

## *Electronic Supplementary Information*

### **Photoresponsive AA/BB supramolecular polymers comprised of stiff-stilbene based guests and bispillar[5]arenes**

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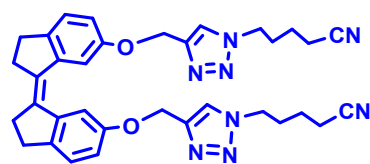
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# 1. NMR and HR-ESI-MS spectra of compound **Z-G**, *E-G* and **H**.



**Z-G**

Chart S1. The structure of compound **Z-G**.

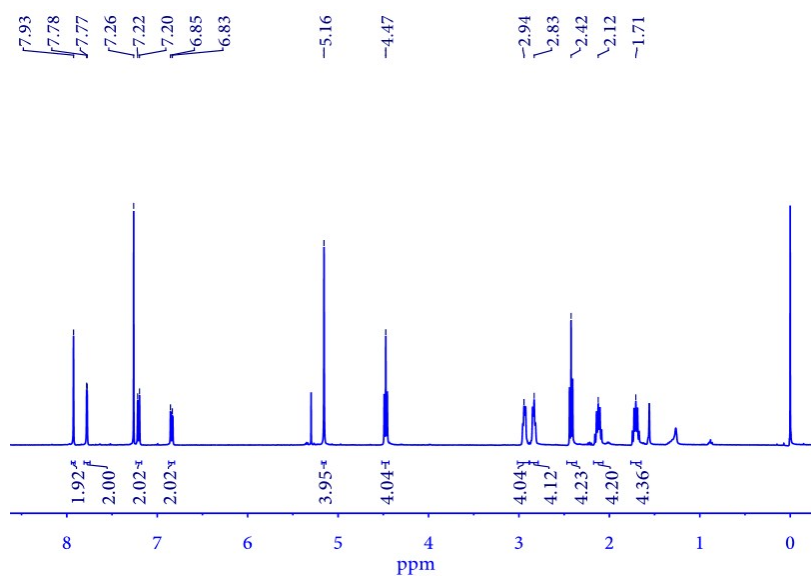


Figure S1.  $^1\text{H}$  NMR spectrum of **Z-G** ( $\text{CDCl}_3$ , 400 MHz).

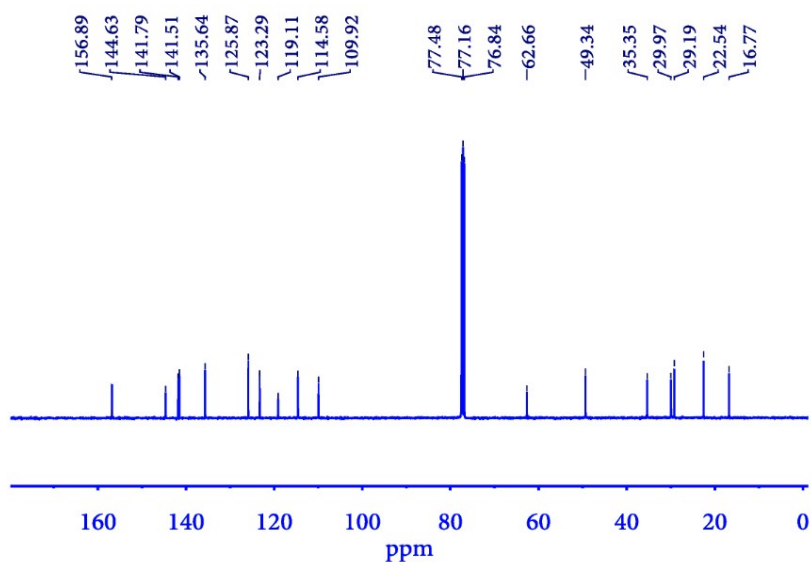


Figure S2.  $^{13}\text{C}$  NMR spectrum of **Z-G** ( $\text{CDCl}_3$ , 100 MHz).

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name FTMS-16110355\_Pos\_20161129\_000006.d  
 Sample WY2016-11-29  
 Comment

Acquisition Date 11/29/2016 10:32:21 AM  
 Instrument Bruker Solarix XR FTMS  
 Operator Peking University

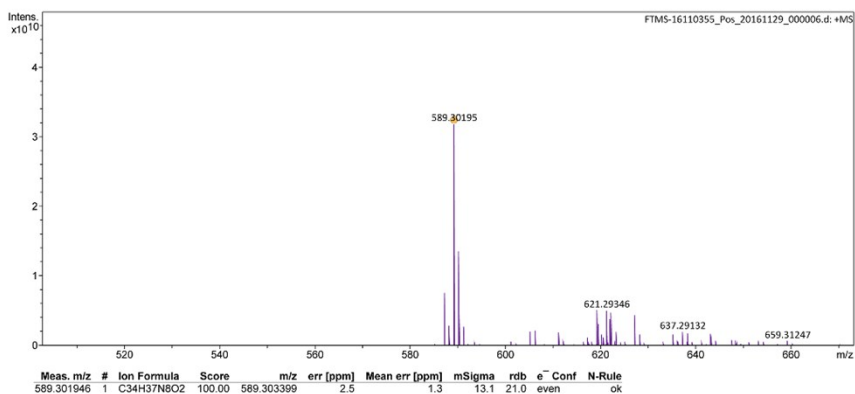
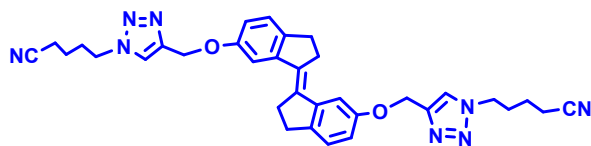


Figure S3. HR-ESI-MS spectrum of **Z-G**.



**E-G**

Chart S2. The structure of compound **E-G**.

The integral area of the **Z-G** proton signal (7.78 ppm) in <sup>1</sup>H NMR spectra is only about 3% of the integral area of **E-G** proton signal, which revealed the almost complete conversion.<sup>[1]</sup>

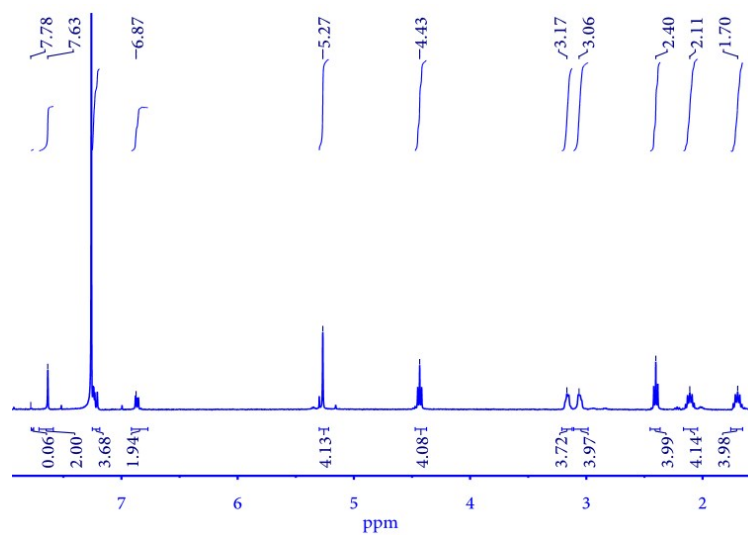


Figure S4.  $^1\text{H}$  NMR spectrum of **E-G** ( $\text{CDCl}_3$ , 400 MHz).

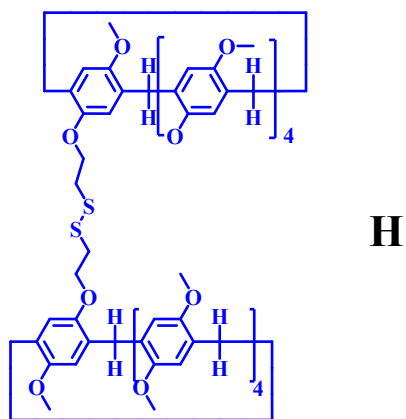


Chart S3. The structure of compound **H**.

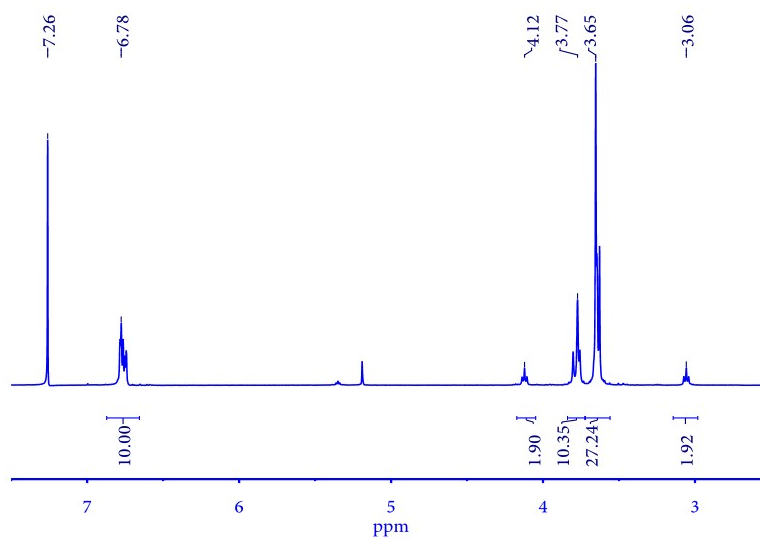


Figure S5.  $^1\text{H}$  NMR spectrum of **H** ( $\text{CDCl}_3$ , 400 MHz).

## 2. Absorption and emission spectra of Z-G and E-G.

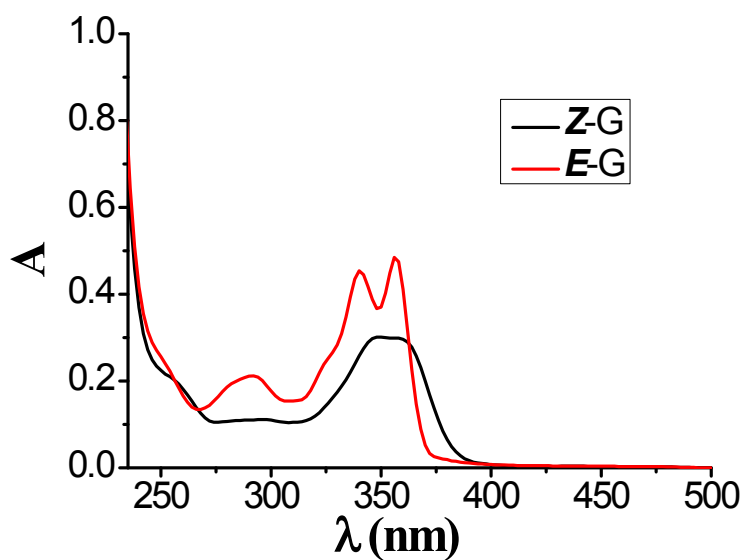


Figure S6. The UV-vis spectra of Z-G and E-G in CH<sub>2</sub>Cl<sub>2</sub> (1.0 × 10<sup>-5</sup> mol/L).

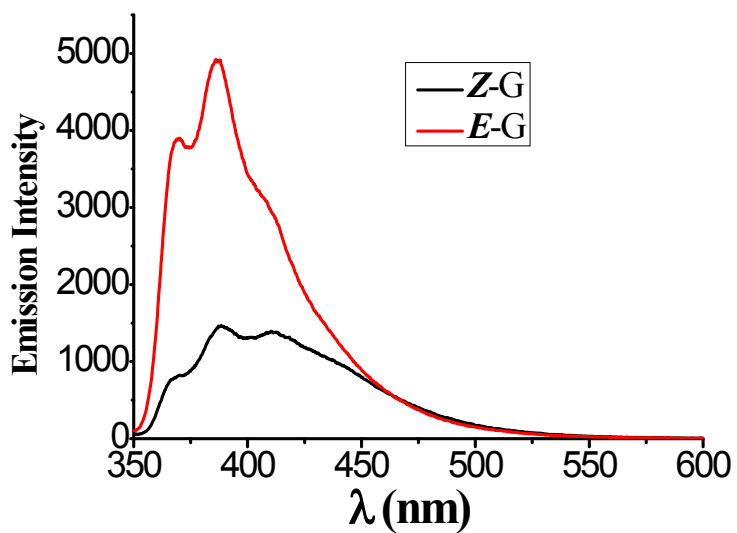


Figure S7. The fluorescence spectra of Z-G and E-G in CH<sub>2</sub>Cl<sub>2</sub> (1.0 × 10<sup>-5</sup> mol/L, λ<sub>ex</sub> = 340 nm).

### 3. COSY spectra of Z-G + H and E-G + H at 150 mM.

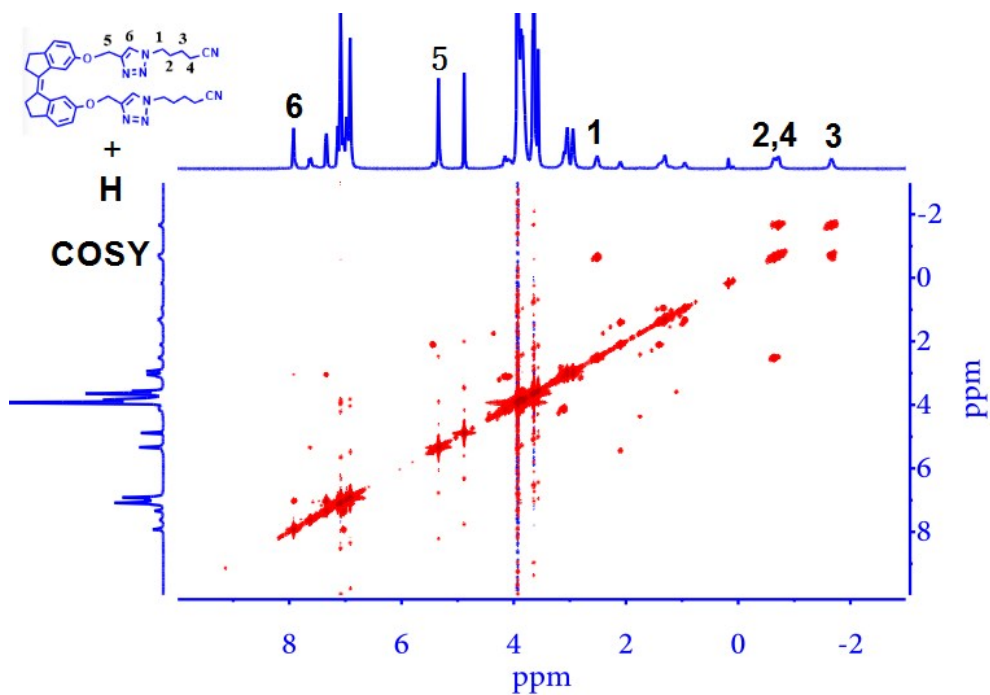


Figure S8. COSY spectrum of a chloroform-d solution of 150 mM Z-G + H.

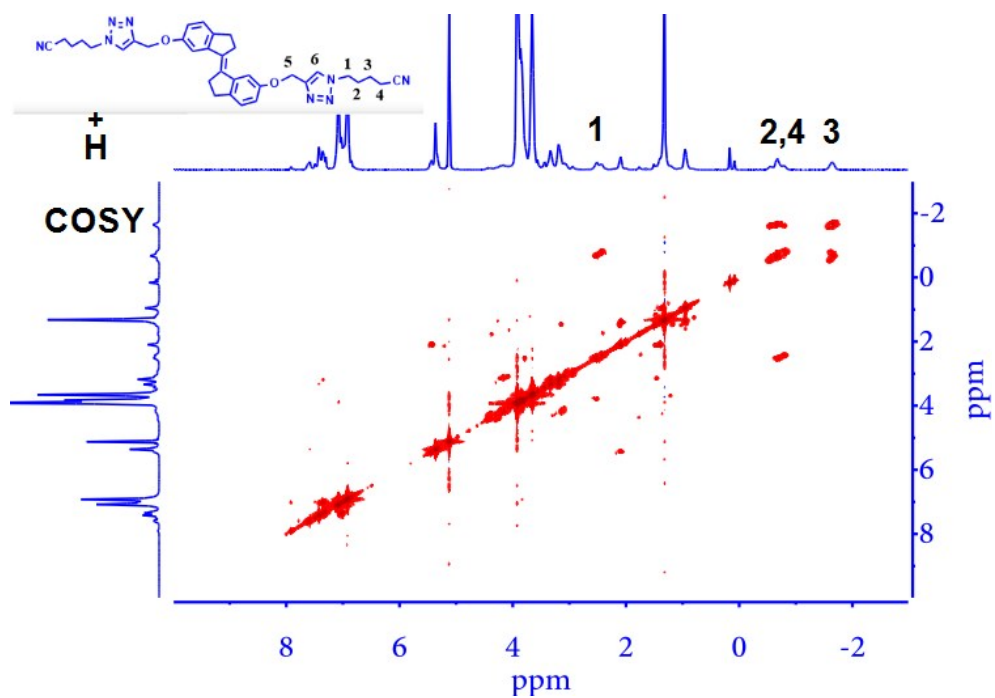


Figure S9. COSY spectrum of a chloroform-d solution of 150 mM E-G + H.

4. ROESY spectra of *Z*-G + H and *E*-G + H at 150 mM.

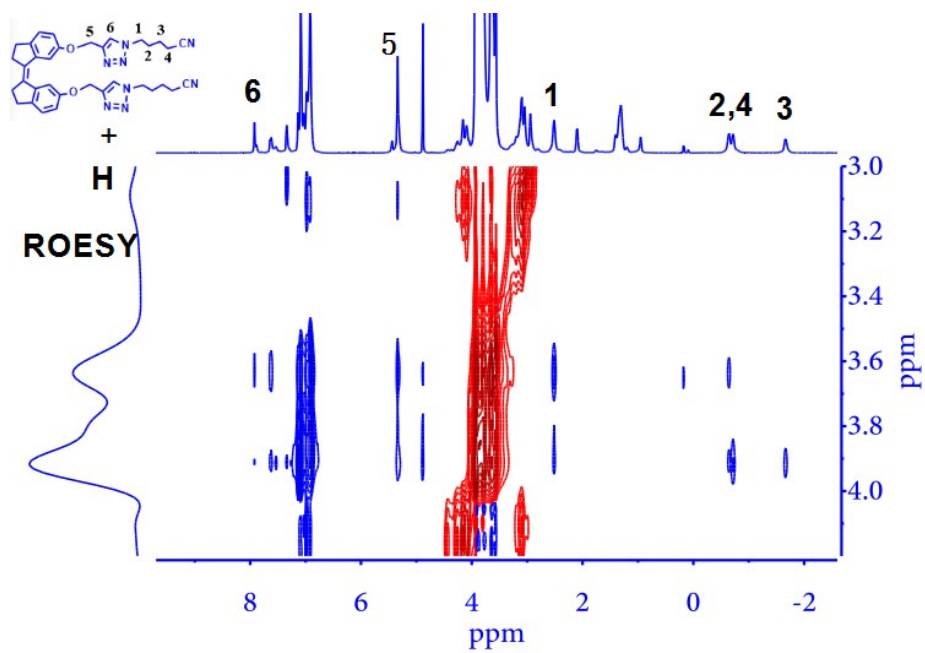


Figure S10. ROESY spectrum of a chloroform-d solution of 150 mM *Z*-G + H.

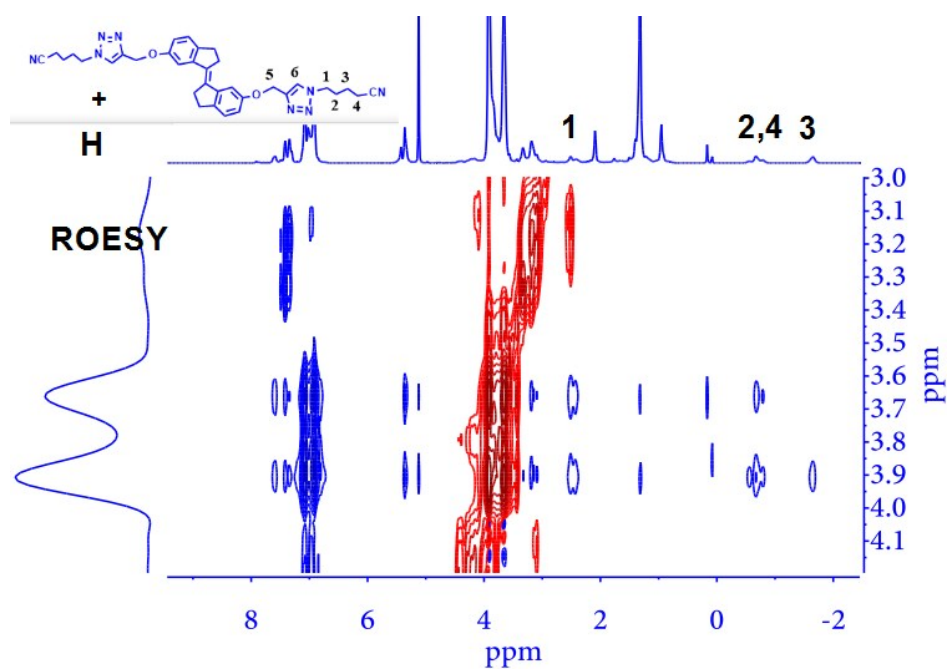
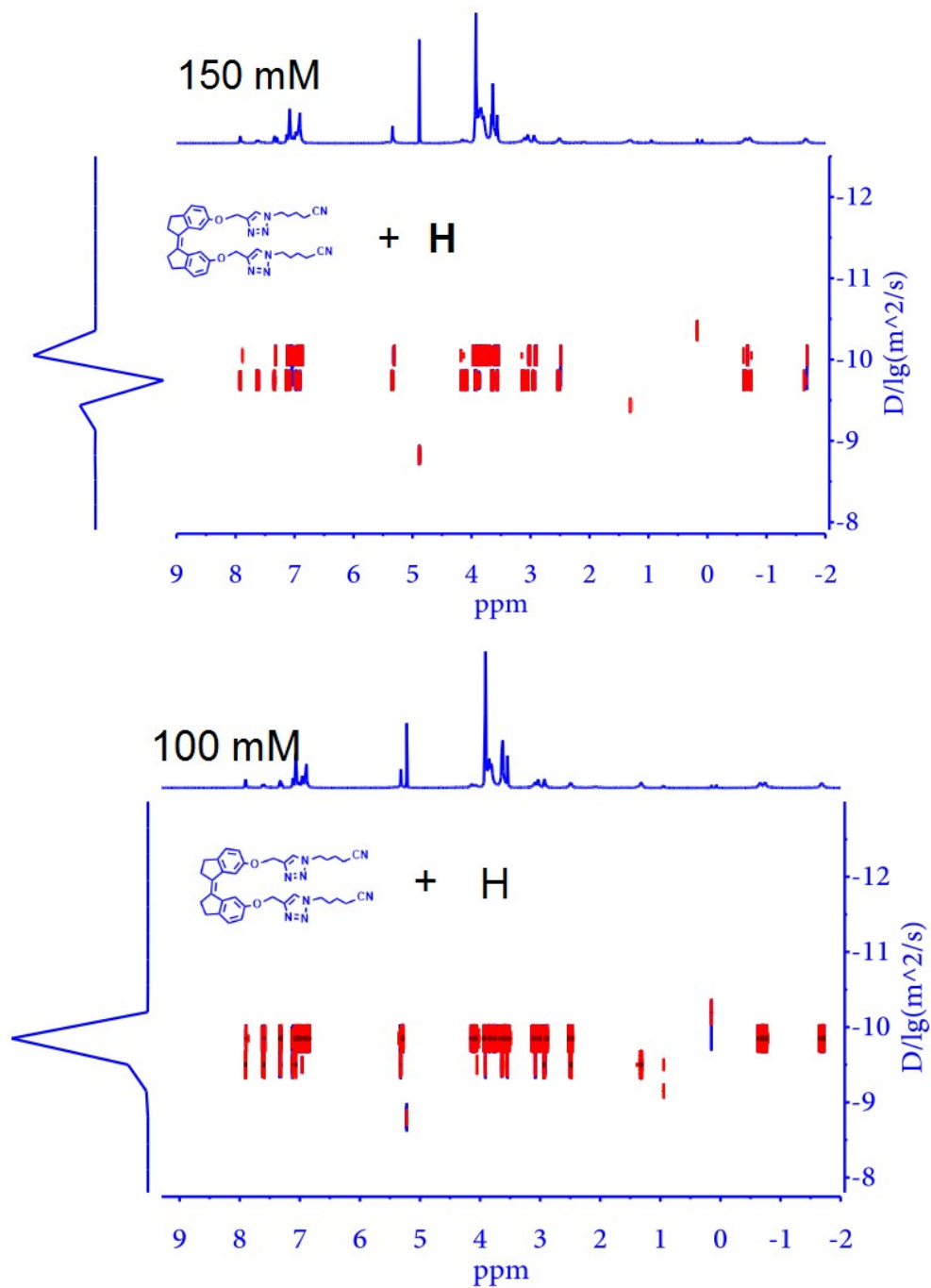
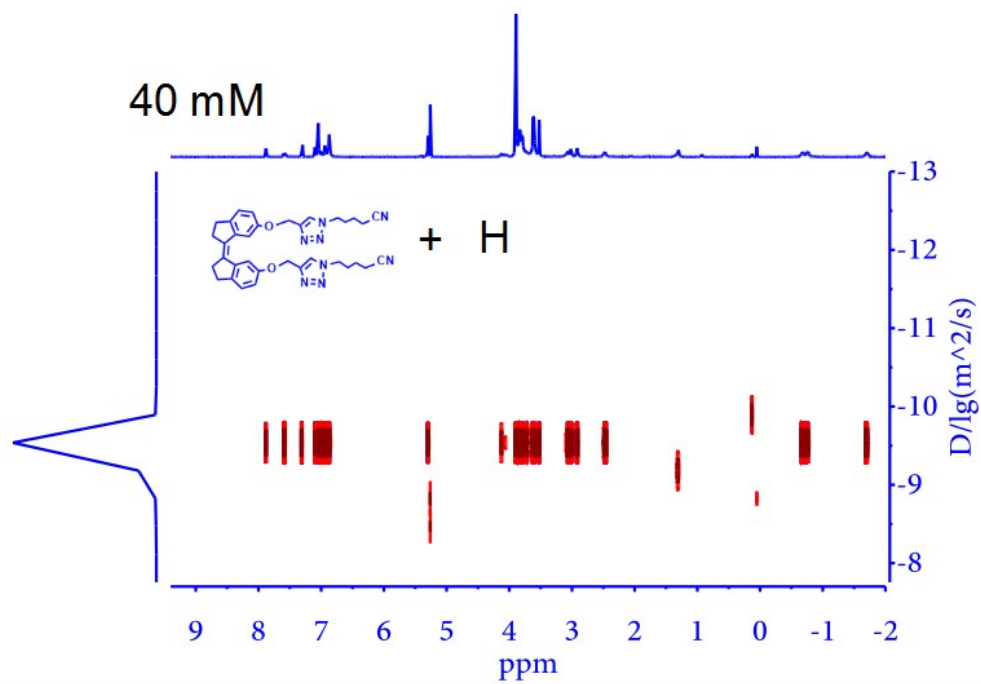
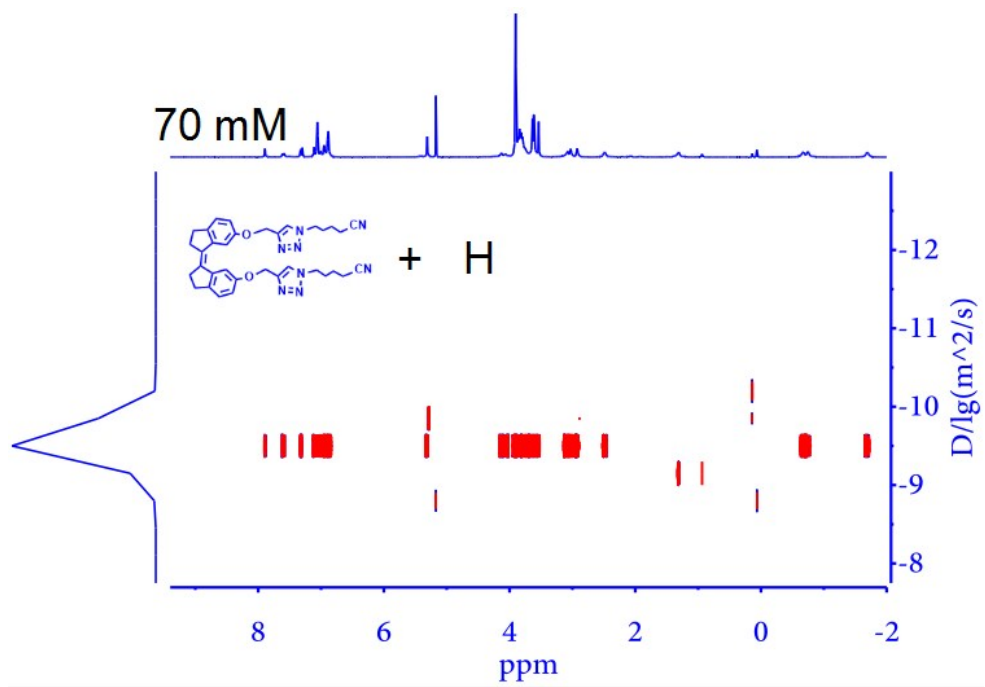


Figure S11. ROESY spectrum of a chloroform-d solution of 150 mM *E*-G + H.

5. DOSY spectra of Z-G + H and E-G + H at 5-150 mM.







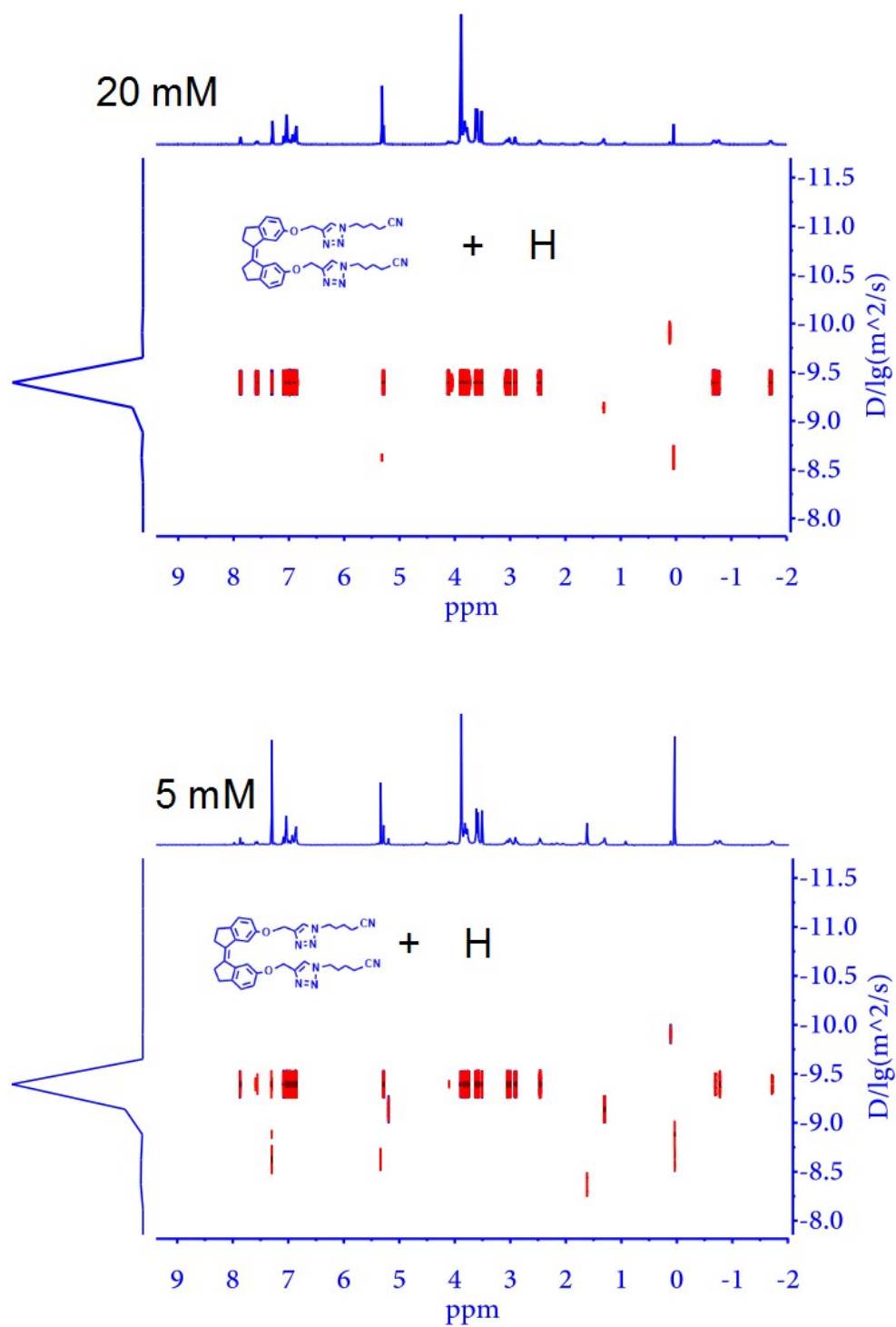
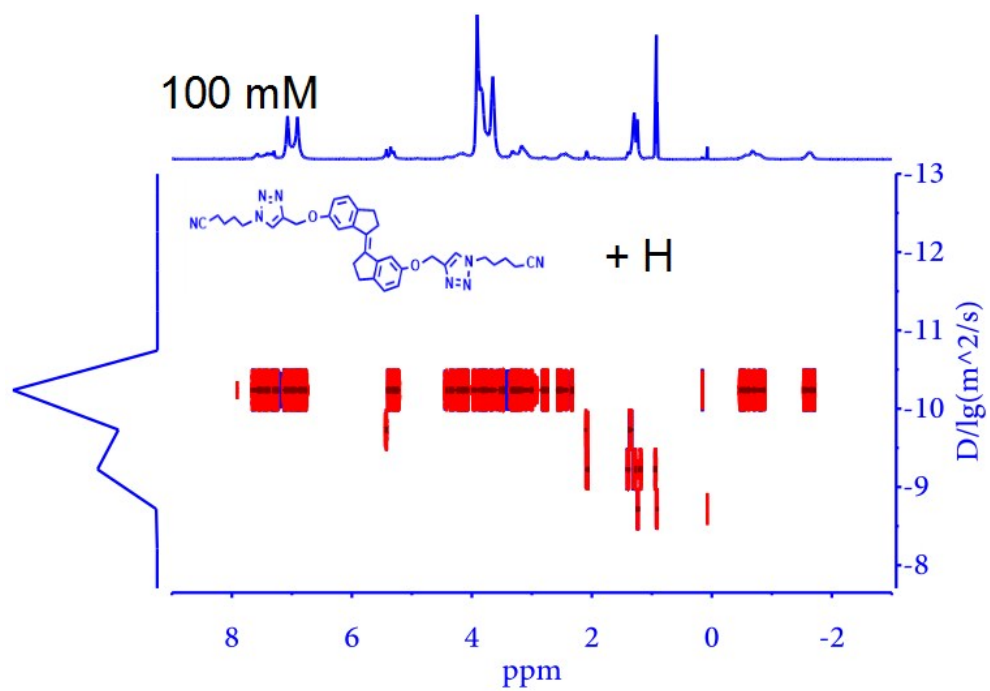
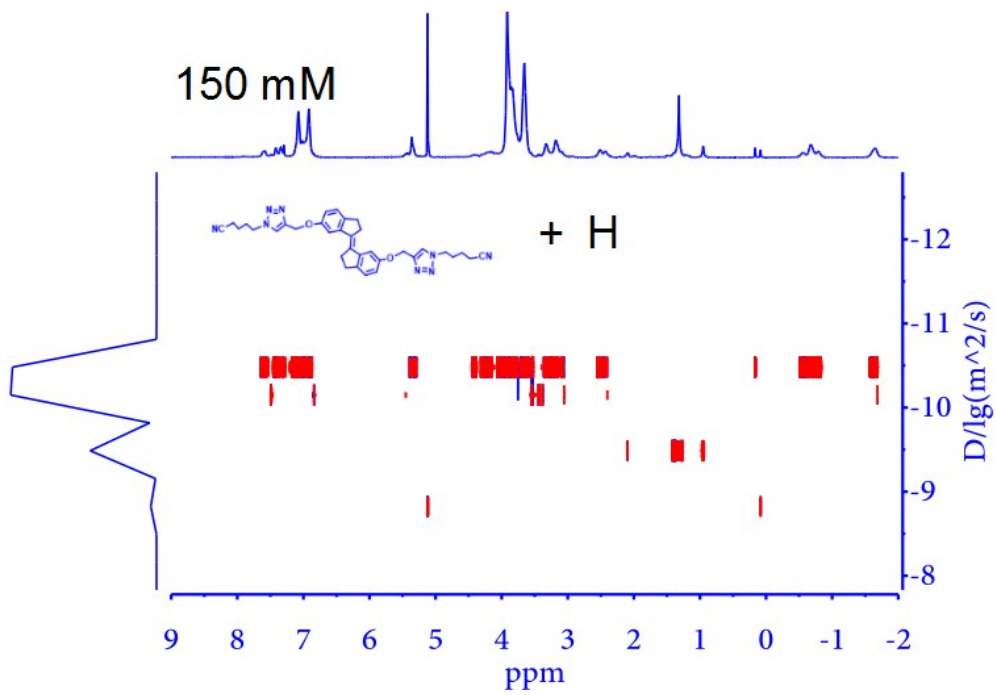
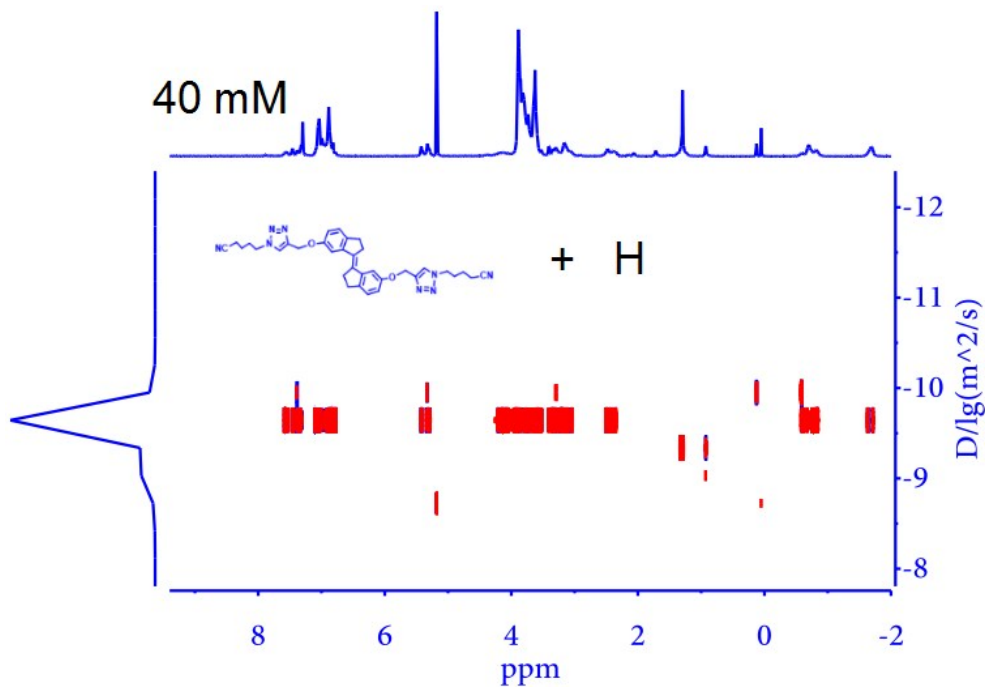
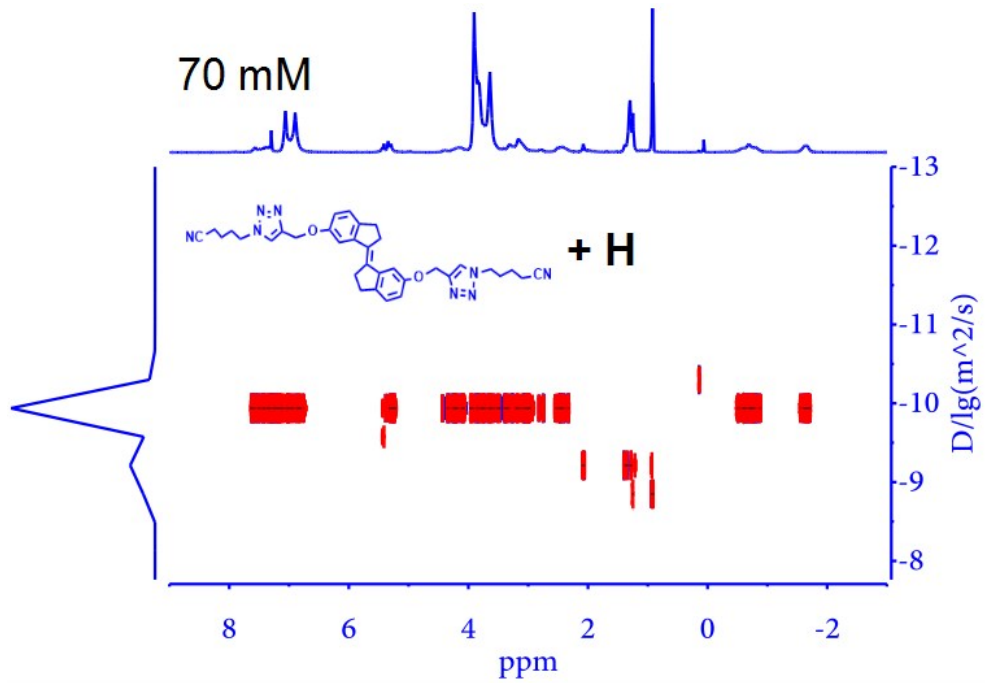


Figure S12. DOSY spectra of **Z-G + H** at 5, 20, 40, 70, 100, 150 mM in  $\text{CDCl}_3$ . (from <sup>1</sup>H NMR spectroscopy 600 MHz,  $\text{CDCl}_3$ , 298 K).





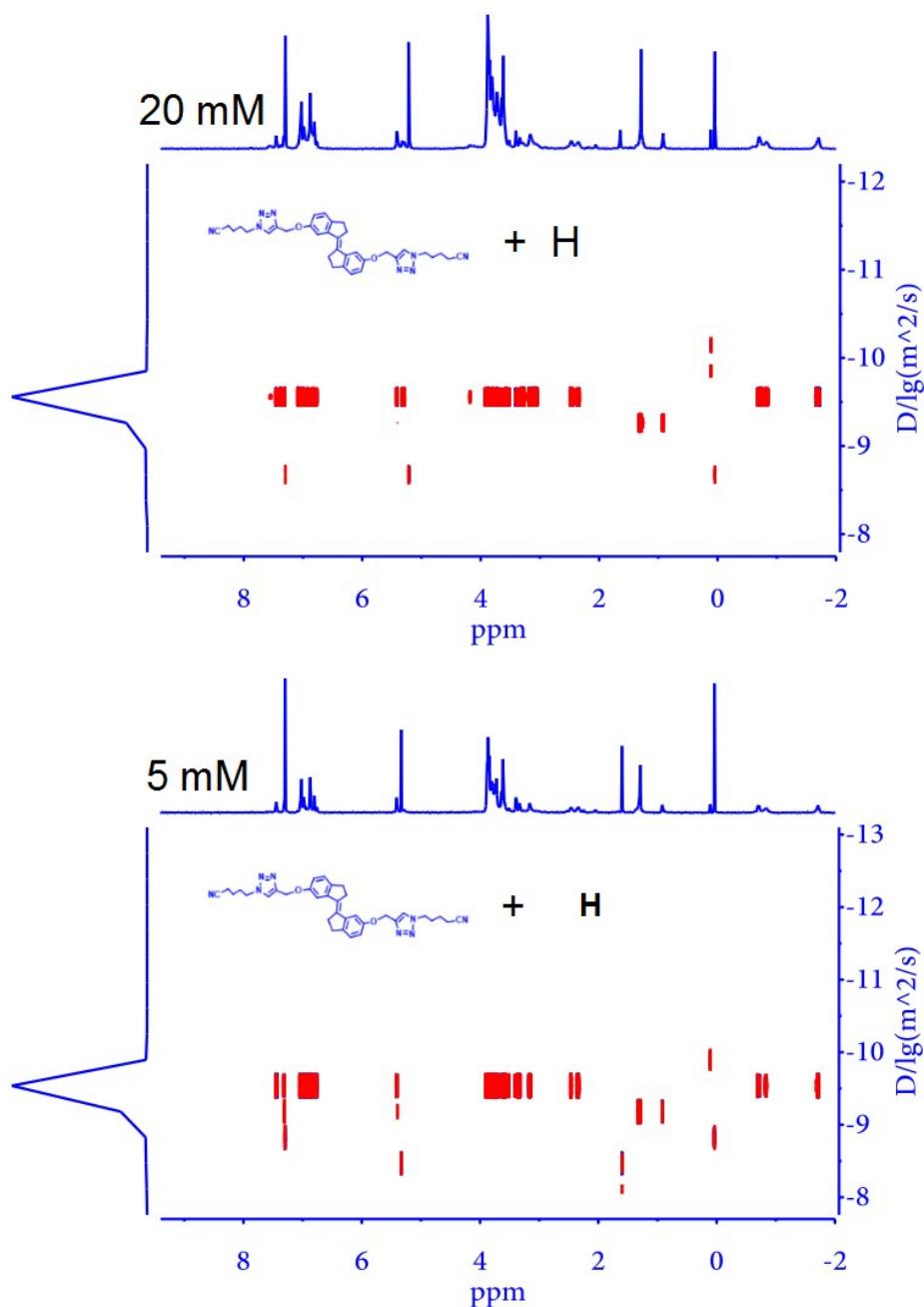


Figure S13. DOSY spectra of *E-G + H* at 5, 20, 40, 70, 100, 150 mM in CDCl<sub>3</sub>. (from <sup>1</sup>H NMR spectroscopy 600 MHz, CDCl<sub>3</sub>, 298 K).

The observation of a sharp decrease in the diffusion coefficient upon increasing concentration of 1:1 mixture of *E-G + H* suggested the formation of linear polymers.<sup>[2]</sup>

We also estimate the average degree of polymerization (DP) of supramolecular polymers at 150 mM roughly from DOSY experiments using following equation:

$$DP = (D_A/D)^3$$

where  $D_A$  is the average diffusion coefficient for the AA and BB monomer ( $3.97 \times 10^{-10} \text{ m}^2\text{s}^{-1}$  at 150 mM),  $D$  is the diffusion coefficient for the sample of supramolecular polymer measured by DOSY ( $3.83 \times 10^{-11} \text{ m}^2\text{s}^{-1}$  at 150 mM). The average degree of polymerization was calculated to be 1110. We realized that this is a very rough estimation.<sup>[3]</sup>

#### 6. Schematic illustration of assembly of 1:1 mixture of *E-G* + H at < 12 mM.

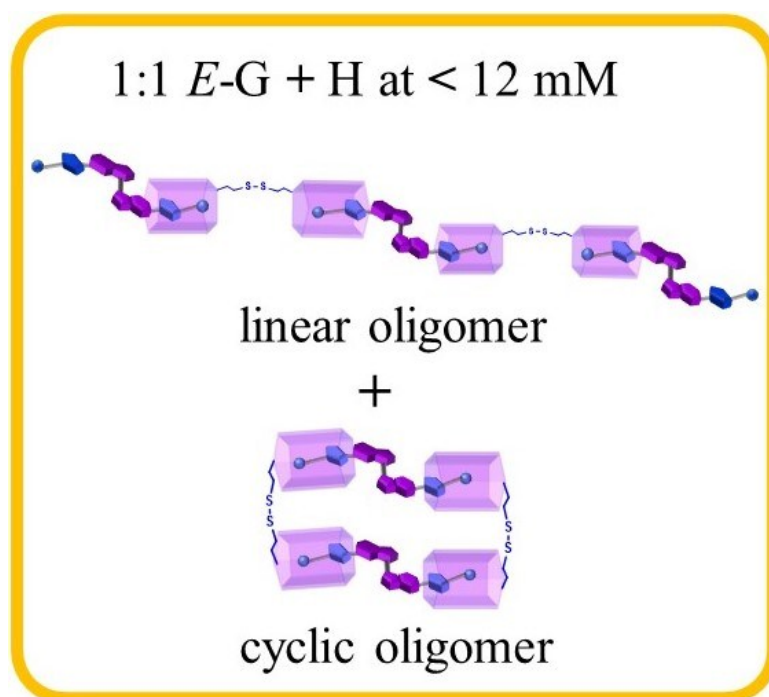


Figure S14. Schematic illustration of assembly of 1:1 mixture of *E-G* + H at < 12 mM.

## 7. DLS experiments

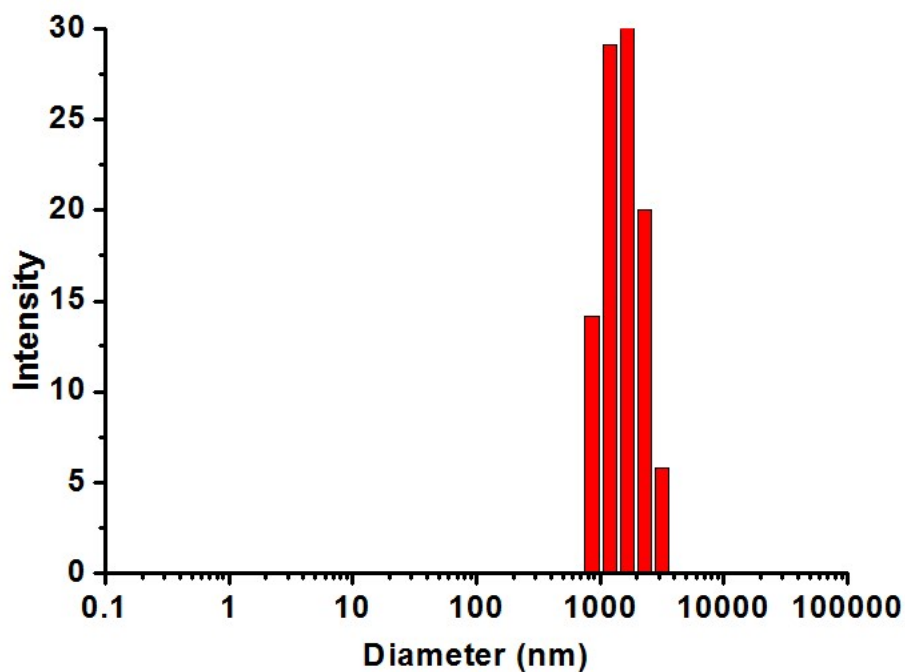
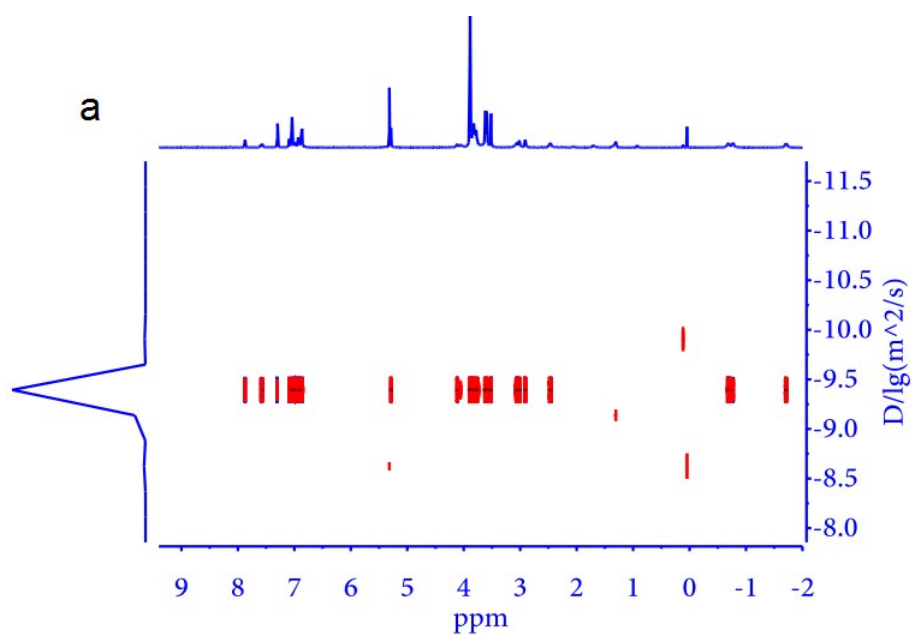


Figure S15. The diameter of supramolecular polymers from 1:1 mixture of *E-G* and *H* at 50 mM determined from DLS.

## 8. Assembly/disassembly behaviour of the AA/BB supramolecular polymers (20 mM) by photo irradiation.



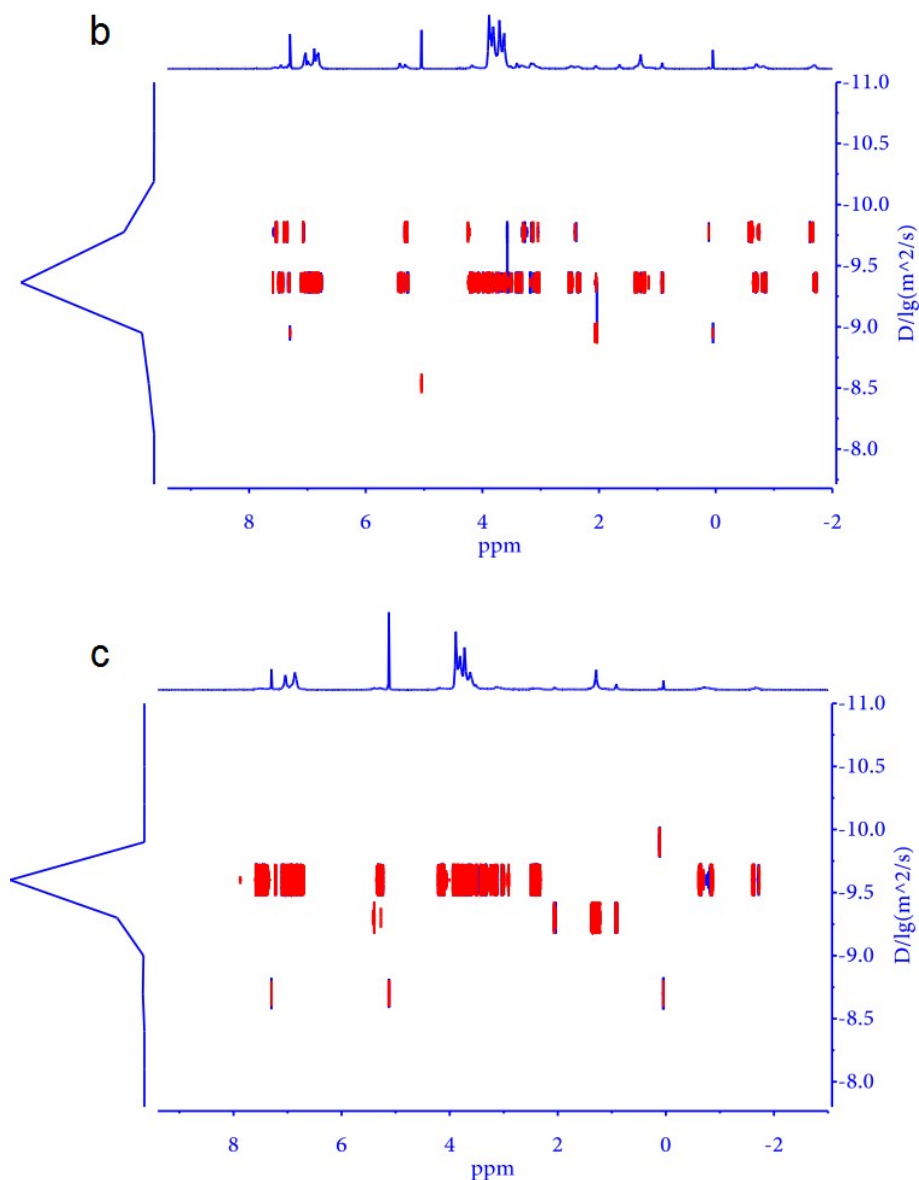


Figure S16. (a) The DOSY spectrum of 1:1 mixture of **Z-G** + **H** at 20 mM. (b) The DOSY spectrum of the mixture after irradiation by 387 nm light. (c) The DOSY spectrum of the mixture from (b) after irradiation by 360 nm light. (600 MHz,  $\text{CDCl}_3$ , 298 K).

The diffusion constant ( $D$ ) of the 20 mM mixture of **Z-G** and **H** was  $(3.57 \pm 0.07) \times 10^{-10} \text{ m}^2\text{s}^{-1}$ . After irradiation by 387 nm light for 80 min, the diffusion constant ( $D$ ) of the mixture was determined to be  $(2.83 \pm 0.12) \times 10^{-10} \text{ m}^2\text{s}^{-1}$ . The decreasing diffusion constant ( $D$ ) indicated the possible formation of polymers due to the transformation from **Z-G** to **E-G** by photo-irradiation. The reverse isomerization was achieved by irradiation at  $> 360 \text{ nm}$ . The diffusion constant ( $D$ ) of the mixture was increased to  $(3.15 \pm 0.07) \times 10^{-10} \text{ m}^2\text{s}^{-1}$ . The changing of  $D$  in the mixture of **Z-G** + **H** before and after irradiation by 387 nm and then 360 nm at 20 mM has similar trend with those at 100 mM.



### 9. Z/E isomerization ratio at different irradiation time.

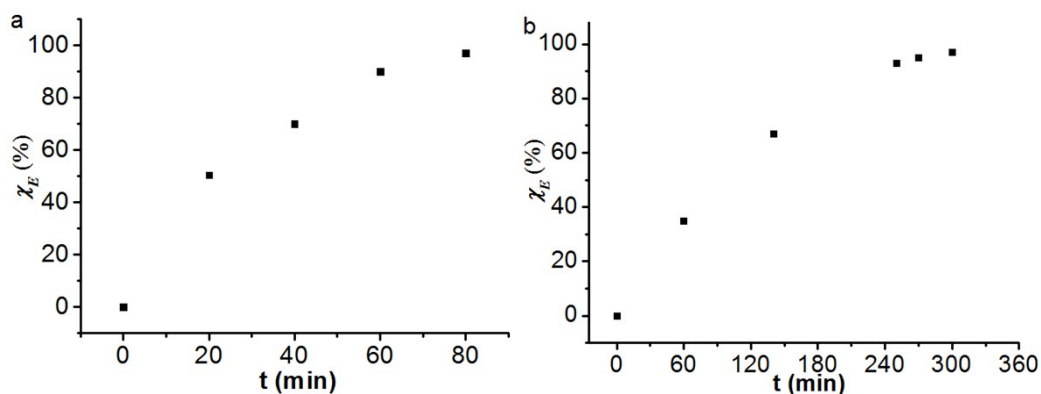


Figure S17. (a) The percentage of *E*-**P** upon irradiation of *Z*-**P** (20 mM) for 0 min, 20 min, 40 min, 60 min and 80 min. (b) The percentage of *E*-**P** when irradiation of *Z*-**P** (100 mM) for 0 min, 60 min, 140 min, 250 min, 270 min and 300 min.

We determined the Z/E isomerization ratio by  $^1\text{H}$  NMR at different irradiation time at 20 mM. The percentage of *E*-**P** is increasing upon irradiation of *Z*-**P** at 387 nm. The percentage of *E*-**P** is 97% at photostationary state. We also determined the Z/E isomerization ratio by  $^1\text{H}$  NMR at different irradiation time at 100 mM. The photoisomerization reaction reached its photostationary state with 95% of *E*-**P** after irradiating *Z*-**P** for 4.5 h.

## 10. UV spectra of 1:1 mixture of Z-G + H at 100 mM.

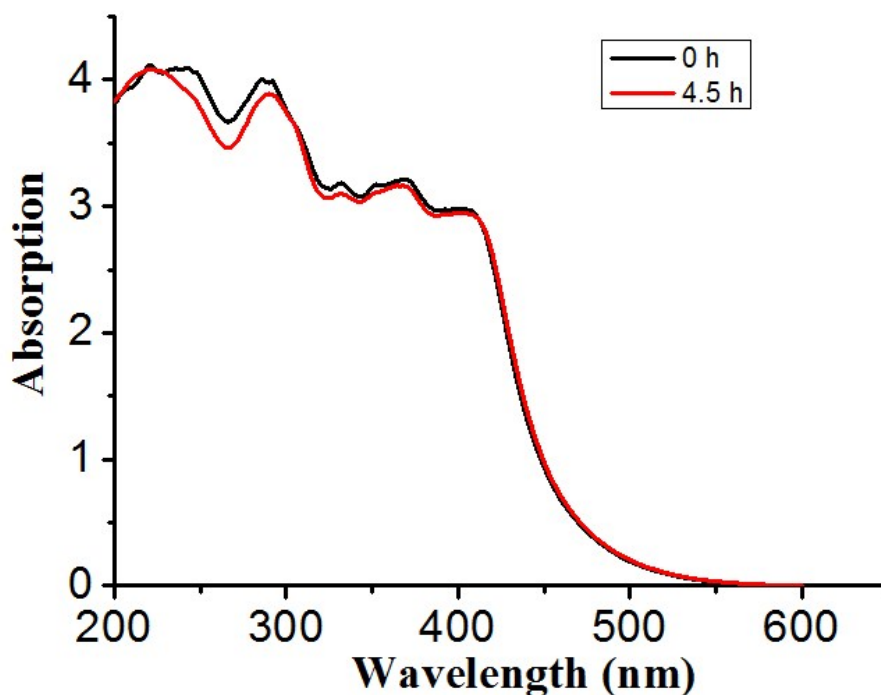


Figure S18. The UV-vis spectra of 1:1 mixture of Z-G + H at 100 mM in CHCl<sub>3</sub> after stay for 0 h and 4.5 h under dark.

## 11. References.

1. Sergey Akbulatov, Yancong Tian and Roman Boulatov, *J. Am. Chem. Soc.*, 2012, **134**, 7620–7623.
2. Chunju Li, Kang Han, Jian Li, Yanyan Zhang, Wei Chen, Yihua Yu and Xueshun Jia, *Chem. -Eur. J.*, 2013, **19**, 11892-11897.
3. Xiaoguang Liu, Jiang-Fei Xu, Zhiqiang Wang and Xi Zhang, *Polym. Chem.*, 2016, **7**, 2333-2336.