

Supporting Information for:

An Air-stable Microwire Radial Heterojunction with High Photoconductivity Based on a New Building Block

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Synthesis of BEHT-DTP. (1) Synthesis of 2,5-bis(methylthio)pyrazine: Sodium thiomethoxide (MeSNa) (5.32 g, 76 mmol) was added into 20 mL dimethylformamide (DMF) with N,N,N',N'-tetramethylethylenediamine (TMEDA) (0.57 mL, 3.8 mmol) and CuI (361 mg, 1.9 mmol) as catalysts under argon atmosphere at 0 °C, followed by adding 2,5- diiodopyrazine (6.3 g, 18.97 mmol in 20 mL DMF) dropwise. The reacted solution was allowed to warm to room temperature after 2 hours and was stirred for another 48 hours. DMF was removed by vacuum distillation and the residue was extracted by chloroform (3 × 50 mL). The organic layer was dried over anhydrous MgSO₄. The crude product was purified by column chromatography on silica gel to give 2,5-bis(methylthio)pyrazine as a pale yellow crystal (2.1 g, 64% yield). ¹H NMR (400 MHz, CDCl₃, δ): 8.28 (s, 2H), 2.53 (s, 6H).

(2) Synthesis of 2,5-diiodo-3,6-bis(methylthio)pyrazine: Under argon atmosphere, n-BuLi (1.6 M in hexane solution, 45.7 mL, 73.1 mmol) was added into THF at -78°C and then 2,2,6,6-tetramethylpiperidine (HTMP) (12.34 mL, 73.1 mmol) was added dropwise. The solution was warmed to 0 °C and stirred for 30 min. After that, the

mixture was cooled down to -78°C . Then, 2,5-bis(methylthio)pyrazine (2.1 g, 12.18 mmol in 5 mL THF) was added and stirred for 2 hours. After that, I_2 (18.57g, 73.1 mmol in 20 mL THF) was added. The reaction was quenched by water (30 mL) and then the solution was warmed to room temperature. After removing the solvent, the residue was purified by column chromatography on silica gel yielding yellow crystals (3.05 g, 59% yield). ^1H NMR (400 MHz, CDCl_3 , δ): 2.48 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3 , δ): 156.51, 115.55, 15.98.

(3) Synthesis of 2,5-dimethylsulfide-3,6-ditrimethylsilylacetylene pyrazine: 2,5-diiodo-3,6-bis(methylthio)pyrazine (1.46 g, 3.45 mmol), CuI (65.4 mg, 0.345 mmol), and bis(triphenylphosphine)palladium(II) dichloride ($\text{Pd}(\text{pph}_3)_2\text{Cl}_2$) (120.6 mg, 0.1725 mmol) were added to 15 mL THF, stirring for 15 min under argon atmosphere. Then, triethylamine (TEA) (15mL) were added dropwise, stirring for 30 min. To the above mixture, trimethylsilylacetylene (HTMS) (2.44 mL, 17.25 mmol) was added and kept for 24 hours in dark at room temperature under argon atmosphere. The solvent was removed and the residue was purified by column chromatography on silica gel yielding bright yellow crystals (610 mg, 48.4% yield). ^1H NMR (400 MHz, CDCl_3 , δ): 2.52 (s, 6H), 0.30 (s, 18H); ^{13}C NMR (101 MHz, CDCl_3 , δ): 152.74, 134.19, 107.18, 99.81, 13.23.

(4) Synthesis of 3,7-diiodo-2,6-bis(trimethylsilyl)dithieno[2,3-b:2',3'-e]pyrazine: 2,5-dimethylsulfide-3,6-ditrimethylsilylacetylene pyrazine (610 mg, 1.67 mmol) was dissolved in dichloromethane (DCM) (20 mL) under argon atmosphere, stirring for 30 min. Then, I_2 (1.69 g, 6.68 mmol in 10 mL dichloromethane) was added dropwise and

kept overnight under argon atmosphere. The excess I₂ was removed by Na₂S₂O₃ solution and the mixture was extracted with chloroform (3×50 mL) followed by drying over anhydrous MgSO₄. The crude was purified by column chromatography on silica gel yielding pale yellow powder (780 mg, 79.4% yield). ¹H NMR (400 MHz, CDCl₃, δ): 0.55 (s, 18H); ¹³C NMR (101 MHz, CDCl₃, δ): 154.37, 149.27, 147.81, 81.89, 0.02.

(5) Synthesis of 3,7-diiododithieno[2,3-b:2',3'-e]pyrazine: 3,7-diiodo-2,6-bis(trimethylsilyl)dithieno[2,3-b:2',3'-e]pyrazine (780 mg, 1.33 mmol) was dissolved in 20 mL THF under argon atmosphere at room temperature. Then, tetrabutylammonium fluoride (TBAF) (1 M in THF, 5.32 mL) was added dropwise and stirred for 4 hours. The solvent was removed and the residue was purified by column chromatography on silica gel, yielding pale yellow powder (520 mg, 88% yield). ¹H NMR (400 MHz, CDCl₃, δ): 8.16 (s, 2H); ¹³C NMR (101 MHz, CDCl₃, δ): 152.39, 146.67, 129.13, 80.18.

(6) Synthesis of 3,7-bis(5-(2-ethylhexyl)thiophen-2-yl)dithieno[2,3-b:2',3'-e]pyrazine (BEHT-DTP): 3,7-diiododithieno[2,3-b:2',3'-e]pyrazine (320 mg, 0.72 mmol), 2-(5-(2-ethylhexyl)thiophene-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan (960 mg, 2.88 mmol), and tetrakis(triphenylphosphine)palladium (Pd(pph₃)₄) (45 mg, 0.036 mmol) were added to 20 mL degassed toluene. After 10 min, Na₂CO₃ aqueous solution (2 M, 5 mL) was added. Then, the solution was subjected to vacuum/argon refill cycles for three times and heated to 85 °C for 24 h under argon atmosphere. The reaction solution was quenched by water (10 mL) and extracted with chloroform (3×30 mL).

The organic layer was washed with brine (3×50 mL) and dried with anhydrous Na₂SO₄. After remove of the solvent, the residue was purified by column chromatography on silica gel, yielding a yellow solid (350 mg, 84% yield). ¹H NMR (400 MHz, CDCl₃, δ): 7.88 (d, J=4.0, 4H), 6.81 (d, J=3.5, 2H), 2.79 (d, J=6.8, 4H), 1.68 (m, 2H), 1.35 (m, 16H), 0.91 (m, 12H). ¹³C NMR (101 MHz, CDCl₃, δ): 153.84, 144.74, 143.38, 133.13, 128.03, 125.81, 125.59, 124.97, 41.49, 34.17, 32.42, 28.90, 25.56, 23.05, 14.18, 10.86. MS (MALDI-TOF) m/z: [M+1]⁺ calcd for C₃₂H₄₀N₂S₄: 581.21; found: 581.2. Anal. calcd for C₃₂H₄₀N₂S₄: C 66.16, H 6.94, N 4.82; found: C 66.52, H 6.92, N 4.78. Thermal gravimetric analysis (TGA) (Figure S11, Supporting Information) showed the decomposition temperature of BEHT-DTP is more than 224 °C.

Materials. The materials used for the synthesis were purchased from J&K Chemical and the solvent was purchased from Beijing Chemical Reagent Co. Ltd..

Characterization. The ¹H NMR and ¹³C NMR spectral were recorded on a 400 MHz AC Bruker spectrometer. Element analysis was conducted on a FLASH EA 1112 element analyzer. Mass spectra measurements were performed on a Bruker Daltonics BIFLEX III MALDI-TOF analyzer using MALDI mode. Cyclic voltammograms were recorded on an electrochemical workstation (CH1860D, CH Instruments) using a Pt button working electrode, a platinum-wire counter electrode and a Ag/AgCl reference electrode. UPS spectra of BEHT-DTP was measured using the ultraviolet photoelectron spectroscope (AXIS Ultra-DLD) with a HeI source ($h\nu = 21.22$ eV) at a pressure of 3.0×10^{-8} Torr. The optical microscopy images were obtained by

dropping the microwire suspension on precleaned cover slides ($24 \times 24 \text{ mm}^2$) and observed by a PSM-1000 microscope. The fluorescence microscopy images were recorded by laser confocal scanning microscope (Olympus 1X71), excited by a mercury lamp. The fluorescence spectra of the single microwire were obtained by dropping their suspensions on precleaned borosilicate glass slides ($15 \times 15 \text{ mm}^2$) and measured by a WITEC NSOM Alpha300 S system with focused laser excitation. Fluorescence spectra of the TDCNQI solution and the BEHT-DTP film were recorded using a Hitachi F-7000 fluorescence spectrometer. The ultraviolet-visible absorption spectra of the compounds were recorded by a Hitachi U3900 spectrophotometer. The sample for TEM imaging was prepared by dropping and drying the core-shell microwire suspension on copper grids and observed by a Hitachi H-7650B microscope with an accelerating voltage of 80 kV. AFM measurement was performed in tapping mode on a Bruker ICON 8 atomic force microscope. The SAED and elemental mapping were obtained by a JEM-2010 TEM with an accelerating voltage of 120 kV. SEM imaging and EDX analyze was performed on a HITACHI S-4300 scanning electron microscope. The molar ratio of TDCNQI to BEHT-DTP in the core-shell microwires was measured by EDX of SEM. In detail, we dissolved the microwires in THF and spin-coated into thin film on a Si wafer. Then, we measured the elemental ratio of F and S of the film, so we could calculate the molar ratio of TDCNQI to BEHT-DTP.

The electrical properties of the photoconductive devices was obtained using a Keithley 4200-SCS semiconductor characterization system and a Semishare SE-4

probe station. The monochromatic light was provided by a Crowntech QEM24-S monochromator guided by a quartz fiber.

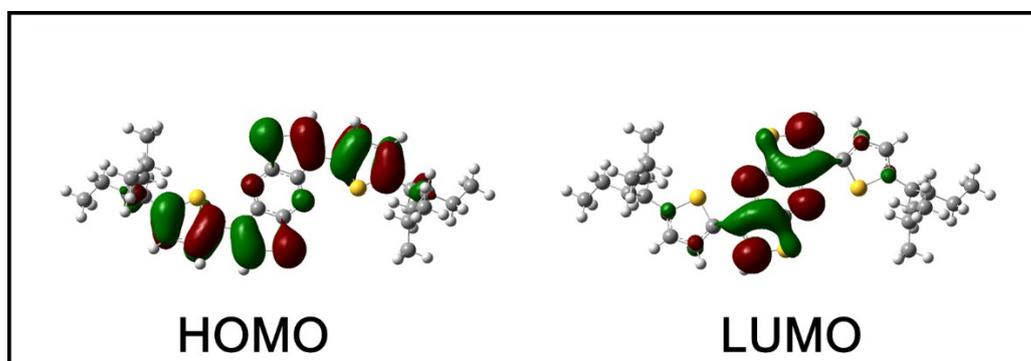


Figure S1. HOMO and LUMO surfaces for BEHT-DTP obtained from DFT calculations at the optimized ground state geometry.

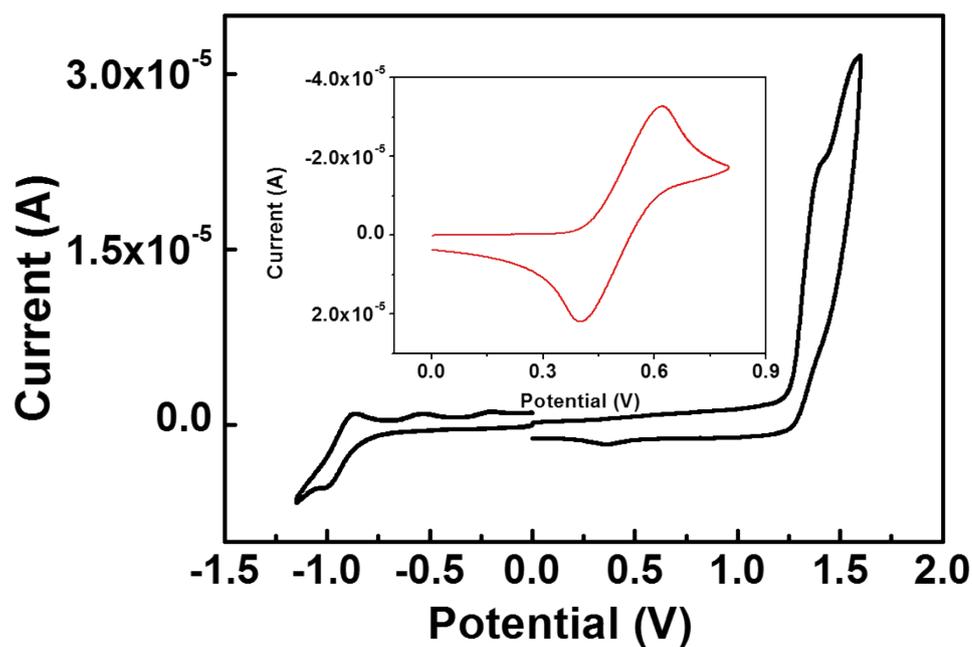


Figure S2. Cyclic voltammogram of BEHT-DTP in dichloromethane with 0.1 M Bu_4NPF_6 as the electrolyte at a potential scan rate of 100 mV s^{-1} . The inset shows the redox curve of ferrocene as an internal reference.

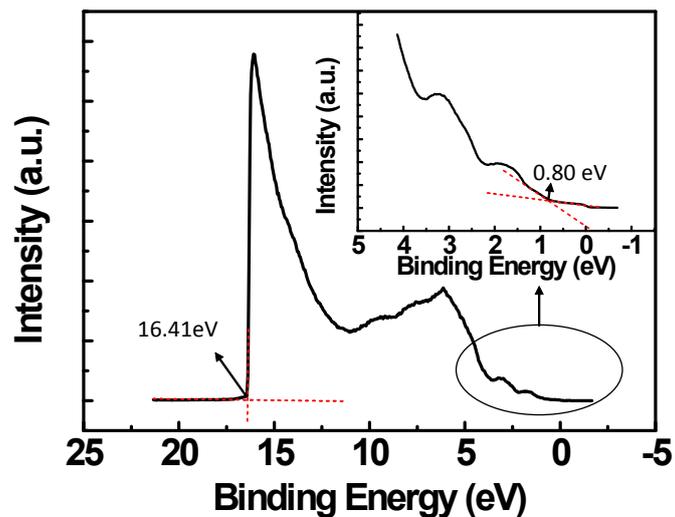


Figure S3. UPS spectra of BEHT-DTP film was measured with a HeI source ($h\nu = 21.22$ eV) at a pressure of 3.0×10^{-8} Torr. The inset shows the amplification of the circled region.

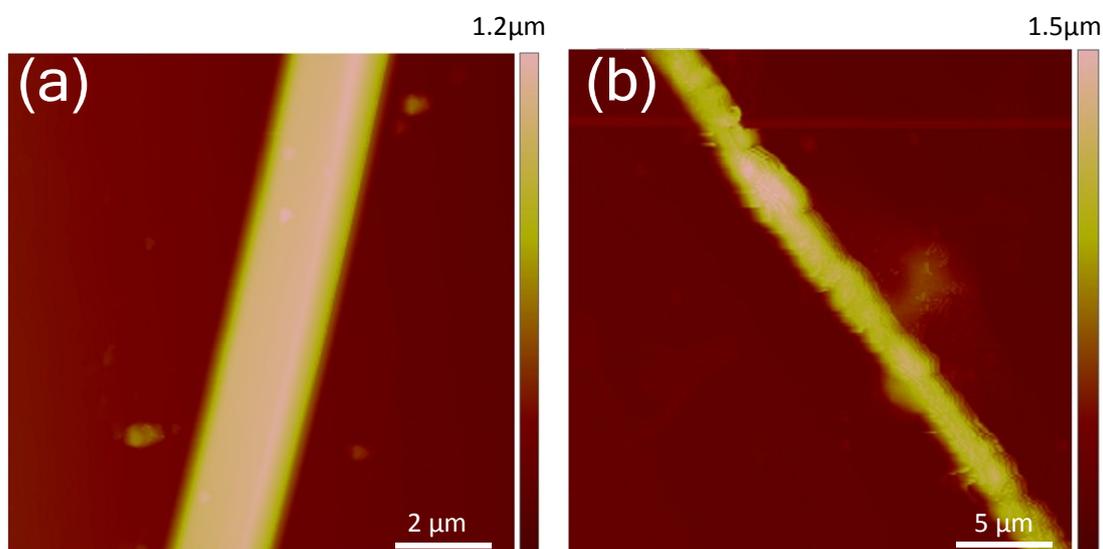


Figure S4. AFM images of the pristine TDCNQI microwire (c) and the TDCNQI@BEHT-DTP p-n heterojunction microwire.

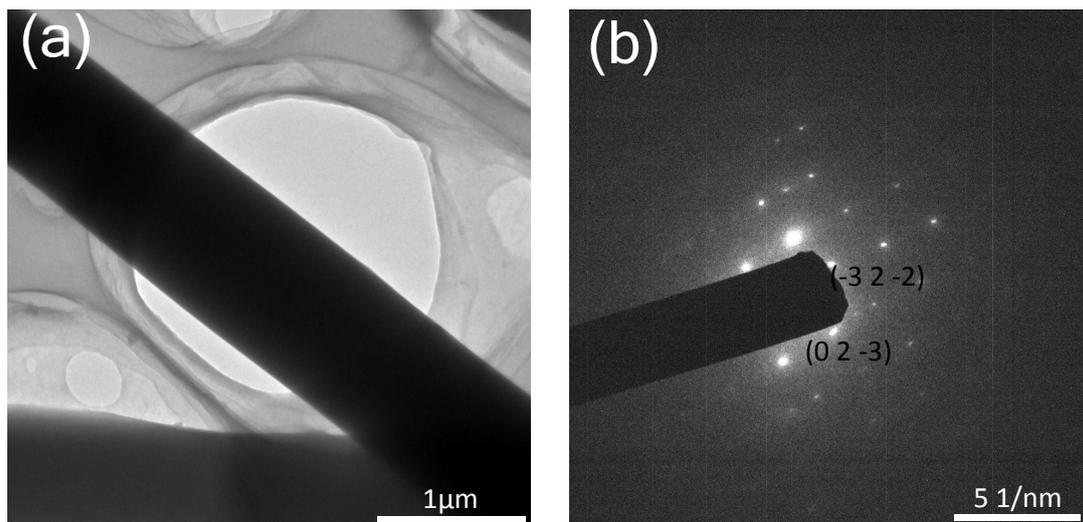


Figure S5. TEM images of the pristine TDCNQI microwire (a) and SAED of the TDCNQI@BEHT-DTP p-n heterojunction microwire (b).

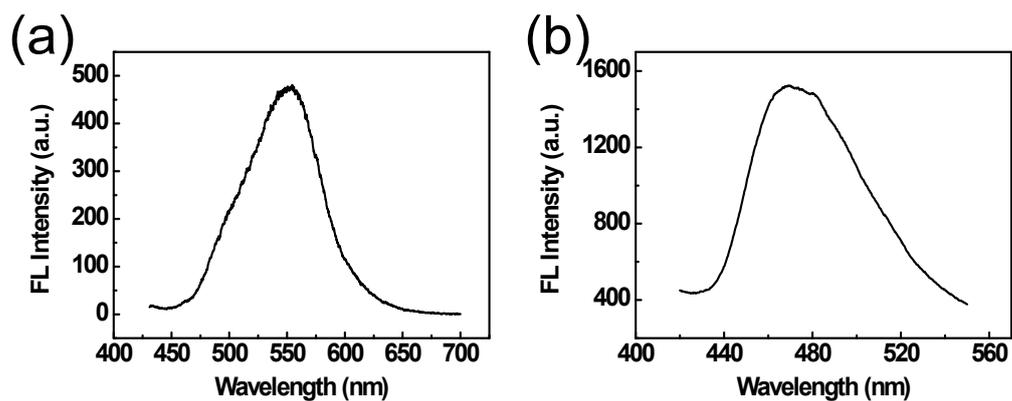


Figure S6. PL emission spectra of (a) TDCNQI in THF solution (The one in films is too weak to be detected by fluorescence spectrometers, so it is not shown here) and (b) BEHT-DTP in film. The excitation wavelengths are 405 and 365 nm, respectively.

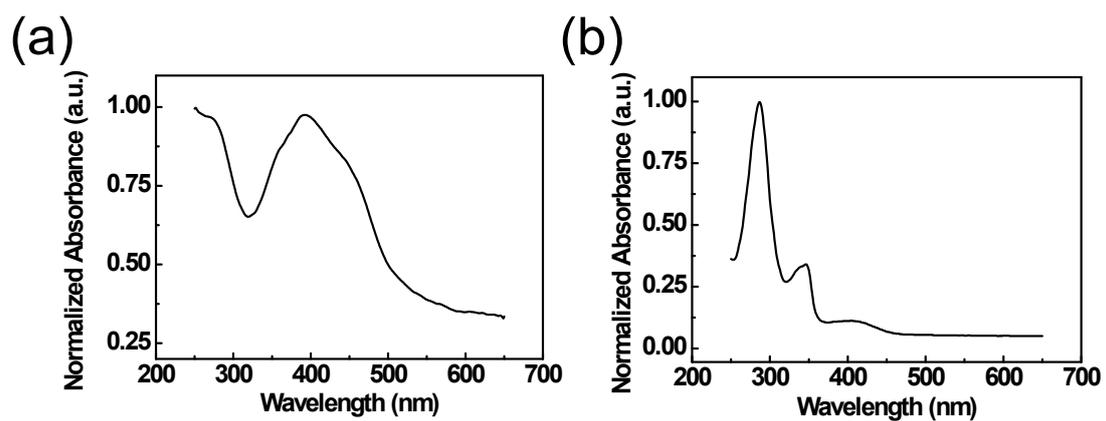


Figure S7. UV absorption spectra of (a) TDCNQI and (b) BEHT-DTP films.

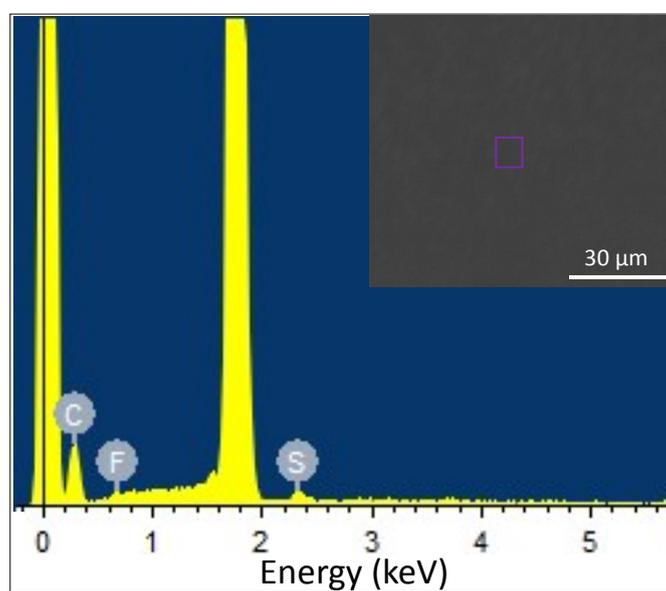


Figure S8. EDX spectral of the thin film of TDCNQI and BEHT-DTP, the inset is the SEM image of the film.

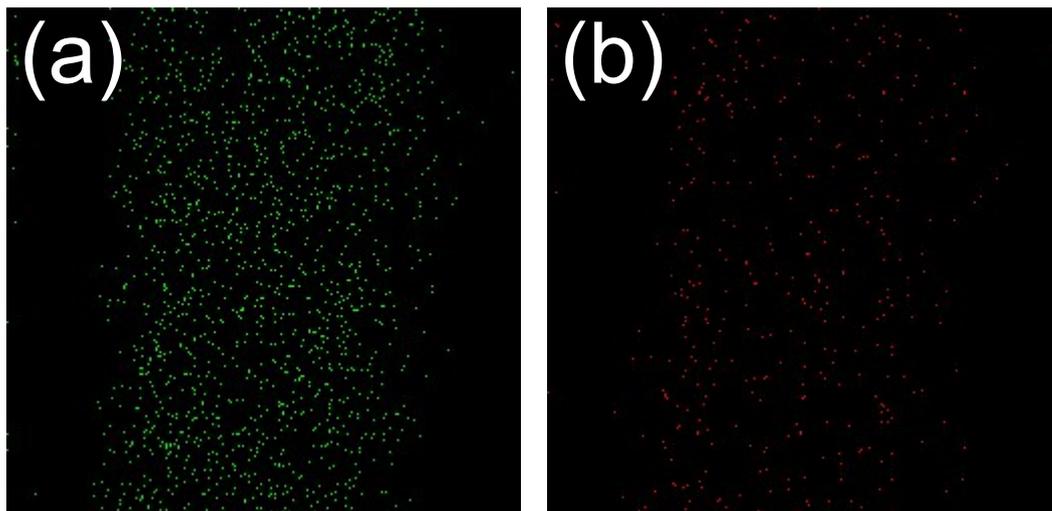


Figure S9. Elemental mapping of S (a) and F (b) concentrations in a TDCNQI@BEHT-DTP core-shell microwire.

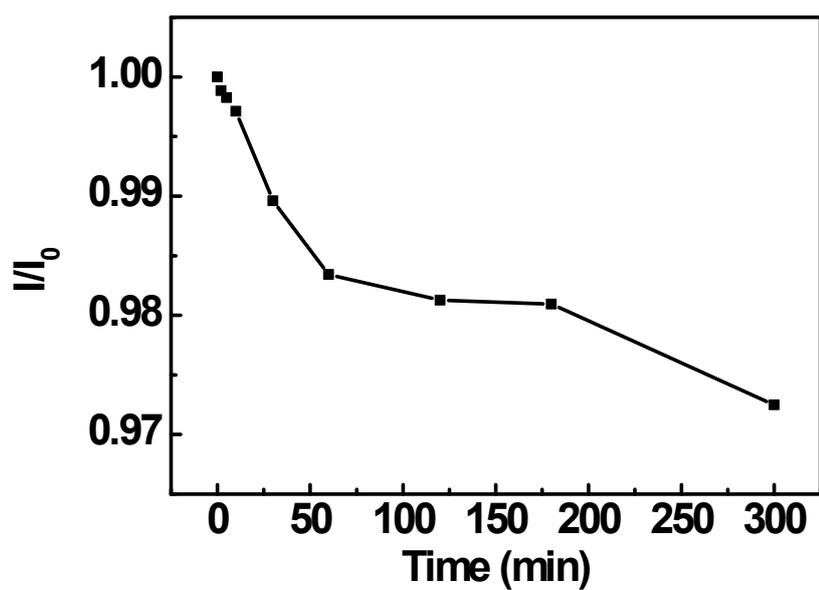


Figure S10. The decay of the current (I) in photoconductive device based on an individual core-shell microwire upon time. I_0 is the initial current value.

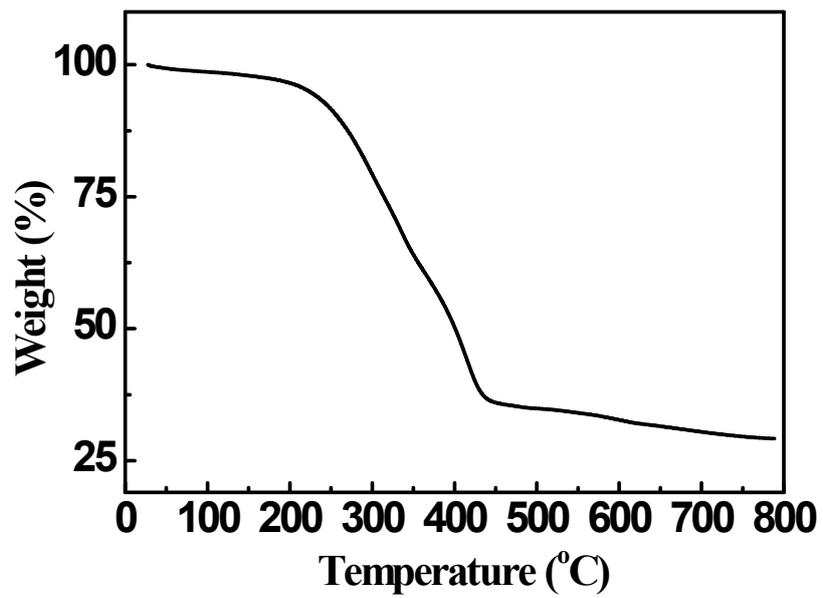


Figure S11. TGA curve of BEHT-DTP.