## **Electronic Supplementary Information (ESI)**

## Liquid-crystalline compounds containing both strong *push-pull* azo chromophore and cholesteryl unit as photoresponsive molecular glass materials

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Scheme S1. Synthetic route of R-Chol.



Figure S1. <sup>1</sup>H NMR spectra of CA-Chol, CN-Chol and NT-Chol.



Figure S2. FT-IR spectra of R-Chol.



Figure S3. POM micrographs of R-Chol, (a) CA-Chol at 168 °C, (b) CN-Chol at 50 °C, (c) CN-Chol at 70 °C, (d) NT-Chol at 90 °C.



Figure S4. X-ray diffraction curves of the R-Chol quenched from the LC state and measured at room temperature.



Figure S5. POM micrograph of the spin-coated film of NT-Chol at room temperature.



Figure S6 DSC curves of R-Chol samples collected from the spin-coated films.



**Figure S7.** 10-fold quasi-crystal produced with interference pattern on the film of CN-Chol: (a) AFM 2D-view image, (b) AFM 3D-view image, (c) optical micrograph in transmittance mode, (d) optical micrograph in refractive mode, (e) photograph of the He-Ne laser diffraction pattern.



**Figure S8.** The scheme for the holographic recording on CA-Chol film. A diodepumped frequency-doubled solid state laser beam with Gaussian profile at 532 nm was split into two equal-intensity beams by using a beam splitter (BS). Several mirrors (M) were used to adjust the beam propagation directions. One beam whose size was controlled by a lens (L1) irradiated onto the CA-Chol film directly. Another beam expanded by two lenses (L2 and L3) was used to record the image of panda and then irradiated onto the same position of the CA-Chol film after collimated by a third lens (L4). The whole recording process was completed in 5-20 seconds. After recording the image of panda, a He-Ne laser (633 nm) was used to read out the hologram recorded on the film.