

Supporting Information

Hybrid Fluorescent Liquid Crystalline Composites: Directed Assembly of Quantum Dots in Liquid Crystalline Block Copolymer Matrices

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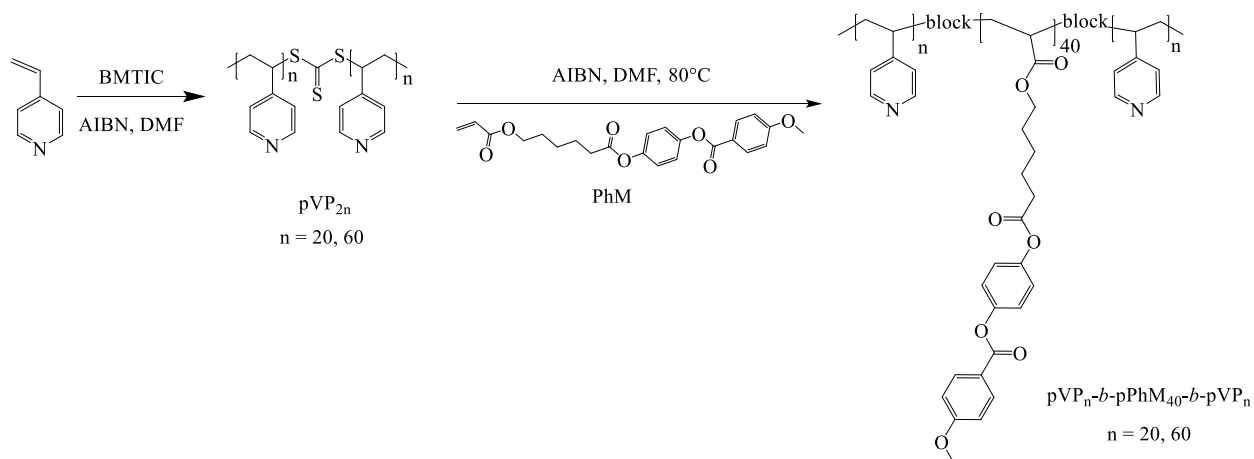
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Synthesis of macromolecular chain transfer agent, pVP₁₂₀

To obtain macromolecular chain transfer agent for triblock copolymers, pVP₁₂₀, 1 g (9.53 mmol) of the as-distilled 4-vinylpyridine, 25 mg (79 μmol) of S,S'-bis(methyl-2-isobutyrate) trithiocarbonate (BMTIC), and 2.7 mg (16.3 μmol) of AIBN were placed in the ampoule; the molar ratio monomer : BMTIC : initiator was 620 : 5 : 1. The solution was poured in an ampoule and blown with argon for 20 min, and the ampoule was sealed. Polymerization was conducted for 24 h at 80°C. After completion of polymerization, the ampoule was cooled with liquid nitrogen and opened. The reaction mixture was diluted with methanol, and the polymer was lyophilized. The yield of the polymer in both cases was ~95%. According to the GPC data, $M_n = 1.2 \times 10^4$ and $M_w/M_n = 1.23$.

Synthesis of the triblock copolymer pVP₆₀-b-pPhM₄₀-b-pVP₆₀

To synthesize the triblock copolymer pVP₆₀-b-pPhM₄₀-b-pVP₆₀, 18 μmol of pVP₁₂₀ (225 mg), 57 μL (38 μmol) of 4-vinylpyridine and p-(6-acryloyloxycaproyloxyphenyl)-p-methoxybenzoate (300 mg, 0.73 mmol) were dissolved in 0.35 mL of DMF. Afterwards, the calculated amount of AIBN solution in DMF was added so that the concentration of the initiator in the reaction mixture was 8×10^{-3} M. The reaction mixture was poured in ampoule, purged with argon and the ampoule was sealed. Polymerization was conducted at 80°C for a day. The block copolymer was isolated by precipitating the reaction mixture into excess diethyl ether. The polymerization product was purified via reprecipitation of the block copolymer from ethyl acetate solution into petroleum ether. The as-purified block copolymers were dried in vacuum at 70°C and characterized by GPC and ¹H NMR spectroscopy.



Scheme S1. Synthetic route of $pVP_n\text{-}b\text{-pPhM}_{40}\text{-}b\text{-pVP}_n$ triblock copolymers.

Tables

Table S1. Molecular weight data and weight fraction of mesogenic PhM units for the copolymers

Polymer	M_n	M_w/M_n	$\omega(\text{PhM})^*$
$pVP_{20}\text{-}b\text{-pPhM}_{40}\text{-}b\text{-pVP}_{20}$	20700	1.60	0.80
$pVP_{60}\text{-}b\text{-pPhM}_{40}\text{-}b\text{-pVP}_{60}$	29100	1.60	0.57
$pPhM_{20}\text{-}b\text{-pVP}_{40}\text{-}b\text{-pPhM}_{20}$	20600	1.55	0.80
$pVP_{120}\text{-}b\text{-pPhM}_{40}$	29500	1.50	0.57
$pVP_{120}\text{-}b\text{-pPhM}_{100}$	53600	1.50	0.77
$pVP_{60}\text{-}b\text{-pPhM}_{40}$	22800	1.60	0.72
$p(\text{VP}_{50}\text{-}r\text{-pPhM}_{50})$	25900	1.40	0.80
$p(\text{VP}_{75}\text{-}r\text{-pPhM}_{25})$	33500	1.40	0.57

*Weight fraction of the PhM block.

Table S2. Phase behavior and morphology of the copolymers

Polymer	Glass transition temperature, °C	Phase behavior*	Microphase separation**
pVP ₂₀ - <i>b</i> -pPhM ₄₀ - <i>b</i> -pVP ₂₀	32	N 110 (0.7) I	U
pVP ₆₀ - <i>b</i> -pPhM ₄₀ - <i>b</i> -pVP ₆₀	33	N 111 (0.3) I	L
pPhM ₂₀ - <i>b</i> -pVP ₄₀ - <i>b</i> -pPhM ₂₀	29	N 91 (0.7) I	U
pVP ₁₂₀ - <i>b</i> -pPhM ₁₀₀	32/144	N 131 (0.6) I	C
pVP ₁₂₀ - <i>b</i> -pPhM ₄₀	33/140	N 118 (0.2) I	L
pVP ₆₀ - <i>b</i> -pPhM ₄₀	33	N 121 (0.8) I	U
p(VP ₅₀ - <i>r</i> -pPhM ₅₀)	51	-	-
p(VP ₇₅ - <i>r</i> -pPhM ₂₅)	65	-	-

*N – a nematic phase. I – an isotropic melt. Isotropization enthalpy (in J g⁻¹) is given in brackets.

**L – a lamellar structure, C – a cylindrical structure, and U – an unclear type of a microphase separated structure, which still contains discrete microphases formed by pVP blocks.

Figures

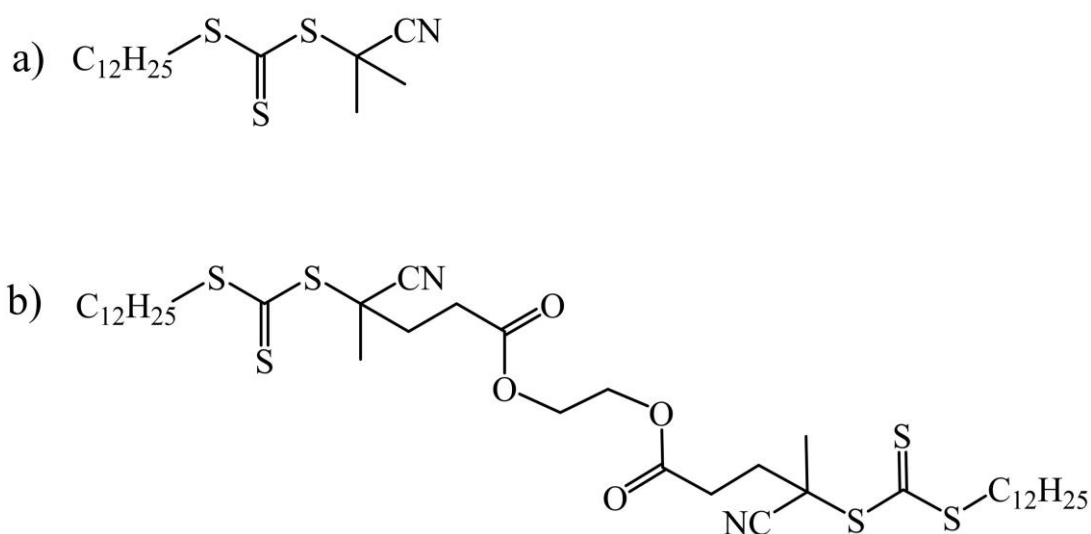


Fig. S1. Chemical structure of the (a) CPDDTC and (b) di-CPDDTC RAFT agents.

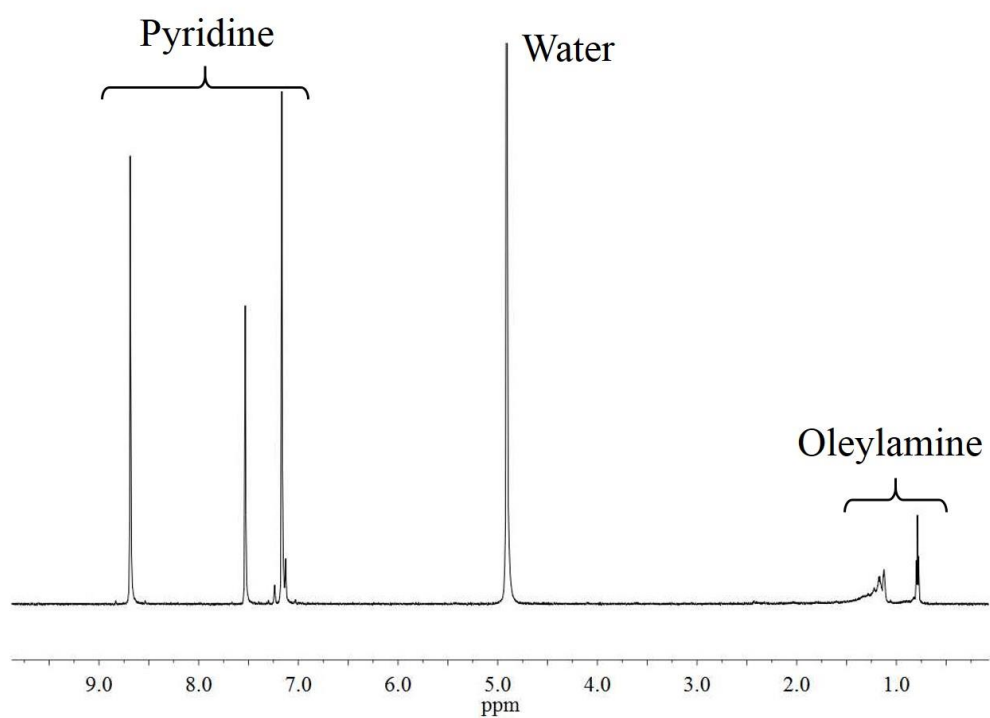


Fig. S2. ¹H NMR spectra of CdSe/ZnS QDs covered with pyridine in pyridine-d₅. The contribution of protonated pyridine containing in pyridine-d₅ was subtracted.

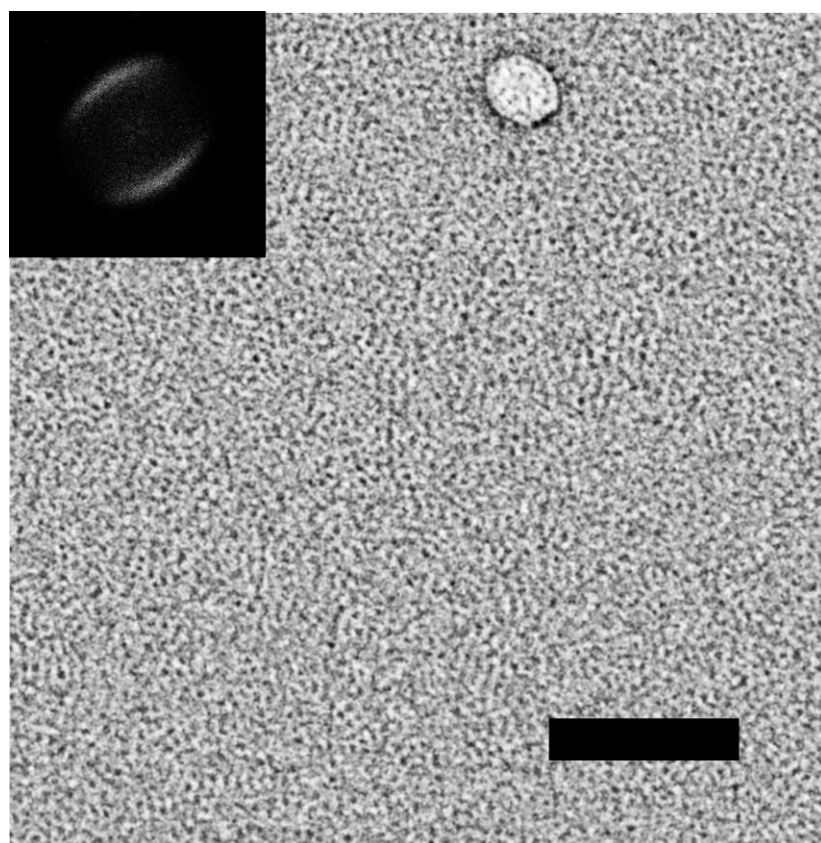


Fig. S3. TEM image of cross section of the pVP₆₀-b-pPhM₄₀ film. The samples were annealed at 140 °C for 3 h and stained with iodine for 1 h. The insets are a corresponding FFT image. Scale bar: 200 nm.

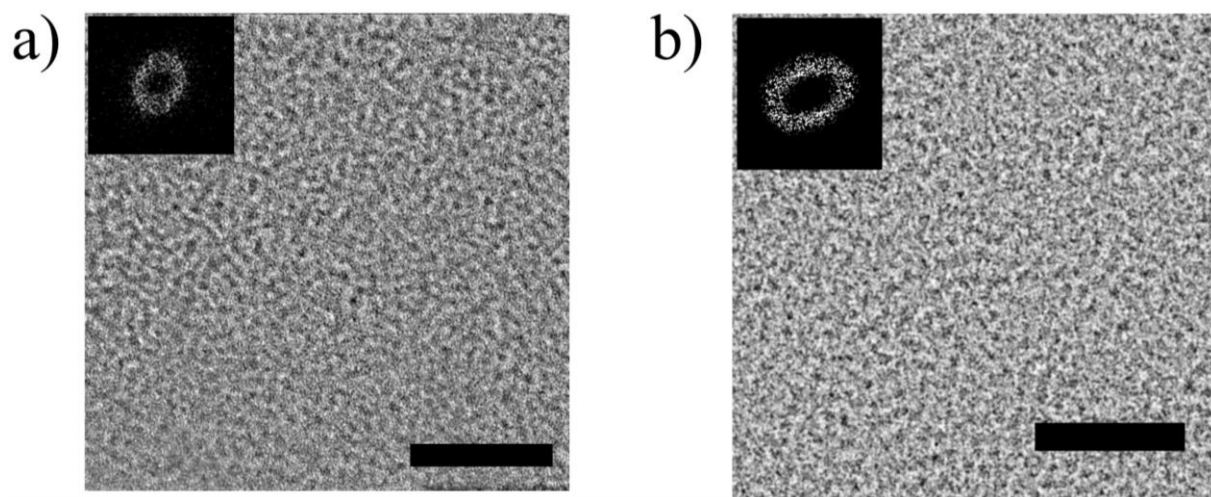


Fig. S4. TEM images of cross sections of the (a) pVP₂₀-b-pPhM₄₀-b-pVP₂₀ and (b) pPhM₂₀-b-pVP₄₀-b-pPhM₂₀ films. The samples were annealed at 140 °C for 3 h and stained with iodine for 1 h. The insets are a corresponding FFT image. Scale bar: 100 nm.

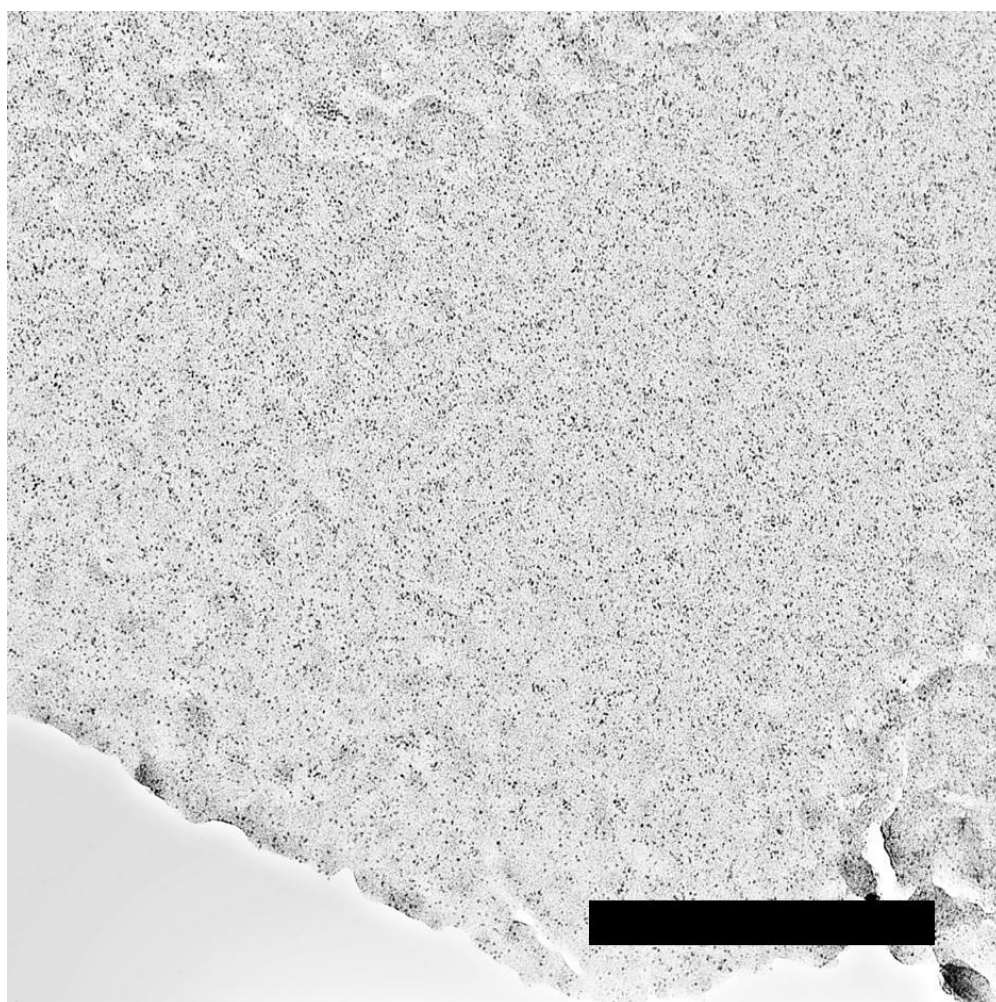


Fig. S5. TEM image of cross section of the V₆₀-LC₄₀-V₆₀ film. The sample was annealed at 140 °C for 3 h. Scale bar: 500 nm.

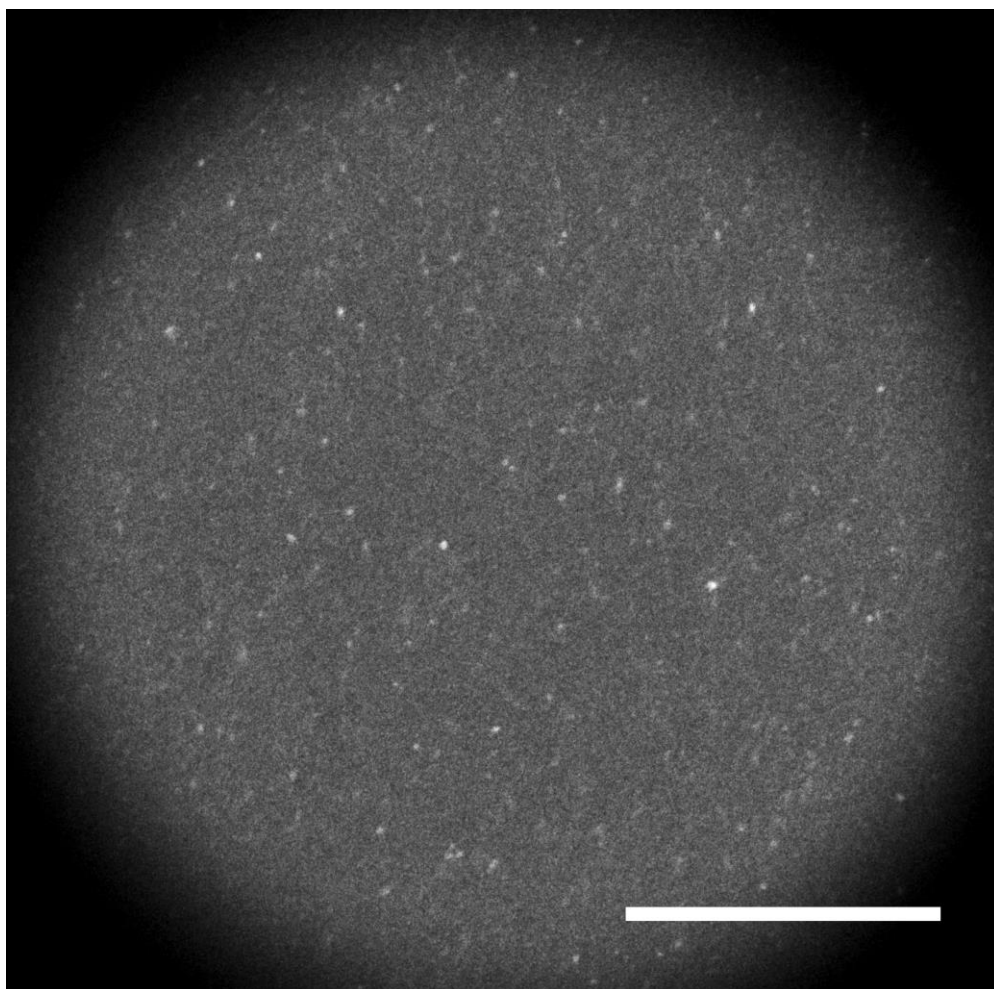


Fig. S6. Dark field TEM image of cross section of the V₆₀-LC₄₀-V₆₀ film. The sample was annealed at 140 °C for 3 h. Scale bar: 200 nm.

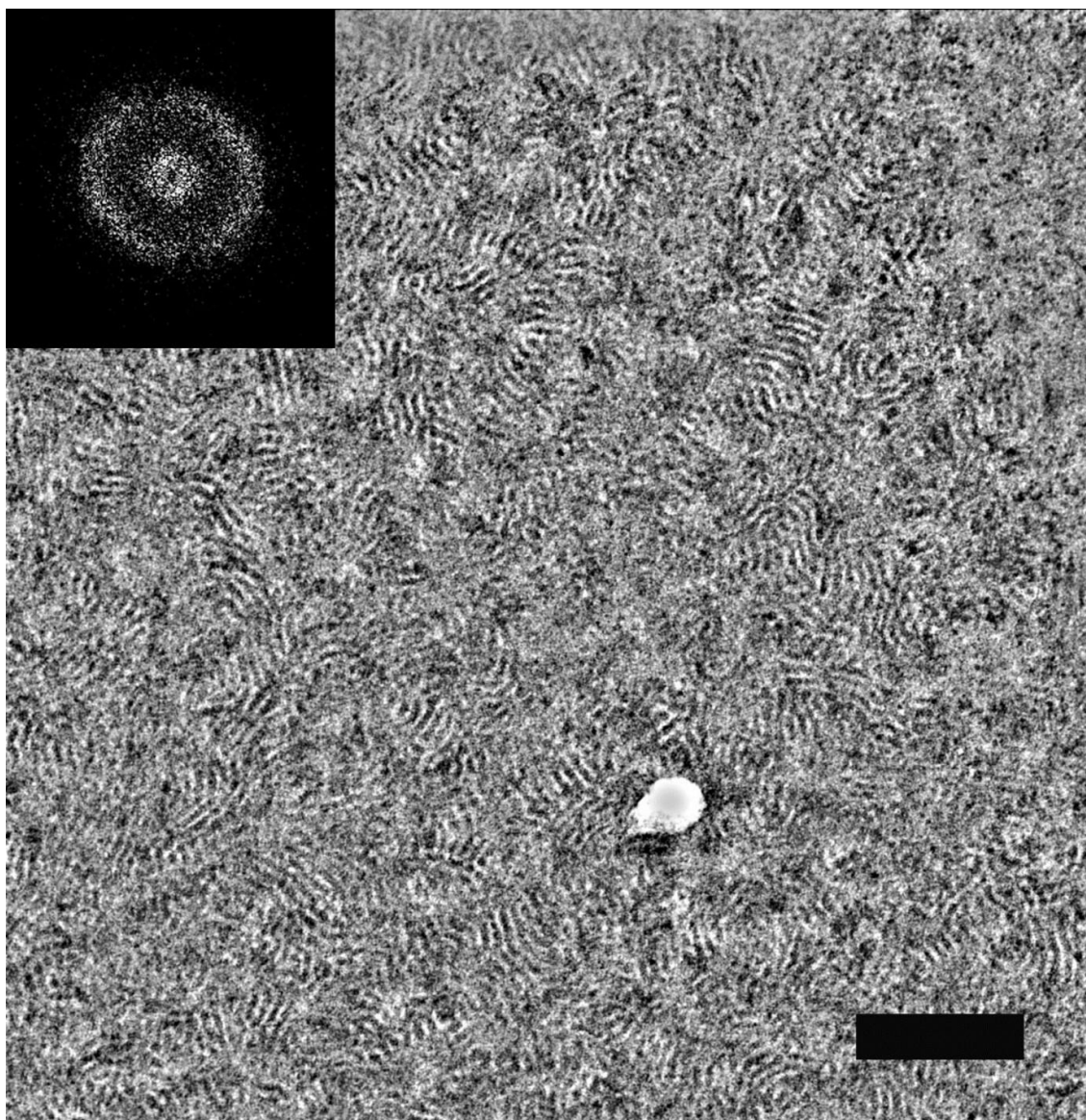


Fig. S7. TEM image of cross section of the V₆₀-LC₄₀-V₆₀ film. The sample was annealed at 140 °C for 3 h and stained with iodine for 30 min. The inset is a corresponding FFT image. Scale bar: 200 nm.

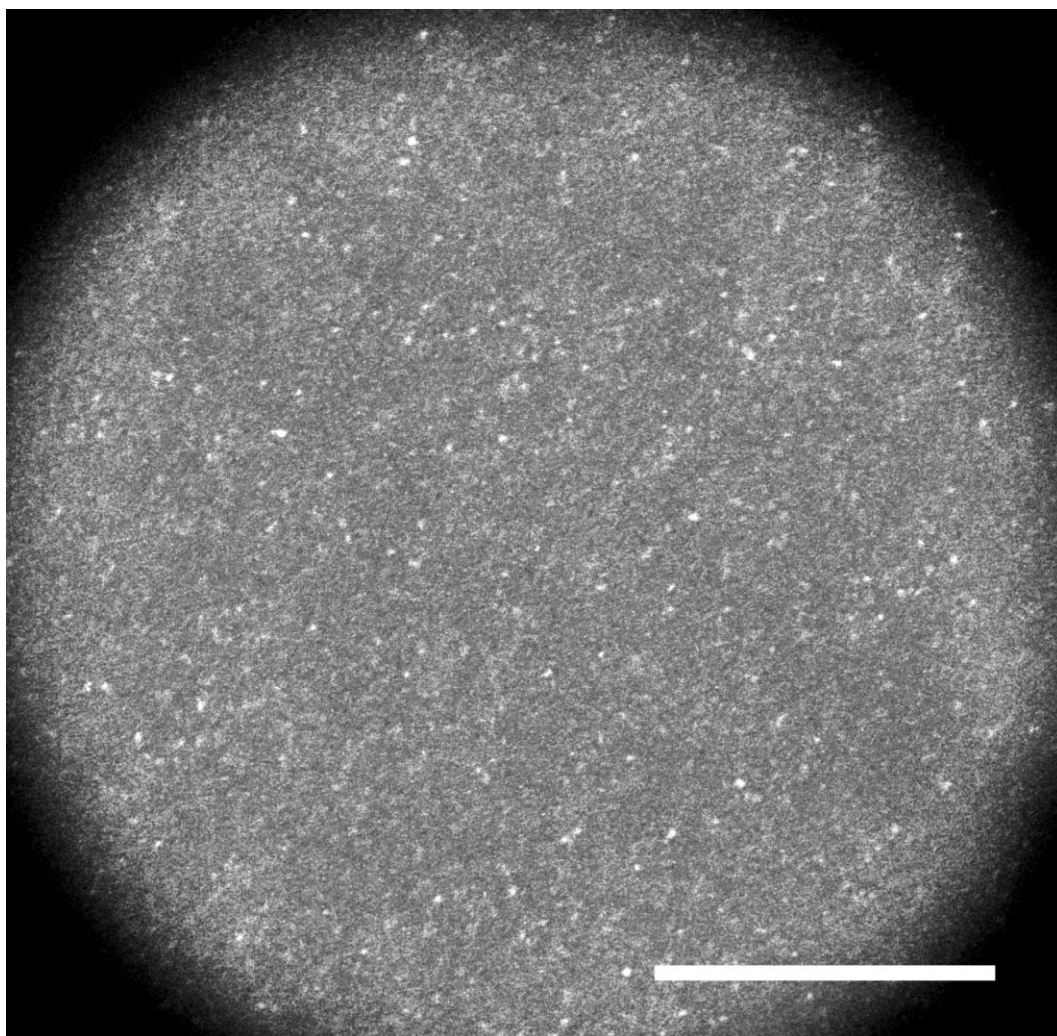


Fig. S8. Dark field TEM image of cross section of the V₁₂₀-LC₄₀ film. The sample was annealed at 140 °C for 3 h. Scale bar: 200 nm.

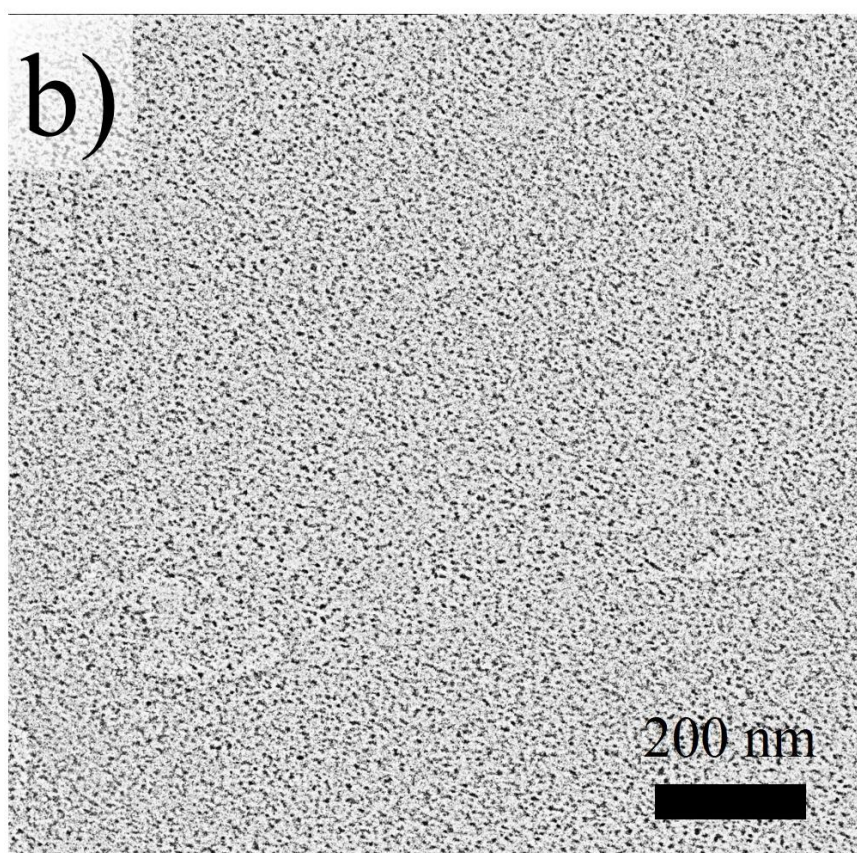
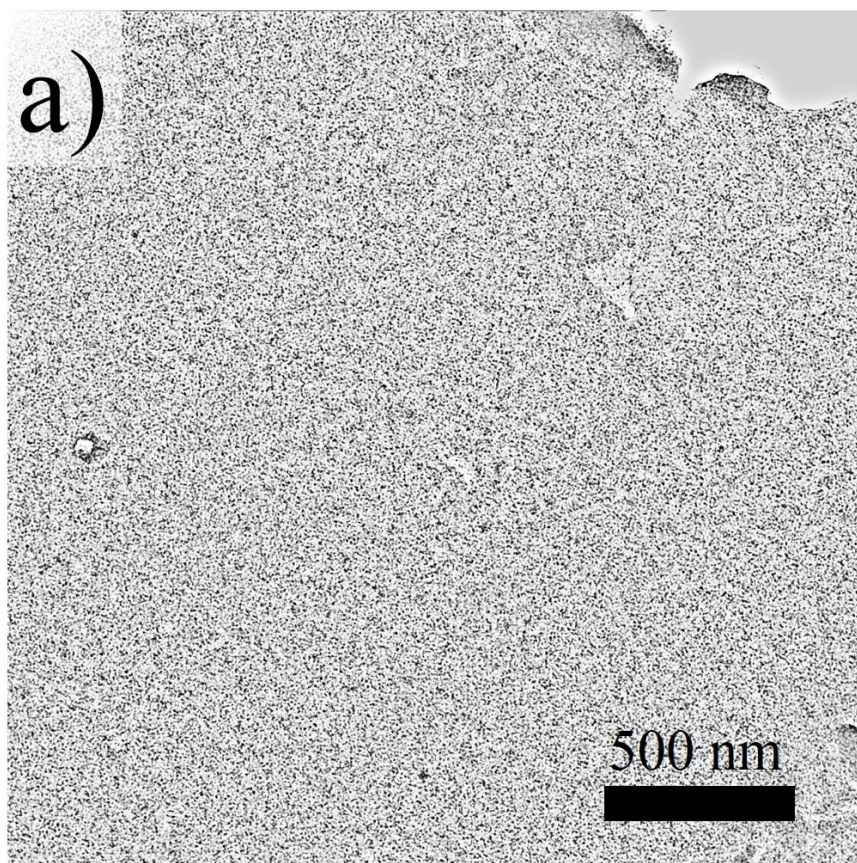


Fig. S9. TEM images of cross sections of the (a) LC₂₀-V₆₀-LC₂₀ and (b) V₆₀-LC₄₀ films. The samples were annealed at 140 °C for 3 h.

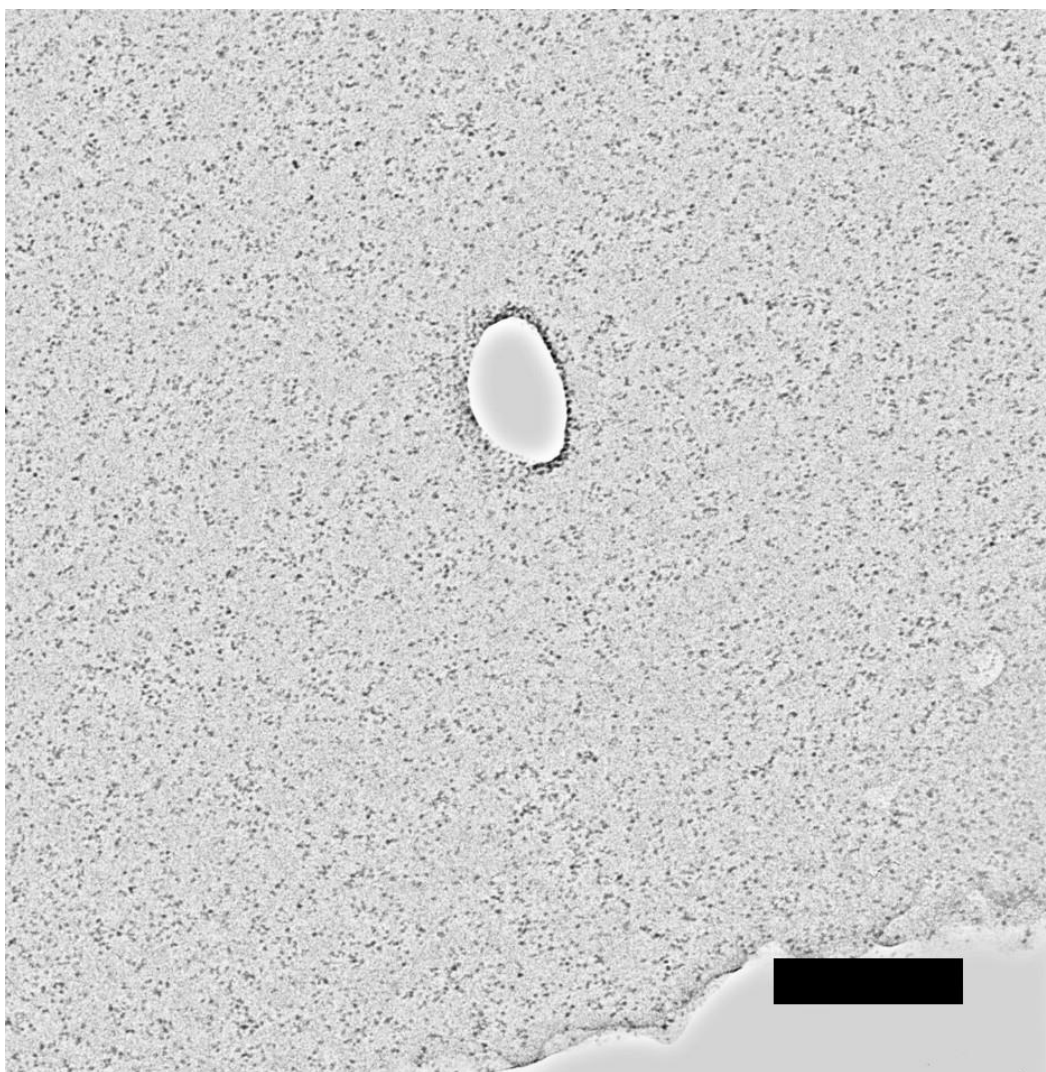


Fig. S10. TEM image of cross section of the VLC-1 film. The samples were annealed at 140 °C for 3 h.

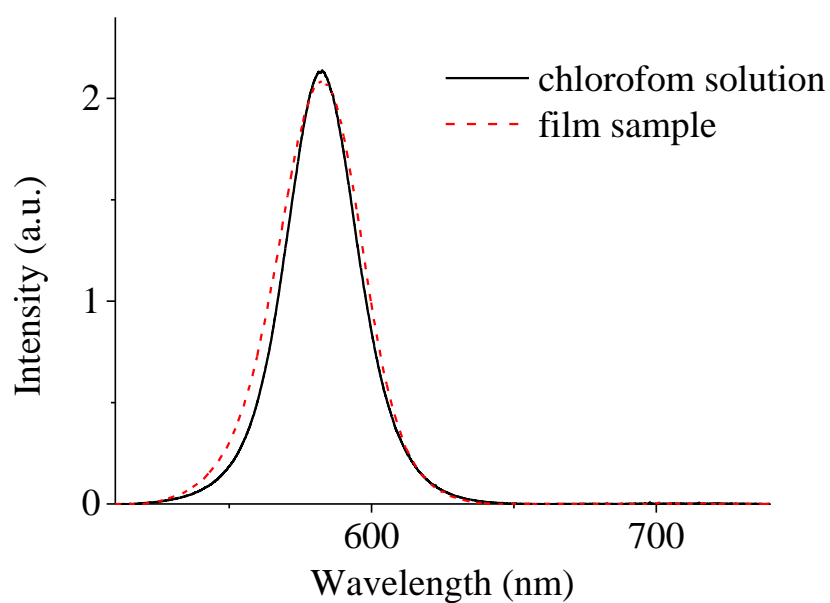


Fig. S11. Fluorescence spectra of the solution of CdSe/ZnS QDs coated with pVP_{60} - b - $pPhM_{40}$ - b - pVP_{60} in chloroform and a film sample of V_{60} - LC_{40} - V_{60} .