

## Supporting Information

### Synthesis of Monodisperse, Highly Emissive, and Size-tunable Cd<sub>3</sub>P<sub>2</sub> Nanocrystals

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#### *Experimental*

**Synthesis:** All chemicals are used as received without further purification. Cd<sub>3</sub>P<sub>2</sub> nanocrystals were prepared as follows: 0.06 mM CdO, 4 ml ODE and 0.2mM oleic acid (OA) were loaded into a 25 ml three-necked flask and heated to 230 °C under Ar flow (no vacuum pumping). In this solution, 1mM tris-trimethylsilyl phosphine (TMS-P) dissolved in 1.0 ml ODE was quickly injected. Subsequently, the growth of Cd<sub>3</sub>P<sub>2</sub> nanocrystals was set at 250 °C for 1 min. (heating rate: 10 °C/min.) After that, the colloidal solution was cooled to room temperature by removing heating mantle. The colloidal solution was mixed with ethanol and the particles were precipitated through centrifugation at 4000 rpm for 15 min. The precipitate was redispersed in hexane and chloroform for further characterization. The dispersed nanocrystals were drop-casted into a carbon-coated Transmission Electron Microscopy (TEM) grid for further characterizations.

**Characterization:** The low-resolution TEM were taken on a JEOL 100CX transmission electron microscope with an acceleration voltage of 100kV. Carbon coated copper grids were dipped in the hexanes or toluene solutions to deposit nanocrystals onto the film. High resolution TEM images (HRTEM) pictures were taken using a Taitan microscope with an acceleration voltage of 300KV. X-ray powder diffraction (XRD) patterns were obtained using a Philips PW1830 X-ray diffractometer. Energy-Dispersive Spectroscopy (EDS): For elemental analysis, a Taitan F30ST (FEI) with a field emission gun operated at 300 kV equipped with an EDAX spectrometer with a Si/Li detector. Optical Measurements: UV-vis spectra were recorded on an HP8453 UV-visible spectrophotometer. Photoluminescence (PL) spectra were taken using a Spex Fluorolog-3 fluorometer.

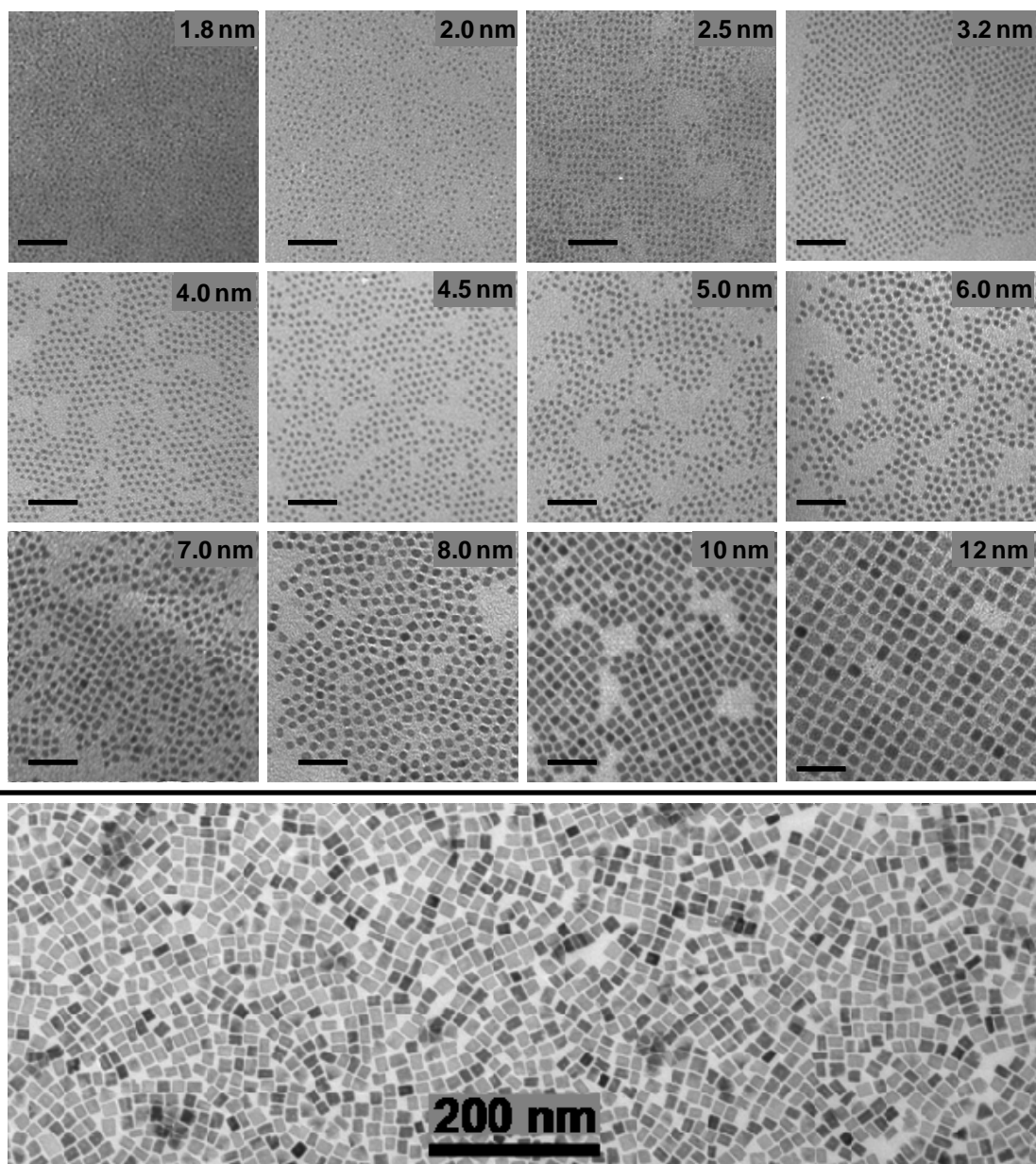


Figure S 1. TEM images of as –prepared  $\text{Cd}_3\text{P}_2$  nanocrystals with various sizes. No size selection was employed for all the samples. The scale bar is 50 nm. (top panel). TEM images of  $\text{Cd}_3\text{P}_2$  nanocrystals with large sizes (20 nm in length). (bottom panel)

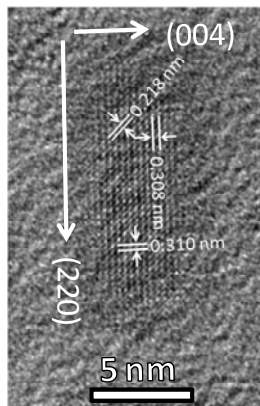
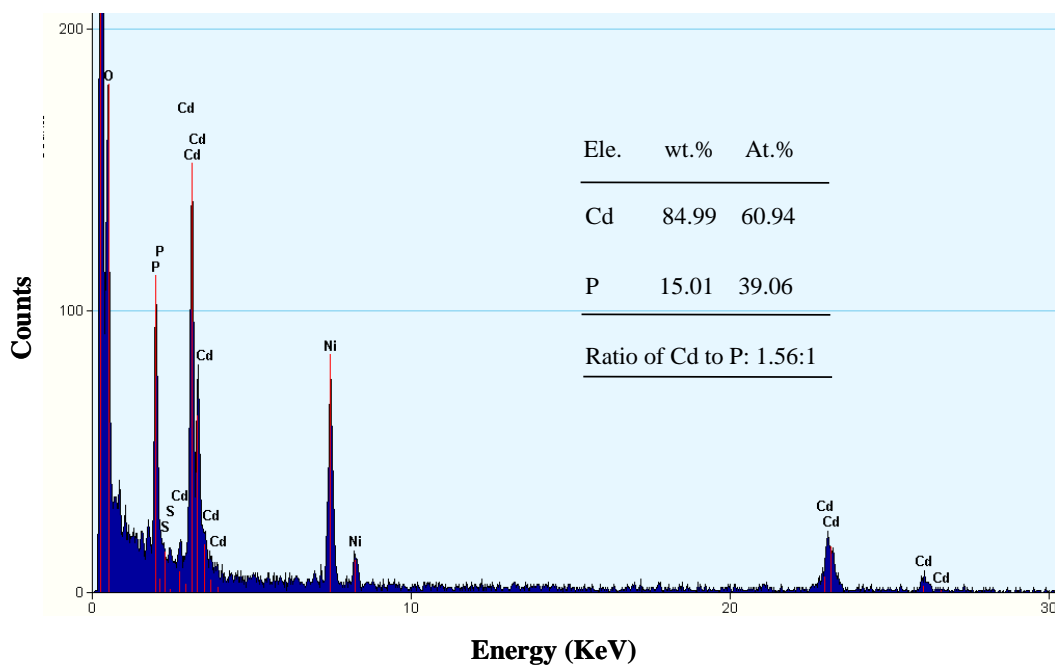


Figure S2. HR-TEM image of Cd<sub>3</sub>P<sub>2</sub> nanocrystals.



**Figure S3** Energy dispersive X-ray Spectrum of the as-prepared 12 nm Cd<sub>3</sub>P<sub>2</sub> nanocrystals. The inset illustrates the composition of the sample.

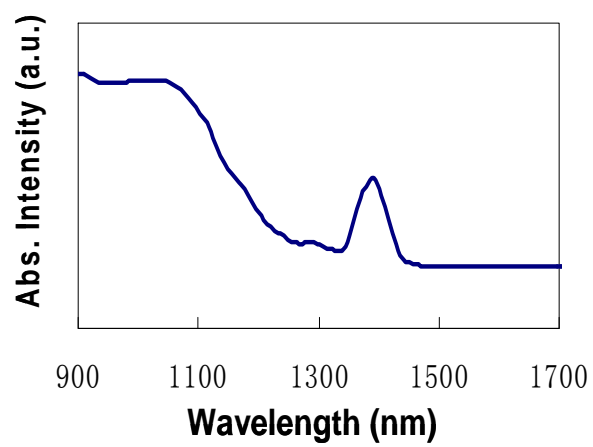


Figure S4. UV-Vis –NIR spectra of Cd<sub>3</sub>P<sub>2</sub> nanocrystals.

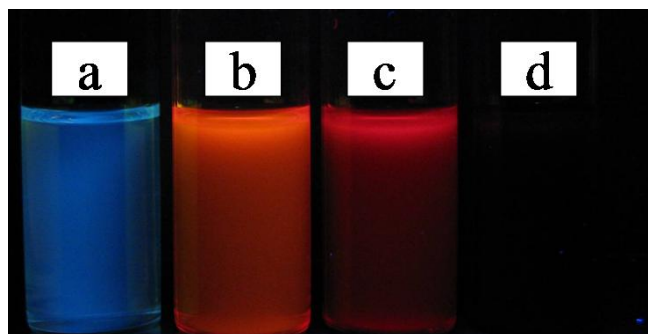


Figure 5. A photograph of several samples emitting from blue to NIR.