Electronic Supplementary Information for

Light-triggered self-assembly of a cyanostilbene-conjugated glutamide from nanobelt to nanotoroid and inversion of circularly polarized luminescence

Xue Jin,[ab] Dong Yang,[bc] Yuqian Jiang, Pengfei Duan*[a] and Minghua Liu*[abcd]

[a] Division of Nanophotonics, CAS Center for Excellence in Nanoscience, CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology (NCNST) No.11 ZhongGuanCun BeiYiTiao, 100190 Beijing, P.R. China.

[b] Beijing National Laboratory for Molecular Science, CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

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

[d] Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, P. R. China.

duanpf@nanoctr.cn or liumh@iccas.ac.cn

1. Experimental section

Materials: All the starting materials and solvents were obtained from commercial suppliers and used as received. Milli-Q water (18.2 MΩ•cm) was used in all cases. 2-phenylacetonitrile and methyl 4-formylbenzoate were purchased from Alfa Aesar. Tert-butanol and potassium tert-butoxide were purchased from TCI. PCNP molecules were synthesized according to synthetic route in Supplementary Information. Cyano-substituted stilbene was synthesized according to the reported procedures. By introducing carboxylic acid moieties to the cyanostilbene, amide condensation reaction with glutamate based amine was carried on using 1-ethyl-3-(3-dimethyllaminopropyl) carbodiimide hydrochloride (EDC•HCl)/1-hydroxybenzotrizole (HOBt) condensation agent. The final compounds were purified by column chromatography and confirmed the molecular structures by ^{1}H NMR, MALDI-TOF-MS.

Characterization: ^{1}H NMR spectra were recorded on a Bruker Advance III 400 (400 MHz) spectrometer. Mass spectra were performed on a BIFLEIII matrix- assisted laser desorption/ionization time of fight mass spectrometry (MALDI-TOF-MS) instrument. SEM was performed on a Hitachi S-4800 FE-SEM 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. FT-IR spectra were recorded on a JASCO FTIR-660 plus spectrophotometer with the resolution of 4 cm^{-1} at room temperature. Samples were first vacuum-dried and made into plates with KBr for FT-IR spectral measurements. XRD analysis was performed on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with $\mathrm{Cu}_{K\alpha}$ radiation (λ=1.5406 Å), which was operated at a voltage of 40 kV and a current of 200 mA. Samples were vacuum-dried for XRD measurements. CD measurements were conducted on a JASCO J-1500 CD spectrometer. UV spectra were obtained on Hitachi U-3900 UV/vis spectrophotometer. CPL measurements were performed with a JASCO CPL-200 spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Cuvettes of 0.1 mm were used for measuring the CD and CPL spectra of samples. Cuvettes of 1 mm were used for measuring the UV–vis, and FL spectra of samples. TEM was performed on Tecnai G2 20 S-TWIN or HT7700 at accelerating voltages of 200 kV, respectively. AFM was performed by using Tapping Mode (Nanoscope IIIa, Digital Instruments) with a Fast-scan B tip. The fully aging assemblies were cast on carbon-coated Cu grids (unstained) or mica slices; the trapped solvent in the assemblies was evaporated under ambient conditions before the TEM or AFM measurements. Fluorescence imaging was performed on an Olympus IX81 inverted fluorescence microscopy with 100 W high-pressure mercury lamp and 100× oil immersion objective, and the exciting wavelength ranges from 325 to 375 nm. Fluorescence lifetimes were measured by Edinburg FLS-980 fluorescence spectrometer (Horiba) using time-correlated single-photon-counting. All operations were performed at room temperature unless otherwise specified.

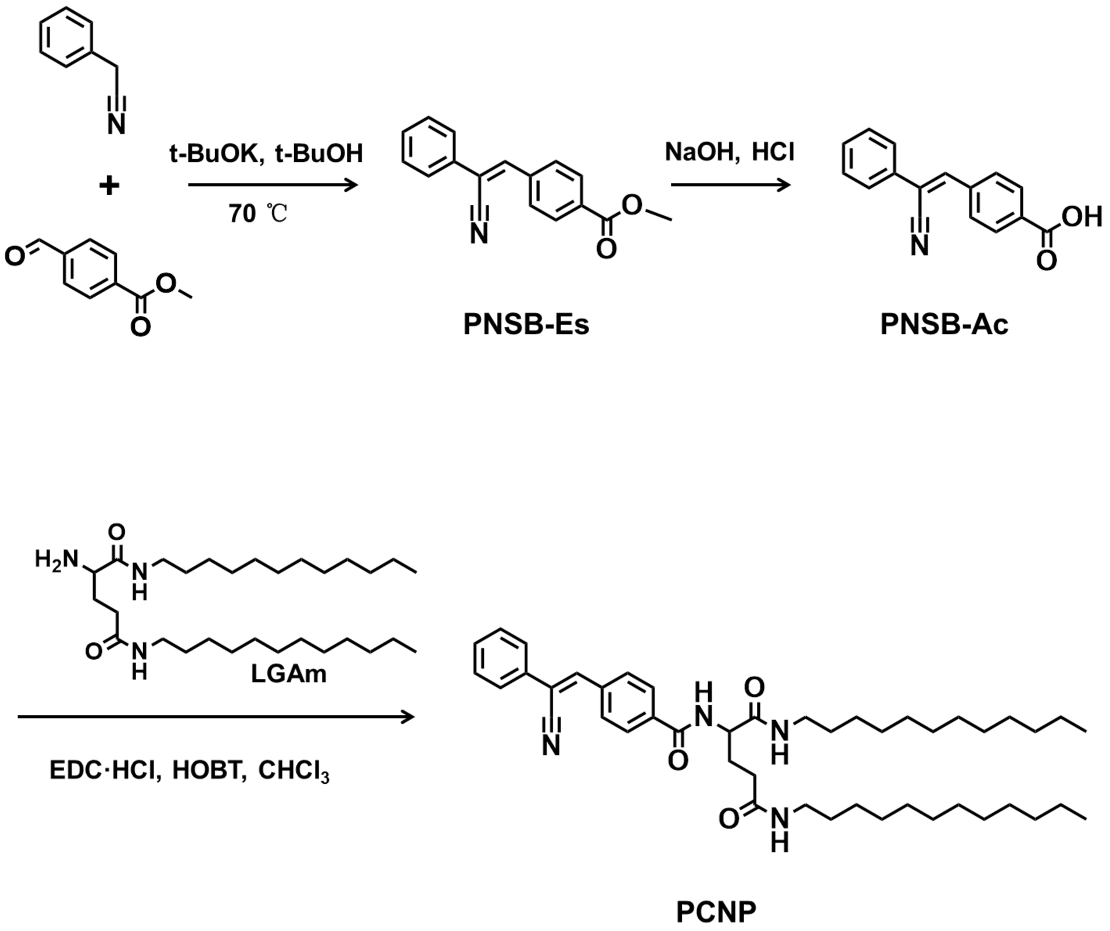

Fig. S1. The synthesize process of PCNP molecule.

Synthesis of PNSB-Es

The ester form PNSB-Es was synthesized according to the reported procedures.[1] Briefly, the mixture of 2-phenylacetonitrile (1.67 g, 1 mmol) and methyl terephthaladehydate (1.64 g, 1 mmol) in tertbutyl alcohol (30 mL) was stirred at 70 ℃. Potassium tert-butoxide (2.31 g, 2.05 mmol) powder was dropped into the mixture and stirred for 6 hours. The resulting precipitate was washed with ethanol, and then dried in vacuum drying box.

Synthesis of PNSB-Ac

The hydrolysis of PNSB-Es was carried on the general procedure. To a suspension of 1.57 g (0.5 mmol) PNSB-Es in 75 mL 1:1 mixture of THF/MeOH, 15 mL of a 2 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 (2 M) was collected by filtration, and washed several times with water yielding 1.27 g (85%) of a white solid. The obtained PNSB-Ac was washed several times by water, ethanol and acetone because of the poor solubility. It was used for next step without further purification.

Synthesis of PCNP

LGAm were synthesized according to previous reported methods.[2] LGAm (2.40 g, 5 mmol) and PNSB-Ac (1.50 g, 5 mmol) were dispersed into a solution of THF/$CHCl_3$ (100 mL, 2:1, v/v). Then EDC•HCl (1.15 g, 6 mmol) and HOBt (0.81 g, 6 mmol) were added. The reaction mixture was stirred at 50 ℃ for 12 h. After removal of solvents, the remained solids were dissolved in THF (20 mL) and then poured into 1% Na_2CO_3 aqueous solution (500 mL). The collected precipitate was purified by column chromatography (CH_2Cl_2/CH_3OH=20/1) over silica gel to yield a white powder (1.53 g, yield: 40%)

^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃, TMS): δ (ppm) 0.86−0.89 (t, 6H, CH_3), 1.15−1.40 (m, 36H, CH_2), 1.46−1.60 (m, 4H, CH_2), 2.05−2.31 (d, 4H, CH_2), 2.39−2.54 (d, 1H, NH), 2.59−2.72 (d, 1H, NH), 3.20-3.37 (m, 4H, CH_2), 4.54−4.66 (d, 1H, CH), 7.07 (s, 1H, NH), 7.40-7.54(m, 2H, Ar-H), 7.58 (s, 1H, Ar-H), 7.67-7.75 (d, 2H, Ar-H), 7.95−8.08 (q, 4H, Ar-H), 8.39 (s, 1H, vinylene). ^{13}C NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ(ppm) 14.13, 22.70, 29.30, 29.33, 29.37, 29.52, 29.57, 29.65, 29.68, 31.93, 39.73, 39.95, 53.37, 113.64, 117.60, 136.13, 127.92, 129.18, 129.36, 129.66, 134.08, 134.96, 136.78, 140.72, 166.55, 171.04, 173.26; MALDI-TOF-MS: calcd. for $C_{45}H_{68}N_4O_3$ m/z=713.1; found $[M+Na]^+$: m/z=735.5. Elemental analysis calcd (%) for $C_{45}H_{68}N_4O_3$: C 75.79, H 9.63, N 7.85; found: C 75.72, H 9.54, N 7.90. The melting point of PCNP is 201.48 ^{o}C.

Preparation of PCNP self-assembled nanostructure

For the self-assembly of the PCNP, H_2O (500 μL) and THF (500 μL) were added into 5 mg PCNP (7 mM) in sealed quartz bottle, and the corresponding mixtures were heated to form transparent solution. Let the solution slowly cool down in the dark, white precipitates with nanobelt morphology gradually formed. For the fabrication of nanotoroids and nanospheres, a 365 nm UV lamp was used to irradiate the solution during the cooling down process. Then, the irradiated samples were stayed in dark for 1 h to complete the assembly. The nanotoroid structures could achieve for 5-120 min UV irradiation. To get the nanospheres, UV irradiation needs to carry on for more than 150 min.

2. Supplementary Figures

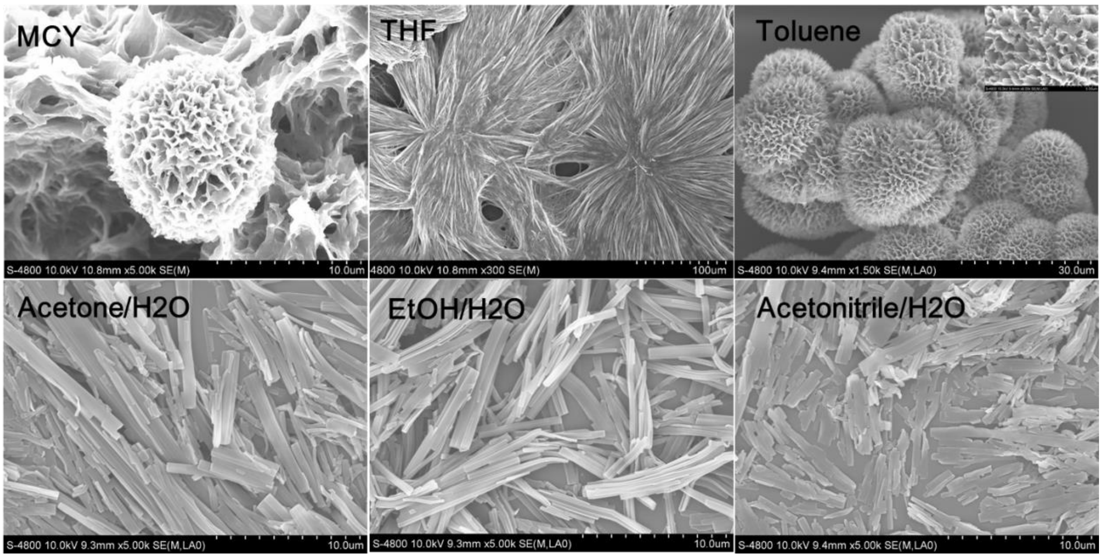

Fig. S2. Methylcyclohexane (MCY), THF, toluene, acetone/water (1:1, v/v) ethanol/H_2O (1:1, v/v), acetonitrile/H_2O (1:1, v/v).

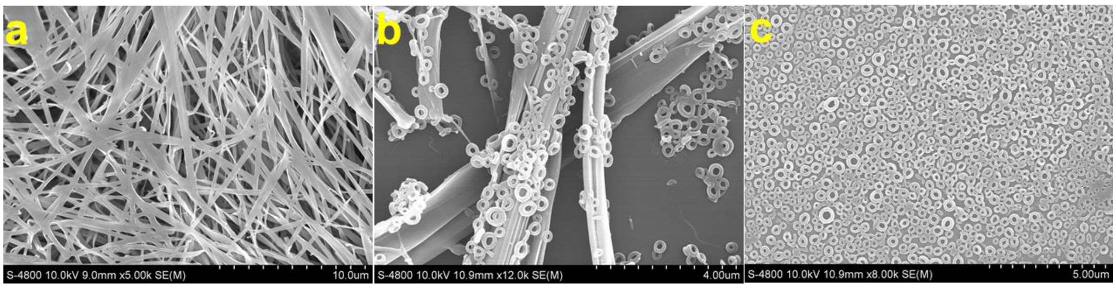

Fig. S3. The sample was assembled in the glass bottle and natural light. a) The morphology of precipation; b) The morphologies of the assemblies at the edge of the precipation; c) The morphology of supernatant.

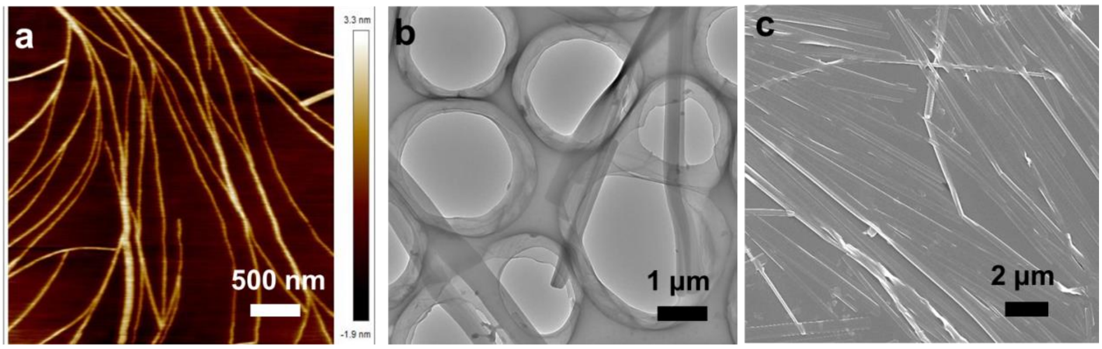

Fig. S4. To prepare the nanobelt sample, the precipitates were diluted by water to achieve good dispersibility. The nanobelts were formed in THF/water (1:1, v/v) without UV irradiation.

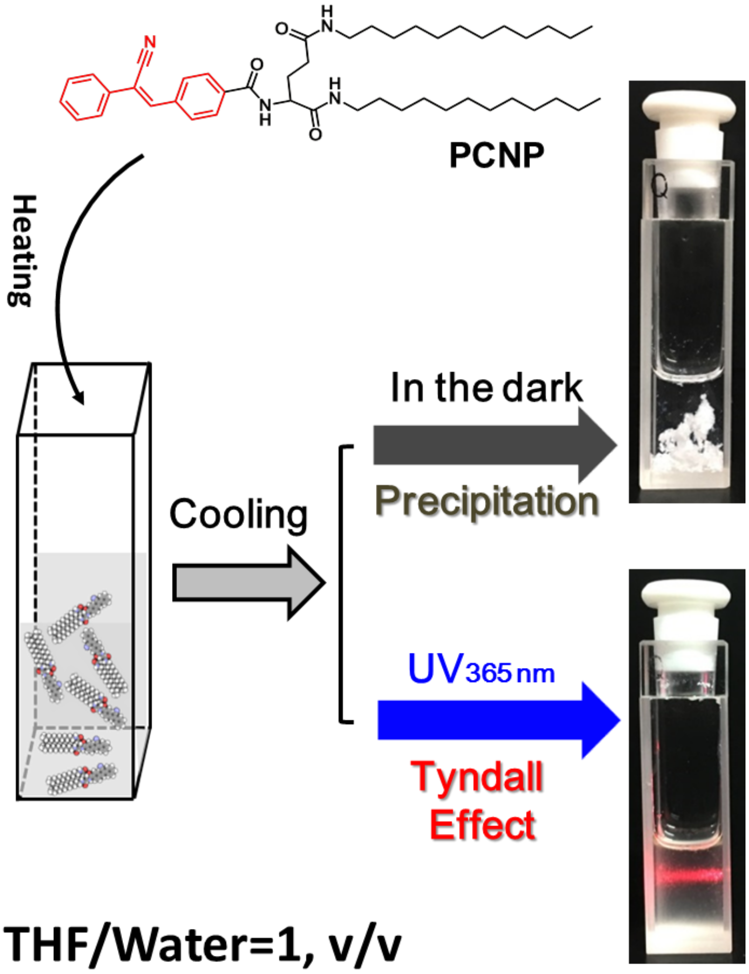

Fig. S5. The PCNP hot solution could form white precipitates after cooling down to room temperature in the dark. If light irradiation (365 nm) was applied, the solution shows a Tyndall effect, indicating the formation of organized nanostructures.

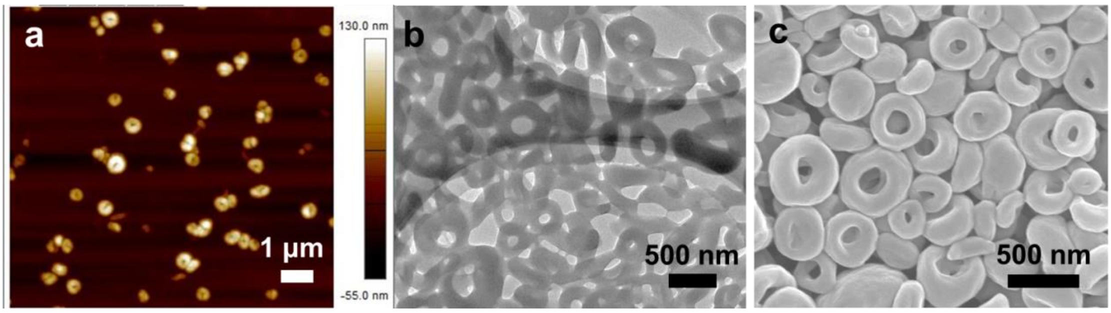

Fig. S6. The solution of nanotoroids was directly cast on the matrix. The nanotoroids were formed in THF/water (1:1, v/v) with 60 min UV irradiation.

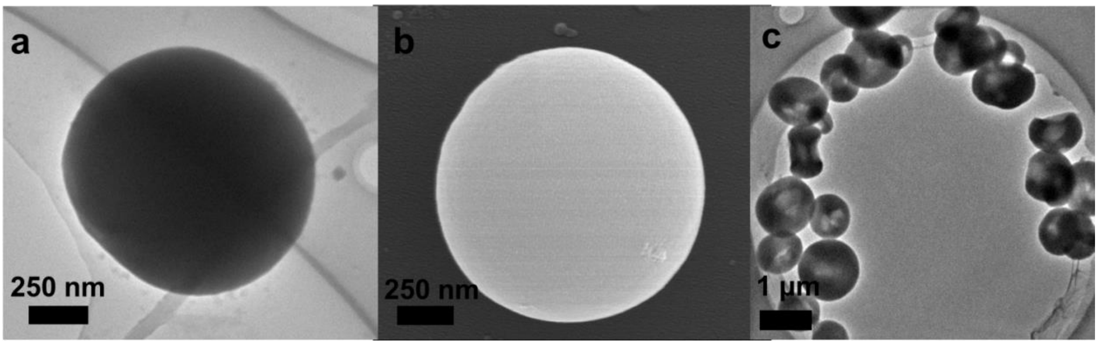

Fig. S7. The solution contained spheres was directly cast on the matrix. Due to the height of the sphere is too high to use AFM measurement, TEM techology was used to carefully observe the nanostructure. From the TEM images, we can see the sphere with a hollow structure, which were formed in THF/water (1:1, v/v) with 150 min UV irradiation.

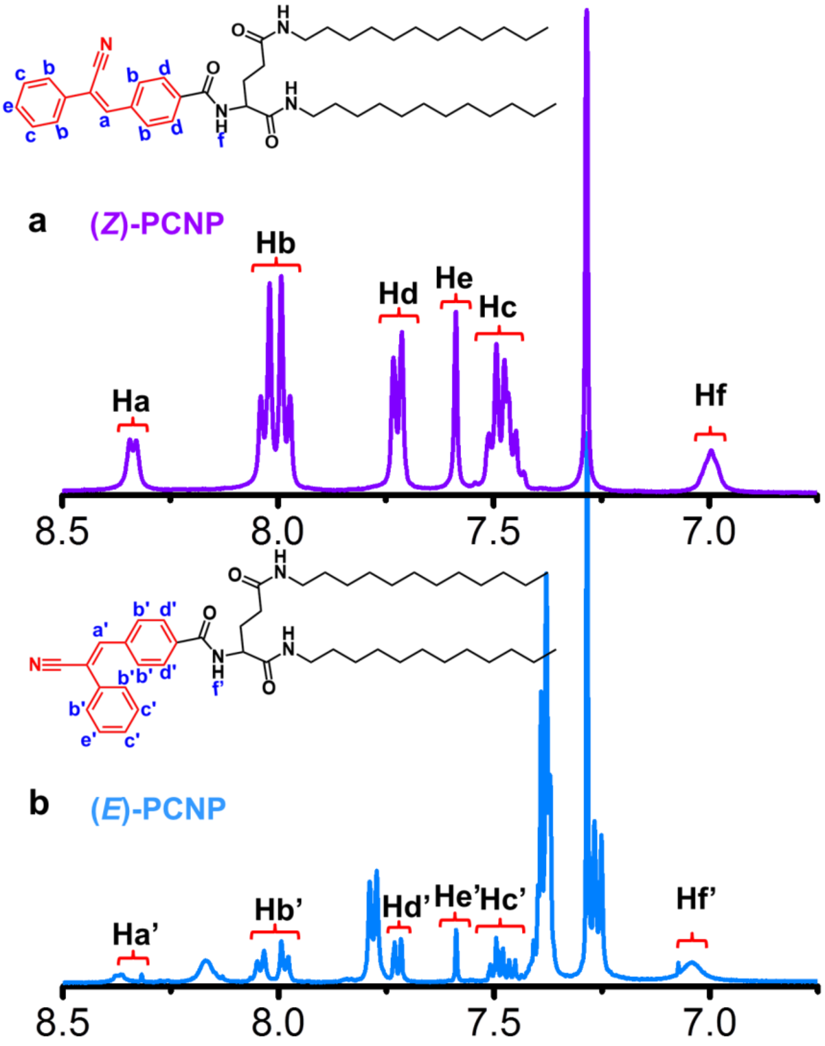

Fig. S8. The NMR spectrum of (*Z*)-PCNP disappearance of the vinylene proton peak at 8.3 ppm as well as appearance of (*E*)-PCNP vinylene proton peak at 8.15 ppm, which confirms the (*Z*)-/(*E*)- photoisomerization of PCNP. The PCNP powders were dissolved in deuterated chloroform. (*E*)-PCNP was obtained by irradiating the sample 30 min with 365 nm ultraviolet light from a lamp (30 mW•cm^{-2}).

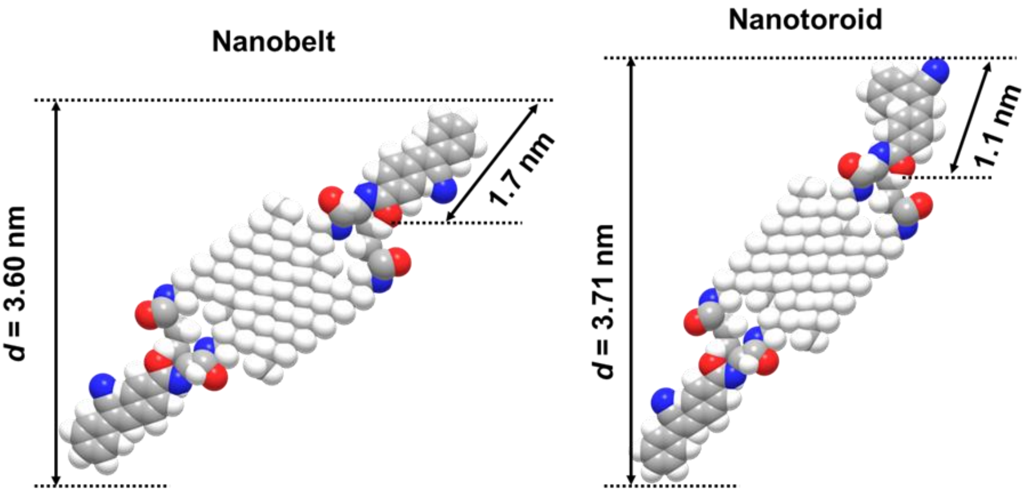

Fig. S9. Bilayer structure formed by PCNP molecules assembly. The possible molecular arrangements of nanobelt and nanotoroid.

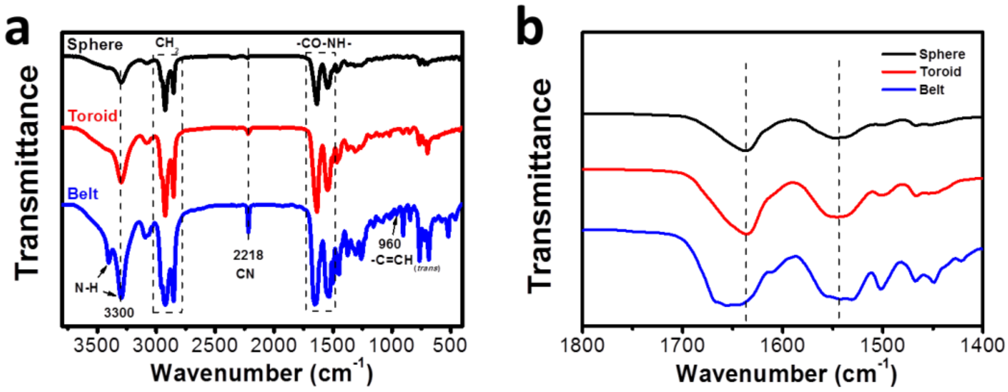

Fig. S10. The FT-IR spectra for three nanostructures. While both nanosphere and nanotoroid showed similar profile, that of the nanobelt showed slight differences in the N-H vibration and amide I band.

Table S1. Fluorescence lifetime fitting results of three nanostructures.

Nanostructure	Components	%	τ (ns)	χ2
Nanobelt	2	17.16	8.12	1.211
		82.84	12.48	
Nanotoroid	2	67.16	5.59	1.231
		32.84	11.35	
Nanosphere	2	55.43	4.33	1.055
		44.57	9.76	

All the samples were cast on the 0.1 mm quartz cuvettes for fluorescence lifetime measurement. The nanostructures were formed in THF/water (1:1, v/v).

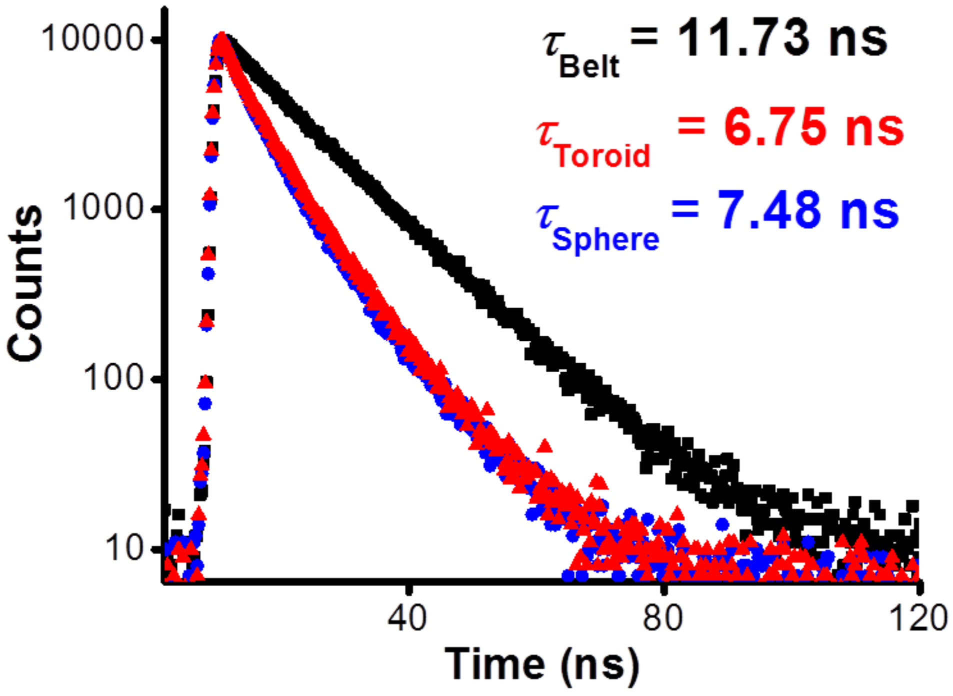

Fig. S11. The as-prepared samples were dropped on the 0.1 mm quartz cuvette, and then carried on the fluorescence lifetime measurement. The nanostructures were formed in THF/water (1:1, v/v).

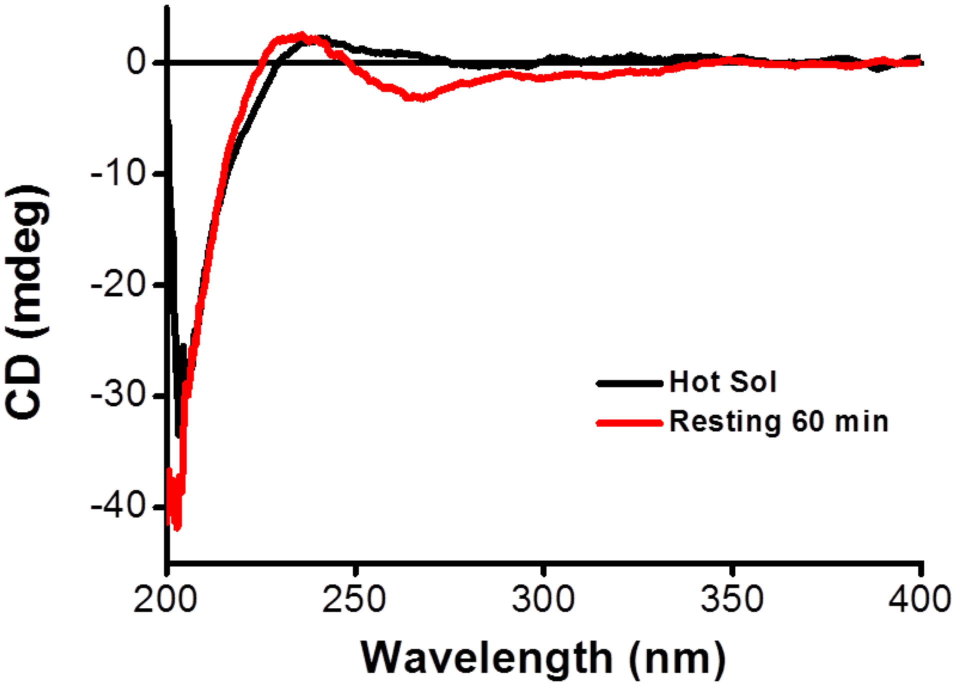

Fig. S12. The hot solution of PCNP was quickly dropped on the 0.1 mm quartz cuvette, and then carried on the CD measurement. After 60 min resting, supramolecular chirality of cyanostilbene corresponding to its absorption range was appeared by the supramolecular assembly. The nanostructures were formed in THF/water (1:1, v/v).

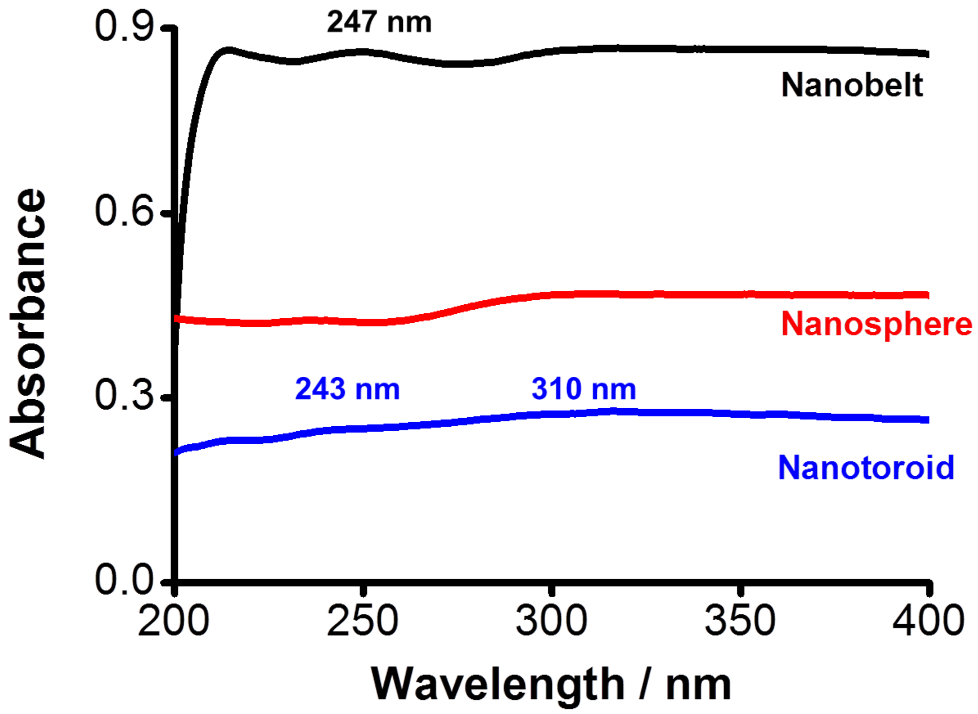

Fig. S13. All the samples were cast on the 0.1 mm quartz cuvettes. Due to the strong scattering, the absorption spectra of nanostructures showed high baseline. The nanostructures were formed in THF/water (1:1, v/v).

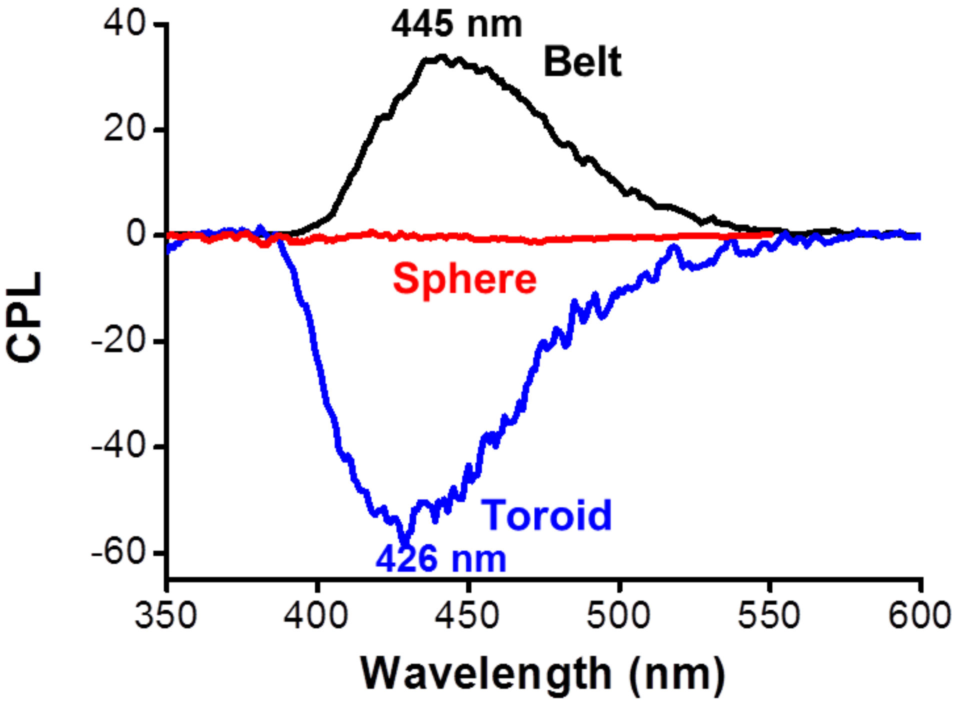

Fig. S14. The samples were excited with 320 nm. Cuvettes of 0.1 mm were used for measuring the CPL spectra. And the samples, either the nanobelt or nanotoroid or nanosphere, were cast on the quartz cuvettes. The nanostructures were formed in THF/water (1:1, v/v).

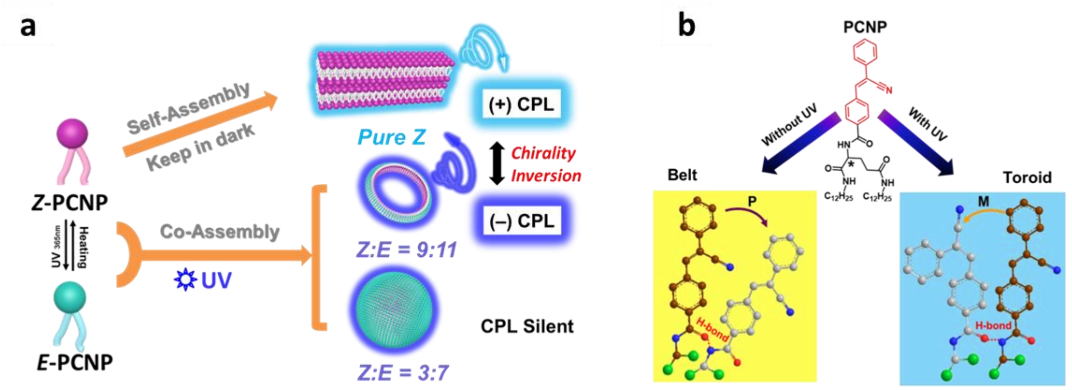

Fig. S15. (a) Schematic presentation of the proposed cooperative assembly processes of (*Z*)- and (*E*)-PCNP, respectively. (*Z*)-PCNP Self-assembled into nanobelt with left hand CPL, while (*Z*)- and (*E*)-PCNP co-assembled into nanotoroid with right hand CPL, the nanosphere showed no CPL. (b) The possible chiral packing mode in nanobelts and nanotoroids.

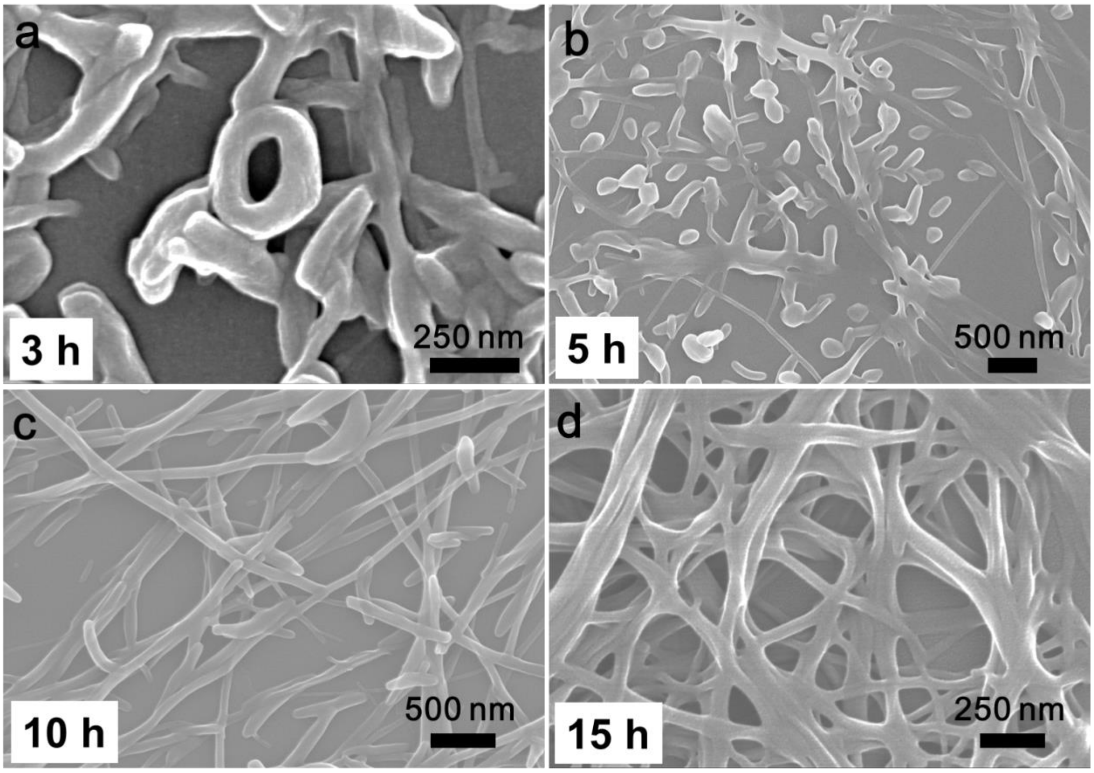

Fig. S16. SEM images of nanotoroid morphologies with different resting time, from (a) to (d). With the prolonged time, the morphology of nanotoroid changed. The nanotoroids gradually transformed into curved nanorods, then, the nanorods extended to form nanofibers. Finally, the solution changed to precipitate with nanofiber structures.

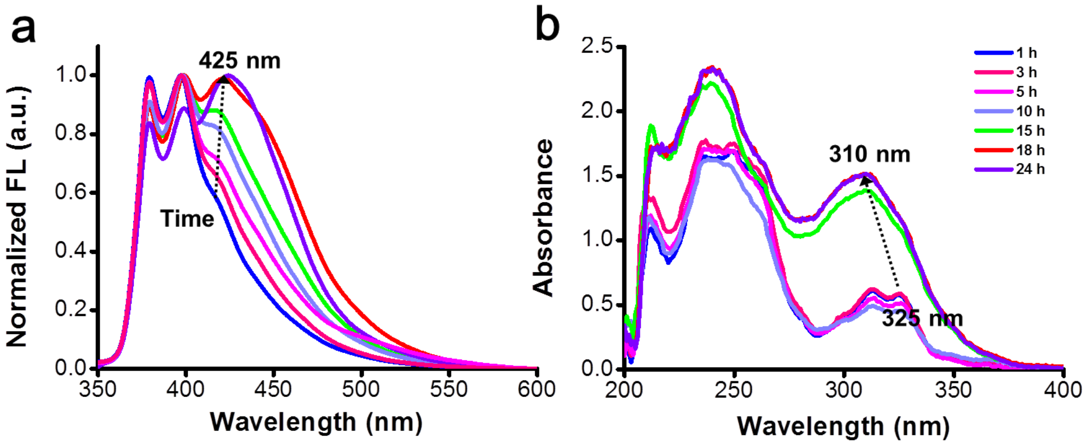

Fig. S17. a) and b) Normalized fluorescence and absorption spectra of the nanotoroids solution with prolonged resting time in the dark. With extending resting time, an emission peak at 425 nm appeared and enhanced. Furthermore, the UV bands at 310 nm increased and broaden. These spectra change were consistent with the morphological transition from nanotoroid to nanobelt. [PCNP]=7 mM.

3. 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).
2. Li Y., Wang T. & Liu M., Gelating-induced supramolecular chirality of achiral porphyrins: chiroptical switch between achiral molecules and chiral assemblies. *Soft Matter*, **3**, 1312-1317 (2007)