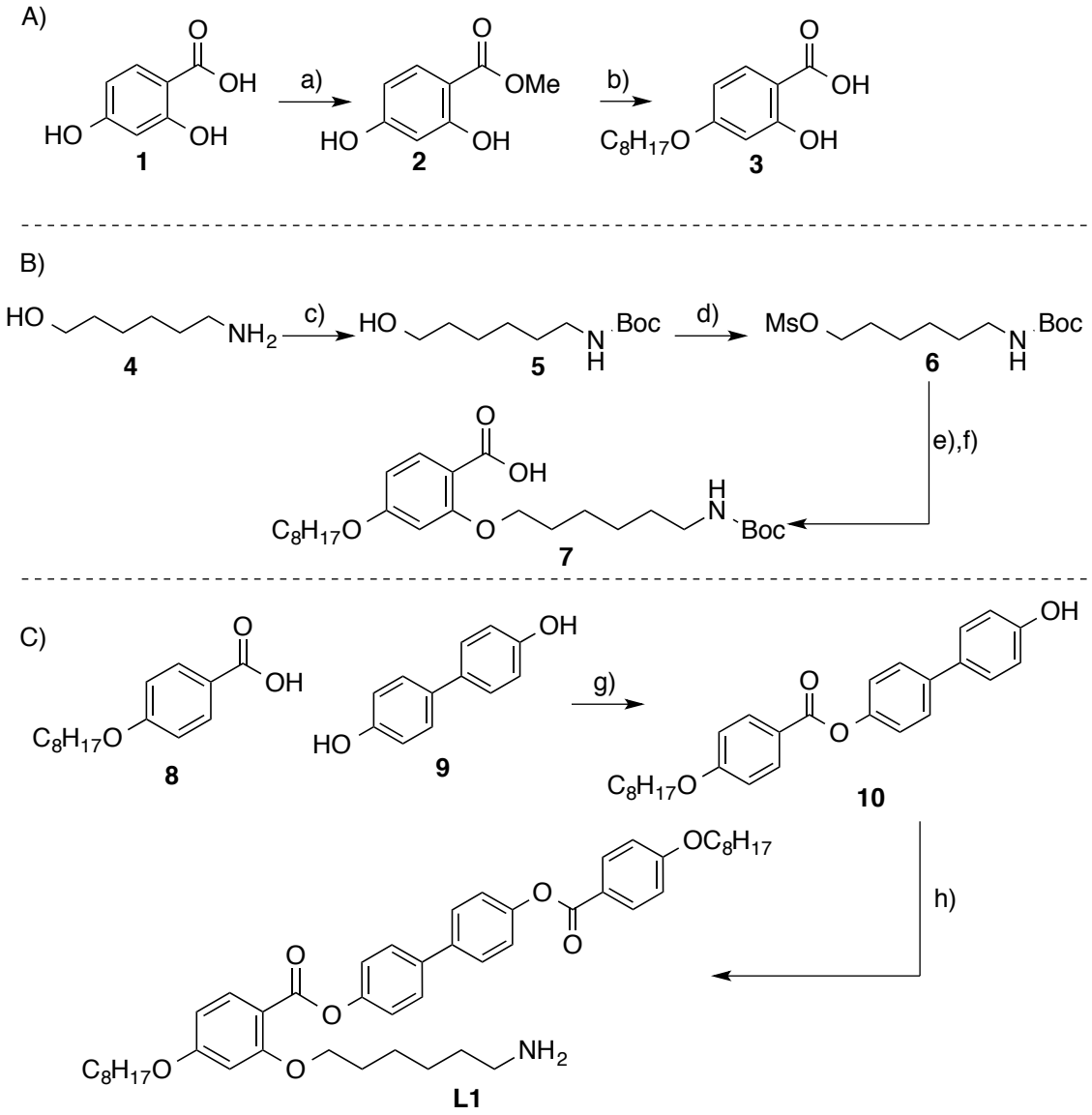
Supplementary Methods

General

Solvents and chemicals were obtained from commercial sources (Aldrich, TCI-America, AK-Scientific and Acros) and used as received. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker DRX-600 equipped with a DCH cryoprobe or a Bruker DRX-500. Chemical shifts (δ) are expressed in parts per million relative to residual $CHCl_3$ or H_2O as internal standards. Proton magnetic resonance (^{1}H NMR) spectra were recorded at either 600 or 500 MHz. Carbon magnetic resonance (^{13}C NMR) spectra were recorded at 150 or 125 MHz. NMR acquisitions were performed at 295 K unless otherwise noted. Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; br s, broad singlet. TLC analysis was performed using precoated silica gel 60 F_{254} plated from EMD Chemicals Inc.

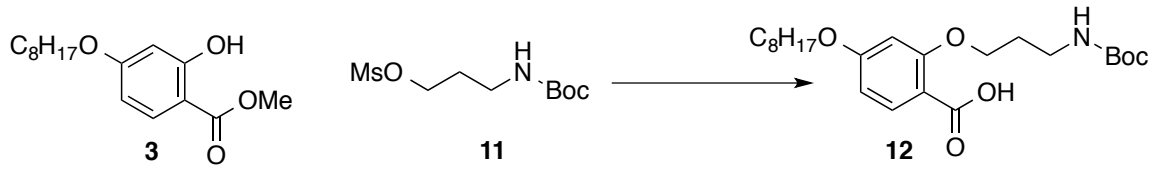
Synthesis of Mesogenic Ligands

General Procedure. The mesogenic ligands were synthesized following our published general procedure.[1] This route involves the preparation of a *para*-alkyated phenol **3** via esterification followed by Williamson etherification selectively at the 4-position. The *ortho*-functionality was then added via coupling with N-Boc mesylate **6**, which was synthesized by *N*-protection followed by *O*-mesylation. The LC-ligand core was obtained by esterification with acid **8** and bis-phenol **9** to give alcohol **10**, which was finally coupled to acid **7** via in situ acid chloride generation. This final coupling both activated the carboxylic acid group and removed the *N*-Boc protection to yield the final ligand **11**. Characterization details for compound **L1** and all subsequent materials are reported in ref 1.



Supplementary Scheme S1 - Synthesis of liquid crystal ligand L1; a) H_2SO_4, MeOH; b) 1-bromooctane, K_2CO_3, 2-butanone; c) $(BOC)_2O$, DCM; d) MsCl, TEA, DCM; e) **3**, KOtBu, KI, 2-butanone; f) NaOH, MeOH; g) DMAP, EDCI, TEA, THF; h) **7**, $SOCl_2$, Toluene

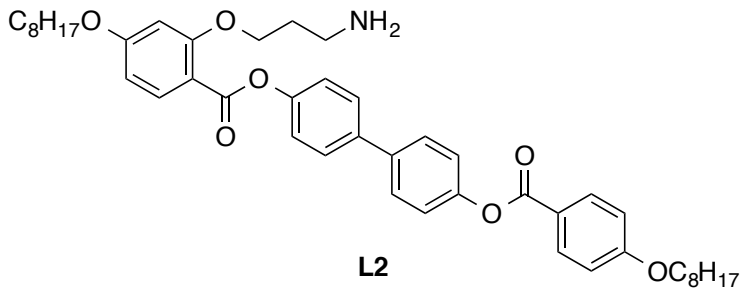
Synthesis of 2-(3-((*tert* butoxycarbonyl)amino)propoxy)-4-(octyloxy)benzoic acid (12)



Methyl 2-hydroxy-4-(octyloxy)benzoate (**3**) (2 g, 7.13 mmol) was dissolved in methy-ethylketone (144 ml). This solution was added to a flask 3-((tert-butoxycarbonyl)amino)propyl methanesulfonate (**11**) (2.168 g, 8.56 mmol). The reaction mixture was treated with KI (1.776 g, 10.70 mmol), and KOtBu (0.961 g, 8.56 mmol) and then heated to reflux. Sample was left to heat for 16hrs then cooled and solvent was removed under vacuum. The residue was extracted with DCM (2 × 50 mL) and then the combined organic fractions were dried with Na_2SO_4 and concentrated on the rotovap. The crude yellow oil was then purified by column chromatography (95:5 Hexane: EtOAc) to obtain methyl 2-(3-((tert-butoxycarbonyl)amino)propoxy)-4-(octyloxy)benzoate (2.1 g, 4.80 mmol) as a clear oil.

This sample was immediately subjected to saponification by treating it with 1M NaOH (16.00 ml, 48.0 mmol) in MeOH (96 mL) and heating the reaction at 55 °C overnight. Solvent was removed by rotovap and the residue was extracted with DCM (3 × 25 mL) and then the combined organic fractions were dried with Na_2SO_4 and concentrated. Crude product was recrystallized from hexanes to give 2-(3-((*tert*-butoxycarbonyl)amino)propoxy)-4-(octyloxy)benzoic acid (**12**) as a white solid (2.68 g, 6.13 mmol, 86 %). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.7 Hz, 1H), 6.60 (dd, *J* = 8.9, 2.2 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 4.99 (d, *J* = 7.2 Hz, 1H), 4.24 (t, *J* = 6.2 Hz, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 3.35 (q, *J* = 6.3 Hz, 2H), 2.14 – 2.05 (m, 2H), 1.84 – 1.75 (m, 2H), 1.43 (s, 11H), 1.38 – 1.25 (m, 8H), 0.89 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.6 , 159.1 , 135.4 , 110.4 , 106.9 , 99.7 , 68.5 , 31.8 , 29.5 , 29.3 , 29.2 , 29.0 , 28.3 , 25.9 , 22.6 , 14.1 .

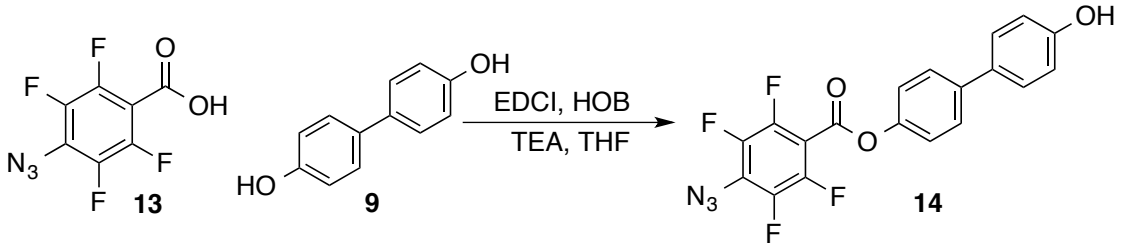
Synthesis of 4'-((4-(octyloxy)benzoyl)oxy)-[1,1'-biphenyl]-4-yl 2-(3-aminopropoxy)-4-(octyloxy)benzoate



L2

Synthesized according to the same general procedure as used for **L1** substituting benzoic acid **12** in place of **7**. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 8.27 – 8.07 (m, 1H), 7.60 (ddd, *J* = 8.7, 4.5, 1.8 Hz, 1H), 7.35 – 7.12 (m, 2H), 7.09 – 6.88 (m, 1H), 6.57 (dd, *J* = 9.0, 2.4 Hz, 0H), 6.37 (d, *J* = 2.4 Hz, 0H), 4.02 (dt, *J* = 22.9, 6.8 Hz, 2H), 3.16 (d, *J* = 8.5 Hz, 1H), 2.32 – 2.00 (m, 1H), 1.95 – 1.66 (m, 2H), 1.62 – 1.10 (m, 8H), 0.90 (dt, *J* = 6.8, 3.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 164.3, 164.2, 163.6, 163.3, 161.7, 150.9, 150.6, 137.6, 137.1, 132.1, 127.8, 122.3, 122.0, 121.9, 114.0, 111.4, 67.8, 31.9, 31.8, 31.8, 29.5, 29.4, 29.3, 29.3, 29.2, 29.1, 26.0, 25.9, 22.7, 22.6, 22.6, 13.9, 13.9, 13.8.

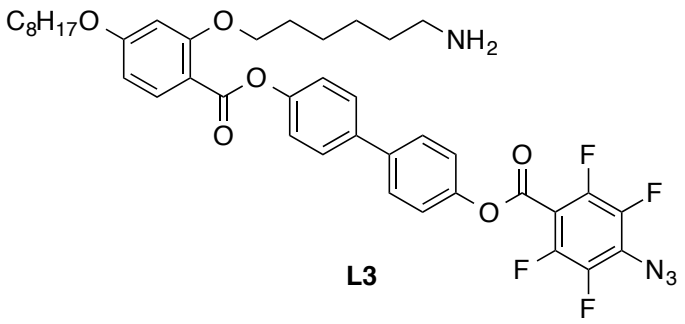
Synthesis of 4'-hydroxy-[1,1'-biphenyl]-4-yl 4-azido-2,3,5,6-tetrafluorobenzoate (14)



4-azido-2,3,5,6-tetrafluorobenzoic acid **13** (3.00 g, 12.76 mmol), [1,1'-biphenyl]-4,4'-diol **9** (2.17 g, 11.64 mmol), and hydroxybenzotriazole (1.90 g, 14.04 mmol) were dissolved in DCM (70 mL). The reaction was cooled to 0°C using an ice bath and then *N*-methylmorpholine (4.21 mL, 38.3 mmol). Finally 1-Ethyl-3-(3-dimethylaminopropyl)carbodimide-HCl (2.69 g, 14.04 mmol) was added and the reaction was allowed to warm to room temperature overnight, giving a milky solution. The reaction mixture was filtered and solids were washed with DCM. The filtrate was cooled to 0°C and then quenched with saturated NH_4Cl. The mixture was

stirred for 15 min and allowed to warm to room temperature over 15 min. The mixture was extracted with DCM (3×40mL) and the combined organic layer was washed with 1M HCl , dried with Na_2SO_4, filtered and evaporated to dryness under vacuum. The residue was treated with MeOH (150mL), heated to reflux, and filtered while hot. The clear filtrate was cooled to room temp to allow crystal to form, which was then isolated by filtration to yield 4'-hydroxy-[1,1'-biphenyl]-4-yl 4-azido-2,3,5,6-tetrafluorobenzoate **14** (2.32g, 5.74 mmol 45% yield). ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.51 (s, 1H), 7.65 (dd, J = 8.7, 1.5 Hz, 2H), 7.50 (dd, J = 8.6, 1.5 Hz, 2H), 7.30 (dd, J = 8.6, 1.5 Hz, 2H), 6.91 (dd, J = 8.6, 1.5 Hz, 2H). ^{13}C NMR (101 MHz, acetone) δ 157.3, 149.0, 139.4, 131.1, 127.9, 127.3, 121.6, 115.7.

Synthesis of 4'-((2-((6-aminohexyl)oxy)-4-(octyloxy)benzoyl)oxy)-[1,1'-biphenyl]-4-yl 4-azido-2,3,5,6-tetrafluorobenzoate (L3)

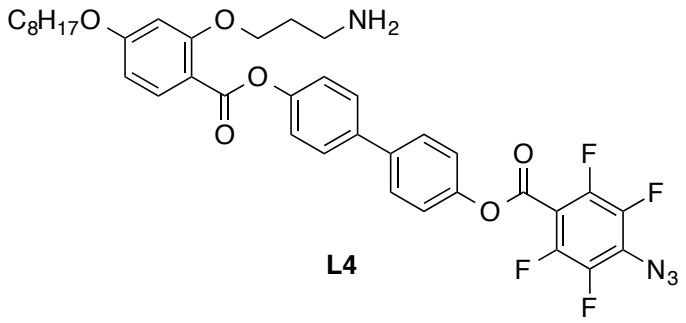


L3

2-((6-((tert-butoxycarbonyl)amino)hexyl)oxy)-4-(octyloxy)benzoic acid **7** (0.99 g, 2.335 mmol) was dissolved in toluene (13.00 mL). Thionyl chloride (0.511 mL, 7.01 mmol) was added dropwise and the reaction was stirred at room temperature for 24 hours. Conversion to the acid chloride was monitored by HPLC. Finally, 4'-hydroxy-[1,1'-biphenyl]-4-yl 4-azido-2,3,5,6-tetrafluorobenzoate **12** (0.99 g, 2.452 mmol) was added and the reaction mixture was heated to 60 °C for 24 hrs. Solvent was removed under vacuum. The residue was dissolved in iPrOH, sonicated and then removed under vacuum. This process was repeated three times, and finally suspended in iPrOH a final time. The crude solids were isolated by centrifugation and the supernatant was separated and disposed. The solids were then recrystallized from EtOH, giving 4'-((2-((6-aminohexyl)oxy)-4-(octyloxy)benzoyl)oxy)-[1,1'-biphenyl]-4-yl 4-azido-2,3,5,6-tetrafluorobenzoate **L3** (0.70g, 0.932 mmol, 39% yield) as a white powder. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.15 (s, 3H), 8.02 (dd, J = 8.9, 1.5 Hz, 1H), 7.60 (td, J = 8.7, 4.2 Hz, 4H), 7.30 – 7.16 (m, 5H), 6.50 (dd, J = 8.9, 2.2 Hz, 1H), 6.45 (d, J = 2.4 Hz, 1H), 3.98 (dt, J = 11.0, 6.2 Hz, 4H), 2.87 (d, J = 9.1 Hz, 2H), 1.95 (s, 2H), 1.88 – 1.57 (m, 6H), 1.61 – 1.10 (m, 15H), 0.99 – 0.82 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 168.6, 165.9, 165.1, 164.4, 163.6, 161.2, 157.6, 150.2, 149.8, 147.8, 144.3, 141.8, 139.1, 138.6, 137.9, 137.2, 134.5, 131.6, 128.1, 127.9, 127.9, 122.3, 122.1, 121.5, 109.16, 108.35, 106.8,

106.1, 104.3, 101.2, 99.4, 68.5, 68.4, 68.1, 39.1, 31.7, 31.7, 29.2, 29.1, 29.0, 28.9, 25.9, 25.8, 22.5, 13.9.

Synthesis of 4'-((2-(3-aminopropoxy)-4-(octyloxy)benzoyl)oxy)-[1,1'-biphenyl]-4-yl 4-azido-2,3,5,6-tetrafluorobenzoate (L4).



L4

Synthesize according to the general protocol used for **L3**, with the substitution of the benzoic acid **12** in place of **7**. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.7 Hz, 1H), 7.70 – 7.43 (m, 4H), 7.33 – 7.10 (m, 4H), 6.57 – 6.39 (m, 1H), 6.38 – 6.27 (m, 1H), 3.94 (p, *J* = 8.5, 7.6 Hz, 4H), 3.14 (s, 2H), 2.13 (s, 2H), 1.84 – 1.61 (m, 2H), 1.50 – 1.11 (m, 12H), 0.92 – 0.77 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 165.9, 165.1, 164.4, 163.6, 161.2, 157.6, 150.2, 149.8, 147.8, 144.3, 141.8, 139.1, 138.6, 137.9, 137.2, 134.5, 131.6, 128.1, 127.96, 127.95, 122.3, 122.1, 121.5, 109.1, 108.3, 106.8, 106.1, 104.3, 101.2, 99.4, 68.5, 68.4, 68.1, 39.1, 31.7, 31.7, 29.2, 29.2, 29.1, 29.1, 29.1, 29.0, 28.9, 28.9, 25.9, 25.8, 22.5, 13.9.

Ligand phase characterization

Each of the ligands synthesized were characterized initially by polarized optical microscopy and Differential scanning calorimetry. Microscopy confirmed that both materials exhibit a smectic and nematic phase. These studies also revealed that the materials could not be heated to the isotropic phase reversibly since that phase transition occurs at approx ~180deg and the materials were not stable at such high temperatures. This was particularly true in the case of the cross-linkable ligands as might be expected. The materials however can be heated to more modest temperatures of ~125 reversibly where they remained in the smectic phase and the crystal to smectic transition observed. L2 appeared to exhibit two distinct smectic phases.

L1 K ➔ Sm
(83.8°C)

L2 K ➔ Sm_1 ➔ Sm_2
(52.9°C) (67.0°C)

Ligand exchange

Total particle ligand density was approximated using thermal gravimetric analysis (TGA). A sample of ODA-QD particles was dried into a TGA sample cup and exposed to a heating program of 5°C per minute from 25°C - 1000°C under a constant stream of compressed air. The percent reduction in mass was used to approximate the total mass of organic ligand (ODA) in the sample. Separately, the concentration of CdSe QD particles was measured spectrometrically. These two values were used to approximate the total ligand coverage and number of ligand exchangeable sites for each particle.

The commercial quantum dots were washed using a precipitation-redispersion scheme. In the process, 1 mL of quantum dot solution was precipitated with 1 mL of methanol. The mixture was centrifuged for 10 min and the supernatant was discarded. The precipitate was then redissolved in 1 mL of toluene and washed two more times. Afterwards the precipitate was dissolved in 1 mL of chloroform. A solution of the **L1** dissolved in toluene (40 mmol) was added to the quantum dot solution, heated to 40 °C, and stirred for 3 hours. The mixture was then taken off heat and left to cool back to room temperature. 2 mL Ethyl Acetate was then added to the ligand exchanged quantum dot solution and centrifuged. The precipitate was washed two more times using a 1:1:2 solution of toluene, chloroform, and ethyl acetate. The precipitate was finally resuspended in 1 mL toluene.

Before and after the ligand exchange the particles were characterized by UV-Vis spectrometry and TGA. We used the QD absorption spectrum to produce a concentration calibration curve from 10 dilutions of the QDs before and after exchange to determine a QD yield of 87.9%. Based on mass difference before and after the exchange and assuming an upper limit of 1 to 1 ligand exchange ratio the percentage of LC ligands from total ligands was 81-70%.

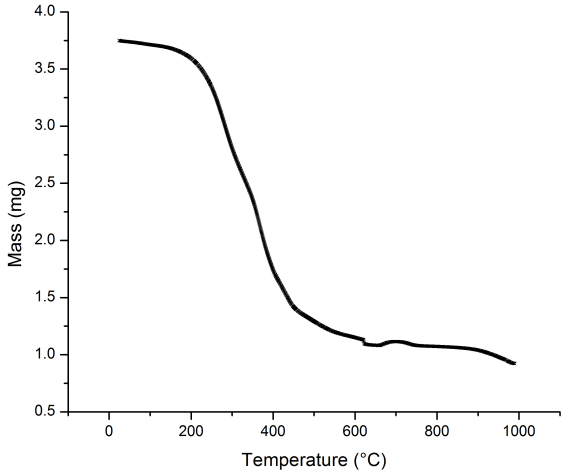


Figure S1. TGA data for the ODA-QD particles used before ligand exchange. The percent reduction in mass was used to approximate the total mass of organic ligand (ODA) in the sample.

Small angle x-ray scattering (SAXS)

X-ray scattering experiments were carried out on beamline 4-2 at the Stanford Synchrotron radiation light source (SSRL). An 11keV beam was used with a beam spot size of 0.3 x 0.1mm at the sample. QD shells dispersed in 5CB were filled into 1 mm quartz capillaries after formation and mounted in a transmission configuration on the beamline in a custom designed sample holder allowing translation and rotation of the capillary. Samples were exposed to the x-ray beam for 1s at three different spots and scattering data collected on a Rayonix MX225-HE CCD detector, with 3072x3072 resolution, 73.242 μm pixel size and 2x2 binning. The data was initially corrected and analyzed using custom software at the beamline to produce 1D scattering plots of intensity as a function of scattering vector, q. Further analysis was carried out using Origin, including peak fitting and further background subtraction as necessary.

Optical Microscopy

Fluorescence microscopy is used to image the spatial distribution of the LC-QDs in the host phase. In all experiments presented here we used CdSe/ZnS core shell QDs with an emission wavelength centered at 620nm. Fluorescence imaging was carried out on an upright Leica DM2500P microscope in reflection mode using a 20x or 40x objective. For fluorescence imaging of QDs with a peak emission at 620 nm, a 515–560 nm band-pass filter with white-light mercury lamp illumination was used. Emission was detected using a 580 nm dichroic mirror and a 590 nm Long pass filter. The microscope can also be used in transition mode with a white light source with crossed polarizers to image sample birefringence. Samples were mounted on standard glass slides under a cover slip, planar liquid crystal alignment was achieved using a rubbed PVA surface coating.

Transmission Electron Microscopy (TEM)

QD shells suspended in 5CB liquid crystal were drop cast onto holey carbon 200 mesh copper grids and imaged without further treatment. The samples were observed using a Jeol 2100 Cryo TEM instrument in the Materials Research Laboratory facility at the University of Illinois, Urbana-Champaign. The instrument has a 0.27 nm point to point resolution and allows for BF/DF imaging, diffraction and high sample tilt. Real time transmission imaging of the sample was captured with a low close mode using a Gatan UltraScan 2k x 2k CCD camera.

[1] Rodarte, A. L.; Nuno, Z. S.; Cao, B. H.; Pandolfi, R. J.; Quint, M. T.; Ghosh, S.; Hein, J. E.; Hirst, L. S. *Chemphyschem* **2014**, *15*, 1413–1421.