

High-efficiency Responsive Smart Windows Fabricated by Carbon Nanotubes Modified by Liquid Crystalline Polymers

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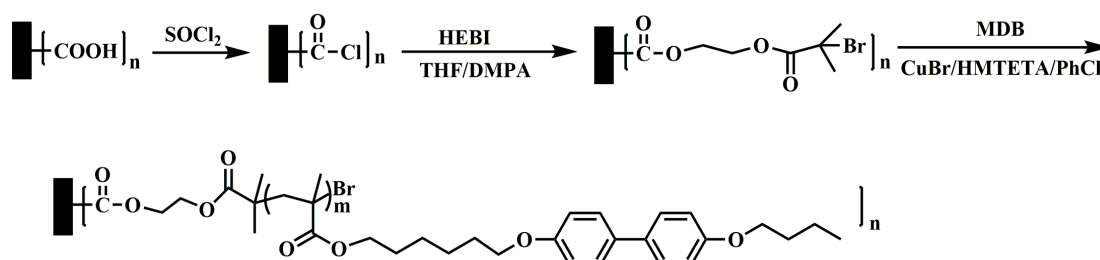
1. Materials.

Photoinitiator Iragcure-651, and photopolymerizable monomer C6M were purchased from Energy Chemical and directly used without any purification. All the LC compounds (4-cyano-4'-pentylbiphenyl (5CB), 4-cyano-4'-heptylbiphenyl (7CB), 4-cyano-4'-octylbiphenyl (8CB), 4-cyano-4'-decylbiphenyl (10CB), 4-cyano-4'-dodecylbiphenyl (12CB), 4-cyano-4'-octanoylbiphenyl (8OCB), 4-cyano-4'-pentylparaterphenyl (5TB)) and chiral dopant S811 were commercially available from Jiangsu Hecheng New Material Co., Ltd. Chlorobenzene was purified according to the previous work. Other solutions and reagents were directly used.

2. Instruments and Measurement.

^1H NMR experiments was recorded on a Bruker ARX400 spectrometer, where tetramethylsilane (TMS) and deuterated chloroform (CDCl_3) were the internal standard and the solvent, respectively. The transmission electron microscope (TEM) experiment was conducted using a JEM-2100F instrument operating with 100 kV accelerating voltage. Fourier transform infrared spectrometer (FT-IR) spectra in the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$ were recorded by a Nicolet 6700 spectrometer. The decomposition temperature of CNT-PDB was determined by thermogravimetric analysis (TGA, TA SDT Q600 instrument) experiment under nitrogen protection at a heating rate of $20\text{ }^\circ\text{C/min}$. TA DSC Q10 calorimeter was used to perform differential scanning calorimetry (DSC) experiment on a programmed heating procedure in nitrogen atmosphere. Contact angle measurements were implemented with a POWEREACH JC2000D1 dynamic contact angle measuring instrument. The orthoscopic and conoscopic images under polarized optical microscopy (POM) were taken under a Leica DM-LM-P with a Mettler FP82HT heating stage. The visible transmittance value was measured by a UV-Vis spectrophotometer (Cary 60). And all photographs were recorded via digital camera (Canon Ixus 125). Infrared imaging (IR) images were recorded by infrared thermal imaging instrument FLIR E4. An 808 nm semiconductor laser source (Center wavelength: $808\pm 3\text{ nm}$, Output power: 8W, Nanjing Latron Laser Company, China) was used to NIR-repsponsive experiments. The vis/NIR spectra and the thermo-optical transmittance were obtained by a UV-vis/NIR spectrophotometer (JASCO V-570) equipped with a hot stage (Linkam LK-600PM) calibrated to an accuracy of $\pm 0.1\text{ K}$. X-ray scattering was performed with Ganesha system (SAXSLAB, U.S.) equipped with a multilayer focused Cu K α radiation as the X-ray source (Genix3D Cu ULD) and a two-dimensional semiconductor detector (Pilatus 100 K, DECTRIS, Swiss).

3. Preparation of CNT-PDB.



Scheme S1. Synthetic route to CNT-PDB.

0.5 g of CNT-COOH and 2 mL of 1,2-dichlorobenzene was added into a flask containing excess thionyl chloride and refluxed at 65°C for 24 h. The solvent was removed under vacuum. The remaining solid was washed three times with anhydrous THF and was vacuum-dried at 25 °C for 0.5 h. A mixture of the solids, 1.0 g (4.67 mmol) of HEBI and 50 mL of anhydrous THF was refluxed for 48 h. The solid was separated through a 0.2 µm polytetrafluoroethylene (PTFE) membrane, thoroughly washed with THF, methanol, and diethyl ether, and then vacuum-dried for 10 h to yield 0.45 g of the initiator CNT-Br.

MDB (0.5 g, 12.2 mmol), CuBr (0.25 mmol), CNT-Br (0.25 mmol), HMTETA (0.25 mmol) and refined chlorobenzene (0.5 g) were added to a glass tube equipped with magnetons, which was sealed under vacuum conditions after repeated five operations of freezing-vacuum-passing nitrogen circulation. Then the glass tube was placed in an oil bath with a magnetic stirrer at 90 °C for 48 h. The glass tube was placed in an ice water bath to terminate the polymerization. The mixture was subsequently dispersed in tetrahydrofuran (THF) and vacuum-filtered using a 0.2 µm PTFE membrane. Then the filtered solid was washed with THF several times to remove PDB and the physically adsorbed compounds. The solid was dissolved in THF and precipitated in anhydrous methanol. The target product of CNT-PDB was dried under vacuum for 48 h (at 40 °C).

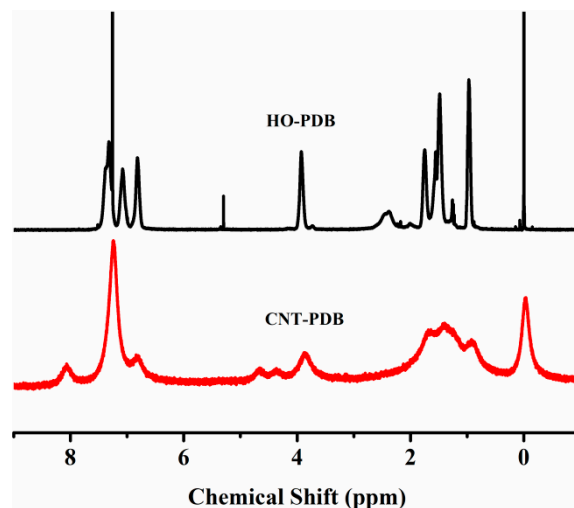


Figure S1. ¹H NMR spectra of polymer HO-PDB and CNT-PDB.

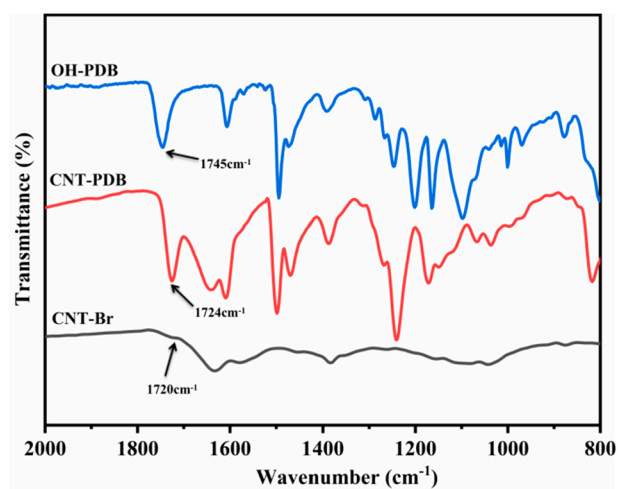


Figure S2. FTIR spectra of HO-PDB, CNT-Br and the polymer brush CNT-PDB.

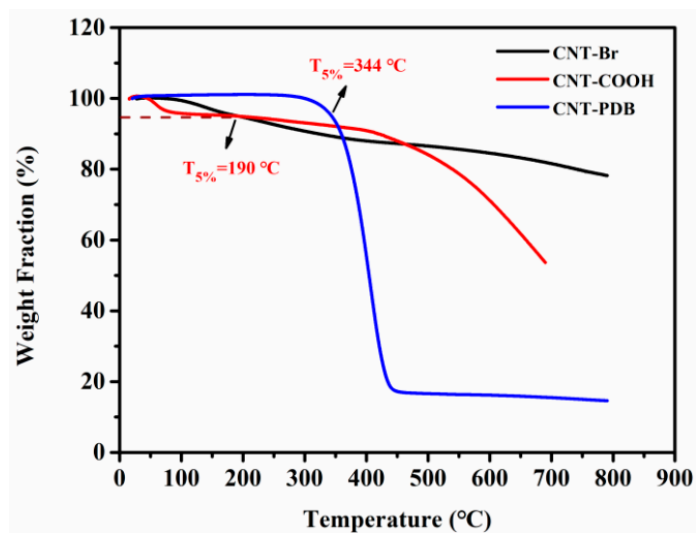


Figure S3. TGA curves of CNT-Br, CNT-COOH and CNT-PDB.

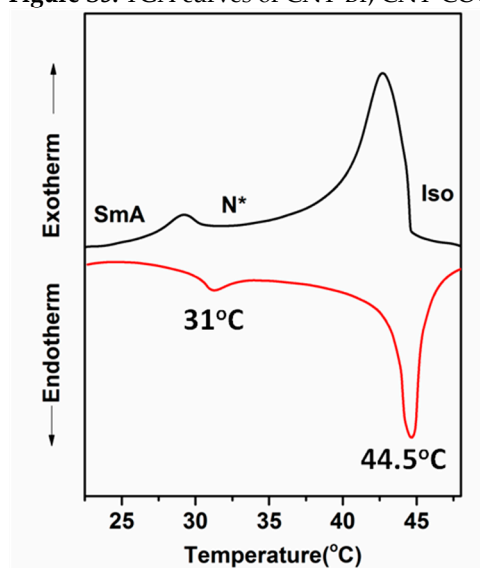


Figure S4. The DSC curve of chiral LC mixture(ChLC).

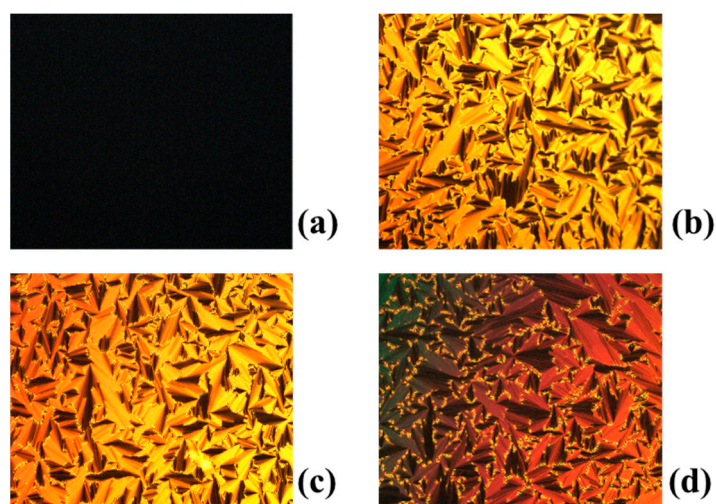


Figure S5. The optical textures of unaligned chiral LC mixture under crossed polarizers at (a) 47.1 °C (Iso), (b) 38.1 °C (N*), (c) 31.2 °C (N* -SmA*), and (d) 26.9 °C (SmA*), respectively. The sample was cooled at 1 °C/minute.

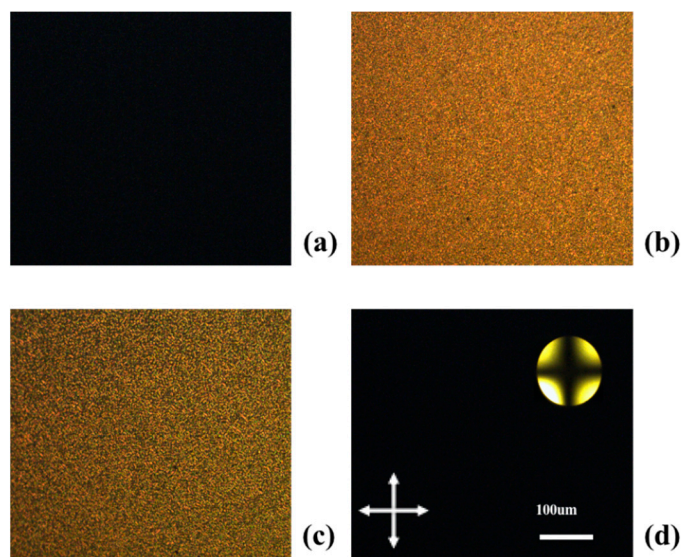


Figure 6. The optical textures of polymer stabilized chiral liquid crystalline thin film. (0.5wt%, 20µm thick cell with homeotropic alignment) under crossed polarizers upon cooling from the isotropic phase at a rate of 1 °C/min. (a) 47 °C (Iso), (b) 38 °C (N*), (c) 31.5 °C (N* -SmA*), and (d) 27 °C (SmA*).

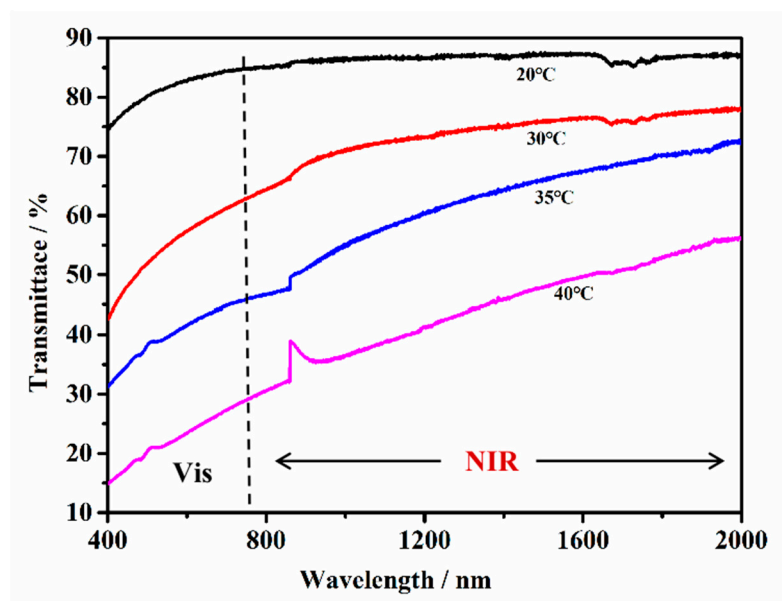


Figure S7. The Vis-NIR transmittance spectra from 400 nm to 2000 nm for the as-made smart window modified with 2 wt% CNT-PDB polymer brush at different environmental temperatures.

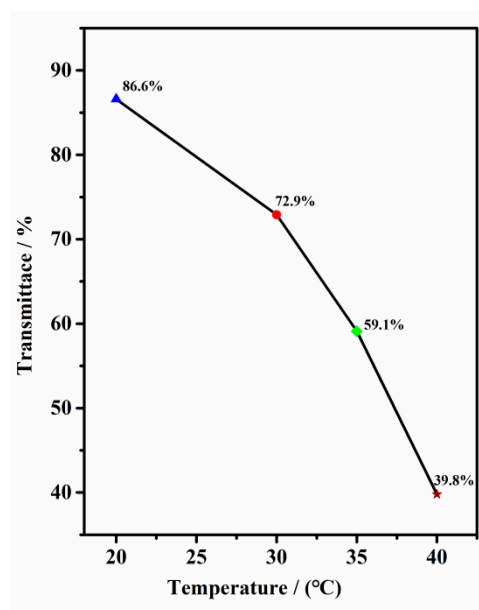


Figure S8. NIR light transmittance at 1150 nm of the as-made smart window modified with 2 wt% CNT-PDB polymer brush during the heating process from 20 to 40 °C (heating rate: 5 °C/min).