

Water Dispersible Semiconductor Nanorod Assemblies via a Facile Phase Transfer and Their Application as Fluorescent Biomarkers

Ambarish Sanyal,^a Tanushree Bala,^a Shafaat Ahmed,^a Ajay Singh,^{b, a} Anna V. Piterina,^c Timothy M. McGloughlin,^c Fathima R. Laffir^a and Kevin M. Ryan^{a, b*}

Supporting Information

The TEM images in Supporting Information Fig. S1 shows a comparison of the inter-rod distance between CdS nanorods assembly obtained by drop coating on a carbon-coated TEM grid from toluene (Fig. S1a) and that of after phase transfer to aqueous medium (Fig. S1b). A careful measurement revealed no significant difference in their inter-rod distance. This further supported the fact that the long chain polymer did not interact with individual nanorods but with a bunch of them, otherwise an increased rod to rod distance would have been observed in transmission electron microscopic image (Fig. S1b). The routine UV-Vis and PL spectra of F88 assisted phase transferred CdS nanorods are presented in Supporting information Fig. S2a. Curve 1 represents the UV-Vis spectra which match well with the reported UV-Vis curve for CdS nanorods having an onset of absorption at ~ 485 nm. This feature can be attributed to excitonic transitions in strongly quantized materials. Photo luminescence curve of the same CdS nanorods phase transferred by F88 excited at 350 nm was presented in curve 2. The photo luminescence emission of pristine F88 (curve 3) was also measured for comparison. Fig. S2b, c illustrate the transmission electron micrographs of F88 protected CdS nanorods after phase transfer to the aqueous medium. Fig. S2b represent the presence of close-packed structure all over the grid in the low magnification similar to that observed when the phase transfer was initiated by F127 (main text, Fig. 1F). Fig. S3 denotes a comparison of the UV-Vis and the PL spectra between the individual

nanorods in toluene and the assembled rods after having phase transferred into the aqueous medium by the block copolymer. A comparison between the 2 states (non assembled individual nanorods in toluene vs the assembled ones in water) would involve a comparison of effects between 2 different media, however similar UV-Vis spectra (Fig. S3a, curves 1 and 2) but a conspicuous difference in the emission spectra was observed. There appears to be a considerable amount of decrease in the intensity of the broad emission band ranging from 580-700 when the rods are assembled in aqueous medium (curve 2 in Fig. S3b) in comparison to individual nanorods in toluene (curve 1 in Fig. S3b), a result which is consistent with the 2D assembly of CdS nanorods in organic medium reported by Chou *et al.* (see reference 14 in main text). This possibly entails significant amount of decrease of the non-radiative transition that occurs when the nanorods are dispersed in a chaotic fashion in toluene environment.

Fig. S4 represents C1s core level spectra with the chemically stripped components of as-synthesised CdS nanorods dispersed in toluene.

Fig. S5 shows an optical micrograph of a droplet of phase transferred CdS nanorods on a glass slide indicating the presence of micron and submicron clusters in solution. The aqueous solution of phase transferred CdS nanorods was filtered through two different pore size filter papers, the first one being Whatman grade 5 (pore size ~ 2.5 micron) and the second one of Millipore (pore size ~ 0.45 micron). In the first case the entire solution passed through (pore size ~ 2.5 micron) and a TEM analysis of the filtrate (Fig. S4B) revealed no difference with Fig. 1F (main text). The photograph of the empty filter paper along with bright yellow filtrate in the glass bottle is given as the inset of Fig. S4B. In the second experiment most of the CdS NRSCs were found to be trapped on the Millipore filter paper (~ 0.45 micron pore) and a very faint yellow coloured filtrate was obtained (inset, Fig. S4C). Interestingly TEM showed no NRSCs but only individual rods dispersed on the grid. It can be inferred from this that the formation of CdS ensembles are real features in solution and do not arise due to

deposition on substrates.

Supporting Information (S1)

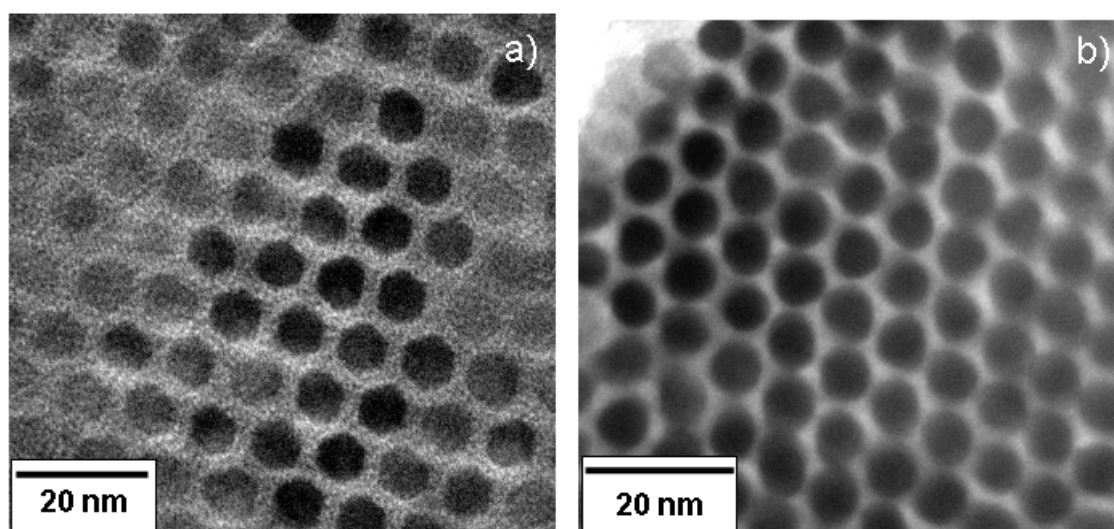


Fig. S1. (a) Representative TEM images of the aligned CdS nanorods in toluene, (b) Similar alignment of CdS nanorods after phase transfer in water via F127 showing negligible change in the inter-rod distance.

Supporting Information (S2)

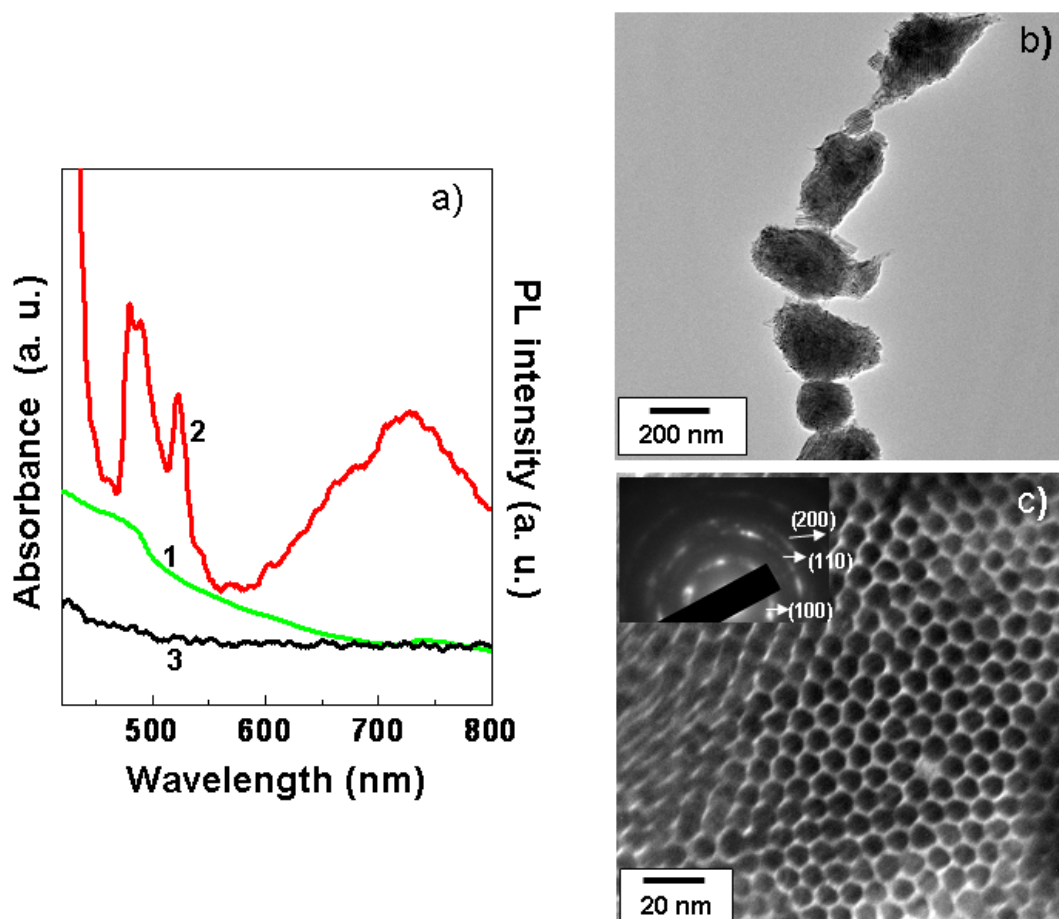


Fig. S2. (a) UV-Vis spectra of CdS nanorods phase transferred with F88 (curve 1) in the aqueous phase. Curves 2 and 3 are the emission spectra from the water dispersible CdS nanorods phase transferred by F88 and the pristine F88 copolymer respectively when an excitation wavelength of 350 nm was used, (b), (c) Representative TEM images of the aligned CdS nanorods in water at progressively higher magnifications after phase transfer with F88. The inset in (c) shows the selected area electron diffraction (SAED) pattern taken from the assembly of CdS nanorods.

Supporting Information (S3)

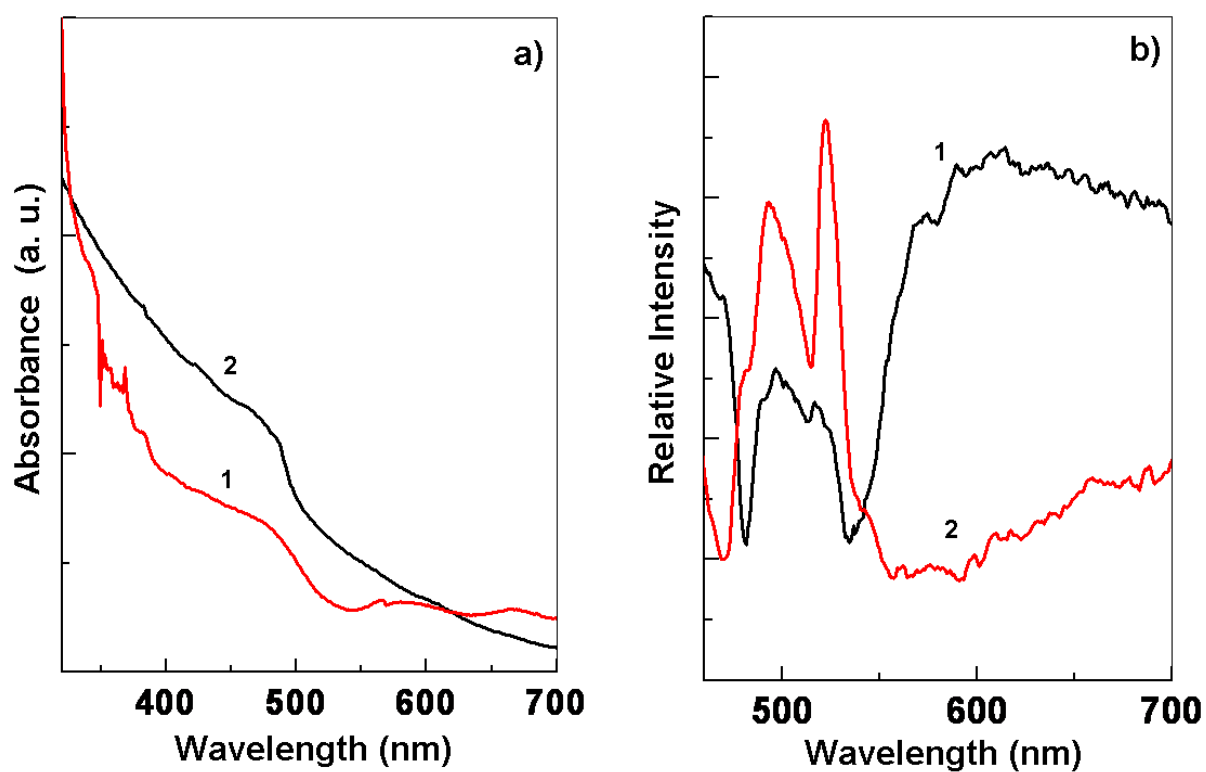


Fig. S3. UV-Vis (a) and PL emission spectra (b) of CdS nanorods as synthesized in the organic phase (curve 1) and after phase transfer with the block copolymer (curve 2) in the aqueous phase.

Supporting Information (S4)

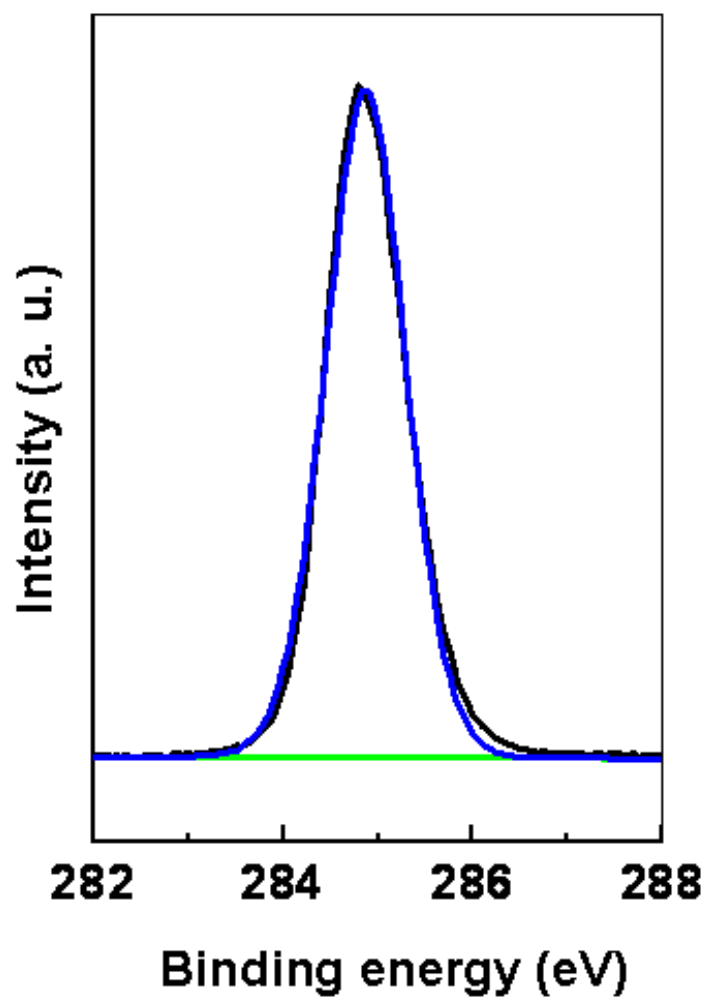


Fig. S4. C1s core level spectra of the as-prepared CdS nanorods dispersed in toluene.

Supporting Information (S5)

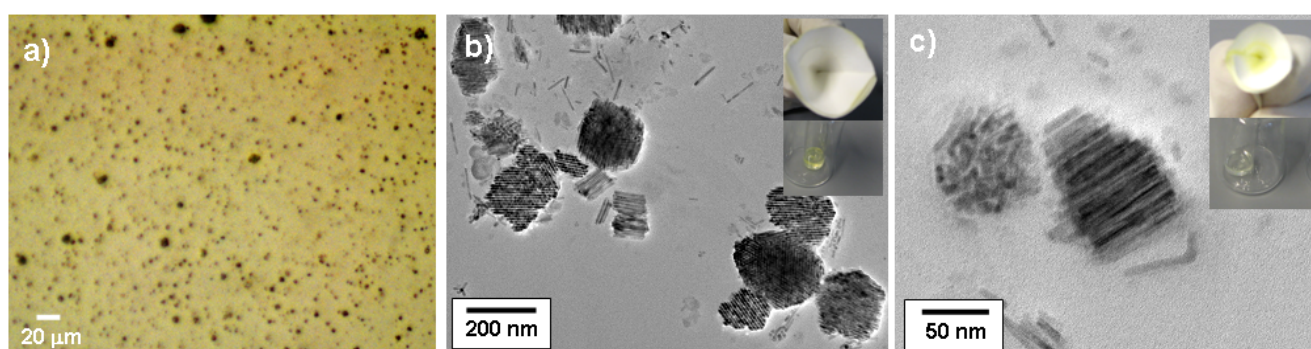


Fig. S5. (a) A low magnification optical image of a droplet on a glass slide. Representative TEM image of the F127 mediated aqueous phase transferred CdS nanorods that have been filtered through Whatman filter grade 5 (b), pore size: 2.5 μm and when filtered through Milipore filter paper (c) pore size: 0.45 μm . The insets in (b) and (c) represent the photographs of the sample vials with the corresponding filter papers containing the filtrate and residue obtained during filtration of the CdS nanorods with 2.5 μm and 0.45 μm filter respectively.