Tunable Circularly Polarized Luminescence from Molecular Assemblies of Chiral AIEgens

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1. Experimental procedures

Compounds 1, 5 and 6 were prepared according to previously reported synthetic procedures and showed identical spectroscopic properties to those reported therein.\[S1\]

![Scheme S1. Synthetic routes of DPCE-ECh and DPEH-ACh based on chiral AIEgens.](image)

1.1. NMR spectra and MS spectra

![Figure S1. $^1$H NMR spectrum of compound 2 in CDCl$_3$](image)
Figure S2. $^{13}$C NMR spectrum of compound 2 in CDCl$_3$

Figure S3. Mass spectrum of compound 2
Figure S4. $^1$H NMR spectrum of compound 3 in CDCl$_3$

Figure S5. $^{13}$C NMR spectrum of compound 3 in CDCl$_3$
Figure S6. Mass spectrum of compound 3

Figure S7. $^1$H NMR spectrum of compound 4 in CDCl$_3$
Figure S8. $^{13}$C NMR spectrum of compound 4 in CDCl$_3$

Figure S9. Mass spectrum of compound 4
Figure S10. $^1$H NMR spectrum of DPCE-ECh in CDCl$_3$

Figure S11. $^{13}$C NMR spectrum of DPCE-ECh in CDCl$_3$
**Figure S12.** The HR-ESI-MS spectrum of DPCE-ECh.

**Figure S13.** $^1$H NMR spectrum of DPCE-ACh in CDCl$_3$
Figure S14. $^{13}$C NMR spectrum of DPCE-ACh in CDCl$_3$.

Figure S15. The HR-ESI-MS spectrum of DPCE-ACh.
Figure S16. TGA curves of DPCE-ECh and DPCE-ACh.

2. Photophysical data

Figure S17. (A) UV-Vis absorption and (B) photoluminescence (PL) spectra of DPCE-ECh and DPCE-ACh in THF at room temperature. Concentration: 10 μM.
Table S1. Photophysical Properties of Chiral AIEgens<sup>a</sup>

<table>
<thead>
<tr>
<th>AIEgens</th>
<th>Solution</th>
<th>Solid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{abs}}$</td>
<td>$\lambda_{\text{em}}$</td>
</tr>
<tr>
<td></td>
<td>[nm]</td>
<td>[nm]</td>
</tr>
<tr>
<td>DPCE-ECh</td>
<td>360</td>
<td>430</td>
</tr>
<tr>
<td>DPCE-ACh</td>
<td>352</td>
<td>430</td>
</tr>
</tbody>
</table>

<sup>a</sup>Abbreviation: $\lambda_{\text{abs}}$ = absorption maximum; $\lambda_{\text{em}}$ = emission maximum; $\Phi_{F, S}$ and $\Phi_{F, P}$ = fluorescence quantum yield in solution and solid powder, respectively; $\tau$ (ns) = fluorescence lifetime.

**Figure S18.** (A-C), PL spectra (A), Plots of the relative PL intensity peak intensity ($I/I_0$) versus the composition of the THF/H$_2$O mixture of DPCE-ECh (B), and fluorescent photographs of DPCE-ECh in THF/H$_2$O mixtures with different $f_w$ (C).
Figure S19. (A-B), PL spectra (A), Plots of the relative PL intensity peak intensity ($I/I_0$) versus the composition of the THF/H$_2$O mixture of DPCE-ACh (B), and fluorescent photographs of DPCE-ACh in THF/H$_2$O mixtures with different $f_w$ (C).

3. Chiroptical data in aggregate suspension.

Figure S20. (A, B) CD spectra of DPCE-ECh (A) and DPCE-ACh (B) in THF (50 µM).
Figure S21. (A, B) CD spectra of DPCE-ECh (A), DPCE-ACh (B) in a mixture solution of THF and H$_2$O (50 µM, $f_w = 20 \%$).

Figure S22. (A, B) CD spectra of DPCE-ECh (A), DPCE-ACh (B) in a mixture solution of THF and H$_2$O (50 µM, $f_w = 30 \%$).
Figure S23. (A, B) CD spectra of DPCE-ECh (A), DPCE-ACh (B) in a mixture solution of THF and H₂O (50 μM, f_w = 40 %).

Figure S24. (A, B) CD spectra of DPCE-ECh (A), DPCE-ACh (B) in a mixture solution of THF and H₂O (50 μM, f_w = 50 %).
Figure S25. (A, B) CD spectra of DPCE-ECh (A), DPCE-ACh (B) in a mixture solution of THF and H$_2$O (50 µM, $f_w = 60\%$).

Figure S26. (A, B) CD spectra of DPCE-ECh (A), DPCE-ACh (B) in a mixture solution of THF and H$_2$O (50 µM, $f_w = 70\%$).
Figure S27. (A, B) CD spectra of DPCE-ECh (A), DPCE-ACh (B) in a mixture solution of THF and H₂O (50 µM, f_w = 80 %).

Figure S28. (A, B) CD spectra of DPCE-ECh (A), DPCE-ACh (B) in a mixture solution of THF and H₂O (50 µM, f_w = 90 %).
Figure S29. (A, B) CPL spectra of DPCE-ECh (A), DPCE-ACh (B) in a solution of THF (50 μM).

Figure S30. (A, B) CPL spectra of DPCE-ECh (A), DPCE-ACh (B) in a mixture solution of and H₂O (50 μM, f_w = 40 %).
Figure S31. (A, B) CPL spectra of DPCE-ECh (A), DPCE-ACh (B) in a mixture solution of and H₂O (50 µM, f_w = 50 %).

Figure S32. (A, B) CPL spectra of DPCE-ECh (A), DPCE-ACh (B) and in a mixture solution of and H₂O (50 µM, f_w = 60 %).
Figure S33. (A, B) CPL spectra of DPCE-ECh (A), DPCE-ACh (B) and in a mixture solution of and H$_2$O (50 $\mu$M, $f_w = 70\%$).

Figure S34. (A, B) CPL spectra of DPCE-ECh (A), DPCE-ACh (B) in a mixture solution of and H$_2$O (50 $\mu$M, $f_w = 80\%$).
Figure S35. (A, B) CPL spectra of DPCE-ECh (A), DPCE-ACh (B) in a mixture solution of and H₂O (50 μM, $f_w = 90\%$).

4. Scanning electron microscopy of DPE-CHOL and DPEH-CHOL.

Figure S36. SEM images of DPCE-ECh obtained from THF/H₂O mixture at $f_w = 40\%$ (A), 60\% (B)
and 90% (C).

**Figure S37.** SEM images of DPCE-ACh obtained from THF/H₂O mixture at $f_w = 40\%$.

**Figure S38.** SEM images of DPCE-ACh obtained from THF/H₂O mixture at $f_w = 50\%$. 
Figure S39. SEM images of DPCE-ACh obtained from THF/H$_2$O mixture at $f_w = 60\%$.

Figure S40. SEM images of DPCE-ACh obtained from THF/H$_2$O mixture at $f_w = 90\%$. 
5. Dynamic UV spectra of DPCE-ACh in suspension.

![Dynamic UV spectra of DPCE-ACh in suspension.](image)

**Figure S41.** Temperature-dependent UV/Vis spectral changes for DPCE-ACh in THF/H$_2$O when f$_w$ = 60%. Conditions: solution concentration: 1×10$^{-5}$ M.

6. Condensed phase data and chiroptical data for neat film of DPCE-ACh
Figure S42. Phase transition of DPCE-ACh as determined from the first cooling (upper columns). DSC scans with rate 5 K min⁻¹. Abbreviation: Cry = solid crystal; S+H: smectic + hexagonal columnar phase; S: smectic phase; iso: isotropic liquid. DSC scans of the second heating and first cooling of DPCE-ECh (5 °C/min, lower picture).

Heating Process

Cooling Process
Figure S43. Polarized optical microscopy (POM) images of DPCE-ACh under crossed polarizers during heating and cooling process (rate: 10 °C/min).

Figure S44. 1D wide angle X-ray diffraction (1D WAXD) pattern of DPCE-ACh on the 1st heating process in different temperature. $2\theta = 2^\circ - 35^\circ$. 
Figure S45. 1D wide angle X-ray diffraction (1D WAXD) pattern of DPCE-ACh on the 1st cooling process in different temperature. $2\theta = 2^\circ - 10^\circ$. 
Figure S46. 1D wide angle X-ray diffraction pattern of DPCE-ACh recorded during the 1st cooling scan at different temperature. (A) $2\theta = 2^\circ - 10^\circ$, (B) $2\theta = 2^\circ - 3.5^\circ$. (C) SAXS profiles of DPCE-ACh with two possible indexations of lamellae and hexagonal array. The data was recorded at 150 °C during the 1st cooling scan.

Figure S47. CD spectra of front and back sides of DPCE-ACh films annealed for 45 min at different temperatures at different rotation angles perpendicular to the light axis. (A) 150 °C (B) 180 °C (C) 190 °C. The film thickness of DPCE-ACh is 50 nm for CD detection.
**Figure S48.** UV spectra of front and back sides of DPCE-ACh films annealed at different temperatures for 45 min.

**Figure S49.** $g_{\text{CD}}$ (415 nm) of DPCE-ACh films annealed for 45 min at temperature of 150-190 °C.
Figure S50. CPL spectra of DPCE-ACh films annealed at 180 °C for 45 min at different rotation angles perpendicular to the light axis (front side).
Figure S51. CPL spectra of DPCE-ACh films annealed 180 °C for 45 min at different rotation angles perpendicular to the light axis (back side).
7. Condensed phase data and chiroptical data for neat film of DPCE-ECh.

**Figure S52.** Polarized optical microscopy (POM) images of DPCE-ECh under crossed polarizers.

**Figure S53.** 1D wide angle X-ray diffraction (1D WAXD) pattern of DPCE-ECh on the 2nd heating process in different temperature. (A) $2\theta = 2^\circ – 35^\circ$, (B) $2\theta = 2^\circ – 6^\circ$. 
**Figure S54.** 1D wide angle X-ray diffraction (1D WAXD) pattern of DPCE-ECh on the 1st cooling process in different temperature. (A) $2\theta = 2^\circ - 35^\circ$, (B) $2\theta = 2^\circ - 6^\circ$.

**Figure S55.** SAXS patterns at different temperatures. Inset: POM image of DPCE-ECh at 100 °C.
Figure S56. The illustration of the shearing geometry

Table S2. The measurement conditions of WAXS and SAXS.

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<thead>
<tr>
<th></th>
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<th>SAXS</th>
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<tbody>
<tr>
<td>SDD</td>
<td>225.831 nm</td>
<td>1219.49 mm</td>
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<tr>
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<td>0.8 × 0.8 mm²</td>
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<tr>
<td>Beam Center</td>
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<td>620.132, 918.9432</td>
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<tr>
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<tr>
<td>Wavelength</td>
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<td>0.134144 nm</td>
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<td>Virtual Detector Mode</td>
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<td>4 images combined</td>
</tr>
<tr>
<td>Exposure Time</td>
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<td>1800 s × 4</td>
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</table>
Figure S57. CD spectra of front and back sides of DPCE-ECh films annealed at different temperatures for 45 min recorded at different rotation angles perpendicular to the light axis. (A) 70 °C (B) 80 °C (C) 90 °C (D) 100 °C (E) 110 °C (F) 120 °C. The film thickness of DPCE-ECh is 50 nm for CD detection.

Figure S58. Diagram of molecular assembly orientation for circularly Bragg phenomenon and non-circularly Bragg phenomenon.
Figure S59. UV spectra of front and back sides of DPCE-ECh films annealed at different temperatures for 45 min recorded at different rotation angles perpendicular to the light axis.

Figure S60. CPL spectra of DPCE-ECh films annealed at 70 °C for 45 min at different rotation angles.
perpendicular to the light axis (front side).

**Figure S61.** CPL spectra of DPCE-ECh films annealed at 70 °C with for 45 min at different rotation angles perpendicular to the light axis (back side).

**Figure S62.** CPL spectra of DPCE-ECh films annealed at 80 °C for 45 min at different rotation angles perpendicular to the light axis (front side).
Figure S63. CPL spectra of DPCE-ECh films annealed at 80 °C for 45 min at different rotation angles perpendicular to the light axis (back side).

Figure S64. CPL spectra of DPCE-ECh films annealed at 90 °C for 45 min at different rotation angles perpendicular to the light axis (front side).
Figure S65. CPL spectra of DPCE-ECh films annealed at 90 °C for 45 min at different rotation angles perpendicular to the light axis (back side).

Figure S66. CPL spectra of DPCE-ECh films annealed at 100 °C for 45 min at different rotation angles perpendicular to the light axis (front side).
Figure S67. CPL spectra of DPCE-ECh films annealed at 100 °C for 45 min at different rotation angle perpendicular to the light axis (back side).

Figure S68. CPL spectra of DPCE-ECh films annealed at 110 °C for 45 min at different rotation angles perpendicular to the light axis (front side).
Figure S69. CPL spectra of t DPCE-ECh films annealed at 110 °C for 45 min at different rotation angles perpendicular to the light axis (back side).

Figure S70. CPL spectra of DPCE-ECh films annealed at 120 °C for 45 min at different rotation angles perpendicular to the light axis (front side).
Figure S71. CPL spectra of DPCE-ECh films annealed at 120 °C for 45 min at different rotation angles perpendicular to the light axis (back side).

Figure S72. SEM textures of DPCE-ECh with layered and arched structures on the fracture plane.
8. References