Electronic Supplementary Material (ESI) for Faraday Discussions.


# Supporting Information

## Optical Anisotropy and Sign Reversal in Layer-by-Layer Assembled Films from Chiral Nanoparticles

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The size of CdS NPs was determined by TEM measurements, as shown in Figure S1, the size of CdS-D and CdS-L is about 3 nm.

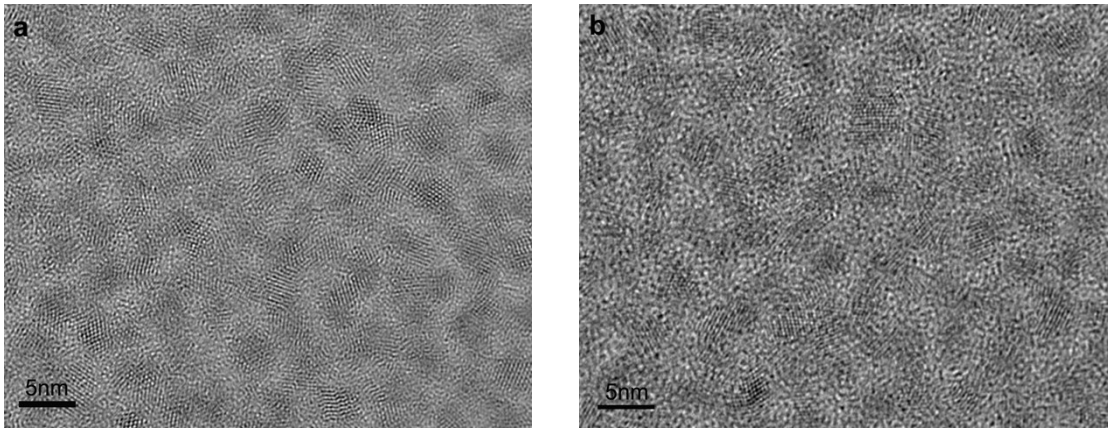


**Figure S1**. TEM images of (a) CdS-D and (b) CdS-L

**Additional data on LBL deposition of film**

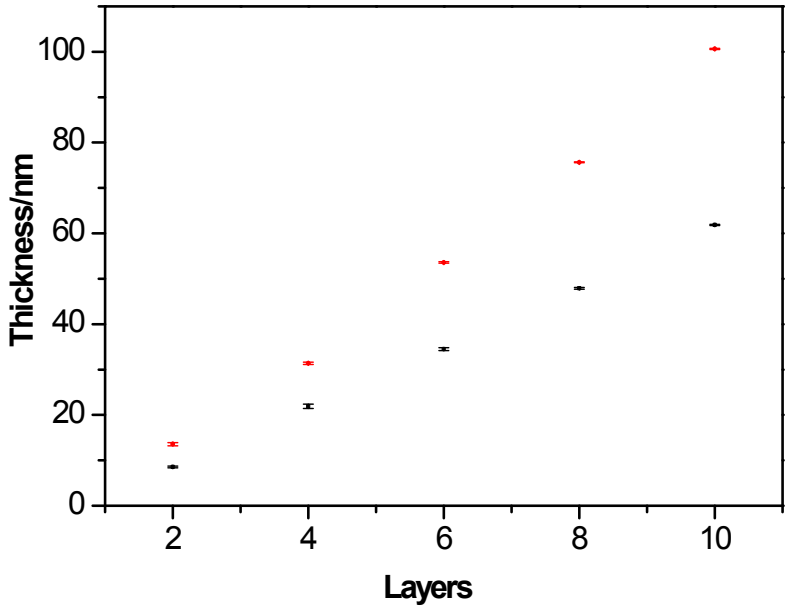


**Figure S2.** Thickness dependence of $D_n$ (black) and $L_n$ (red) films on number of layers

**Calculations of Chirooptical Activity of the Films under assumption that experimentally measure polarization rotation primarily originates from interactions of incident photons with chiral NPs.**

From Lambert-Beer's Law, one can define a molar absorption

$$\Delta\varepsilon = \frac{\Delta A}{c \cdot b} \qquad (1)$$

Which is independent of the concentration $c$, expressed in mol·L$^{-1}$, and of the pathlength b, expressed in cm. The circular dichroism is defined as the difference $\Delta A = A^{D} - A^{L}$, where $A^{D}$ and $A^{L}$ are the absorptions of left and right circularly polarized light, respectively. The output of CD spectrometers is usually measured as ellipticity $\theta$ (in mdeg), related to $\Delta A$ through $\theta$ (mdeg)=33000$\Delta A$.

In our research, the concentration of CdS NPs in the LBL film can be expressed as

$$c = \frac{N_{NP} / NA}{V_{film}},$$

here $N_{NP}$ is the number of CdS NPs in LBL film, NA is Avogadro constant, $V_{film}$ is the volume of LBL film. For calculating c, we need to know the weight percent of

CdS NPs in LBL film, the density of CdS($\rho_{CdS}$=4.82g/cm$^3$)and PDDA($\rho_{PDDA}$=1.26 g/cm$^3$) and the volume of one CdS NPs, which can be calculated by $V_{NP}=\frac{4}{3}\pi R^3$, R can be obtained from TEM images (R=1.5nm, see Figure S1).

The TGA curves of pure PDDA and LBL films were obtained under $N_2$ flow. The data (wt%=73%) of 600℃ was used as the weight percent of CdS NPs in LBL film.

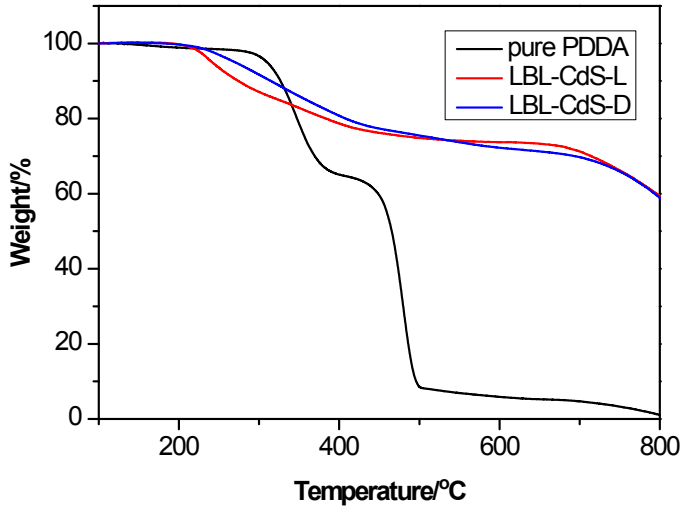


**Figure S3.** TGA curves of LBL films and pure PDDA under $N_2$ flow

$$TGA(wt\%)=\frac{M_{NPs}}{M_{NPs}+M_{PDDA}}$$
$$=\frac{\rho_{CdS}\cdot N_{NPs}V_{NP}}{\rho_{CdS}\cdot N_{NPs}V_{NP}+\rho_{PDDA}\cdot V_{PDDA}}$$
$$=\frac{\rho_{CdS}\cdot N_{NPs}V_{NP}}{\rho_{CdS}\cdot N_{NPs}V_{NP}+\rho_{PDDA}(V_{film}-N_{NPs}V_{NP})}$$
$$=\frac{\rho_{CdS}\cdot N_{NPs}}{V_{NP}(\rho_{CdS}-\rho_{PDDA})+\rho_{PDDA}\frac{V_{film}}{N_{NPs}}}$$

$$\therefore \frac{V_{film}}{N_{NPs}}=\frac{\rho_{CdS}\cdot V_{NP}}{TGA(wt\%)\cdot\rho_{PDDA}}-\frac{V_{NP}(\rho_{CdS}-\rho_{PDDA})}{\rho_{PDDA}}$$

$$=\frac{4.82\times\frac{4}{3}\pi\times(1.5\times10^{-9})^3}{0.73\times1.26}-\frac{\frac{4}{3}\pi\times(1.5\times10^{-9})^3\times(4.82-1.26)}{1.26}$$
$$=34.14\times10^{-27}m^3$$
$$=34.14\times10^{-24}L^3$$

$$c = \frac{N_{NP} / NA}{V_{film}} = \frac{1}{34.14 \times 10^{-24} L \times 6.022 \times 10^{23} mol^{-1}} = 0.0486 mol / L$$

The path length of CE measurement in LBL films is 15 or 20 bilayers, but the thickness data listed in Table S1 is the films on silicon wafer substrate, only 15 or 20 layers, so the path length used in equation (1) should be 2 times of the thickness measured by ellipsometer. Figure S4 is SEM images of fracture surface of LBL films at 15 and 20 layers on the silicon substrate.

**Table S1. Ellipsometric and SEM thickness of prepared films.**

| Film/Cycles | Ellipsometer(nm)/SEM(nm) |
|---|---|
| $D_{15}$ | 115/115.0 |
| $D_{20}$ | 169/177.5 |
| $L_{15}$ | 135/121.6 |
| $L_{20}$ | 187/222.6 |

So, for $D_{20}$ at the wavelength of 396nm, $\theta$=2.8 mdeg, b=169nm×2=338nm=$338\times10^{-7}$ cm, c = 0.0486 mol/L

$$\Delta\varepsilon = \frac{\Delta A}{c \cdot b} = \frac{\theta}{33000 \times c \times b} = \frac{2.80368}{33000 \times 0.0486 \times 338 \times 10^{-7}} = 51.7$$

**Table S2. Δε of $D_{15}$, $D_{20}$, $L_{15}$ and $L_{20}$ at different wavelength.**

| Film | Δε($cm^{-1}M^{-1}$) /λ | |
|---|---|---|
| $D_{15}$ | -18.5 /343nm | 48.6/396nm |
| $D_{20}$ | -12.6 /343nm | 51.7/396nm |
| $L_{15}$ | 54.0/347nm | -41.2/397nm |
| $L_{20}$ | 71.5/347nm | -95.6/397nm |

**Table S3. Δε of some organic molecules and bio-molecules.**

| Samples | | λ(Δε) |
|---|---|---|
| Natural products[1] | Dendryphiellin F | 257nm(+36.9)/234nm(-19.0) |
| | Abscisic acid | 265nm(+44.3)/233nm(-36.5) |

| | | |
|---|---|---|
| | calycanthine | 259nm(+18)/240nm(-20.0) |
| | quassin | 266nm(+10.4)/242nm(-9.5) |
| | Arnottn II | 261nm(-79)/221nm(+39) |
| | vinblastine | 228nm(+31)/214nm(-73.4) |
| RNA[2] | A-form | 170nm(-25)/190nm(+33) |
| | A′ -form | 170nm(-25)/189nm(+35) |
| | A-form$(A{\cdot}U)_{20}$ | 167nm(-39)/187nm(+43) |
| | A-form$(G{\cdot}C)_{20}$ | 173nm(-20)/189nm(+47) |
| DNA[2] | A-form | 170nm(-25)/190nm(+34) |
| | B-form | 170nm(-15)/190nm(+14) |
| | B-form$(A{\cdot}T)_{20}$ | 168nm(-22)/186nm(+25) |
| | B-form$(G{\cdot}C)_{20}$ | 174nm(-17)/190nm(+22) |

**Transition Densities from TD-DFT Calculation of CdS-D.**
Details of the calculations are described in the main article. Hydrogen atoms were excluded for better visualization. Red surfaces correspond to regions with electronic density smaller than the ground state whereas while blue surfaces correspond to increased electronic density. All surfaces are plotted with an isovalue of 0.0005 *e/bohr³*. The names of the bands correspond to those used in the discussion of the experimental circular dichroism spectra (Figure 3 in the main article).

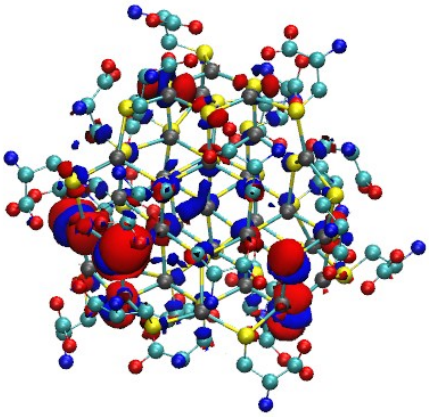

**Figure S4 –** Transition at λ=382 nm (ChiNP390 band).

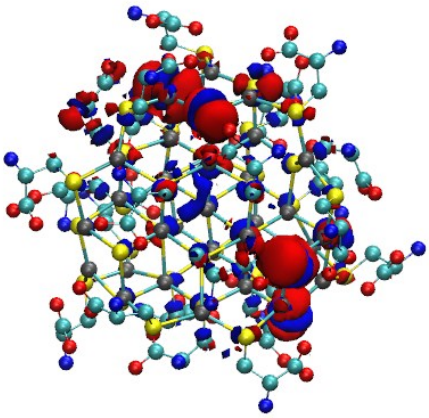

**Figure S5 –** Transition at λ=380 nm (ChiNP390 band).

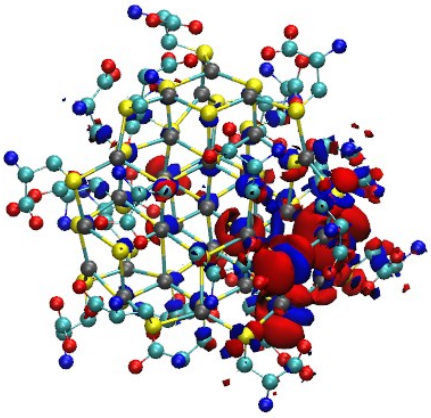

**Figure S6 –** Transition at λ=374 nm (ChiNP390 band).

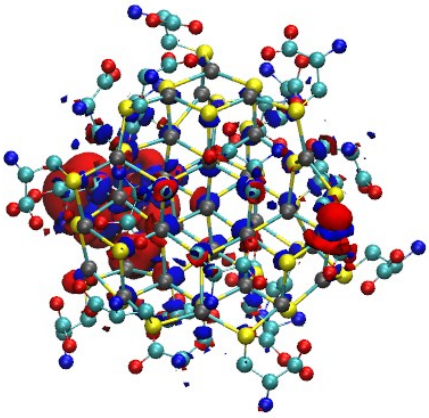

**Figure S7 –** Transition at λ=346 nm (ChiNP357 band).

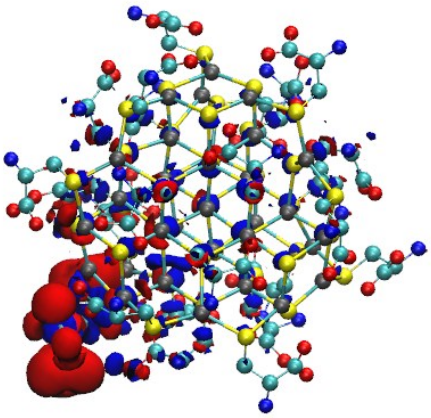

**Figure S8 –** Transition at λ=345 nm (ChiNP357 band).

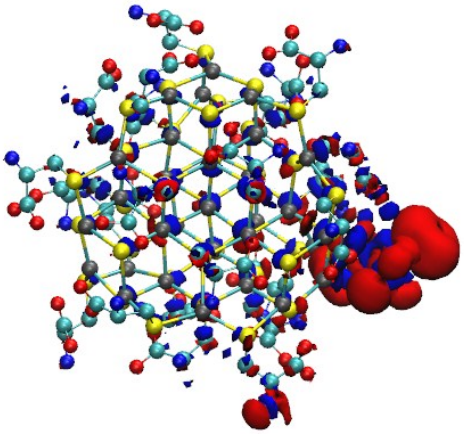

**Figure S9 –** Transition at λ=341 nm (ChiNP357 band).

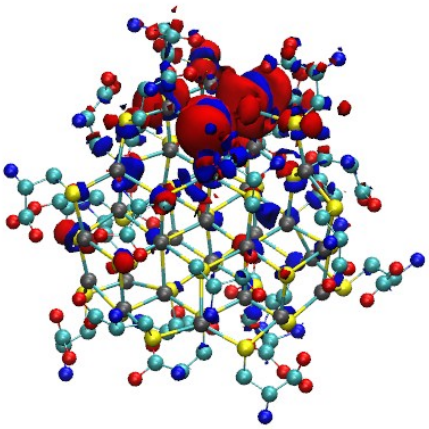

**Figure S10 –** Transition at λ=306 nm (ChiNP310 band).

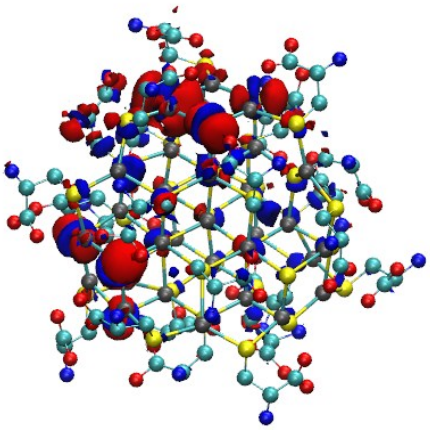

**Figure S11 –** Transition at λ=304 nm (ChiNP310 band).

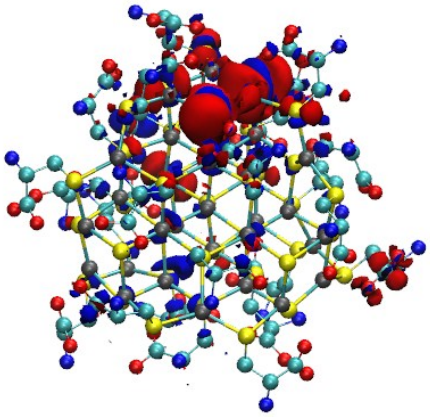

**Figure S12 –** Transition at λ=302 nm (ChiNP310 band).

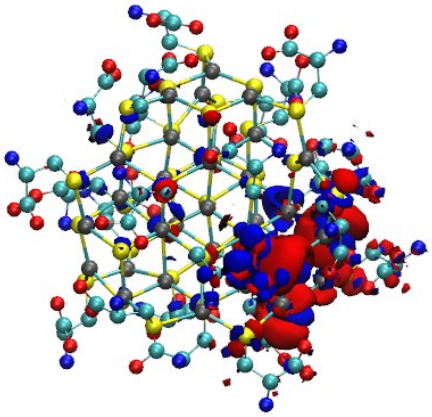

**Figure S13 –** Transition at λ=300 nm (ChiNP310 band).

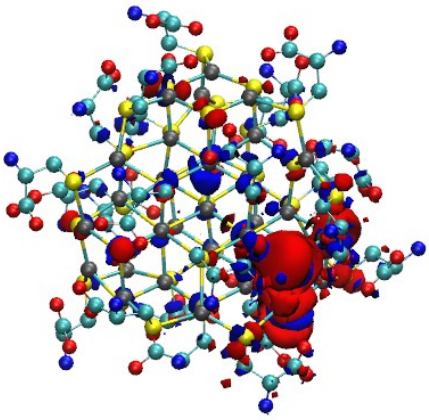

**Figure S14 –** Transition at λ=299 nm (ChiNP310 band).

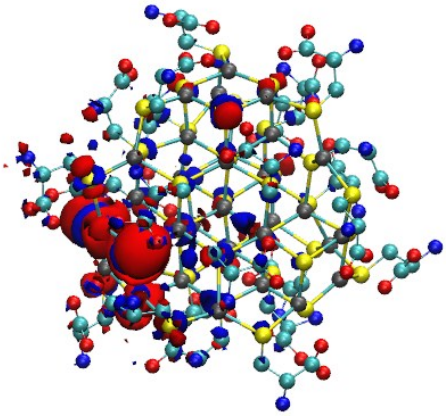

**Figure S15 –** Transition at λ=293 nm (ChiNP310 band).

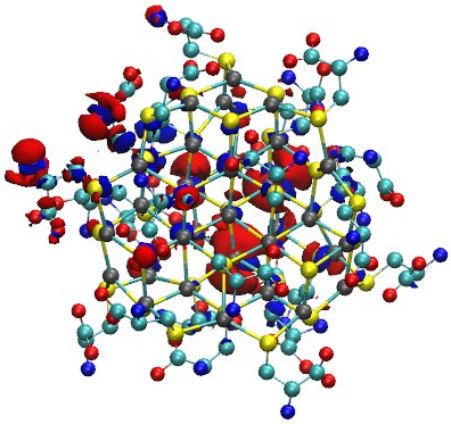

**Figure S16 –** Transition at λ=292 nm (ChiNP310 band).

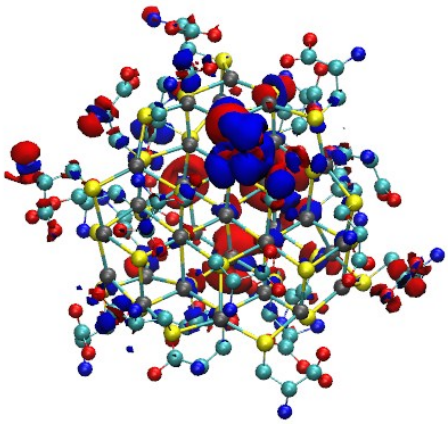

**Figure S17 –** Transition at λ=290 nm (ChiNP290 band).

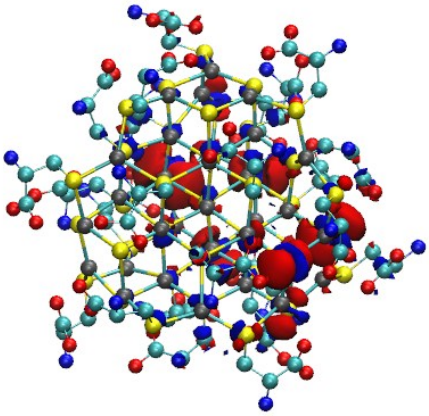

**Figure S18 –** Transition at λ=289 nm (ChiNP290 band).

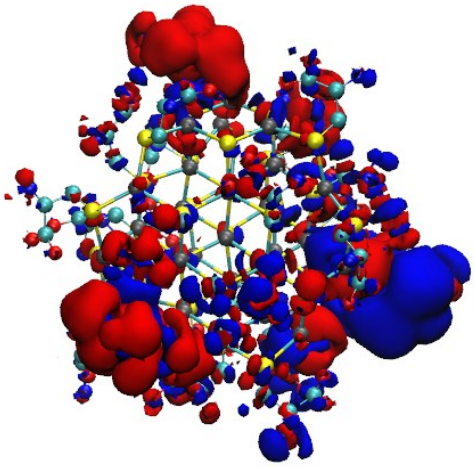

**Figure S19 –** Transition at λ=281 nm (ChiNP290 band).

**REFERENCES**


1. Berova, N.; Bari, L. D.; Pescitelli, G. Application of Electronic Circular Dichroism in Configurational and Conformational Analysis of Organic Compounds. *Chem. Soc. Rev.*, **2007**, 36, 914-931.
2. Rizzo, V.; Schellman, J. A. Matrix-Method Calculation of Linear and Circular Dichroism Spectra of Nucleic Acids and Polynucleotides. *Biopolymers.* **1984**, 23, 435-470.