

## Supporting Information For

### Effects of Multivalent Ligand Interactions on Surface-Induced Ordering of Liquid Crystals

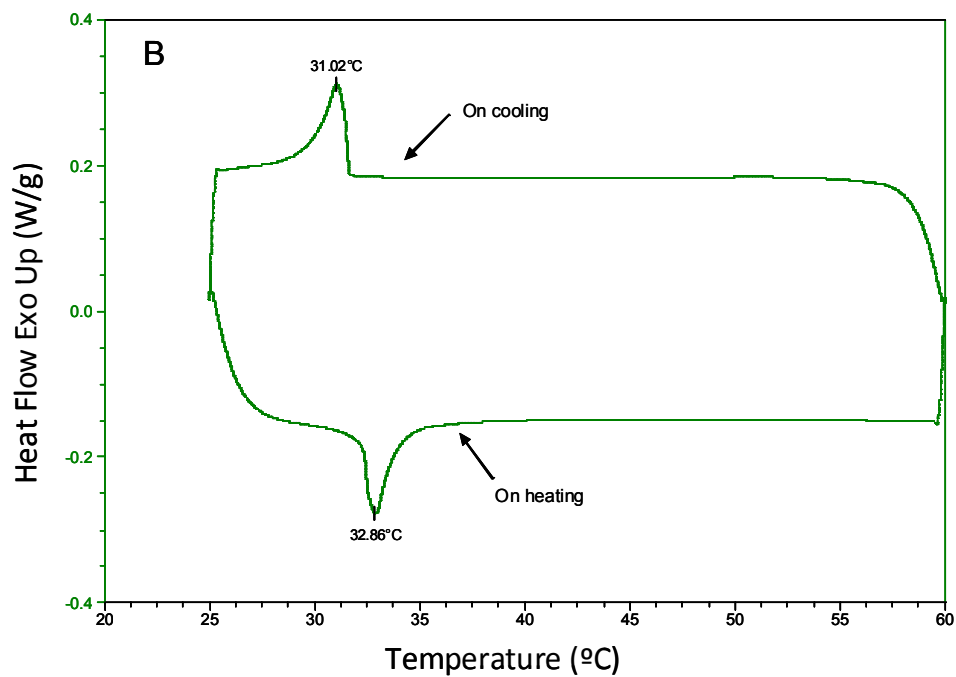
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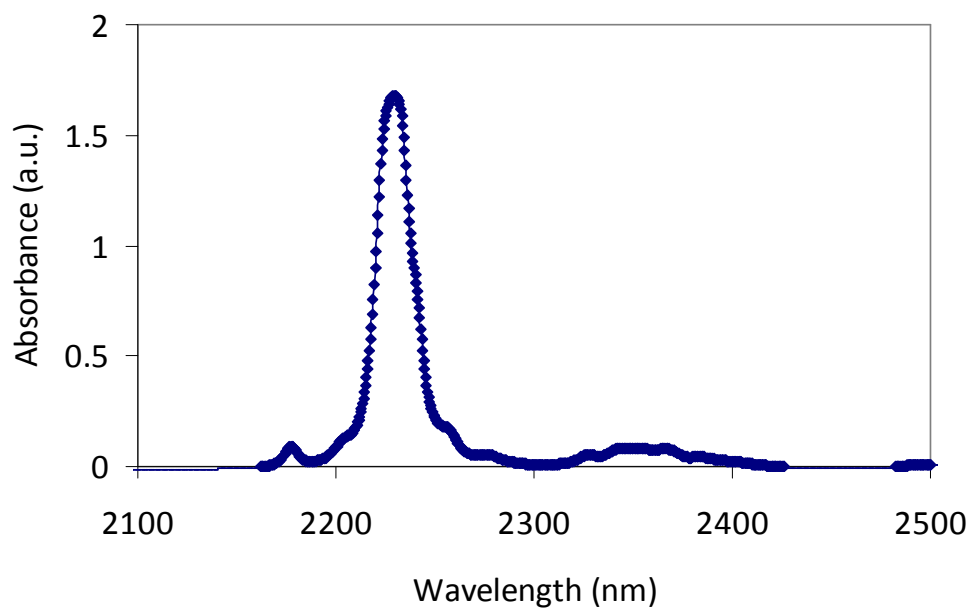
#### Experimental

**Synthesis of 4-pentyl-3',4'-dicyanobiphenyl (DCB).** First 4-pentyl aniline was diazotized in presence of  $\text{NaNO}_2/\text{HCl}$  to produce the diazonium salt. Briefly, 4-pentyl aniline in concentrated hydrochloric acid was cooled to  $0^\circ\text{C}$  and stirred while  $\text{NaNO}_2$  was added in portions, keeping the temperature below  $5^\circ\text{C}$ . After the addition was complete, the reaction mixture was stirred for an additional 15 min at  $0^\circ\text{C}$ . The *in situ* diazonium salt was then reacted with 1, 2 dibromobenzene and in presence of  $\text{NaOH}$  to give 4-pentyl-3',4'-dibromobiphenyl. The crude product was then refluxed for 6 hours with  $\text{CuCN}$  in presence of dry DMF. The excess DMF was removed under vacuum and the resulting residue was passed through a silica column to afford the desired material. The solid compound was then recrystallized twice from methanol to furnish the pure material (10% yield). Selected data for DCB:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (s, 1H), 7.92 (d, 1H), 7.8 (d, 1H), 7.6 (d, 2H), 2.5 (t, 2H), 0.9 (t, 3H), 1.0-1.5 (m, 6H). IR:  $2227\text{ cm}^{-1}$ . Elemental analysis: Calculated for  $\text{C}_{19}\text{H}_{18}\text{N}_2$ , C 83.16, H 6.57, N 10.21%; found C 82.72, H 6.15, N 9.89%. DSC: Cr  $52^\circ\text{C}$  I (Cr = crystalline phase, I = isotropic).

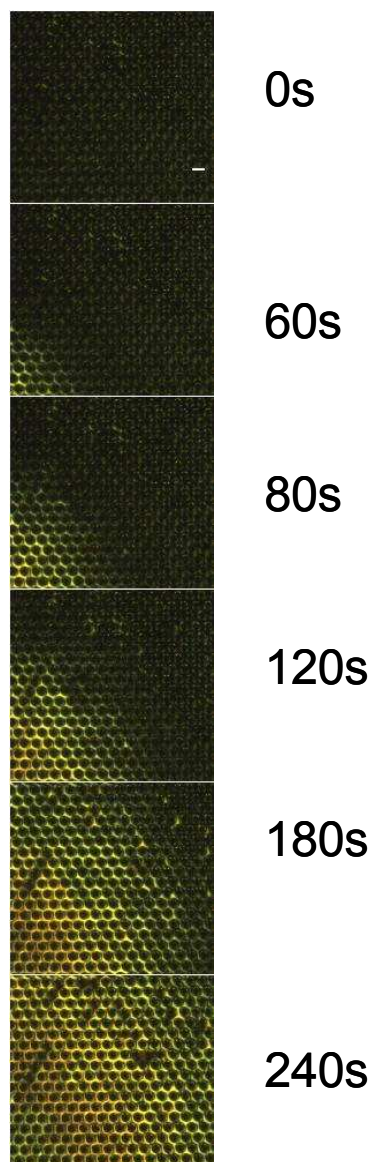
**Preparation of LC Mixtures from 5CB and DCB.** We added a small wt% of DCB (dicyanobiphenyl) to 5CB and then heated the mixture above  $T_{\text{NI}}$ . The mixture was then vortexed for 30s to obtain a homogenous suspension. To determine if DCB was miscible with 5CB, we performed DSC (1 wt% DCB in 5CB, see Figure S1). The mixture exhibited only one transition at around  $33^\circ\text{C}$ : No peak was evident in the region of the melting temperature of pure DCB ( $\sim 52^\circ\text{C}$ ). This suggests that DCB is miscible with 5CB.



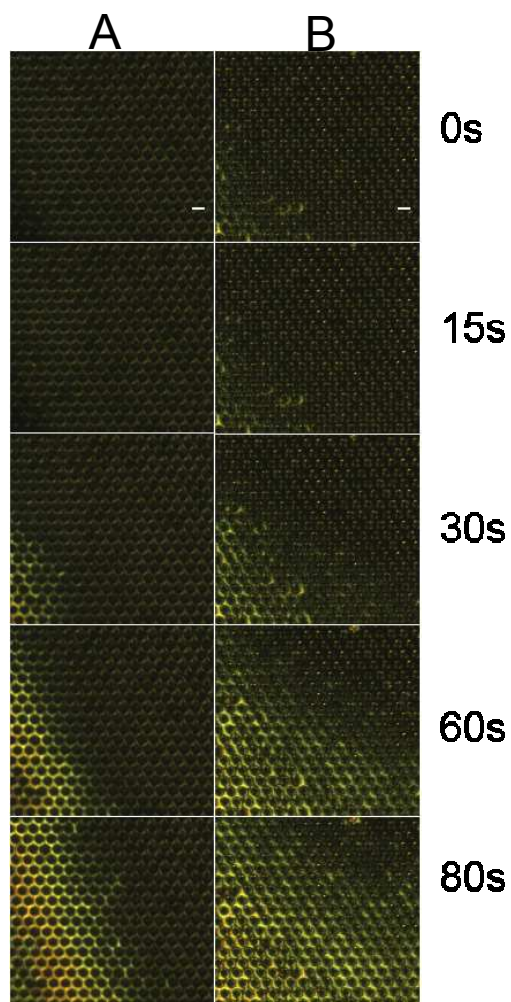
**Figure S1.** Dsc traces for 1 wt% DCB in 5CB on heating and cooling (scan rate 2°C/min).



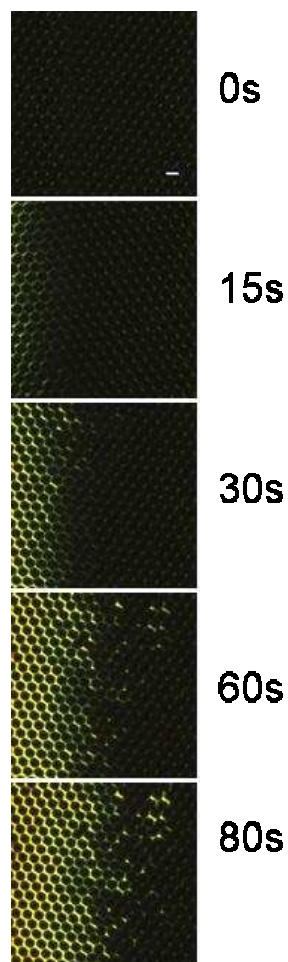
**Figure S2.** IR spectrum of benzonitrile solution. It exhibited a single peak at 2230  $\text{cm}^{-1}$  which corresponds to the stretching of the nitrile group of benzonitrile.



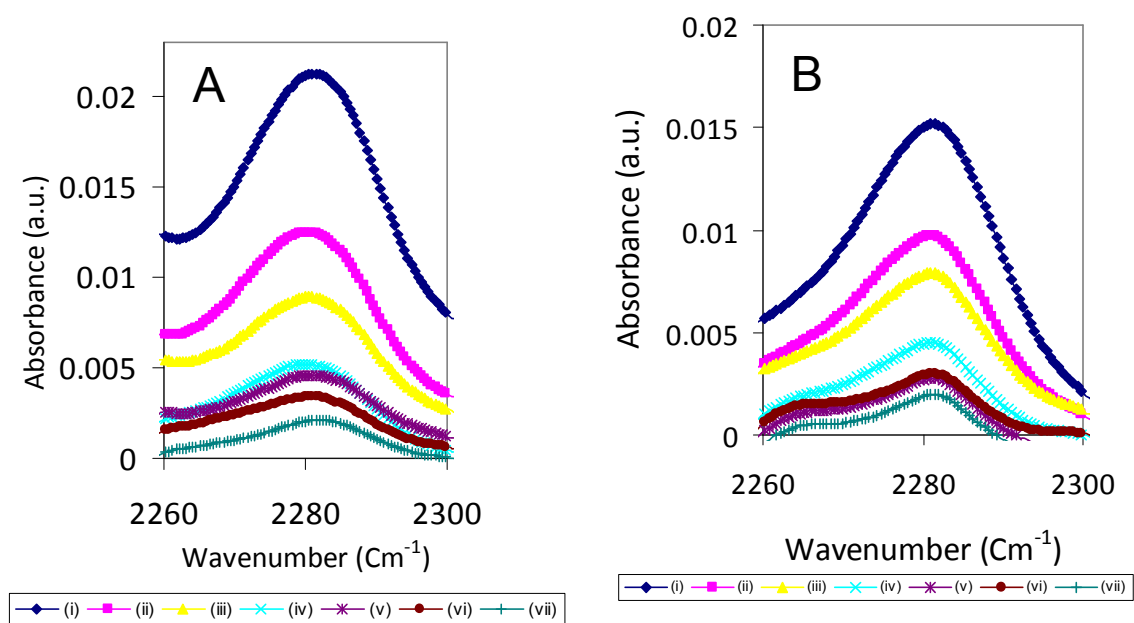
**Figure S3.** Optical images (crossed polars) of a mixture of 5CB containing 2.0 wt% DCB showing the time-dependent response of the LCs hosted in micropillar arrays to a vapor of DMMP (Scale bar = 50  $\mu\text{m}$ ).



**Figure S4.** Optical images (crossed polars) of mixtures of 5CB containing 0.9 wt% (A), 1.5 wt % (B) of DCB, showing the time-dependent change in optical appearance caused by exposure to DMMP supported on chemically functionalized  $\text{Cu}^{2+}$  surfaces hosted within micropillar array. The micropillars were coated with excess copper perchlorate salt and then rinsed with ethanol prior to use (Scale bar = 50  $\mu\text{m}$ ).



**Figure S5.** Optical images (crossed polars) of mixtures of 5CB containing 2 wt% DCB showing the time-dependent change in optical appearance caused by exposure to DMMP supported on chemically functionalized  $\text{Cu}^{2+}$  surfaces hosted within micropillar array. The micropillars were coated with excess copper perchlorate salt (Scale bar = 50  $\mu\text{m}$ ).



**Figure S6.** Difference IR spectra (A) obtained after the addition of DMMP [(i) 0 mM (ii) 10 mM (iii) 20 mM (iv) 40 mM (v) 60 mM (vi) 80 mM (vii) 100 mM] to a solution of 5 mM copper perchlorate in benzonitrile and (B) after addition of the same concentration of DMMP to 2 wt% DCB in benzonitrile solutions (B), respectively.