Supporting information for

High efficiency hybrid solar cells using post-deposition ligand

exchange by monothiols

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1. Experimental section

Synthesis of CdSe QDs

In a typical synthetic process, CdO (76 mg), trioctylphosphine oxide (TOPO, 3.0 g) and oleic acid (3.0 ml) were added into the reactor and the mixture was heated to 280-290 °C under vigorous stirring in the nitrogen atmosphere. Se (80 mg) was added into trioctylphosphine (TOP, 1.0 ml) and sonicated until the solution became clear. Then the Se-TOP solution was quickly injected into the mixture of CdO, TOPO and oleic acid. After 5 min reaction, the hot solution was quickly transferred into toluene (5 ml). The as-prepared CdSe QDs were washed in methanol and separated by centrifugation for two times, and were then dispersed in pyridine (15 ml) and stirred for 24 h in nitrogen. The resulting nanocrystals were washed by hexane and separated by centrifugation. The final products were dried by blow of nitrogen. In our synthesis, the sizes of CdSe QDs were controlled by adjusting the injection temperature and the growth temperature. Typically, higher injection temperature and higher growth temperature resulted in larger size of CdSe QDs.

Device fabrication

P3HT:CdSe QDs blend solution was prepared by dispersing CdSe QDs (30 mg) and dissolving P3HT (Luminescence Technology Corp., 3.3 mg) in a mixture of chlorobenzene and pyridine (v: v = 9:1, 1 ml) and stirred overnight.

Our hybrid solar cells were fabricated on glass substrates commercially pre-coated with a layer of indium tin oxide (ITO). Prior to fabrication, the substrates were cleaned using detergent, deionized water, acetone, isopropanol consecutively for every 15 min, and then treated in an ultraviolet ozone generator for 15 min before being spin-coated with poly(3,4-ethylenedioxythiophene): aqueous poly(styrenesulfonate) (PEDOT:PSS) dispersions (Baytron P AI4083). After baking the PEDOT:PSS in air at 140 °C for 15 min, the substrates were transferred to a glovebox for spin coating of P3HT:CdSe active layer with the thickness of about 80 nm. For the sample that undergoes ligand exchange, the substrate was dipped in the 0.1 M thiols (in acetonitrile) solution for 30-40 s, followed by a rinse with pure acetonitrile. Then all the samples were annealed at 150 °C for 30 min. Subsequently, samples were loaded into a vacuum deposition chamber (background pressure \approx 5×10^{-4} Pa) to deposit 100 nm thick aluminum cathode with a shadow mask (device area of 9 mm²). For electron mobility measurement in the P3HT:CdSe blend films, the electron-only devices were fabricated in a structure of glass/Al/P3HT:CdSe/Al, for which a layer of 100 nm thick Al was first deposited onto the glass substrate and then the P3HT:CdSe solution was spin coated on the Al-covered substrate followed by depositing a layer of 100 nm thick Al. The treatments of the active layer were the

same as fabrication of hybrid solar cells and the area for those electron-only devices was 9 mm².

Device characterization

The current density–voltage (*J–V*) curves were measured with Keithley236 measurement source units at room temperature in air. The photocurrent was measured under a calibrated solar simulator (Abet 300 W) at 100 mW cm⁻², and the light intensity was calibrated with a standard photovoltaic (PV) reference cell. External quantum efficiency (EQE) spectrum was measured with Stanford lock-in amplifier 8300 unit. The absorption spectra of the samples on ITO/PEDOT:PSS substrates were recorded on a UV-visible spectrophotometer (UV-2450, Shimadzu Corporation, Japan). The morphological structures of the P3HT:CdSe blend thin films were investigated by the CM200 transmission electron microscope (TEM) at 160 KV. The ITO/glass substrates successively coated with PEDOT:PSS and P3HT:CdSe films were immersed in deionized water overnight to dissolve PEDOT:PSS. A carbon-coated copper grid was then used to pick up the P3HT:CdSe blend films floating on the water surface. The hybrid films were dried naturally in air and loaded into the TEM for characterization.

The electron mobility of the blends was measured using the space-charge-limited current (SCLC) method. However, in the blend devices, the presence of ohmic contacts at both interfaces could lead to a SCLC, which is a combination of both hole and electron current. Therefore, in order to measure the SCLC of one type of charge carrier, the other one have to be suppressed by a large injection barrier, resulting in a hole-only or electron-only diode device. The device characteristics were extracted by modeling the dark current under forward bias using the SCLC expression described by the Mott – Gurney law:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_e \frac{V^2}{L^3} \tag{1}$$

Here, $\varepsilon_r \approx 6$ is the average dielectric constant of the hybrid film, ε_0 is the permittivity of the free space, μ_e is electron mobility, $L \approx 100$ nm is the thickness of the film, and V is the applied voltage.

2. Absorption spectrum and TEM image of CdSe QDs



Fig. S1. Absorption spectrum of CdSe QDs in toluene solution. Inset is a TEM image of the as-synthesized CdSe QDs. The CdSe QDs were ~6.7 nm in size.



3. External quantum efficiency (EQE) for hybrid solar cells

Fig. S2. External quantum efficiency (EQE) for hybrid solar cells (ITO/PEDOT:PSS/P3HT: CdSe/Al) before and after ligand exchange by different thiols.

4. TEM images of P3HT:CdSe QDs blend films before and after ligand exchange by *n*BT



Fig. S3. TEM images of P3HT: CdSe QDs blend films before (a) and after (b) ligand exchange by *n*BT.