Supporting Information

Liquid crystalline block copolymers as adaptive agents for compatibility between CdSe/ZnS quantum dots and low-molecular-weight liquid crystals

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Experimental section

Materials

Chloroform, pyridine, methanol, hexane and 4′-pentyl-4-biphenylcarbonitrile (5CB) were purchased from Aldrich. Chloroform was passed through aluminum oxide and distilled. Pyridine were dried over KOH and distilled over CaH_2. RM257 were purchased from Synthon (Fig. S1a). CdSe/ZnS quantum dots (QDs) covered with oleylamine and surrounded by TOPO matrix were synthesized according to a previous literature.[1] HexSorb and BuSorb (Fig. S1b and c, respectively) were synthesized as described previously.[2] Synthesis of LC triblock copolymers were performed by reversible addition-fragmentation transfer polymerization (Scheme 1) as described previously.[3]

Preparation of the inorganic-polymer composites

Ligand exchange technique: the replacement of oleylamine by pyridine

To substitute pyridine for oleylamine ligand covering CdSe/ZnS QDs ligand exchange procedure was used according to a previous literaturee.[4] Firstly, QDs were precipitated three times from chloroform solution into methanol to remove TOP/TOPO matrix. Then 100 mg of QDs were dispersed in 20 ml of anhydrous pyridine and the mixture was placed in an ampoule, which was purged with argon for 40 min. The ampoule was sealed and heated to 90 °C for 24 h. After that, the reaction mixture was cooled to room temperature,

ampoule was opened and QDs were precipitated into hexane. The precipitate of QDs was collected by centrifugation, washed by an excess of hexane and dried under vacuum. To achieve the highest possible replacement of oleylamine by pyridine, described procedure was repeated three times. Obtained QDs coated with pyridine were stored as a pyridine solution under argon atmosphere at 0°C.

Ligand exchange technique: the replacement of pyridine by triblock copolymer

The preparation of pVP_{60}-5% is given here as a typical example. 2.6 mg of QDs covered with pyridine and dispersed in pyridine (150 μl) were added to 47.4 mg of pVP_{60}-*b*-$pPhM_{40}$-*b*-pVP_{60} dissolved in chloroform (1 ml). Then, the resulting mixture was thoroughly stirred for 3 h. and solvents were removed under reduced pressure. The obtained solid product was dispersed in 1 ml of chloroform and dried under reduced pressure again. The latter procedure was repeated five times. The other composites were prepared via a similar procedure by changing the ratio between QDs and a block copolymer.

Preparation of dispersion of QDs decorated with LC block copolymer in low-molecular-weight cholesteric LC

RM257 (12.5 mg), 5CB (30.1 mg), HexSorb (1.5 mg), BuSorb (1.35 mg) and pVP_{60}-10% (5 mg) were dissolved in 1 ml of chloroform. The obtained mixture was thoroughly stirred and dried under reduced pressure. Then, the mixture was placed into the 20 μm-thick plane-parallel glass cell, both inner surfaces of which were coated with rubbed polyimide layer (ZLI 2650). Sample was annealed at room temperature for 48 h.

Instrumental measurements

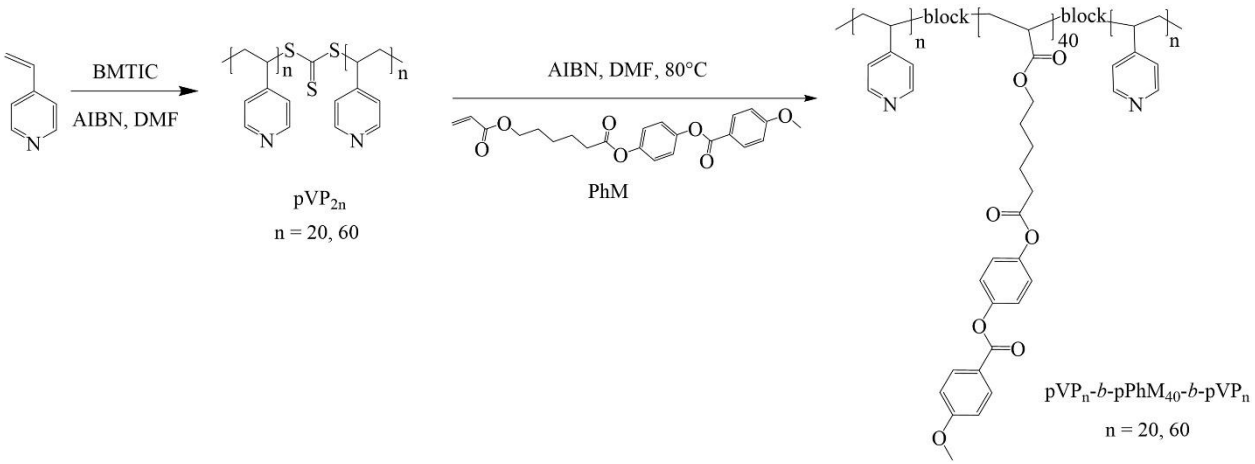
Polarizing optical microscopic (POM) observations were conducted on an Axio Vert. A1 (Carl Zeiss) microscope equipped with a CCD camera and a hot stage. Fluorescence microscopy observations were performed using Micromed 3 LUM microscope (LOMO).

The phase transition temperatures of the polymers were studied by differential scanning calorimetry (DSC) with a PerkinElmer DSC-7 thermal analyzer with a scanning rate of 10 K/min. Samples were prepared as 10–20 mg pellets. Samples were first heated above isotropic melt to remove thermal history.

To prepare samples of the composites for TEM measurements following procedure was used. Firstly, using dispersion of composite in chloroform films were prepared by drop-casting on PTFE substrate. The obtained films were annealed at 140 °C for 3 h. Then, annealed samples were embedded in an epoxy resin and cured overnight. The sample was subsequently microtomed to a thickness of about 50 nm using a Reichert-Gung ultramicrotome with a diamond knife (Diatome) at room temperature. The microtomed sections were floated on water and subsequently placed on copper grids. To obtain contrast during TEM, the samples were stained with iodine for 1 h. TEM images were taken with a LEO 912 AB Omega transmission electron microscope (Carl Zeiss) operating at an accelerating voltage of 100 kV.

Absorbance spectra of the composites were recorded by Unicam UV-500 UV-Vis spectrophotometer. Fluorescence spectra were recorded using an M266 automated monochromator/spectrograph (SOLAR Laser Systems, Belarus) equipped with a CCD U2C-16H7317 (Ormins, Belarus), a homemade light-collecting inverted system using a 100X/0.80 MPLAPON lens (Olympus, Japan) and a homemade confocal unit with two 100-mm objective lenses. Exciting light was cut off by Semrock 488-nm RazorEdge® ultrasteep longpass edge filters (Semrock, USA). Fluorescence of QDs was excited by an KLM-473/h-150 laser (Plazma, Russia) operating at 473 nm. An incident light intensity was equal to 50 mW/cm^2 as measured with a LaserMate-Q (Coherent) intensity meter. ^{1}H NMR spectra of the inorganic-polymer composites in the form of 3% solutions in $CDCl_3$ were recorded on a Bruker DRX500 instrument.

Confocal fluorescence microscopy image was obtained by FluoView 300 scanning system configured on an IX81 inverted microscope platform equipped with a 60 × 1.2 NA water immersion lens (Olympus, Center Valley, PA). The QDs were excited at λ = 457 nm. The sample was formed between two coverslips (25 × 25 mm, Fisher Scientific).



Scheme 1. Synthetic route of pVP_n-b-$pPhM_{40}$-b-pVP_n triblock copolymers.

Table S1. The composition of the mixture of CLC and pVP_{60}-10%.

Component	Content (wt. %)
BuSorb	2.8
HexSorb	3.0
5CB	59.4
RM257	24.8
pVP_{60}-*b*-$pPhM_{40}$-*b*-pVP_{60}	9
CdSe/ZnS QDs	1

Figures

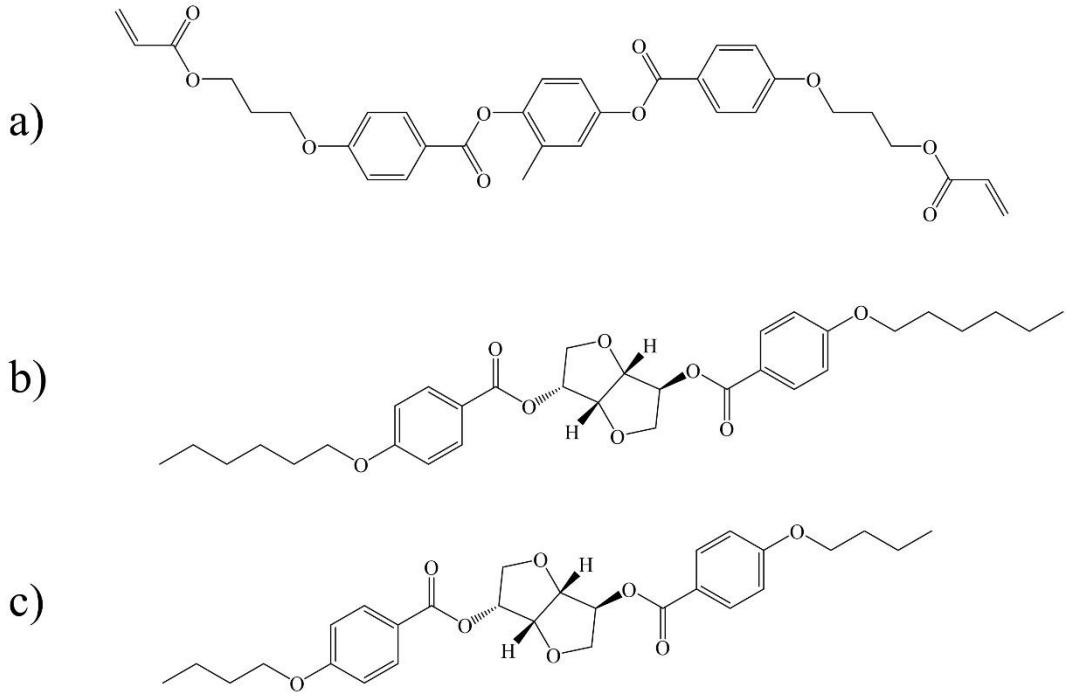


Fig. S 1 Chemical structures of RM257 (a), HexSorb (b), BuSorb (c).

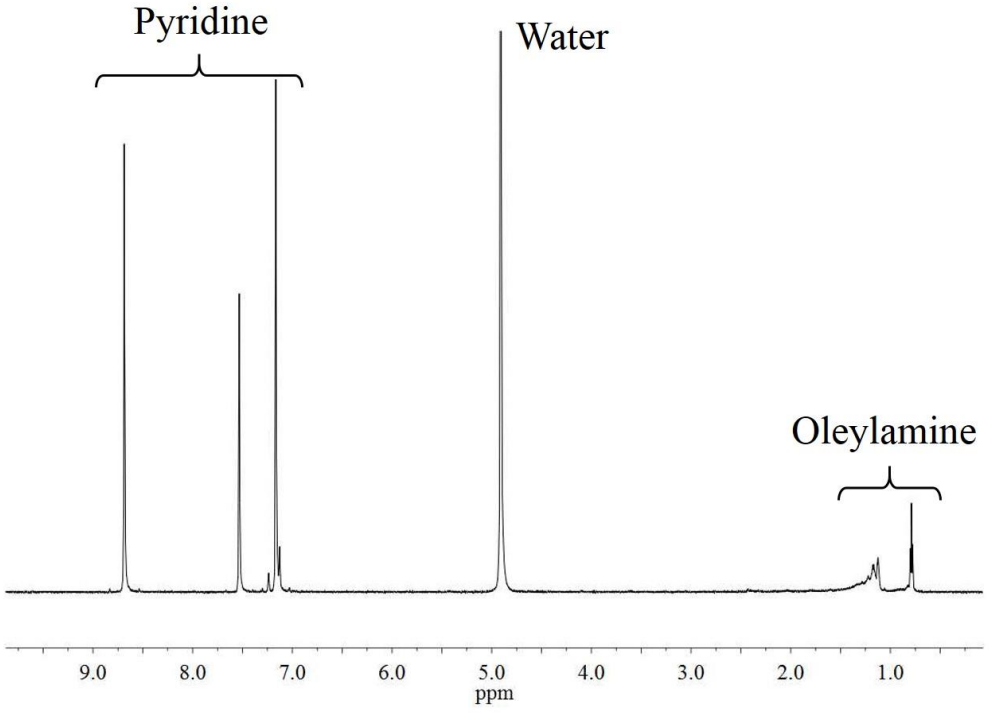


Fig. S 2 ^{1}H NMR spectra of CdSe/ZnS QDs covered with pyridine in pyridine-d_5. The contribution of protonated pyridine containing in pyridine-d_5 was subtracted.

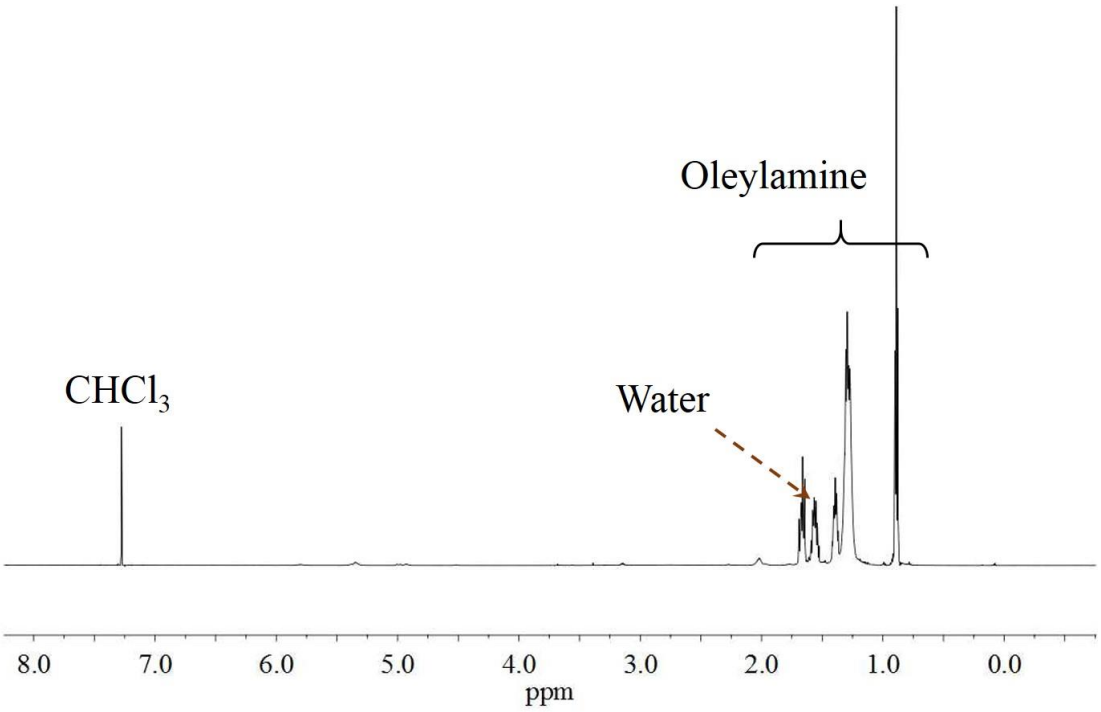


Fig. S 3 ^{1}H NMR spectra of CdSe/ZnS QDs covered with oleylamine in $CDCl_3$.

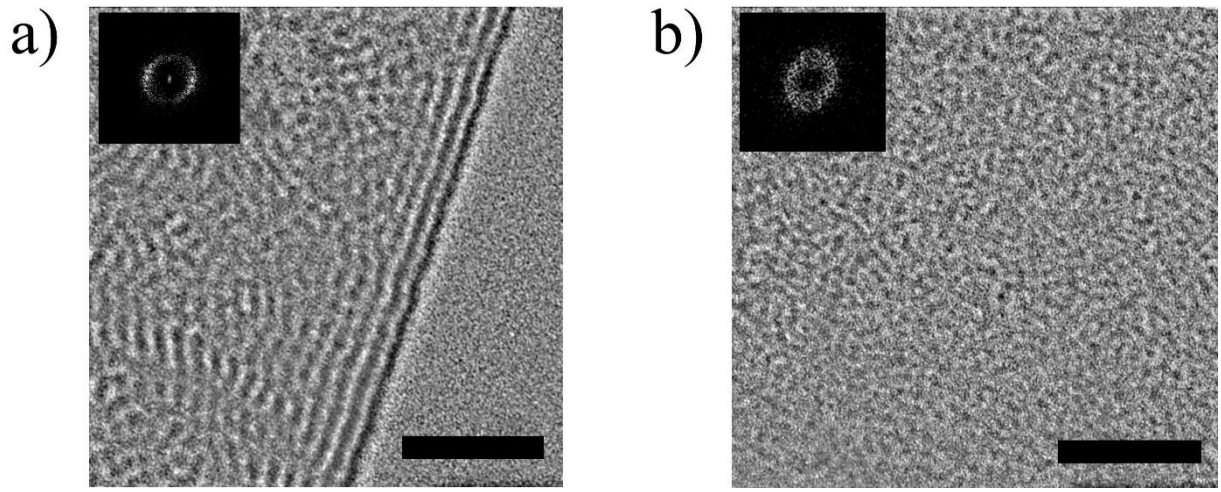


Fig. S 4 TEM images of cross sections of pVP_{60}-b-$pPhM_{40}$-b-pVP_{60} (a) and pVP_{20}-b-$pPhM_{40}$-b-pVP_{20} (b). The samples were annealed at 140 °C for 3 h and stained with iodine for 1 h. The insets are a corresponding FFT image. Scale bar: 100 nm.

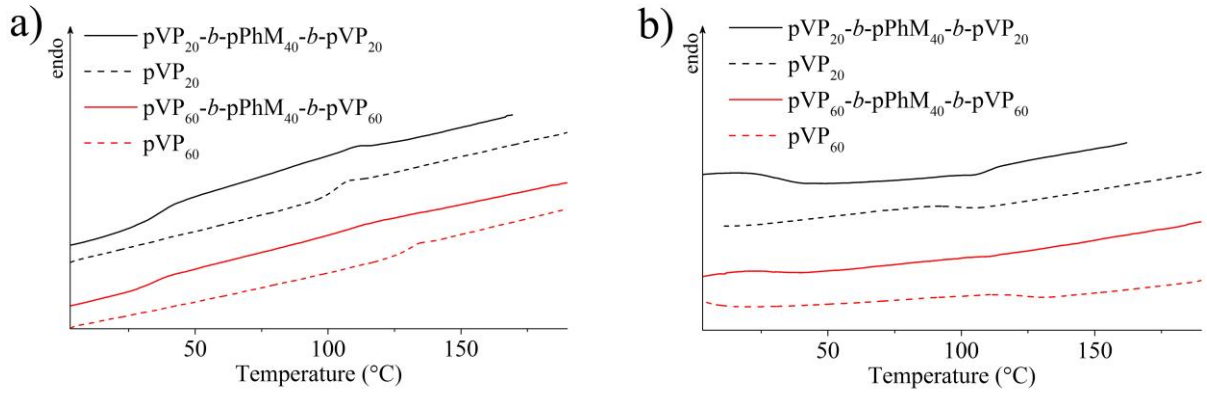


Fig. S 5 DSC curves of samples of pVP_{60}, pVP_{20}, pVP_{60}-b-$pPhM_{40}$-b-pVP_{60} and pVP_{20}-b-$pPhM_{40}$-b-pVP_{20}: second heating (a) and second cooling (b).

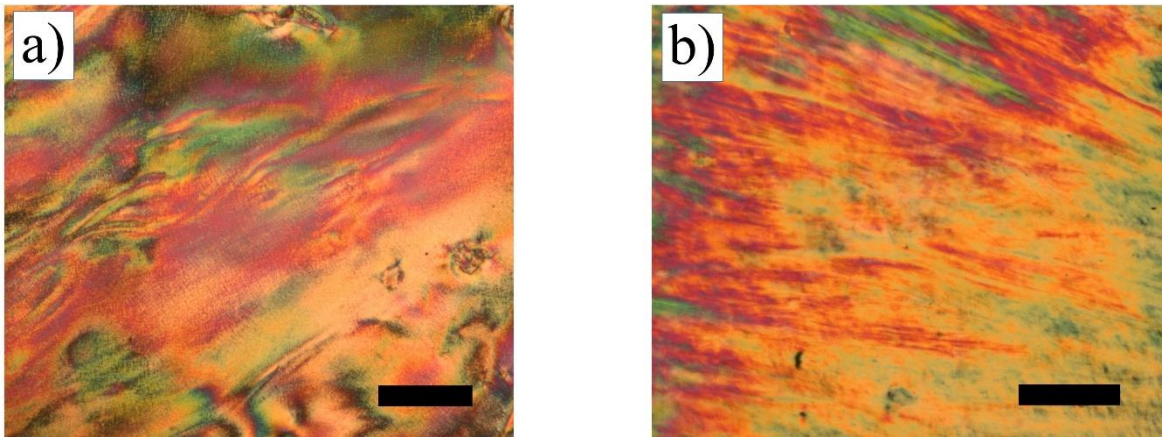


Fig. S 6 POM images of samples of pVP_{20}-b-$pPhM_{40}$-b-pVP_{20} (a) and pVP_{60}-b-$pPhM_{40}$-b-pVP_{60} (b). The samples were annealed at 100 °C for 3 h. Scale bar: 100 μm.

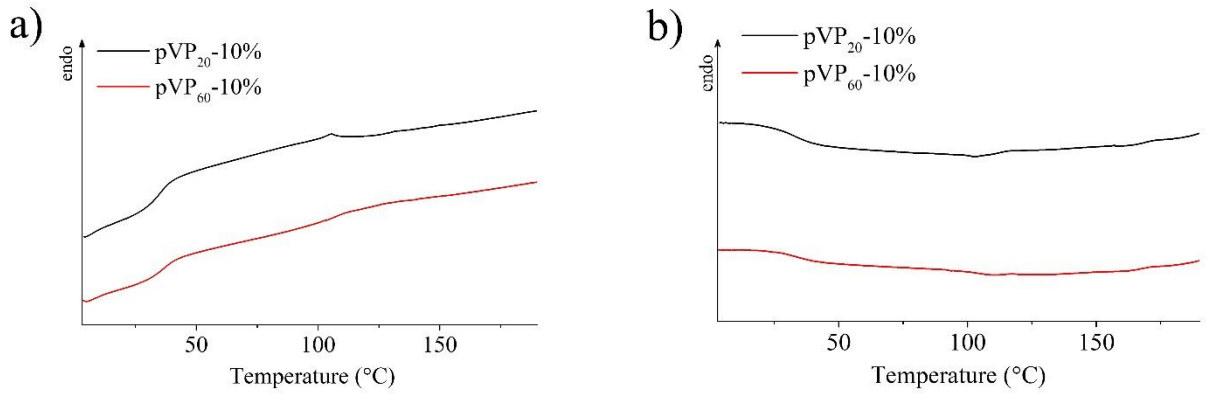


Fig. S 7 DSC curves of samples of pVP_{60}-10% and pVP_{20}-10%: second heating (a) and second cooling (b).

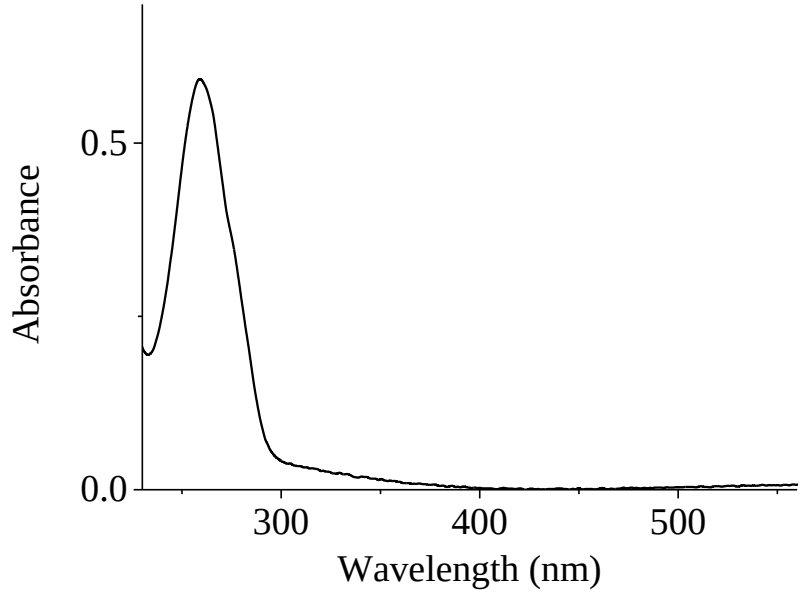


Fig. S 8 Absorbance spectra of a film sample of pVP_{60}-b-$pPhM_{40}$-b-pVP_{60}.

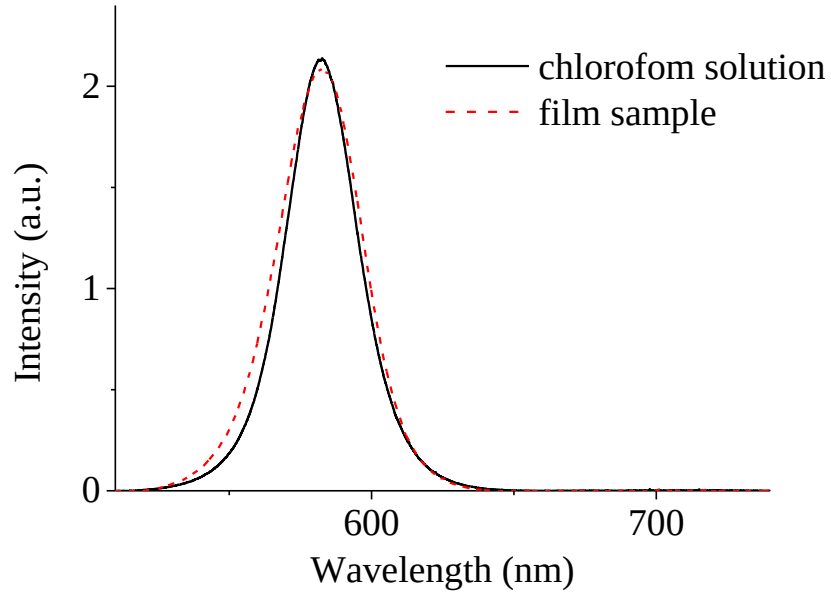


Fig. S 9 Fluorescence spectra of the solution of CdSe/ZnS QDs coated with pVP_{60}-b-$pPhM_{40}$-b-pVP_{60} in chloroform and a film sample of pVP_{60}-10%.

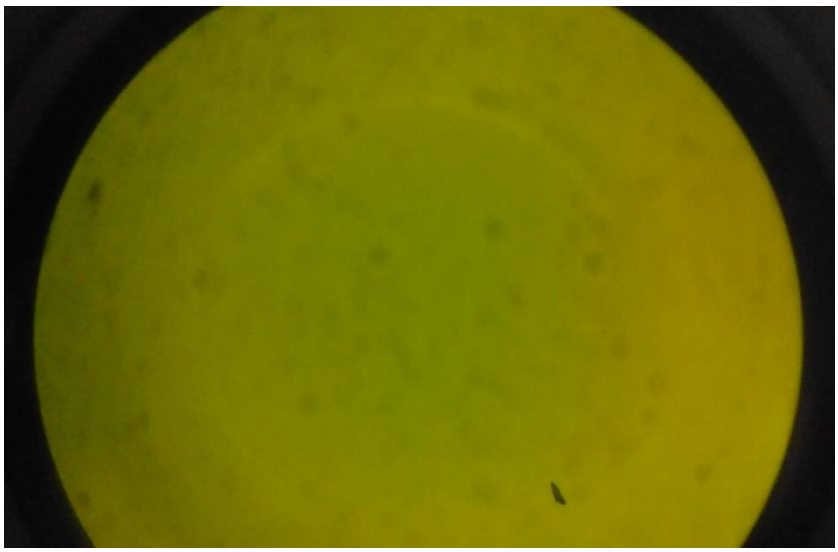


Fig. S 10 Fluorescence microscopy image of 20 μm-thick optical cell filled with the mixture of CLC and pVP_{60}-10%.

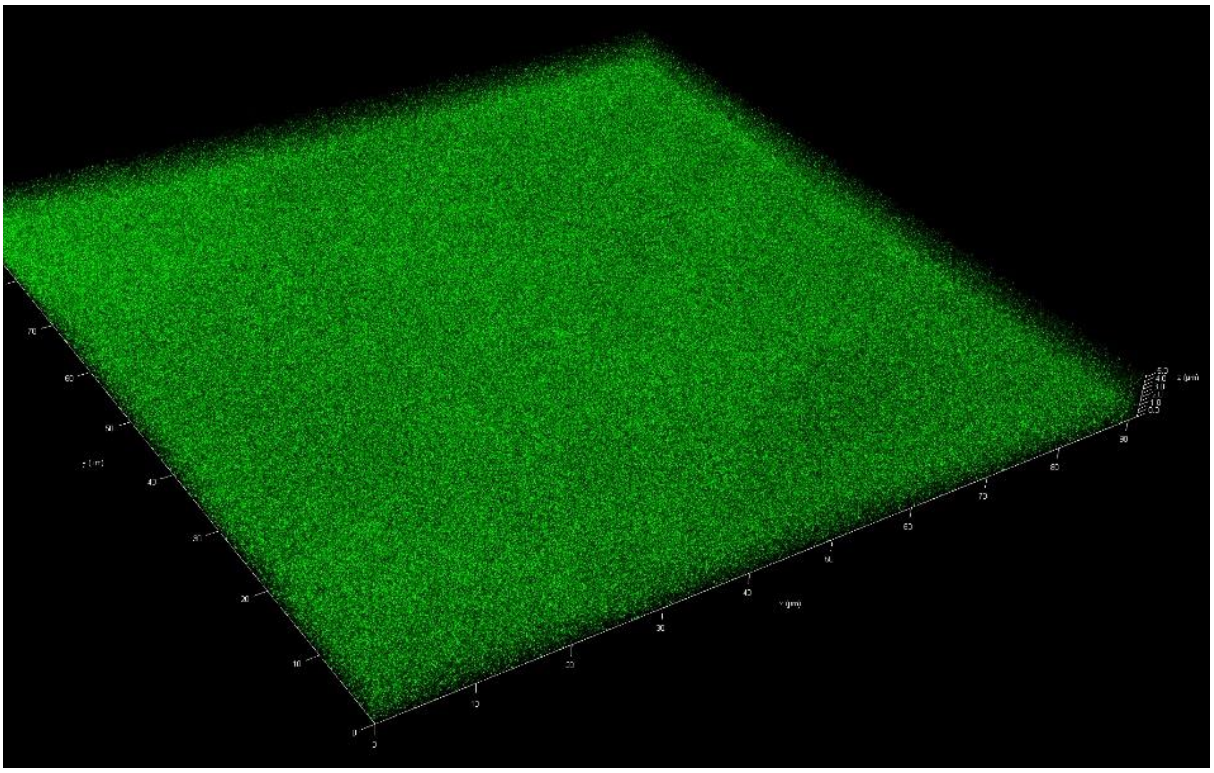


Fig. S 11. Confocal microscopy image of the mixture of CLC and pVP_{60}-10%.

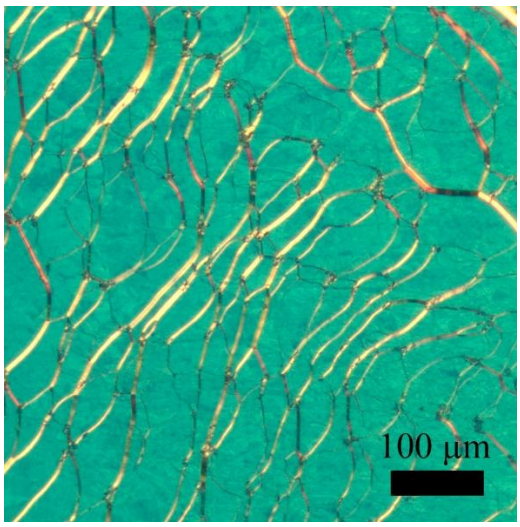


Fig. S 12. POM image of the mixture of CLC and pVP_{60}-10%.

References

1 V. Krivenkov, P. Samokhvalov, M. Zvaigzne, I. Martynov, A. Chistyakov and I. Nabiev, *J. Phys. Chem. C*, 2018, **122**, 15761–15771.

2 A. Bobrovsky, A. Ryabchun, A. Medvedev and V. Shibaev, *J. Photochem. Photobiol. A Chem.*, 2009, **206**, 46–52.

3 M. A. Bugakov, N. I. Boiko, E. V. Chernikova, S. S. Abramchuk and V. P. Shibaev, *Polym. Sci. Ser. C*, 2018, **60**, 3–13.

4 Q. Li, B. Sun, I. a. Kinloch, D. Zhi, H. Sirringhaus and A. H. Windle, *Chem. Mater.*, 2006, **18**, 164–168.