Supporting Information

Thermo-responsive Shape and Optical Memories of Photonic Composite Film Enabled by Glassy Liquid Crystalline Polymer Networks

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1 Characterization of AC6CN, A6OCM, C4M and C6M



AC6CN: ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.19 (d, J = 8.6 Hz, 2H), 7.77 (d, J = 7.9 Hz, 2H), 7.71 (d, J = 8.3Hz, 2H), 7.66 (d, J = 8.3Hz, 2H), 7.35 (d, J = 8.3Hz, 2H), 7.01 (d, J = 8.6Hz, 2H), 6.44 (d, J = 17.3Hz,1H), 6.20-6.11 (m, 1H), 5.85 (d, J = 10.5Hz, 1H),



A6OCB: ¹H NMR (600 MHz, CDCl₃, δ): 7.68 (d, J =7.1 Hz, 2H, aryl H), 7.63 (d, J =6.6 Hz, 2H, aryl H), 7.52 (d, J =7.9 Hz, 2H, aryl H),6.98 (d, J = 8.5 Hz, 2H, aryl H), 6.40 (d,

J =17.1 Hz, 1H, vinyl), 6.12 (dd, J =10.5 Hz, 17.5 Hz, 1H, vinyl), 5.81 (d, J=10.5Hz,1H, vinyl), 4.17 (t, J=6.7Hz, 2H, -OCH₂), 4.01 (t, J=6.7Hz, 2H, -OCH₂), 1.83 (m, 2H, CH₂), 1.72 (m, 2H, CH₂), 1.60–1.42 (m, 4H, CH₂)



Fig. S1 (c): ¹H NMR of C4M in CDCl₃

C4M: ¹H NMR (400 MHz, CDCl3), δ (ppm): 8.18 (t, *J* = 9.3 Hz, 4H), 7.22-7.08 (m, 3H), 7.04-6.97 (m, 4H), 6.44 (d, *J* = 17.3Hz, 2H), 6.20-6.11 (m, 2H), 5.86 (d, *J* = 10.2Hz, 2H), 4.29 (t, *J* = 5.3Hz, 4H), 4.13 (t, *J* = 5.3Hz, 4H), 2.27 (s, 3H), 2.00-1.88(m, 8H).



Fig. S1 (d): ¹H NMR of C6M in CDCl₃

C6M: ¹H NMR (600 MHz, CDCl₃, δ): 8.15 (dd, J =8.9 Hz,15.5Hz, 4H, aryl H), 7.17 (d, J =8.6 Hz, 1H, aryl H), 7.13 (d, J =2.5 Hz, 1H, aryl H), 7.08 (dd, J =2.78 Hz,8.61Hz, 1H,

aryl H), 6.97 (t, J =8.2 Hz, 4H, aryl H), 6.41 (dd, J =1.2Hz,17.3 Hz, 2H, vinyl), 6.12 (dd, J =10.4 Hz, 17.4 Hz, 2H, vinyl),5.83 (dd, J=1.4Hz,10.4Hz,2H, vinyl), 4.19 (t, J=6.7Hz, 4H, -OCH₂), 4.06 (m, 4H, -OCH₂), 2.24 (s, 3H, -CH₃), 1.85 (m, 4H, CH₂), 1.73 (m, 4H, CH₂), 1.60–1.42 (m, 8H, CH₂).

2 Thermodynamic properties of the LCN



Fig. S2 DSC curve of the LCN 3 Angle dependence of the PBG in the photonic composite film

Here the photonic film sample was rotated by every 10° according to the measured standard, and all the reflectance measurements were manipulated at the condition that the angle between detecting beam and samples was 90°. As shown in Fig. S3, the PBG position undergoes a blue-shift and the corresponding peak intensity has a great decrease as the rotated angle is increased. All these observations demonstrate that both the location and intensity of PBG peak of the photonic film has angle dependence.



Fig. S3 PBG as a function of angle in the photonic composite film