Supplementary Information

Polymer-Grafted ZnO Nanorods Enhance Optical Nonlinearity of Oligothiophene-Doped Liquid Crystals

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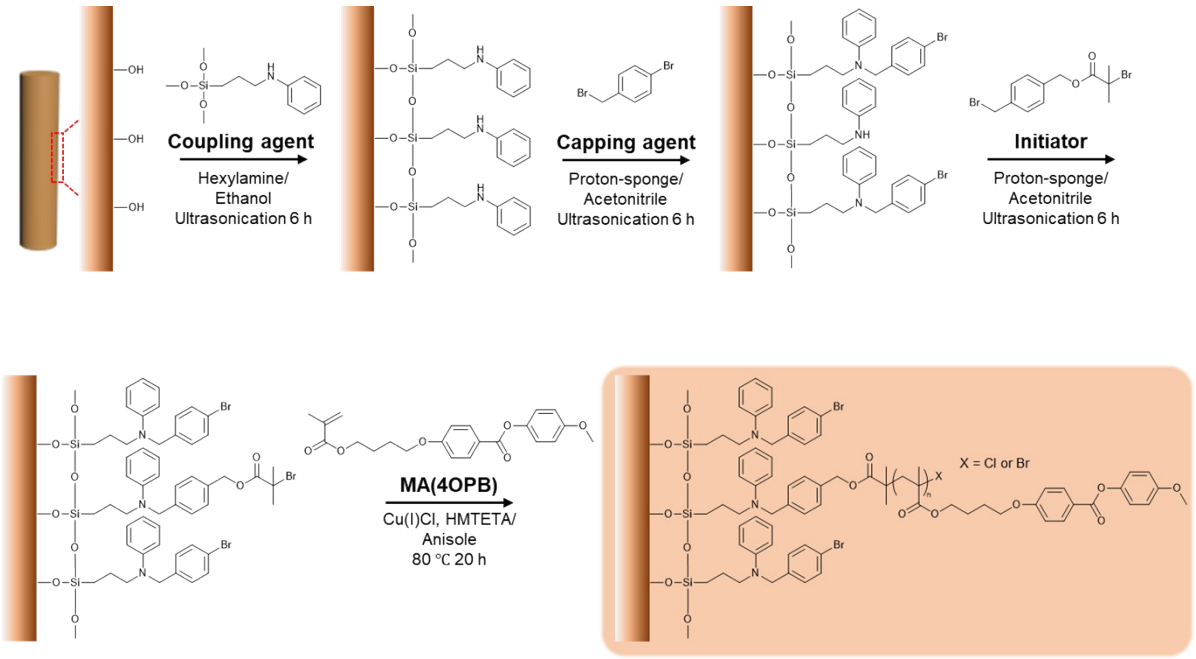

Fig. S1 Schematic representation of the synthesis of polymer-grafted ZnO nanorods.[1] The density of initiator modification was controlled to 1.01 nm^{-2}.

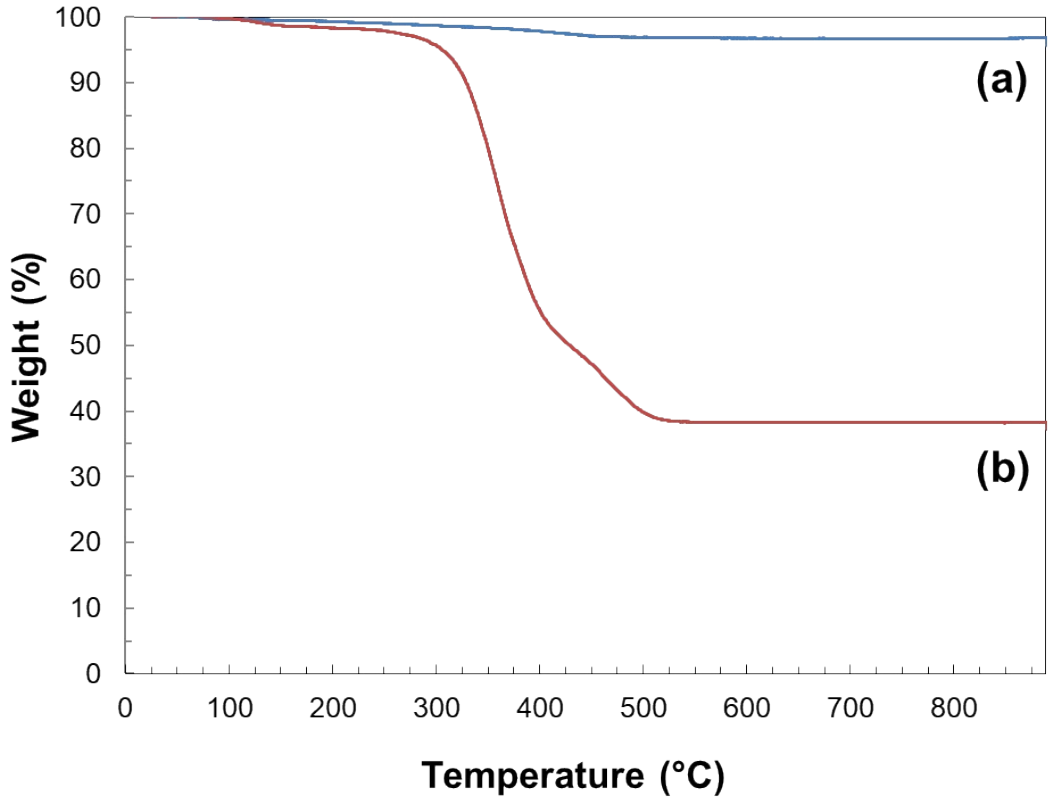

Fig. S2 TGA curves of (a) ZnO and (b) ZnO-PMA(4OPB) nanorods at a heating rate of 10 °C min^{-1}.

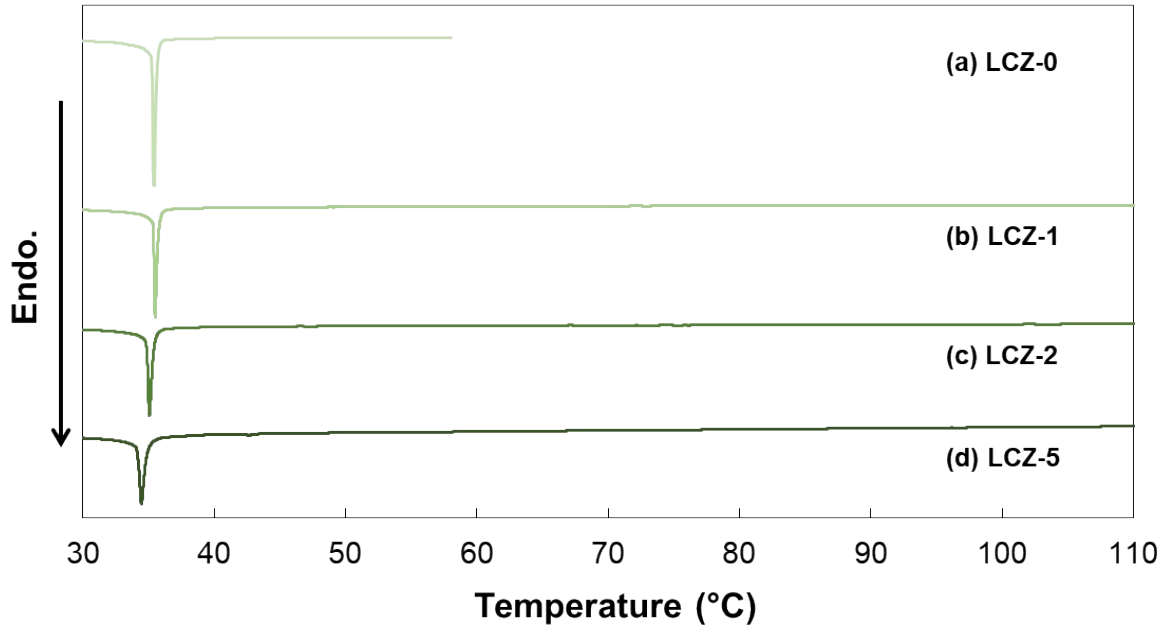

Fig. S3 DSC thermograms of (a) LCZ-0, (b) LCZ-1, (c) LCZ-2, and (d) LCZ-5 on the third heating process. The scanning rate is 1 °C min^{-1}.

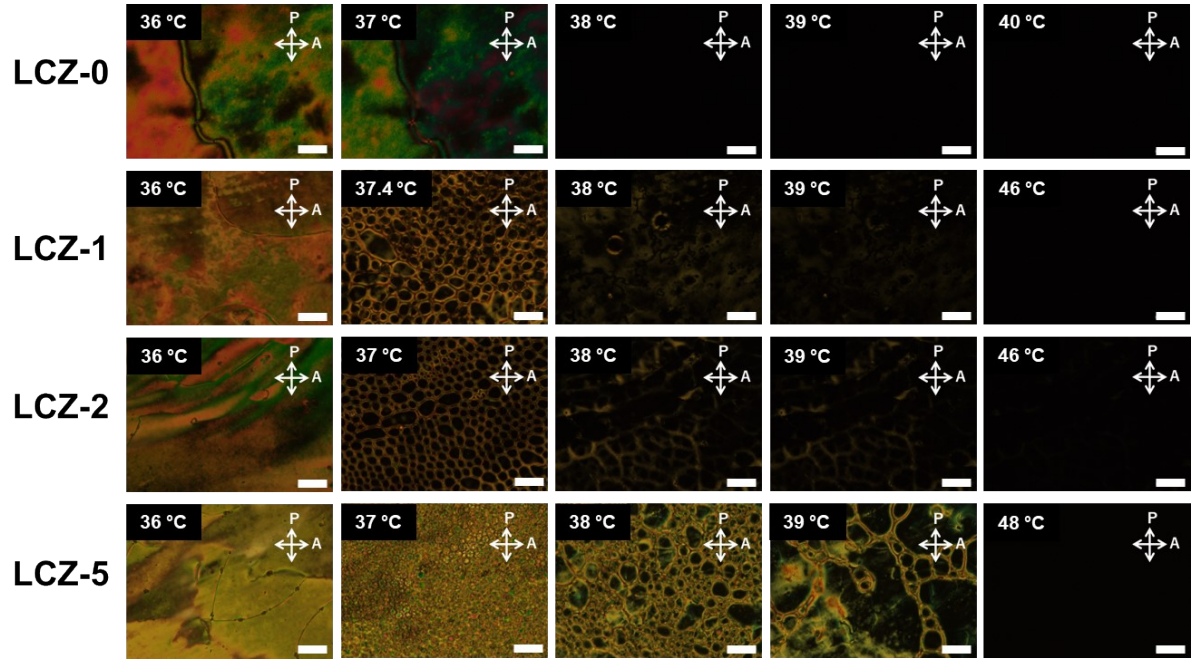

Fig. S4 Polarized optical micrographs of LCZ-*X*. The samples were heated to their isotropic temperature at a scanning rate of 1 °C min^{-1}. The scale bar is 50 μm.

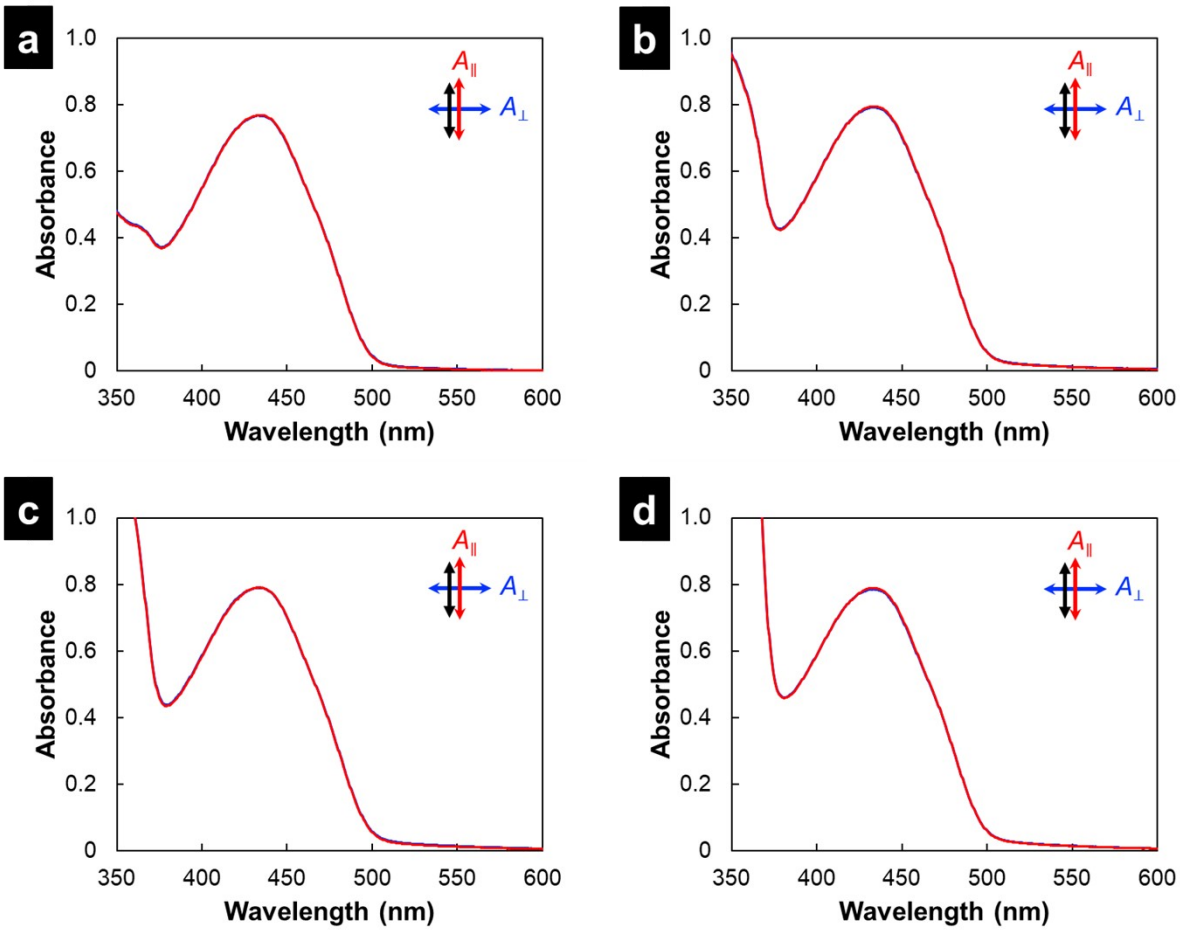

Fig. S5 Polarized UV-vis absorption spectra of LC cells containing LCZ-*X*. (a) LCZ-0, (b) LCZ-1, (c) LCZ-2, and (d) LCZ-5. $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to the injection direction (black arrow) of the sample.

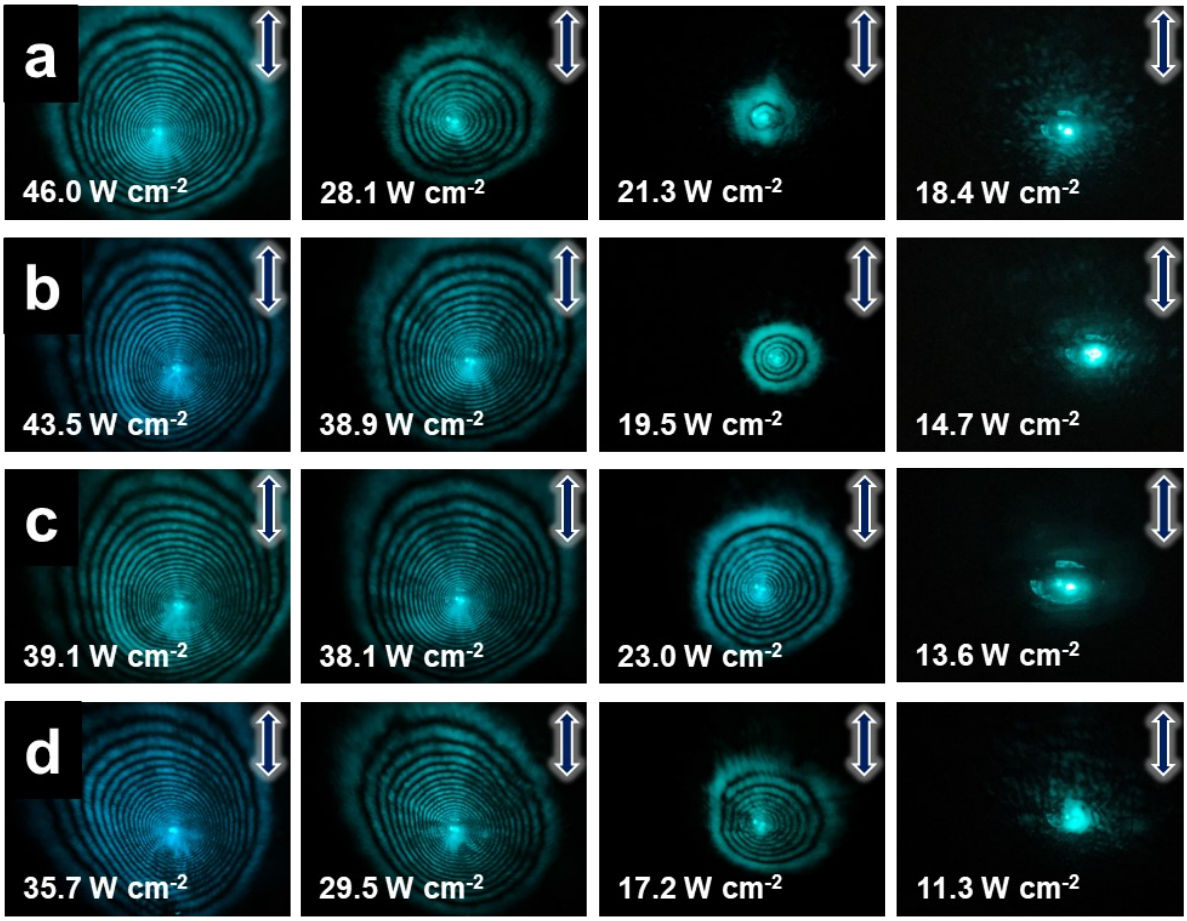

Fig. S6 Diffraction rings formation of LCZ-*X*. Photographs of the diffraction ring patterns arising from the homeotropic-to-planar molecular reorientation in the LC cells of LCZ-0 (a), LCZ-1 (b), LCZ-2 (c), and LCZ-5 (d) at different light intensities. The blue arrow represents the direction of the polarized light.

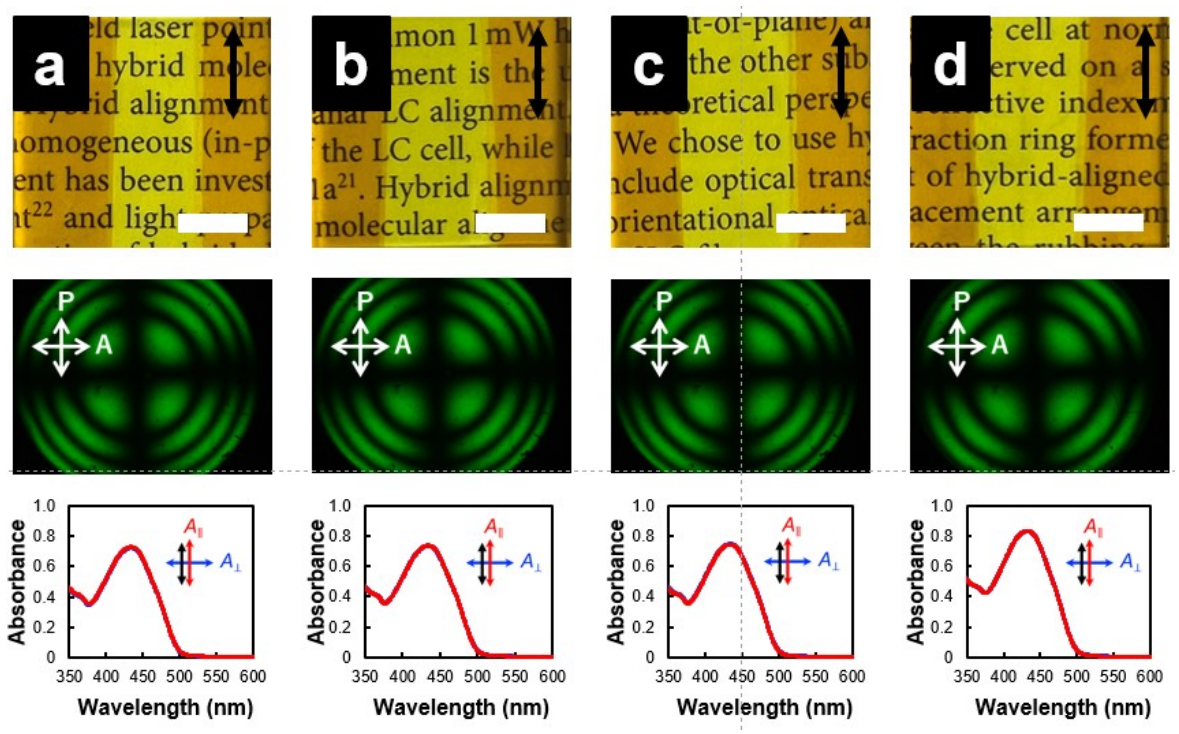

Fig. S7 Photographs (top), conoscopic POM images (middle), and polarized UV-vis absorption spectra (bottom) of TR5-doped 5CB containing PMA(4OPB) in homeotropic cells at the concentrations of 0 (a), 0.39 (b), 0.78 (c), and 1.98 (d) mol%. $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to the injection direction (black arrow) of the sample. The scale bar is 5 mm.

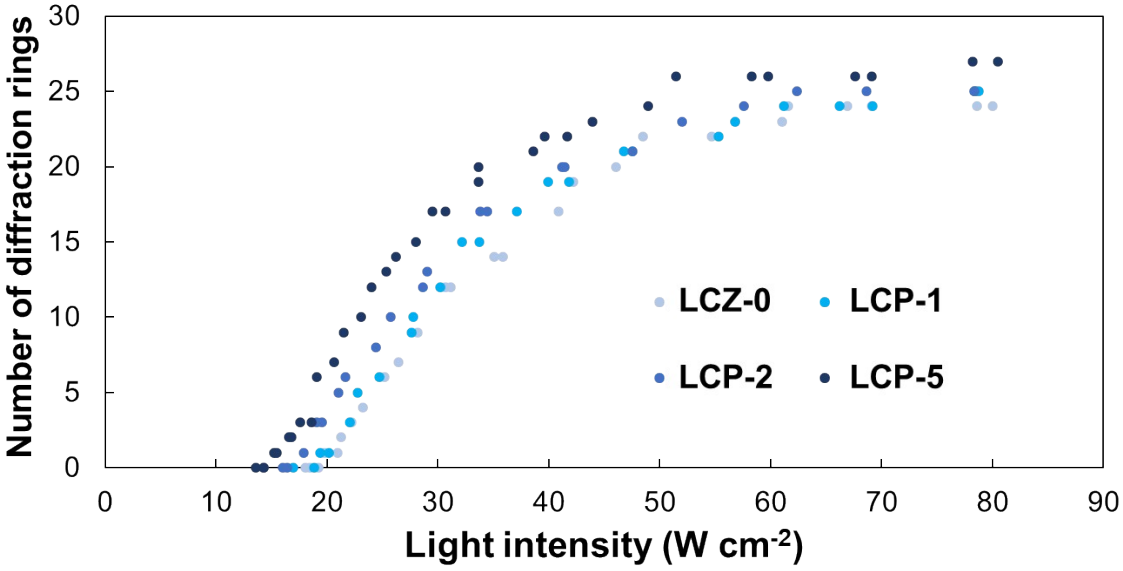

Fig. S8 Number of diffraction rings as a function of light intensity for oligothiophene-doped LC systems containing homopolymers at different concentrations.

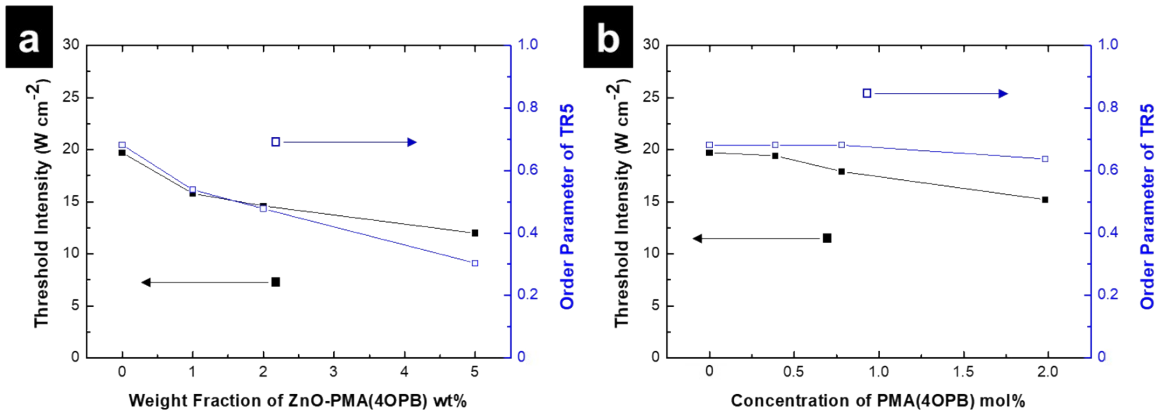

Fig. S9 The threshold intensity and order parameter of TR5 molecules in LC systems containing (a) LCZ-*X* and (b) homopolymers. To evaluate the order parameter of these LC systems, homogeneous LC cells were prepared by the following steps. Two commercially available glass substrates (2.5 cm × 2.5 cm) were ultrasonically cleaned with 2-propanol for 30 min. Subsequently, the glass substrates were treated with a UV-ozone cleaner for 10 min. A precursor solution (AL-1254, JSR Corporation, Tokyo, Japan) was spin-coated on the glass substrate to form a uniform homogeneous alignment layer. After the spin-coating, the glass substrates were treated at 220 °C for 2 h and consequently rubbed in one direction using a rubbing apparatus (MRG-100, EHC, Tokyo, Japan) to yield surface-treated glass substrates that can align LC molecules homogeneously. Next, the glass cells were fabricated by sandwiching two surface-treated glass substrates with 20 μm-thick polyimide tapes. The mixtures of TR5/5CB containing polymer-grafted nanorods or homopolymer were injected into the glass cells by capillary actions then annealed at 70 °C to induce a homogeneous alignment of TR5, host LC, and polymer-grafted nanorods. Then, the order parameter of TR5 in LC systems containing polymer-grafted nanorods and homopolymer was estimated by measuring the polarized UV-Vis spectra for every sample and using the following equation[2]: $S = (A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp})$, where $A_{\parallel}$ and $A_{\perp}$ are the polarized absorbances parallel and perpendicular to the rubbing direction of the alignment layers, respectively. The maximum absorbance of TR5 was used to evaluate the order parameter of oligothiophene-doped LC systems containing polymer-grafted nanorods and homopolymers.

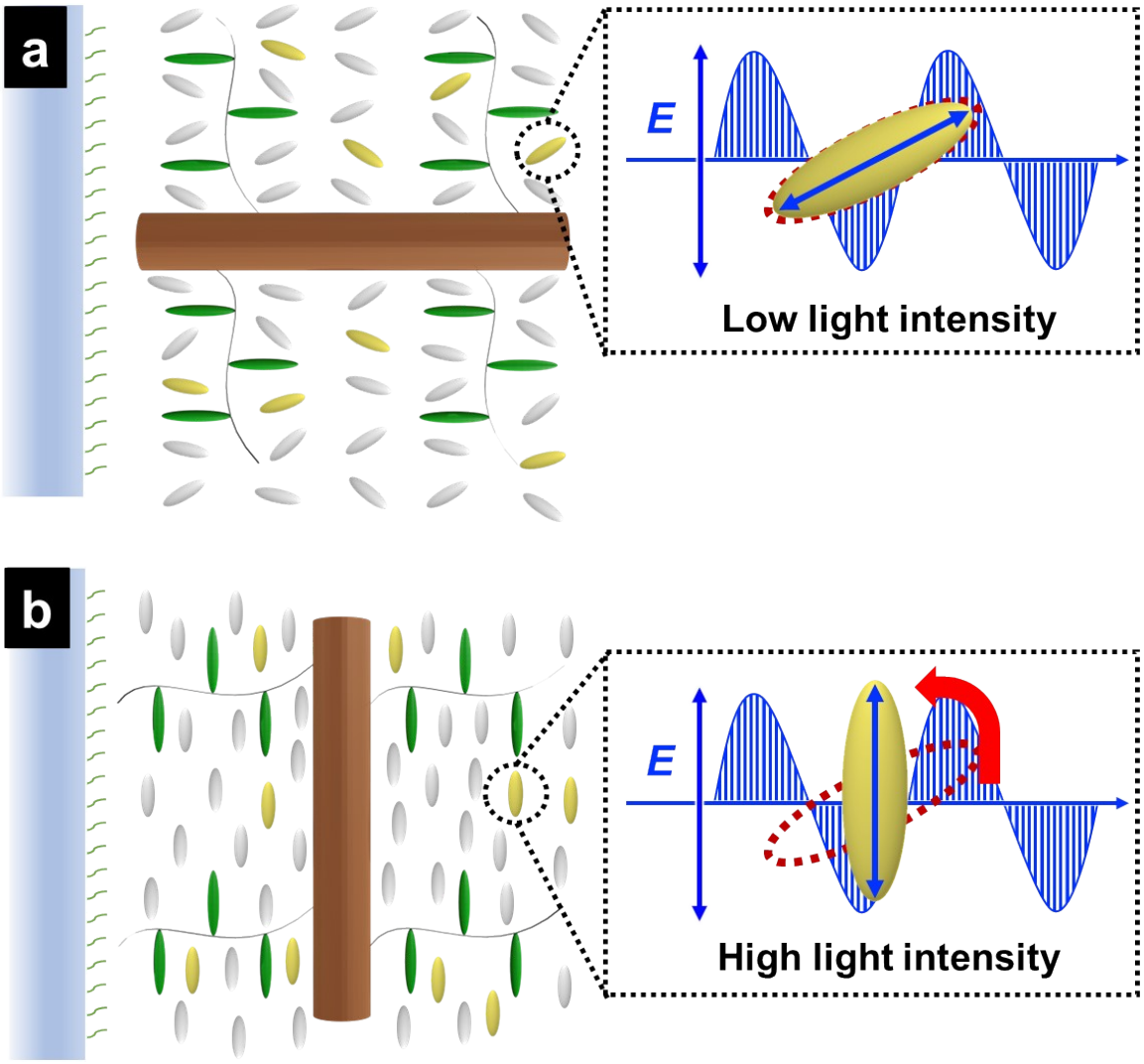

Fig. S10 Schematic illustrations of the molecular reorientation of LCZ-*X*. (a) At low light intensity, no reorientation of molecules is induced. The addition of polymer-grafted nanorods induces a slight disordering of molecules. (b) The polymer-grafted nanorods were reoriented parallel to the glass substrate at high light intensities due to the cooperative molecular interactions between the mesogens of the grafted polymers and the molecules. The inset shows the reorientation of the TR5 molecules parallel to the polarization direction of optical electric field when light intensity is increased to a certain threshold.

Table S1 The compositions of all oligothiophene-doped LC systems containing homopolymers.

Sample	Compositions (mol%)	
	TR5/5CB [a]	PMA(4OPB)
LCZ-0	100	0
LCP-1	99.61	0.39
LCP-2	99.22	0.78
LCP-5	98.02	1.98

[a] The guest-dye, TR5, is doped into 5CB at a dye concentration of 0.1 mol%.

Table S2 Characteristics of oligothiophene-doped LC systems containing homopolymer. [a]

Sample	Absorbance at 488 nm [a]	Threshold Intensity (W cm^{-2})	Max. # of Rings
LCZ-0	0.166	19.7	24
LCP-1	0.161	19.4	25
LCP-2	0.161	17.9	25
LCP-5	0.176	15.2	27

[a] Determined by polarized UV-vis absorption spectroscopy.

【References】

1. S. Kubo, R. Taguchi, S. Hadano, M. Narita, O. Watanabe, T. Iyoda and M. Nakagawa, *ACS Appl. Mater. Interfaces*, 2014, **6**, 811–818.
2. M. Kondo, M. Sugimoto, M. Yamada, Y. Naka, J.-I. Mamiya, M. Kinoshita, A. Shishido, Y. Yu and T. Ikeda, *J. Mater. Chem.*, 2010, **20**, 117–122.