

**Supporting Information**  
**for**  
**A self-assembled photoresponsive gel consisting of**  
**chiral nanofibers**

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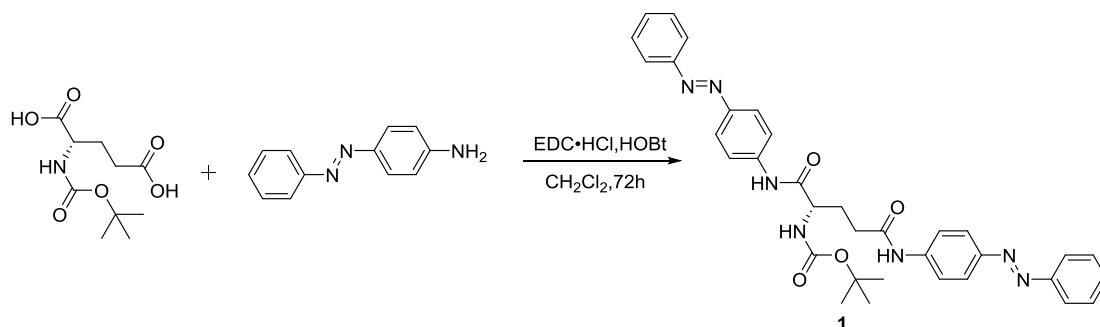
**Additional schemes and figures, general remarks, synthesis and  
characterization data, including copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra**

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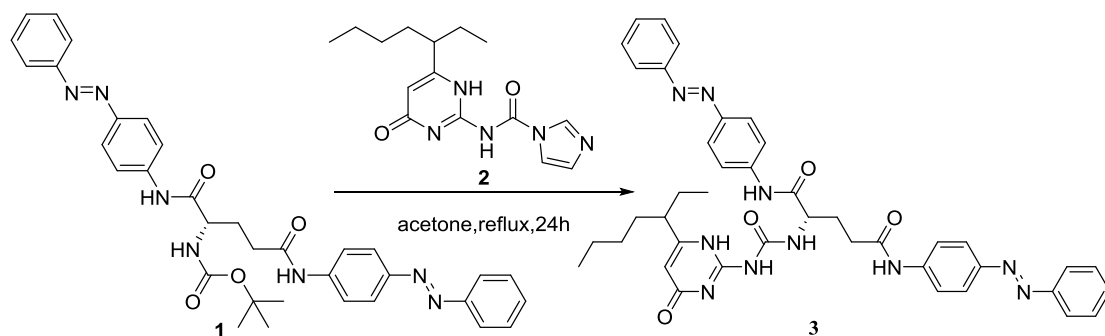
## General information

All reagents were purchased from commercial sources and used without further purification unless otherwise indicated. Compound **2** was prepared easily according to the literature method [1].  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-400 spectrometer in  $\text{DMSO-}d_6$  using tetramethylsilane (TMS) as the internal standard. High-resolution mass spectra (HRMS) were recorded on a Waters LCT Premier XE spectrometer using standard conditions. The UV-vis absorption spectra were obtained on a Varian Cary 100 spectrometer and a Varian Cary Eclipse (1 cm quartz cell was used). The UV irradiations (254 nm and 365 nm) were performed by a handheld UV lamp with an output power of 6 W. The light of 420 nm was performed by a lamp with an output power of 2  $\text{W}/\text{cm}^2$ . SEM images were obtained by using Hitachi S-3400N scanning electron microscope and NOVA Nano SEM450 ultra-high-resolution field emission scanning electron microscope. The rheological experiment of the resulting organogel was carried out on MARS III instrument. CD spectra were recorded on a JASCO J-810 spectropolarimeter at 25 °C.



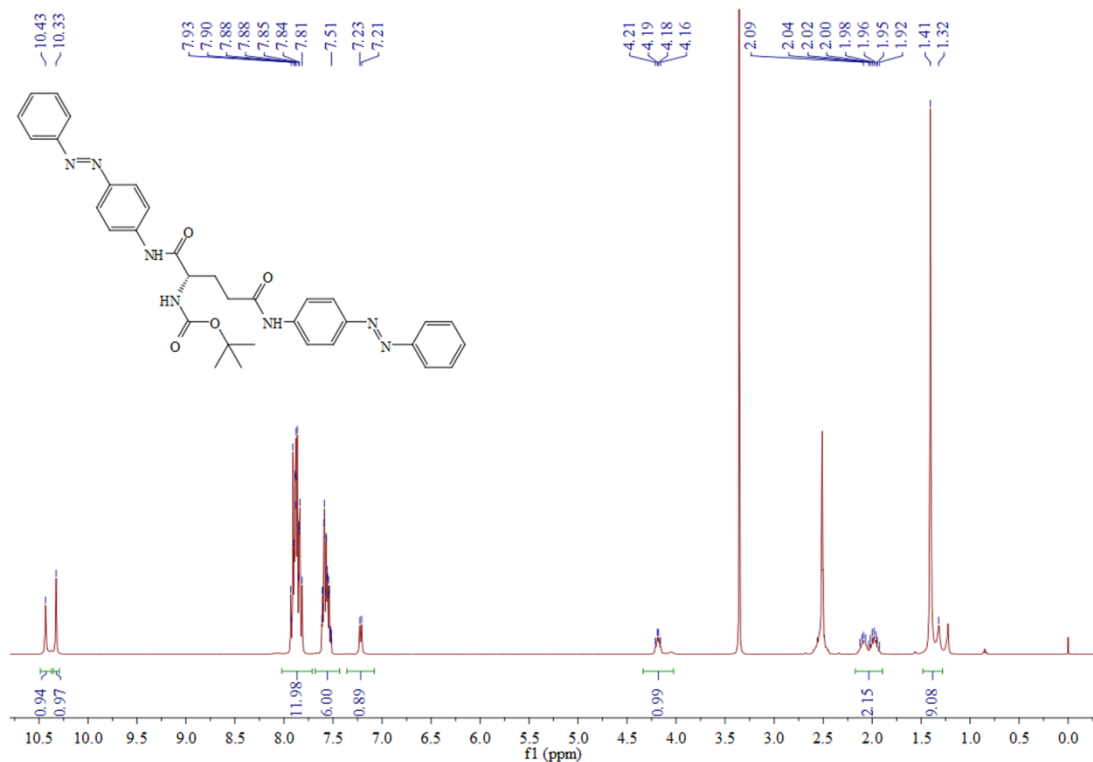
### Scheme S1: Synthesis of compound 1.

1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride ( $\text{EDC}\cdot\text{HCl}$ , 8.04 g, 0.044 mol) and 1-hydroxybenzotriazole (HOBT, 5.94 g, 0.044 mol) were added into 200 mL  $\text{CH}_2\text{Cl}_2$  solution of Boc-L-glutamic acid (5 g, 0.02 mol) and 4-aminoazobenzene (7.8838 g, 0.04 mol), then the obtained mixture was stirred at room temperature for 72 h under an Ar atmosphere. The obtained yellow solid was isolated by filtration and washed three times with  $\text{CH}_2\text{Cl}_2$ . The crude product was recrystallized from THF/ $\text{H}_2\text{O}$  to yield compound **1** as a yellow solid (10.53 g, 87% yield).  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  10.43 (s, 1H), 10.33 (s, 1H), 8.02 – 7.71 (m, 12H), 7.68 – 7.43 (m, 6H), 7.22 (d,  $J = 7.6$  Hz, 1H), 4.18 (dd,  $J = 13.5, 7.9$  Hz, 1H), 2.17 – 1.90 (m, 2H), 1.36 (d,  $J = 34.1$  Hz, 9H).  $^{13}\text{C}$  NMR (400 MHz, DMSO)  $\delta$  171.44, 170.83, 155.43, 151.99, 147.58, 147.35, 142.35, 142.05, 131.04, 130.97, 129.38, 123.64, 122.32, 122.28, 119.50, 119.17, 78.23, 54.78, 32.92, 28.17, 27.07, 25.09. HRMS  $[\text{M} + \text{H}]^+$  calculated for  $\text{C}_{34}\text{H}_{36}\text{N}_7\text{O}_4^+$  606.2829, found 606.2830.

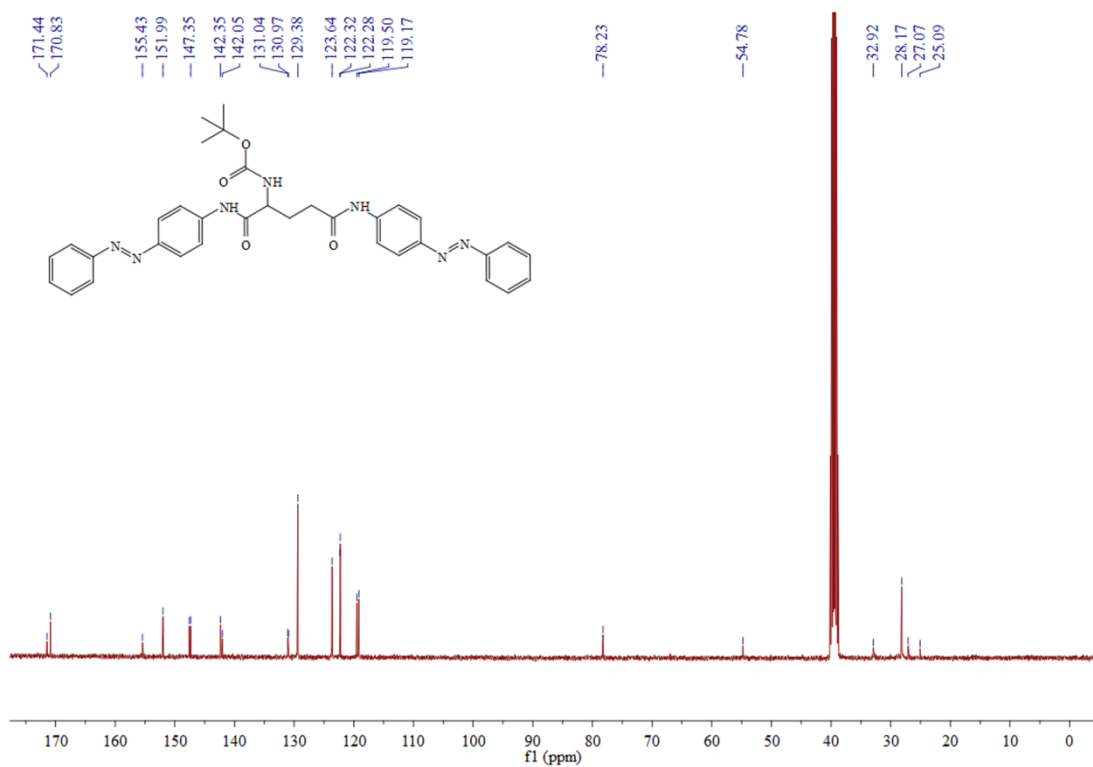


**Scheme S2: Synthesis of compound 3.**

Five mL trifluoroacetic acid was dropped into the 25 mL  $\text{CH}_2\text{Cl}_2$  solution of compound **1** (1.0 g, 1.65 mmol), then the mixture was stirred at room temperature for 2 h under an Ar atmosphere. Evaporation of the resulting red solution was performed under reduced pressure, and a small amount of  $\text{CH}_2\text{Cl}_2$  was added frequently into the bottle until the trifluoroacetic acid was removed entirely. The resulting yellow solid was added into an acetone solution of compound **2** (1.2205 g, 4.03 mmol) under Ar atmosphere, then the mixture was heated at reflux for 24 h. Evaporation of the resulting solution under reduced pressure and the further purification was carried out by column chromatography using  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (50:1, v/v) and  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (10:1, v/v) to afford yellow solid **3** (620 mg, 62.5% yield).  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  11.29 (s, 1H), 10.67 (s, 1H), 10.34 (s, 1H), 9.68 (s, 1H), 8.30 (s, 1H), 8.01 – 7.68 (m, 12H), 7.68 – 7.43 (m, 6H), 5.77 (s, 1H), 4.64 (s, 1H), 2.22 (dd,  $J = 13.5, 6.0$  Hz, 2H), 2.05 (dd,  $J = 13.6, 6.7$  Hz, 1H), 1.55 (dd,  $J = 15.8, 10.0$  Hz, 4H), 1.29 – 1.04 (m, 6H), 0.85 – 0.71 (m, 6H).  $^{13}\text{C}$  NMR (400 MHz, DMSO)  $\delta$  170.51, 151.99, 147.79, 147.34, 142.30, 141.65, 131.11, 130.96, 129.41, 129.37, 123.57, 122.34, 122.26, 119.70, 119.17, 53.14, 29.13, 22.15, 13.86, 11.84. HRMS  $[\text{M} + \text{Na}]^+$  calculated for  $\text{C}_{41}\text{H}_{44}\text{N}_{10}\text{O}_4\text{Na}^+$  763.3445, found 763.3443.



**Figure S1:** <sup>1</sup>H NMR of compound 1.



**Figure S2:** <sup>13</sup>C NMR of compound 1.

## Single Mass Analysis

Tolerance = 30.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

167 formula(e) evaluated with 8 results within limits (up to 1 best isotopic matches for each mass)

Elements Used:

C: 0-53 H: 0-49 N: 0-7 O: 0-4

TIAN-H

ECUST institute of Fine Chem

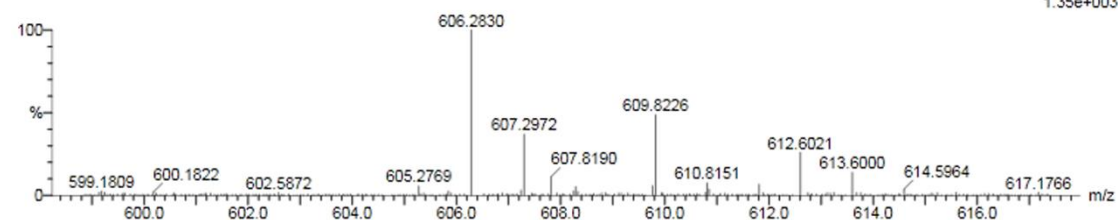
30-Nov-2017

16:02:43

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1.35e+003

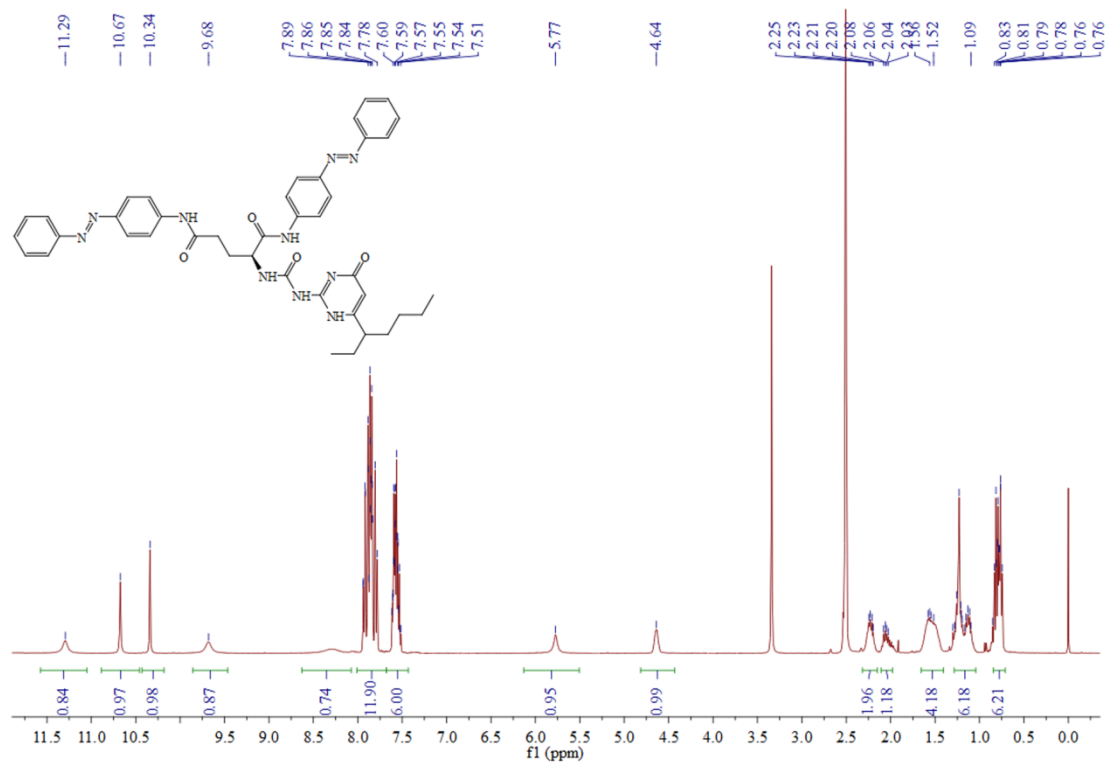
TH-HD-005 17 (0.620) Cm (17:20)

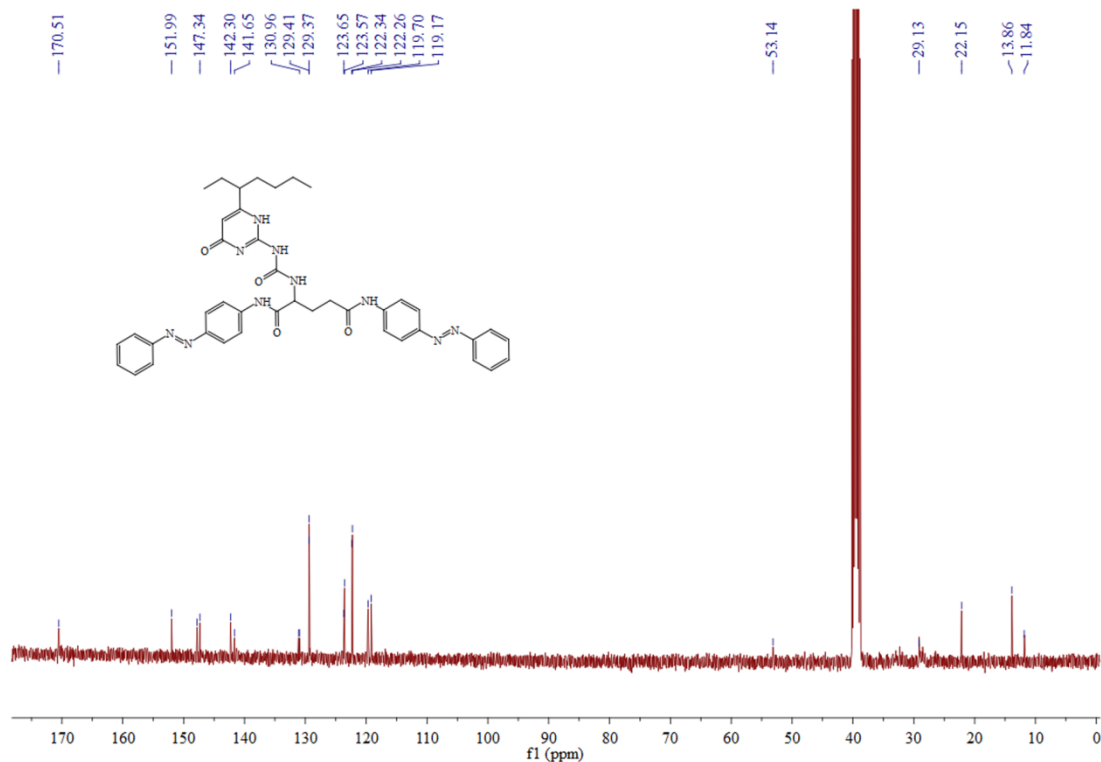


Minimum: 30.0 30.0 -1.5  
 Maximum: 30.0 30.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
606.2830	606.2829	0.1	0.2	20.5	99.7	0.0	C34 H36 N7 O4

Figure S3: HRMS of compound 1.

Figure S4: <sup>1</sup>H NMR of compound 3.



**Figure S5:**  $^{13}\text{C}$  NMR of compound 3.

**Elemental Composition Report**

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**Single Mass Analysis**

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

88 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

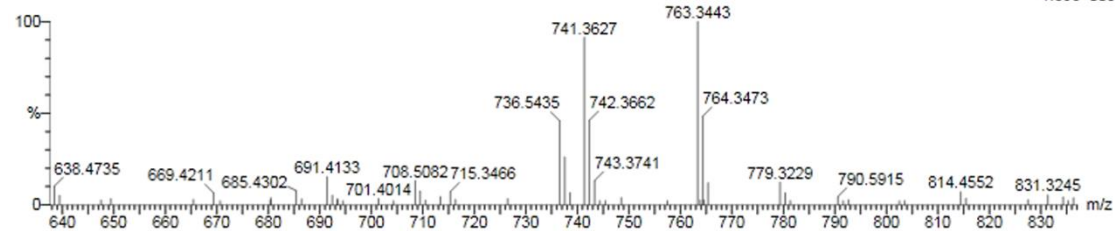
Elements Used:

C: 0-42 H: 0-46 N: 0-10 O: 0-4 Na: 0-1

ZOU-L

TH-HD-21 200 (5.055) Cm (186.202)

2: TOF MS ES+  
1.89e+003



Minimum:

Maximum: 5.0 5.0 -1.5

Mass Calc. Mass mDa PPM DBE i-FIT i-FIT (Norm) Formula

763.3443 763.3445 -0.2 -0.3 24.5 23.9 0.0 C41 H44 N10 O4 Na

**Figure S6:** HRMS of compound 3.

## Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

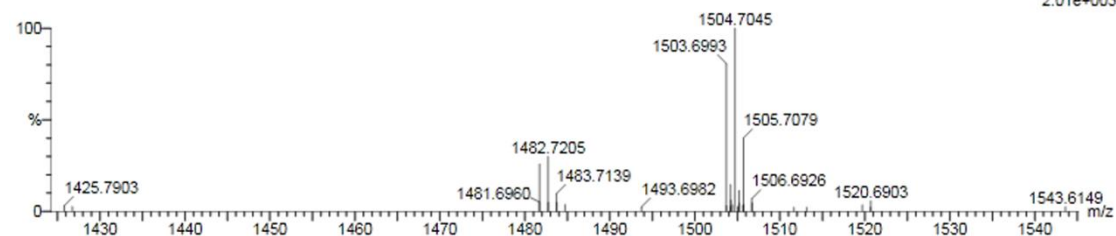
327 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-82 H: 0-88 N: 0-20 O: 0-8 Na: 0-1

ZOU-L

TH-HD-21 112 (2.831) Cm (109:152)

2: TOF MS ES+  
2.01e+003

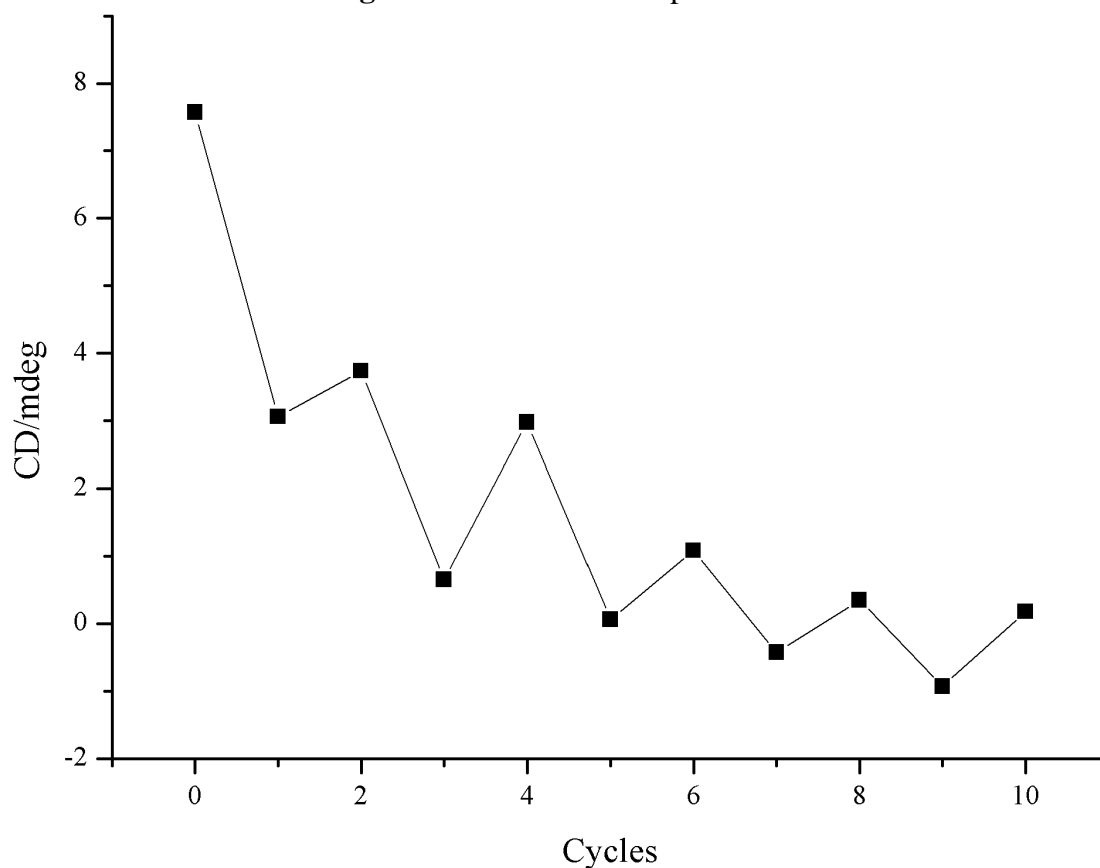
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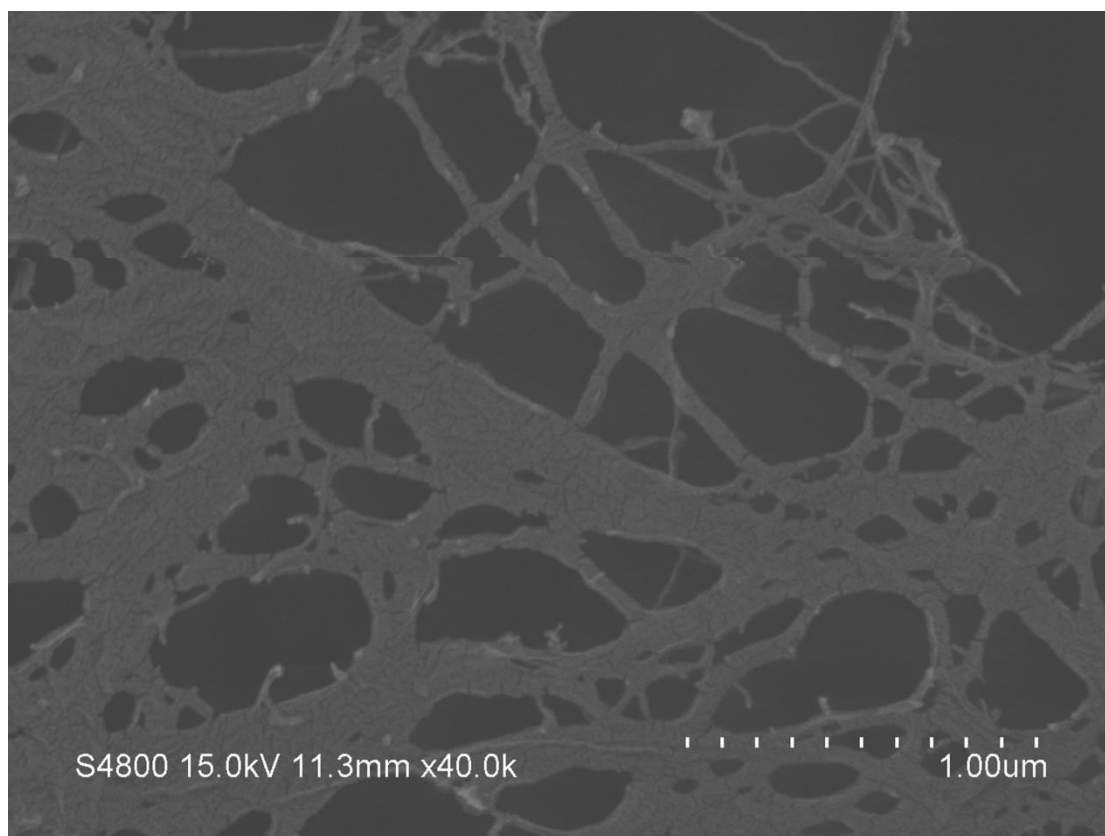
Maximum:

5.0 5.0 -1.5  
50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
1503.6993	1503.6992	0.1	0.1	48.5	78.5	0.0	C82 H88 N20 O8 Na

Figure S7: HRMS of compound 3.

Figure S8: Fatigue resistance of compound 3 in tetrachloromethane ( $3 \times 10^{-5}$  mol/L) under 365 nm/420 nm irradiation.



**Figure S9:** FESEM image of the microstructure obtain by assembled compound **3** in benzene.

#### References

1. Keizer H.; Sijbesma R.; Meijer EW. *European Journal of Organic Chemistry*, **2010**, 2553-2555. doi:10.1002/ejoc.200300752