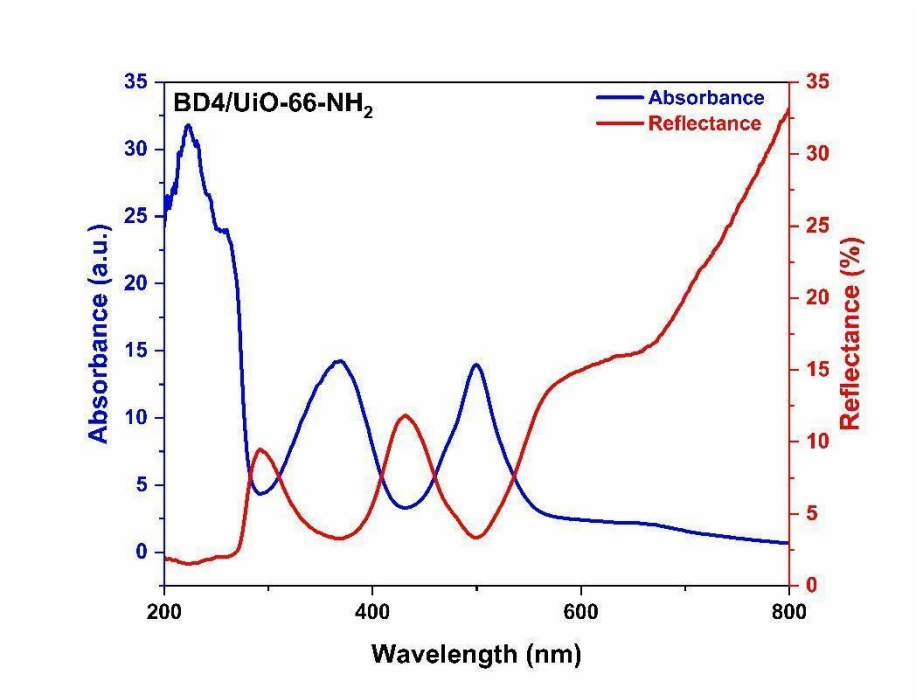


Fig. S17: Absorbance and reflectance spectrums of BD4/UiO-66-NH_2.

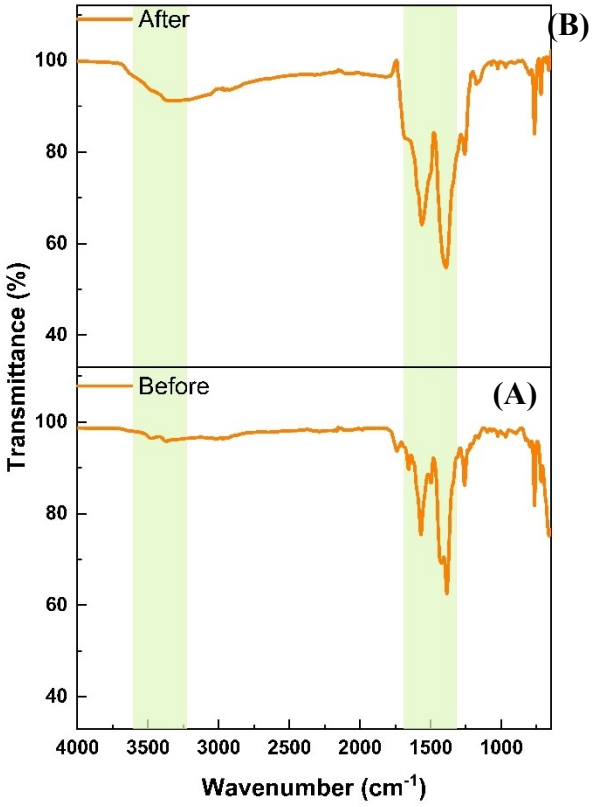


Fig. S18: FTIR spectra of BD4/UiO-66-NH_2 (A) before, (B) after HER

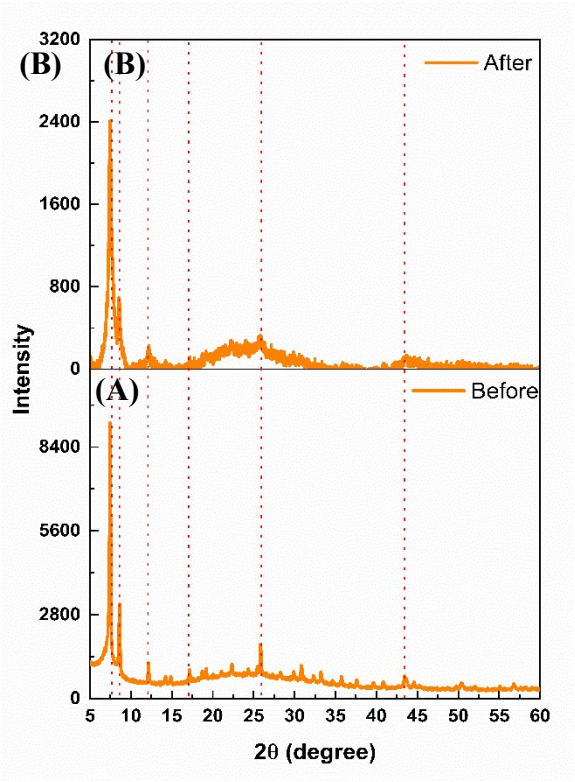


Fig. S19: PXRD pattern of BD4/UiO-66-NH_2 (A) before, (B) after HER

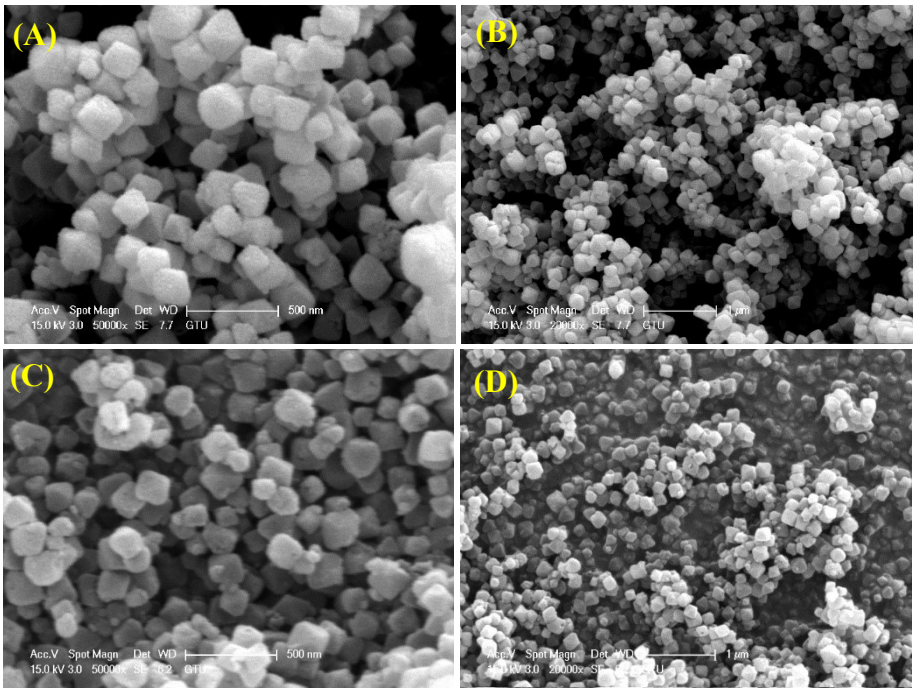


Fig. S20: SEM images of BD4/UiO-66-NH2 (A, B) before, (C, D) after HER

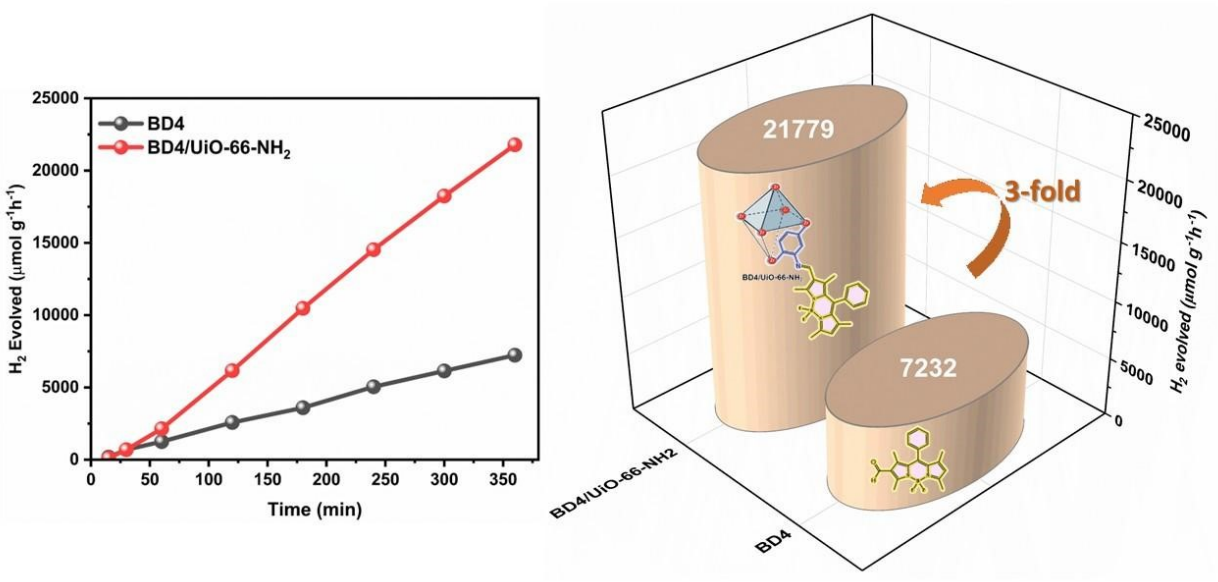


Fig. S21: H_2 Evolution Comparison of BD4 and BD4/UiO-66-NH_2