Electronic Supplementary Information

Stimuli-responsive Circularly Polarized Luminescence Film with Tunable Emission

Huli Yu\(^{a,b}\), Biao Zhao\(^{a,b}\), Jinbao Guo\(^b\), Kai Pan\(^b\), and Jianping Deng\(^*\)\(^{a,b}\)

\(^a\)State Key Laboratory of Chemical Resource Engineering and \(^b\)College of Materials Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China
Table S1 XPS results of sulfur content in CNCs. ..........................................................3
Figure S1 UV absorption spectra of released MD or PD .................................................3
Figure S2 TEM images of CNCs ..................................................................................3
Figure S3 CD spectra of CNCs films prepared at different pH ......................................4
Figure S4 SEM image of the film prepared by lower sulfur content CNC.........................4
Figure S5. CD and PL spectra of PD/CNC films with different mass ratio.......................5
Figure S6 Colorless homogeneous CNC film................................................................5
Figure S7 CD and transmission spectra of PD/CNC film rotated at different angles........6
Figure S8 Fluorescence photograph of PD solution with acid-base sensitivity .............6
Figure S9 Chemical structure change of PD in protonation-deprotonation process ......7
Figure S10 CD spectra of the PD/CNC film treated by NH$_3$ or HCl..............................7
Figure S11 CPL and DC spectra after 10 cycles of adsorbing HCl-NH$_3$.........................8
Figure S12 SEM images of composite films swelled by different water content.............8
Figure S13 CD and transmission spectra of red color film treated by NH$_3$ or HCl ........8
Figure S14 CD, UV, CPL and DC spectra of the water-soaked PD/CNC film.................9
Figure S15 CPL and DC spectra of the PD/CNC film responsive to solvents.................10
Reference......................................................................................................................10
Table S1. Sulfur content in CNCs treated by rotary evaporation for different time.\(^a\)

<table>
<thead>
<tr>
<th></th>
<th>CNC-0 h</th>
<th>CNC-1.5 h</th>
<th>CNC-3 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.88</td>
<td>0.67</td>
<td>&lt;0.4</td>
</tr>
</tbody>
</table>

\(^a\)According to XPS measurement.

Figure S1. UV absorption spectra of released dansyl monomer (MD) or polymer of dansyl monomer (PD) from MD/CNC or PD/CNC films.

A trace of dansyl monomer was released from MD/CNC film after 4 cycles of acid-base responsibility. However, no PD released from PD/CNC film was detected even after 10 cycles of acid-base responsibility. These results prove that PD is more suitable for repeatedly responding.

Figure S2. TEM image of CNCs. The average length of CNC is about 144 nm. The length of 200 particles were measured from TEM images by using the Image J software.
Figure S3. CD spectra of CNCs films prepared at different pH by adding HCl or NaOH. Strong CD signals occurred at the pH range of 0.1–12, indicating wider pH range for the assembly of CNCs.

Figure S4. The SEM image of the film prepared by lower sulfur content (< 0.4 wt%) CNC. No pseudo-layered helical structure was observed, indicating chiral liquid crystal structure is not formed in the film.
**Figure S5.** CD and PL spectra of PD/CNC composite films with different mass ratio $M_{PD}/M_{CNC}=1/480$, PD-CNC-r1; $M_{PD}/M_{CNC}=2/480$, PD-CNC-r2; $M_{PD}/M_{CNC}=3/480$, PD-CNC-r3. $M_{PD}/M_{CNC}$, wt/wt.

**Figure S6.** Digital photograph of homogeneous CNC film on black background. The diameter of the polystyrene Petri dish is 6 cm.
**Figure S7.** The CD spectra of PD/CNC composite film rotated at different degree.

CNC films with chiral liquid crystal structure selectively reflect left-handed circularly polarized light, while permitting right-handed circular polarized light to pass through. In the transmission spectra, there was almost no change for PD/CNC film at different degree. The result indicates that the change of transmitted right-handed circular polarized light intensity is negligible. Therefore, it can be inferred that there is almost no change in the CD spectra of different degree, indicating the negligible effect of linear dichroism.

**Figure S8.** The fluorescence photograph of PD solution with acid-base sensitivity. NaOH, NaHCO$_3$, Na(CO$_3$)$_2$, NH$_3$·H$_2$O and ethylenediamine could be used as the base. HCl, CH$_3$COOH, H$_2$SO$_4$ could be used as the acid.
**Figure S9.** Chemical structure change of PD in the protonation-deprotonation process.

**Figure S10.** CD spectra of PD/CNC composite film. By adsorbing NH$_3$ or HCl gas, the CD signals of composite film showed no change, indicating the chiral structure of the composite film was not affected by base or acid.
Figure S11. The CPL and corresponding DC spectra of the solid composite film after 10 cycles of adsorbing HCl-NH$_3$.

![Figure S11](image)

Figure S12. SEM images of PD/CNC composite films swelled by different water content. The thickness of the composite film was increased with water content, indicating the helical pitch (p) of cholesteric structure increased by water swelling. Wetted sample were freeze-dried for SEM measurement.

![Figure S12](image)
Figure S13. CD and transmission spectra of red color PD/CNC films by water swelling (75 wt% of water content). The films adsorbed NH$_3$ for 60 s and HCl for 20 s in advance, respectively. Then films were infiltrated by water until red color appeared. There was no difference in CD and reflection results of NH$_3$ or HCl treated films, indicating that PD had no influence on the structural color change of composite films.

Figure S14. CD, UV, CPL and DC spectra of the water-soaked PD/CNC composite film. The inset was magnified CD spectra at the wavelength between 270 and 400 nm. The film was infiltrated in water for 24 h. There was no induced CD signal
observed at the wavelength from 300 to 400 nm, between which the corresponding UV absorption appeared.\textsuperscript{1} Besides, no induced L-CPL was generated.\textsuperscript{2} These resulted indicated that PD retained achiral and no chiral induction phenomenon occurred in the composite film.

Figure S15. CPL and DC spectra of the PD/CNC film responsive to DMF and DMSO.

Reference
