Organic photodiodes constructed from a single radial heterojunction microwire

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Materials. Alq_3 was purchased from Jinlin Optical and Electronic Materials Co. Ltd. P3HT (Mw=50 000-70 000) was obtained from Rieke Matals, Inc. The organic solvent was purchased from Beijing Chemical Reagent Co. Ltd..

Characterization. The fluorescence microscopy and bright field images were recorded by laser confocal scanning microscope (Olympus 1X73), excited by a mercury lamp. The ultraviolet-visible absorption spectra was recorded by a Hitachi U3900 spectrophotometer. AFM measurement was performed on a Nanoscope IIIa atomic force microscope in tapping mode. SEM imaging was performed on a HITACHI S-4300 scanning electron microscope. The TEM images, SAED and elemental mapping were obtained by a JEM-2010 TEM with an accelerating voltage of 120 kV. The electricity characteristics were carried out by Keithley 4200-SCS semiconductor characterization system connected to a Semishare SE-4 probe station in ambient environment. The monochromatic light was provided by a Crowntech QEM24-S monochromator guided by a quartz fiber.

The external quantum yield (EQE) for the microwire was obtained by measuring the photocurrent of the device under illumination of monochromatic light with different wavelengths. The power of the monochromatic light (P_m) was detected by a silicon photodetector (Newport 918D-UV-OD3R), and the diameter of incident light beam was approximately 3.0 mm，thus the incident irradiance can be estimated as I_{irr}. The effective microwire area (A) was taken as the wire diameter (2.0 μm) multiplied by the gap length (~24.0μm), thus, the incident radiant energy delivered to the microwire per second is $I_{irr}A$. Corresponding to the photon energy E_p of photons with different wavelengths, the quantity of incident photons per second can be estimated as $I_{irr}A/ E_p$. Meanwhile, the quantity of photogenerated electrons (N_e) pass through the microwire per second can be estimated from the photocurrent, therefore, the EQE can be calculated by $N_eE_p/ I_{irr}A$.

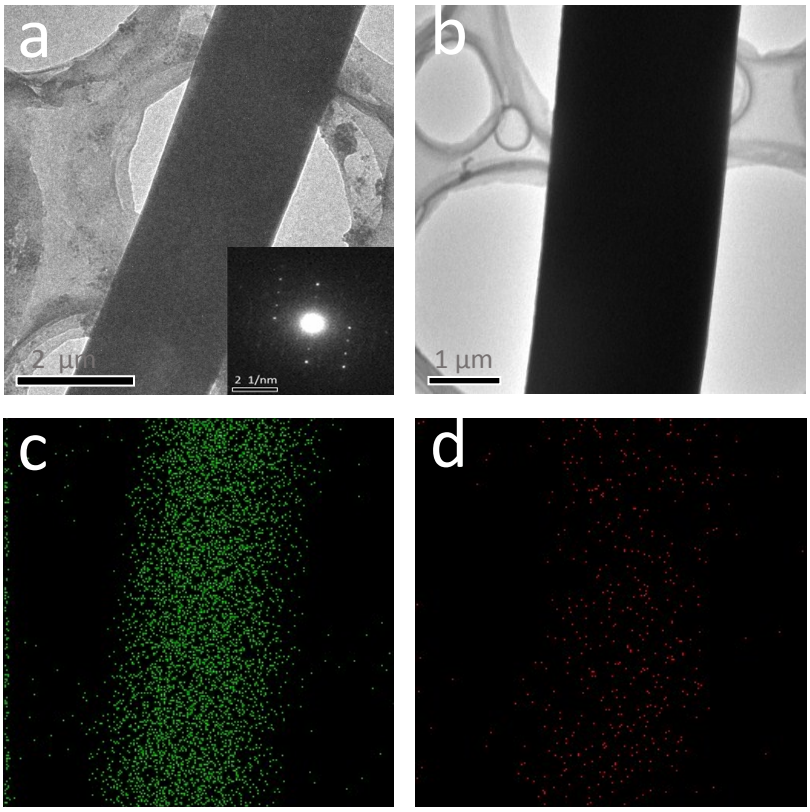

Figure S1. TEM images of a neat Alq_3 microwire with its SAED pattern (a) and the heterojunction microwire (b), together with the elemental mapping of aluminum (c) and sulfur (d) for the heterojunction microwire.

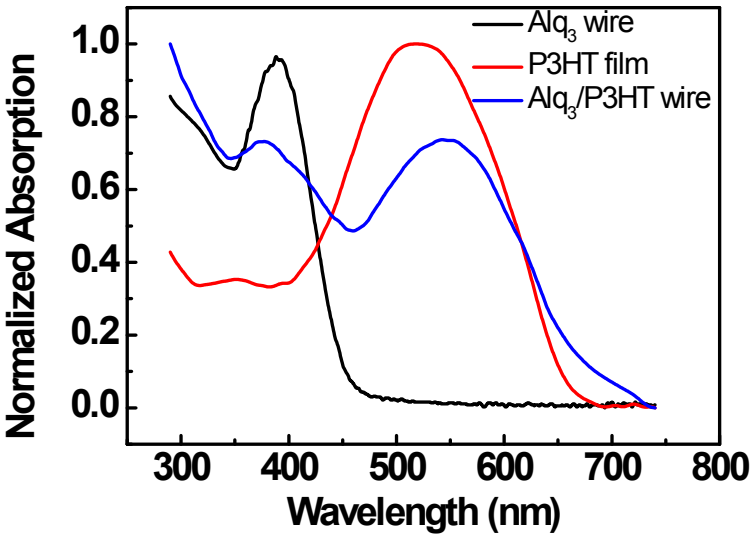

Figure S2. The UV-Vis absorption spectra of the Alq_3 microwires, P3HT film and heterojunction microwires.

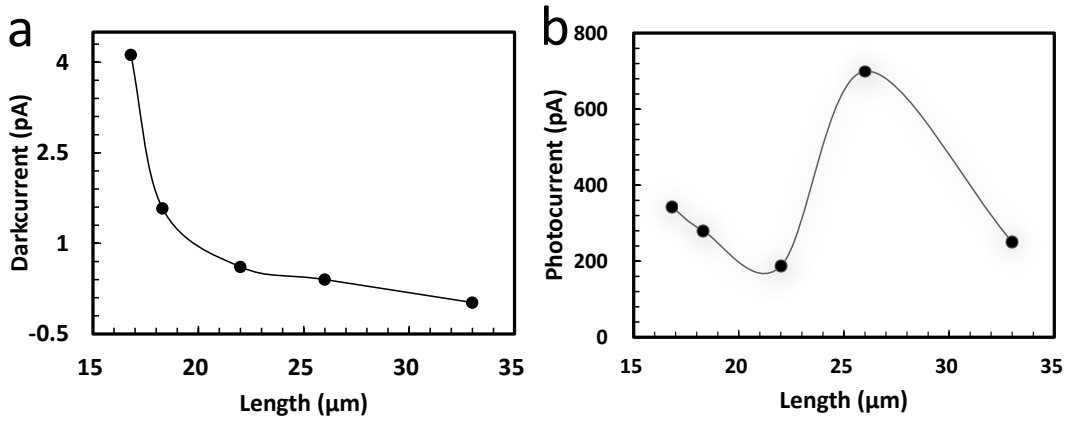

Figure S3. The changes of dark current (a) and photocurrent (illuminated by imitated white light of 79.4 mW/cm^2 from a tungsten lamp) (b) of the heterojunction microwire device at -10 V bias with the increase of the microwire length between the two electrodes.

Molecular Dynamics (MD) Simulations Procedure

In order to investigate the interaction of Alq_3 and P3HT in the THF solution, we simulated a system comprising Alq_3 crystal and a segment of P3HT (the oligomer). The crystallogrcaphic information (CIF file) of a α-phase Alq_3 was obtained from CCDC, Refcode: QATMON01. The geometry of THF and 5 repeating units of P3HT (the oligomer, P3HT5) were optimized by density functionally theory (DFT) calculations based on B3LYP/6-31G* level using Gaussian 09.[1]

We used the optimized potentials for liquid simulations-all atom (OPLS-AA) force field for the molecular dynamics simulations. The OPLS-AA force field parameters for Alq_3 are adopted from the reference.[2] The original OPLS-AA force field lacks the partial atomic charges for THF and P3HT5. We obtained it using the Merz-Kollmann (MK) scheme, where charges are calculated from the electrostatic potential.[3]

For constructing the interface of MD simulation system, we first calculated a bulk of P3HT5 dissolved in THF. After stabilizing this system under the constant temperature, constant pressure (NPT) ensemble, the interface was constructed by aligning the (001) crystal face of a pure 5×5×5 supercell of Alq_3 to the bulk system along Z-axis.

The system was evolved under the constant temperature, constant volume (NVT) ensemble dynamics for 5 ns at 300 K. In order to confirm Alq_3 to be a crystal, the position of Al atom were frozen during the simulations. The MD simulations were carried out using the Gromacs 5.0.4 package.[4] The *g_energy* module was used to calculate and visualize the short-range Lennard-Jones interaction energies E(LJ-SR) and Coulomb interaction energies E(Coul-SR) between Alq_3 and P3HT5. The last 2 ns structure was selected for analysis because the interaction energy E(Coul -SR) has become stable from this time point. The average over the last 2 ns of E(LJ-SR) and E(Coul -SR) are −786.7 and −27.2 KJ/mol, respectively. The E(LJ-SR) was larger than E(Coul -SR), indicating that the interaction between Alq_3 and P3HT5 is dominated by hydrophobic.

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