

*Supporting Information*

## **Confined Synthesis of CdSe Quantum Dots in the Pores of Metal-Organic Frameworks**

Takuo Wakaoka<sup>1</sup>, Kenji Hirai<sup>2</sup>, Koji Murayama<sup>1</sup>, Yoshihiko Takano<sup>1</sup>, Hiroshi Takagi<sup>1</sup>, Shuhei Furukawa<sup>2</sup>, Susumu Kitagawa<sup>2</sup>

<sup>1</sup>*Murata Manufacturing Co., Ltd., Nagaokakyo-shi, Kyoto 617-8555, Japan*

<sup>2</sup>*Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan*

## **Contents**

|   |              |
|---|--------------|
| <b>Experimental procedures</b>  | <b>3–4</b>   |
| <b>Analytical methods</b>   | <b>5</b>     |
| <b>XRD measurements of PCPs</b>   | <b>6–7</b>   |
| <b>STEM and EDS images of PCPs</b>  | <b>8–13</b>  |
| <b>Photoluminescence</b>  | <b>14–15</b> |
| <b>QD calculations – The size and surface atom ratios of CdSe nanoparticles</b> | <b>16–17</b> |

## Reactants and solvents

Trimethyl 1,3,5-benzenetricarboxylate (3CH<sub>3</sub>BTC), 2-amino terephthalic acid (NH<sub>2</sub>BDC), CdO, and octadecene were purchased from Sigma-Aldrich. N,N-dimethylformamide (DMF) was purchased from Wako Pure Chemical Industries. AlCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, and stearic acid were purchased from Nacalai Tesque. Selenium was purchased from Kojundo Chemical Laboratory. Tributylphosphine was purchased from Kanto Chemical. Unless otherwise noted, all chemicals were used as received and without further purification.

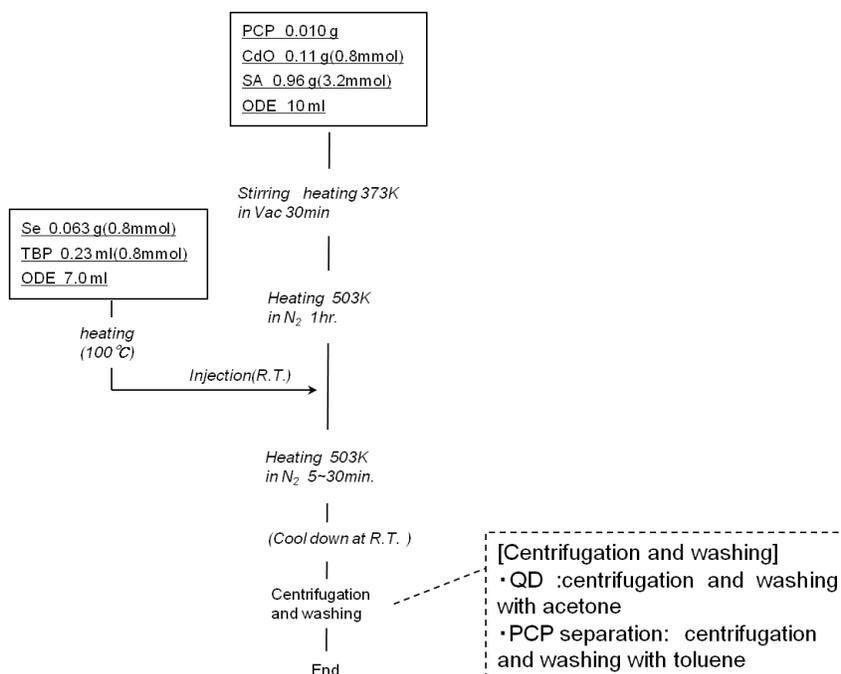
## Synthesis of PCPs

MIL-101(Al)-NH<sub>2</sub> was synthesised by solvothermal treatment using DMF as a solvent. The starting reactants were 0.51 g AlCl<sub>3</sub>·6H<sub>2</sub>O, 0.56 g NH<sub>2</sub>BDC, 30 mL DMF. The reactants were placed in a Teflon<sup>®</sup>-lined autoclave and heated for 72 h at 403K in an oven under static conditions. The resulting yellow powder was filtered under vacuum and washed with acetone. To remove organic species trapped within the pores, the samples were activated in boiling methanol overnight and stored at 373K.

MIL-100(Fe) was synthesised by solvothermal treatment using water as a solvent. A mixture of 0.16 g FeCl<sub>3</sub>·6H<sub>2</sub>O and 0.14 g 3CH<sub>3</sub>BTC, dispersed in 5 mL of water, was heated for 3 days at 403K in a Teflon-lined autoclave. The resulting orange solid was recovered by filtration, washed with acetone, and dried in air.

## Quantum dot growth in PCPs

Figure S1 shows the process used to grow confined quantum dots (QDs) in the pores of PCPs. The PCPs were added to a Cd precursor solution containing CdO and stearic acid, a complexing agent, in octadecene. The mixture was heated to 503K. To form the initial CdSe nucleus, a Se precursor solution, composed of Se and tributylphosphine as a complexing agent in octadecene, was quickly injected into the Cd solution containing the PCPs. The resulting mixture was cooled by injection of the room-temperature precursor solution. The mixture was heated to 503K and maintained for a prescribed time. After the prescribed time, the mixture was cooled to room temperature and the PCPs were washed and precipitated from the solution.



**Figure S1.** Quantum dot (QD) fabrication in PCP pores.

## **TEM, STEM, and EDS measurements**

Transmission electron micrographs (TEM) were acquired with JEM-2200FS and HITACHI HD-2300A instruments. TEM-energy dispersive X-ray spectroscopy (EDS) measurements were performed on JED-2300T and Genesis XM4 machines.

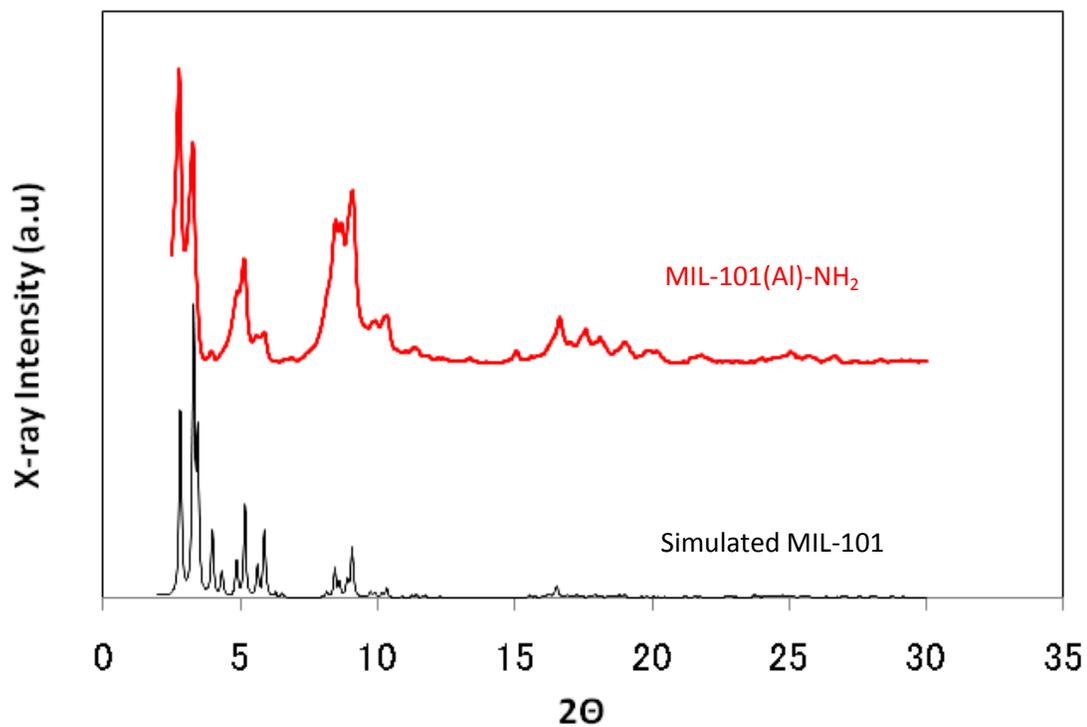
Cross-sectional PCP micrographs were obtained from thin layers of resin-impregnated powder samples cut on an ultramicrotome.

## **Optical analyses**

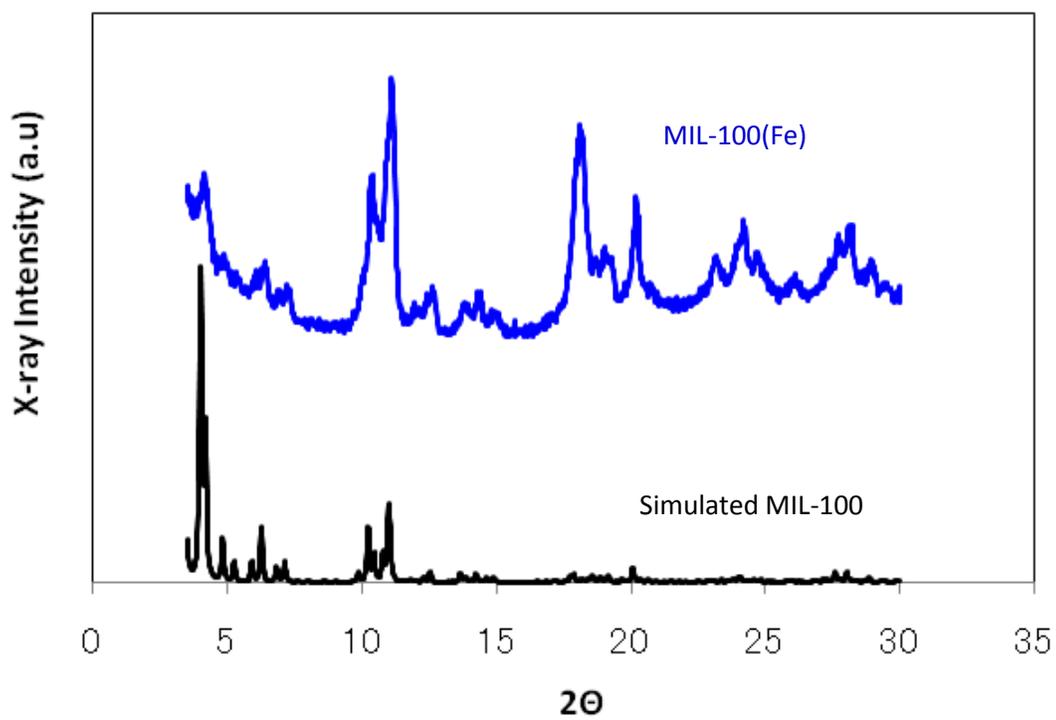
Photoluminescence (PL) of PCP suspensions with dispersed CdSe QDs was measured using a C9920-02 Absolute PL quantum yields measurement system (HAMAMATSU photonics). This system comprises a 150-W Xe lamp excitation light source, a monochromator, an integrating sphere, and a CCD spectrometer, which allows for simultaneous detection of the whole spectral range. Measurements can be acquired from liquid samples in a quartz cell, powders on a tray, and films on a substrate with any excitation wavelength from 250 to 800 nm. The PL spectra of PCPs with CdSe QDs were acquired from sample liquids and films at room temperature.

Low-temperature PL was measured using an instrument built in our laboratory, comprising a He-Cd laser excitation source (KIMMON electric, 325 nm, max 45 mW), vacuum chamber with a sample stage capable of cooling to 12K via cryostat, monochromator (Instruments SA , TRIAX series 320) capable of scanning wavelengths using a wire, mechanical chopper, lock-in amplifier, and photomultiplier (HAMAMATSU photonics, R636-10).

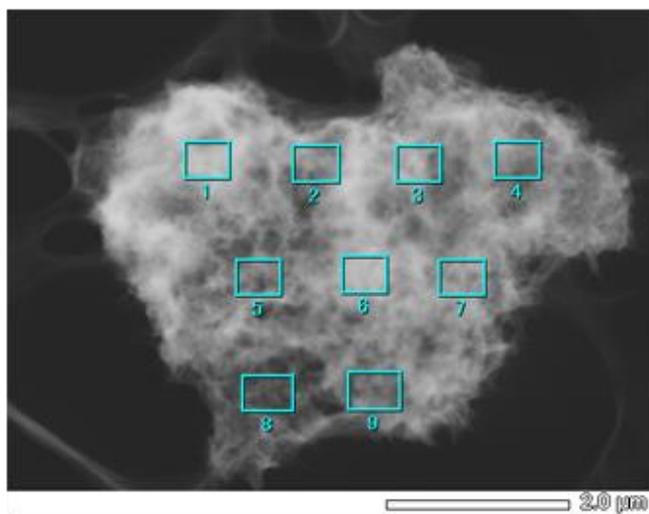
Samples were prepared as follows. Precipitate containing PCPs with aggregated QDs was placed on Si substrates and dried under vacuum. The excitation laser was mechanically chopped and incident on the sample. PL intensity was detected at the photomultiplier via the lock-in amplifier, and data were recorded on a PC.



**Figure S2.** X-ray diffraction (XRD) diffractograms (copper radiation) of samples of MIL-101(AI)-NH<sub>2</sub>.

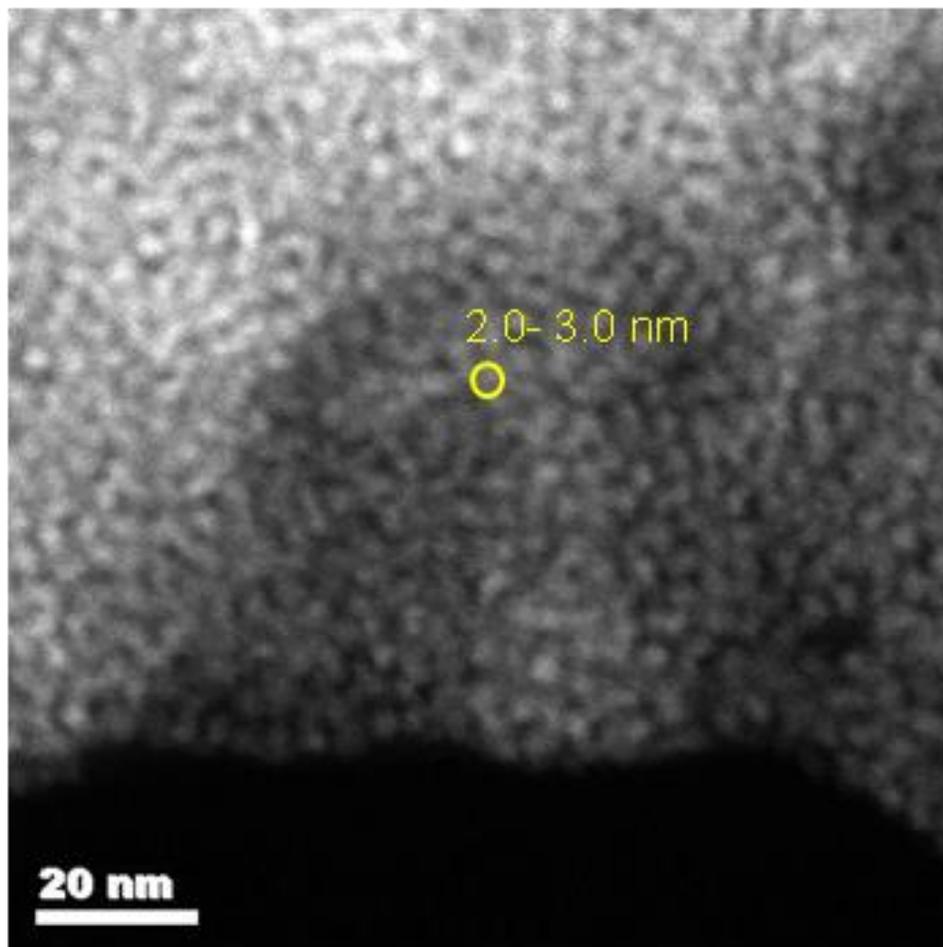


**Figure S3.** XRD diffractograms (copper radiation) of samples of MIL-100(Fe).

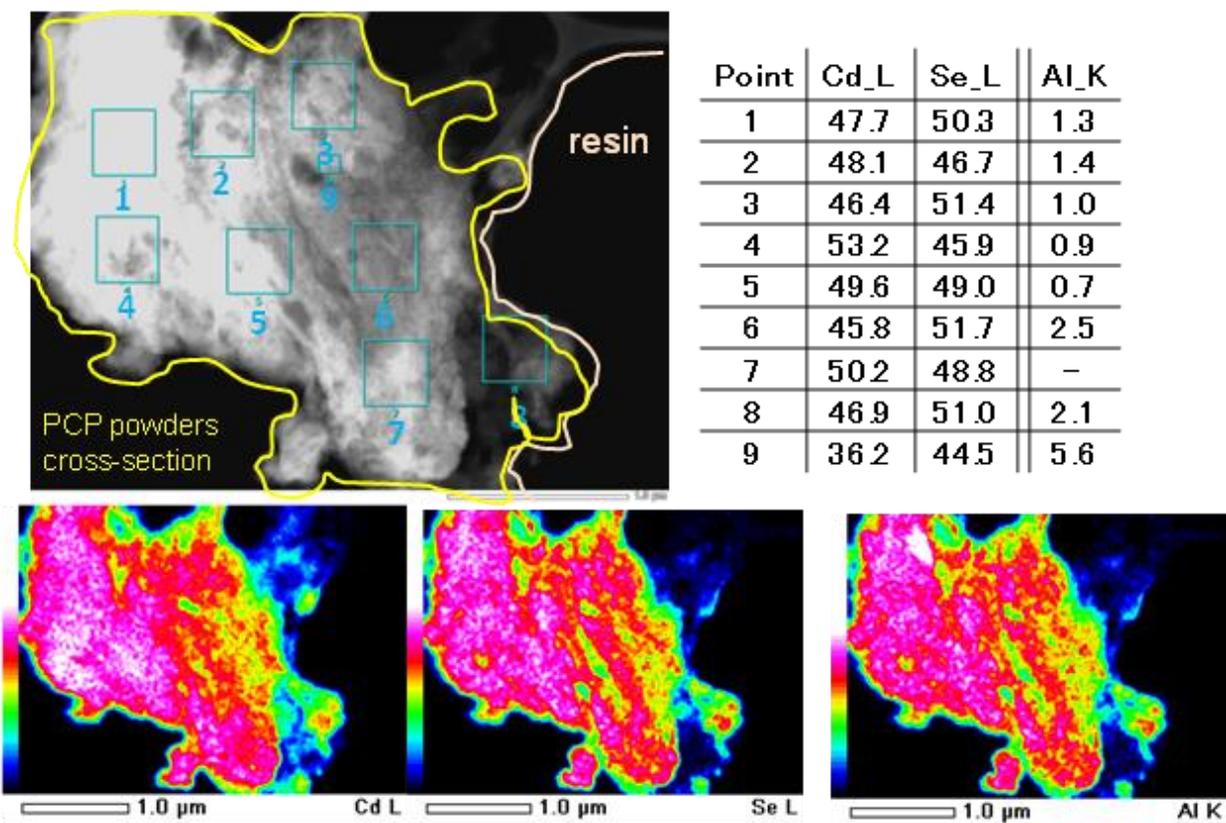


| Point | Cd_L | Se_L | Al_K |
|-------|------|------|------|
| 1     | 342  | 383  | 232  |
| 2     | 345  | 393  | 219  |
| 3     | 35.0 | 37.5 | 22.9 |
| 4     | 34.7 | 35.8 | 22.6 |
| 5     | 40.9 | 37.1 | 17.2 |
| 6     | 36.4 | 36.1 | 21.4 |
| 7     | 37.4 | 38.7 | 19.5 |
| 8     | 39.9 | 40.6 | 15.7 |
| 9     | 38.9 | 37.8 | 18.3 |

**Figure S4.** STEM-EDS image of a MIL-101 (Al)-NH<sub>2</sub> surface supporting CdSe nanoparticles.

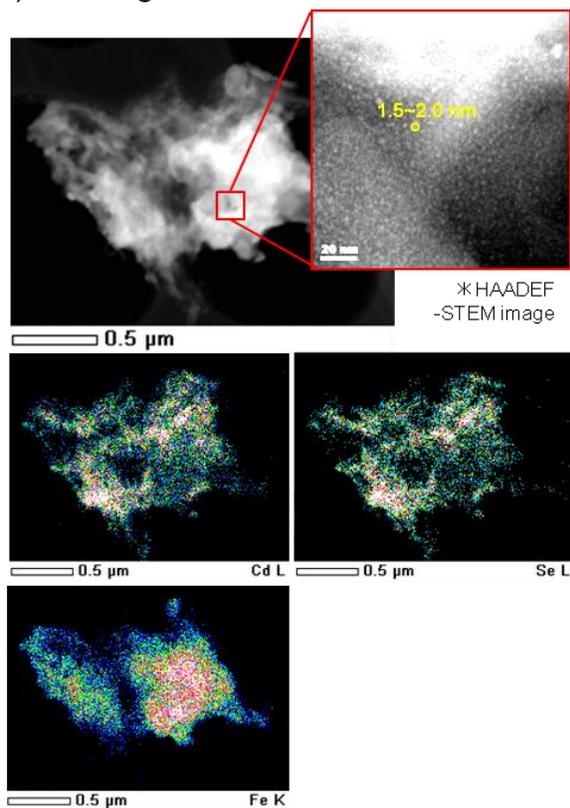


**Figure S5.** STEM image of a MIL-101 (Al)-NH<sub>2</sub> cross-section supporting CdSe nanoparticles.

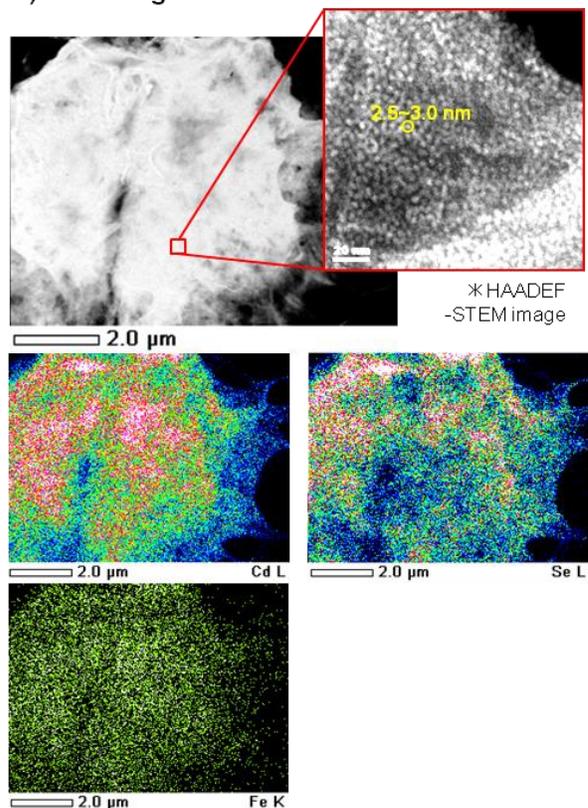


**Figure S6.** STEM-EDS images of MIL-101 (Al)-NH<sub>2</sub> cross-sections supporting CdSe nanoparticles.

a) Nuclear growth time: 5 min

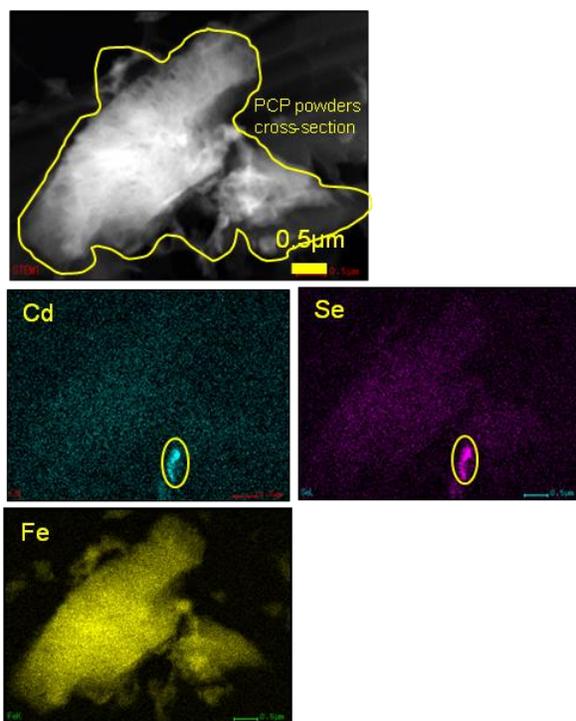


b) Nuclear growth time: 30 min

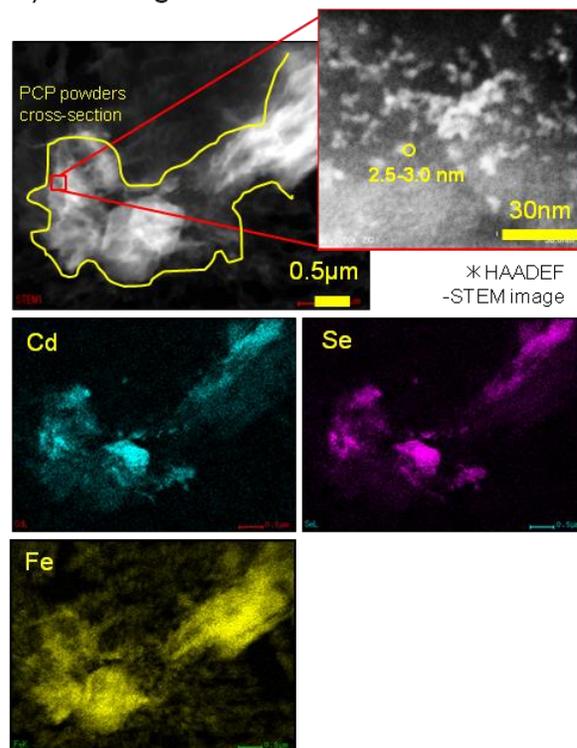


**Figure S7.** EDS images and STEM images of MIL-100 (Fe) surfaces supporting CdSe nanoparticles.

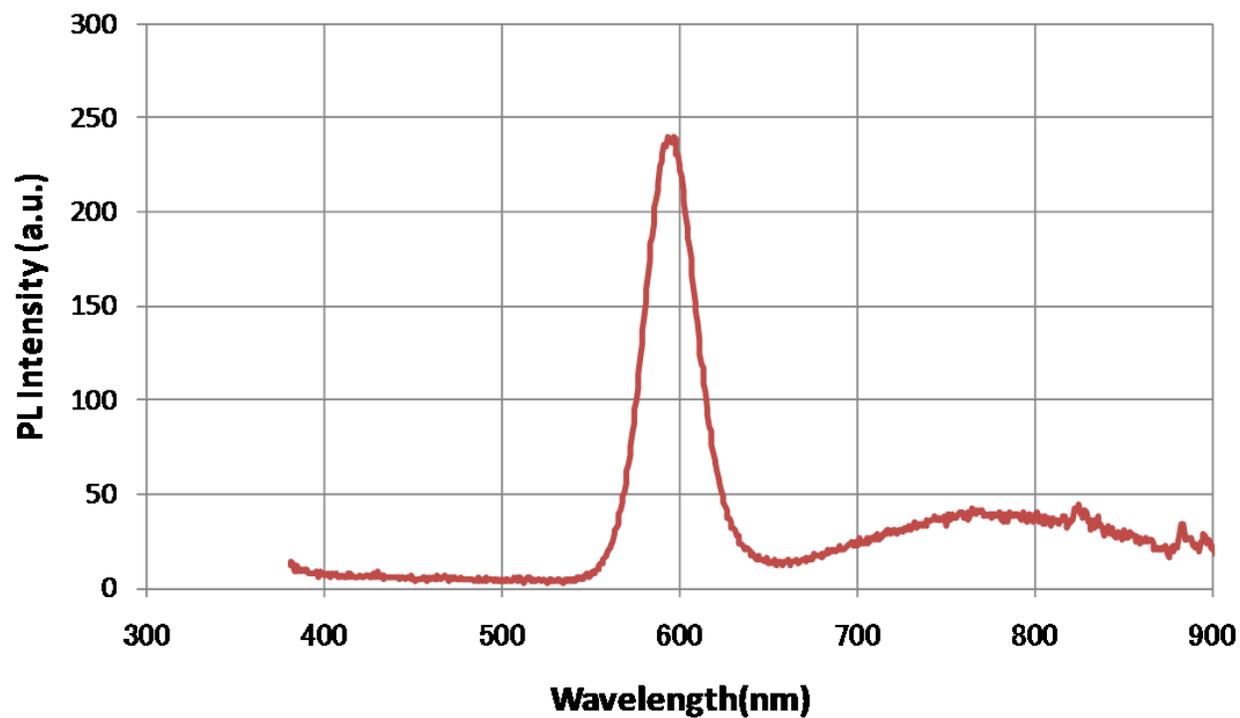
a) Nuclear growth time: 5 min



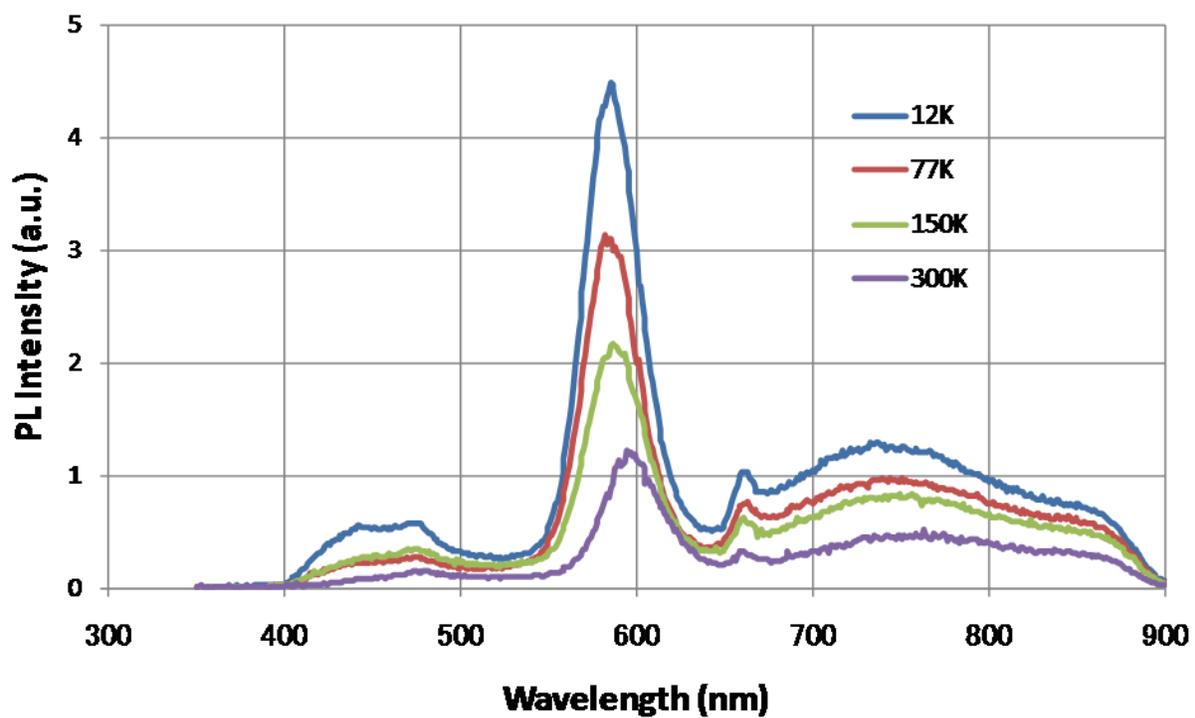
b) Nuclear growth time: 30 min



**Figure S8.** EDS images and STEM images of MIL-100 (Fe) cross-sections supporting CdSe nanoparticles.



**Figure S9.** A photoluminescence (PL) spectrum acquired at room temperature from the supernatant following separation of the PCPs. This spectrum represents the emission of QDs located outside the pores of PCPs and dispersed in solution.



**Figure S10.** PL spectra, acquired at several temperatures, of MIL-101(Al)-NH<sub>2</sub> containing supported CdSe QDs.



**Table S1.** The calculated number of Cd atoms exposed on the CdSe surface.

| CdSeparticle size(nm) | particle volume(nm <sup>3</sup> ) | the number of unit cell per a particle | the number of Cd atoms per a particle | the number of Se atoms per a particle | core size (nm) | core volume(nm <sup>3</sup> ) | the number of unit cell per a core | the number of Cd atoms per a core | the number of Se atoms per a core |
|-----------------------|-----------------------------------|--|---------------------------------------|---------------------------------------|----------------|-------------------------------|------------------------------------|-----------------------------------|-----------------------------------|
| 1.70                  | 2.57                              | 7.64                                   | 45.83                                 | 45.83                                 | 0.92           | 0.41                          | 1.21                               | 7.25                              | 7.25                              |
| 1.80                  | 3.05                              | 9.07                                   | 54.41                                 | 54.41                                 | 1.02           | 0.55                          | 1.65                               | 9.89                              | 9.89                              |

\*core is particle which except for the one atom thick surface layer (nm)

| CdSeparticle size(nm) | surface atomic ratio | Cd atoms exposed on the surface |
|-----------------------|----------------------|---------------------------------|
| 1.70                  | 84.2%                | 38.6                            |
| 1.80                  | 81.8%                | 44.5                            |