Electronic Supplementary Information for

Chiral amine triggered self-assembly of achiral emissive molecules into circularly polarized luminescent supramolecular assemblies

Yutao Sang,[ad] Dong Yang,[ad] Pengfei Duan,[bd] and Minghua Liu*[acd]

[a] CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P.R. China.

[b] National Center for Nanoscience and Technology, China, P.R. China, 100190.

[c] Collaborative Innovation Centre of Chemical Science and Engineering, Tianjin, P. R. China.

[d] University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

E-mail: liumh@iccas.ac.cn; Tel: +86-10-82615803

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1. Experimental Section

1.1 Materials

All the starting materials and solvents were obtained from commercial suppliers and used as received. Benzoyl chloride, isophthaloyl chloride and 1,3,5-benzenetricarbonyl trichloride were purchased from Acros. 4-Aminobenzyl cyanide was purchased from J&K. Methyl 4-formylbenzoate were purchased from Alfa Aesar. Milli-Q water (18.2 MΩ cm^{-1}) was used in all cases. The experimental details for the synthesis of ***C1***, ***C2*** and ***C3*** are provided in the Synthetic procedures.

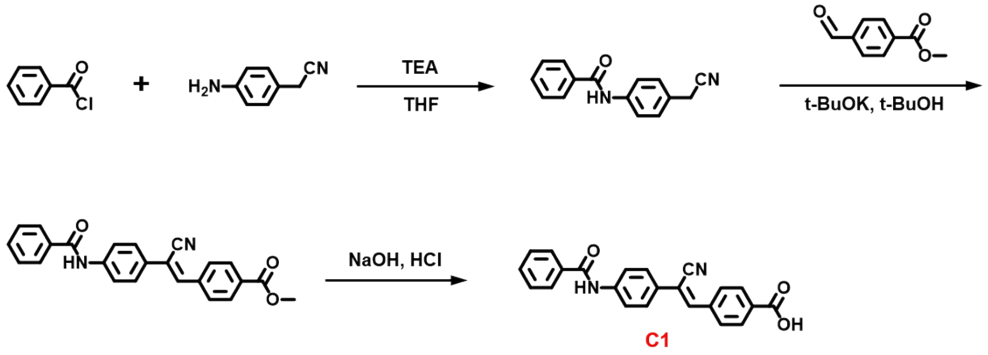
1.2 Characterizations

1H NMR spectra were recorded on Bruker AV400 (400 MHz) and Bruker Fourier 300 (300 MHz) spectrometer with TMS as internal standard at 298 K. Mass spectral data were obtained by using a BIFLEIII matrix-assisted laser desorption/ionization time of fight mass spectrometry (MALDI-TOF MS) instrument. UV-vis spectra and fluorescence spectra were obtained using JASCO UV-550 spectrometer and Hitachi F-4500 fluorescence spectrophotometer, respectively. Circular Dichroism (CD) and Linear dichroism (LD) Spectra were was performed on a JASCO J-1500 spectrophotometer. For the measurement of the CD spectra, the cuvette was placed perpendicular to the light path of CD spectrometer and rotated within the cuvette plane to rule out the possibility of the birefringency phenomena and eliminate the possible angle dependence of the CD signal. Scanning Electron Microscopy (SEM) images were recorded on a Hitachi S-4800 FE-SEM instrument with an accelerating voltage of 10 kV. Before SEM measurement, the samples on silicon wafers were coated with a thin layer of Pt to increase the contrast. Fourier transform-infrared (FT-IR) studies were performed with a JASCO FTIR-660 spectrometer. Samples were vacuum-dried and made into plates with KBr for FT-IR spectral measurements. X-ray Diffraction (XRD) analysis was performed on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with Cu Kα radiation (λ = 1.5406 Å), which was operated at a voltage of 40 kV and a current of 200 mA. Samples were cast on glass substrates and vacuum-dried for XRD measurements. Circularly polarized luminescence (CPL) measurements were performed with a JASCO CPL-200 spectrometer. The CD, LD, CPL, UV-vis spectra and fluorescence spectra were recorded in sandwich type quartz cuvettes with an optical path length of 0.1 mm. The magnitude of CPL can be evaluated by the luminescence dissymmetry factor (g_{lum}), which is defined as $g_{\mathrm{lum}} = 2 \times (I_L - I_R)/(I_L + I_R)$, where I_L and I_R refer to the intensity of left- and right-handed CPL, respectively. Experimentally, the value of g_{lum} is defined as g_{lum} = [ellipticity/(32980/ln10)]/total fluorescence intensity at the CPL extremum. Similarly, the magnitude of CD can be evaluated by dissymmetry factor (g_{CD}), which is defined as $g_{\mathrm{CD}} = 2 \times (\varepsilon_L - \varepsilon_R)/(\varepsilon_L + \varepsilon_R)$, where ε_L and ε_R refer to the extinction coefficients for left- and right-handed circularly polarised light, respectively. Experimentally, the value of g_{CD} is defined as g_{CD} = [ellipticity/32980]/absorbance at the CD extremum. DLS measurements were conducted on Zetasizer Nano ZS ZEN3600 (Nano ZS, Malvern Instruments). The scattering angle was set at 173°. A screw-capped quartz cuvette was used for the measurements. The temperature for measurements was kept at 25 ℃.

1.3 Methods

A typical procedure for the DAC/***C3*** complex in dimethylformamide (DMF) is as follows: ***C3*** (3 mg) was first dissolved in a sealed tube containing DMF by shaking, and then DMF solution containing DAC was injected in with a pipette. Then ultrasonic treatment was performed for five minutes in order to obtain well-dispersed suspension.

1.4 Synthetic procedures



Scheme S1. Synthesis of ***C1***.

In a typical experiment, A THF solution (10 mL) of benzoyl chloride (1.12 g, 8 mmol) was added to a solution containing 4-aminobenzyl cyanide (1.06 g, 8 mmol) and triethylamine (2.20 mL, 16 mmol) in 200 mL THF. The resulting mixture was stirred at room temperature overnight and then filtered to remove the precipitate. The resulting filtrate was concentrated by rotary evaporation and a white color precipitate was obtained after adding 100 mL methanol. The solid precipitate was used for next step without purification. The next step was synthesized according to the typical reported procedures of cyano-substituted stilbene.[1] Briefly, the mixture of the resulting precipitate (236.27 mg, 1 mmol) and methyl terephthaladehydate (164.16 mg, 1 mmol) in tertbutyl alcohol (30 mL) was stirred at 50 °C. Potassium tert-butoxide (224.42 g, 2 mmol) powder was dropped into the mixture and stirred for 2 hours. The resulting precipitate was used for next step without purification. The following hydrolysis was carried on the general procedure. To a suspension of 191.21 mg (0.5 mmol) precipitate in 75 mL 1:1 mixture of THF/MeOH, 5 mL of a 0.5 M KOH aqueous solution was added. The mixture was allowed to reflux for 3 h. THF was removed under reduced pressure and the resulting suspension was diluted with water. The precipitate formed by acidification with aqueous HCl (1 M) was collected by filtration, washed several times by water, ethanol and acetone. This clean product was dried to give a light yellow powder. Yield = 82%. ^{1}H NMR (300 MHz, d_6-DMSO, δ, ppm): 13.18 (s, 1H), 10.51 (s, 1H), 8.09-7.98 (m, 9H), 7.83-7.80 (d, 2H), 7.65-7.54 (m, 3H). ^{13}C NMR (75.49 MHz, d_6-DMSO, δ, ppm) 167.17, 166.21, 141.06, 140.46, 138.38, 135.11, 132.25, 130.21, 129.53, 128.88, 128.21, 126.93, 120.92, 118.02, 112.53. MALDI-TOF MS: calcd. For $C_{23}H_{16}N_2O_3$ M$^+$: m/z = 368.39; found: m/z = 368.39.

C2 and ***C3*** were prepared with the above method except that benzoyl chloride was replaced by isophthaloyl chloride and 1,3,5-benzenetricarbonyl trichloride. Meanwhile, the corresponding reactants were scaled up compared with the synthesis of ***C1***. ***C2***, yield = 75%.^{1}H NMR (300 MHz, d_6-DMSO, δ, ppm): 13.11 (s, 2H), 10.69 (s, 2H), 8.60 (s, 1H), 8.22-8.19 (d, 2H), 8.11-7.99 (m, 14H), 7.85-7.83 (d, 4H), 7.77-7.72 (t, 1H). ^{13}C NMR (100.62 MHz, d_6-DMSO, δ, ppm) 167.17, 165.67, 140.90, 140.61, 138.35, 135.38, 132.36, 131.42, 130.22, 129.54, 129.19, 129.11, 127.64, 127.01, 121.02, 118.02, 112.52. MALDI-TOF MS: calcd. For $C_{40}H_{26}N_4O_6$ M$^+$: m/z = 658.67; found: m/z = 658.67. ***C3***, yield = 66%. ^{1}H NMR (300 MHz, d_6-DMSO, δ, ppm): 13.08 (s, 3H), 10.87 (s, 3H), 8.80 (s, 3H), 8.13-7.99 (m, 21H), 7.88-7.85 (d, 6H). ^{13}C NMR (100.62 MHz, d_6-DMSO, δ, ppm) 167.13, 142.14, 138.16, 134.92, 133.93, 132.52, 130.19, 131.10, 129.89, 129.67, 129.63, 126.46, 127.64, 117.96, 122.90. MALDI-TOF MS: calcd. For $C_{57}H_{36}N_6O_9$ M^+: m/z = 948.95; found: m/z = 948.95.

2. Supplementary Figures

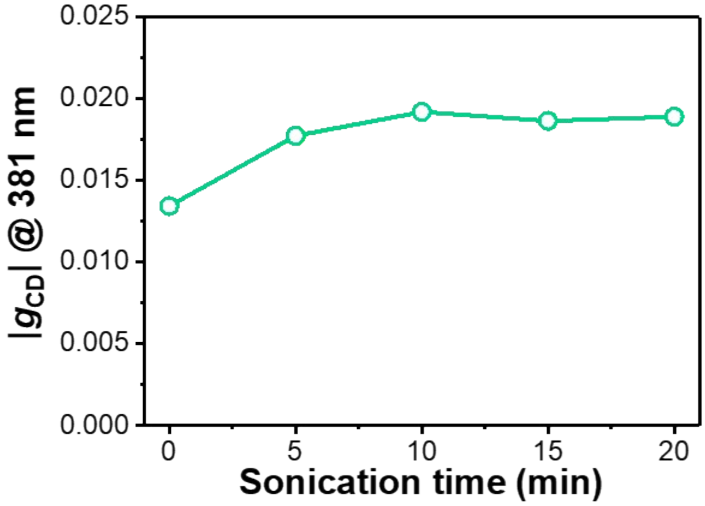


Fig. S1 The |*g*CD| values of DAC/***C3*** under diverse sonication time. [***C3***] = 3.16 mM. [DAC] = 4.74 mM.

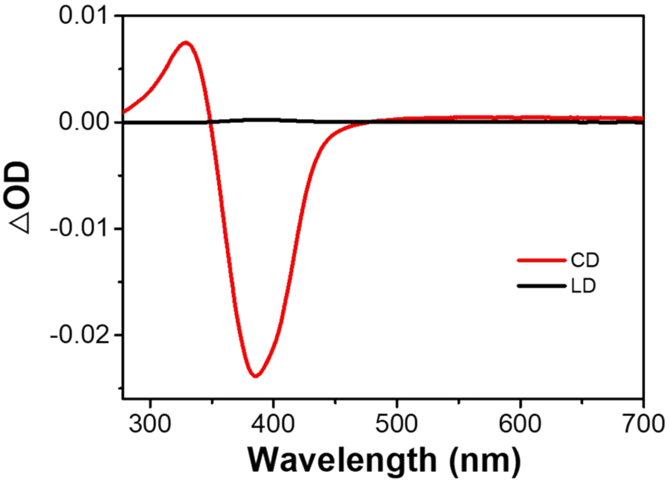


Fig. S2 The typical CD and LD spectra of the DAC/***C3*** in DMF, which are unified as the same unit (Δ OD). [***C3***] = 3.16 mM; [DAC] = 4.74 mM.

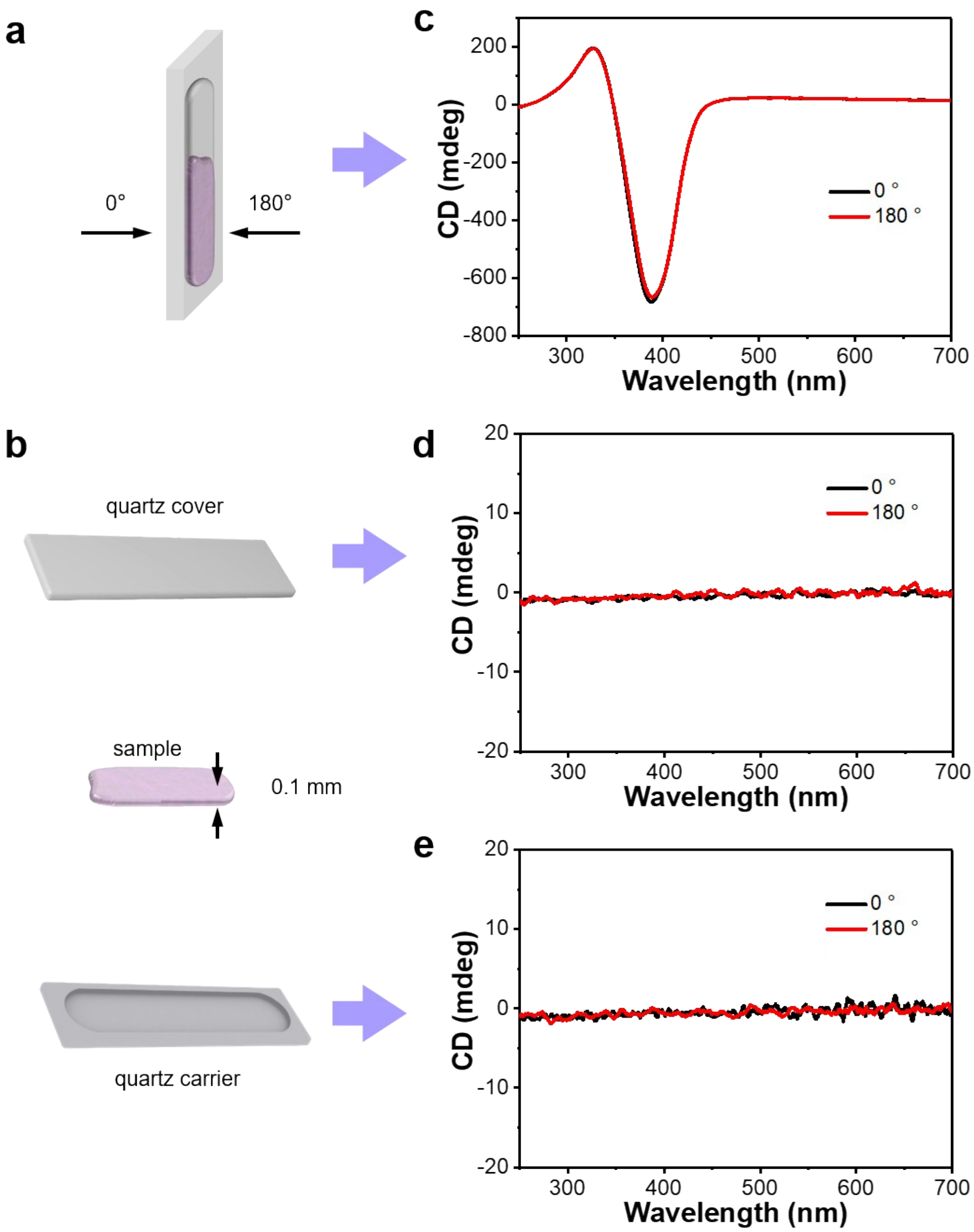


Fig. S3 (a) Schematic representation and (b) the components of sandwich-type quartz cuvette. CD spectra of (c) *S*-DAC/***C3*** assemblies, (d) the quartz carrier and (e) quartz cover measured at 0° and 180°. [***C3***] = 3.16 mM. [DAC] = 4.74 mM.

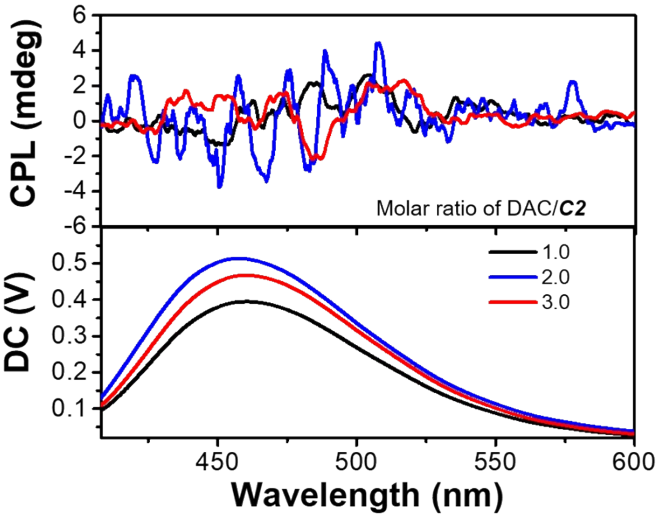


Fig. S4 CPL spectra of the DAC/***C2*** with different molar ratios excited at 350 nm. The concentration of ***C2*** was kept constant as 3.16 mM.

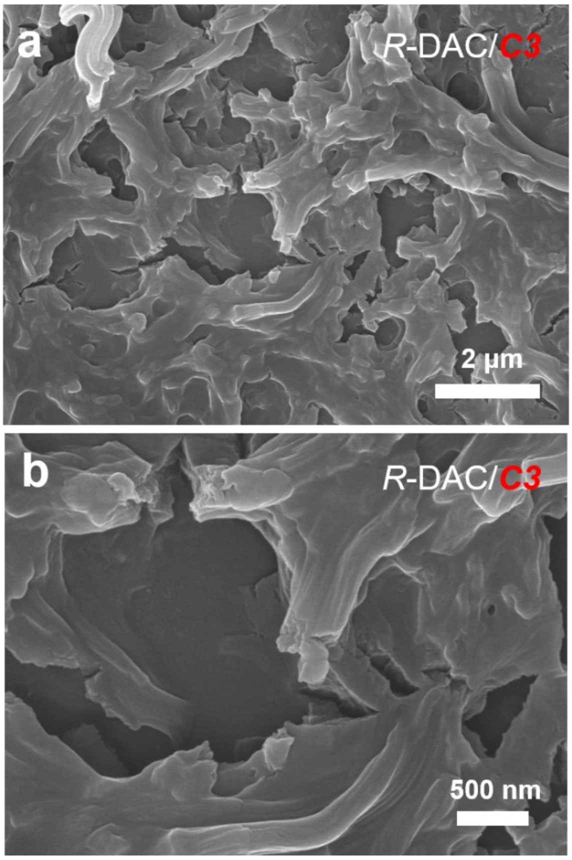


Fig. S5 SEM images of the self-assembled structure at nanoscale for *R*-DAC/***C3***. [***C3***] = 3.16 mM; [DAC] = 4.74 mM.

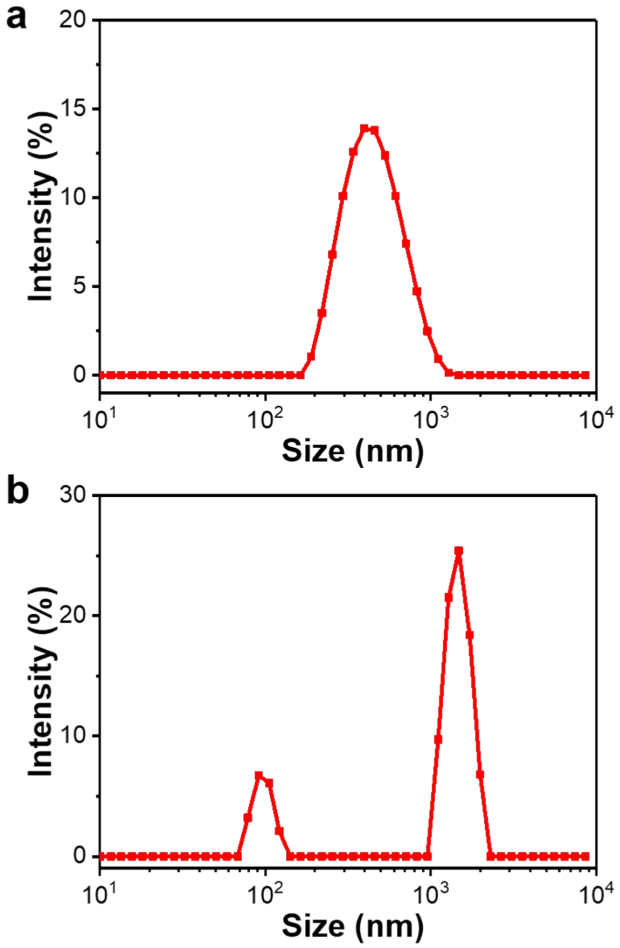


Fig. S6 DLS result for (a) DAC/***C3*** and (b) DAC/***C2*** in DMF at 25℃. [*C3*] = [*C2*]= 3.16 mM. [*S*-DAC] = 3.16 mM for DAC/***C2*** and 4.74 mM for DAC/***C3***, respectively.

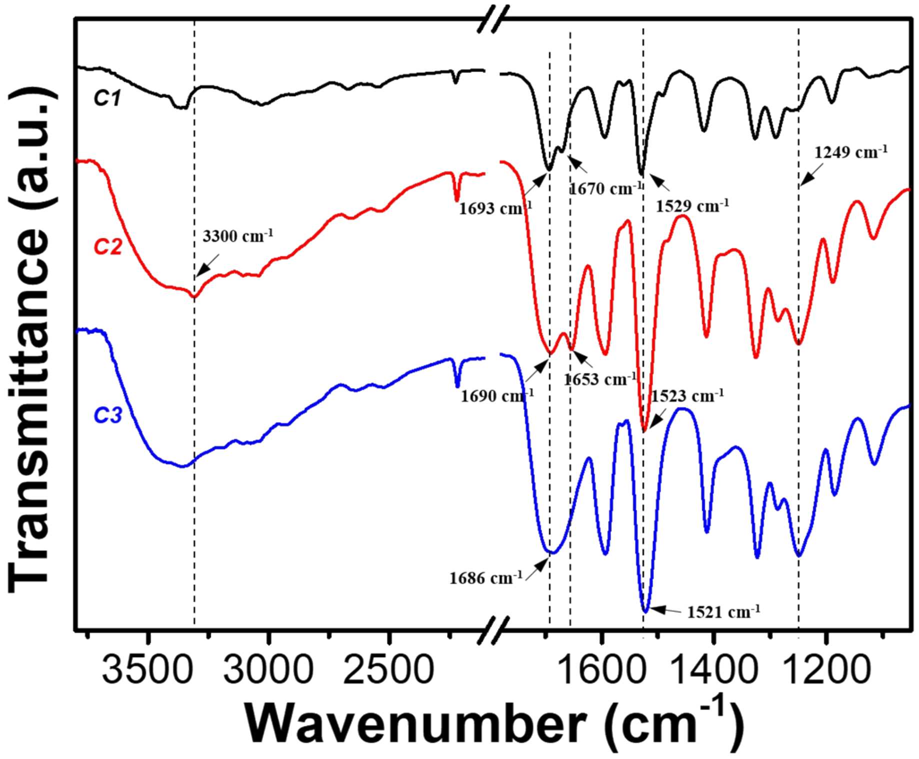


Fig. S7 FTIR spectra of ***C1*** (black curve), ***C2*** (red curve) and ***C3*** (blue curve).

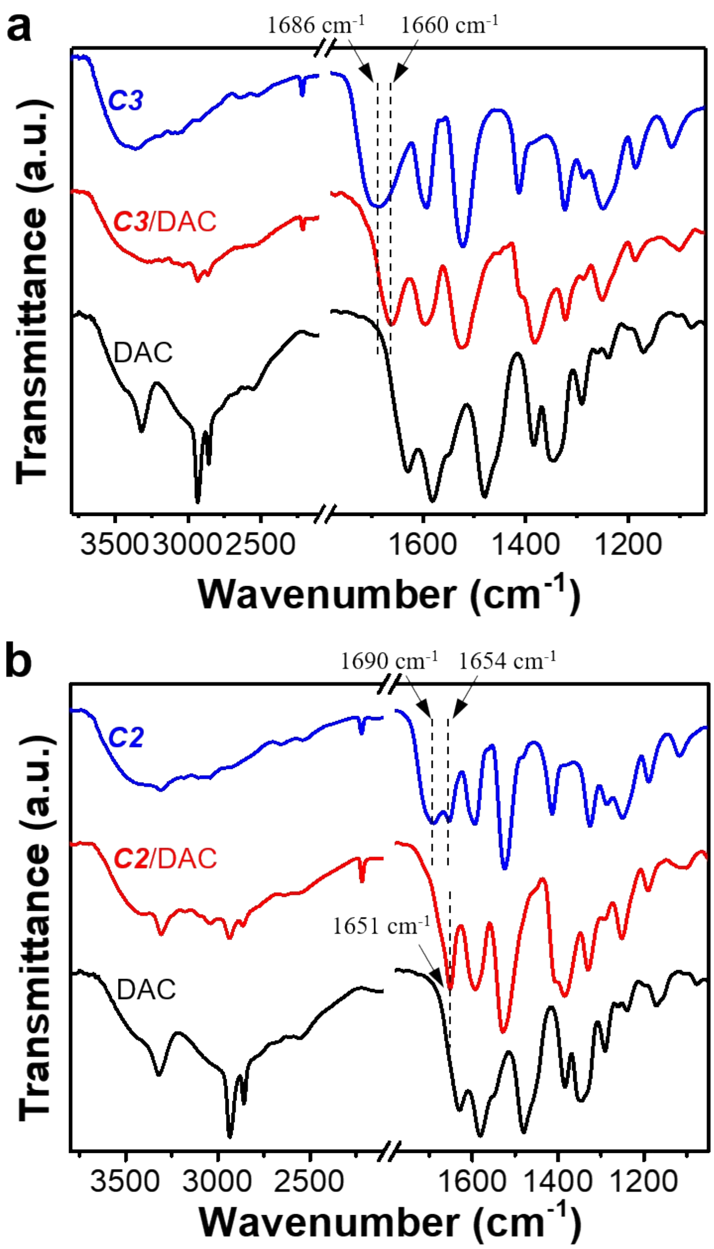


Fig. S8 FTIR spectra of (a) ***C3*** (blue curve), DAC/***C3*** (red curve), DAC (black curve), and (b) ***C2*** (blue curve), DAC/***C2*** (red curve), DAC (black curve).

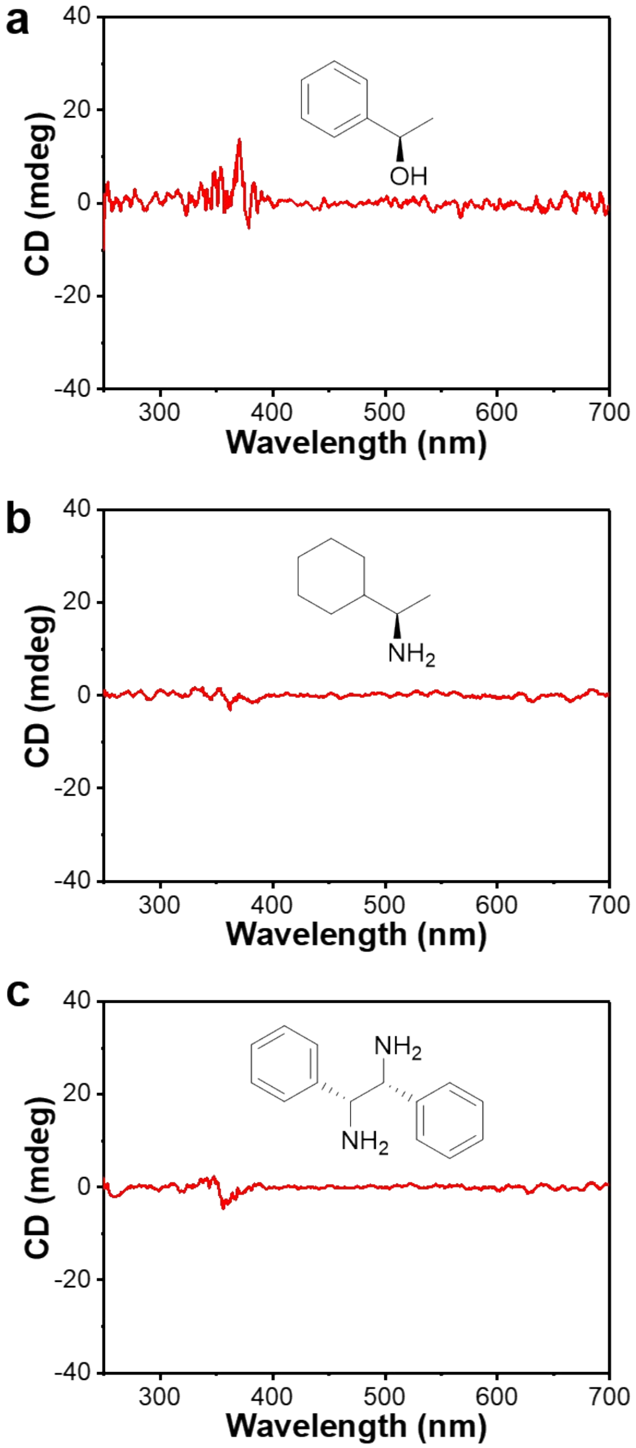


Fig. S9 The molecular structures of chiral additives and corrsponding CD spectra with ***C3*** in DMF. [***C3***] = 3.16 mM. [1-phenylethanol] = [1-cyclohexyl ethylamine] = 6.32 mM, [1,2-diphenylethylenediamine] = 4.74 mM.

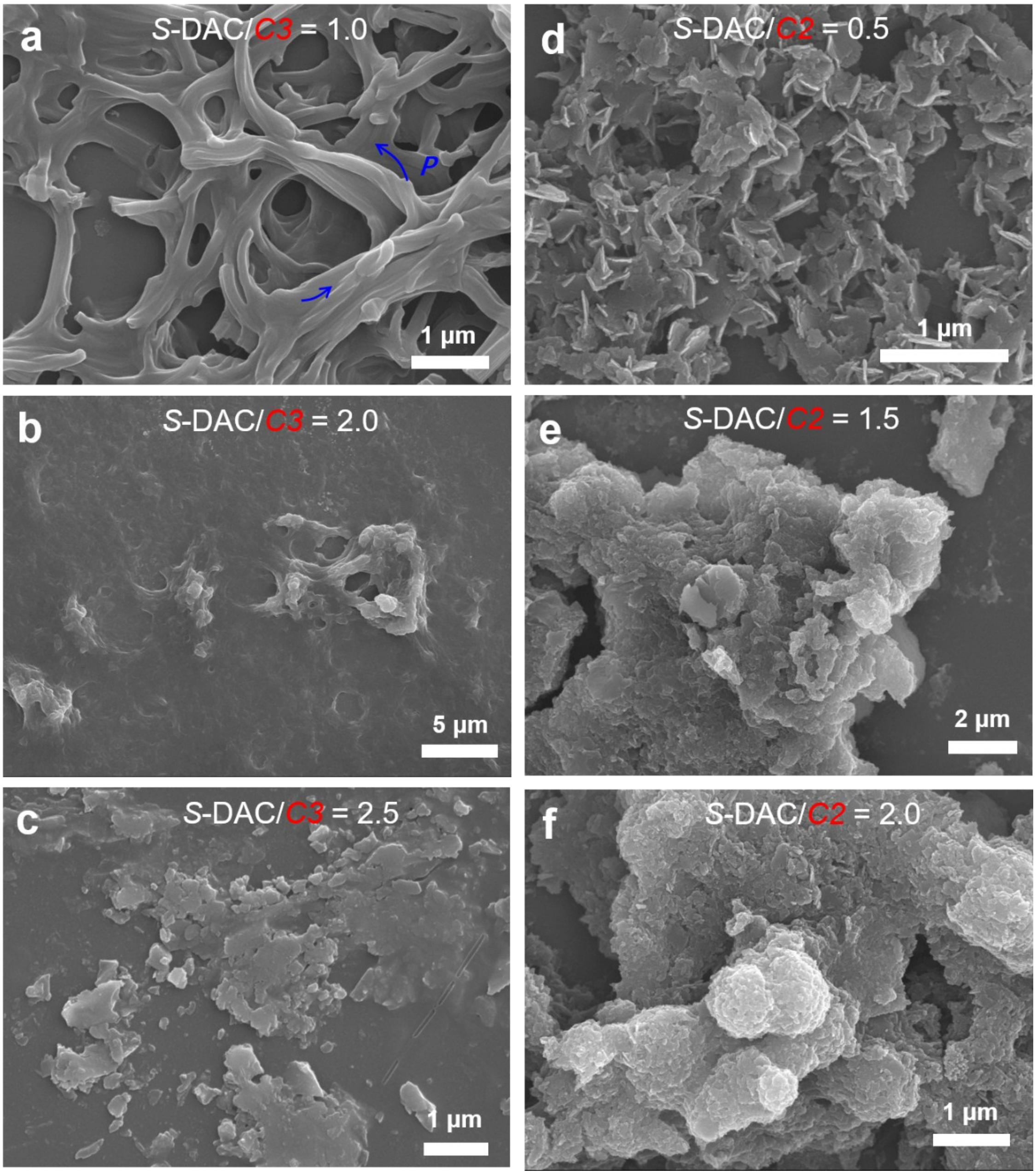


Fig. S10 SEM images of (a-c) DAC/***C3*** and (d-f) DAC/***C2*** with different molar ratios.

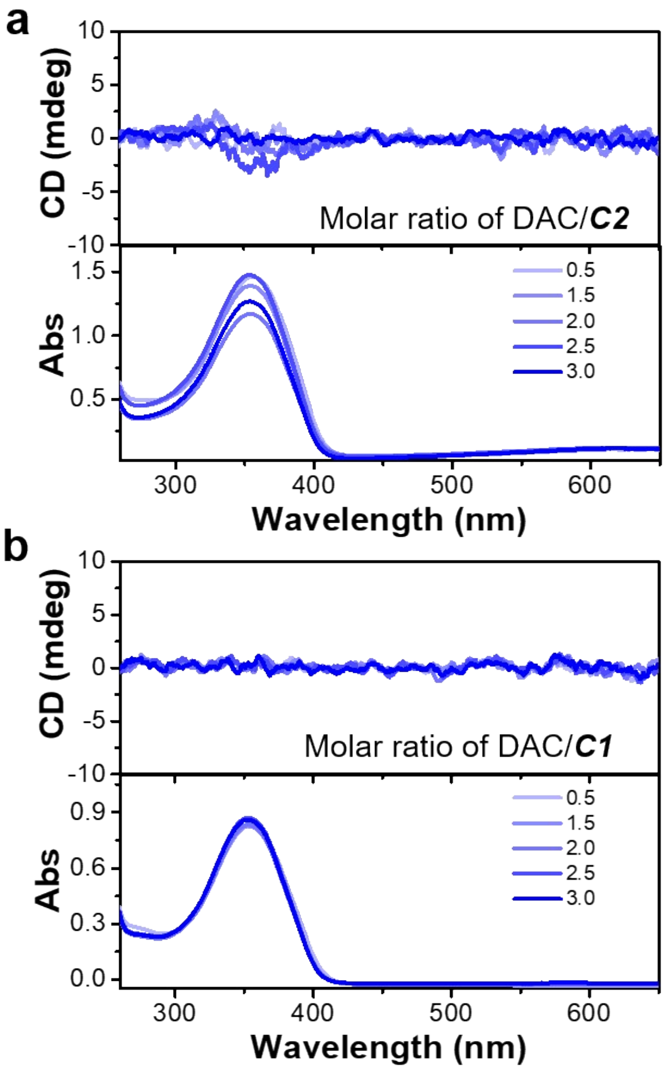


Fig. S11 CD spectra of the (a) DAC/***C2*** and (b) DAC/***C1*** with different molar ratios. The concentration of ***C2*** and ***C1*** were kept constantly as 3.16 mM.

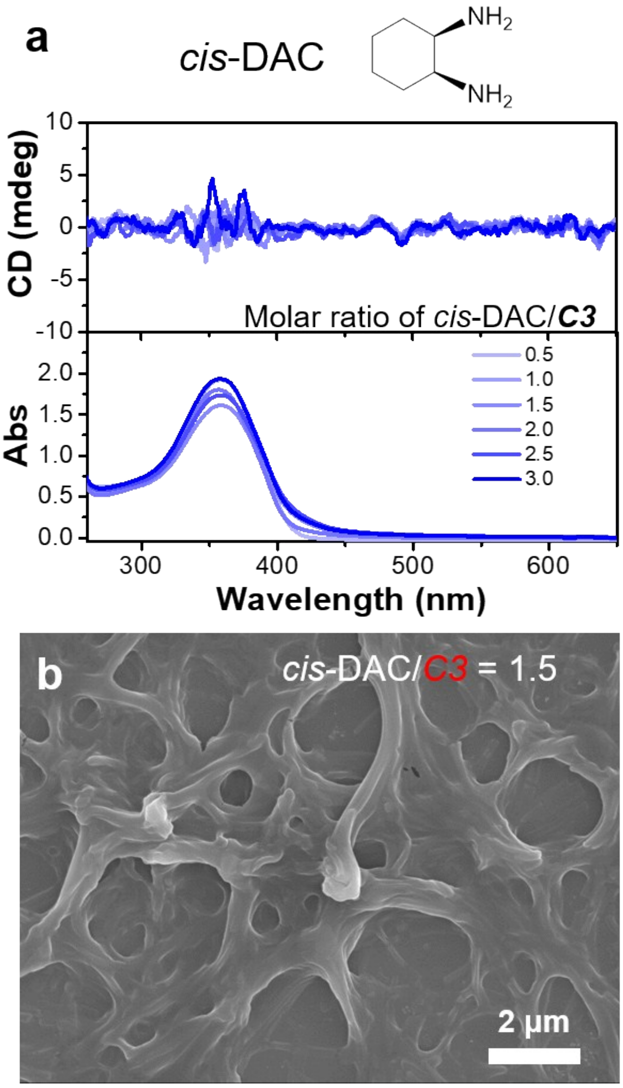


Fig. S12 (a) Molecular structures of *cis*-DAC and the CD spectra of the *cis*-DAC/***C3*** with different molar ratios. (b) SEM images of *cis*-DAC/***C3***. The concentration of ***C3*** was kept constantly as 3.16 mM.

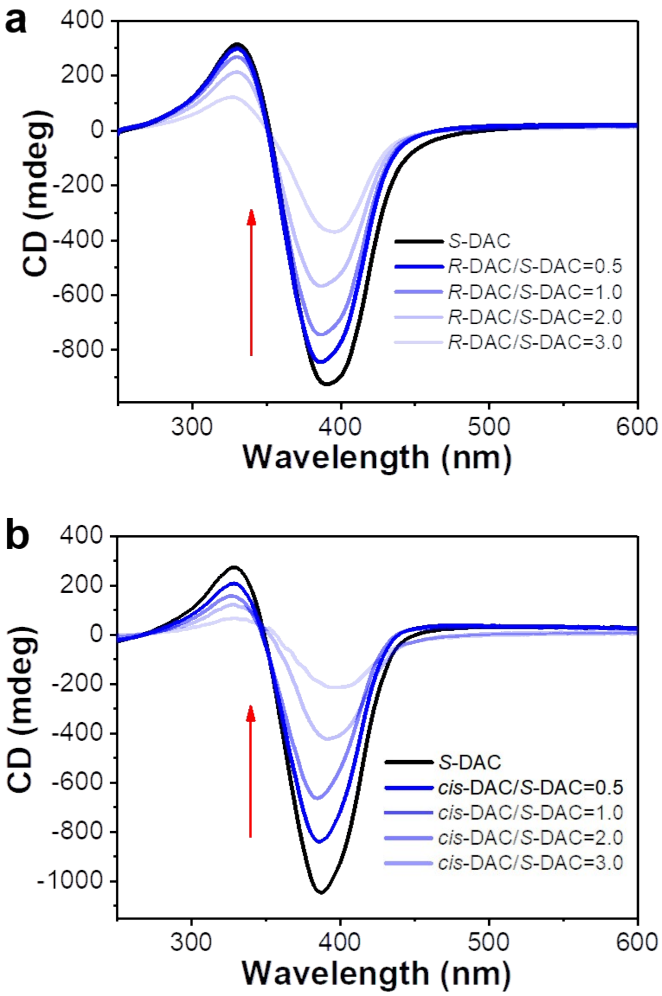


Fig. S13 CD spectra of *S*-DAC/***C3*** complex at 6 hours after various molar ratio of (a) *R*-DAC and (b) *cis*-DAC. [***C3***] = 3.16 mM; [*S*-DAC] = 4.74 mM.

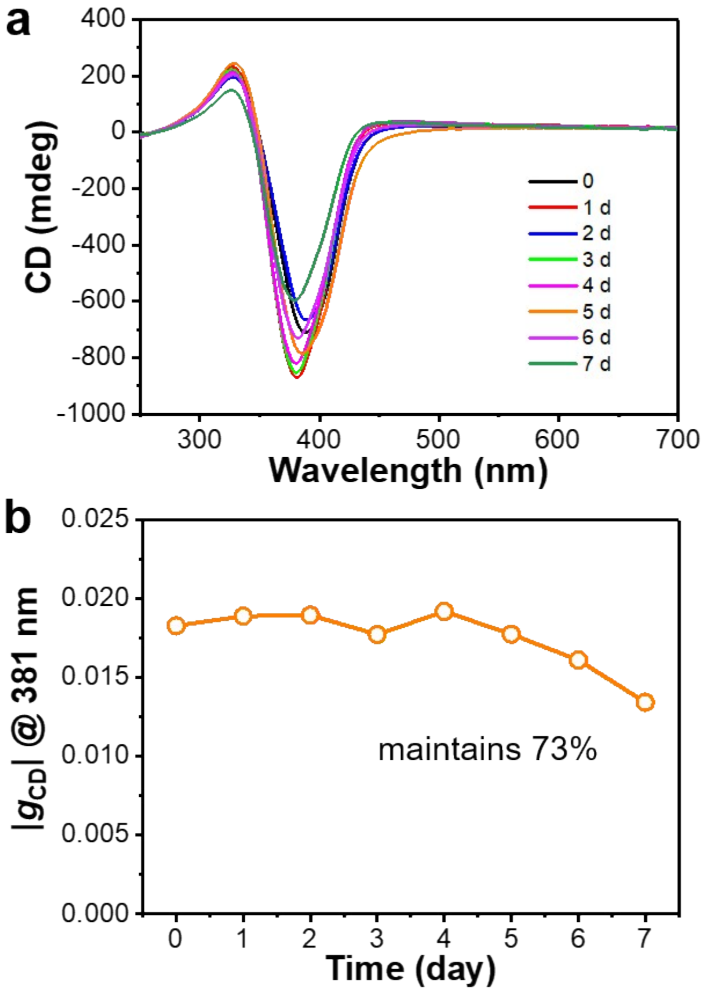


Fig. S14 (a) CD spectra and (b) Corresponding $|g_{\mathrm{CD}}|$ values of *S*-DAC/***C3*** assemblies measured at different times. [***C3***] = 3.16 mM. [*S*-DAC] = 4.74 mM.

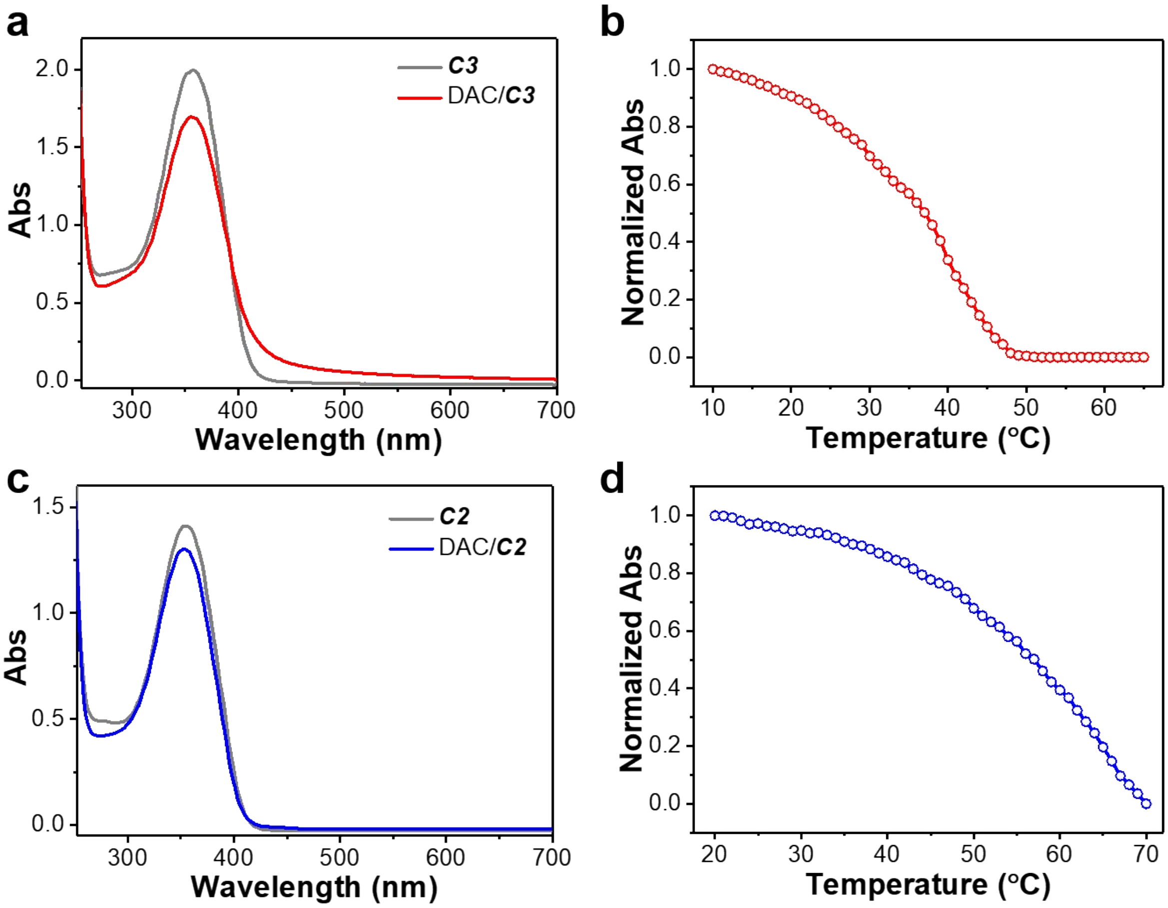


Fig. S15 (a) UV-vis absorbance spectra of ***C3*** and DAC/***C3*** in DMF. (b) Absorption data of DAC/***C3*** at 430 nm plotted as a function of temperature. (c) UV-vis absorbance spectra of ***C2*** and DAC/***C2*** in DMF. (d) Absorption data of DAC/***C2*** at 405 nm plotted as a function of temperature. [***C2***] = [***C3***] = 3.16 mM. [*S*-DAC] = 3.16 mM for DAC/***C2*** and 4.74 mM for DAC/***C3***, respectively.

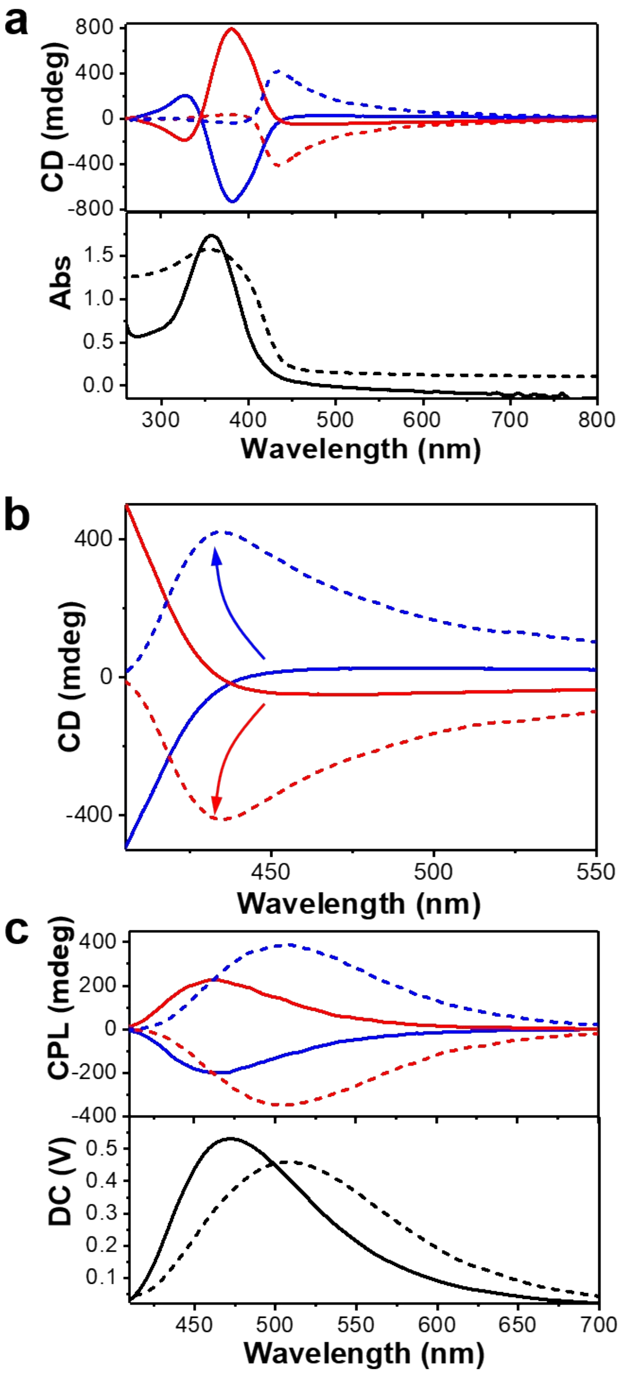


Fig. S16 (a, b) CD and (c) CPL spectra of DAC/***C3*** suspension (solid curves) and thin films (dashed curves). (b) shows the expanded portion of CD spectra in (a). The red and blue curves represent *R*-DAC/***C3*** and *S*-DAC/***C3*** assemblies, respectively. [***C3***] = 3.16 mM. [DAC] = 4.74 mM.

Supplementary References

1. Yoon S. J. & Park S., Polymorphic and mechanochromic luminescence modulation in the highly emissive dicyanodistyrylbenzene crystal: secondary bonding interaction in molecular stacking assembly. *J. Mater. Chem.*, **21**, 8338-8346 (2011).