

Supplementary information for

Thermomechanically Controlled Fluorescence Anisotropy in Thin Films of InP/ZnS Quantum Dots

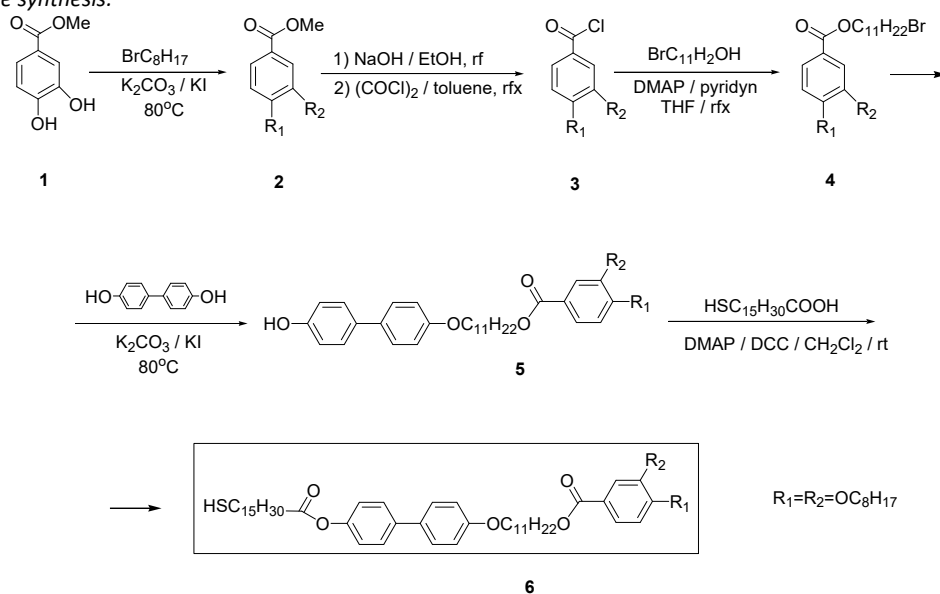
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Supplementary Note 1. InP/ZnS QDs Synthesis: Tessier et al. protocol was modified and 100 mg (0.45 mmol) indium (III) chloride (Sigma Aldrich, 99.999% trace metal basis), 300 mg (2.2 mmol) zinc chloride (Sigma Aldrich, 99.999% trace metal basis), and 5 ml OAm (Acros, 80-90% grade) was mixed in a three-necked flask, and heated to 120°C for 1h in vacuum conditions. Then nitrogen flow was opened and the temperature increased to 180°C. 0.45 ml of tris(diethylamino)phosphine ((DEA)₃P, Sigma Aldrich, 97%) was swiftly injected. After 20 min 1 ml of sulfur stock solution (360 mg of sulfur powder (Sigma Aldrich, ≥99.0%) in 5 ml of trioctylphosphine (TOP, Sigma Aldrich, 97%), sonicated) was added dropwise. After 40 min the temperature increased to 200 °C, and after the next 60 min zinc stock solution (1 g zinc stearate (Sigma Aldrich, technical grade) suspended in 4 ml 1-octadecene (ODE, Alfa Aesar, 90%)) was added dropwise and the temperature increased to 220°C. After 30 min 0.7 ml of sulfur stock solution was injected, and the temperature increased to 240°C. After 30 min 2 ml of zinc stock solution (0.5 g zinc stearate suspended in 2 ml ODE) was added and the temperature increased to 260°C. The reaction was stopped after 30 min by cooling down at room temperature.

20 ml of toluene (used as received) was added to the reaction mixture and centrifuged (7 000 rpm for 5min) to remove an excess of organic compounds. Then, QDs aggregate was dispersed in toluene and a portion of acetone (antisolvent for QDs) was added. Then, the dispersion was centrifuged (7 000 rpm for 5min) yielding a fraction of size-focused QDs. The procedure for size fractioning was repeated by adding additional portions of acetone and consecutive centrifugations. The size of QDs inorganic core was estimated to be 2.8 nm diameter based on small-angle x-ray scattering studies (assuming a spherical shape of the scattering object) and transmission electron microscopy (Figure 1b in the main text). Due to the small size of QDs, their tendency to form isotropic phase when drop casted onto a solid substrate (as evidenced with small-angle x-ray diffraction studies, Figure S1b), and ability to fit x-ray scattering data assuming a spherical shape of scattering nanobjects, we refer to these QDs as quasi-isotropic.

Supplementary Note 2. L synthesis.

Scheme of the synthesis:



Materials: All reactants were bought from Sigma-Aldrich and used without further purification. Solvents were dried over molecular sieves before use.

Synthesis of the 3,4-bis-octyloxy-benzoic acid methyl ester (2):

Into the solution of 15g (0.89mol) of methyl 3,4-dihydroxybenzoate (1) in 300ml of DMF, a 30.8g (0.22mol) of anhydrous K₂CO₃ and 37g (0.22mol) of KI was added. Next 43g (0.22mol) of 1-bromooctane was added dropwise. The mixture was vigorously stirred at a temperature of 80°C for 24h. After cooling to room temperature the mixture was poured into 1 L of cold water with ice. The precipitate was filtrated and recrystallized from ethanol. The product was purified by column chromatography with chloroform as an eluent to yield 18 g (96%) of a white solid.

¹H NMR: (300MHz, CDCl₃) δ: 7,63 (1H; dd; J=8,3Hz; J=2Hz); 7,53 (1H; d; J=2Hz); 6,86 (1H; d; J=8,3Hz); 4,11 – 3.96 (4H; m); 3,88 (3H; s); 1,94 – 1,73 (4H; m); 1,59 – 1,18 (20H; m); 1.0 – 0.8 (6H; m).

Synthesis of the 3,4-bis-octyloxy-benzoyl chloride (3):

18.3g (0.046 mol) of NaOH diluted in 10ml of distillate water was added in portions to the mixture of 18 g (0.46 mol) of compound **2** in 250 ml of ethanol. The reaction mixture was stirred under reflux for 12h. After cooling to room temperature the precipitate was filtrated and dried under vacuum for 24h to give 17.2g (95%) of a white solid. 10g (25 mmol) of the dry, crude product was dissolved in anhydrous toluene. Then, 10 ml (0.17 mol) of oxalyl chloride was added dropwise. The reaction mixture was stirred under reflux for 8h; then, it was cooled to room temperature and filtrated to separate inorganic wastes. The solution was concentrated to give a bright yellow residue which was dried under vacuum and used in the next reaction without further purification. Yield 10.3g (100%).

Synthesis of the 3,4-bis-octyloxy-benzoic acid 11-bromo-undecyl ester (4):

2 ml of anhydrous pyridine and a catalytic amount of dimethylamine pyridine (DMAP) was added to the solution of 1.5g (6 mmol) of 11-bromoundecan-1-ol in 10 ml of anhydrous THF. Next, the solution of 2g (5 mmol) of compound **3** was added dropwise. The mixture was stirred at 70°C for 16h. The solvent was removed and the residue was purified by column chromatography (eluent - toluene) and crystallized from ethanol to yield 1.5 g (60%) of a white solid.

¹H NMR: (300MHz, CDCl₃) δ: 7,63 (1H; dd; J=8,3Hz; J=2Hz); 7,53 (1H; d; J=2Hz); 6,86 (1H; d; J=8,3Hz); 4,28 (2H; t; J=6,9Hz); 4,11 – 3.96 (4H; m); 3,40 (2H; t; J=6,1Hz); 1,94 – 1,73 (4H; m); 1,59 – 1,18 (20H;m); 1.0 – 0.8 (6H; m).

Synthesis of the 3,4-bis-octyloxy-benzoic acid 11-(4'-hydroxy-biphenyl-4-yloxy)-undecyl ester (5):

0.9g (6.5 mmol) of K₂CO₃ and 1.1g (6.5 mmol) KI were added to the solution of 1g (5.5 mmol) of 4,4'-biphenol in 100 ml of dimethylformamide (DMF). Next, 1.6g (2.2 mmol) of compound **9** dissolved in DMF was added dropwise. The reaction mixture was stirred at 80°C for 24h. After cooling down to room temperature the mixture was poured into the water with ice. The precipitate was filtrated and dried under the vacuum. The crude product was purified by column chromatography (eluent - toluene) to give 790 mg (50%) of a white solid.

¹H NMR: (300MHz, CDCl₃) δ: 7,63 (1H; dd; J=8,4Hz; J=1,8Hz); 7,54 (1H; d; J=1,8Hz); 7,48-7,38 (4H; m); 6,93 (2H; d; J=8,7Hz); 6,91 – 6,83 (3H; m); 4,99 (1H, br, s,) 4,28 (2H; t; ; J=6,9Hz); 4,09 – 4,01 (4H; m); 3,98 (2H; t; ; J=6,6Hz); 1,91 – 1,69 (8H; m); 1,53 – 1,4 (8H;m); 1,4 – 1,2 (26H;m); 0,94 – 0,81 (6H; m). ¹³C NMR (75MHz, CDCl₃) δ 166.48; 158.4; 154.8; 153.27; 148.6; 133.8; 133.3; 128.0; 127.8; 123.6; 122.9; 115.72; 114.89; 114.47; 112.05; 69.44; 69.16; 68.22; 65.09; 31.96; 29.67; 29.51; 29.48; 29.39; 29.31; 29.2; 28.91; 26.19; 26.15; 22.81; 14.24.

Synthesis of the 3,4-bis-octyloxy-benzoic acid 10-[4'-(16-mercapto-hexadecanoyloxy)-biphenyl-4-yloxy]-decyl ester (6):

0.18g (0.62 mmol) of 16-mercaptohexadecanoic acid and a catalytic amount of DMAP were added to the solution of 0.4g (0.57 mmol) of compound **5** in 40 ml of dry CH₂Cl₂. Next, 0.14g (0.69 mmol) of dicyclohexylcarbodiimide (DCC) was added. The reaction mixture was stirred at room temperature for 12h. The precipitate was filtrated and the filtrate was evaporated to dryness. The crude product was purified by column chromatography (eluent - toluene) to give 390 mg (70%) of a white solid.

¹H NMR: (300MHz, CDCl₃) δ: 7.63 (1H, dd, J₁=2.1 Hz, J₂=8.4 Hz); 7.57 – 7.50 (3H, m); 7.47 (2H, d, J=9.0Hz); 7.11 (2H, d, J=8.7 Hz); 6.95 (2H, d, J=8.7 Hz); 6.86 (1H, d, J=8.4 Hz); 4.28 (2H, t, J=6.6 Hz); 4.12 – 3.92 (6H, m); 2.63 – 2.45 (4H, m); 1.9-1.69 (8H, m); 1.67 – 1.54 (2H, m); 1.52 – 1.2 (58H, m); 0.95 – 0.82 (6H, m); ¹³C NMR (75MHz, CDCl₃) δ: 172.59; 166.74; 158.89; 153.26; 149.79; 148.62; 138.70; 132.87; 128.20; 127.77; 123.56; 122.92; 121.9; 114.92; 114.46; 112.04; 69.42; 69.14; 68.22; 65.03; 34.82; 34.97; 31.96; 31.94; 29.78; 29.72; 29.66; 29.6; 29.5; 29.48; 29.41; 29.32; 29.26; 29.21 28.92; 26.19; 26.15; 26.1; 25.11; 24.8; 22.80; 14.23;

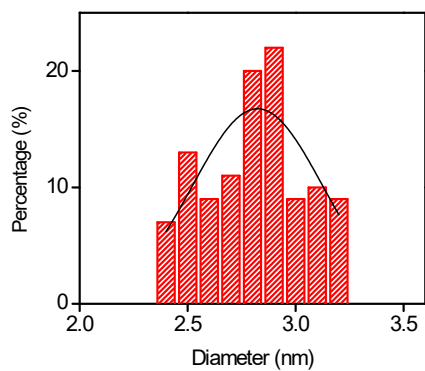
Supplementary Note 3. Measurement methods.

Optical measurements: Fluorescence was measured with modified Fluorolog 3-2-IHR320-TCSPC Horiba- Jobin Yvon fluorimeter in front face detection mode. The initial organic coating of the glass substrate was removed with water with soap, acetone, and then the initially cleaned glass was subject to UV-ozone cleaning (Ossila, 5 min). These films were prepared by drop-casting QDs dispersions in toluene using a freshly prepared coverslip. Thermal annealing was conducted using a temperature control stage Linkam TP 93 with 0.1K resolution. Fluorescence data were collected and processed with FluorEssence software. Uniformly aligned samples were prepared by thermal annealing of the drop casted material, followed by heating to 40 or 80 °C, and applying a mechanical shearing force using a metal spatula.

Structural Measurements: X-Ray structural characterization was performed using the Bruker Nanostar system (Cu K α radiation, parallel beam formed by cross-coupled Goebel mirrors, and a 3-pinhole collimation system, VANTEC 2000 area detector). The sample temperature was controlled with 0.1K resolution. Dispersion of QDs in toluene was drop casted on Kapton tape and the samples were thermally annealed. TEM images were taken using JEM 1400 microscope (JEOL Co., Japan) equipped with a high-resolution digital camera CCD MORADA G2 (EMSIS GmbH, Germany). HR- TEM micrographs and HAADF EDS and elemental analysis were performed with TALOS F200X field electron emission cathode X-FEG and electron beam energy 80 – 200 keV, equipped with four detector system Super X EDS and 120 mm² surfaces of detection (Biological and Chemical Research Centre, University of Warsaw).

Supplementary Figures and Tables.

a)



b)

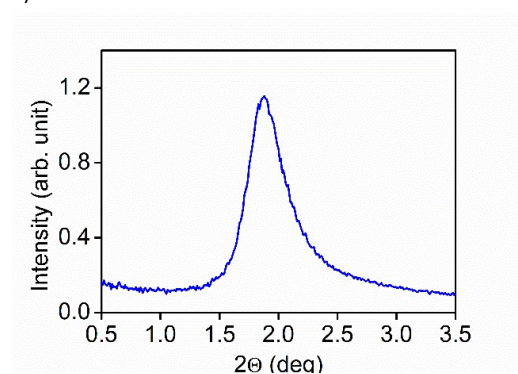
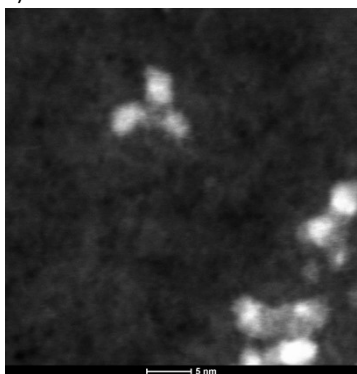


Figure S1. InP/ZnS QDs size distribution a) The size distribution of QDs based on the TEM image. The average size of NCs 2.9 ± 0.3 nm. b) SAXRD

a)



b)

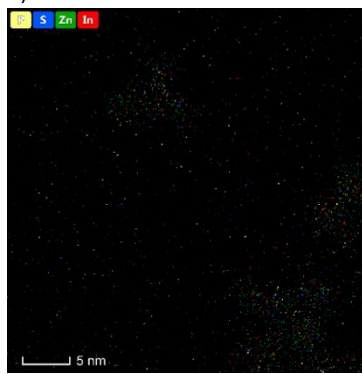


Figure S2. (a) Dark field mode HR-TEM micrograph of tetrahedral-shaped NCs. (b) HAADF EDS elemental distribution. Excess of zinc and sulfur on the surface of NCs confirms the core/shell structure of anisotropic NCs.

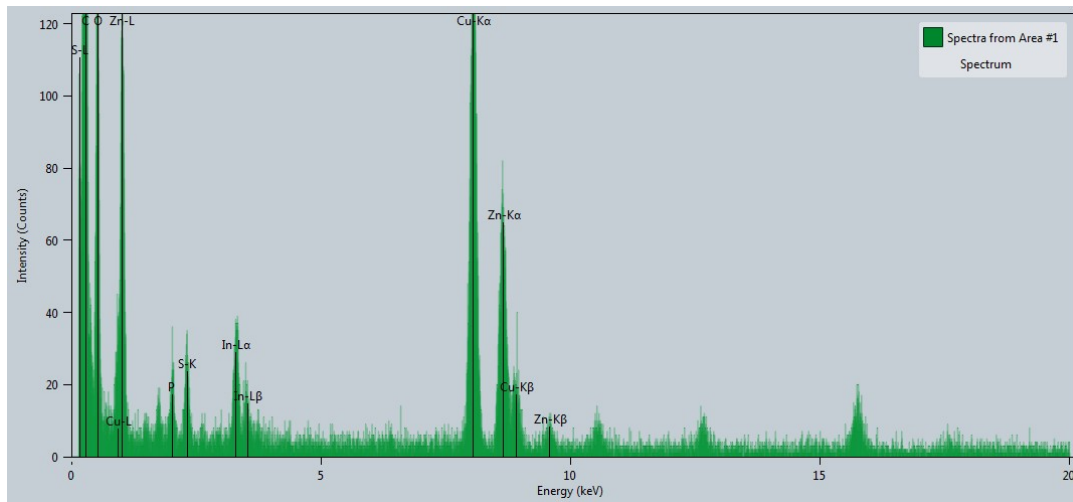


Figure S3. High-angle Annular Dark-Field Energy Dispersive X-ray Spectroscopy (HAADF EDS) of InP/ZnS QDs; the presence of indium, sulfur, phosphor, and zinc elements in QDs was confirmed. A high amount of copper is coming from the TEM grid.

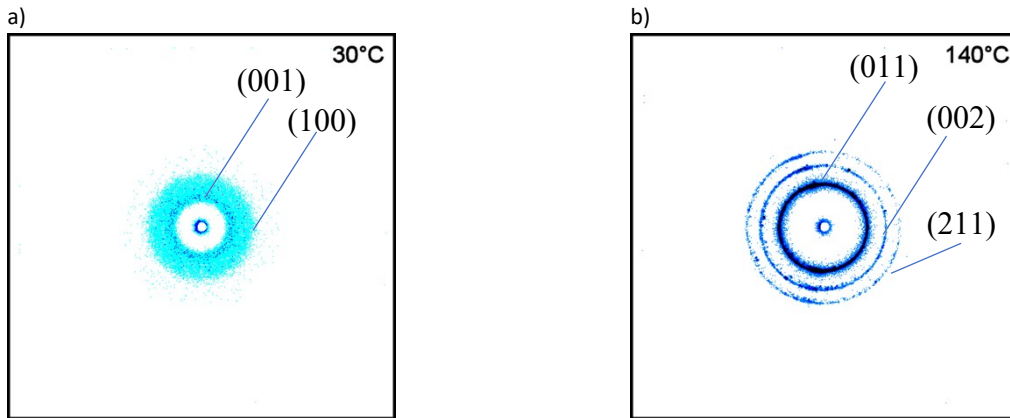


Figure S4. QDs/L SAXRD diffractograms collected at a) 30°C, b)140°C.

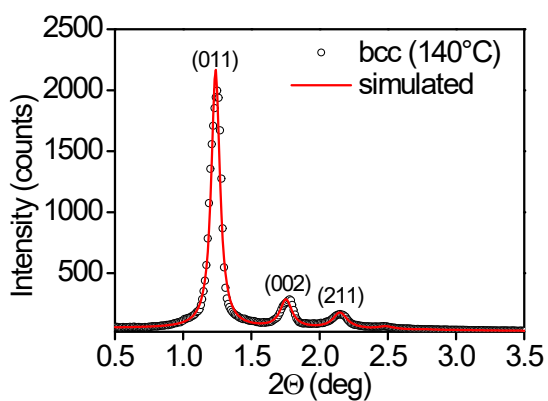


Figure S5. SAXRD diffractogram of QDs/L assemblies forming bcc structure. Signals indexed as (011), (002), (211) correspond to 7.1, 5.0, and 4.1 nm, respectively.

Table S1. Unit cell parameters for the structures formed by QDs/L hybrid material, and estimated volume per single hybrid quantum dot.

	unit cell parameters [nm]	$V_{\text{QDs/LC}}$ [nm ³]
QDs/LC (30°C): Lam	$a = 7.2^*$ $c = 10.5$	470
QDs/LC (140°C): bcc	$a = 10.0$	500

* mean in-plane interparticle distance

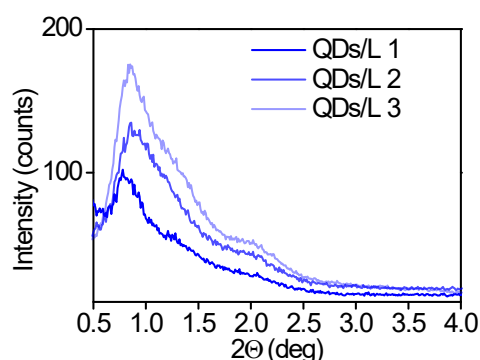


Figure S6. SAXRD diffractograms of three QDs/L samples in 30°C. Ligand exchanges were performed on three independently produced batches of QDs. Reproducibility of the hybrid material preparation is not affected by intrinsic properties of an individual batch, that is in all cases SAXRD diffractograms characteristic signals were recorded. Small fluctuations of the position of the main XRD signal is most probably due to small variations of the QDs size in separate batches.

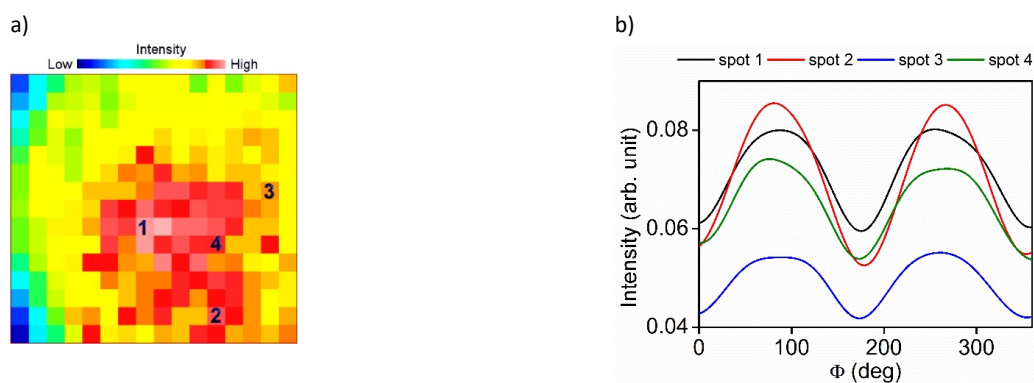


Figure S7. SAXRD measurements of QDs/L/40 on glass substrate a) diffraction intensity map, for the 3 mm x 3 mm sample. The diffraction was collected from four random spots to confirm macroscopic anisotropy of the sample later tested on spectrofluorometer. Variations of intensity of diffracted signals originates from the variable thickness of the material in different areas of the sample. b) Azimuthal integration of main diffraction signal corresponding to layer periodicity, collected from four different spots of QDs/L/40 sample, evidencing common layer orientation in the whole macroscopic sample.

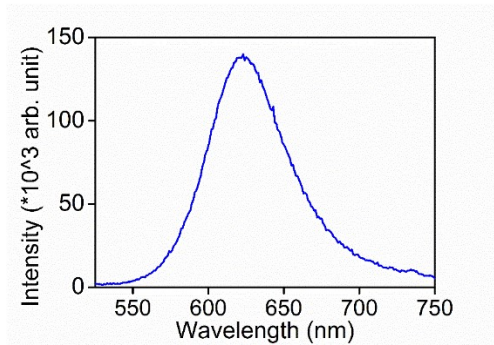


Figure S8. Fluorescence spectra of a heat annealed QDs/LC material (thin film, QDs forming a lamellar structure). Emission band maxima is placed at ~ 623 nm, FWHM ~ 62 nm.

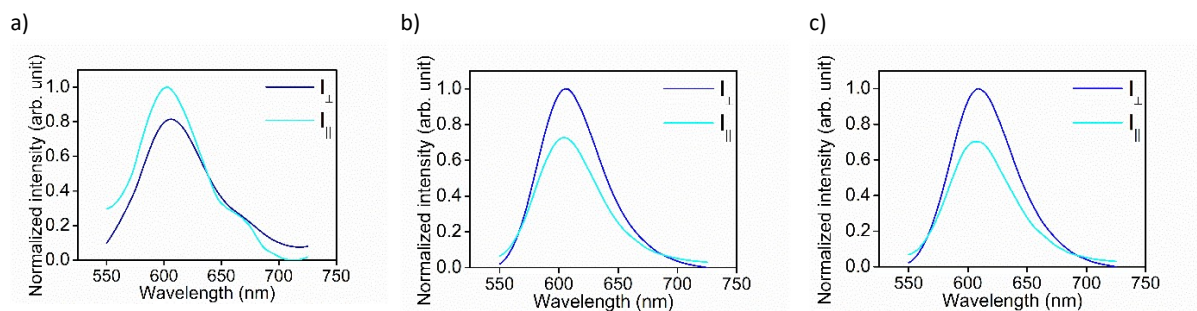


Figure S9. FA measurements of QDs/L/40. a) Data shown in Figure 3b in the main text. b) Sample rotated 90 deg in the plane of the glass substrate. c) Sample rotated and heated up to 140°C; note that the initial sample orientation remains after phase transition to the bcc phase which results in detected FA however, the overall emission intensity is significantly lower at elevated temperature.

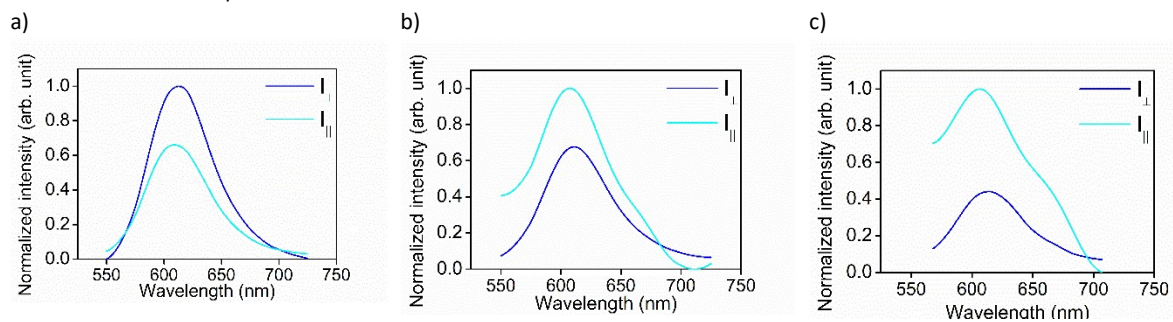


Figure S10. FA measurements of QDs/L/80. a) Data shown in Figure 3d in the main text. b) Sample rotated 90 deg in the plane of the glass substrate. c) Sample rotated and heated up to 140°C; note that the initial sample orientation remains after phase transition to the bcc phase which results in detected FA however, the overall emission intensity is significantly lower at elevated temperature.

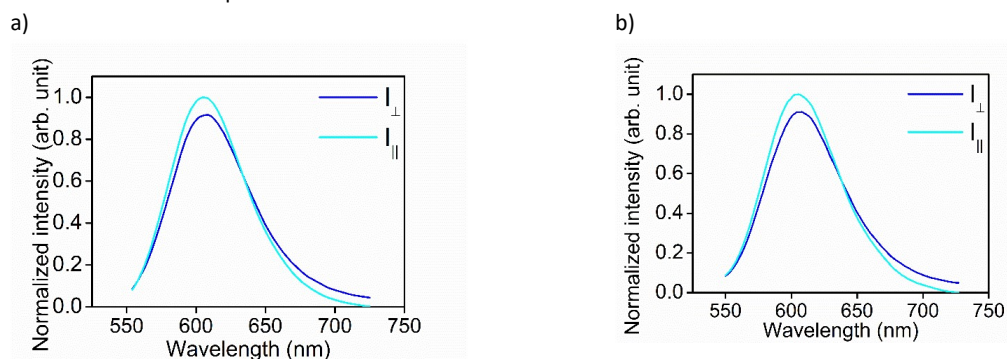


Figure S11. FA measurements of InP/ZnS QDs coated with DDT in a neat state, the sample prepared on glass without shearing. a) Measurements at 30°C. b) Measurements at 140°C. Based on this data, the ratio of the polarized component to the total intensity r can be calculated. The obtained values for emission band maxima, an order of magnitude lower than in the case of aligned QDs/L/40 and QDs/L/80, may come from the intrinsic anisotropic structure of QDs. It is worth noting that this interpretation is further strengthened by detecting polarization P , defined as $P = (I_{||} - I_{\perp}) / (I_{||} + I_{\perp})$ in thin-films

of our nanocomposites, on the order of 0.004 for DDT-capped QDs vs. 0.105 for QDs/L/40 and -0.205 for QDs/L/80. In the case of DDT-capped QDs (which form only short-range ordered assemblies), the value of P suggests that observed polarization anisotropy is related to intrinsic properties of individual building blocks, thus much higher P values are observed for LC-capped QDs are almost exclusively caused by the anisotropy of long-range ordered assemblies.