Supporting Information

Double-responding circularly polarized luminescence based on the mechanic and temperature-induced assemblies of cyano-distyrylbenzene hydrogen-bonding liquid crystal

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1. General

The chemical reagents were purphased from Aladdin Aladdin reagent company and J&K Chemicals. TLC examination was carried out on pre-coated glass plates. Silica gel (200-300 mesh) was applied as adsorbent for column chromatography. NMR spectra were measured on a Bruker-ARX 400 instrument with TMS as internal standard. Bruker mass spectrometer was used for investigation of MS spectra. The phase transition behavior under POM was studied by Leica DMRX with a hot stage of Linkam THMSE 600. Thermal analysis was measured on Thermal Analysis Q100 under N₂ atmosphere. XRD analysis were obtained on SEIFERT-FPM (XRD7) with Cu K α 1.5406 Å as the radiation source with 40 kV, 30 mA power. UV-Vis spectra were examined on Varian spectrometer. Fluorescence spectra were collected on a Hitachi F-4500 spectrometer. The fluorescence absolute values (Φ_F) were obtained on an Edinburgh Instruments FLS920 Fluorescence Spectrometer with a 6-inch integrating sphere.

2. The synthetic process and characteristic spectra.



Scheme S1. The synthetic routes for CDB-1Ch and CDB-2Ch.

2.1 Synthesis of compound 2.

Piperidine (0.3 mL) was added in a stirred THF (30 mL) solution of compound **1** (0.5 g, 3.1 mmol) and 4-nitrophenylacetonitrile (0.5 g, 3.1 mmol). The reaction mixture was stirred at 65 °C for 5 h until the reaction was complete as judged by TLC, after which CH₃OH (100 mL) was added into the reaction mixture to afford precipitation. The precipitation was filtered to provide a yellow compound **2** in yield of 86%.

Compound **2**: ¹H NMR (400 MHz, DMSO-d₆): δ ppm: 10.35 (s, 1H, NH), 8.35 (d, *J* = 12.0 Hz, 2H, ArH), 8.22 (s, 1H, CH), 8.02 (d, *J* = 12.0 Hz, 2H, ArH), 7.99 (d, *J* = 12.0 Hz, 2H, ArH), 7.78 (d, *J* = 12.0 Hz, 2H, ArH), 2.10 (s, 3H, CH₃). MALDI-TOF-MS (C₁₇H₁₃N₃O₃) Calcd. for *m*/*z* = 307.0957, found: *m*/*z* = 307.9966 (MH⁺), 330.9820 (MNa⁺), 346.9723 (MK⁺).

2.2 Synthesis of compound 3.

The mixture of compound **2** (0.5 g, 1.6 mmol) and concentrated hydrochloric acid (10 mL) in dioxane (30 mL) was stirred at 100 °C for 8 h. Then the reaction mixture was neutralized with Na₂CO₃ until pH = 7. H₂O (100 mL) was added in this mixture to give precipitation. The precipitation was filtered to afford compound **3** in yield of 72%.

Compound **3**: ¹H NMR (400 MHz, DMSO-d₆): δ ppm: 8.28 (d, *J* = 8.0 Hz, 2H, ArH), 8.00 (s, 1H, CH), 7.91 (d, *J* = 8.0 Hz, 2H, ArH), 7.83 (d, *J* = 8.0 Hz, 2H, ArH), 6.68 (d, *J* = 8.0 Hz, 2H, ArH), 3.39 (bs, 2H, NH₂). MALDI-TOF-MS (C₁₅H₁₁N₃O₂) Calcd. for *m*/*z* = 265.0851, found: *m*/*z* = 265.5423 (M⁺).

2.3 Synthesis of compound 4.

 Na_2S (0.5 g, 6.4 mmol) was added into a THF (30 mL) solution of compound **3** (0.6 g, 2.3 mmol). The reaction mixture was stirred at 65 °C for 8 h until the reaction was completed as judged by TLC analysis. Then the reaction mixture was partitioned by EtOAc (50 mL) and H₂O (50 mL). The EtOAc layer was seperated and concentrated *in vacuo*. The residue was treated by CH₃OH (100 mL) to afford precipitation. After filtration, compound **4** was collected as yellow solid in yield of 74%.

Compound 4: ¹H NMR (400 M Hz, DMSO-d₆): δ ppm: 7.64 (d, *J* = 8.0 Hz, 2H, ArH), 7.41 (s, 1H, CH), 7.32 (d, *J* = 8.0 Hz, 2H, ArH), 6.62 (d, *J* = 8.0 Hz, 4H, ArH), 5.69 (bs, 4H, NH₂). MALDI-TOF-MS (C₁₅H₁₃N₃) Calcd. for *m*/*z* = 235.1109, found: *m*/*z* = 235.8357 (M⁺), 258.3109 (MNa⁺), 274.3219 (MK⁺).

2.4 Synthesis of compound 6.

Compound **3** (0.6 g, 2.3 mmol) was dissolved in DCM (30 mL) and stirred for 0.5 h at 0 °C. Then compound **5** (1.0 g, 2.3 mmol) and pridine (0.2 mL) was added in the solution. The reaction mixture was further stirred at 0 °C for 4 h until the reaction was used out as judged by TLC analysis. After reaction, the reaction mixture was concentrated under reduced pressure. The residue was treated by hexane (50 mL) to afford compound **6** in yield of 80%.

Compound 6: ¹H NMR (400 M Hz, CDCl₃): δ ppm: 8.29 (d, *J* = 8.0 Hz, 2H, ArH), 7.94 (d, *J* = 8.0 Hz, 2H, ArH), 7.82 (d, *J* = 8.0 Hz, 2H, ArH), 7.60 (s, 1H, CH), 7.54(d, *J* = 8.0 Hz, 2H, ArH), 6.85 (s, 1H, NH), 5.41(bs, 1H, CH=C), 4.62 (bs, 1H, CH), 0.64-2.48 (m, 43H, cholesterol unit). MALDI-TOF-MS (C₄₃H₅₅N₃O₄) Calcd.for *m*/*z* = 677.4193, found: *m*/*z* = 700.7819 (MNa⁺).

2.5 Synthesis of CDB-1Ch

 Na_2S (0.5 g, 6.4 mmol) was added in the THF (30 mL) solution of compound **6** (1.1 g, 1.7 mmol). The reaction mixture was stirred at 65 °C for 8 h. TLC detection suggested the disappearance of materials. Then the solvent was distilled under reduced pressure. The resulting crude oil was purified by silica gel

column chromatography (eluent: hexane/ $CH_2Cl_2=7:3$) to obtain **CDB-1Ch** as yellow solid in yiled of 67%.

CDB-1Ch: ¹H NMR (400 M Hz, CDCl₃): δ ppm: 7.82 (d, *J* = 8.0 Hz, 2H, ArH), 7.46 (d, *J* = 8.0 Hz, 4H, ArH), 7.30 (s, 1H, CH), 6.72 (d, *J* = 8.0 Hz, 2H, ArH), 6.70 (s, 1H, NH), 5.41 (bs, 1H, CH=C), 4.62(bs, 1H, CH), 3.86 (bs, 2H, NH₂), 0.66-2.45 (m, 43H, cholesterol unit). ¹³C NMR (100 MHz, CDCl₃), δ ppm: 152.81, 147.33, 141.15, 139.54, 137.58, 130.74, 130.22, 128.94, 127.17, 124.49, 122.66, 118.24, 114.96, 109.72, 75.31, 56.70, 56.16, 50.09, 38.25, 36.96, 36.59, 31.92, 28.25, 27.84, 24.24, 23.87, 22.85, 22.59, 21.06, 19.35, 18.74, 11.72. MALDI-TOF-MS (C₄₃H₅₇N₃O₂) Calcd for *m*/*z* = 647.4451, found: *m*/*z* = 647.8050 (MNa⁺). Anal.calcd for C₄₃H₅₇N₃O₂: C 79.71, H 8.87, N 6.49; found C 79.74, H 8.79, N 6.41.

2.6 Synthesis of CDB-2Ch

Compound 4 (0.15 g, 0.65 mmol) and compound 5 (0.55 g, 1.3 mmol) was dissolved in DCM (30 mL). The reaction mixture was stirred for 4 h at 0 °C by using pyridine (0.2 mL) as catalyst. TLC analysis suggested the fulfilment of reaction. The CH_2Cl_2 solvent was evapotated by reduced pressure and the residue was precipitated by hexane (50 mL) to afford yellow product **CDB-2Ch** in yield of 78%.

CDB-2Ch: ¹H NMR (400 M Hz, CDCl₃): δ ppm: 7.85 (d, *J* = 8.0 Hz, 2H, ArH), 7.69 (d, *J* = 8.0 Hz, 2H, ArH), 7.48 (d, *J* = 8.0 Hz, 2H, ArH), 7.45 (d, *J* = 8.0 Hz, 2H, ArH), 7.39 (s, 1H, CH), 6.75 (s, 1H, ArH), 6.68 (s, 1H, NH), 5.41 (bs, 2H, CH=C), 4.62 (bs, 2H, CH), 0.66-2.49 (m, 86H, cholesterol unit). ¹³C NMR (100 M Hz, CDCl₃), δ ppm: 152.67, 140.11, 139.58, 138.68, 136.14, 130.23, 129.16, 128.64, 126.32, 122.75, 118.86, 118.25, 118.06, 108.90, 75.18, 56.70, 55.97, 49.86, 39.63, 39.54, 38.45, 36.96, 36.58, 36.09, 35.82, 31.89, 28.25, 24.30, 23.67, 22.84, 11.88. MALDI-TOF-MS (C₇₁H₁₀₁N₃O₄) Calcd for *m*/*z* = 1059.7792, found: *m*/*z* = 1060.2519 (M⁺). Anal.calcd for C₇₁H₁₀₁N₃O₄: C 80.41, H 9.60, N 3.96; found C 80.36, H 9.63, N 3.90.







Figure S2. MALDI-TOF-MS spectrum of compound 2



Figure S4. MALDI-TOF-MS spectrum of compound 3







Figure S6. MALDI-TOF-MS spectrum of compound 4



Figure S7. The ¹H NMR spectrum of compound **6**



Figure S8. MALDI-TOF-MS spectrum of compound 6



Figure S9. The ¹H NMR spectrum of CDB-1Ch



Figure S10. The ¹³C NMR spectrum of CDB-1Ch



Figure S11. MALDI-TOF-MS spectrum of CDB-1Ch



Figure S12. The ¹H NMR spectrum of **CDB-1Ch**



Figure S14. The MALDI-TOF-MS spectrum of CDB-2Ch



Figure S15. The emission spectra ($\lambda_{ex} = 365 \text{ nm}$) of **DCB-1Ch** in different states. Insets their photographs in different solid states under 365 nm UV light.



Figure S16. The XRD traces of **DCB-1Ch** in different states.



Figure S17. The FTIR spectra of **DCB-1Ch** in different states.



Figure S18. The emission spectra ($\lambda_{ex} = 365 \text{ nm}$) of **DCB-2Ch** in different states. Insets their photographs in different solid states under 365 nm UV illumination.



Figure S19. The XRD traces of **DCB-2Ch** in different states.



Figure S20. FTIR spectra of **DCB-2Ch** in different states.



Figure S21. CPL spectra of **DCB-1Ch** in pristine state.



Figure S22. CPL spectra of **DCB-1Ch** in ground state.



Figure S23. CPL spectra of DCB-1Ch in fumed state.



Figure S24. CD spectra of **DCB-1Ch** in different states.



Figure S25. UV–vis spectra of **DCB-1Ch** in THF/H₂O (2:8) solution (2×10^{-6} M) and solid film.



Figure S26. CD spectra of **DCB-2Ch** in different states.



Figure S27. UV–vis spectra of **DCB-2Ch** in THF/H₂O (2:8) solutions (2×10^{-6} M) and solid film.



Figure S28. CPL spectra of **DCB-2Ch** in pristine state.



Figure S29. CPL spectra of DCB-2Ch in ground state.



Figure S30. DSC curves of **DCB-1Ch** and **DCB-2Ch** upon the cooling and second heating cycles at a scanning rate of 10 °C min⁻¹



Figure S31. POM images of **DCB-1Ch** in the mesophase at 145 °C



Figure S32. POM images of **DCB-1Ch** in the mesophase at 160 $^{\circ}$ C



Figure S33. POM images of **DCB-1Ch** in the mesophase at 165 °C



Figure S34. POM images of **DCB-2Ch** in the mesophase at 240 °C

Compoun	Phase	$d_{\rm obs}({\rm \AA})$	$D_{\rm cal}({\rm \AA})$	Miller	Lattice parameters (Å,
da	(T/°C),			S	Lattice area S (Å ²),
(L/ Å)	symmetr			indice	Molecular volume $V(Å^3)$
	У			s hk	
DCB-1Ch	Col _{r1}	35.06	35.06	11	a = 61.35, b =42.73, S =
(32.0)	(145)	30.67	30.67	20	2621.5, V = 11272.4, Z =
	p2mm	25.10	24.91	21	10.4
		17.32	17.53	22	
		15.03	14.77	32	
		14.55	14.44	41	
		11.46	11.68	33	
		8.60	8.76	44	
		4.30 (h)			
	Col _{r1}	29.08	29.08	11	a = 55.00, b = 34.26, S =
	(165)	14.88	14.54	22	1884.3, V = 8969.3, Z =
	p2mm	11.18	11.18	13	8.3
		9.79	9.69	33	
		8.21	8.56	04	
		5.98	6.13	45	
		5.81	5.81	55	
		4.76 (h)			
DCB-2Ch	Col (240)	38.33	38.33	10	a = 38.33, b = 20.83, S =
(45.5)	p2mm	20.83	20.83	01	798.4, V = 3984.1, Z =
		13.71	14.10	21	2.2
		10.029	10.05	12	
		8.2135	8.07	32	
		5.9017	6.10	33	
		5.4326	5.21	04	
		4.99 (h)			

Table S1. Results of (hkl) indexation of XRD profiles at a given temperature (T/°C) of mesophase

^aThe molecular length (L); d_{obs} : spacing observed; d_{cal} : spacing calculated; Z: number of molecules per columnar slice of thickness h.



Figure S35 The emission spectra (λ_{ex} = 365 nm) of **DCB-1Ch** at 25 °C, 145 °C, 165 °C and 220 °C, respectively.



Figure S36 The emission spectra (λ_{ex} = 365 nm) of **DCB-2Ch** at 25 °C and 240 °C, respectively.



Figure S37. CPL spectrum of DCB-1Ch at 145 °C.



Figure S38. CPL spectrum of **DCB-1Ch** at 165 °C.



Figure S39. CPL spectrum of DCB-1Ch at 220 °C.



Figure S40. CPL spectrum of DCB-2Ch at 240 °C.



Figure S41. Emission spectra of **DCB-1Ch** in THF-water system (20 μ M) with different water fractions (f_w), excited at $\lambda_{ex} = 365$ nm. (Insert: The plot of intensity vs f_w and their pictures in pure THF and THF/H₂O (2:8) solutions).



Figure S42. Emission spectra of **DCB-2Ch** in THF-water system (20 μ M) with different water fractions (f_w), excited at $\lambda_{ex} = 365$ nm. (Insert: The plot of intensity vs f_w and their pictures in pure THF and THF/H₂O (2:8) solutions).



Figure S43. DFT calculated HOMO and LUMO of **DCB-1Ch** and **DCB-2Ch** with corresponding energy

gap.



Figure S44. The film thickness of CDB-2Ch in mesophase.



Figure S45. CPL spectra of **CDB-2Ch** in mesophase at different rotation angles (0°, 90°, 180° and 270°) perpendicular to the light axis.



Figure S46 The g_{abs} of **DCB-1Ch** in different states.



Figure S47 The g_{abs} of **DCB-2Ch** in different states.



Figure S48 emission anisotropic spectra of CDB-1Ch and CDB-2Ch in different states.



Figure S49 The XRD trace of DCB-1Ch in mesophase at 165 °C and the proposed molecular stacking in rectangular columnar mesophase.