

Supporting Information for

Millimeter-scale assembly of CdSe Nanorods into smectic superstructures by solvent drying kinetics

(DOI: 10.1002/adma.200800125)

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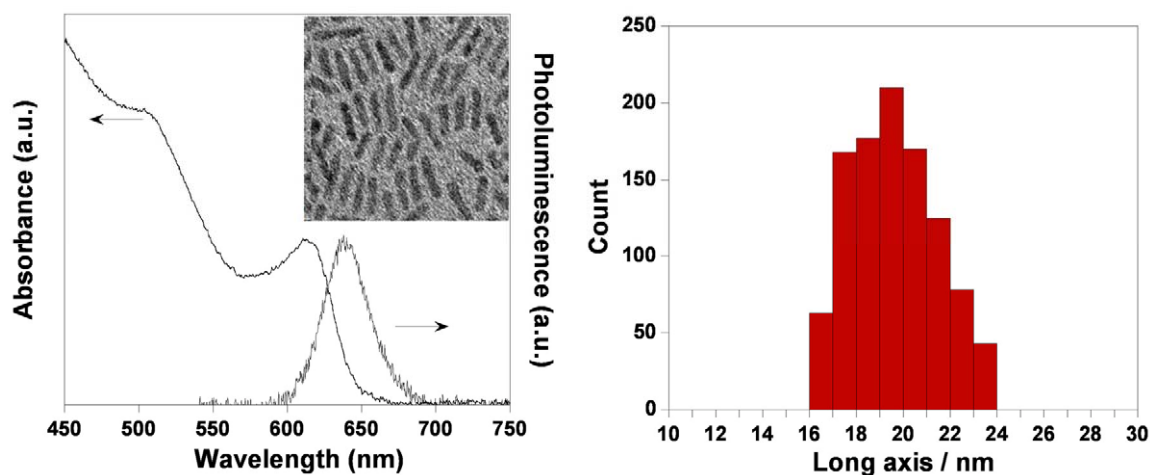


Figure S1. left: Absorption and emission spectra of 5×20 nm NRs, recorded in hexane, using USB2000 and USB4000-FL spectrometers, respectively, from Ocean Optics. The excitonic peak is at 614 nm and the emission at 638 nm (FWHM = 34 nm, excitation: 518 nm LED, 35 μ W). The inset shows a TEM image of the same sample drop-cast from hexane/octane (9/1) solution onto a holey carbon TEM grid. The width of the TEM image corresponds to 100 nm. **right:** Statistical analysis of TEM images of over 1000 NRs (using ImageJ software) revealed an averaged rod length of 19.6 ± 1.8 nm, i.e. the polydispersity in length was $\sim 9\%$. The size distribution in diameter was $< 5\%$.

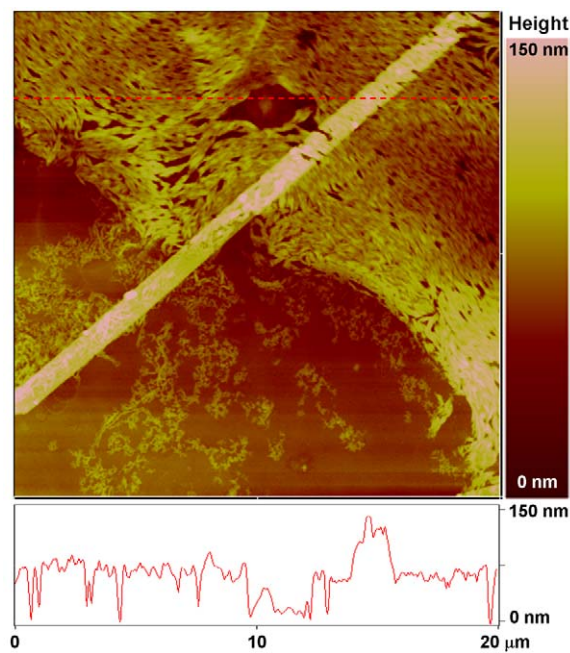


Figure S2. $20 \times 20 \mu\text{m}$ AFM image of CdSe NR superstructures with its corresponding height analysis along the red dashed line. The bright, diagonal structure is a gold wire patterned on the Si_3N_4 substrate with electron beam lithography. There are void regions within these NR superstructures and the AFM height analysis shows that these voids are indeed primarily empty.

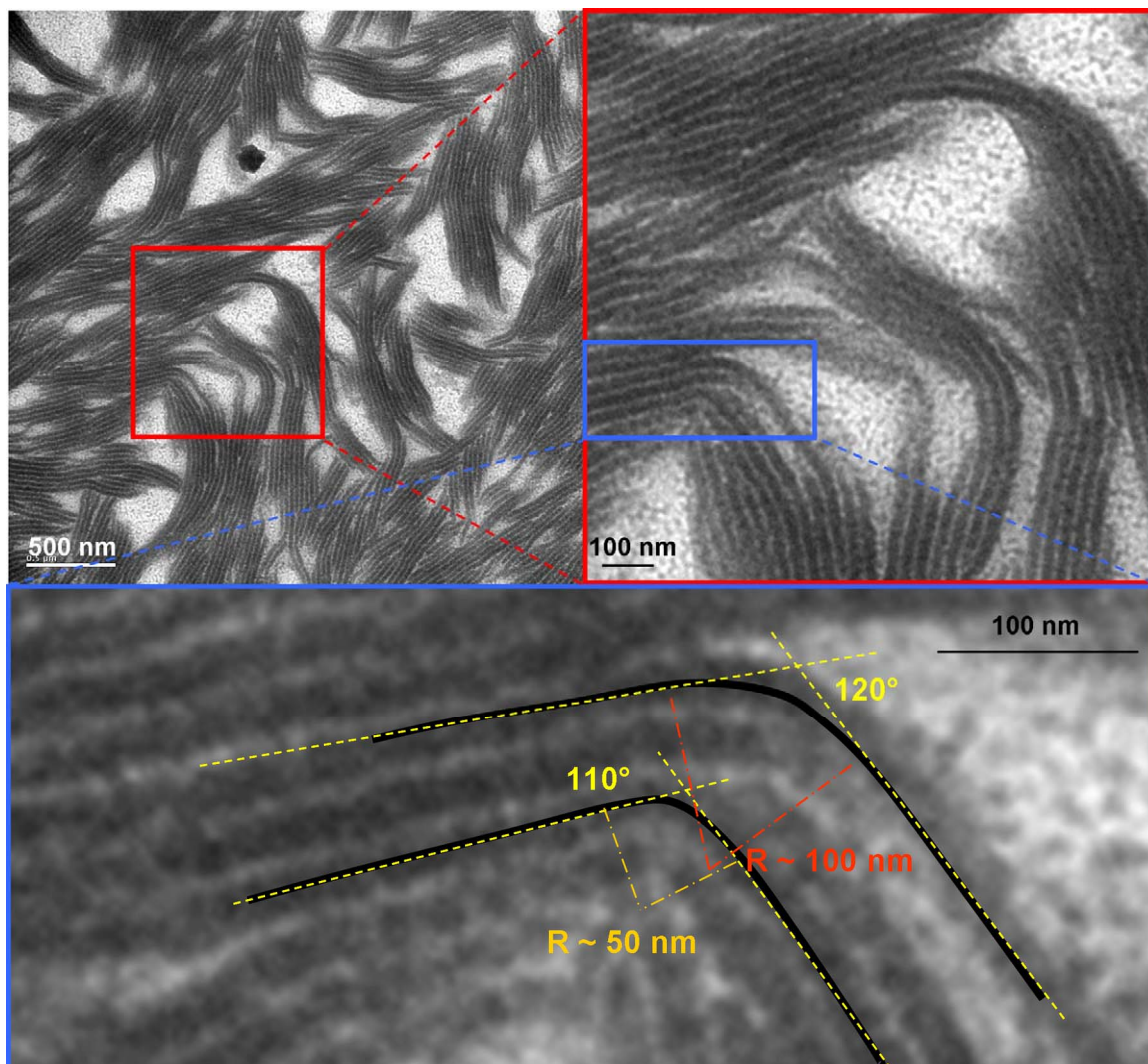


Figure S3. TEM images of strongly bent CdSe NR-tracks with increasing magnification. Some of the bends shown here are 90-120° and occur over as little as ~150 nm. More common are curvatures of ~120-150° occurring over ~500 nm (e.g. in the top right image)

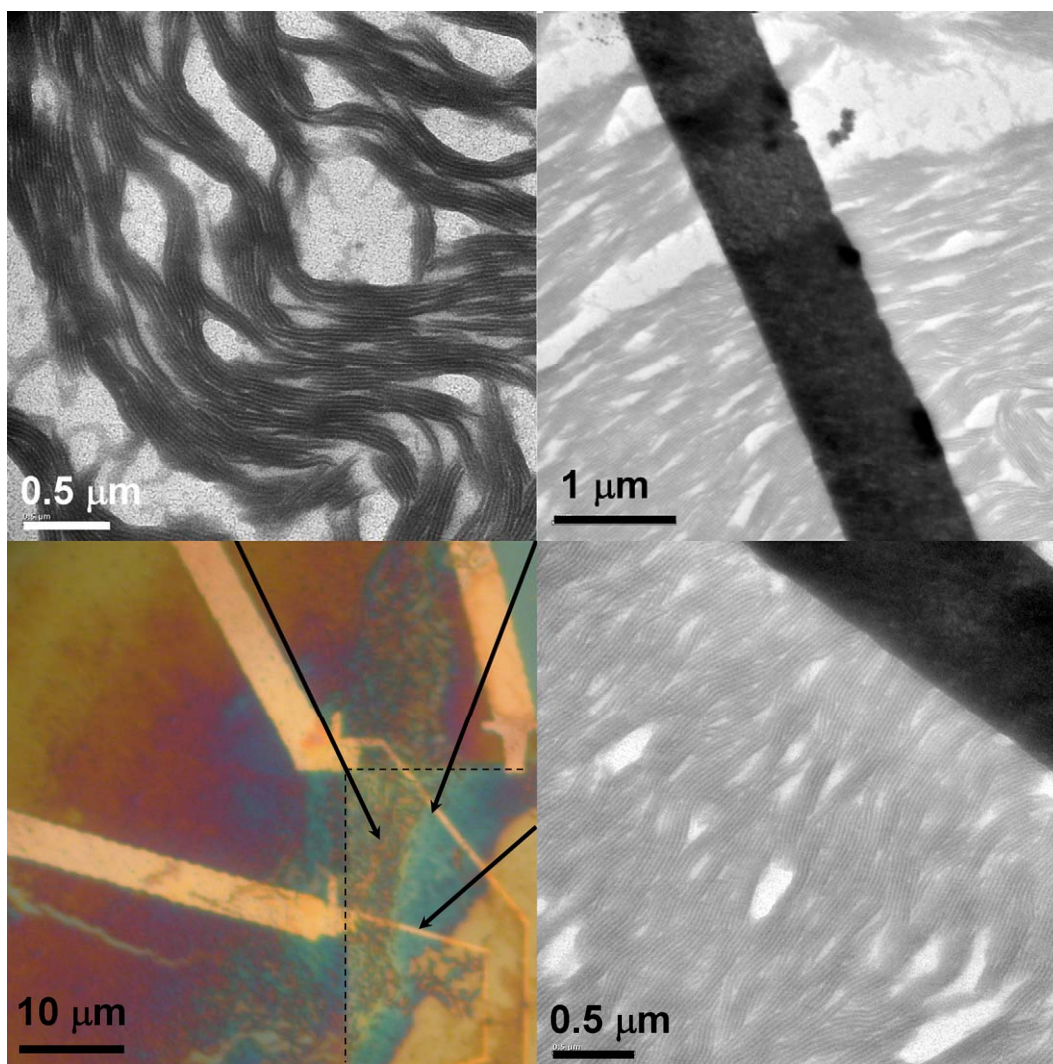


Figure S4. Optical micrograph of a Si_3N_4 membrane device, containing some gold patterns, covered by a film of CdSe NRs, obtained by drop-casting a medium-concentrated solution ($\sim 5 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$ in hexane/octane (9/1)). The border of the window region is marked with a dashed line for clarity. The extended coffee-stain ring ($\sim 30\text{--}50 \mu\text{m}$ thick), formed during the solvent evaporation, was partially on this window region and could be imaged with TEM. TEM images, corresponding to the locations indicated by the arrows, show different assembly superstructures: there are extended dense lamellar-like structures as well as less dense regions showing strongly bent superstructures. AFM images in regions outside the window reveal qualitatively similar superstructures to the ones imaged by TEM (cf. **Figure S2**).

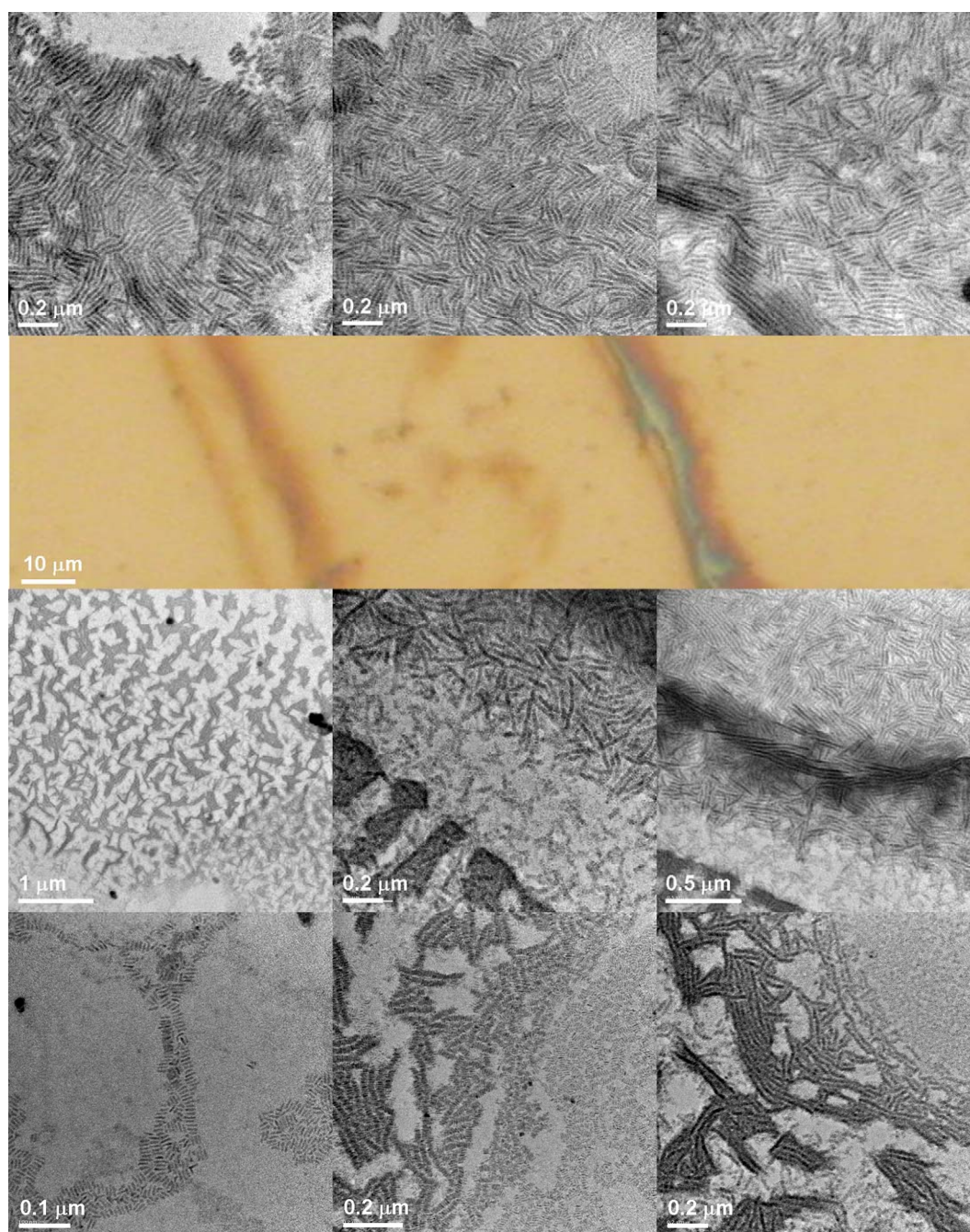


Figure S5. In addition to extended coffee-stain regions (cf. **Figure S4**) multiple thinner rings ($\sim 10\ \mu\text{m}$) can be observed, e.g., as shown in the optical micrograph (2nd row). Such regions exhibit a greater structural diversity of assembly patterns: the dense middle part of the coffee-stain is still characterized by relatively long tracks packing closely together (top row)), though the extent of long-range order is not as dramatic as in **Figure S4**. The perimeter of this dense region represents far more discontinuities and cluster-type assemblies of shorter NR tracks (3rd row; the right image shows the transitional region between the denser and the more sparse regime). Finally, toward the inner part of the initial droplet, the tracks get shorter and the overall coverage is lower (bottom row): monolayer coverage (middle) or submonolayer assemblies (left) can be observed.

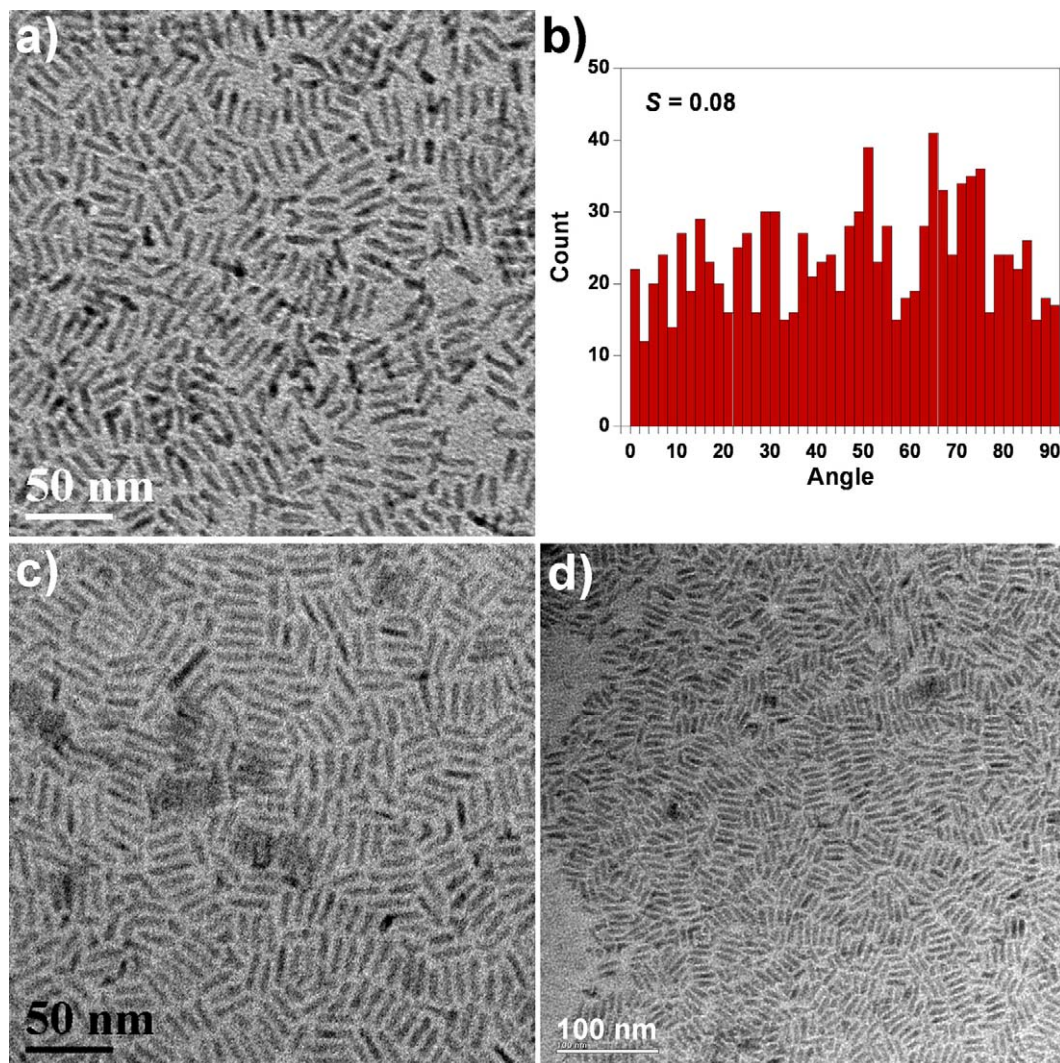


Figure S6. *a,c)* TEM images of CdSe NRs drop-cast from hexane/octane (9/1) solvent mixtures on holey TEM grids (**a**) and on Si_3N_4 membranes (**c**). These rods show an isotropic arrangement with an overall order parameter close to zero as shown in (**b**), where the statistical analysis of the assembly on TEM grids in terms of the angular distribution of the rods is represented. The rods tend to align side-to-side into tracks of usually 5-10 rods (but some also longer) and to some extent several of such tracks stack together due to end-to-end interactions between the rods. The assembly on Si_3N_4 seems slightly more homogenous compared to the holey carbon grids as the solvent can evaporate more uniformly. **d)** TEM images of the same CdSe NRs drop cast from a 1/1 hexane/octane solution on Si_3N_4 membranes. A few longer tracks containing up to 20 rods in parallel can be observed, but a statistical analysis of the images show no significant difference to the assembly patterns obtained for the 9/1 solvent mixture, suggesting that the higher percentage of a higher boiling solvent has only a minor contribution. Similarly, using pure octane solutions (images not shown here) for the drop-cast did not yield longer tracks; to the contrary, the overall homogeneity of the monolayer was slightly reduced. In some regions of the substrate, obtained from the 9/1 hexane/octane mixture, we have also observed micro-scale areas with NRs exhibiting strong unidirectional orientation (cf. **Figure S10**).

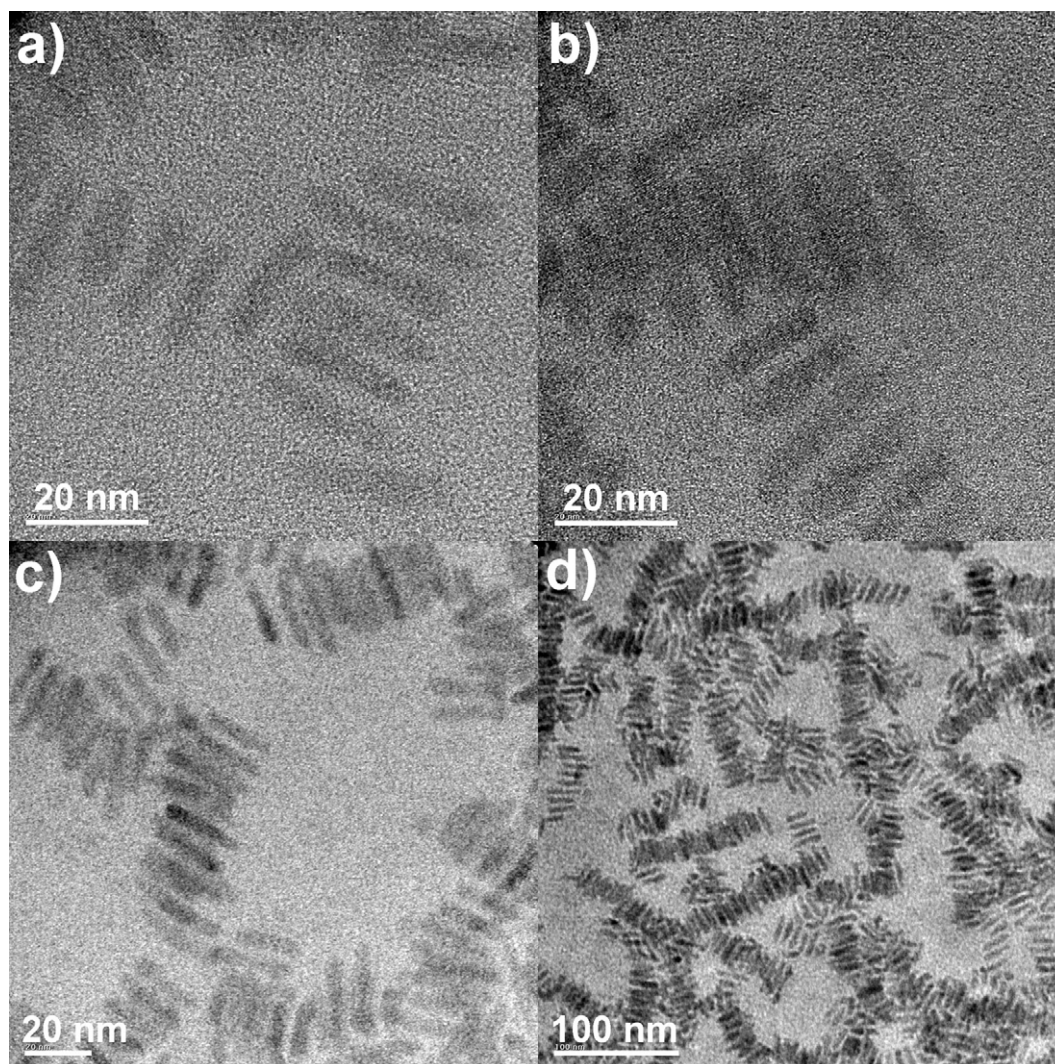


Figure S7. TEM images of the formation of short CdSe NR tracks. **a)** monolayer of CdSe NRs organized side-to-side in short tracks of <10 NRs. **b,c)** a second layer of NRs starts to fill the interstitial spaces to form a apparently denser track containing ~ 10 NRs per layer. The arrangement of each layer with respect to the next one is offset in a zigzag-manner. **d)** zoom-out image showing several multilayer tracks of up to ~ 20 NR-length (per layer) showing no significant short-range order with respect to neighboring tracks.

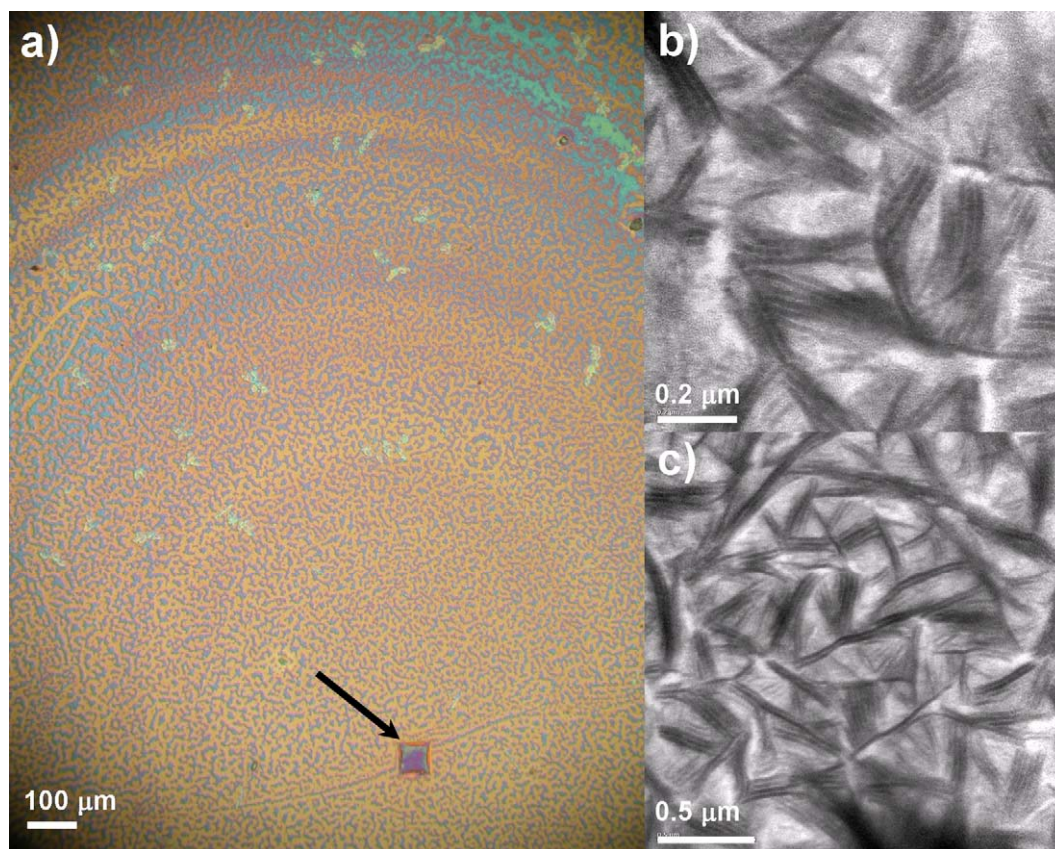


Figure S8. a) Optical micrograph of a Si_3N_4 membrane device covered by a film of CdSe NRs obtained by drop-casting a concentrated solution ($5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ in hexane/octane (9/1)). The $50 \times 50 \mu\text{m}^2$ membrane window is indicated by the arrow. The film is homogenous over the whole substrate ranging over $5 \times 5 \text{ mm}^2$, though some slightly darker regions similar to “coffee-stains” can be seen. b,c) TEM images of this CdSe NRs’ film taken in the window region. Throughout the entire area such dense clusters of NR tracks can be observed. Each of these cluster-like structures contains ~ 5 -10 tracks, ~ 200 -500 nm in length, arranged in parallel, but showing no extended long-range order.

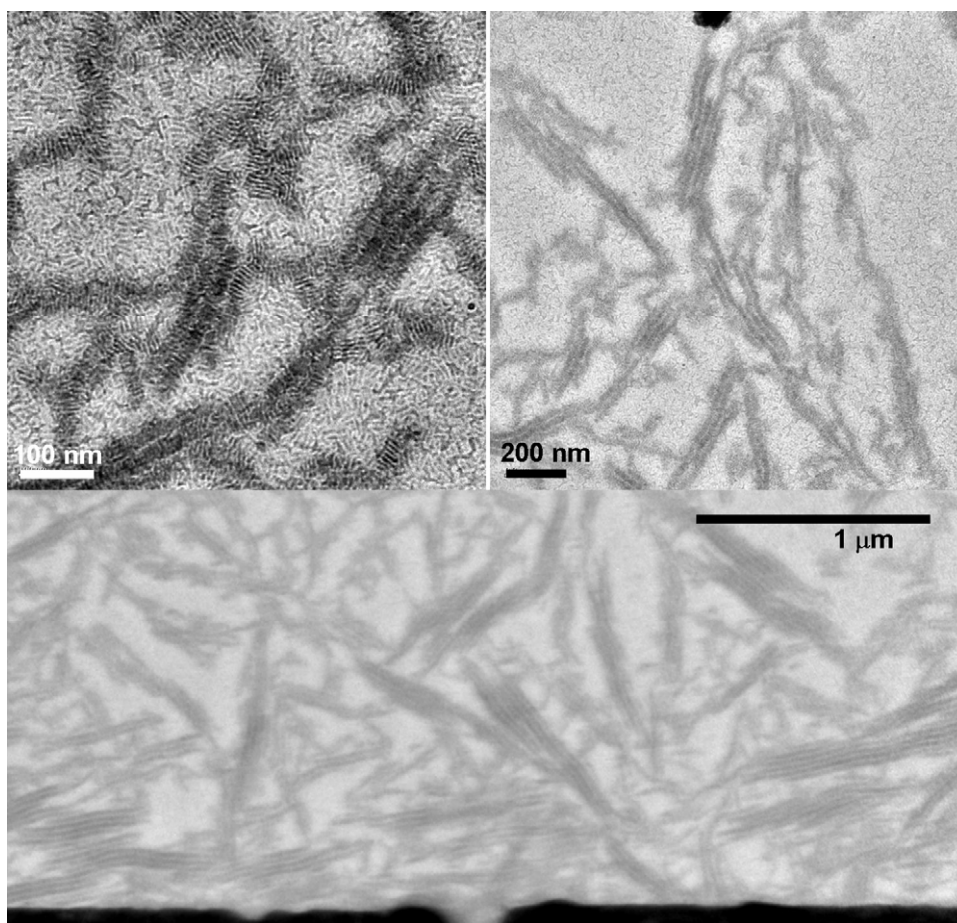


Figure S9. TEM images (with different magnifications) of CdSe NRs tracks that are several hundred nm long and start to align parallel to each other due to attractive capillary forces. When approaching a pinning site, such as the patterned gold wire in the bottom image, these track-bundles pack preferably parallel to this pinning site. This arrangement can be seen as a preliminary step toward the extended lamellar phase in the coffee-stain region (cf. **Figure S4**). Further away from the pinning site, the track-bundles are more randomly oriented, but also exhibit attractive interactions with neighboring tracks.

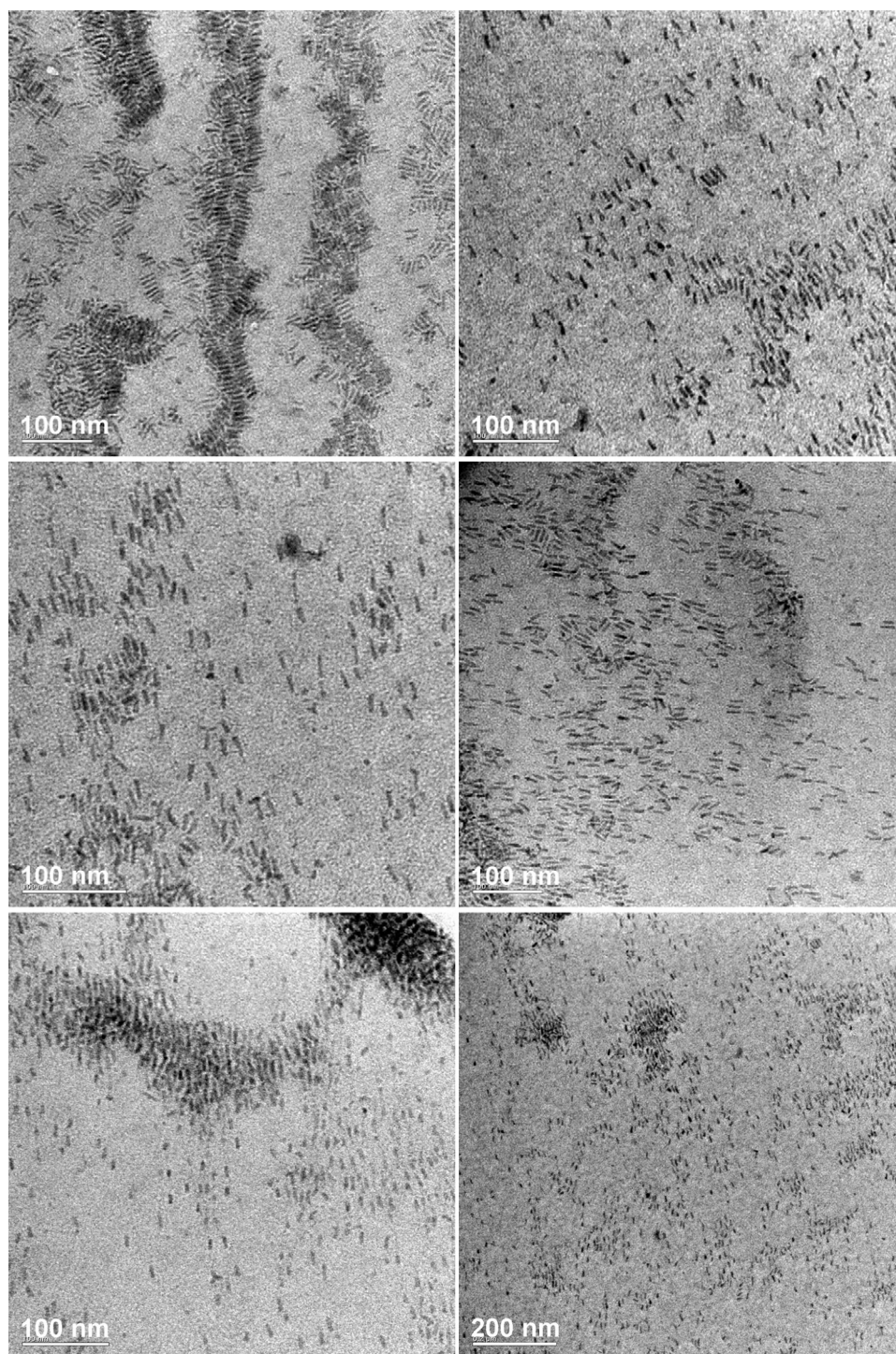


Figure S10. TEM images of NRs exhibiting a high degree of unidirectional orientation. These regions extend over several μm and have been found repeatedly. This kind of orientation might originate from flow alignment.