

Supporting Information for:

**Reconfigurable Nanorod Films: An In-Situ Study of
the Relationship Between Tunable Nanorod
Orientation and their Optical Properties of Self-
Assembled Thin Films**

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1. EXPERIMENTAL SECTION

- 1.1. **Materials.** Cadmium oxide (CdO, 99.99%), propylphosphonic acid (PPA, 95%), tri-n-octylphosphine oxide (TOPO, 99%), toluene (ACS Reagent, 95%), 1,2-dichlorobenzene (99 %), elemental selenium (pellets, 99.99% trace metals basis), elemental sulfur (99%), and anhydrous n-hexane, acetonitrile, toluene, methanol, and ethanol were purchased from Sigma-Aldrich and used without further processing. Tri-n-octylphosphine (97%) was purchased from Strem Chemicals. n-Octadecylphosphonic acid was purchased from Polycarbon Industries
- 1.2. **NR Synthesis.** *CdSe/CdS NRs.* Dot-in-rod CdSe/CdS nanostructures were synthesized by modifying the seeded synthesis approach presented by Carbone *et al.*¹ For the synthesis of the CdSe seeds, a 25 mL three-neck flask was loaded with 60 mg of CdO, 280 mg of ODP, and 3.3 g of TOPO and heated to 150°C under vacuum with stirring for 2 hours. 1.7 M TOP:Se was prepared by mixing with a magnetic stirbar 3.60 g TOP and 580 mg selenium pellets in a vial under nitrogen. After the cadmium phosphonate precursor was exposed to sufficient vacuum, the flask is heated to 370°C until the contents were optically clear. A 1.5 g quantity of TOP was then injected into the flask, and the contents were allowed to return to an injection temperature of 370°C. To grow 3.9 nm CdSe seeds, 450 µL of 1.7 M TOP:Se was swiftly injected into the flask. The temperature controller was immediately set to 350°C, and the flask was maintained at this temperature for 3 minutes. Upon reaching the desired size, the heating mantle was disengaged from the flask, and the solution was quenched by introducing 10 mL of room temperature anhydrous toluene when the solution reached 160°C and submerging the flask into an ice bath. The CdSe NCs were washed by two cycles of precipitation and redissolution in equal volumes of methanol and toluene. After a third precipitation in methanol, the seeds were dried under nitrogen and stored in a glove box. Prior to the synthesis of the seeded rods, a stock solution of equimolar TOP:S was prepared by combining 15 g of TOP with 1.2 g of elemental sulfur in a vial with stirring and heat (100°C) overnight. To prepare the seeded heterostructures, a 50 mL three-neck flask was loaded with 60 mg of CdO, 290 mg of ODP, 60 mg of PPA, and 3 g of TOPO and heated to 150°C under vacuum with stirring for 2 hours. After sufficient vacuum, the flask was heated to 350°C until the precursor became optically clear. At this point, 1.5 g of TOP was injected into the flask, and the contents were allowed to return to the injection temperature of 350°C. The seed solution was prepared by sonicating the previously synthesized and dried CdSe NCs with TOP so that the solution reached a concentration of 400 µM. 200 µL of the TOP-solvated CdSe NCs are mixed with 1.62 g of the equimolar TOP:S. When the injection temperature stabilized, this TOP:S mixture was injected into the flask, and the rods were allowed to grow for 8 minutes. The heating mantle was then disengaged from the flask, and the solution was quenched by introducing 10 mL of room temperature anhydrous toluene when the solution reached 160°C and submerging the flask into an ice bath. The NRs were washed by two cycles of precipitation and redissolution in equal volumes of methanol and toluene, and redispersed to a solution concentration of 5 mg/mL.

- 1.3. **Electron Microscopy.** Transmission electron micrographs were collected on an FEI Tecnai T12 operating at 120 kV. Scanning electron micrographs were recorded on a LEO-1550-FESEM.
- 1.4. **Grazing-incidence Scattering.** Grazing incidence small angle X-ray scattering (GISAXS) measurements were performed on beam line D1 of the Cornell High Energy Synchrotron Source (CHESS) using monochromatic radiation of wavelength $\lambda = 1.117$ Å with a bandwidth $\Delta\lambda/\lambda$ of 1.5%. The X-ray beam was produced by a hardbent dipole magnet of the Cornell storage ring and monochromatized with Mo:B4C synthetic multilayers with a period of 30 Å. The D1 area detector (MedOptics) is a fiber-coupled CCD camera with a pixel size of 46.9 μm by 46.9 μm and a total of 1024×1024 pixels with a 14-bit dynamical range per pixel. Typical read-out time per image was below 5 s. The images were dark current corrected, distortion-corrected, and flat-field corrected by the acquisition software. The sample to detector distance was 946 mm, as determined using a silver behenate powder standard. The incident angle of the X-ray beam was varied from 0.25 to 0.5° i.e., slightly above the silicon critical angle. Typical exposure times ranged from 0.1 to 1.0 s. Scattering images were calibrated and integrated using the Fit2D software. GISAXS diffraction peaks were indexed and fitted using in-house software.² After well-ordered GISAXS images were obtained, GIWAXS patterns on the same sample spot were recorded on Fuji image plates, and scanned for digital processing with a GE Healthcare Typhoon FLA-7000 image plate reader. Image plates were letter sized with 2000 x 2500 pixels and a 100 μm pixel size. For typical exposures of 2s an image plate was placed in a holder at 180 mm from the sample; the holder could be quickly slid in and out of scattering position on a rail. The intense scattering close to the direct beam was blocked with lead tape. Digital images were also analyzed using Fit2D. For in-situ GISAXS/GIWAXS measurements, we used a custom-made vapor chamber with an aperture cut through the sample stage to enable the transmission of light for optical absorbance spectroscopy. A colloidal NR film deposited on an optically transparent substrate is positioned on the sample stage. The top of the stage was sealed, and a spectrometer was positioned on the cover to obtain optical transmission measurements. X-ray beams passed the chamber through Kapton windows. The sample is located on an elevated block and liquid solvent can be injected into the chamber through a long Teflon capillary from outside the hutch. A flow system delivered N₂ gas to modulate solvent vapor concentration inside the chamber. GISAXS peaks were indexed and fitted using our in-house software. A critical angle of 0.17 degree was found to give the best fit with our NR samples.
- 1.5. **In-situ solvent vapor annealing at elevated temperature.** The inlet gas line was affixed to a thermocouple, which indicated that the temperature at the end attached to the solvent chamber was maintained at a regular temperature of 80°C. When the heated gas is reintroduced into the chamber, the solvent takes approximately 10 minutes to evaporate from the interior into the outlet. During this period, a scattering pattern was captured with an integration time of 1 second every minute during film wetting and evaporation, and every 30 seconds when order begins to recover.

- 1.6. **In-situ Optical Transmission.** Optical transmission spectra of the NR arrays were simultaneously captured with scattering patterns during the assembly process. Optical spectra were obtained using a Filmetrics F30 Transmission Spectrometer fitted to the roof of the cell. The incident light was generated by a Navitar microscope white light source with an adjustable halogen lamp. The light was introduced into the chamber by reflection using an angled mirror.
- 1.7. **Photoluminescence Emission.** A 420 nm tunable diode laser served as the light source for photoluminescence (PL) emission studies. A sample with standing rods were used for all experiments. The excitation beam was shone perpendicular to the sample substrate. A monochromator and detector was placed 90 degrees to the excitation beam. A linear polarizer was positioned between the sample and the detector to vary the polarization. A half wave-plate was placed between the polarizer and the detector. With every corresponding rotation of the polarizer, the half wave-plate was rotated accordingly such that the polarization of light entering the grating and the detector is kept constant.
- 1.8. **Ex-situ optical absorbance.** For the ex-situ measurement a prepared sample of perpendicular NR was used. In contrast to the in-situ experiment, the polarization of the incident light was varied while the NR orientation remained static. In this case a grazing incidence geometry is needed rather than the unpolarized transmission geometry of the in-situ study. In either case the light polarization was perpendicular or parallel to the NR, and the detailed ex-situ measurement confirmed our interpretation of the in-situ data.

2. LENGTH DISTRIBUTION OF COLLOIDAL NANORODS

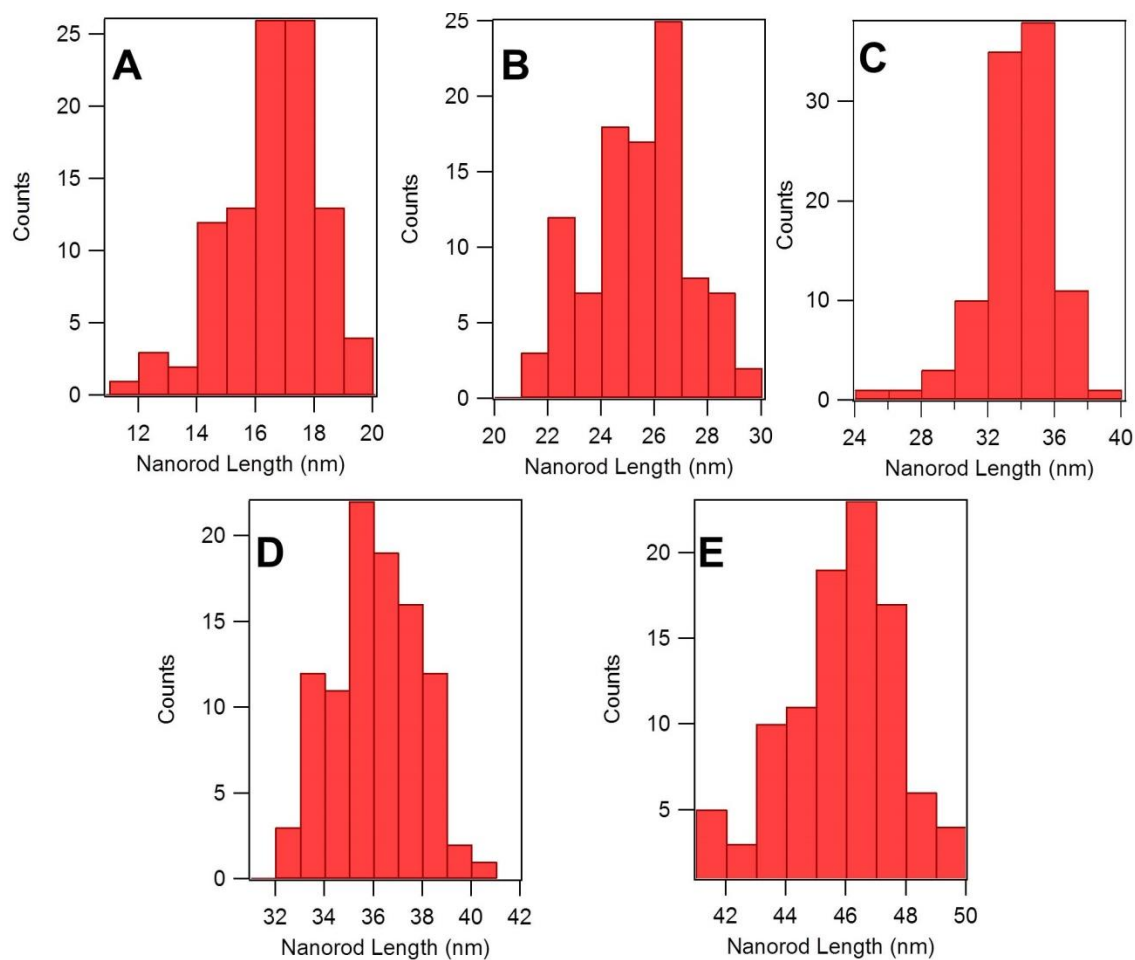


Figure S1. Size histograms of different lengths of CdSe/CdS colloidal nanorods assembled into thin films. An average of 100 rods were sampled from TEM images, depicting an average length of a) 16.5 ± 1.6 nm, b) 25.3 ± 2.1 nm, c) 33.7 ± 2.1 nm, d) 36.1 ± 1.9 nm, and e) 45.9 ± 2.0 nm.

3. EXPERIMENTAL CELL AND HUTCH EXPERIMENTAL SETUP

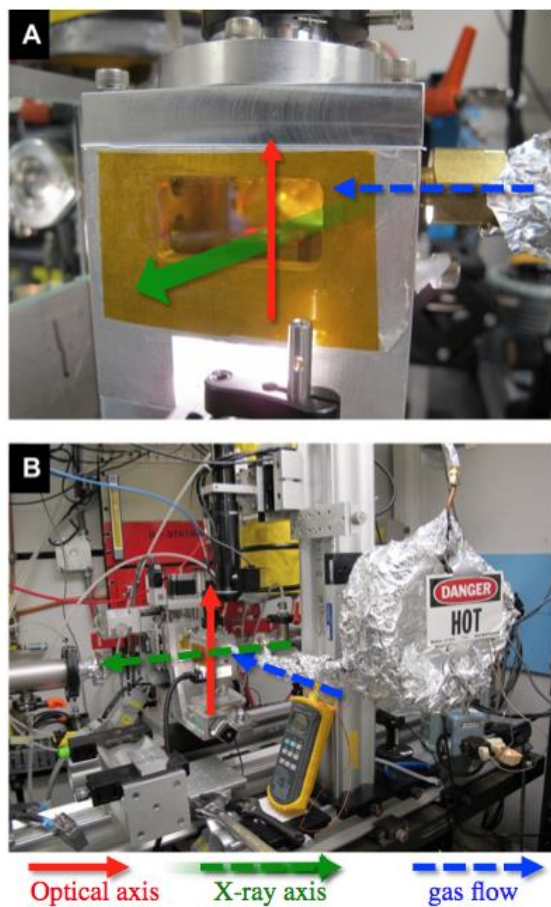


Figure S2. a) Images showing the cell used to swell self-assembled films of colloidal nanorods. b) The hutch containing the cell and the gas heating element used to drive solvent out of the nanorod system. The arrangement of optical axis, X-ray beam axis and gas flow are indicated by colored arrows.

4. GISAXS PATTERNS OF THE STRUCTURE EVOLUTION OF COLLOIDAL NRs WITH VARIABLE LENGTH IN RESPONSE TO SOLVENT VAPOR ANNEALING

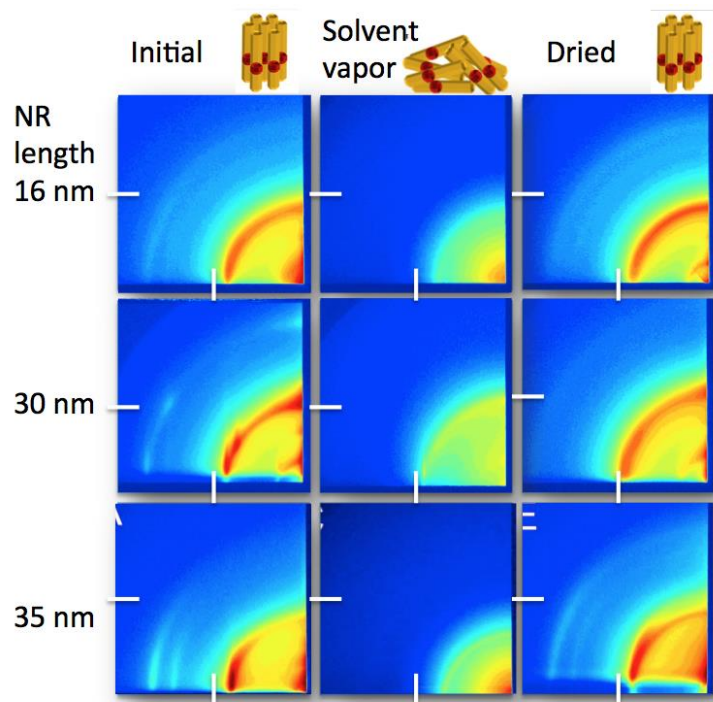


Figure S3. GISAXS of NR films with 16, 30, and 35 nm length. GISAXS data illustrate the similarity in the structure evolution of variable length NRs in response to solvent vapor annealing. Initially formed NR films are well-ordered (left panel), upon exposure to DCB solvent vapor the NR films disorder (middle panel), and re-assembly upon drying (right panel). Tick mark denotes $q=1/\text{nm}$.

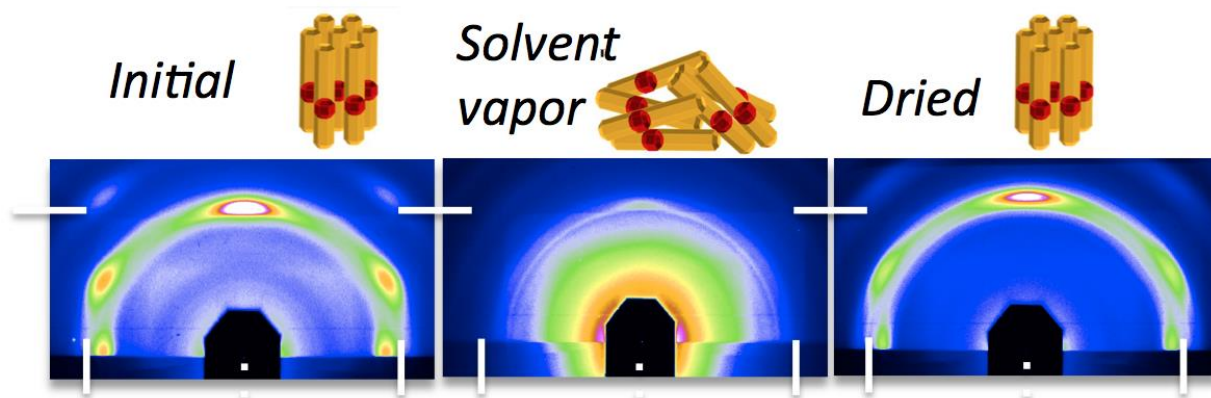


Figure S4. GIWAXS of NR films with 35 nm length. Wide-angle scattering data illustrate the similarity in the structure evolution of NRs in response to solvent vapor annealing. Initially formed NR films are well-ordered (left panel), upon exposure to DCB solvent vapor the NR films disorder (middle panel), and re-assembly upon drying (right panel). Tick mark denotes $q=10/\text{nm}$

5. NR ORIENTATION RELATIVE TO THE SUBSTRATE

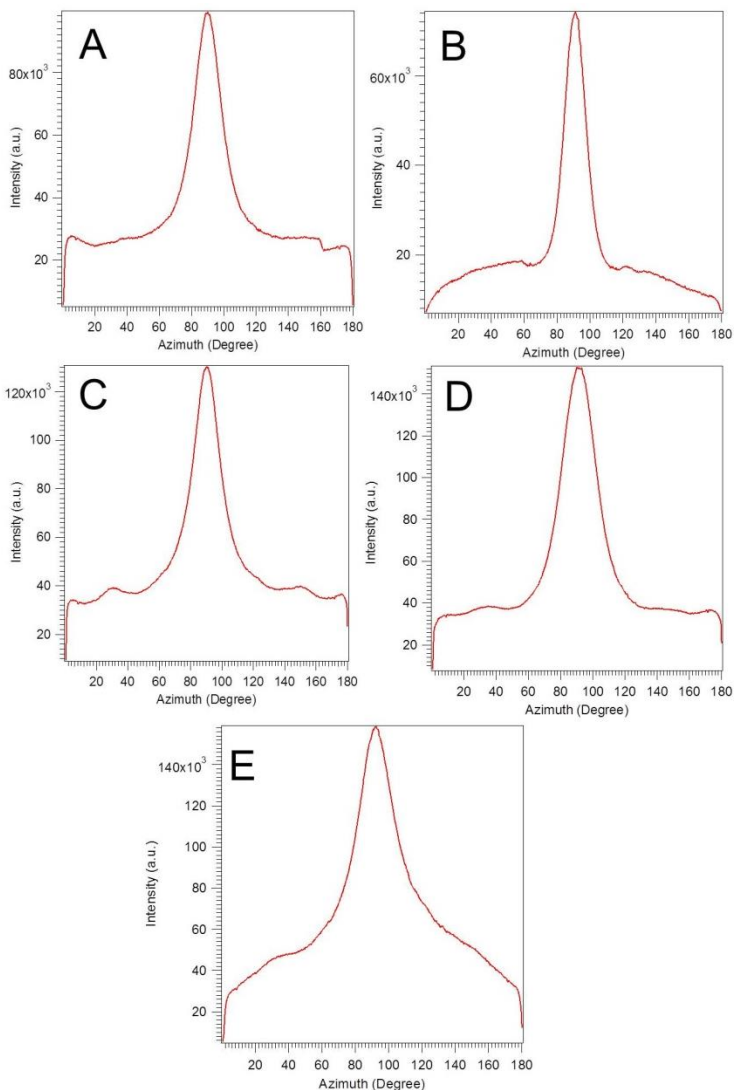


Figure S5. Azimuthal spread of the (002) reflection in GIWAXS patterns of NR films with varying length a) 16.5 ± 1.6 nm, b) 25.3 ± 2.1 nm, c) 33.7 ± 2.1 nm, d) 36.1 ± 1.9 nm, and e) 45.9 ± 2.0 nm. The narrow azimuthal spread of the (002) reflection indicates that NRs assemble into arrangements with their long axis aligned normal to the substrate.

6. OPTICAL CHARACTERIZATION OF NR FILMS

Ex-situ optical reference measurements on a well-aligned sample of vertical NR. In this case the NR sample was fixed, while the polarization vector of the light source could be aligned from parallel (0deg) to perpendicular (90deg) to the NR. The measurements confirm the results from the *in-situ* measurements that the optical adsorption is highest, when the polarization vector is parallel to the NR axis.

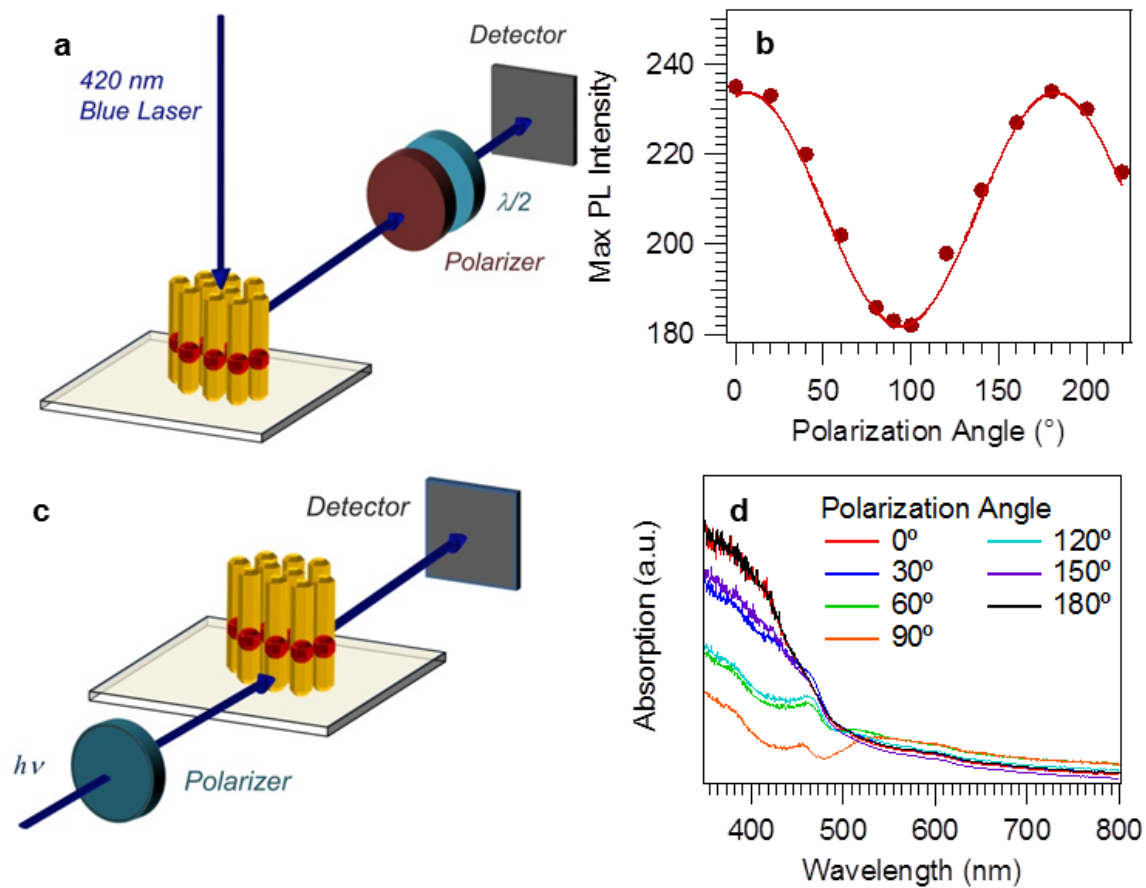


Figure S6: (a) Experimental configuration for photoluminescence measurements and (b) maximum photoluminescence intensity as a function of polarization for an NR array of 46.9 nm rods. (c) Experimental configuration for polarization dependent absorption of the NR film and (d) absorption spectra for a NR array prepared with 46.9 nm long (AR: 9) rods corresponding with its different structural configurations.

7. REFERENCES

(1) Carbone, L.; Nobile, C.; De Giorgi, M.; Sala, F. D.; Morello, G.; Pompa, P.; Hytch, M.; Snoeck, E.; Fiore, A.; Franchini, I. R.; Nadasan, M.; Silvestre, A. F.; Chiodo, L.; Kudera, S.; Cingolani, R.; Krahne, R.; Manna, L. *Nano Lett* **2007**, 7, 2942.