

Reversible Electric Switching of NDI Molecular Wires by Orthogonal Stimuli

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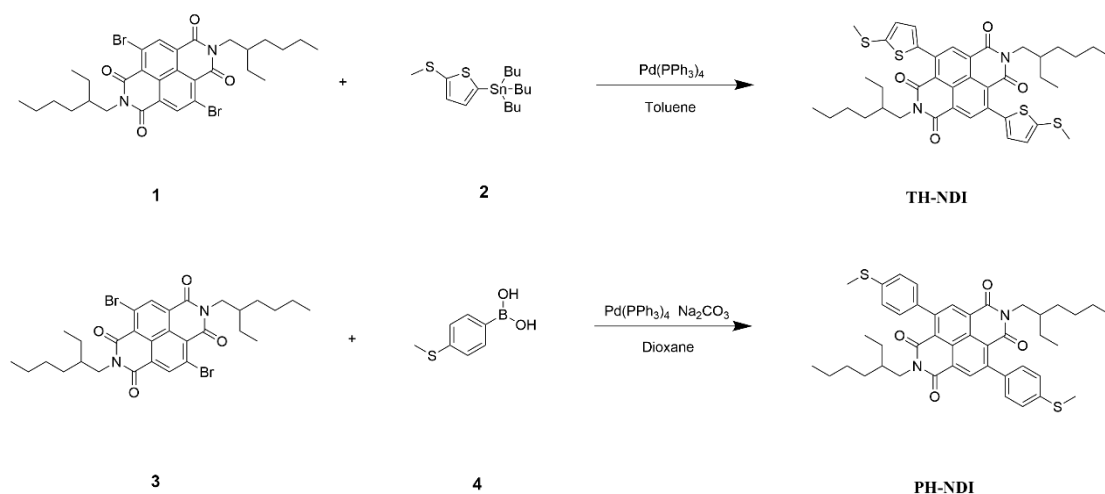
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Section S1. Syntheses of TH-NDI and PH-NDI



Scheme S1. Synthetic routes of TH-NDI and PH-NDI.

Th-NDI: Br-NDI-Br (**1**, 200mg, 0.308 mmol) and Pd(PPh₃)₄ (35.59 mg, 0.0308 mmol) were added into 50 mL Schlenk tube, followed by degassing for 15 min. The degassed toluene was injected into the tube and the solution was stirred at 95 °C for 12 hrs. Then dibutyl(5-(methylthio)thiophen-2-yl)(propyl)stannane (**2**, 516.55 mg, 1.232 mmol) was added and the reaction mixture was stirred overnight 95 °C. The mixture was cooled to room temperature and extracted with EA. The EA solution was concentrated by evaporation under vacuum. The residue was purified via chromatography on a silica gel column using DCM/PE=1:1 as eluent to give Th-NDI a purple solid 160 mg, yielding: 69%. ¹H NMR (400 MHz, CDCl₃) δ 8.72 (s 2H), 7.20 (d, *J* = 3.72 Hz, 2H), 7.11 (d, *J* = 3.76, 2H), 4.09(dd, *J* = 4.56 Hz, 3.12Hz 4H), 2.60 (s, 6H), 1.37-1.27 (m, 16H), 0.92-0.85 (m, 12H), ¹³C NMR (101 MHz, CDCl₃) δ 162.6, 162.4, 142.1, 141.6, 139.4, 136.5, 130.1, 129.2, 127.5, 125.4, 122.7, 44.6, 37.8, 30.7, 28.6, 23.9, 23.1, 21.6, 14.1, 10.6. HRMS(EI-TOF): C₄₀H₄₆N₂O₄S₄ *m/z* [M⁺] calcd for 746.2340; found: 746.2342.

Ph-NDI: Br-NDI-Br (**3**, 200mg, 0.308 mmol), 4-(methylthio)phenylboronic acid (**4**, 155.25 mg, 0.924 mmol), Na₂CO₃ (130.58 mg, 1.232 mmol) and Pd(PPh₃)₄ (17.80 mg, 0.0154 mmol) were added into 100 mL Schlenk tube under argon atmosphere. The degassed dioxane (10 ml) and H₂O (2 ml) were added, and the reaction mixture was

stirred for 12 hrs at 95 °C. The mixture was cooled to room temperature and extracted with EA and washed with water. The solvent was concentrated by evaporation under vacuum. The residue was purified via chromatography on a silica gel column using DCM/PE=1:1 as eluent to give the product PH-NDI as orange solid 169 mg, yielding: 75%. ¹H NMR (400 MHz, CDCl₃) δ 8.63 (s, 2H), 7.38-7.33 (m, 8H), 4.06 (dd, J=2.68Hz, 4.84Hz 4H), 2.57 (s, 6H), 1.35 - 1.24 (m, 16H), 0.90 – 0.86 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 162.9, 162.7, 147.1, 139.4, 136.8, 136.00, 128.8, 127.3, 126.00, 125.5, 122.8, 44.5, 37.7, 30.6, 28.5, 23.9, 23.1, 15.5, 14.1, 10.6. HRMS(EI-TOF): C₄₄H₅₀N₂O₄S₂ m/z [M⁺] calcd for 734.3212; found: 734.3214.

Section S2. Cyclic voltammograms of **TH-NDI** and **PH-NDI**

The cyclic voltammetry measurements were performed in a three-electrode system with a Pt wire as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and a glassy carbon electrode as the working electrode. The electrolyte was Bu_4NPF_6 . The ferrocene was used as external standard.

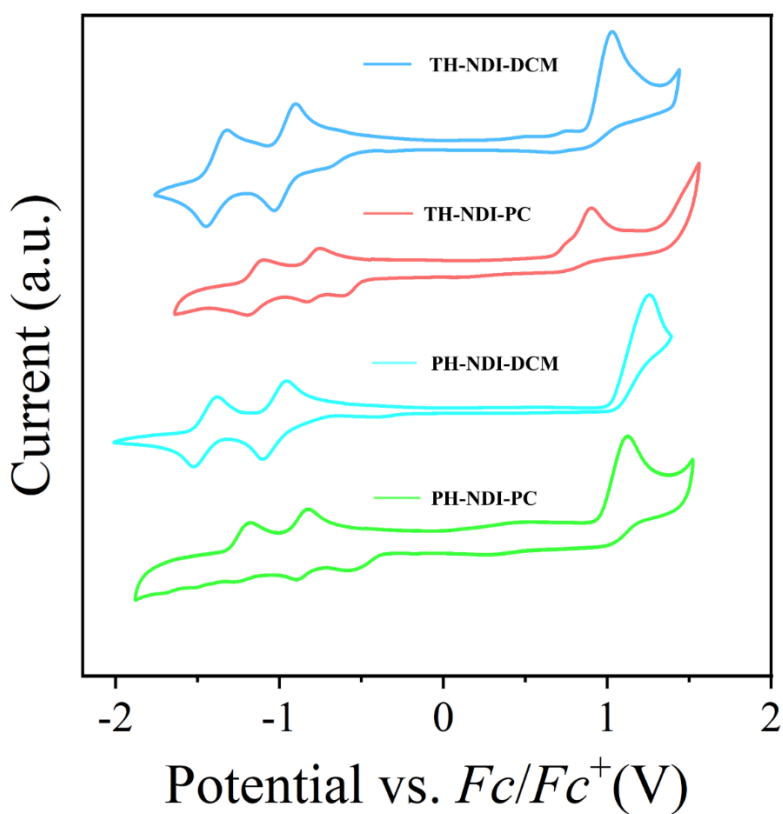


Fig. S1. Cyclic voltammograms of **TH-NDI** and **PH-NDI** compounds in DCM and PC solutions at a scan rate of 100 mV s^{-1} .

Section S3. The conductance of TH-NDI and PH-NDI junctions

Single-molecule conductance measurements were carried out using the Xtech scanning tunneling microscope break junction (STM-BJ) instrument, and the data were analyzed using XMe opensource code (Weiruijingyi, China). The single-molecule conductance was measured under ambient conditions using a STM. During the measurements, 5 μL of 0.1mM target molecule in 1,2,4-trichlorobenzene (TCB) or propylene carbonate (PC) were prepared and dropped onto the substrate in situ.

The polar solvent (PC) tends to uplift the background noise due to the leakage current. To reduce area of the electrode exposed to solvent, the STM tip is etched electronically in the solution of ethanol/hydrochloric acid (1:1) at a constant potential of 5 V, then insulated with Apiezon wax. For the measurements in TCB solvent, the gold wire is flamed by hydrogen flame gun to form gold bead (diameter~1 mm).

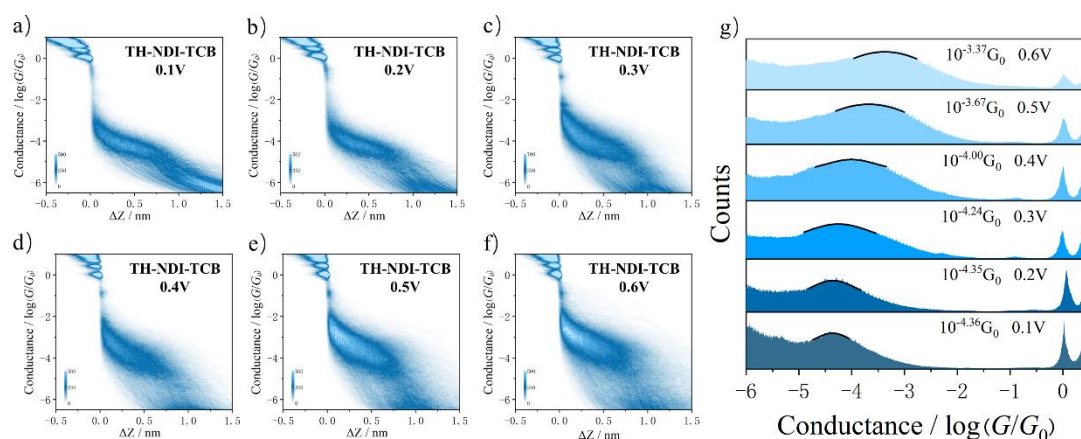


Fig. S2. The conductance of TH-NDI junction in low polar TCB solution. (a-f) 2D conductance-displacement histograms at different bias voltages. (g) The bias dependence of 1D conductance histograms.

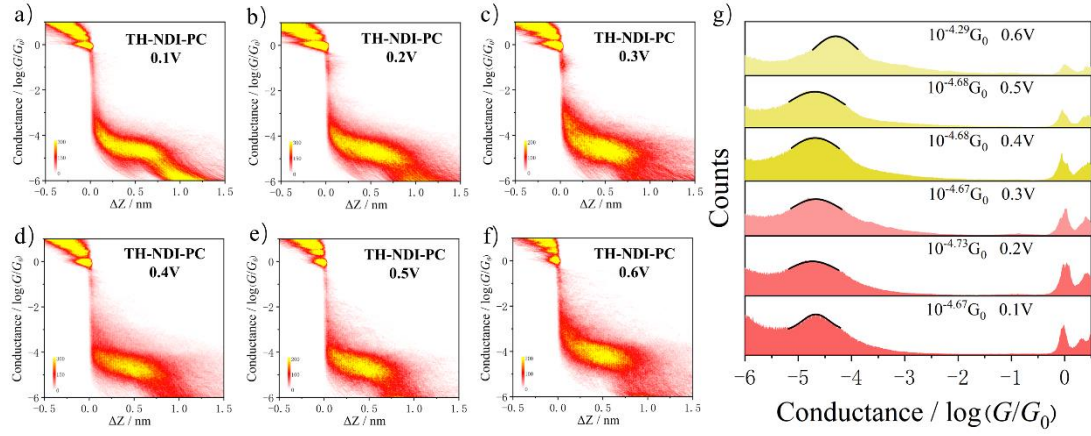


Fig. S3. The conductance of TH-NDI junction in high polar PC solution. (a-f) 2D conductance-displacement histograms at different bias voltage. (g) The bias dependence of 1D conductance histograms.

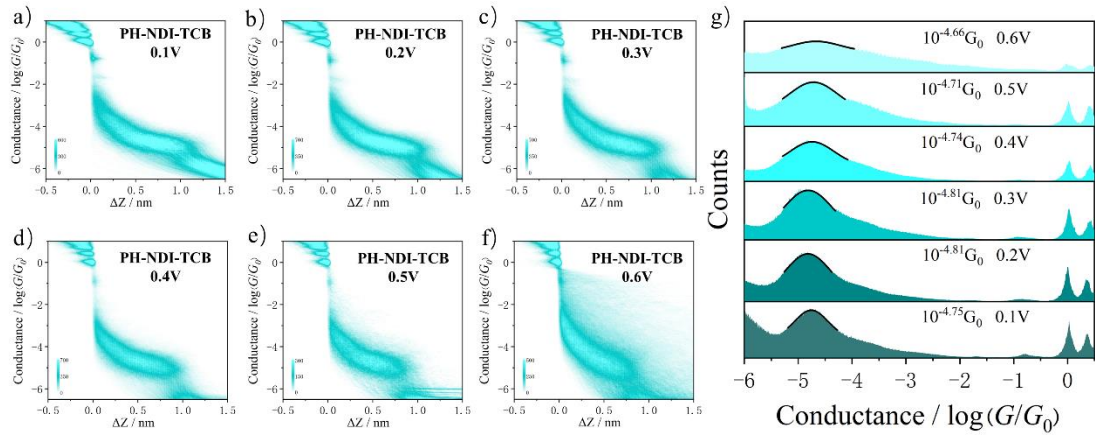


Fig. S4. The conductance of PH-NDI junction in low polar TCB solution. (a-f) 2D conductance-displacement histograms at different bias voltages. (g) The bias dependence of 1D conductance histograms.

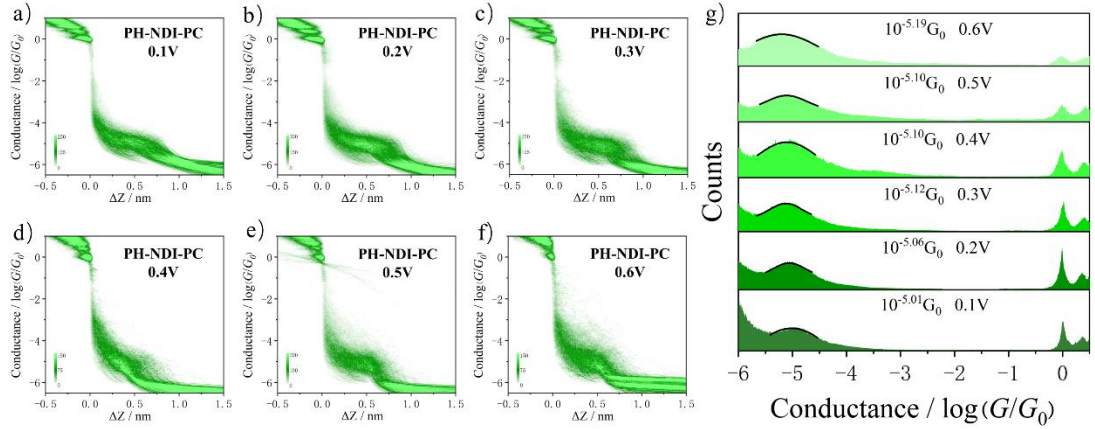


Fig. S5. The conductance of PH-NDI junction in high polar PC solution. (a-f) 2D conductance-displacement histograms at different bias voltage. (g) The bias dependence of 1D conductance histograms.

Section S4. Displacement-distribution histograms of **TH-NDI** and **PH-NDI** junctions.

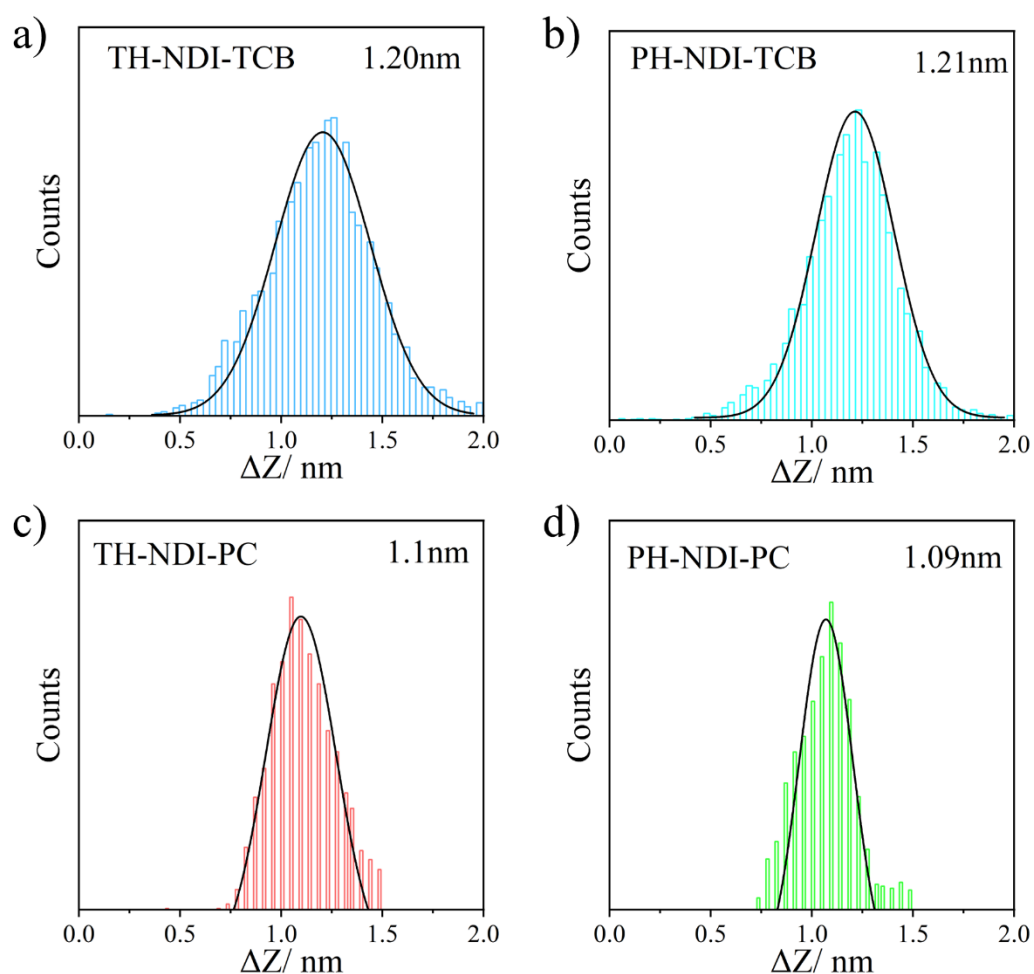


Fig. S6. The displacement-distribution histograms of TH-NDI and PH-NDI junctions under bias voltage of 0.1 V. (a) TH-NDI in TCB, (b) PH-NDI in TCB, (c) TH-NDI in PC, and (d) PH-NDI in PC.

Fig. S6 shows the displacement-distribution histograms of NDI molecule-based junctions during the stretching process under bias voltage of 0.1 V. These histograms were fitted by Gaussian functions. By adding the snapback distance of 0.5 nm^{1,2}, the characterized lengths of the molecular junctions were determined to be 1.70 nm for **TH-NDI-TCB**, 1.71 nm for **PH-NDI-TCB**, 1.6 nm for **TH-NDI-PC** and 1.59 nm for **PH-NDI-PC**.

Section S5. Single-molecule conductance for **TH-NDI** at the gate voltage window from -0.6V to 0.6V

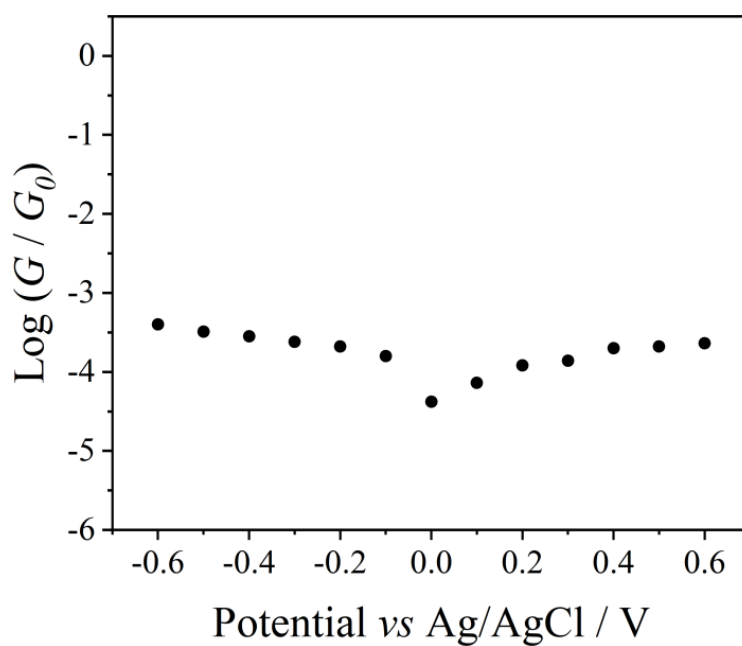


Fig. S7. Single-molecule conductance for **TH-NDI** at the gate voltage window from -0.6V to 0.6V, while keeping the bias voltage at 0.6V.

Section S6. Theoretical calculation

In order to simplify the analysis, the alkyl chains of NDI- molecules were replaced with methyl groups. The optimized molecular geometries were obtained using the B3LYP functional with the 6-31G (d, p) basis set in the Gaussian 09 package. Frequency analysis was performed at the same level to confirm that the optimized structures were at the minimum energy states. To construct the devices, the optimized molecules were inserted into the gap between two gold electrodes, which were cut into pyramid structures. The sulfur atoms were used as anchoring groups and placed at the top of the pyramids to form a single-molecule junction. For the **TH-NDI** junction, the anchoring atom was mounted on the second layer of the pyramid to simulate the interaction between the thiophene ring and the electrode. The device optimization and transmission spectra were calculated using the Atomistix Toolkit (ATK) software package with nonequilibrium Green's functions. The generalized gradient approximation with the Perdew-Burke-Ernzerhof functional was used to approximate the exchange-correlation potential.

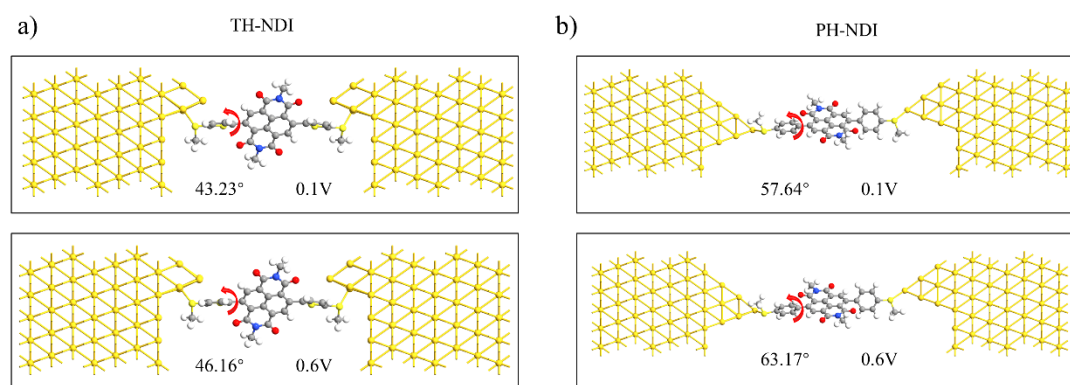


Fig. S8 The change of dihedral angle in the junction of **TH-NDI** at 0.1V and 0.6 V. (b) The change of dihedral angle in the junction of **PH-NDI** at 0.1V and 0.6 V.

We compared the dihedral angles between NDI moiety and thiophene/phenylene ring at bias voltages of 0.1 and 0.6V. The angles are determined to be 43.23°/46.16° and 57.64°/63.17° at 0.1V/0.6V for TH-NDI and PH-NDI, respectively. It has been reported that electron transmission is proportional to $\cos^2\Phi$, where Φ is the torsion angle of conjugated molecules. The dihedral angles of TH-NDI and PH-NDI fluctuate in a very small range, proving the change of planarity has a negligible effect on the molecular conductance.

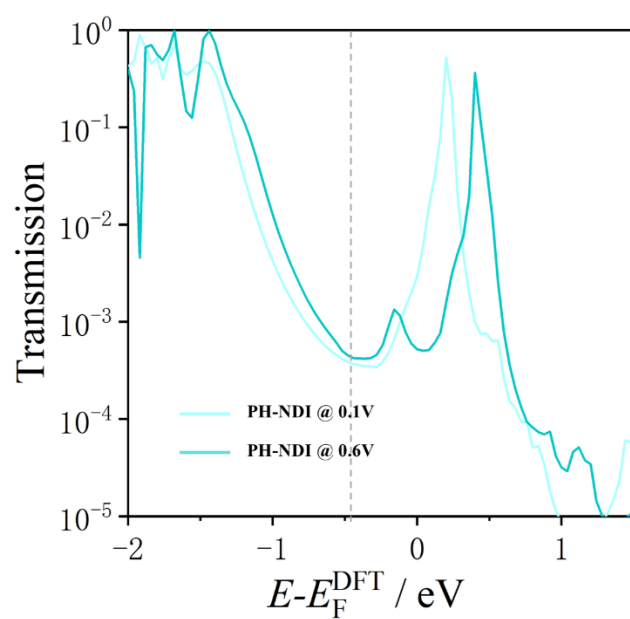


Fig. S9. The comparison of transmission spectra for **PH-NDI** junctions at bias voltage of 0.1 V and 0.6 V, respectively.

Section S7. ^1H NMR, ^{13}C NMR, and MS spectra.

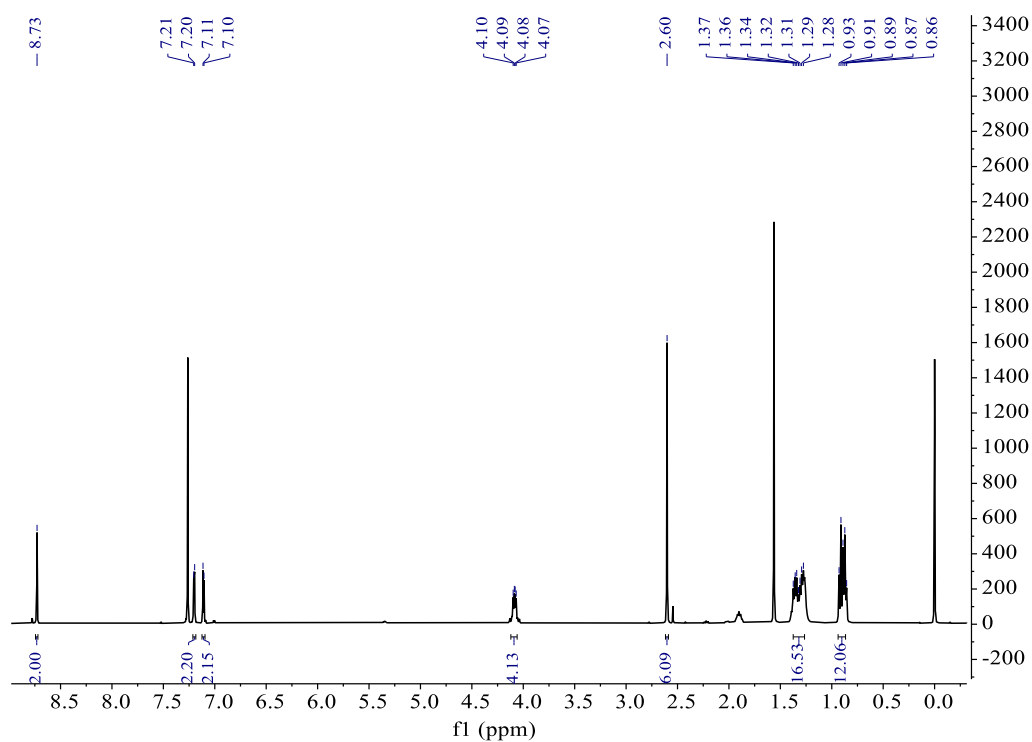


Fig. S10. ^1H NMR spectrum of TH-NDI in CDCl_3 .

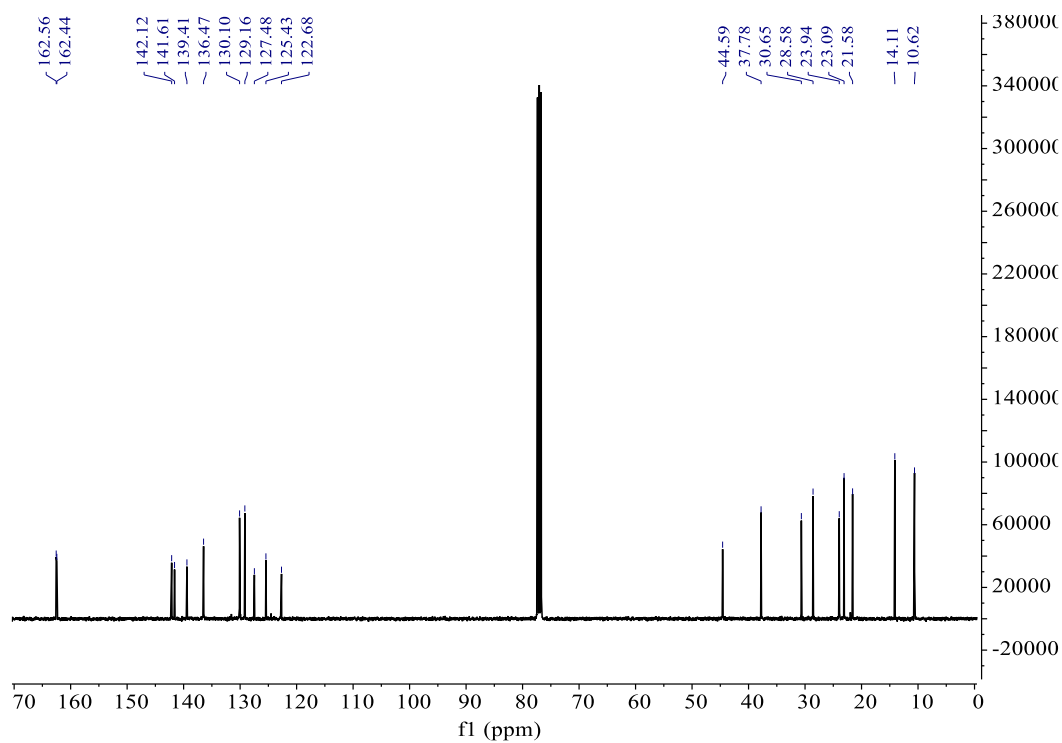


Fig. S11. ^{13}C NMR spectrum of TH-NDI in CDCl_3 .

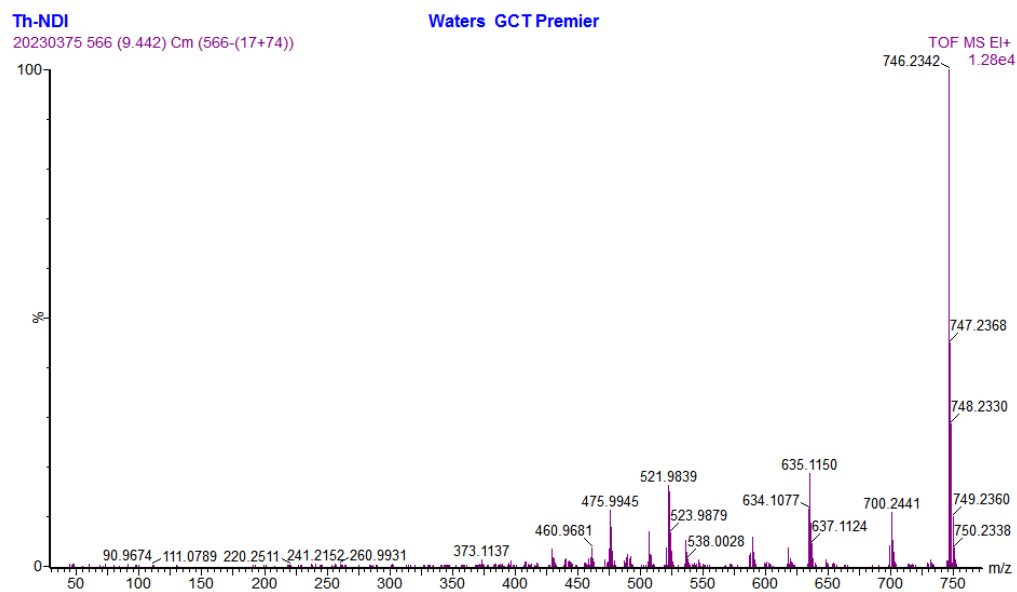


Fig. S12. HRMS spectrum of TH-NDI.

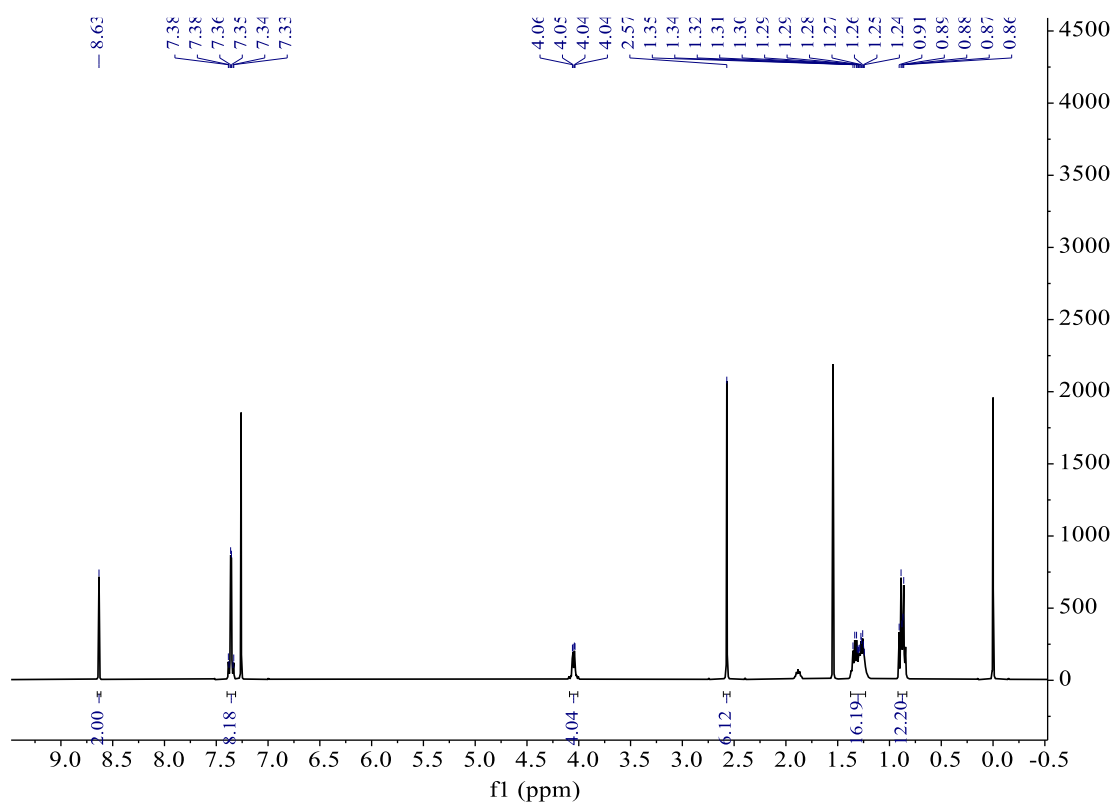


Fig. S13. ^1H NMR spectrum of PH-NDI in CDCl_3 .

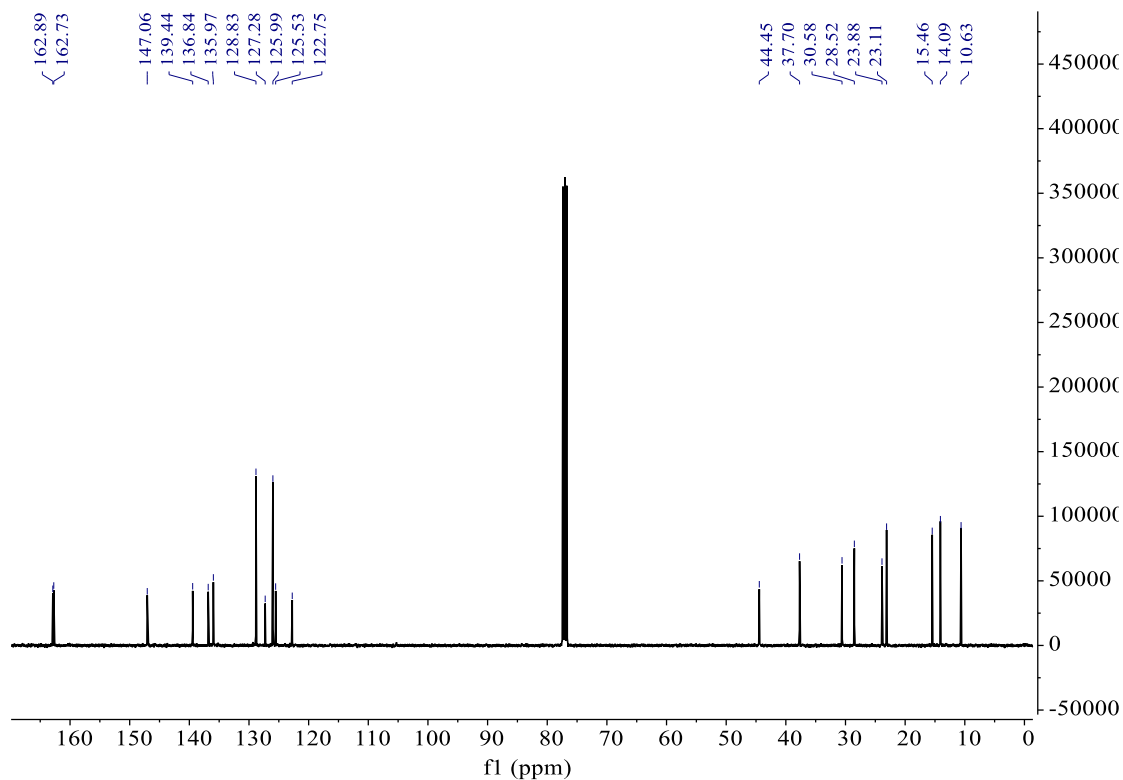


Fig. S14. ^{13}C NMR spectrum of **PH-NDI** in CDCl_3 .

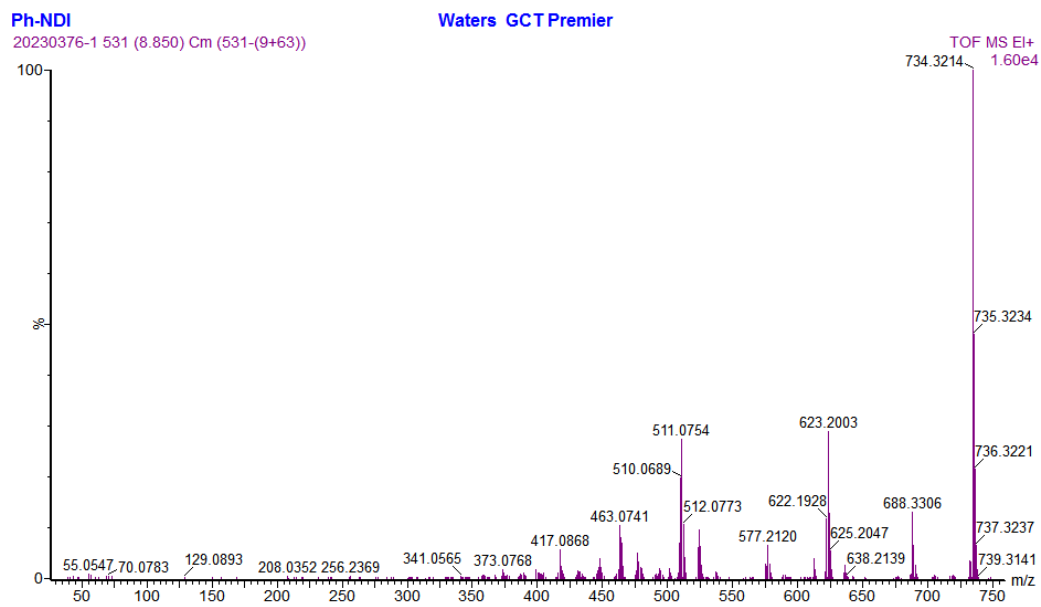


Fig. S15. HRMS spectrum of **PH-NDI**.

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