Electronic Supplementary Information for

Nanotrumpets and circularly polarized luminescent nanotwists hierarchically self-assembled from an achiral C_3-symmetric ester

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Contents

1. Experimental Section

1.1 Materials

All the starting materials and solvents were obtained from commercial suppliers and used as received. 1,3,5-Benzenetricarbonyl trichloride was purchased from Acros. Methyl 6-amino-2-naphthoate was purchased from TCI. Milli-Q water (18.2 MΩ cm^{-1}) was used in all cases. The experimental details for the synthesis of BTANM is provided in the Supporting Information.

1.2 Characterizations

1H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 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. Elemental analysis was performed on a Thermo Flash EA-1112 Series NCHS-O analyzer. 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-810 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. The CPL spectra were obtained using a JASCO CPL-200 spectrometer. 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 (FTIR) studies were performed with a JASCO FTIR-660 spectrometer. 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.

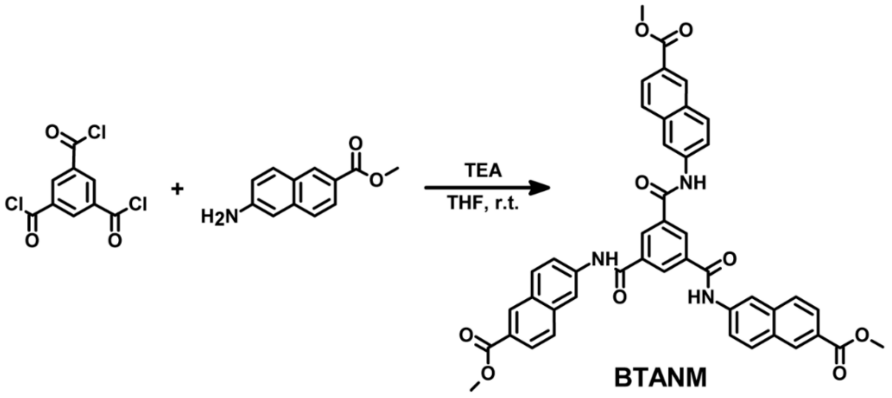
1.3 Methods

A typical procedure for the gels formation in the mixture of dimethylformamide (DMF) and H_2O is as follows: BTANM (5 mg) was first dissolved in a sealed tube containing DMF by shaking, and then Milli-Q water was injected in with a pipette. A white gel slowly formed after 2 hours finally. Gelation was confirmed by the absence of flow, as observed by the tube inversion method. The magnitude of the CD signal is defined as $g_{\mathrm{CD}} = 2 \times (\varepsilon_{\mathrm{L}} - \varepsilon_{\mathrm{R}})/(\varepsilon_{\mathrm{L}} - \varepsilon_{\mathrm{R}})$, 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 400 nm. The magnitude of CPL can be evaluated by the luminescence dissymmetry factor (g_{lum}), which is defined as $g_{\mathrm{lum}} = 2 \times (I_{\mathrm{L}} - I_{\mathrm{R}})/(I_{\mathrm{L}} + I_{\mathrm{R}})$, where I_{L} and I_{R} refer to the intensity of left- and right-handed CPL, respectively. Experimentally, the value of glum is defined as g_{lum} = [ellipticity/(32980/ln 10)]/total fluorescence intensity at the CPL extremum.

1.4 Synthetic procedures

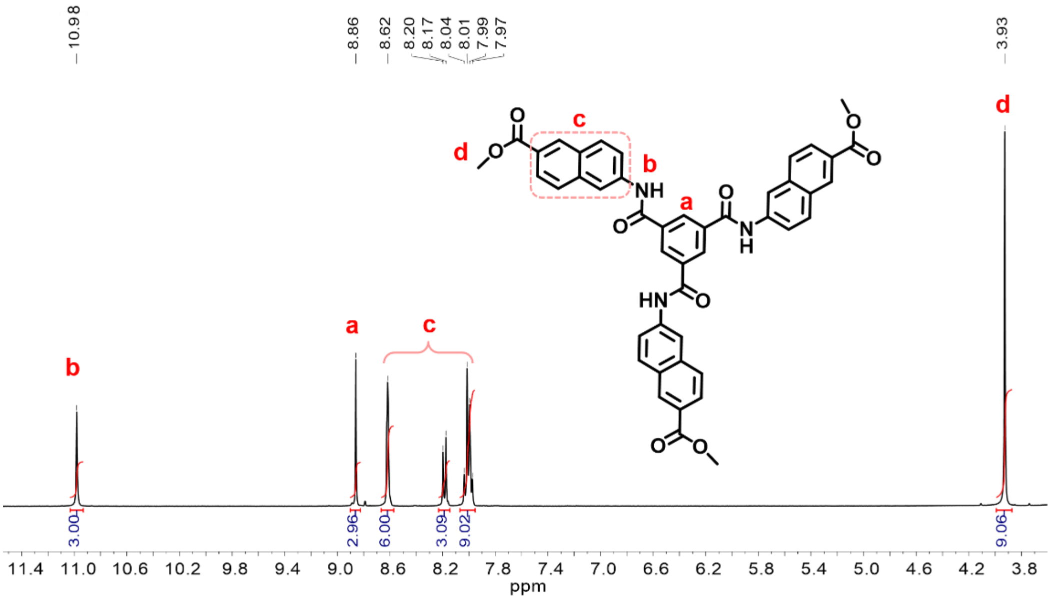
The methyl naphthoate-substituted benzenetriester (BTANM) was prepared by treating 1, 3, 5-benzenetricarbonyl trichloride with methyl 6-amino-2-naphthoate as shown in Scheme S1.

Scheme S1. Synthesis of BTANM.



A THF solution (10 mL) of 1,3,5-benzenetricarbonyl trichloride (0.33 g, 1.24 mmol) was added to a solution containing methyl 6-amino-2-naphthoate (1 g, 4.97 mmol) and triethylamine (1.37 mL, 9.94 mmol) in 25 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 filtered, followed by washing on the filter paper consecutively with water (20 mL) and methanol (20 mL). This clean product was dried under reduced pressure. Yield = 87%. ^{1}H NMR (400 MHz, d$_6$-DMSO, δ, ppm): 3.93 (s, 9H, CH$_3$), 7.99-8.01 (m, 9H, Ar-H), 8.17-8.20 (d, 3H, Ar-H), 8.61-8.63 (d, 6H, Ar-H), 8.86 (s, 3H, Ar-H), 11.00 (s, 3H, N-H). MALDI-TOF MS: calcd. For $C_{45}H_{33}N_3O_9$ M$^+$: m/z = 759.77; found [M+Na]$^+$: m/z = 782.7. Elemental Analysis: calcd. for $C_{45}H_{33}N_3O_9$: C 71.14, H 4.38, N 5.53; found: C 71.05, H 4.15, N 5.62.

1H NMR spectra of BTANM in DMSO-d6.



2. Supplementary Tables and Figures

Table S1. Solubility of BTANM in various solvents.

Solvent	Phase [a]	Solvent	Phase
H_2O	I	acetonitrile	I
ethyl acetate	I	$CHCl_3$	I
methanol	I	CH_2Cl_2	I
ethanol	I	acetone	I
THF	I	toluene	I
DMF	S	n-hexane	I
DMSO	S	cyclohexane	I

[a] S: soluble; I: insoluble

Table S2. The effect of DMF/H_2O volume ratio on gelation properties of BTANM.

Volume ratio [a]	Phase [b]
10	S
9	PG
8	PG
7	G
6	G
5	G
4	G
3	G
2	G
1	G
0.67	G
0.43	PG
0.25	PG
0.11	P

[a] The total volume of DMF/H_2O mixture is 1 mL and the concentration of BTANM is 6.58 mM.

[b] S: solution; PG: partial gel; G: stable gel; P: precipitate.

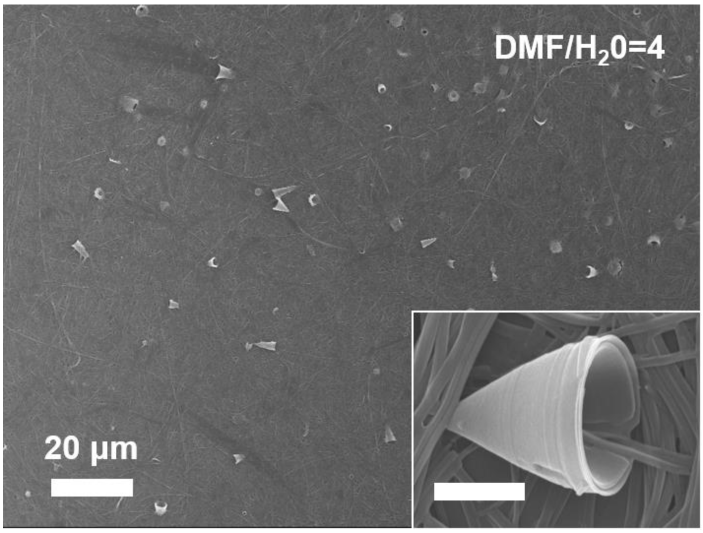


Fig. S1 SEM images of BTANM at the volume ratio of DMF/H_2O=4. The insets show the expanded trumpet-like nanostructures; scale bar: 1 μm.

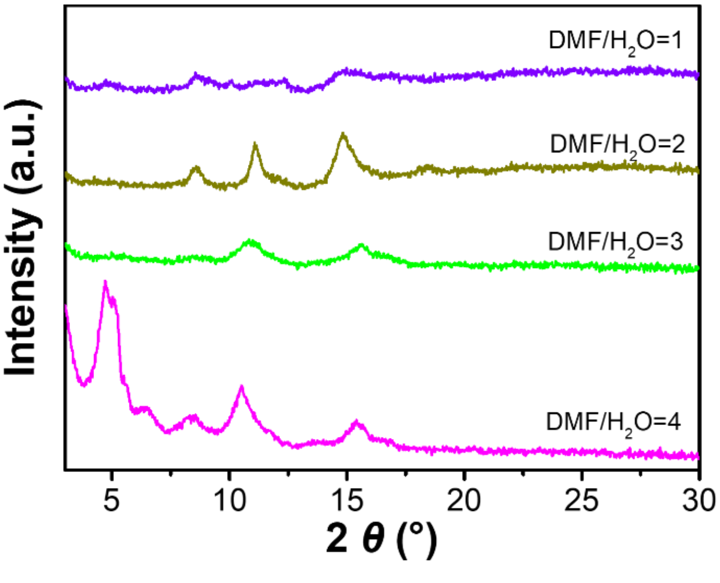


Fig. S2 XRD pattern of BTANM.

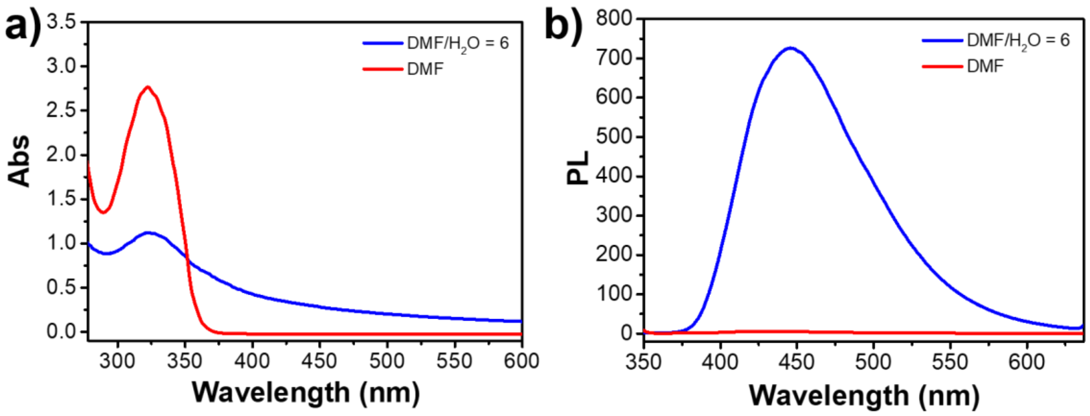


Fig. S3 (a) UV−vis and (b) fluorescence spectra (λ_{ex}=325 nm) of the BTANM (6.58 mmol) in DMF/H_2O=6 (blue line) and DMF (red line).

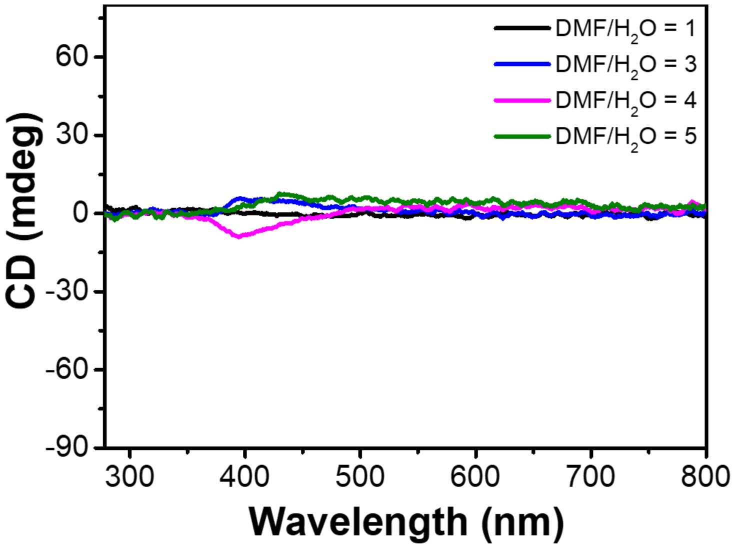


Fig. S4 CD spectra of BTANM (6.58 mmol) at various volume ratio of DMF/H_2O.

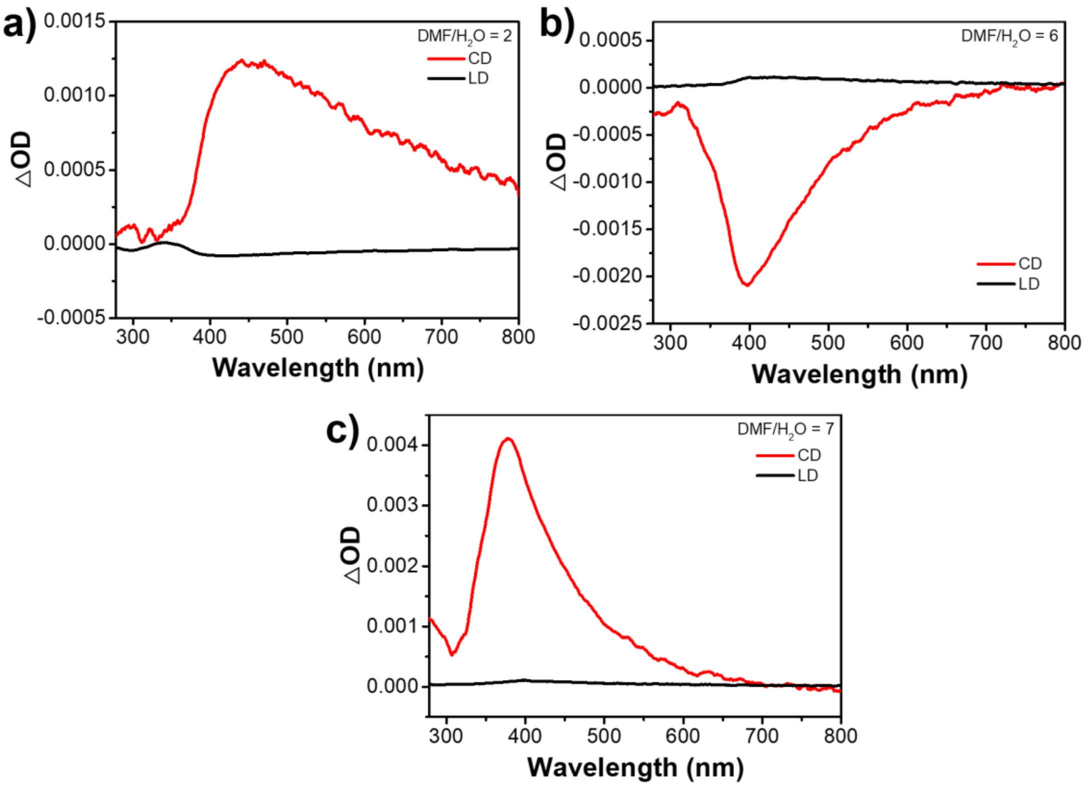


Fig. S5 The typical CD and LD spectra of the BTANM assemblies, which are unified as the same unit (Δ OD).

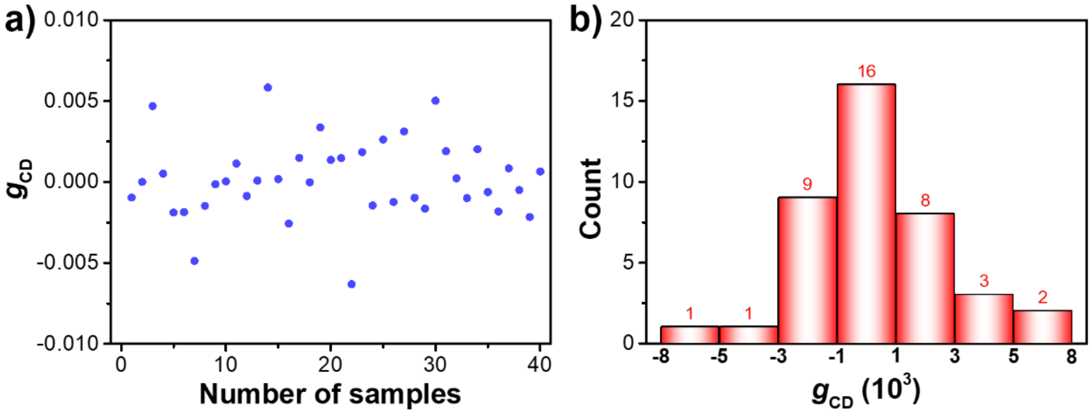


Fig. S6 (a) The statistical distribution of the handedness and intensity of the CD signals around 400 nm from 40 samples of BTANM gels at DMF/H_2O=7. (b) Histogram of CD intensity for 40 samples.

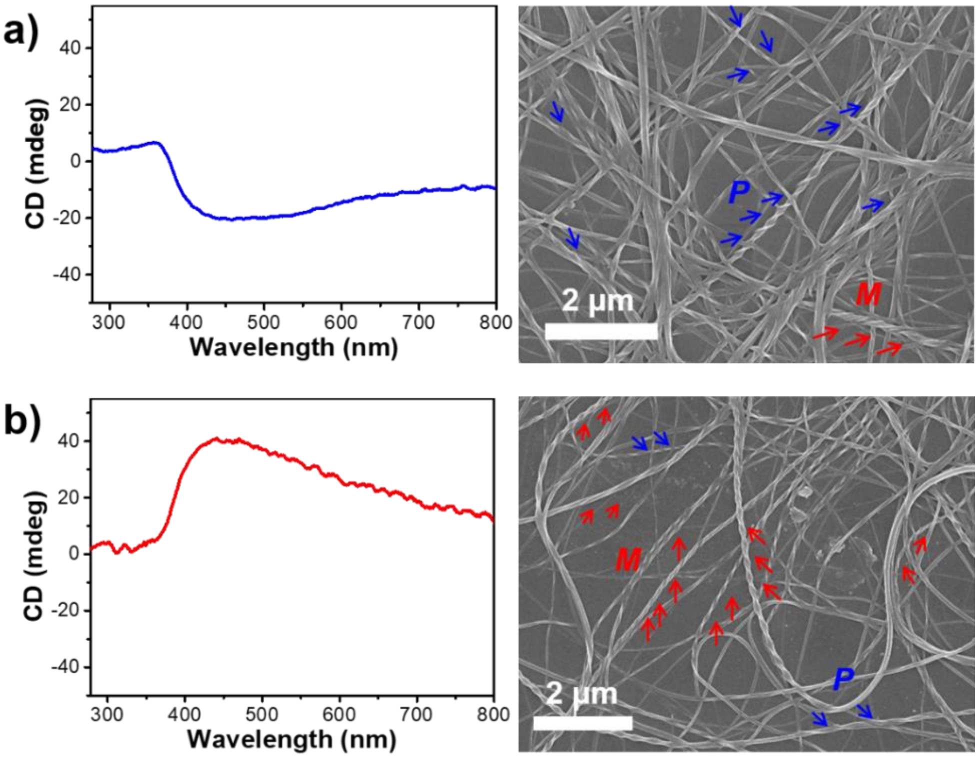


Fig. S7 CD spectra and SEM images of optically active BTANM gels formed in DMF/H_2O = 2. (a) When the *P* twists outnumber the *M* twists, the CD spectrum shows a negative Cotton effect, (b) while if the *M* twists outnumber the *P* twists, the CD spectrum shows a positive Cotton effect.