Supporting Information

Photo-induced Electron Recombination Dynamics in CdSe/P3HT Hybrid Heterojunctions.

Josep Albero\textsuperscript{a}, Eugenia Martínez-Ferrero\textsuperscript{a} Jon Ajuria\textsuperscript{c}, Christoph Waldauf\textsuperscript{c}
Roberto Pacios\textsuperscript{c} and Emilio Palomares\textsuperscript{a,b,*}


\textsuperscript{c} Ikerlan, S. Coop. Pº J. M. Arizmendiarréta, 2. 20500 Arrasate-Mondragon. Gipuzkoa. Spain.
Experimental Section:

**QD preparation:** CdSe quantum dots (QD) were synthesized using the wet chemical synthetic method previously described by Nazeeruddin et al. with few modifications.\(^1\) A selenium (Se) solution was prepared by mixing 0.4 g of Se powder (-100 mesh, 99.99%), 10 mL of technical-grade trioctylphosphine (TOP; 90%), and 0.2 mL of anhydrous toluene (99.8%). 20 g of technical-grade trioctylphosphine oxide (TOPO; 90%) and 0.25 g of cadmium acetate dihydrate (98%) were placed in a round-bottomed flask and heated until 150°C. The solution was purged with argon during the whole reaction. When all the TOPO was dissolved the solution was heated up to 290°C. At this temperature, the Se solution was quickly injected into the reaction vessel through a rubber septum. The heat was removed 15 minutes later and the resulting solution was cooled to room temperature. The CdSe quantum dots were precipitated with a copious amount of methanol and collected by centrifugation and decantation. The precipitated CdSe quantum dots were recovered by adding a small amount of chloroform and re-precipitated with methanol. This purification process was repeated three times. To obtain the pyridine coated QD, the TOPO-coated CdSe were dissolved in 40 mL of pyridine and refluxed at 90°C overnight under dark conditions. Pyridine-coated CdSe were precipitated with hexane and collected by centrifugation and decantation (three times). The precipitate was dissolved in a mixture of pyridine and chloroform (8:92, v/v), and saved as stock solution in a concentration of 15 mg/mL. The nanoparticle’s size, analyzed by Transmission Electron Microscopy, is 4 nm.

**Film preparation:** For the film preparation, variable amounts of rr-P3HT, purchased from Rieke, and CdSe nanocrystal stock solution were mixed in order to get a final concentration of 15 mg/mL in Chloroform:Pyridine (92:8, v/v) and the desired percentage of P3HT:CdSe. The resulting solutions were stirred and heated at 50°C for 2 hours. Finally, a drop of the P3HT/CdSe solution was deposited onto a pre-cleaned glass slide of 2 x 2 cm², and spin coated at 2000 rpm for 30 seconds. The films were aged at 140°C for 5 minutes. Atomic Force Microscopy of the samples (AFM) was performed on tapping mode on a Molecular Imaging model Pico SPM II (pico +).

**Device preparation:** Pre-cleaned ITO substrates were used as anode. Over the ITO substrate a thin layer (40nm) of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)
(PEDOT:PSS) was deposited by spin coating. After annealing (100°C) the PEDOT:PSS layer, the P3HT:CdSe blend films were deposited by spin coating, obtaining 150 nm thickness. The films were annealed at 140°C. Finally, thermal evaporation of 20 nm Ca and 200 nm Ag was done at 10^-6 mbar. The final area of the devices is of 9 mm².

Spectroscopical characterization: The UV-Visible spectra were recorded using a Shimadzu UV-1700 spectrophotometer. The fluorescence emission properties were measured under ambient conditions using an Aminco Bowman Series 2 luminescence spectrometer equipped with a temperature controller and a holder for films and solid samples. Time Correlated Single Photon Counting (TCSPC) experiments were carried out with Lifespec-red picosecond fluorescence lifetime spectrophotometer from Edinburgh Instruments® equipped with lasers as excitation sources. The instrument response was always shorter than 300 ps measured at full width half maximum (FWHM). The samples were measured at wavelength of 670 nm after excitation at 405 nm. The transient absorbance experiments were recorded using a home-built system as reported before.² The samples were measured with a probe wavelength of 980 nm and an excitation source of 470 nm. Laser intensity pulse was 86.7 μJ/cm², repetition rate 1 Hz.
Figure S1. UV-Vis (up) and Emission photoluminescence spectra (down) for the hybrid thin films with increasing CdSe concentration. Excitation wavelength is 405 nm.
References:
