## Supplementary Information:

# Photophysical Properties of Spherical Aggregations of CdS Nanocrystals Capped with A Chromophoric Surface Agent†

**Qiong Zhang,[a] Yuanhao Gao,[a] Shengyi Zhang,[a] Jieying Wu,[a] Hongping Zhou,[a] and Jiaxiang Yang [a], Baokang Jin[a], Yupeng Tian*[,a, b, c],**

## Table of Contents

Page

## X-ray crystal structure determination for $CdS_2L$:

The single-crystal diffraction data were collected on a Bruker Apex2 CCD diffractometer with MoKα radiation using ω-scan mode ($\lambda$ = 0.71073 Å).[1] The structure was solved with direct methods using the Sir97 program and refined anisotropically with SHELXTL using the full-matrix least-squares procedure.[2] All the nonhydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL, using the full-matrix least-squares procedure. The hydrogen atom positions were geometrically idealized and allowed to ride on their atoms and fixed displacement parameters. Details of data collection and refinement are given in Table S1.

## TPA cross-section (δ)

The TPA cross sections ($\delta$) are determined by comparing their TPEF to that of fluorescein in DMF, according to the following equation [3]:

$$\delta = \delta_{ref} \frac{\Phi_{ref}}{\Phi} \frac{c_{ref}}{c} \frac{n_{ref}}{n} \frac{F}{F_{ref}}$$

Here, the subscripts *ref* stands for the reference molecule. $\delta$ is the TPA cross-section value, $c$ is the concentration of solution, $n$ is the refractive index of the solution, $F$ is the TPEF integral intensities of the solution emitted at the exciting wavelength, and $\Phi$ is the fluorescence quantum yield. The $\delta_{ref}$ value of reference was taken from the literature[4].

The squared dependence of induced fluorescence power and incident laser intensity was observed and the log–log plot of the fluorescence signal vs. excited light power provided direct evidence for two-photon excited process (**Figure S7**). However, with the increasing of incident irradiances, the power of emitting fluorescence deviated from the second-order power law and decreased gradually. This deviation may be attributed to some other nonlinear optical processes, such as stimulated emission, excited-state absorption and ground-state depletion.[5, 6]

## The fluorescence lifetime measurement

Time-resolved decay curves were measured on HORIBA HuoroMax-4P time-resolved fluorescence spectrometer. The decays were analyzed by the "least-squares". The quality of the exponential fits was evaluated by the goodness of fit ($\chi^2$).

**Table S1.** Crystal Data of **$CdS_2L$**

| | | | |
|---|---|---|---|
| crystal size(mm) | 0.21 x 0.11 x 0.09 | volume ($Å^3$) | 3447(2) |
| morphology | red blocks | *Z* | 4 |
| formula | C41 H36 Cd N4 S2 | density(g/ml) | 1.467 |
| formula weight | 761.26 | F(000) | 1560 |
| temperature/K | 173(2) | θ (min, max) | 1.07, 25.00 |
| wavelength(Å) | 0.71069 | *h,k,l* (min, max) | (-23,21), (-12,12), (-19,20) |
| crystal system | Monoclinic | no. refln measured | 23696 |
| space group | $P2_1/c$ | no.unique reflns | 6057 |
| *a* (Å) | 19.958(5) | no.of parameters | 434 |
| *b* (Å) | 10.403(5) | R_obs | 0.0739 |
| *c* (Å) | 17.406(5) | $wR_2$_all | 0.1543 |
| | | $\Delta\rho_{max}$(e $Å^{-3}$) | +1.755 |
| *β* (°) | 107.496(5) | $\Delta\rho_{min}$(e $Å^{-3}$) | -0.440 |
| | | GoF | 1.005 |

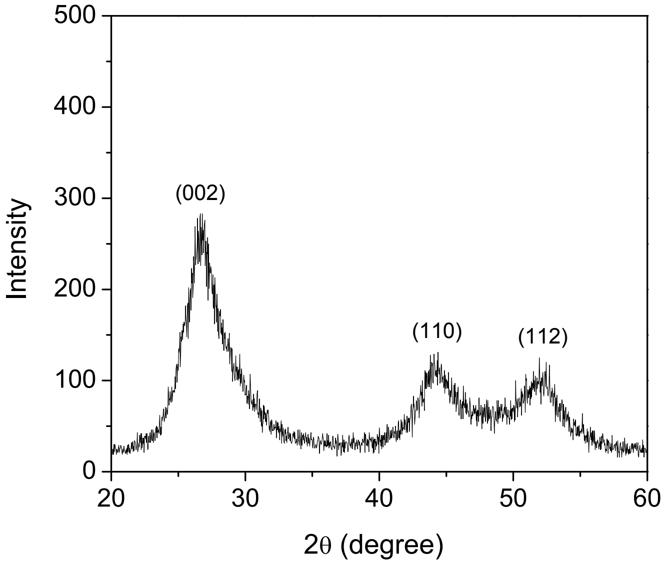

**Fig. S1.** XRD pattern of the spherical aggregates of L-capped CdS nanocrystals

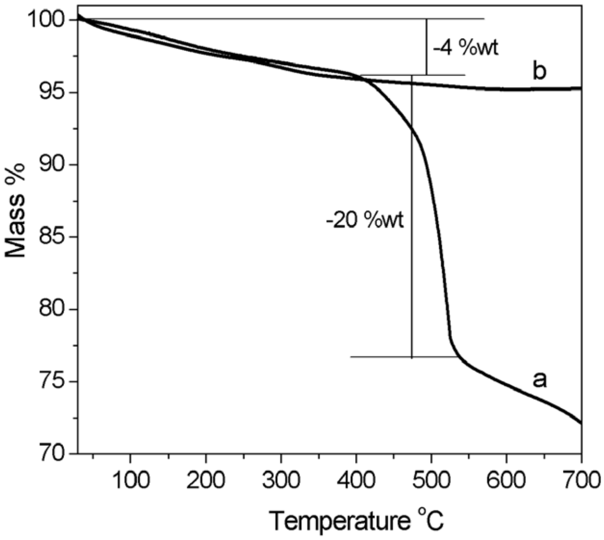

**Fig. S2.** TGA diagram: a) the spherical aggregates of L-capped CdS nanocrystals; b) pure CdS nanorods

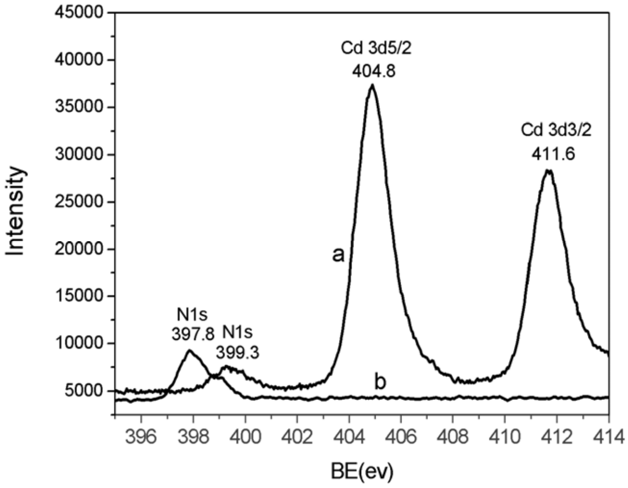

**Fig. S3.** X-ray photoelectron spectra (XPS) in the N 1s and Cd 3d regions: a) spherical aggregates of L-capped CdS nanocrystals; b) pure ligand L.

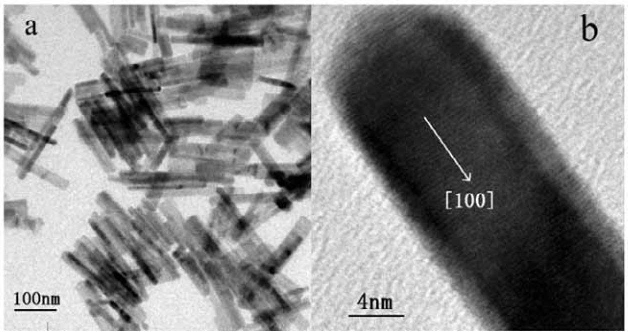

**Fig. S4** (a) TEM image of the pure CdS nanorods prepared without the L. (b) A high-resolution TEM image of CdS nanorod that shows lattice fringes perpendicular to be the (100) direction

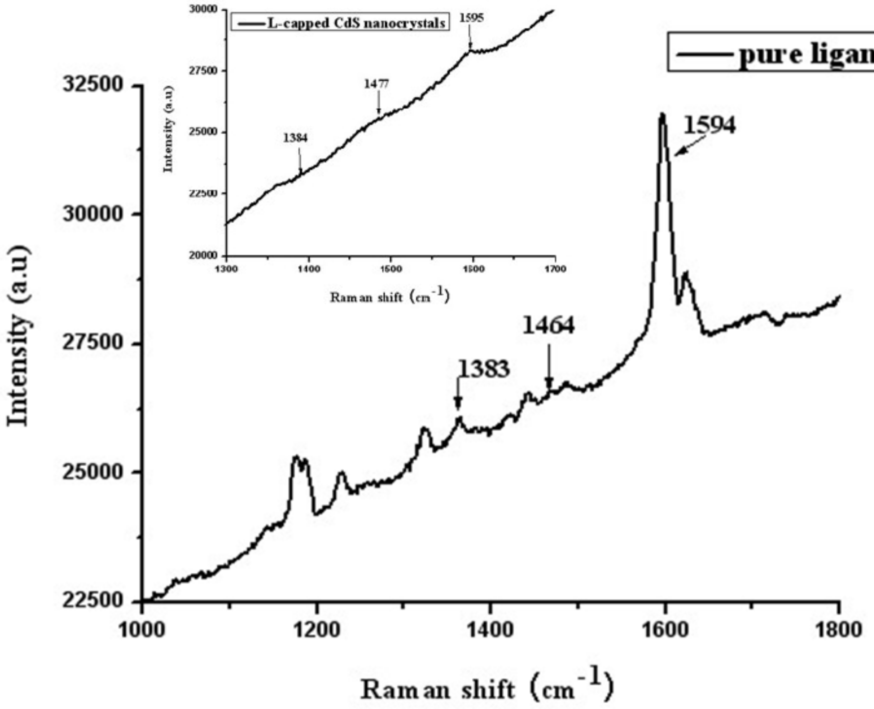

**Fig. S5** A comparison of the Raman spectra of pure ligand and L-capped CdS nanocrystals

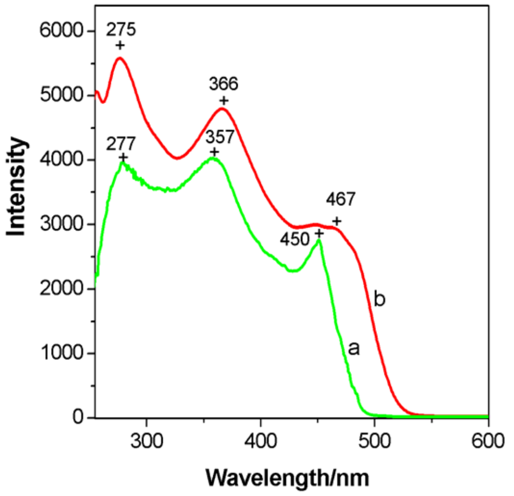

**Fig. S6** Electronic absorption spectra in solid state of a) L, and b) The spherical aggregates of L-capped CdS nanocrystals.

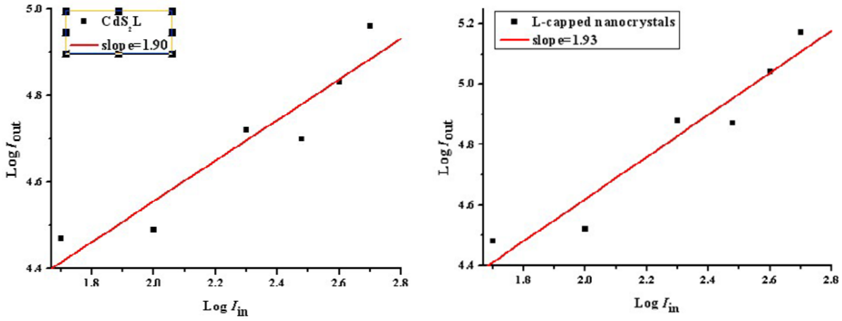

**Figure S7.** Log-Log linear of squared dependence of induced fluorescence signal of

**$CdS_2L$** and **L-capped CdS nanocrystals** in DMF solvent ($1.0 \times 10^{-3}$ mol $L^{-1}$) and incident irradiance intensity.

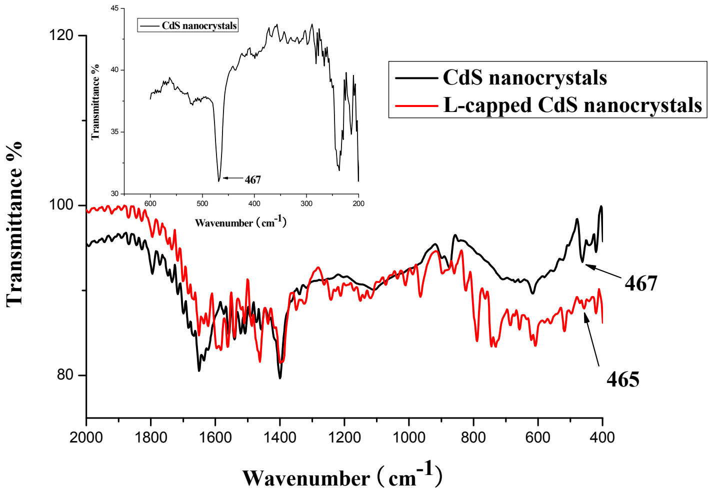

**Fig. S8** IR spectra: L-capped CdS nanocrystals and CdS nanocrystals. Inset figure: Far-IR spectrum of CdS nanocrystals.

## References

(1) Bruker (2005), APEX2 Software Suite (Version 2.0-2), Bruker AXS Inc., Madison, Wisconsin, USA.

(2) a) Bruker (1997), SHELXTL, Structure Determination Programs. Version 5.1, Bruker AXS, Inc., Madison, Wisconsin, USA; b) Farrugia, L. J. *J. Appl. Cryst.* 1999, **32**, 837-838; c) G. M. Sheldrick, (1997) SHELX97, Programs for Crystal Structure Analysis (Release 97-2), University of Gotingen, Germany.

(3) Xu C, Webb WW. Measurement of two-photon excitation cross sections of molecular fluorophores with data from 690 to 1050 nm. J. Opt. Soc. Am. B 1997; 13:481-491.

(4) Varnavski O, Goodson T, Sukhomlinova L, Twieg R. Ultrafast exciton dynamics in a branched molecule investigated by time-resolved fluorescence, transient absorption, and three-pulse photon echo peak shift measurements. J. Phys. Chem. B 2004;

108:10484-10492.

(5) Xu, C.; Zipfel, W.; Shear, J. B.; Williams, R. M.; Webb, W. W. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 10763–10768.

(6) Picot, A.; Malvolti, F.; Le Guennic, B.; Baldeck, P. L.; Williams, J. A. G.; Andraud, C.; Maury, O. *Inorg. Chem.* **2007**, *46*, 2659–2665.