

Electronic Supplementary Information

Connecting the (quantum) dots: Towards hybrid photovoltaic devices based on chalcogenide gels

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Materials

Selenium powder (99.5%), stearic acid (95%), diethylzinc (1M, in hexane), Bis(trimethylsilyl)sulfide, trioctylphosphine oxide (TOPO, 90%), tetranitromethane (TNM), and 11-mercaptoundecanoic acid (MUA, 95%) were purchased from Aldrich. Trioctylphosphine (TOP, 97%) and cadmium oxide (99.999%) were purchased from Strem Chemicals and tetramethylammonium hydroxide pentahydrate (TMAH, 97%) was purchased from ACROS. Toluene, methanol and ethyl acetate were purchased from Mallinckrodt. TOPO was distilled before use; all other chemicals were used as received.

Synthesis of CdSe(ZnS) core(shell) QDs

In a typical synthesis of QDs, a mixture of 0.0514 g (0.4 mmol) of cadmium oxide, 0.5 g (1.76 mmol) of stearic acid and 3.7768 g (9.77 mmol) of trioctylphosphine oxide were heated to 300 °C under argon flow to generate a homogeneous colorless solution and then a solution of selenium containing 0.0316 g (0.4 mmol) of selenium powder in 2.4 mL of trioctylphosphine was injected and QDs were grown for two hours. To make the ZnS Shell, a mixture of 0.6 ml of diethyl zinc solution (1M) in hexane, 0.12 mL of bis(trimethylsilyl)sulfide (0.57 mmol) and 2 ml of trioctylphosphine was slowly injected over a time period of 15 minutes (the total molar ratio of the injection solution was CdSe:ZnS 1:1.4) using a syringe pump at 180 °C and followed by annealing at 75 °C for five hours. As-prepared CdSe(ZnS) core(shell) QDs were purified by

repeated cycles of dispersion in toluene and precipitation with methanol. The additional washing steps were performed to remove excess organic ligands.

Synthesis of CdSe(ZnS) aerogels

0.3678 g (1.6 mmol) of MUA was dissolved in 10 mL of methanol and the pH increased up to ~10 using TMAH. The MUA solution was added to the purified QDs and shaken vigorously to achieve complete ligand exchange (Cd:MUA molar ratio of 1:4, based on original moles of Cd employed in the synthesis). The resulting MUA capped nanocrystals were washed with ethyl acetate two times and then dispersed in methanol (10 mL of methanol in two vials) and gelation was initiated by adding 50 μ L of TNM (3% methanolic solution). Wet gels were aged for several days and exchanged with acetone to remove byproducts, followed by liquid CO₂ exchange in a critical point drier, and drying by supercritical extraction, resulting in the formation of aerogels. More details on the supercritical extraction procedure can be found in ref. 1.

Deposition of hybrid films

Films were deposited on plain or indium tin oxide (ITO) coated glass cleaned by sonication in acetone, isopropanol and chloroform. QDs or aerogel dispersions in toluene were drop-casted, and P3HT and hybrid P3HT:aerogel and P3HT:QDs mixtures in toluene were spin-coated (1500 rpm, 40s) onto the substrates. For reliable comparisons, QDs isolated from the same synthesis batch that was used to prepare aerogels were used in all studies.

Fourier transform infrared spectroscopy (FTIR)

Fig. S1 shows the FTIR spectrum of the CdSe(ZnS) aerogel, obtained using a Bruker TENSOR 27 FT-IR spectrometer (Bruker Optics, inc.). Dried gel was combined with KBr and pressed into a 15 mm pellet using a Carver Hydraulic Press. The process of gelation usually leaves unoxidized thiolates (typically about 15 % by mole relative to the starting material), which remain bound to the surface of the gel network.

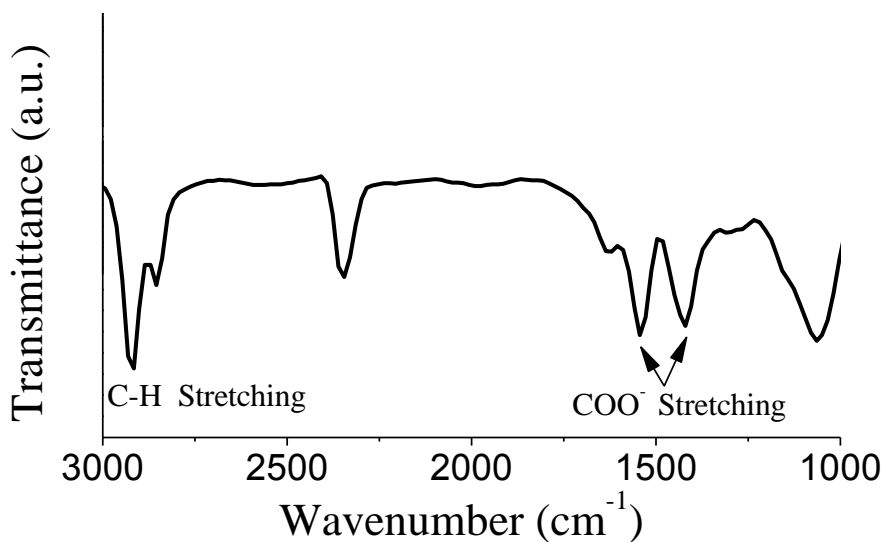


Figure S1. FTIR spectra of CdSe(ZnS) aerogel with C-H stretching and symmetric and asymmetric stretching of caboxylate of residual MUA ligands labeled.

High-resolution transmission electron microscopy (TEM)

All TEM samples were prepared by drop casting toluene dispersions of the materials onto carbon-coated copper grids. The analyses were conducted in the bright field mode using a JEOL FasTEM 2010 HR TEM analytical electron microscope operating at an accelerating voltage of 200 kV. Fig. S2 shows high resolution of TEM images of the CdSe(ZnS) aerogel.

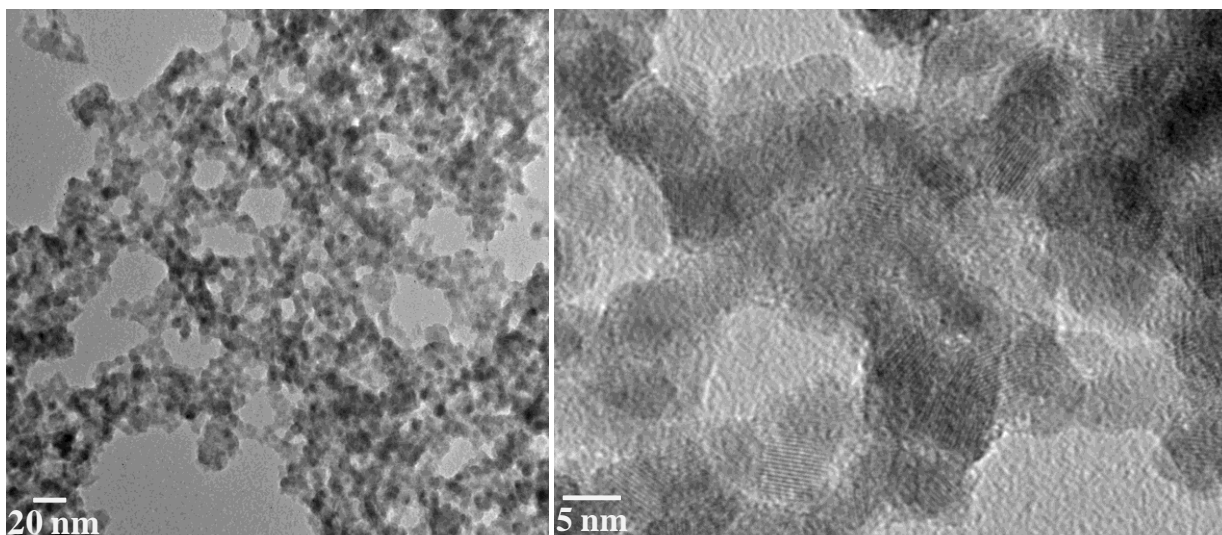


Figure S2. TEM images of CdSe(ZnS) aerogel. The presence of end to end connected QDs (joints) is visible in the images.

Absorption spectra

Absorption spectra of QDs and aerogels (dispersed in toluene), P3HT (film) and P3HT:aerogel and P3HT:QDs hybrid films were obtained on a Hewlett-Packard (HP) 8453 spectrophotometer. The steady-state absorption spectra as a function of increasing CdSe(ZnS) QDs concentration in P3HT:QDs hybrid films is displayed in Fig. S3. There is an enhancement in light scattering as the CdSe(ZnS):P3HT ratio is increased.

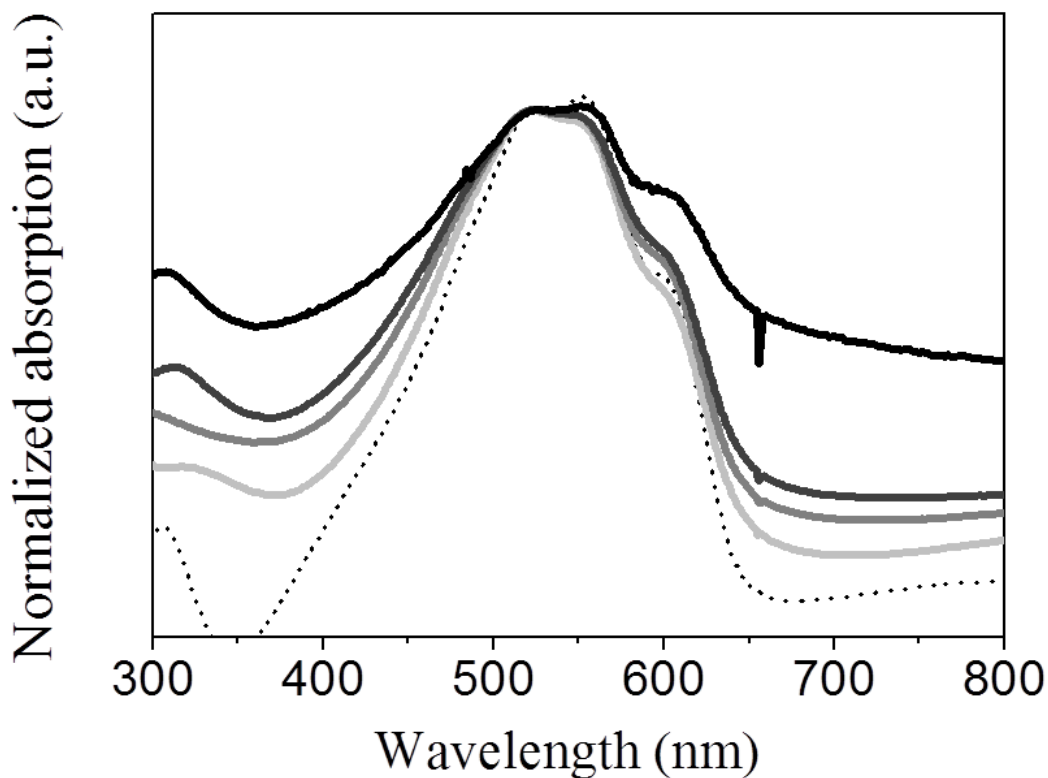


Fig. S3. Steady-state absorption spectra of hybrid films of P3HT:QDs with different weight ratios of CdSe(ZnS): (·····) 0 wt%, (—) 50 wt%, (—) 67 wt%, (—) 80 wt% and (—) 90 wt%. Spectra are normalized by the fraction of photons absorbed at 550 nm.

Chronoamperometry

Chronoamperometry measurements were obtained in a three-electrode cell connected to a Eco Chemie Autolab PGSTAT10 potentiostat. Ag/AgCl and a Pt wire were employed as reference electrode and as counter-electrode, respectively, and a 0.1 M aqueous solution of

Na_2SO_4 saturated with O_2 was used as electrolyte. Working electrodes with active area of 1 cm^2 were prepared by depositing films of QDs, aerogels, P3HT, P3HT:aerogel and P3HT:QDs onto ITO-coated glass. The current characteristics were recorded as function of time, while repeated on-off cycles of light illumination (100 mW cm^{-2}) were applied. Fig. S4 shows the photocurrent responses for photoelectrodes based on bare P3HT, aerogels or QDs. Upon light illumination, prompt photocurrent generation in each electrode was observed. Aerogels and QDs show n-type behavior, while P3HT presents a p-type behavior, consistent with a preferential charge transport of electrons in the inorganic materials and holes in the polymer film. Fig. S5 shows chronoamperometry measurements of P3HT: CdSe (core only) aerogel hybrid films containing different concentrations of aerogels. Fig. S6 schematically displays the charge transfer processes expected in P3HT-, CdSe(ZnS)- and hybrid P3HT-CdSe(ZnS)-based systems.

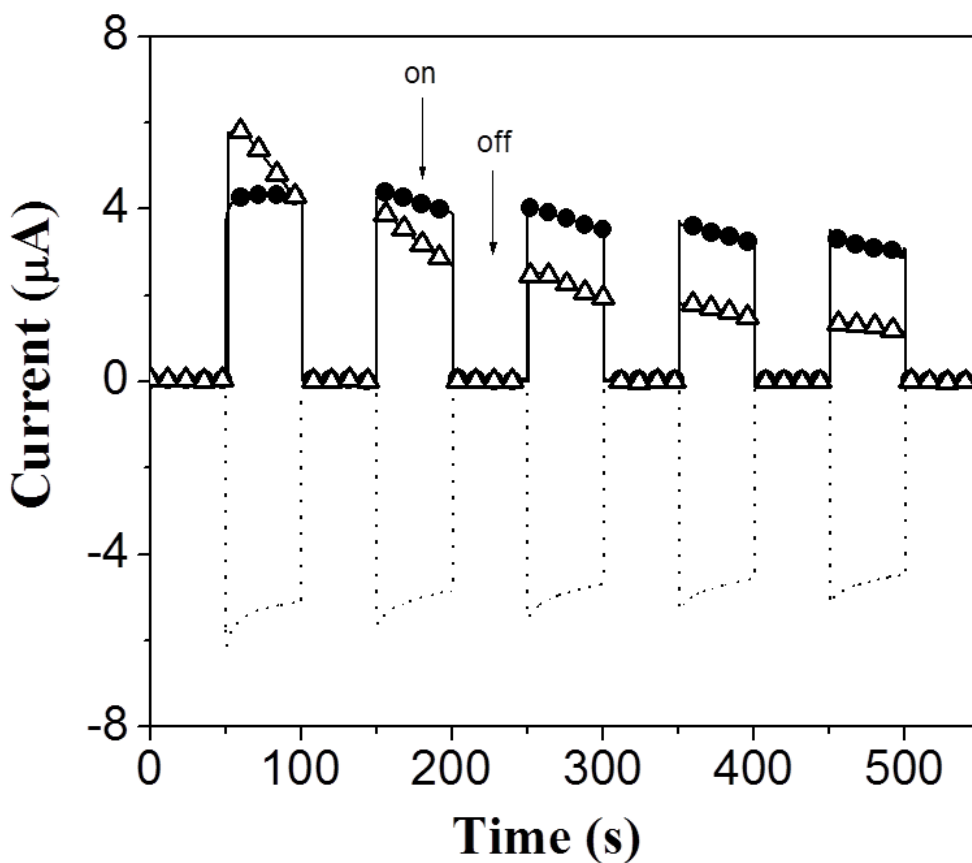


Fig. S4. Photocurrent responses under white light ($\lambda > 300 \text{ nm}$, 100 mW cm^{-2}) of films of (.....) P3HT, (Δ) CdSe(ZnS) QDs and (\bullet) CdSe(ZnS) aerogel deposited onto ITO-glass substrates, in the presence of a $0.1 \text{ M Na}_2\text{SO}_4$ electrolyte saturated with O_2 .

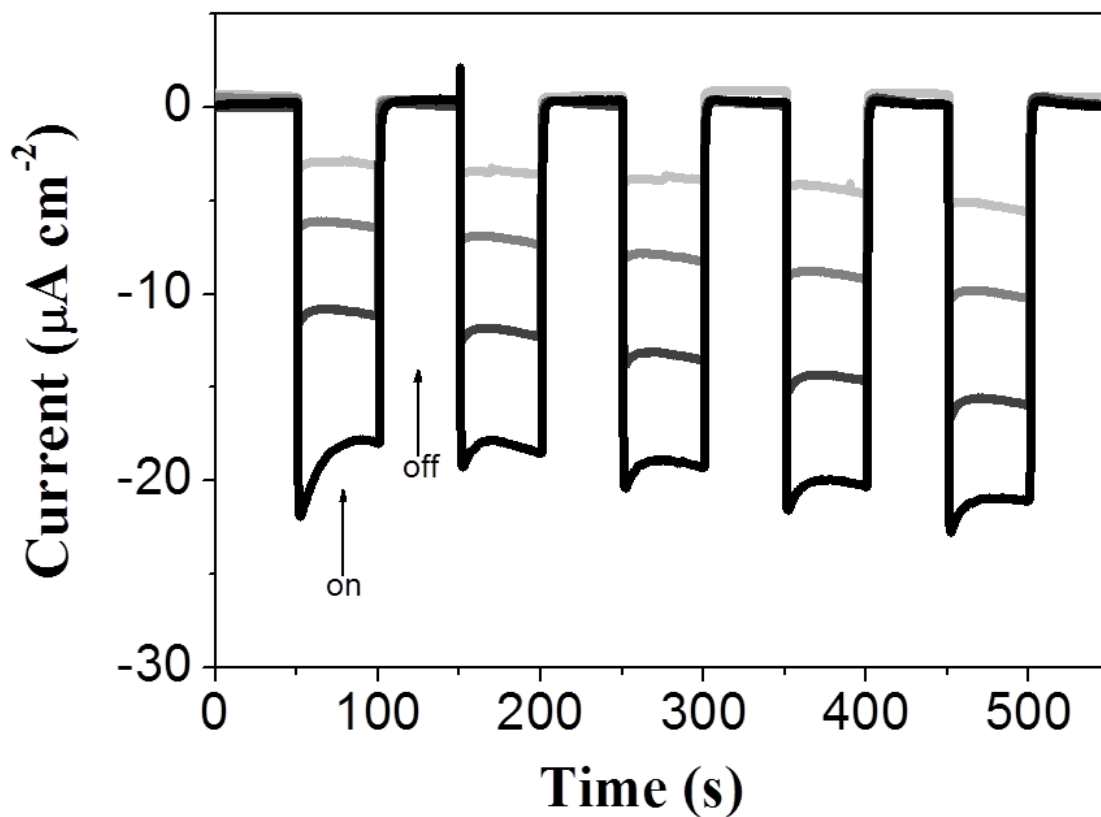


Fig S5. Photocurrent responses under white light ($\lambda > 300 \text{ nm}$, 100 mW cm^{-2}) of films of P3HT:CdSe (core only) aerogel, with (—) 50 wt%, (—) 67 wt%, (—) 80 wt% and (—) 90 wt% of CdSe, in the presence of a 0.1 M Na_2SO_4 electrolyte saturated with O_2 .

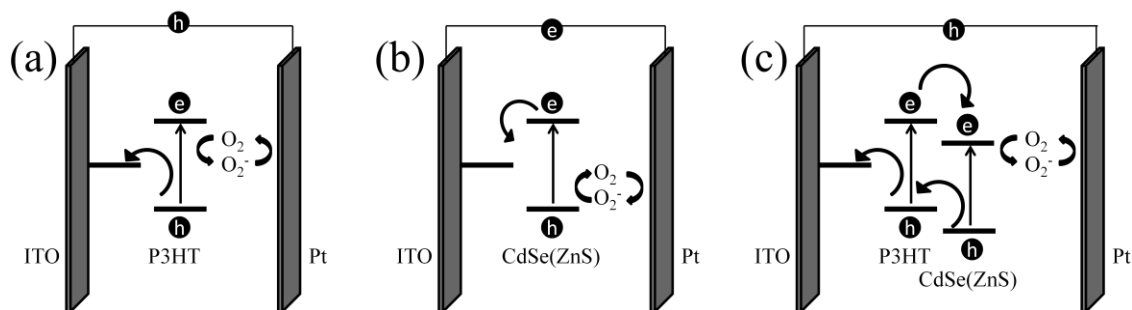


Fig. S6. Scheme of charge transfer processes expected for systems containing electrodes based on (a) P3HT, (b) CdSe(ZnS) QDs or aerogel, and (c) P3HT:CdSe(ZnS) hybrid films, in the presence of a 0.1 M Na_2SO_4 electrolyte saturated with O_2 electrolyte and under white light irradiation.

Transient absorption spectroscopy (TAS)

Microsecond to millisecond laser-based transient absorption spectroscopy was used to determine the yield of charge pair generation and the charge recombination dynamics following photoexcitation of the films. TAS kinetic traces were taken using a simultaneous pump and probe set up. A pulsed nitrogen laser (Photon Technology International GL-3300) was used to excite a dye laser (Photon Technology International GL-301), producing emission at 510 nm which was directed at the sample to induce its electronic excitation. A quartz halogen lamp (Bentham IL1) and photodiode were used to measure the absorption characteristics of the samples, while monochromators (Photon Technology International) were employed to refine the probe wavelength.

Atomic Force Microscopy (AFM)

The morphology of films deposited onto glass slides were analyzed using a NanoSurf easy scan 2 flex AFM microscope operating in tapping mode. Fig. S7 shows that hybrid films containing aerogels are rougher than films containing QDs: the root mean square (RMS) roughness was estimated to be ca. 110 nm and ca. 70 nm for samples containing 90 wt% of aerogel and QDs, respectively. In all samples, the presence of large clusters/aggregates can be seen. In aerogel-based samples, the clusters/aggregates appear to be well spread out in the film, while in QDs-based samples they appear more concentrated in certain regions. The morphology of P3HT films containing 90 wt% or 50 wt% of aerogels have similar features. This is possibly related to the pre-assembled interconnected network, which preserves its structure, even after mixing with the polymer, as evidenced in HRTEM images. In the QDs-based samples, the 50 wt% sample have finer domains compared to the 90 wt% sample.

In all cases, the roughness is very high compared to organic P3HT:PCBM mixtures used in solar cells. Efficient charge photogeneration requires the morphology of the donor-acceptor film to be structured on the exciton diffusion length of the donor material (typically on the order of 10 nm). This condition is necessary to ensure that photogenerated excitons are in close proximity (within the exciton diffusion length) of the donor-acceptor heterojunction where they can undergo dissociation into electrons and holes. Further studies are underway to prepare hybrid polymer:aerogel films with smoother morphologies.

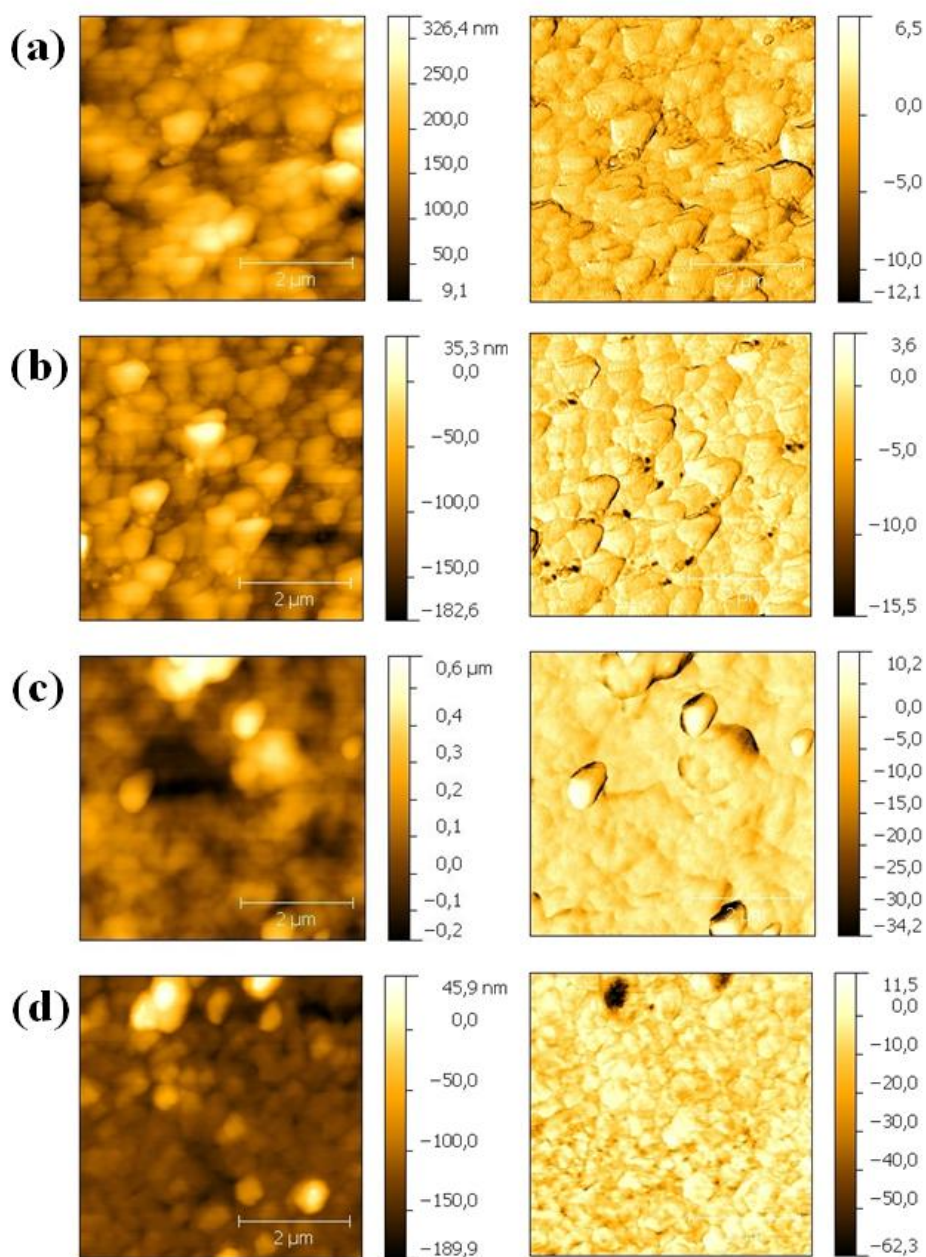


Fig. S7. AFM images obtained in tapping mode for P3HT films containing (a) 90 wt% and (b) 50 wt% of CdSe@ZnS aerogel or (c) 90 wt% and (d) 50 wt% of CdSe@ZnS QDs, deposited onto glass slides. Left images show topography, while right images show phase information. The scan area is 5 μm x 5 μm and the scale bar indicates 2 μm in all images.