Supplementary Materials

Chemically Bonded N-PDI-P/WO_3 Organic-Inorganic Heterojunction with Improved Photoelectrochemical Performance

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1. Materials

All reagents and chemicals were purchased from commercial sources (Aladdin, Acros, Sigma, TCI, Alfa, Shanghai Macklin Biochemical Co., or Sinopharm Chemical ReagentCo.) and used without further purification except statements. Solvents (toluene and $CHCl_3$) were distilled by standard procedures before used for organic synthesis.

2. Synthesis

N-PDI-P was successfully synthesized by following the procedure shown in Fig S1. 3,4,9,10-Perylenetetracarboxylic dianhydride was hydrolyzed in 5% KOH solution to obtained an aqueous solution of compound 2, the solution was adjusted the pH≈9 with 20% dilute hydrochloric acid, K_2CO_3 and Methyl trioctyl ammonium chloride (Aliquat 336) together with 1-Bromohexane were added, the reaction mixture was refluxed for 18 hours to obtain compound 3; Compound 3 and p-Toluenesulfonic acid monohydrate were dissolved in n-Heptane and toluene mixed solvent, after refluxing for 5 h, deionized water was added , the product was extracted with CH_2Cl_2 and the organic phase was evaporated to obtain compound 4; Compound 4, 1-naphthylamine and imidazole were mixed, the mixture was stirred at reflux under high temperature for 5h, after this time deionized water was added, the solution was adjusted with 20% dilute hydrochloric acid for neutral, the mixture was suction filtered and washed with water, then solid was dried and further purification was carried out by column chromatography to obtain compound 5; Compound 5 and *p*-toluenesulfonic acid monohydrate were dissolved in toluene , the mixture was stirred at reflux for 4h, toluene was removed by vacuum, the compound was sonicated in distilled water, the mixture was suction filtered and solid was dried to obtain compound 6; Compound 6 and L-phenylalanine tert-butyl ester were mixed with imidazole. After refluxing for 5 h, deionized water was added, precipitation was filtered and washed with water until neutral. The solid was dried and purified by silica gel column chromatography to obtain N-PDI-P. ^1H NMR (500 MHz, $CDCl_3$) δ ppm: 8.74 (d, 2H), 8.62 (d, 2H), 8.57 (q, 4H), 7.43-8.00 (m, 7H), 7.07-7.23 (m, 5H), 6.00 (dd, 1H), 3.71 (dd, 1H), 3.53 (dd, 1H), 1.50 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ ppm: 168.41, 163.64, 162.89, 135.18, 134.78, 132.09, 131.70, 130.10, 129.71, 129.21, 128.31, 127.26, 126.79, 126.46, 125.66, 123.56, 123.20, 123.01, 121.80, 82.25, 55.40, 35.02, 28.01; MS (MALDI-TOF): *m/z* = 720.2 $[M]^+$; Elemental analysis: calcd (%) for $C_{47}H_{32}N_2O_6$: C 78.32, H 4.48, N 3.89; found C 78.53, H 4.46, N 4.10.

During the synthesis process, phenylalanine was used directly for the final imidization. However, along with the reaction progressed, the reaction solution gradually became colorless and precipitated a red-black solid, which was insoluble in common organic solvents such as CH_3CH_2OH and CH_2Cl_2. As a result, the solid product cannot be purified and we did not gain the final product by this method. Finally, we utilized phenylalanine tert-butyl ester to obtain N-PDI-P which has nice solubility in common organic solvents. By its nice solubility, the proposed solution preparation method, which is cheap and easy, can be used to prepare organic-inorganic composite materials.

3. Supporting Figs

Figure S1. Synthetic Route for N-PDI-P

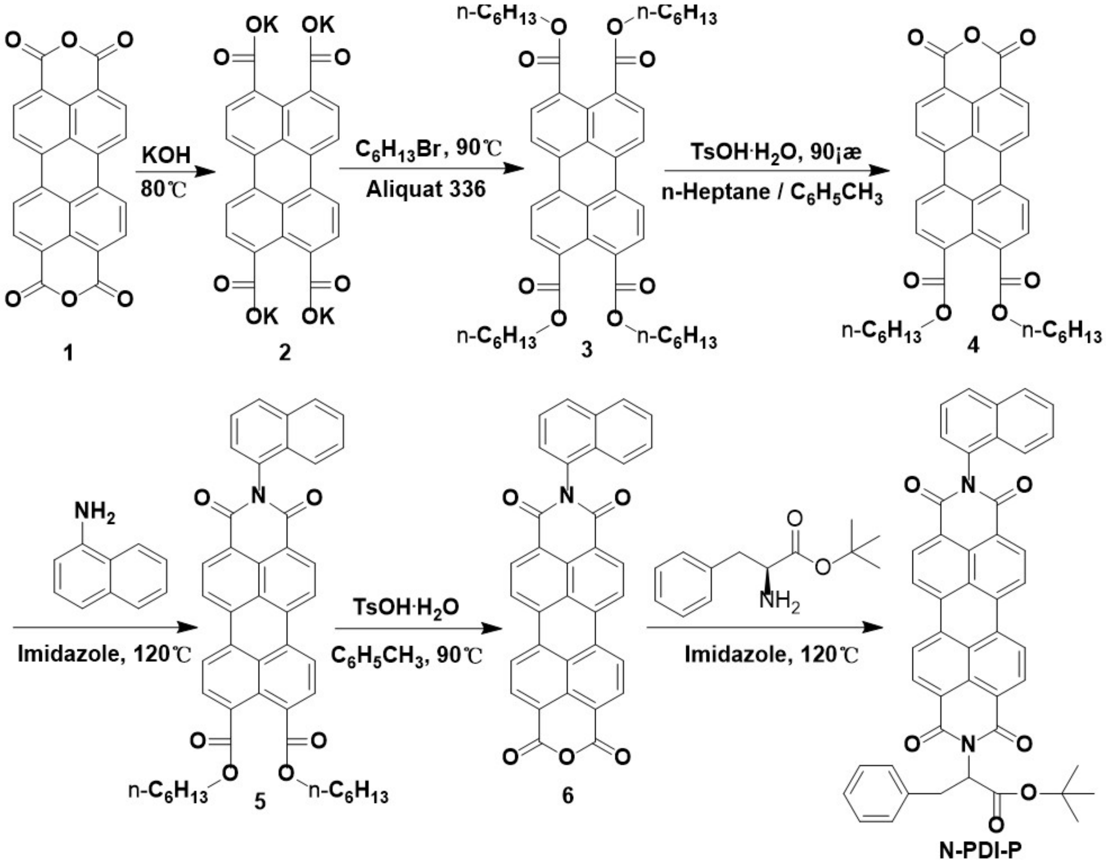


Figure S2. (a)SEM image of PDI-WO_3 composites prepared by immersion for 4 days and EDS spectroscopy with elemental mapping of (b)C, (c)O, (d)W and (e)N

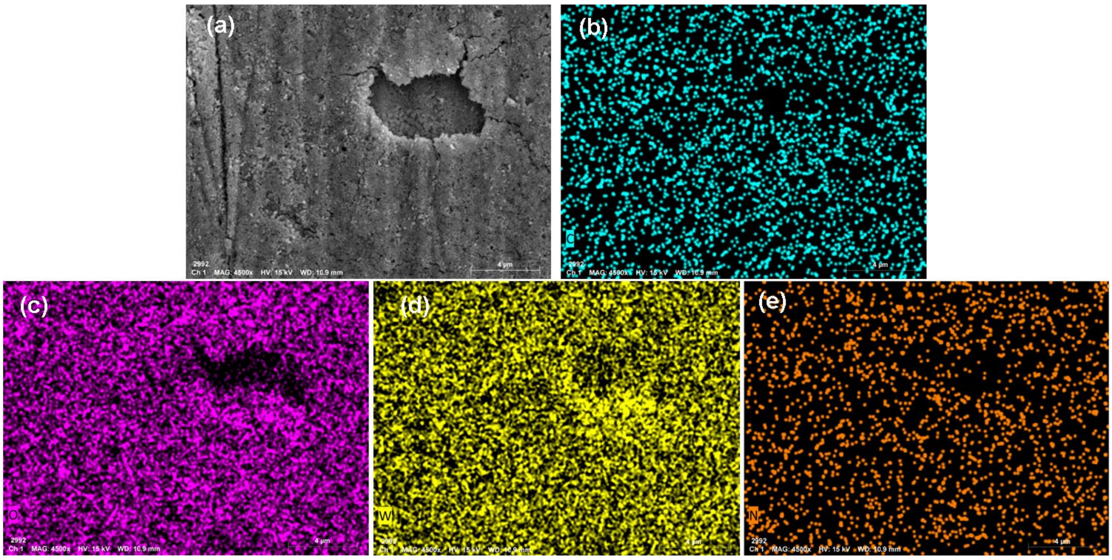


Figure S3. XPS spectra: (**a**) survey spectrum of the prepared N-PDI-P/WO_3 composite and high-resolution spectra showing (**b**) the W $4f_{7/2}$, W $4f_{5/2}$ and W 5p peaks.

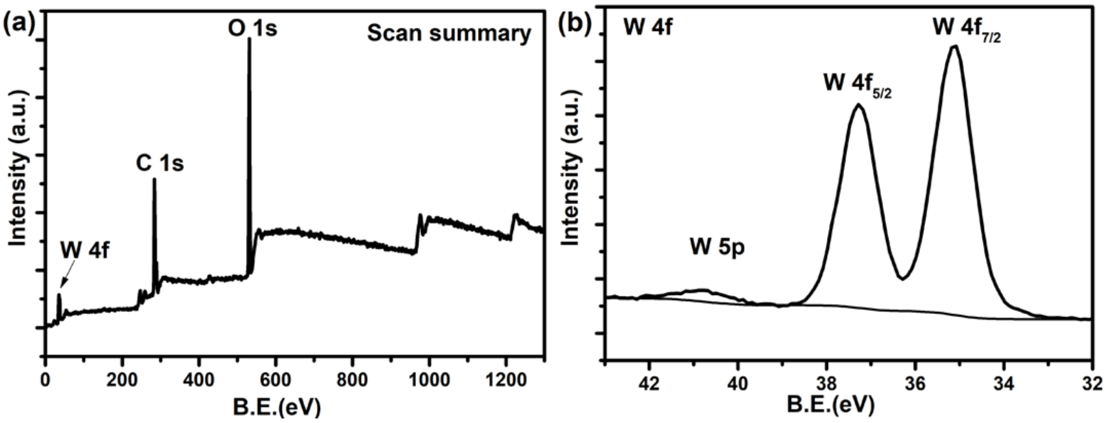


Figure S4. (a) UV-Vis curve and (b) CV curve of N-PDI-P

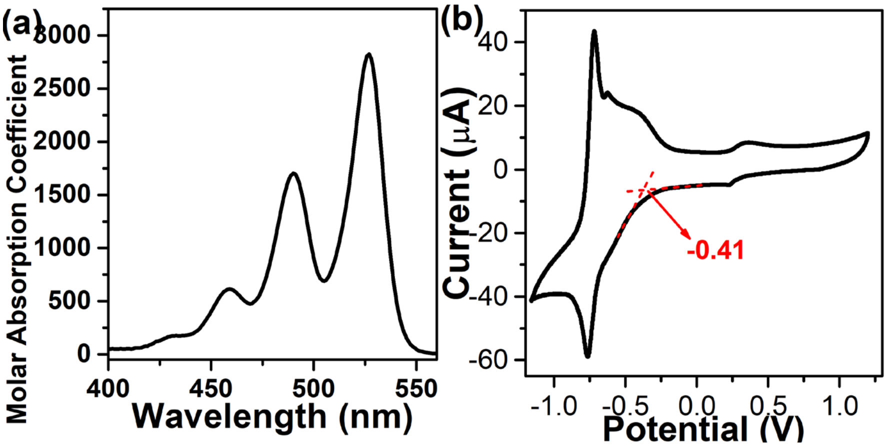
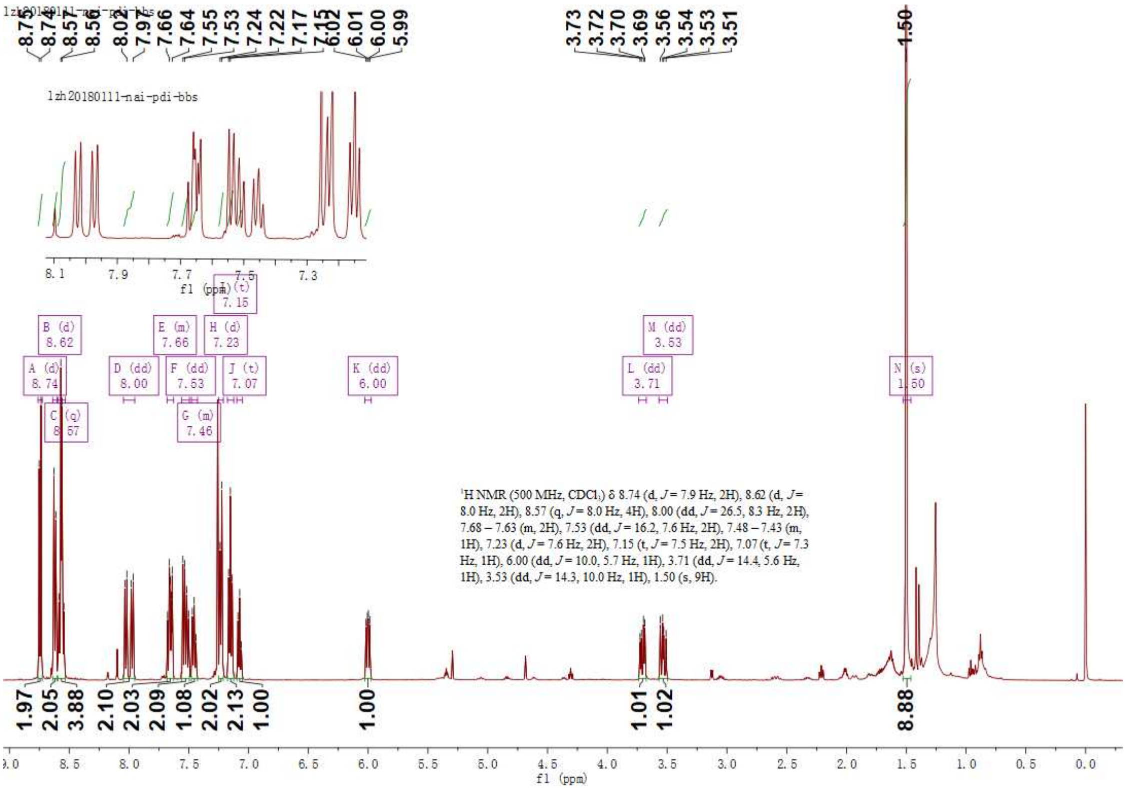


Figure S5. The ^{1}H NMR spectra of N-PDI-P.



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 7.9 Hz, 2H), 8.62 (d, *J* = 8.0 Hz, 2H), 8.57 (q, *J* = 8.0 Hz, 4H), 8.00 (dd, *J* = 26.5, 8.3 Hz, 2H), 7.68 – 7.63 (m, 2H), 7.53 (dd, *J* = 16.2, 7.6 Hz, 2H), 7.48 – 7.43 (m, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.00 (dd, *J* = 10.0, 5.7 Hz, 1H), 3.71 (dd, *J* = 14.4, 5.6 Hz, 1H), 3.53 (dd, *J* = 14.3, 10.0 Hz, 1H), 1.50 (s, 9H).

Figure S6. The ^{13}C NMR spectra of N-PDI-P.

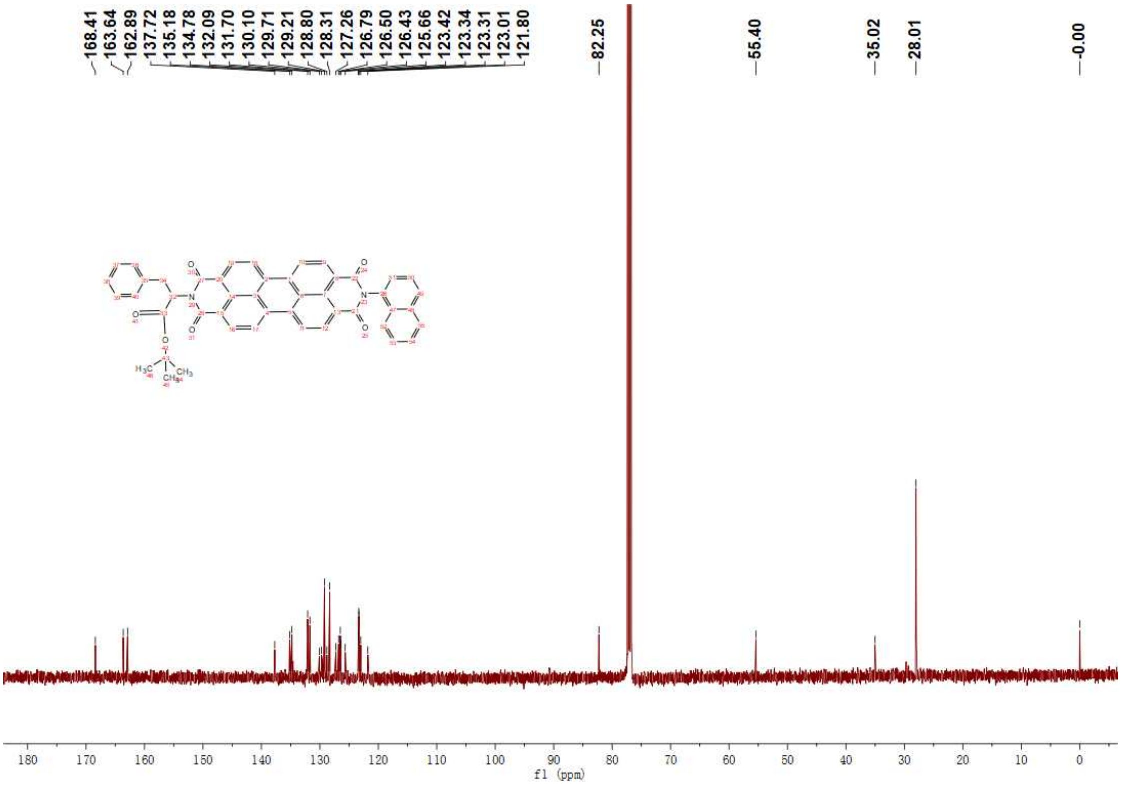
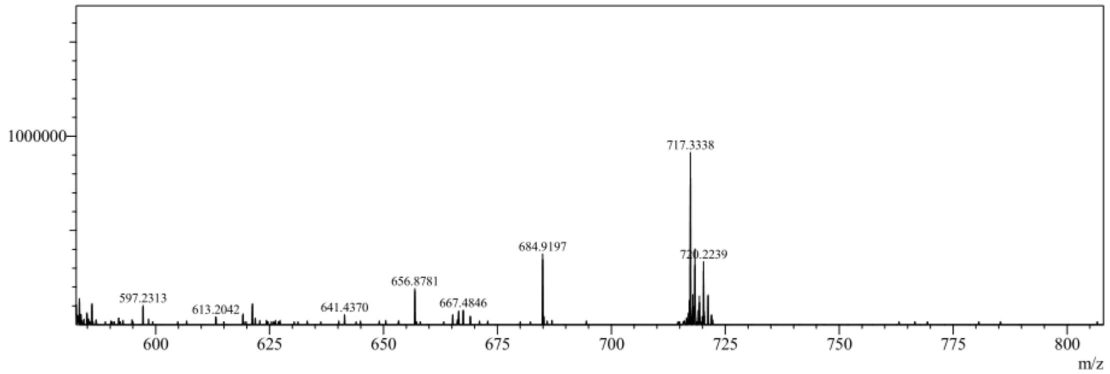


Figure S7. The MS spectra of N-PDI-P.



4. Supporting table

Table S1. Decay times measured around the PL peak from time-resolved PL for **N-PDI-P** on W, **N-PDI-P** on WO$_3$ and **N-PDI-P**/WO$_3$.

	B1	τ_1/ns	B2	τ_2/ns	τ/us
N-PDI-P on W	1384	21.80	5.99*10^{10}	1.18	1.18
N-PDI-P on WO3	2.13*10^{10}	1.11	2.13*10^{10}	1.11	1.11
N-PDI-P/WO3	8.34*10^{13}	0.75	8.34*10^{13}	0.75	0.75