

Supporting Information

Photo-driven morphological transformations of supramolecular polymers actuated by an overcrowded alkene switch

Wen-Jing Liang, Jing-Jing Yu, Qi Zhang, Chang-Shun Ma, Zhao-Tao Shi, Da-Hui Qu *

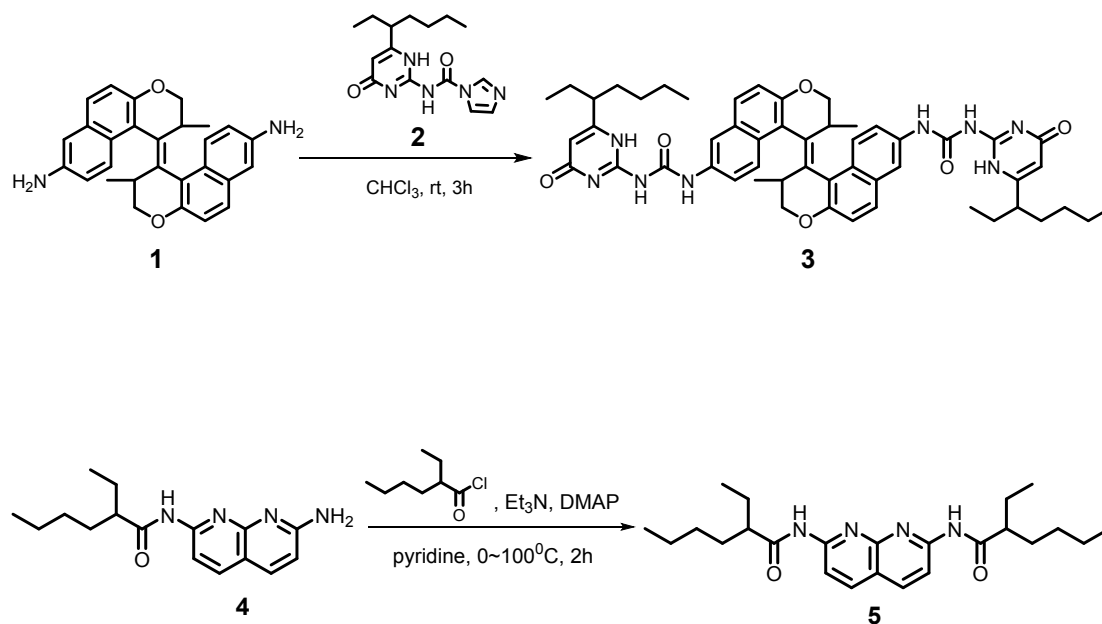
1. Experimental Section.....	2
1.1 General Methods and Details.....	2
1.2 Synthesis.....	3
2. Structural characterization of <i>trans</i> OAS-Upy.....	6
2.1 ¹ H- ¹ H COSY spectra of <i>trans</i> OAS-Upy.....	6
2.2 2D Rosey spectra spectra of <i>trans</i> OAS-Upy.....	7
3. Photostationary state (PPS) of <i>trans</i> OAS-Upy.....	7
4. Properties of supramolecular polymers.....	8
4.1 ¹ H NMR changes of <i>trans</i> OAS-Upy at different concentrations.....	8
4.2 Specific viscosity changes of <i>trans</i> OAS-Upy at different concentrations.....	8
4.3 DOSY spectra of OAS-Upy.....	9
5. Sizes and morphologies of OAS-Upy.....	10
5.1 Changeable DLS of <i>trans</i> OAS-Upy after UV irradiation.....	10
5.2 High resolution TEM images of OAS-Upy.....	10
6. Depolymerization of OAS-Upy supramolecular polymers.....	11
6.1 ¹ H NMR changes of <i>trans</i> OAS-Upy after adding Napy monomers.....	12
7. References.....	12
8. Appendix.....	13

1. Experimental Section

1.1 General Methods and Details

Chemicals were purchased from Acros, Aldrich, Fluka, Adamas, or Merck and used as received unless otherwise stated. Solvents were reagent grade, which were dried and distilled prior to use according to standard procedures. All reactions were carried out under an atmosphere of dry nitrogen unless otherwise stated. ^1H NMR, ^{13}C NMR, DOSY and 2D ROESY NMR spectra were measured on a Bruker AV-400 and AV-500 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on a LCT Premier XE mass spectrometer. UV-Vis absorption spectra were recorded on Varian Cary 100 spectrometer (1 cm, quartz cells). The UV light resource were obtained on a PerfectLight PL-LED 100. Viscosity measurements were carried out with Ubbelohde microdilution viscometers at 298 K in chloroform. DLS were measured on MALV RN, ZETA SIZER, Model ZEN3600, 303K. TEM images were recorded on a JEOL JEM-1400 and JEM-2100 apparatus, and the samples were prepared by casting dilute solution on copper sheet.

1.2 Synthesis



Scheme S1. Synthetic route of *trans* OAS-Upy and Napy

Compound **1** has been synthesized according to the previous procedure as a yellow solid¹. Compound **2** and compound **4** was synthesized according to previously reports^{2,3}.

Synthesis of OAS-Upy

To a solution of compound **1** (150 mg, 0.35 mmol, 1equiv) in chloroform was added compound **2** (322 mg, 1.06 mmol, 3 equiv), Then the mixture was stirred at room temperature under Ar for 3 h. After that, the reaction solution was extracted by DCM and 2M hydrochloric acid, then washed with saturated NaHCO_3 aqueous solution and water successively, the organic layer was dried by Na_2SO_4 , and the solvent was removed though reduced pressure to get a crude product, Subsequent purification by chromatography on silica using DCM/MeOH (100:1) as eluent yielded compound OAS-Upy (206 mg, 65%) as a yellow-green solid. $^1\text{HNMR}$ (400MHz, CDCl_3 , 298K) δ (ppm): 13.23 (s, 2H), 12.45 (s, 2H), 12.40 (s, 2H), 8.17 (s, 4H), 7.83 (s, 2H), 7.12 (s, 2H), 7.05 (s, 2H), 5.99 (s, 2H), 4.10 (d, $J = 6.8$ Hz, 4H), 2.79 (s, 2H), 2.38 (s, 2H),

1.66 (m, 8H), 1.26 (m, 8H), 1.12 (s, 6H), 0.91 (m, 12H). ^{13}C NMR (100MHz, CDCl_3 , 298K) δ (ppm): 173.07, 155.71, 154.95, 154.79, 151.48, 133.24, 131.13, 129.39, 128.83, 125.15, 121.40, 118.68, 118.25, 114.45, 106.55, 74.02, 45.41, 32.89, 32.82, 29.61, 29.38, 26.61, 22.60, 22.42, 14.03, 13.82, 11.66. HRMS (ESI) (m/z): $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{52}\text{H}_{60}\text{N}_8\text{O}_6$ 893.4709, found 893.4739.

Synthesis of Napy

To a solution of compound **4** in (100 mg, 0.35 mmol, 1equiv) anhydrous pyridine was added triethylamine (42 mg, 0.42 mmol, 1.2 equiv) and catalytic amount of DMAP, the mixture was placed in an ice bath, 2-ethylhexanoyl chloride (68 mg, 0.42 mmol, 1.2 equiv) was added dropwise to the reaction solution slowly. Then the ice bath was removed, the reaction solution was placed in an oil bath and heated to reflux for 2 hours. After that, the solvent was removed under reduced pressure. The residue was extracted by DCM and 2M hydrochloric acid, then washed with water successively, the organic layer was dried by Na_2SO_4 , and the solvent was removed through reduced pressure to get a crude product, Subsequent purification by chromatography on silica using PE/DCM (50:1) as eluent yielded compound **Napy** (122 mg, 85%) as a white solid. ^1H NMR (400MHz, CDCl_3 , 298K) δ (ppm): 8.48 (d, $J = 8.8$ Hz, 2H), 8.43 (s, 2H), 8.14 (d, $J = 8.8$, 2H), 2.23 (m, 2H), 1.69-1.78 (m, 4H), 1.46-1.64 (m, 4H), 1.27-1.36 (m, 8H), 0.96 (t, $J = 7.6$ Hz, 6H), 0.82-0.90 (m, 6H). All the data are consistent with previous literature⁴.

2. Structural characterization of *trans* OAS-Upy

2.1 ^1H - ^1H COSY spectra of *trans* OAS-Upy

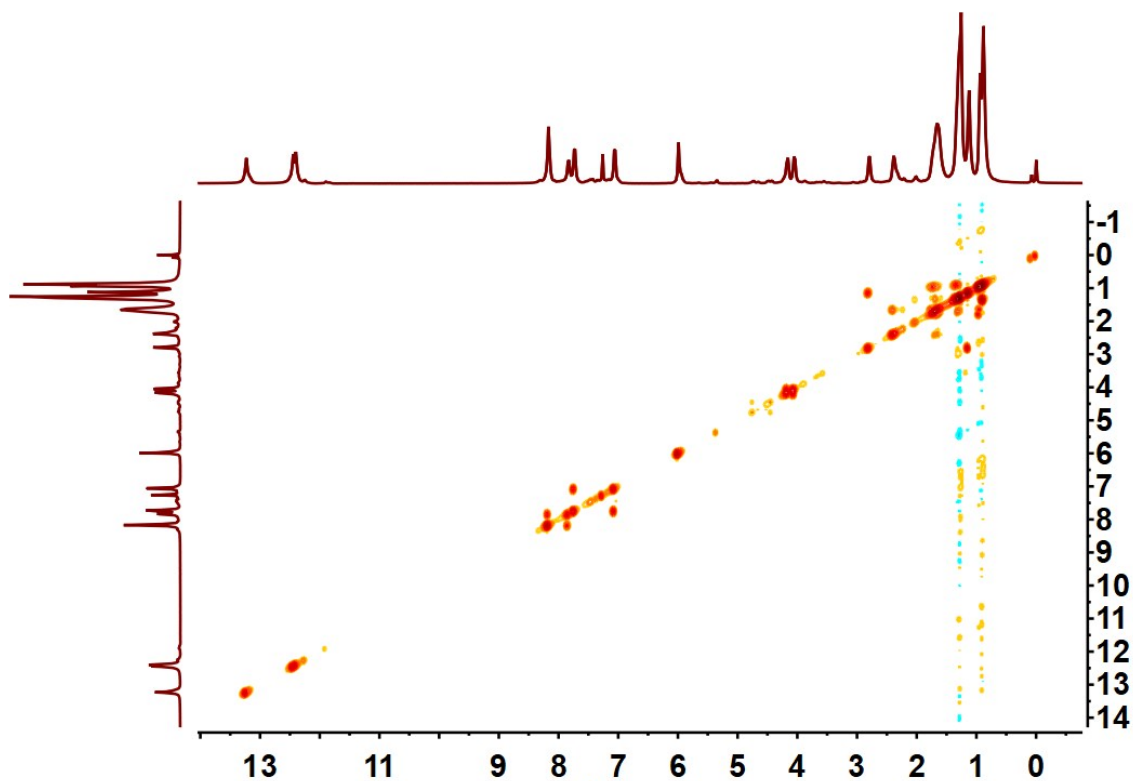


Figure S1. ^1H - ^1H COSY spectrum of *trans* OAS-Upy (500 MHz, CDCl_3 , 298K)

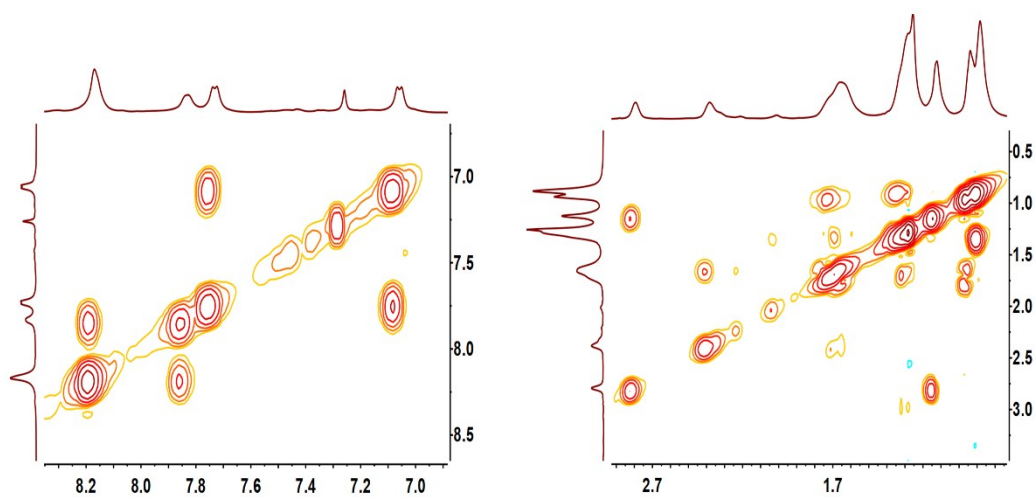


Figure S2. Partial ^1H - ^1H COSY spectra of *trans* OAS-Upy (500 MHz, CDCl_3 , 298K)

2.2 2D Rosey spectra spectra of *trans* OAS-Upy

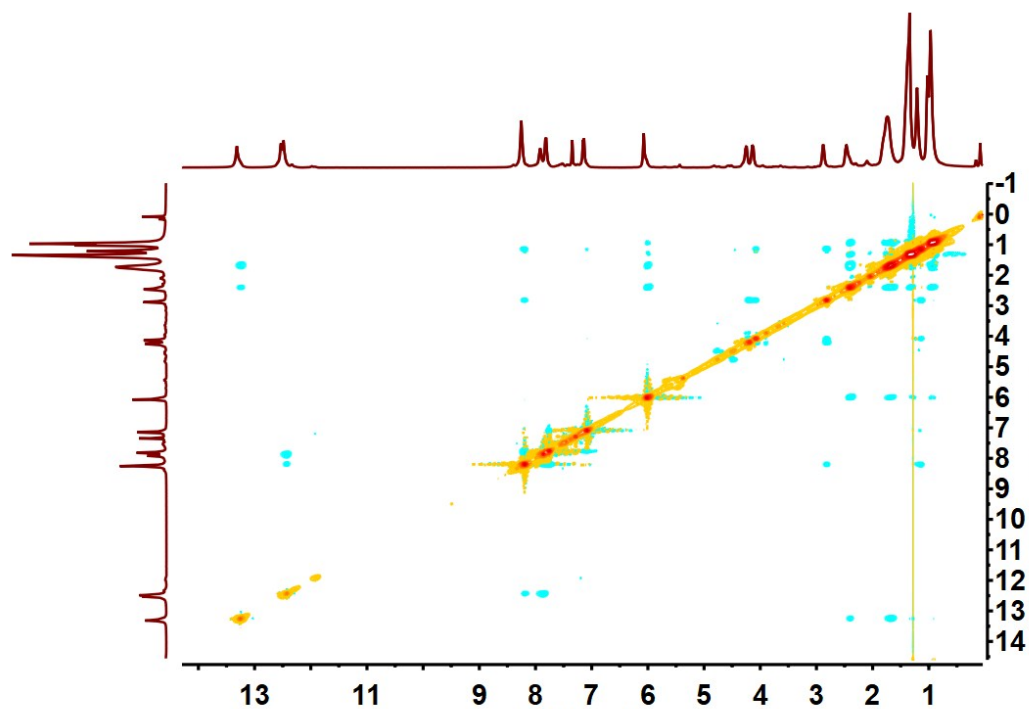


Figure S3. 2D Rosey spectrum of *trans* OAS-Upy (500 MHz, CDCl₃, 298K)

3. Photostationary state (PPS) of *trans* OAS-Upy

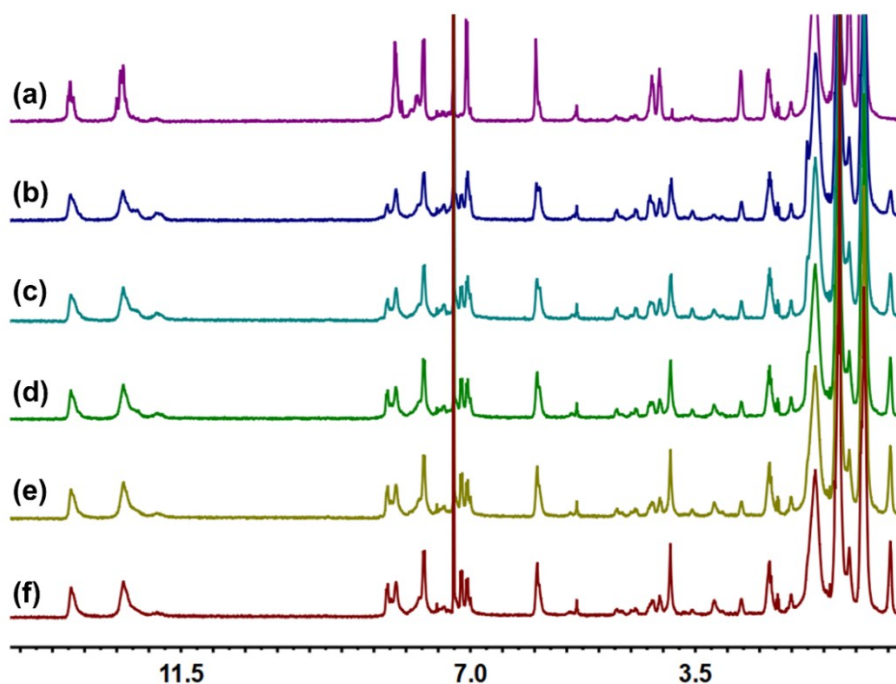


Figure S4. ¹H NMR spectra of *trans* OAS-Upy (400 MHz, CDCl₃, 298K) after UV (365nm) irradiation versus different time: a) 10 min; b) 15 min; c) 20min; d) 40 min; e) 60 min; f) 90 min.

4. Properties of supramolecular polymers

4.1 ^1H NMR changes of *trans* OAS-Upy at different concentrations

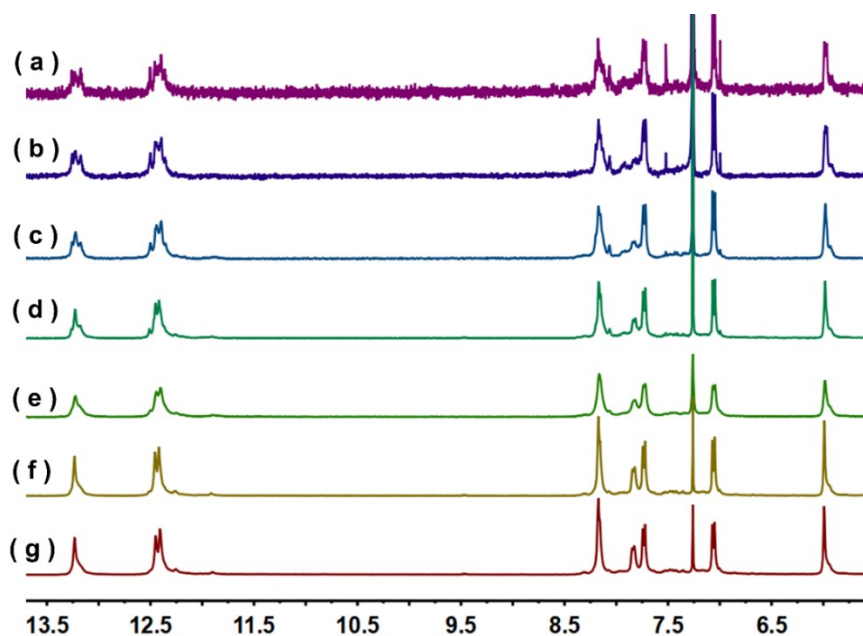


Figure S5. Partial ^1H NMR spectra of *trans* OAS-Upy (400 MHz, CDCl_3 , 298K) at various concentrations: a) 1 mM; b) 5 mM; c) 10mM; d) 20 mM; e) 50 mM; f) 70 mM; g) 100 mM.

4.2 Specific viscosity changes of *trans* OAS-Upy at different concentrations

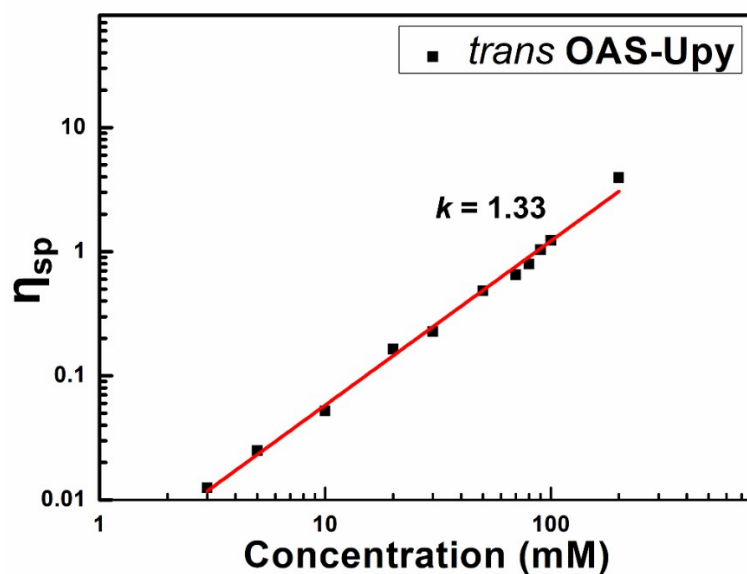


Figure S6. Specific viscosity (η_{sp}) of *trans* OAS-Upy (CHCl_3 , 25°C) versus the concentration.

4.3 DOSY spectra of OAS-Upy

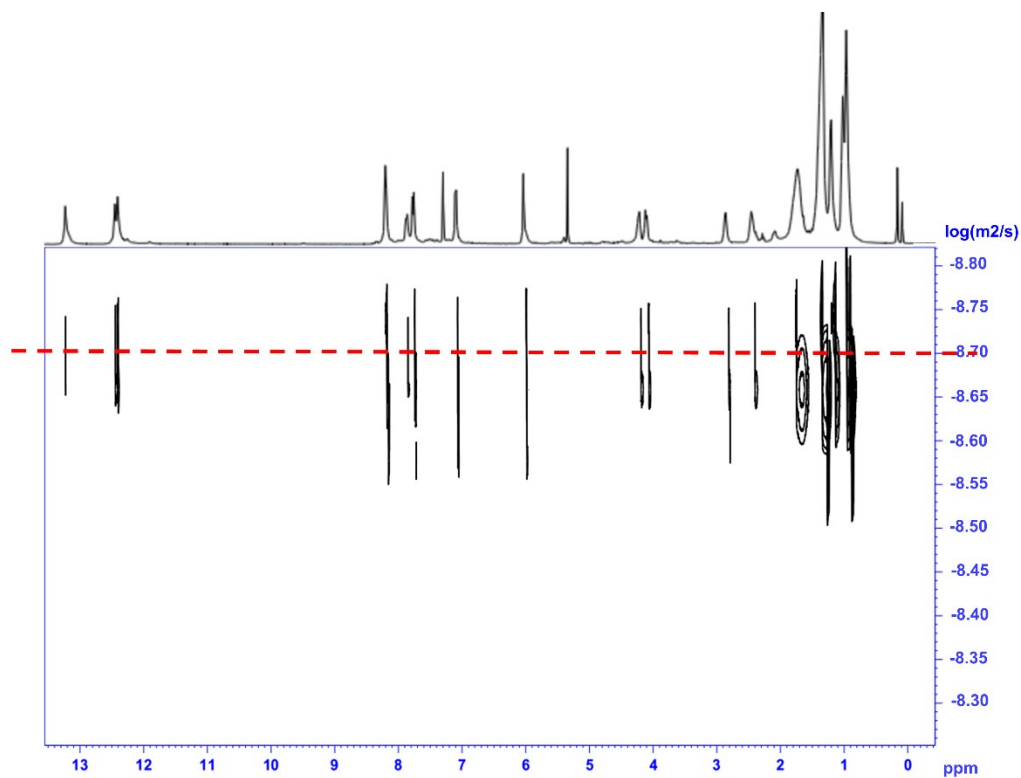


Figure S7. DOSY spectrum of *trans* OAS-Upy (20 mM in CHCl_3 , 298K)

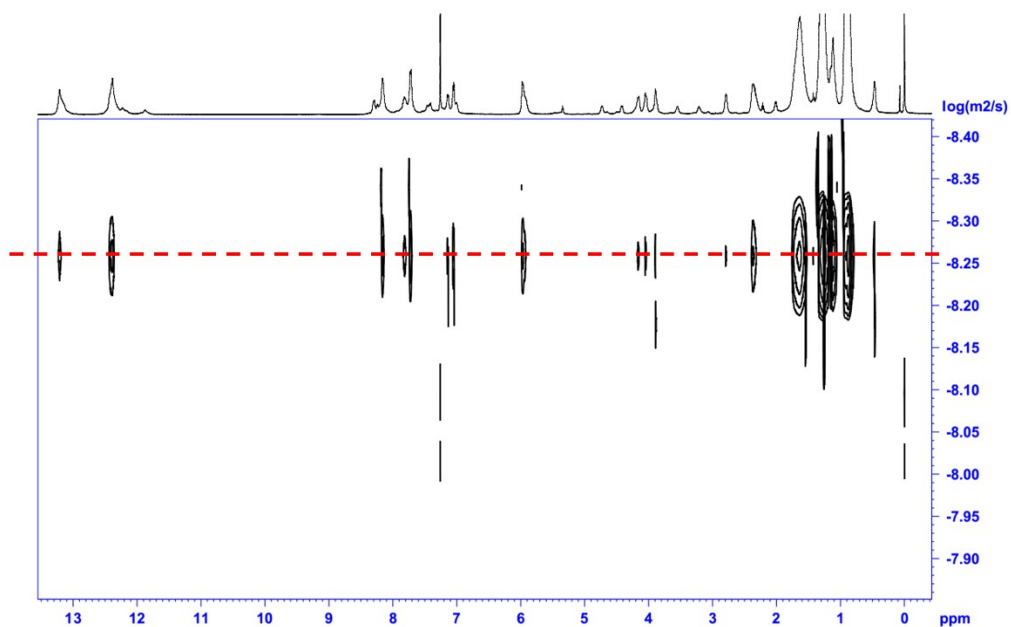


Figure S8. DOSY spectrum of *trans* OAS-Upy after UV irradiation for 60 min (20 mM in CHCl_3 , 298K)

5. Sizes and morphologies of OAS-Upy

5.1 Changeable DLS of *trans* OAS-Upy after UV irradiation

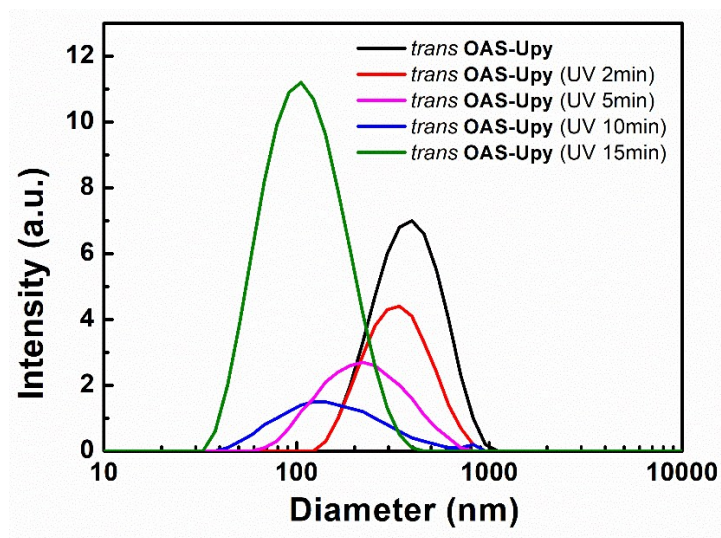


Figure S9. The sizes changes of *trans* OAS-Upy after UV (365nm) irradiation for various time (2min~15min).

5.2 High resolution TEM images of OAS-Upy

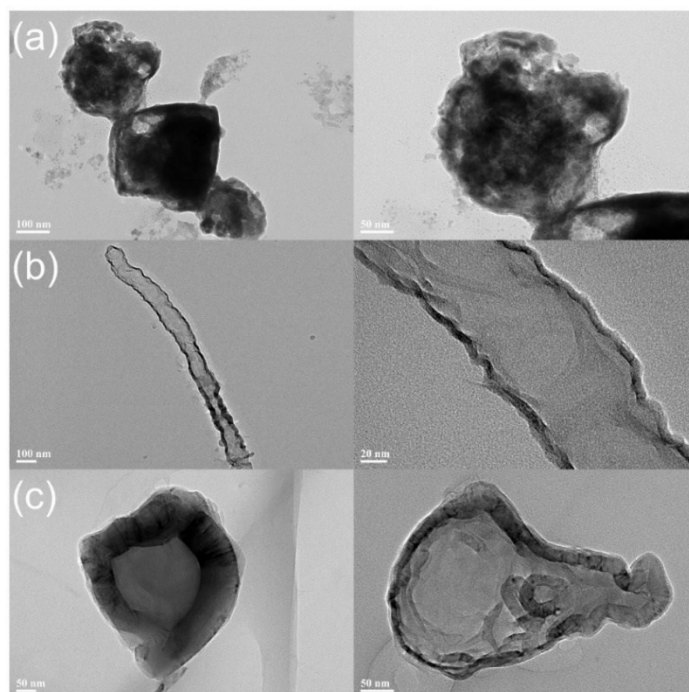
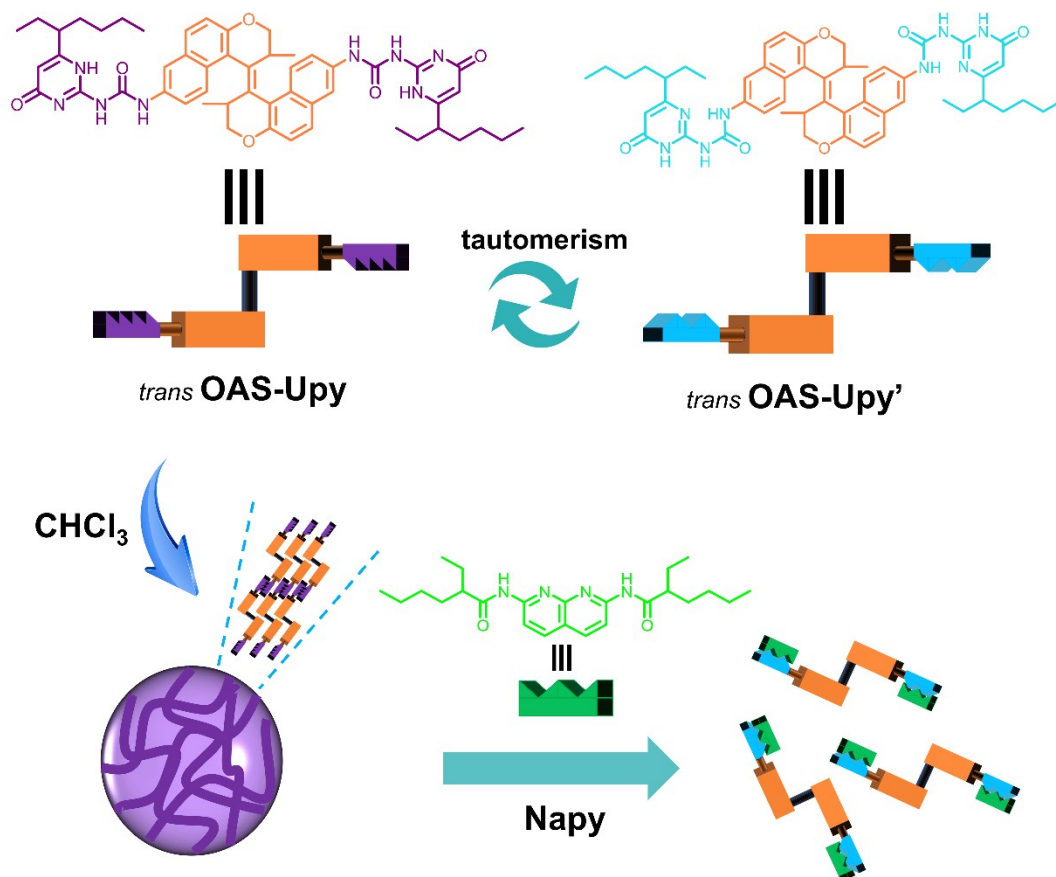


Figure S10. (a) TEM images of *trans* OAS-Upy aggregates; (b) TEM images of *trans* OAS-Upy aggregates after UV (365 nm) irradiation for 15 min; (c) TEM images of *cis* OAS-Upy after heating (50°C) under darkness for 30 min, all the TEM tested onto copper grid (1×10^{-5} M in CHCl_3).

6. Depolymerization of OAS-Upy supramolecular polymers



Scheme S2. (a) The chemical structure and tautomerism of *trans* OAS-Upy; (b) Graphical representation for the depolymerization of *trans* OAS-Upy in chloroform solution.

As shown in the scheme S2, in the initial state, *trans* OAS-Upy could form spherical polymers via intermolecular quadruple hydrogen bonding and π - π stacking interactions. After adding the Napy monomers to the above system, the Upy groups of *trans* OAS-Upy would firstly undergo a tautomerism from DDAA arrays to ADDA arrays, then a stronger quadruple hydrogen bonding complex was formed between *trans* OAS-Upy' and Napy monomer via ADDA-DAAD arrays. As a result, the quadruple hydrogen bonding system formed by *trans* OAS-Upy could be completely disturbed, the well-defined polymers would depolymerize.

6.1 ^1H NMR changes of *trans* OAS-U_{py} after adding Napy monomers

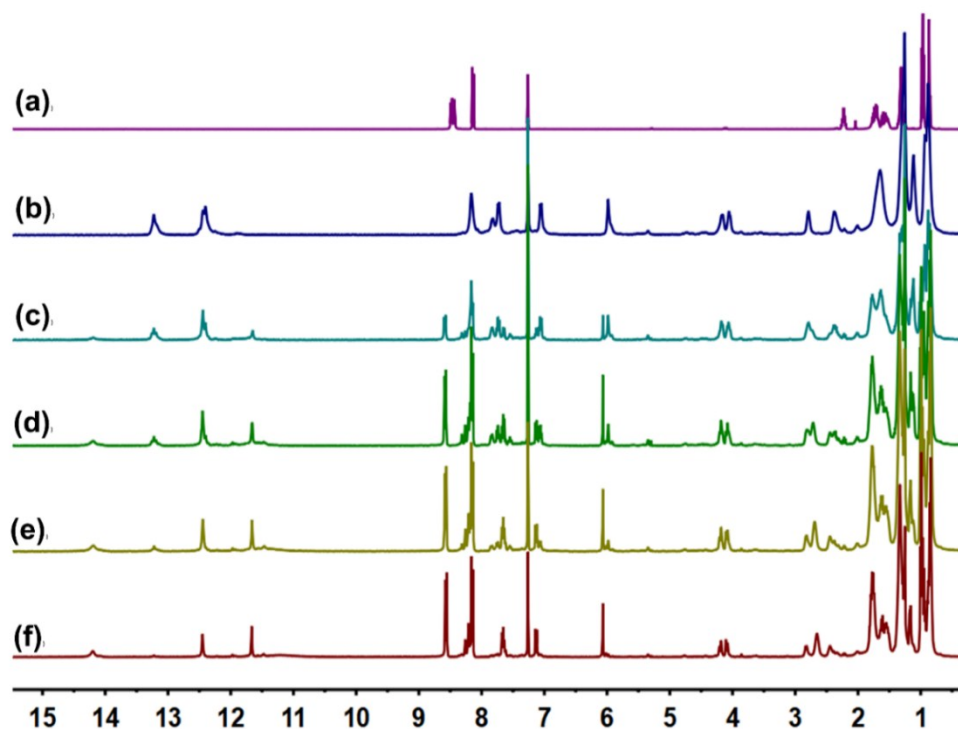


Figure S11. ^1H NMR spectra (400 MHz, CDCl_3 , 298K) of 10 mM *trans* OAS-U_{py} upon progressive addition of Napy: a) Napy; b) 0 equiv; c) 0.5 equiv; d) 1.0 equiv; e) 1.5equiv; f) 2.0 equiv.

7. References

1. J. J. Yu, Q. Z. Cao, Q. Zhang, S. Yang, D. H. Qu, H. Tian, *Chem. Commun.*, **2016**, 52, 12056-12059;
2. H. M. Keizer, J. J. Gonzalez, M. Segura, P. Prados, R. P. Sijbesma, E. W. Meijer, J. de Mendoza, *Chem. Eur. J.*, **2005**, 11, 4602-4608.
3. C. A. Anderson, P. G. Taylor, M. A. Zeller, S. C. Zimmerman, *J. Org. Chem.*, **2010**, 75, 4848-4851.
4. G. B. W. L. Ligthart, H. Ohkawa, R. P. Sijbesma, E. W. Meijer, *J. Org. Chem.*, **2006**, 71, 375-378.

8. Appendix

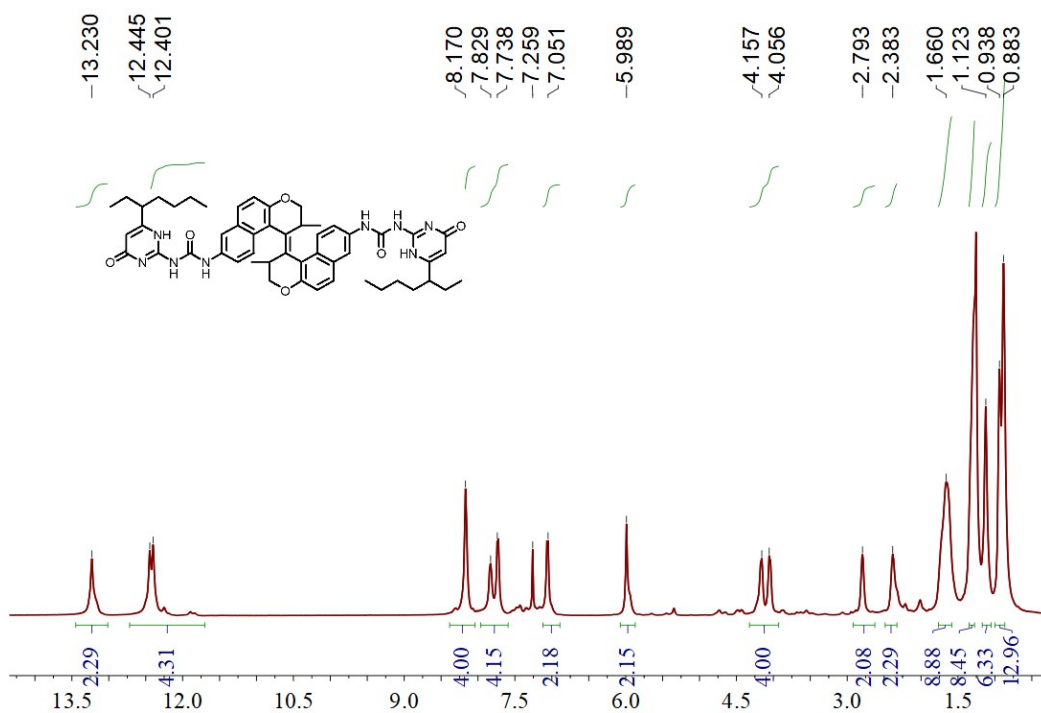


Figure S12. ¹H NMR spectrum of *trans* OAS-Upy (400 MHz, CDCl₃, 298K)

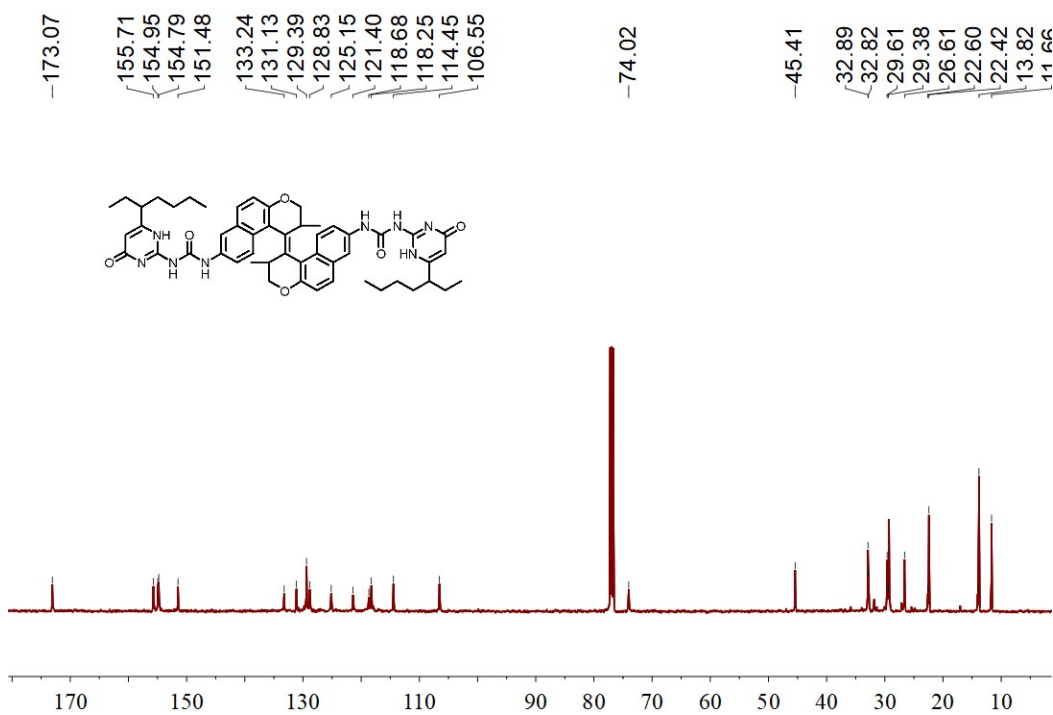


Figure S13. ¹³C NMR spectrum of *trans* OAS-Upy (100 MHz, CDCl₃, 298K)

Single Mass Analysis

Tolerance = 50.0 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

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

Elements Used:

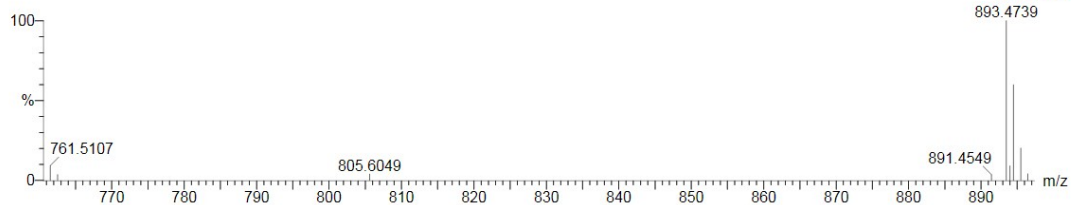
C: 0-52 H: 0-61 N: 0-8 O: 0-6

DH-QU

ECUST institute of Fine Chem

QD-YJJ-005 10 (0.168) Cm (6:10)

29-Oct-2015
21:04:08
1: TOF MS ES+
9.08e+003
893.4739



Minimum: -1.5
Maximum: 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
893.4739	893.4714	2.5	2.8	26.5	23.2	0.0	C52 H61 N8 O6

Figure S14. ESI-MS spectrum of *trans* OAS-Upy