# Supplementary information

**CPL-triggered construction of one-dimensional supramolecular helical conducting nanofibers with superior performance in chiroptical sensing**

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**Methods and Characterization.** Meso-Tetra(4-carboxyphenyl)porphyrin(TCPP) were synthesized in analogy to the previous procedure[1]. 10, 12-Pentacosadiynoic acid (PCDA) were purchased from Tokyo Chemical Industry Co., Ltd., and was purified to remove the polymerized part before use. Ethane diamine was purchased from Sigma-Aldrich Co. LLC, and used without further purification. Ethylenediamine-substituded Pentacosadiacetylene (EPDA) were synthesized in analogy to the previous procedure[2]. The achiral porphyrin derivatives 4,4',4'',4'''-(porphyrin-5,10,15,20 -tetrayl)tetrakis(N-(2-(pentacosa-10,12-diynamido)ethyl)benzamide) (TPPDA) were synthesized in analogy to the previous procedure. The molecular structure, synthetic route were shown in Figure S1. $^{1}$H-NMR spectra and MALDITOF mass characterizations confirmed the synthesis of TPPDA successfully (Figure S2 and Fig.3). All other solvents and reagents were of analytical grade and were used without further purification excepted for chloroform. Milli-Q water (18.25 MΩ cm) was used in all cases. The gel (6mg $mL^{-1}$) was obtained after cooling a hot chloroform solution of TPPDA (at 60°C) into room temperature. The CPL (290-390 nm), generated by Babinet-Soleil prism from ultra-high pressure mercury lamp, were used for the asymmetric assembly process. The light intensity was approximately 0.04 mW $cm^{-2}$. In a typical run, TPPDA solution (6mg in 1mL dry chloroform) was heated to 60°C and maintain for 30 minutes, then hot TPPDA chloroform solution was cooled to room temperature and subsequently irradiated with left- or right-handed CPL for 20minutes. Then above samples were preserved in the dark for 6 h and a transparent purple gel could be obtained. The preparation of xerogel film was obtained by spin-coating method, chloroform was removed in reduced pressure subsequently.

FTIR experiments were performed on a MAGNA 750 FT-IR spectrometer. The ultraviolet-visible (UV-Vis) spectra were recorded by a SHIMADZU UV-2550 PC spectrophotometer, optical cells (63 μm or 1 mm optical path length) were used for UV-vis and CD measurements.1H-NMR spectra experiments were carried out at 55°C with a JEOL FX-90Q NMR 400 MHz spectrometer. Matrix-assisted laser desorption ionization time-of-flight (MALDITOF) mass spectra were acquired on a Bruker UltraflexIII TOF/TOF mass spectrometer (Bruker Daltonics, Tnc., Billerica, MA) equip with a Nd: YAG laser (355 nm). XRD measurements were performed with a Rigaku AX-G by using a CuKα (λ = 0.154 nm) beam. The circular dichroism (CD) spectra were measured by using JASCO CD spectrometer J-1000. TEM images were recorded on a JEOL-2000 microscope that operated at 200 kV.

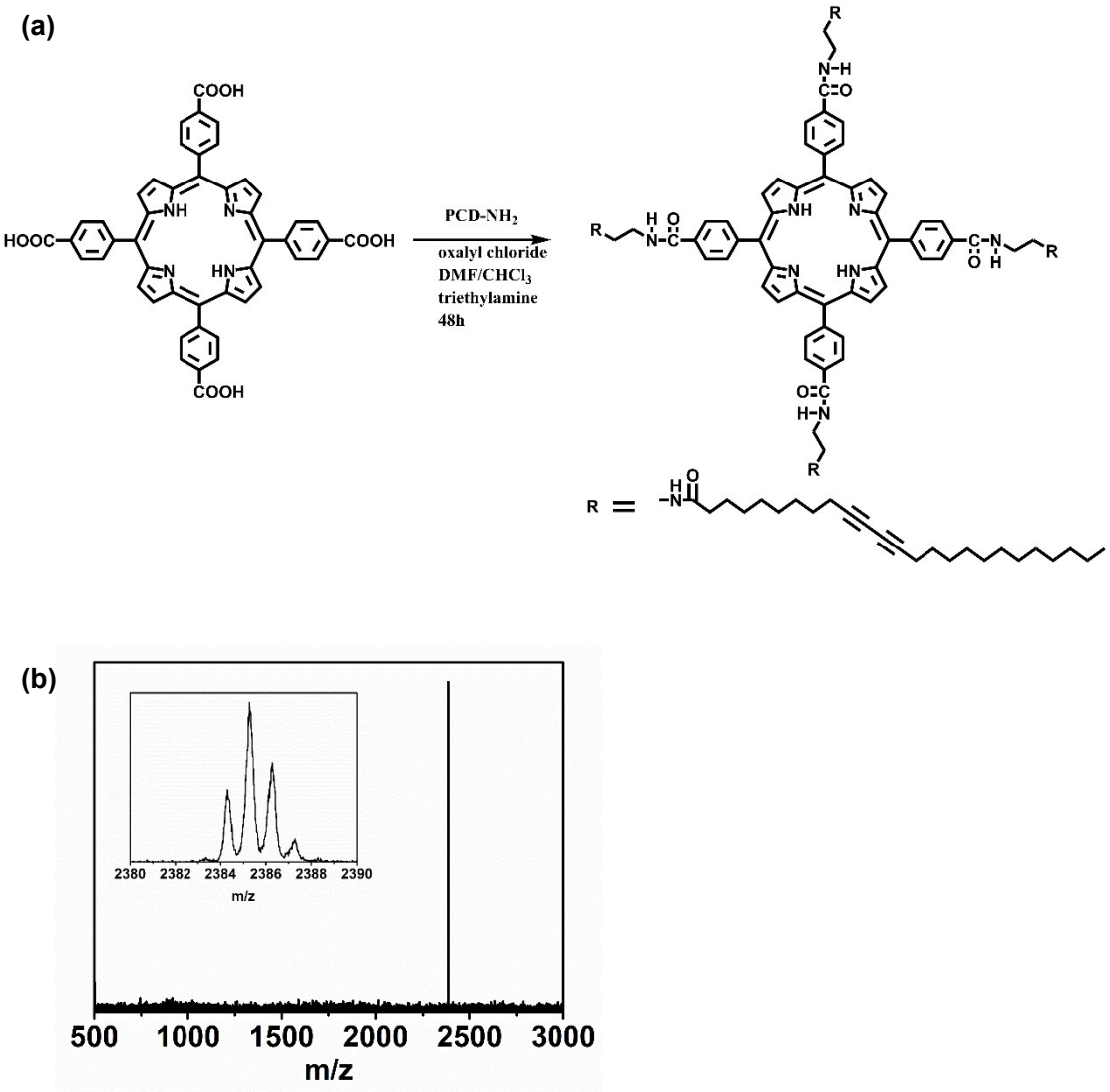


**Figure S1:** Molecular synthesis. (a) Synthetic route and characterization of 4,4',4",4"'-(porphyrin-5,10,15,20-tetrayl)tetrakis(N-(2-(pentacosa-10,12-diynamido)ethyl) benzamide) (TPPDA). (b) MALDITOF spectra of TPPDA. Insert: The amplified MALDITOF spectrum of TPPDA.

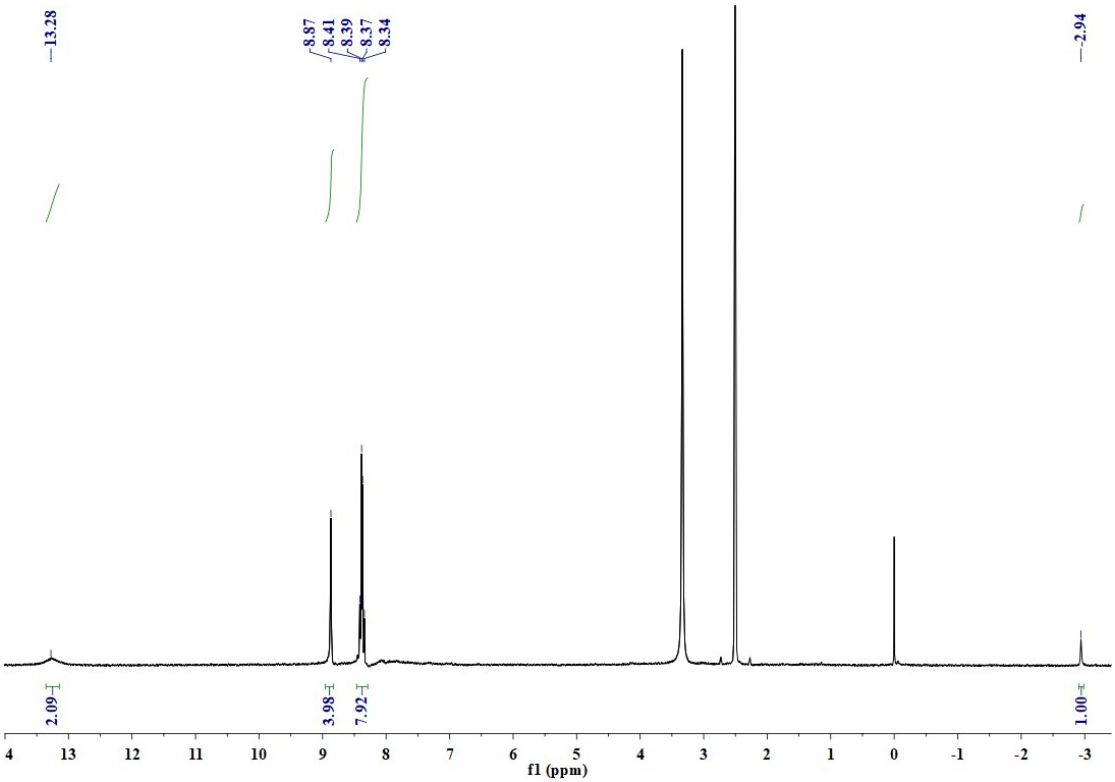


**Figure S2:** [1]H NMR of TCPP (300 MHz, DMSO). δ 13.28 (s, 4H, COOH), 8.87 (s, 8H, pyrrole CH), 8.38 (q, J = 8.3 Hz, 16H, ArCH), -2.94 (s, 2H, NH).

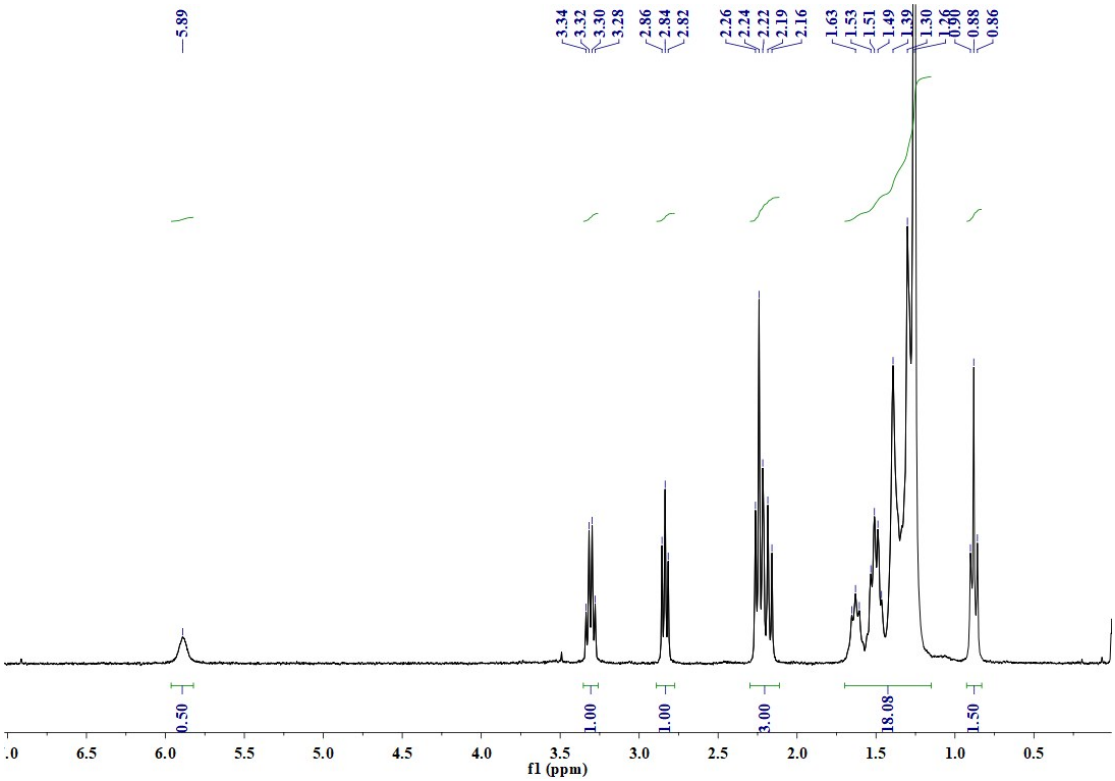


**Figure S3:** [1]H NMR of EPDA (300 MHz, $CDCl_3$). δ 5.89 (s, 1H, CONH), 3.31 (dd, *J* = 11.6, 5.7 Hz, 2H, CONH$CH_2$), 2.84 (t, *J* = 5.9 Hz, 2H, $CH_2NH_2$), 2.30 – 2.11 (m, 6H, $CH_2$NHCO, $CH_2C{\equiv}C{-}C{\equiv}CCH_2$), 1.70 – 1.15 (m, 34H, NHCOCH$_2$ $(CH_2)_6$ $CH_2C{\equiv}C$, $C{\equiv}CCH_2(CH_2)_{10}CH_3$, $CH_2NH_2$), 0.88 (t, *J* = 6.6 Hz, 3H).

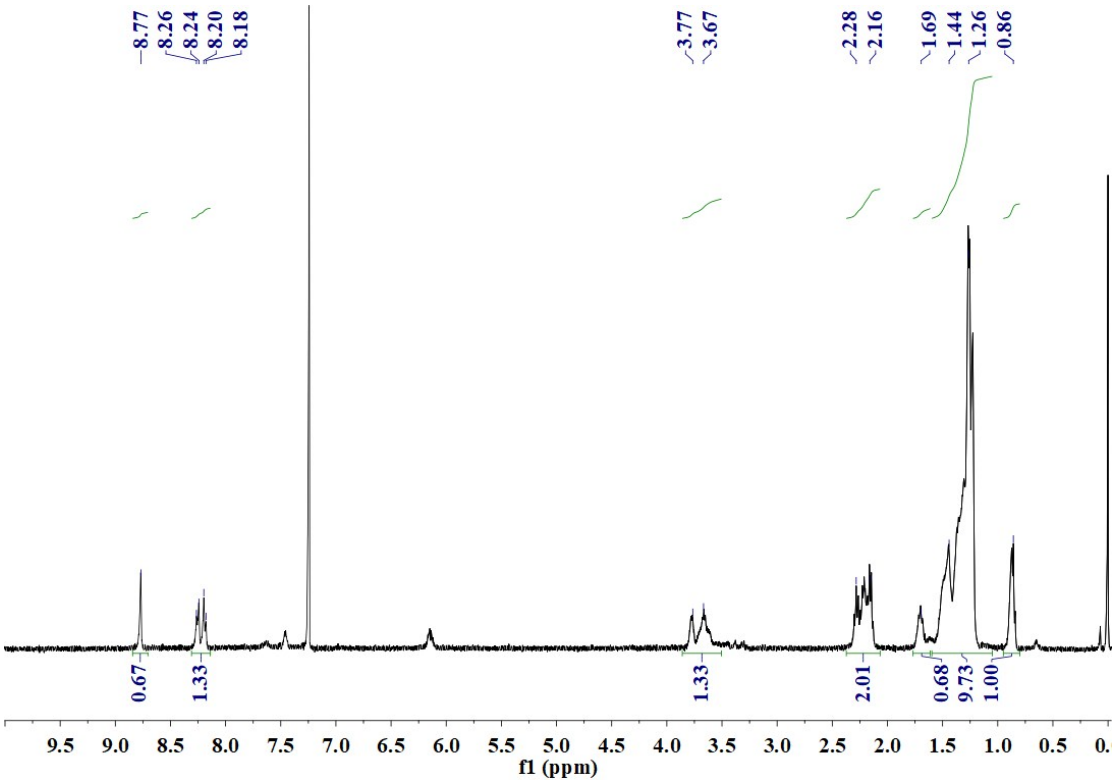


**Figure S4:** $^{1}$H NMR of TPPDA (400 MHz, $CDCl_3$). δ 8.76 (s, 8H, pyrrole CH), 8.24 (d, $J$ = 7.6 Hz, 8H, ArH), 8.18 (d, $J$ = 7.7 Hz, 8H, ArH), 7.41 (s, 4H, CONH), 8.76 (s, 4H, NHCO) 3.77 (m, 8H, CONH$CH_2$), 3.66 (m, 8H, $CH_2$NHCO), 2.28 (t, $J$ = 7.7 Hz, 8H, NHCO$CH_2$), 2.20-2.10 (m, 16H, $CH_2$C≡C−C≡C$CH_2$), 1.73-1.65 (m, 8H, NHCOCH$_2$$CH_2$), 1.42-1.17 (m, 120H, NHCOCH$_2$CH$_2$$(CH_2)_5$ $CH_2$C≡C, C≡CCH$_2$$(CH_2)_{10}$$CH_3$), 0.86 (t, $J$ = 6.5 Hz, 12H, $CH_2$$CH_3$).

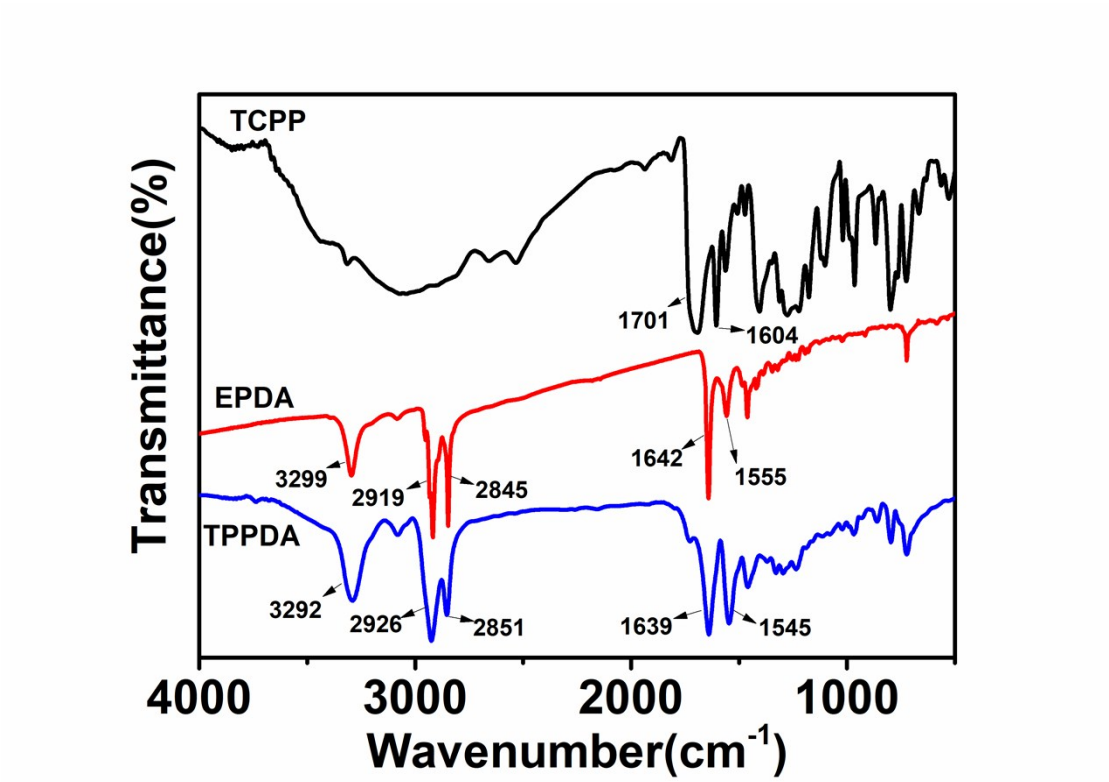


**Figure S5:** FT-IR characterizations of the synthesis of TPPDA. TCPP (upper), EPDA (middle), TPPDA (lower). Significant changes in the wavenumber region corresponding to the N-H and O-H stretching bands were detected and a shift of the C=O stretching band to lower wavenumbers indicated the synthesis of the TPPDA molecules.

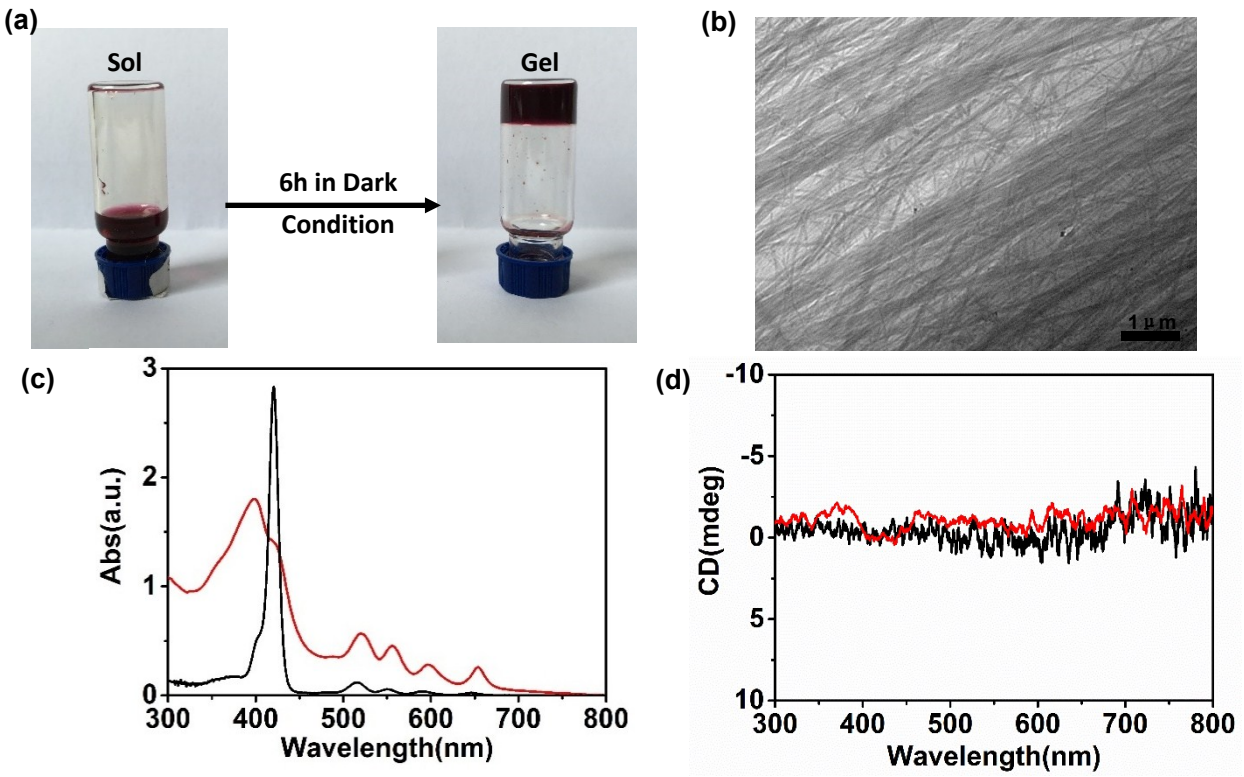


**Figure S6:** Images and Spectra analysis of TPPDA gel. (a) Pictures of TPPDA solution (left) and gel (right). (b) TEM images of the TPPDA gel without UV irradiation. (c) UV and (d) CD spectra of TPPDA solution (black line) and gel (red line) of TPPDA.

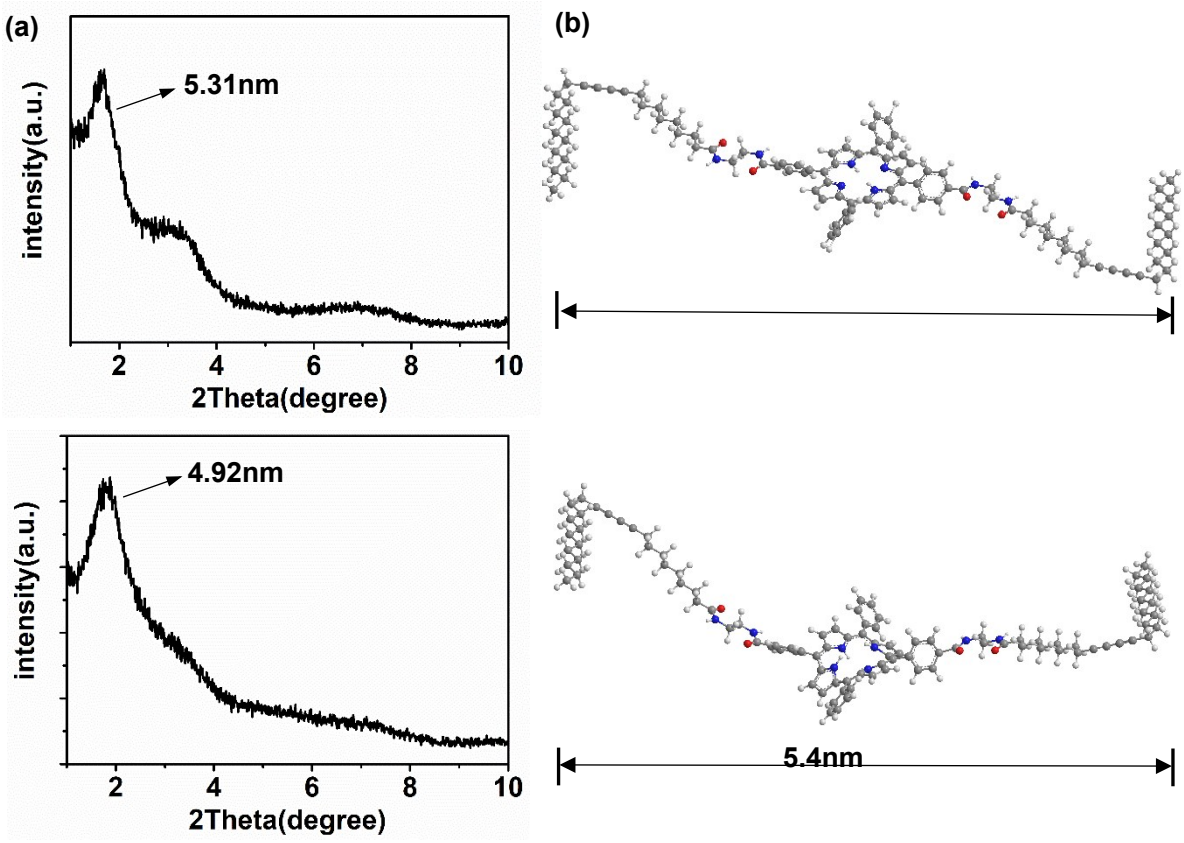


**Figure S7:** XRD profile of TPPDA assemblies with and without photo irradiation. (a) XRD profile of the xerogel prepared from chloroform gel of TPPDA without photo irradiation. (b) Molecular model of free base TPPDA, two peripheral alkyl chains were omitted for clarity. (c) XRD profile of the xerogel prepared from chloroform gel of TPPDA with photo irradiation. (d) Molecular model of protonated TPPDA, two peripheral alkyl chains were omitted for clarity.

**4.97nm**

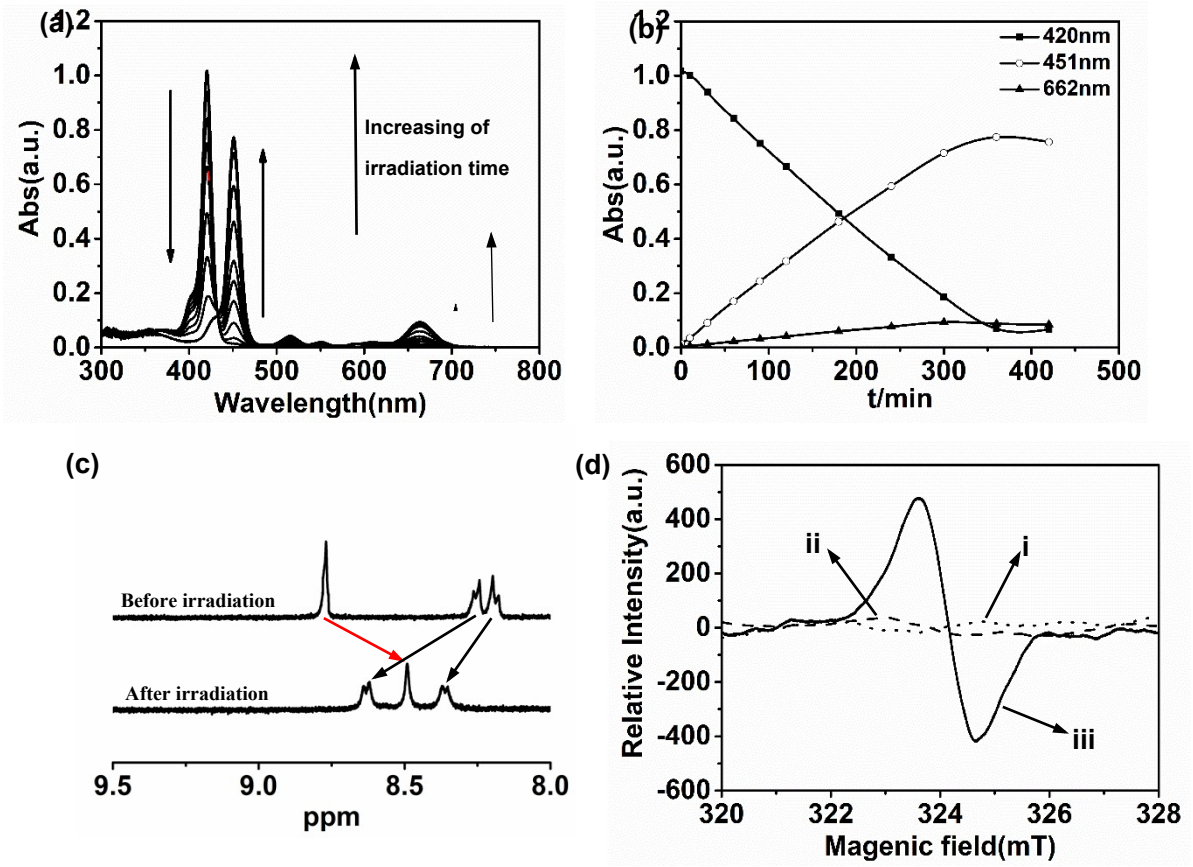


**Figure S8:** Spectra change of TPPDA solution under photo irradiation. (a) UV spectra change upon irradiation (0.04 mW/cm$^2$); (b) Plots of the absorption intensity change at λ=420, 451,662 nm as a function of the irradiation time. (c) $^1$H NMR spectra of TPPDA $CDCl_3$ solution before(upper) and after(lower) irradiation. The arrows indicates the chemical shifts of the hydrogen atoms on pyrrole ring (red) and benzene ring (black). (d) ESR spectra of (i) pure chloroform, (ii) TPPDA chloroform solution without irradiation, (iii) TPPDA chloroform solution irradiated with UV light.

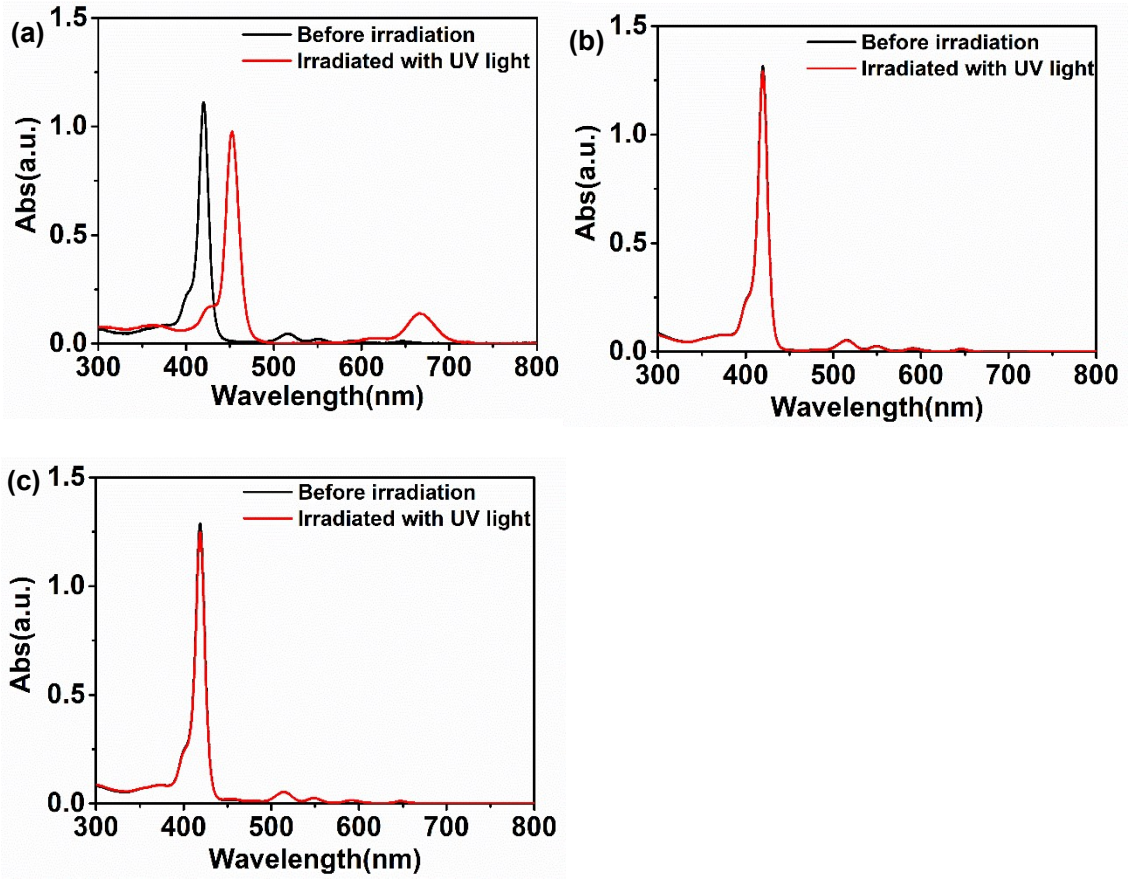


**Figure S9:** UV spectra of TPPDA in Dichloromethane, DMF and THF irradiated with normal UV**.** (a) Dichloromethane solution; (b) DMF solution; (c) THF solution. (2min, 3mW $cm^{-2}$).

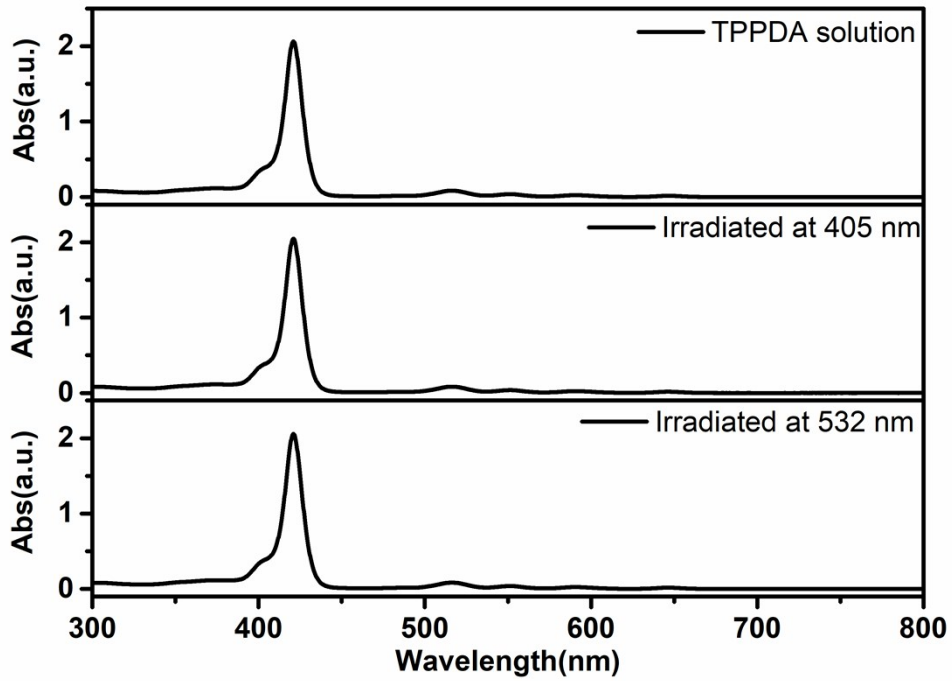


**Figure S10:** UV spectra of TPPDA solution in chloroform irradiated at 405 and 532 nm. (a) UV spectra of TPPDA solution in chloroform; (b) Irradiated at 405 nm for 5 minutes (5mW $cm^{-2}$); (c) Irradiated at 532 nm for 5 minutes (5mW $cm^{-2}$).

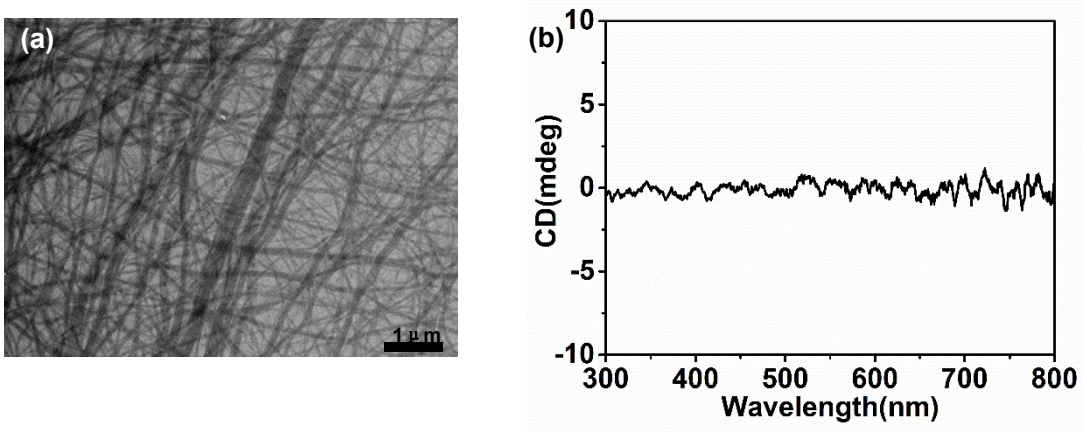


**Figure S11:** TEM and CD of TPPDA assemblies irradiated with normal UV. (a) TEM images (b) CD spectrum of the aggregates of TPPDA by evaporation of $CHCl_3$ solution with normal UV irradiation (20min, 0.04mW $cm^{-2}$).

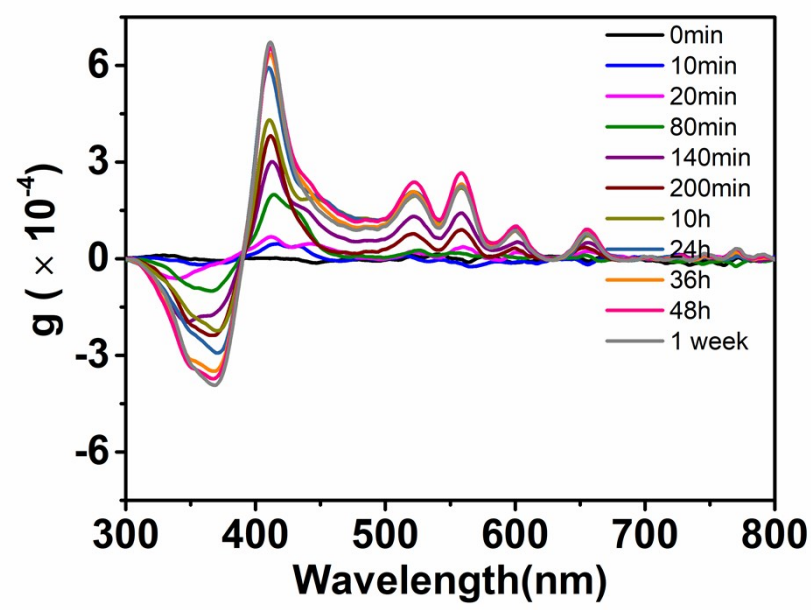


**Figure S12:** Time-dependent g values of the organogel obtained with 20-minutes R-CPL irradiation in the initial stage.

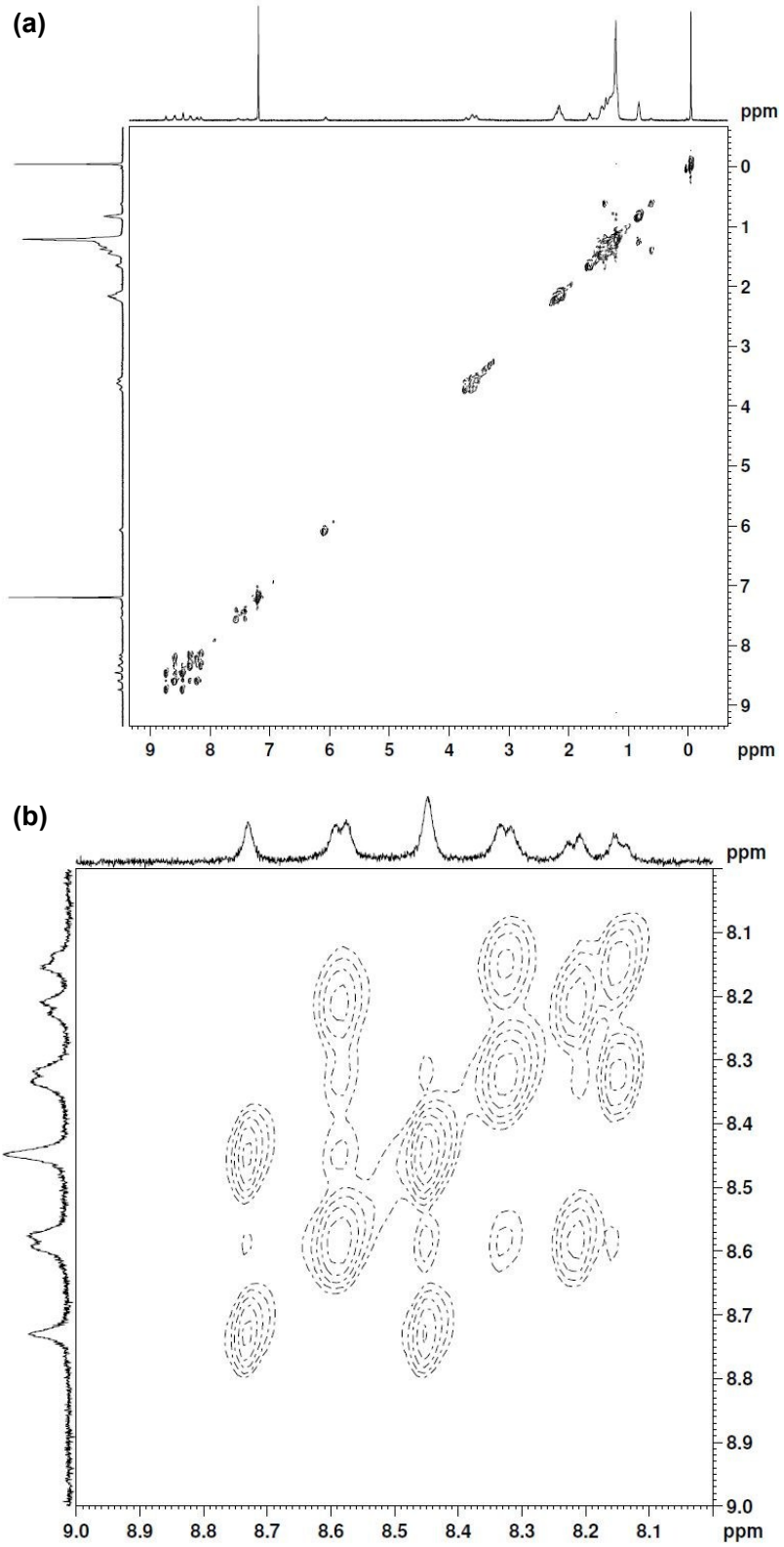


**Figure S13:** (a) 2D-NOESY spectra of free base TPPDA and protonated TPPDA co-assembly system; (b) Amplified spectrum between 8-9 ppm. We could distinguish the peaks corresponding to the free base TPPDA (8.77, 8.24, 8.18) and the protonated TPPDA (8.63, 8.50, 8.41). Strong correlations can be seen between the free base

TPPDA and protonated TPPDA. The correlations at (8.63 and 8.24 ppm), (8.41 and 8.18 ppm) corresponding to phenyl protons, and correlations at (8.77 and 8.50 ppm) indicates the interaction between the pyrrole protons of the neighboring molecules. These results showed that the co-assembly behavior of the free base TPPDA and protonated TPPDA.

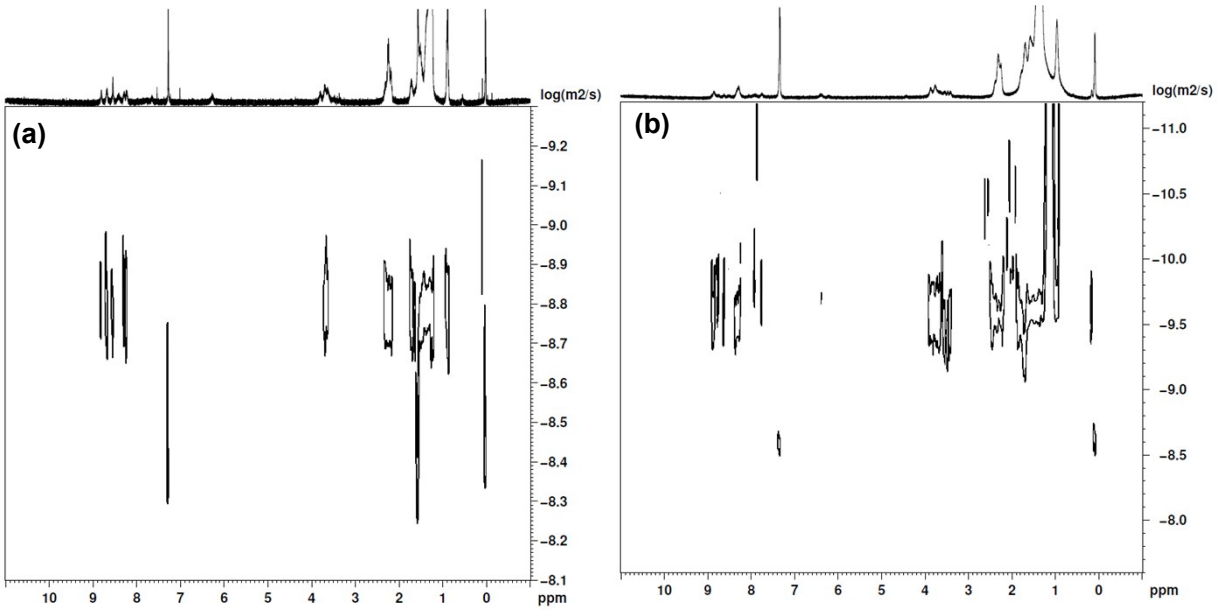


**Figure S14:** DOSY NMR spectra (400 MHz, $CDCl_3$, 298 K) of free base TPPDA and protonated TPPDA co-assembly system at different concentration of monomer. (a) $1.4\times10^{-3}$M, (b) $7\times10^{-3}$M. Upon increasing the concentration from 1.4 mM to 7 mM, the diffusion coefficient values drop from $1.61\times10^{-9}m^2s^{-1}$ to $2.01\times10^{-10}m^2s^{-1}$. Hence, it supports concentration-dependent size expansion of the supramolecular polymer networks and the co-assembly behavior of free base TPPDA and protonated TPPDA.

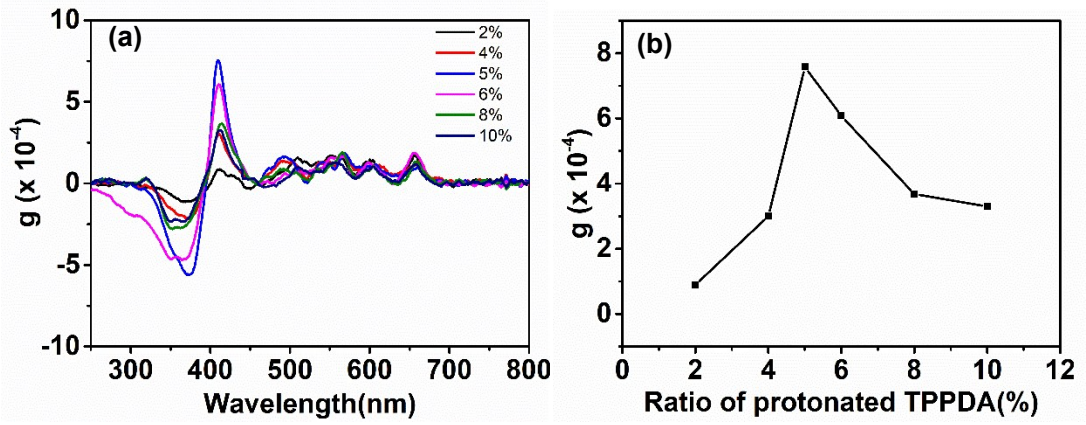


**Figure S15:** G- factor of TPPDA assemblies with different irradiation time at the initial stage. (a) G-factor of the organogel with different radio of protonated TPPDA, 2%, 4%, 5%, 6%, 8%, 10% corresponding to R-CPL irradiation time of approximately 12, 18, 21, 24, 30, 35 minutes; (b) Plots of the g-factor value change at l=410nm as a function of the radio of protonated TPPDA.

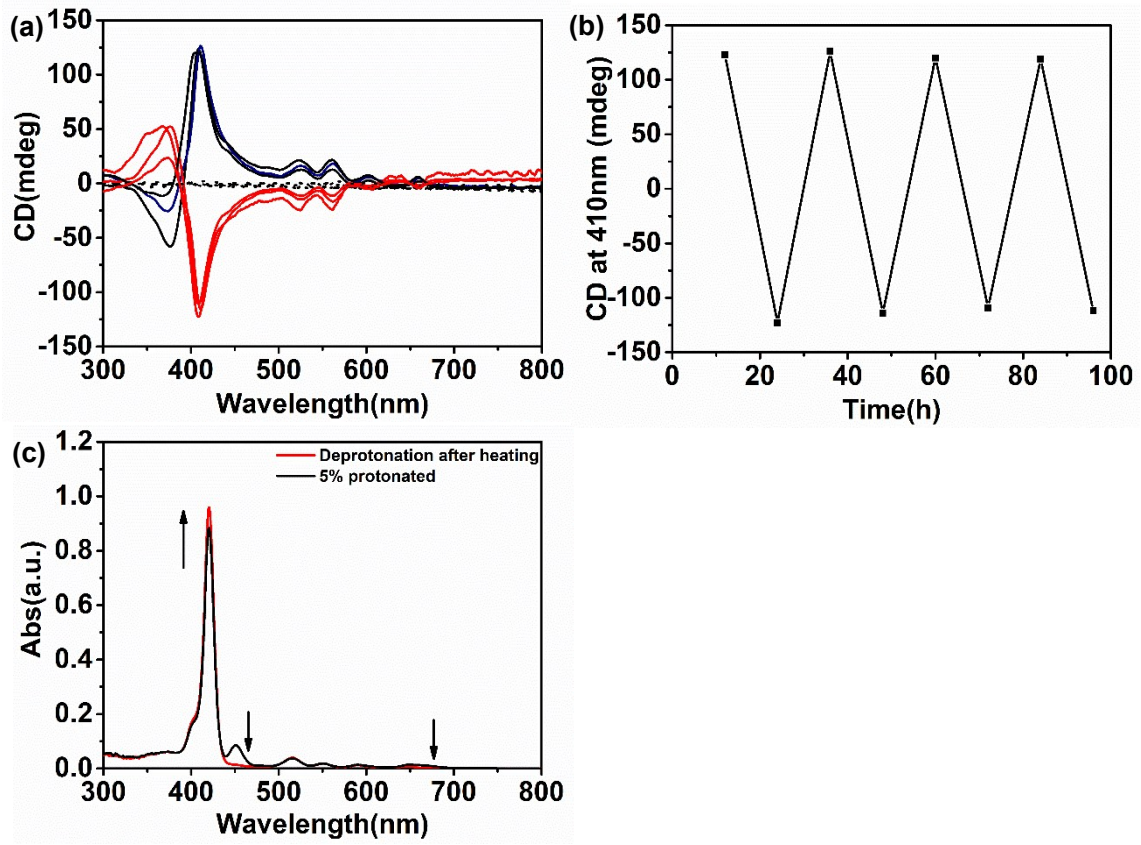


**Figure S16:** Modulation of supramolecular chirality. (a) CD spectra of the chiral gel irradiated with R-CPL (black solid line) and L-CPL (red solid line) reversibly, CD spectra of achiral gel formed after heating and cooling of the chiral gel (dashed line); (b) Time-dependent CD values at 410nm in three circles. (c) UV spectra of the solution with 5% protonated TPPDA and deprotonation after heating or placed in dark for days.

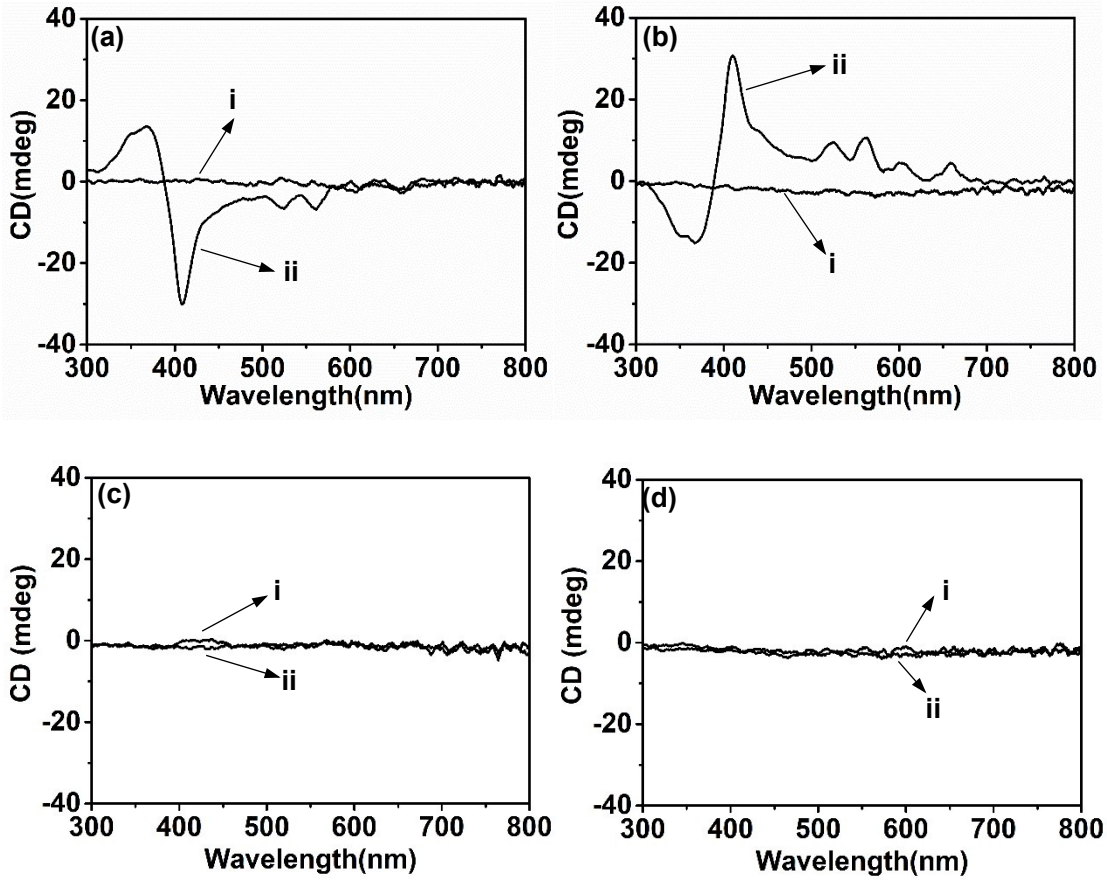


**Figure S17:** CD spectra of the organogel using ready-made chiral gel as seed (1/100). (a) CD spectra of organogel prepared from (i) normal gel without any treatment and (ii) using left-handed organogel as chiral seed; (b) CD spectra of organogel prepared from (i) normal gel without any treatment and (ii) using right-handed organogel as chiral seed. (c) CD spectra of organogel prepared from (i) normal gel without any treatment and (ii) using left-handed polymerized xerogel as chiral seed; (d) CD spectra of organogel prepared from (i) normal gel without any treatment and (ii) using right-handed polymerized xerogel as chiral seed.

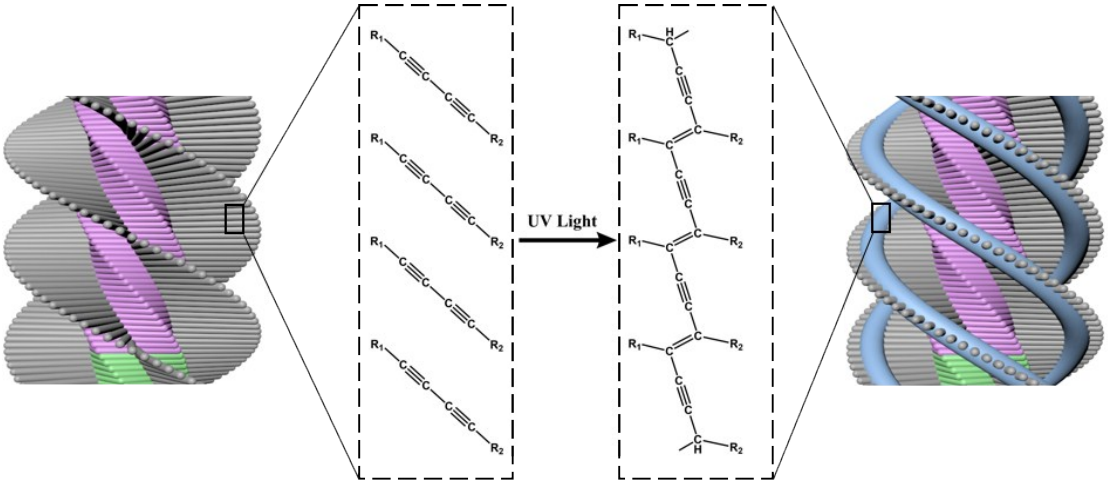


**Figure S18**: Structure and photopolymerization process of DA moieties in TPPDA under 254 nm light irradiation. Porphyrin core and alkyl chains are omitted for clarity.

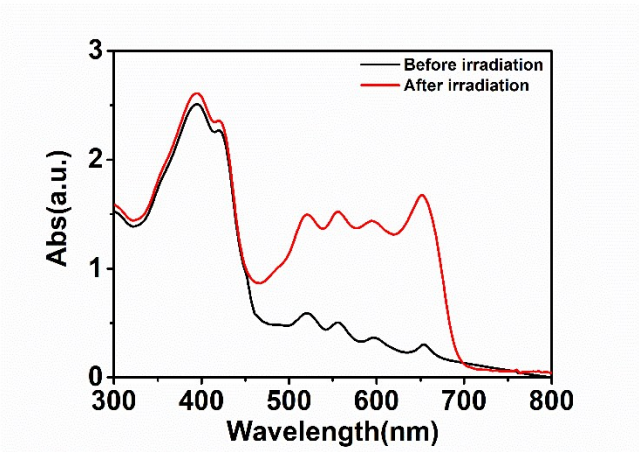


**Figure S19:** Photo initiated polymerization of diacetylene moieties of TPPDA. UV spectra of TPPDA xerogel film before and after irradiation with 254 nm light.

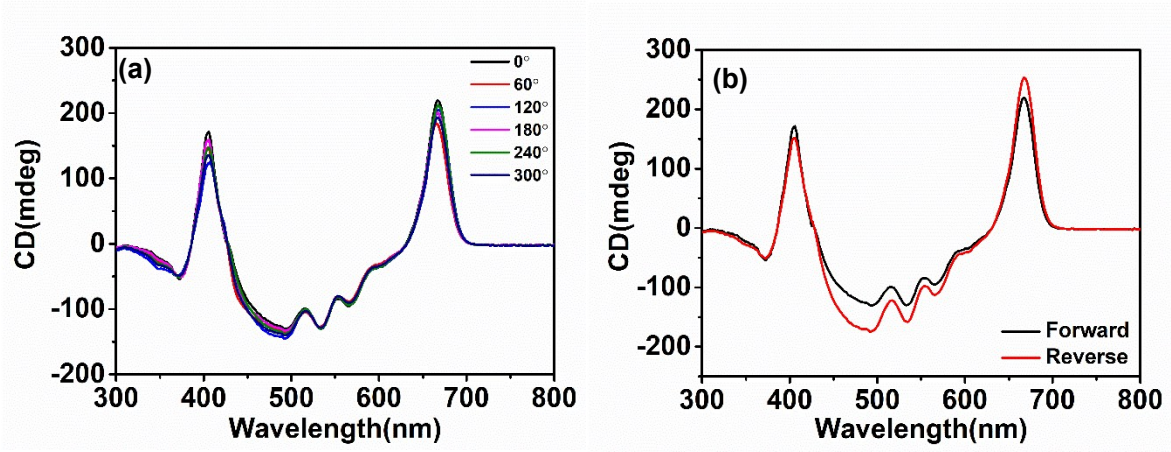


**Figure S20:** (a) CD spectra of TPPDA xerogel film at various rotation angles about surface normal for the samples; (b) Forward and reverse CD spectra of TPPDA xerogel film.

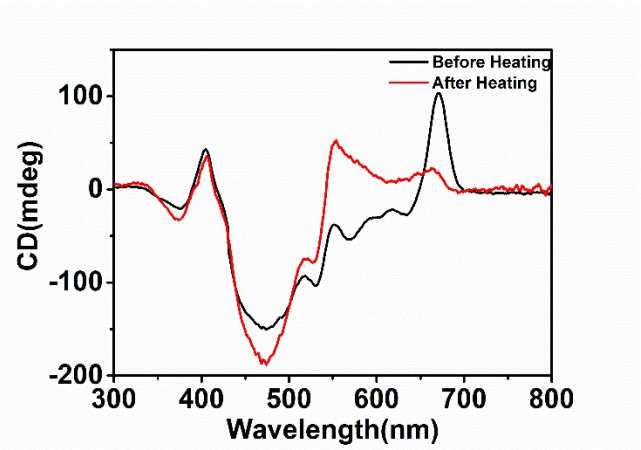


**Figure S21:** CD spectra of TPPDA xerogel film after heating at 90°C.

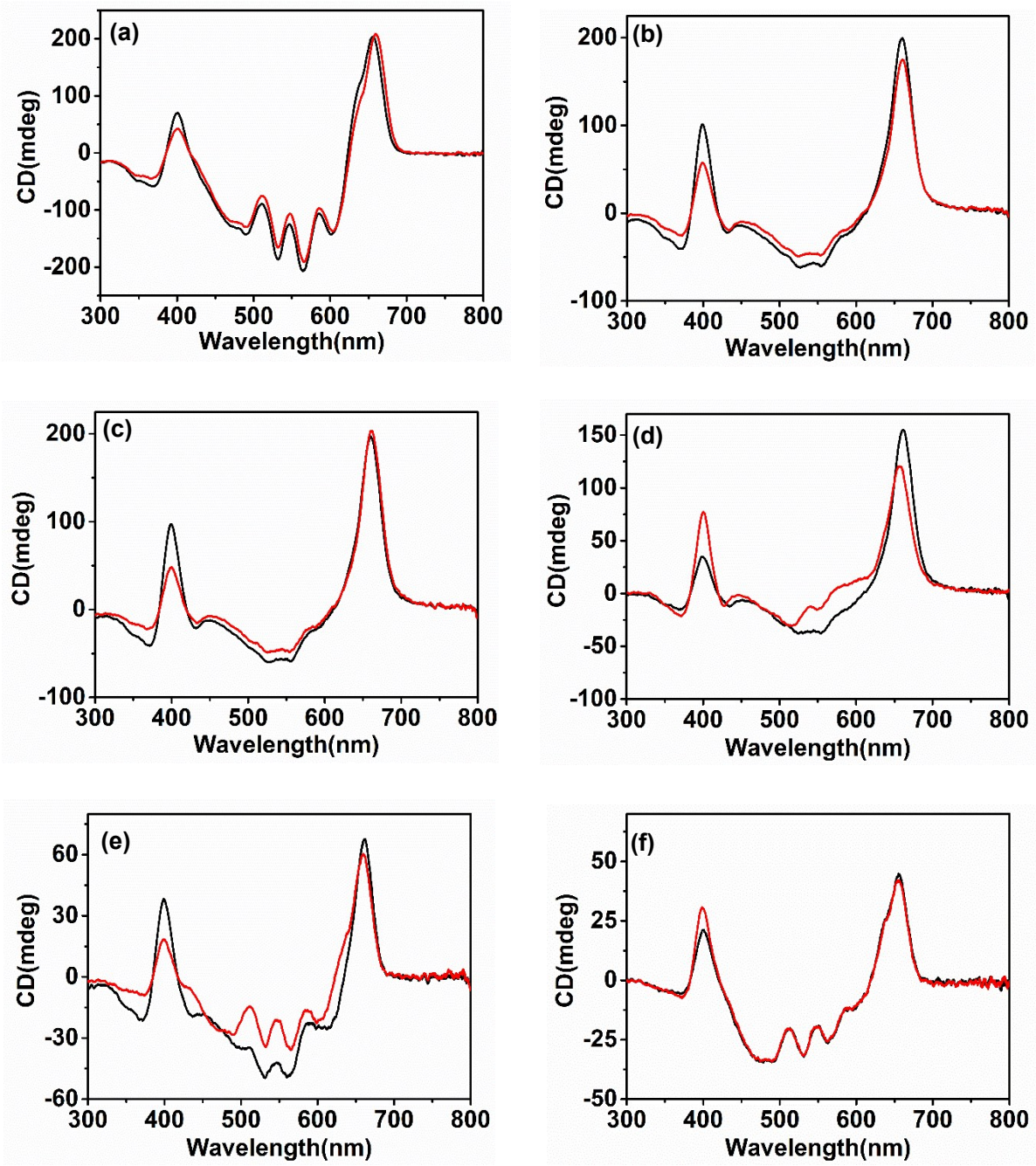


**Figure S22:** CD spectra of polymerized TPPDA film before (black line) and after (red line) treatment. (a) Immersed in hybridization buffer solution (pH=4) for 3 minutes; (b) Immersed in hybridization buffer solution (pH=10) for 3 minutes; (c) Immersed in chloroform for 3 minutes; (d) Immersed in dichloromethane for 3 minutes; (e) Immersed in tetrahydrofuran for 3 minutes; (f) Immersed in DMF for 3 minutes.

# References


1. L. J. Twyman, A. Ellis and P. J. Gittins, *Macromolecules*, 2011, **44**, 6365-6369.

2. W. Hu, Y. Chen, H. Jiang, J. Li, G. Zou, Q. Zhang, D. Zhang, P. Wang and H. Ming, *Adv Mater*, 2014, **26**, 3136-3141.