Electronic Supplementary Material (ESI) for Polymer Chemistry.

Photoresponsive Supramolecular Polymers Based on Quadruple Hydrogen-Bonding and a Photochromic Azobenzene Motif

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Supporting Information

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Synthesis and Characterization

2-(1-imidazolylcarbonylamino)-6-methyl-4[1*H*]-pyrimidinone (2)

This compound was prepared as reported by Sze et al.[1] A mixture of 6-methylisocytosine (5.0 g, 0.04 mol) and 1,1'-carbonyldiimidazole (8.43 g, 0.052 mol) in dry THF (100 mL) was refluxed for 12 h. The suspension was cooled to 25 °C and filtered. The solid was washed with acetone (20 mL) three times and dried in vacuum oven to afford a white solid (8.62 g, 98%). Compound **2** was used in the subsequent step without further purification. ^{1}H NMR (300 MHz, CD_3OD): δ 7.69 (s, 1H), 7.05 (s, 2H), 5.94 (s, 1H), 2.22 (s, 3H).

1-(2-Hydroxyethyl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea (3)

This compound was prepared as reported by Meijer et al. with slight modification.[2] A mixture of imidazolide **2** (5.0 g, 22.8 mmol) and ethanolamine (2.9 mL, 48.3 mmol) was stirred in dry THF (100 mL) under a nitrogen atmosphere. Dry triethylamine (3 mL) was added to the suspension, and then the mixture was stirred at 50 °C for 24 h. The solution was allowed to cool to room temperature and 100 mL acetone was added. The white precipitate was filtered and rinsed with water and then acetone. After dried under vacuum, the product **3** was obtained as a white solid (3.48 g, 72%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.55 (s, 1H), 9.80 (s, 1H), 7.50 (s, 1H), 5.77 (s, 1H), 4.81 (s, 1H), 3.45 (m, 2H), 3.21(m, 2H), 2.10 (s, 3H).

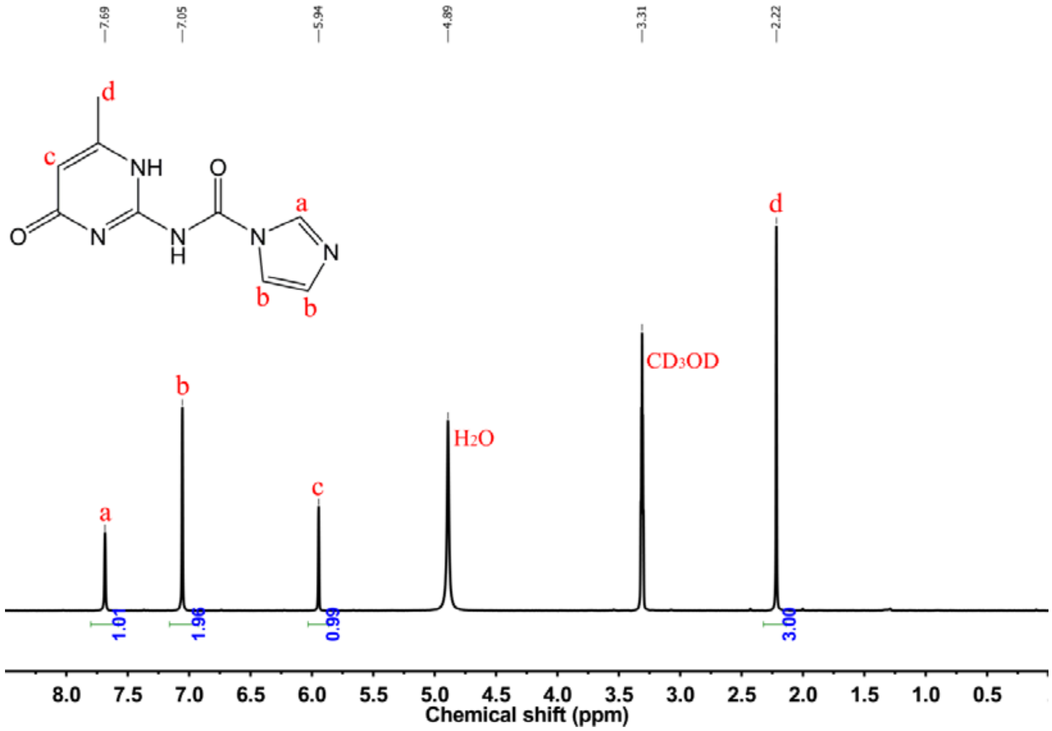


Figure S1. ^{1}H NMR spectrum of compound **2** in CD_3OD.

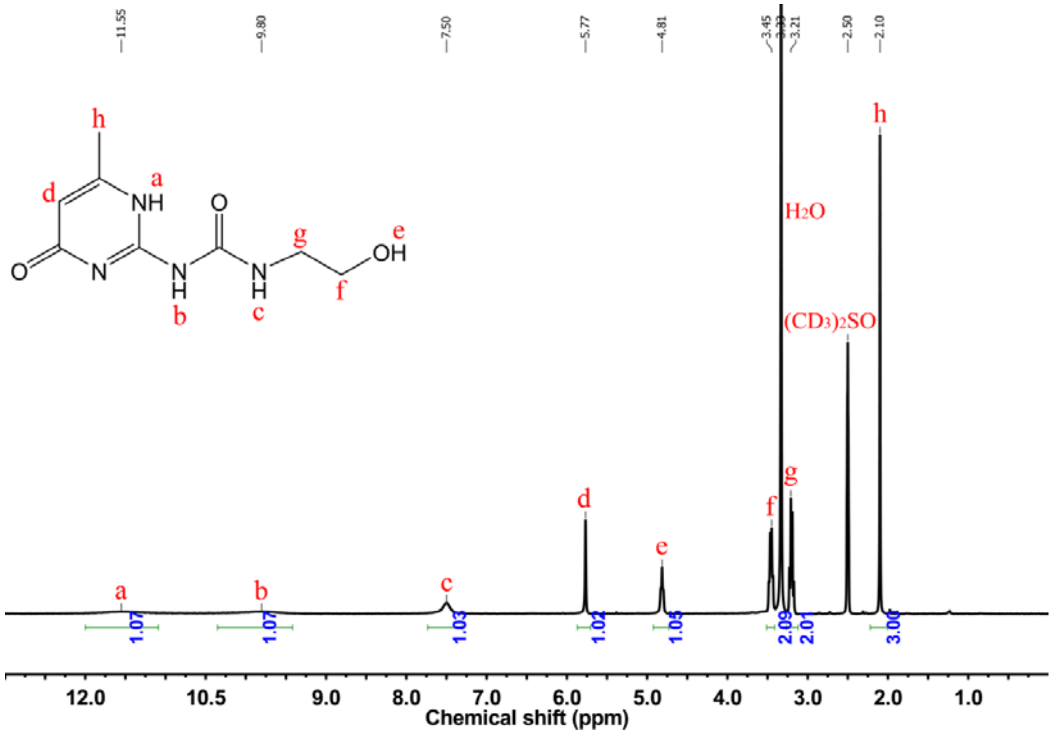


Figure S2. ^{1}H NMR spectrum of compound **3** in DMSO-d_6.

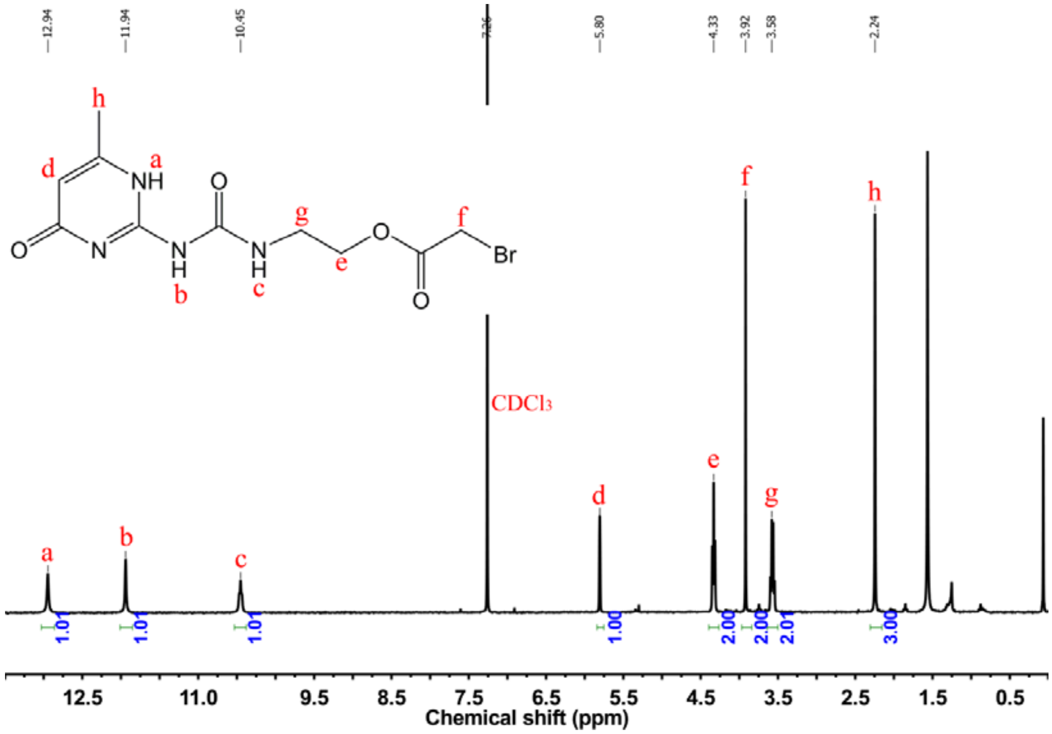


Figure S3. ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

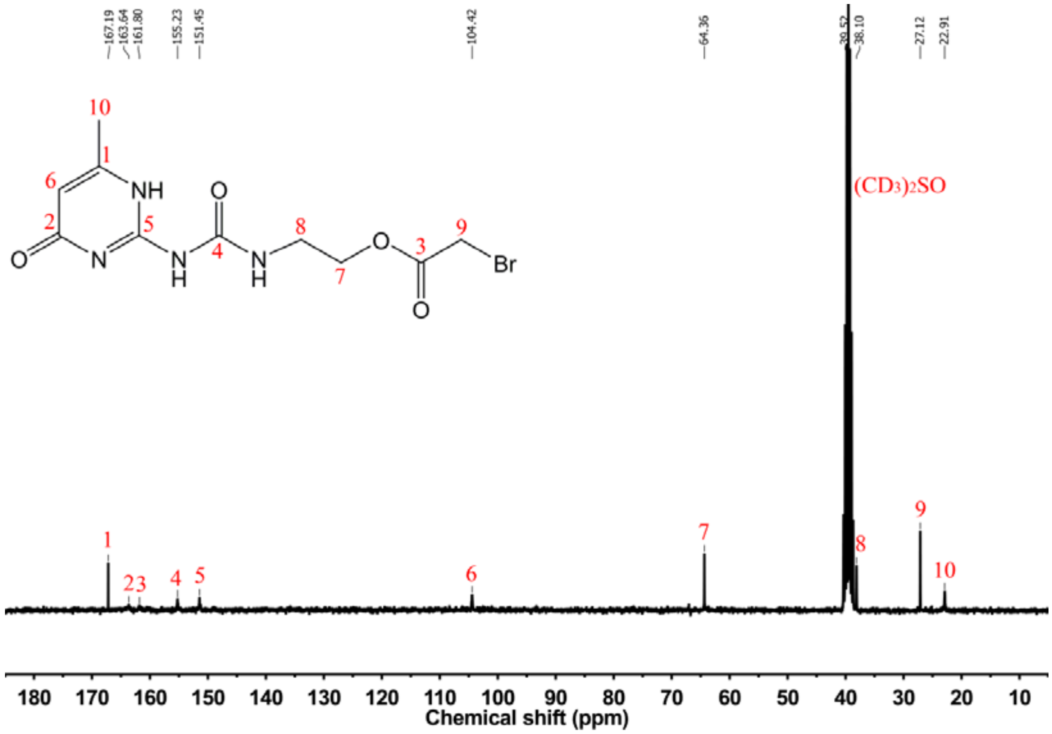


Figure S4. ^{13}C NMR spectrum of compound **4** in DMSO-d_6.

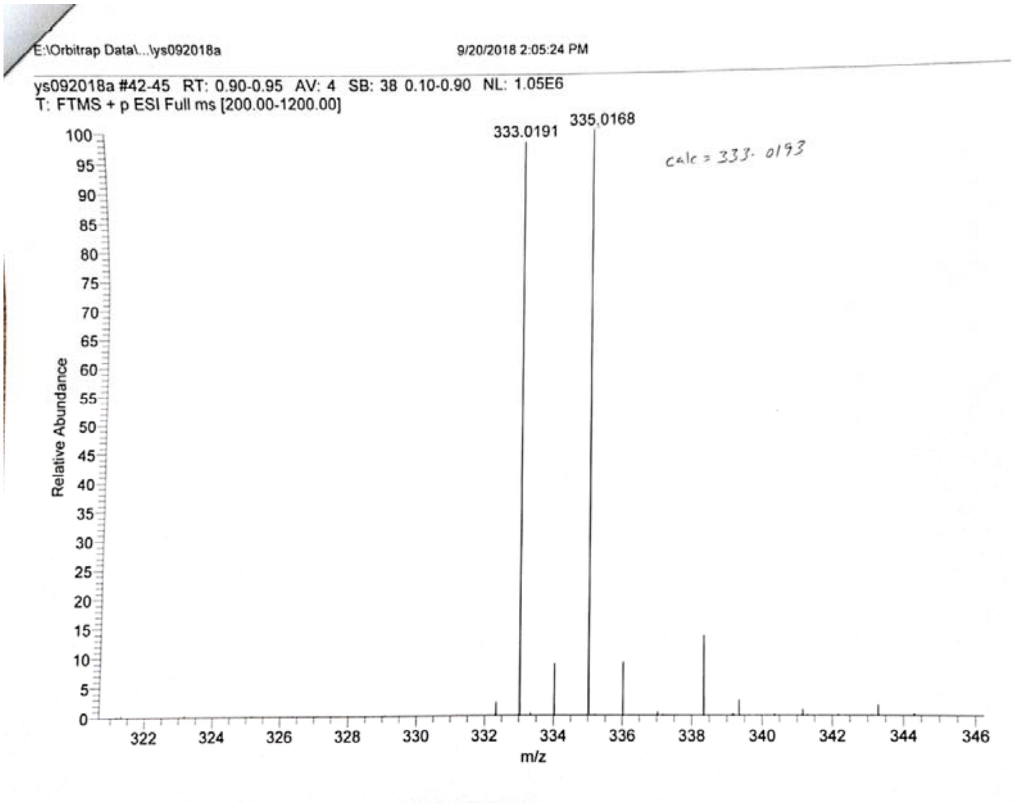


Figure S5. HR-ESI-MS spectrum of compound **4**.

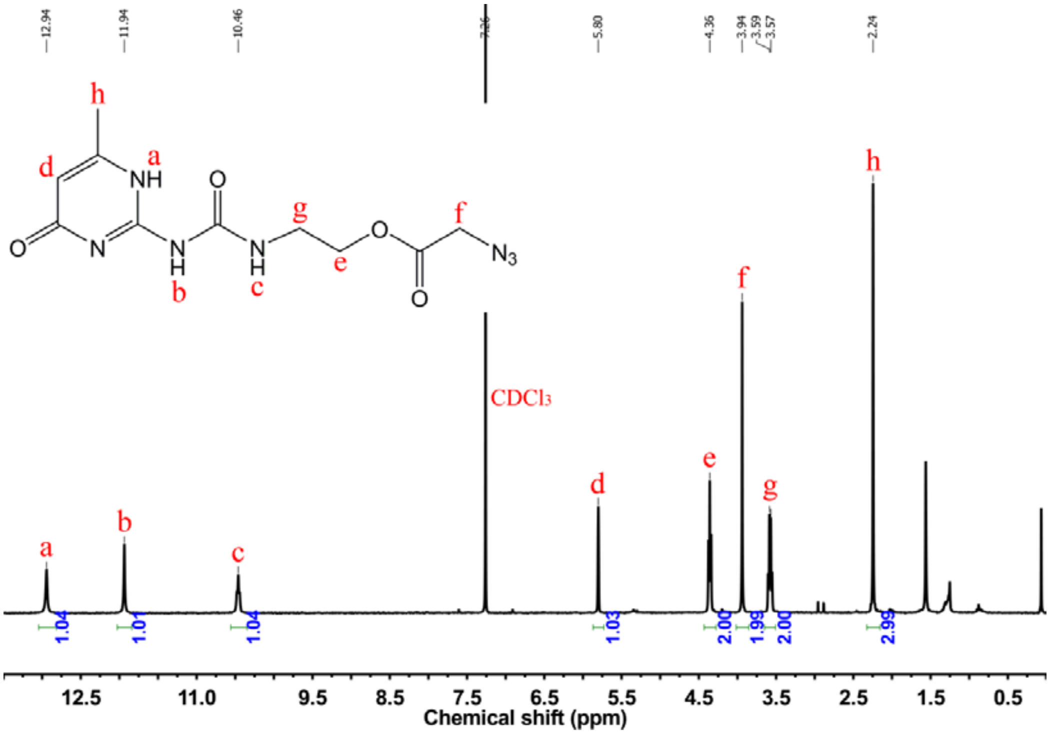


Figure S6. ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

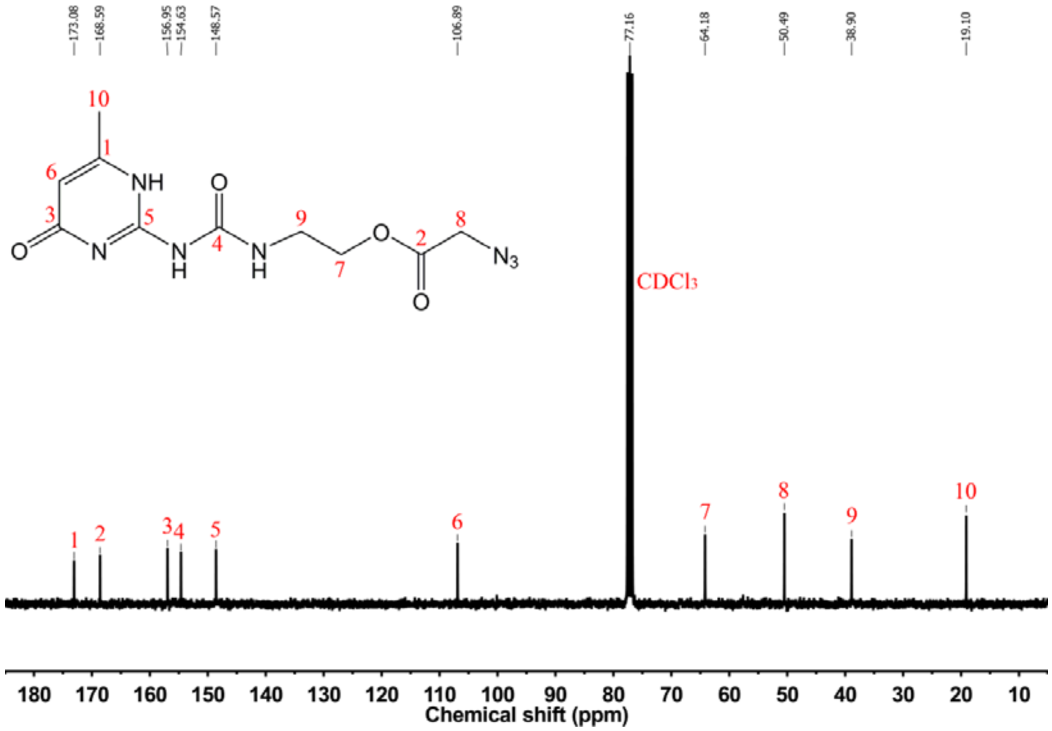


Figure S7. ^{13}C NMR spectrum of compound **5** in CDCl₃.

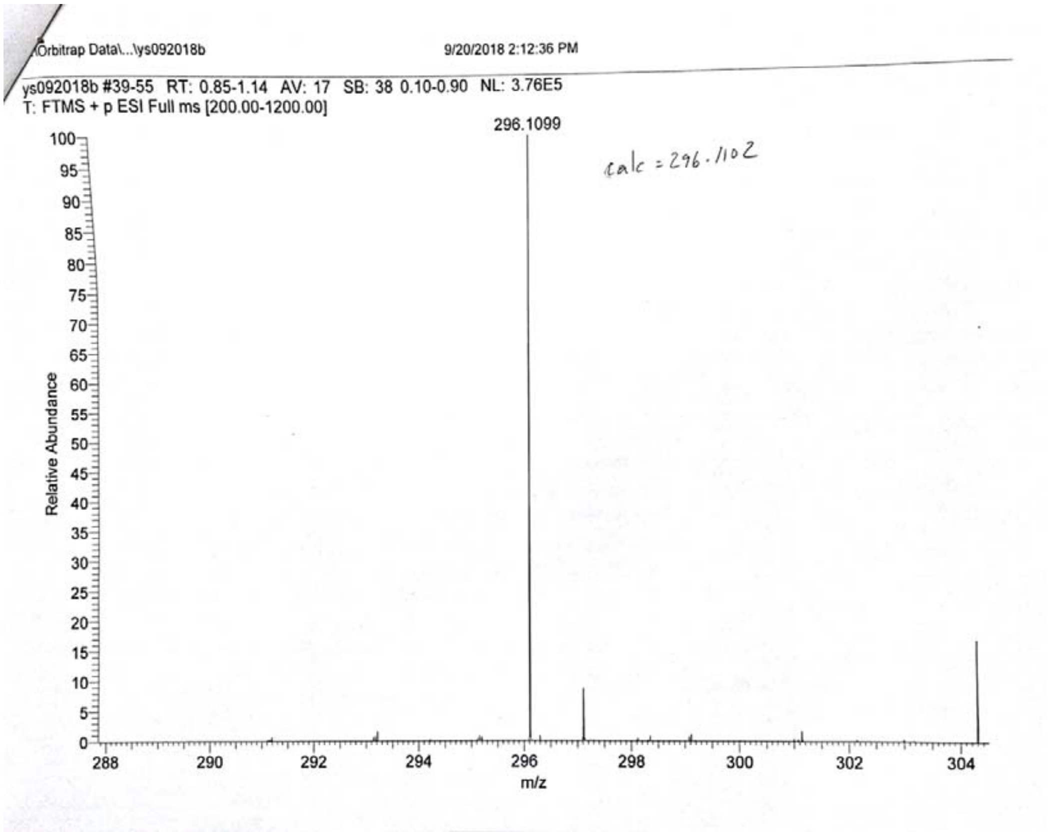


Figure S8. HR-ESI-MS spectrum of compound **5**.

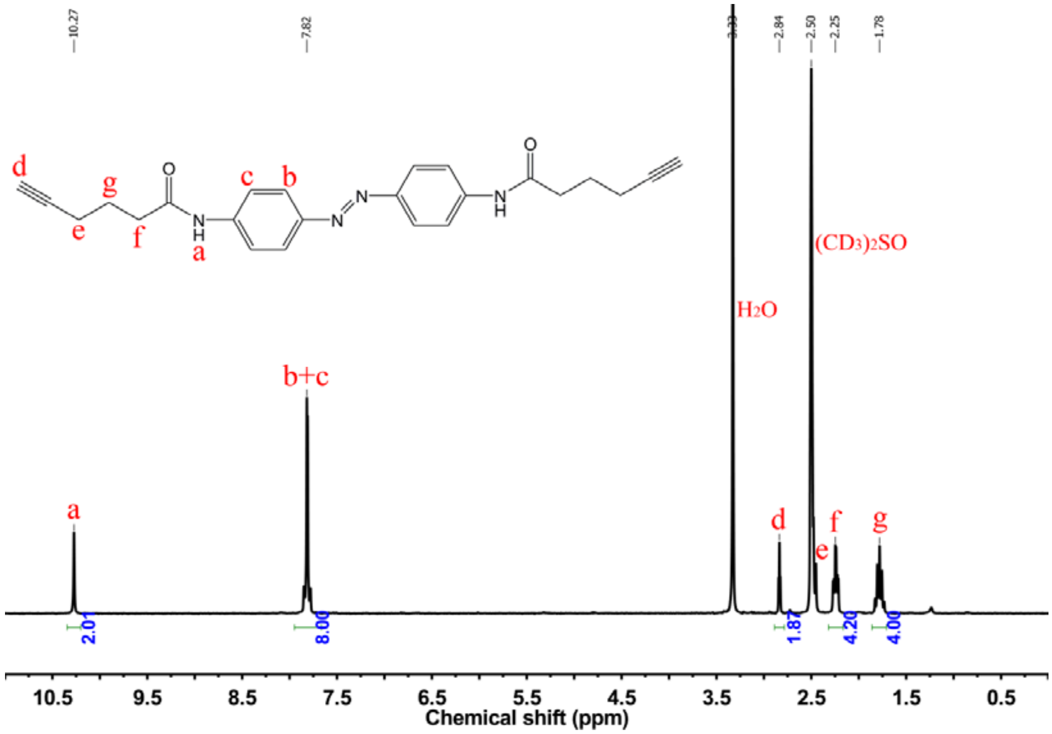


Figure S9. ^{1}H NMR spectrum of compound **6** in DMSO-d_6.

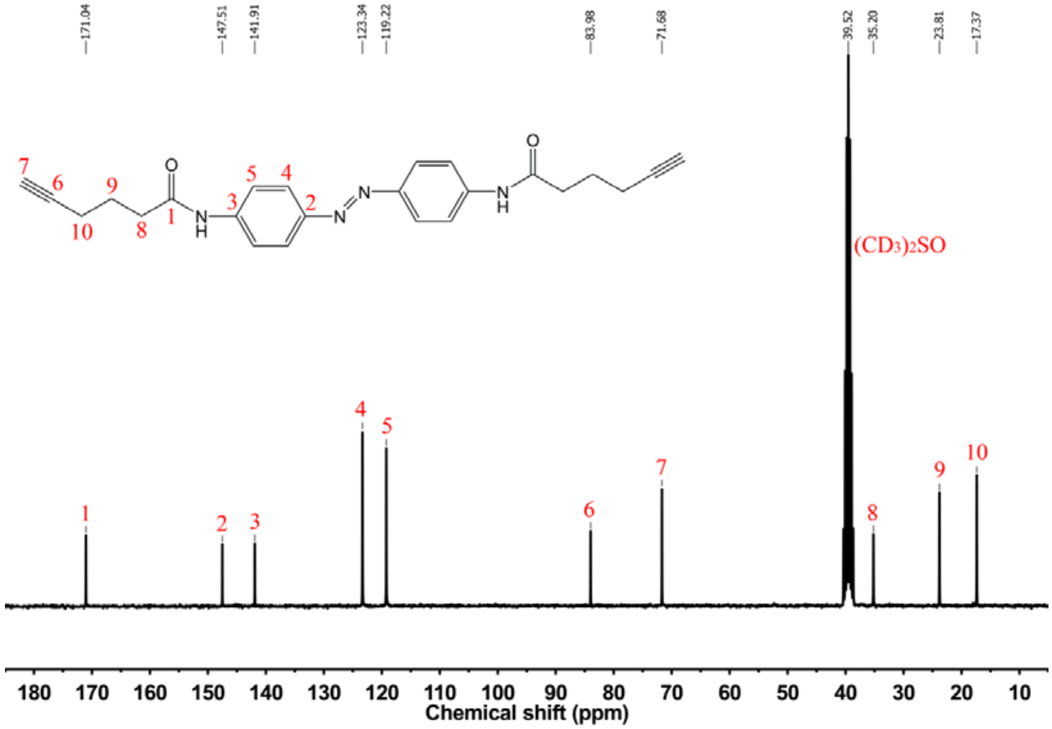


Figure S10. ^{13}C NMR spectrum of compound **6** in DMSO-d_6.

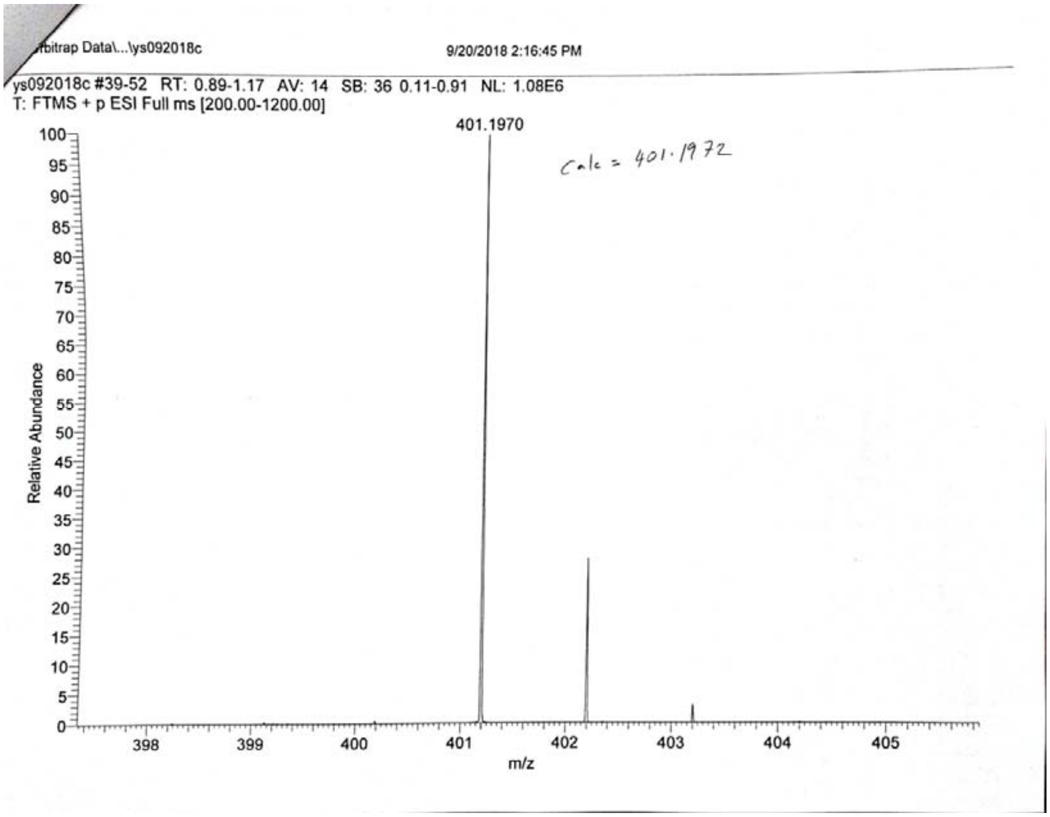


Figure S11. HR-ESI-MS spectrum of compound **6**.

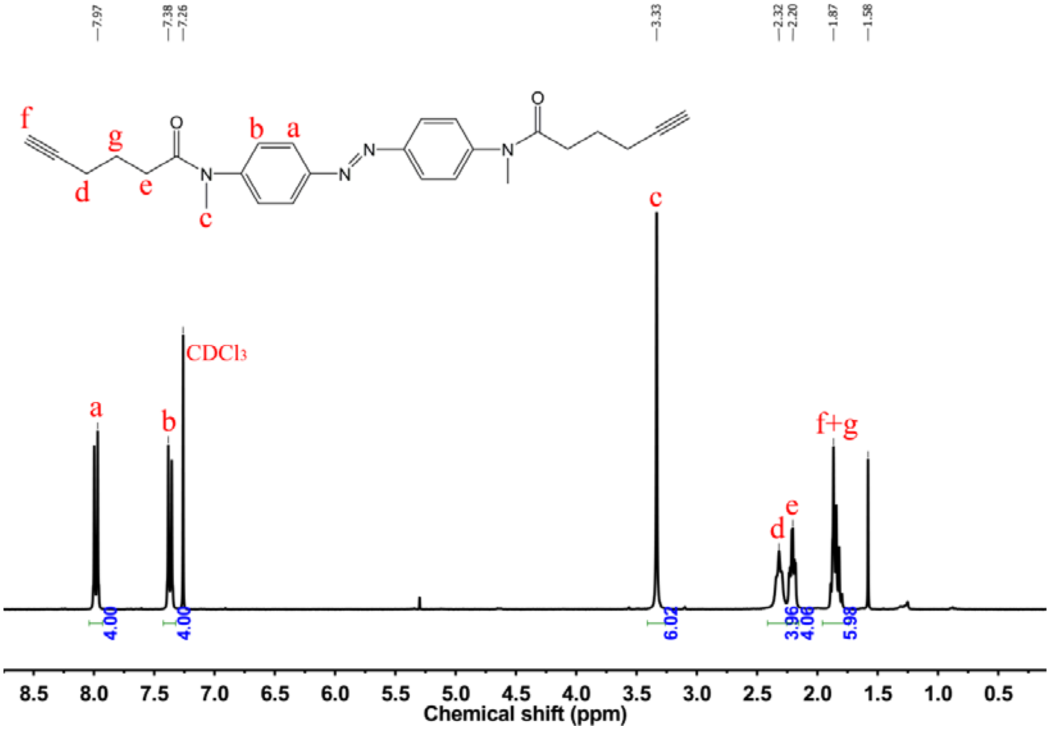


Figure S12. ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

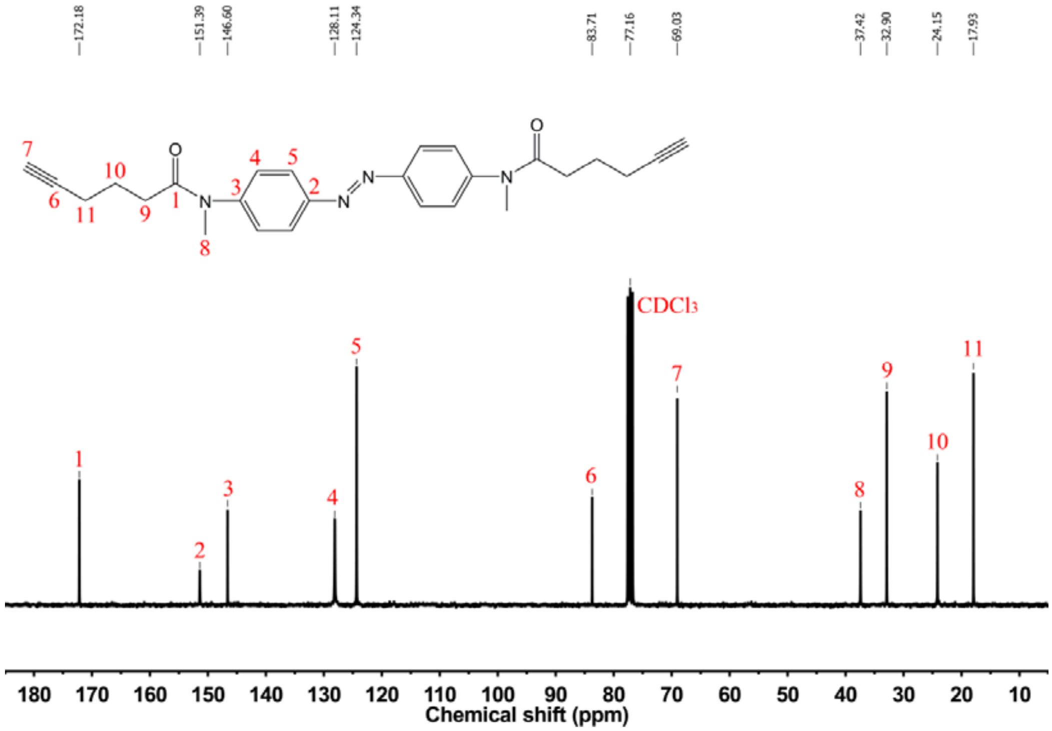


Figure S13. ^{13}C NMR spectrum of compound **7** in $CDCl_3$.

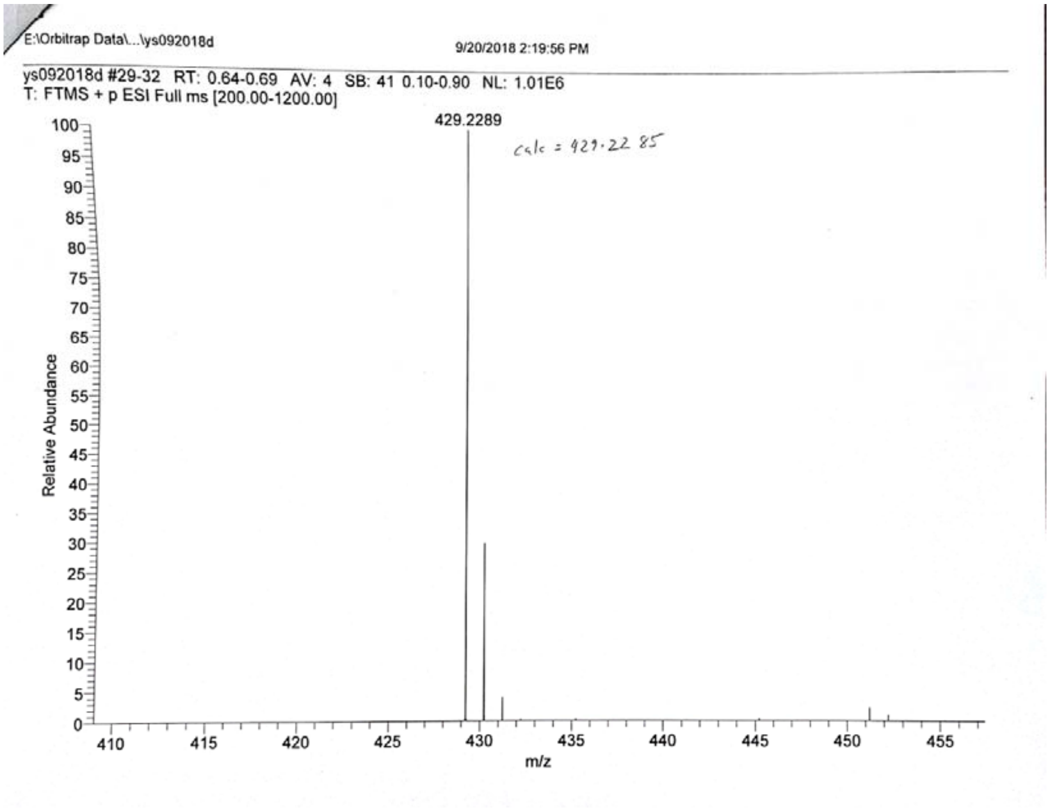


Figure S14. HR-ESI-MS spectrum of compound **7**.

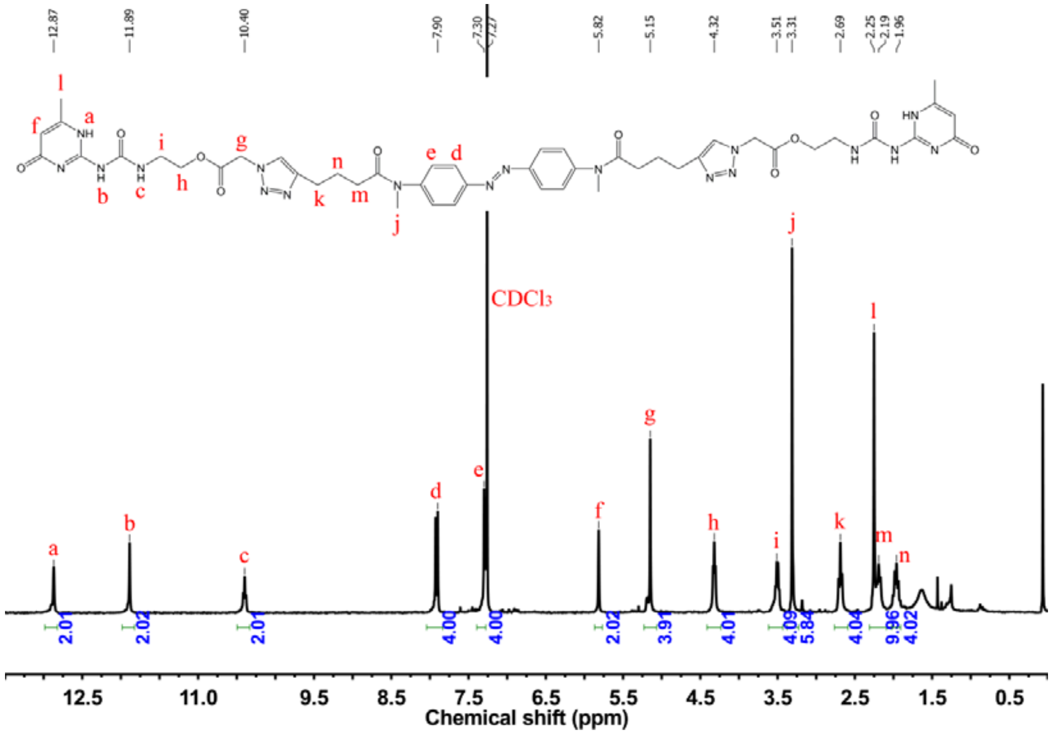


Figure S15. ^{1}H NMR spectrum of monomer (*E*)-**1** in CDCl$_3$.

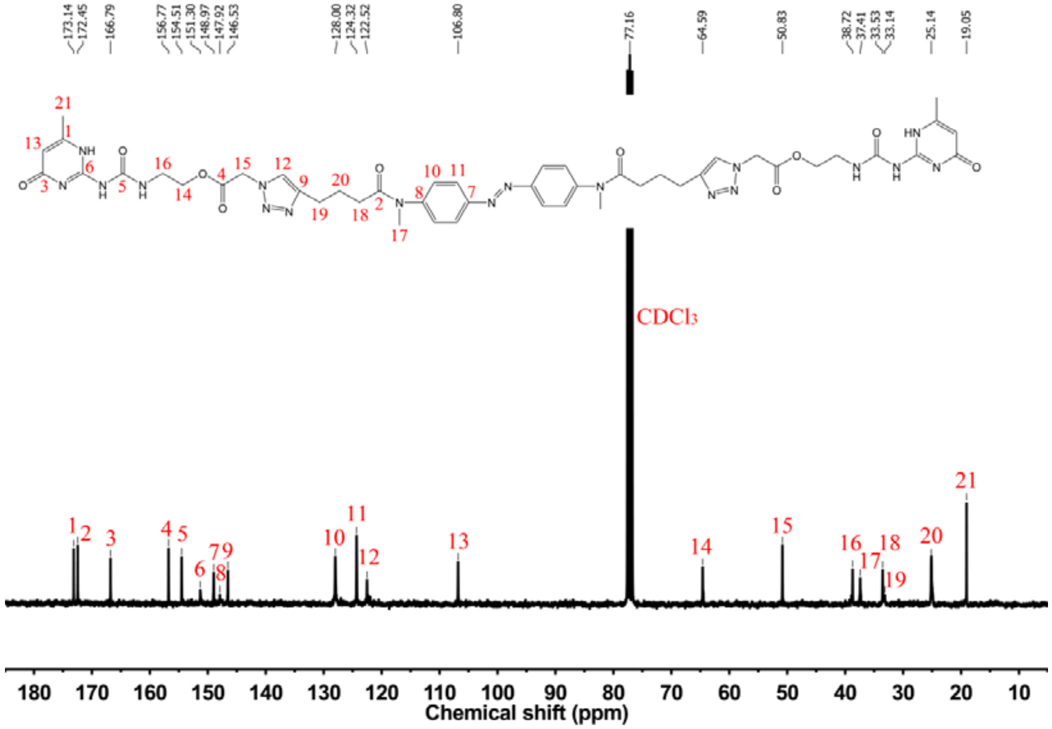


Figure S16. ^{13}C NMR spectrum of monomer (*E*)-**1** in CDCl$_3$.

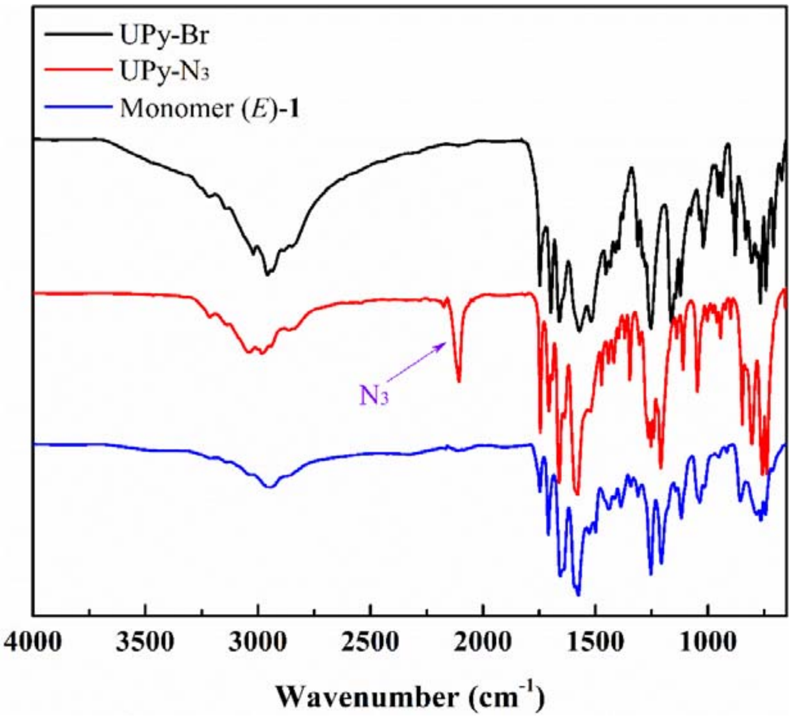
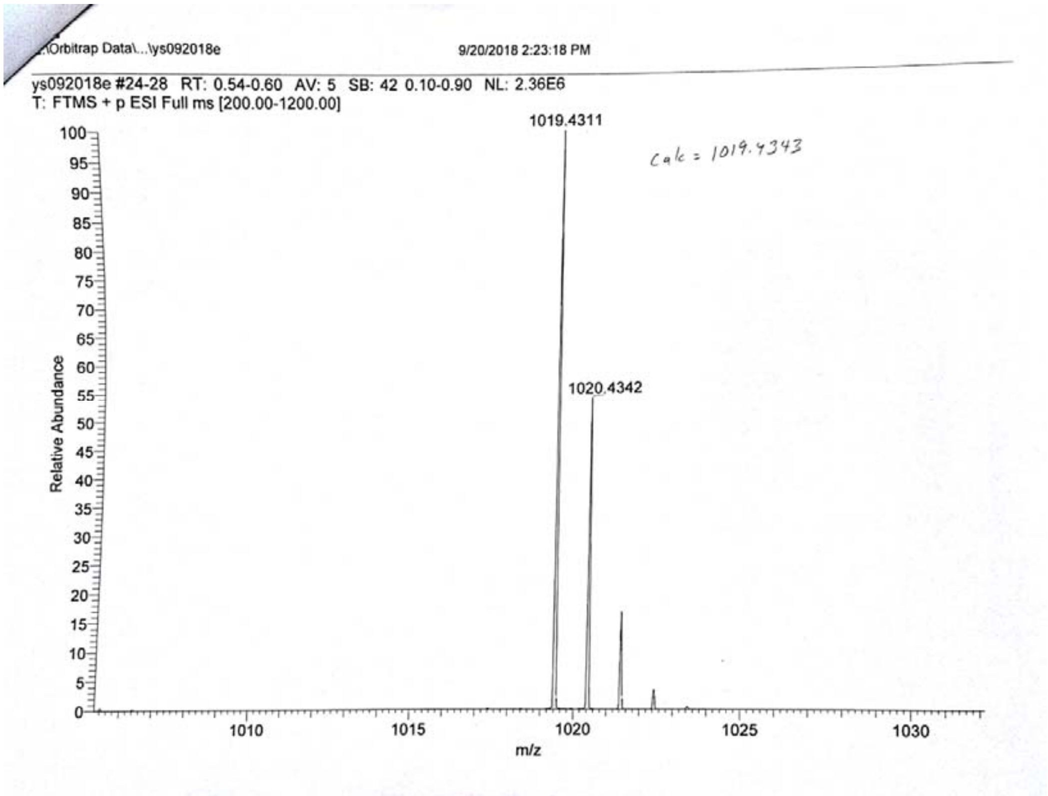


Figure S17. FTIR spectra of UPy-Br, UPy-N$_3$ and monomer (*E*)-**1**.



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T: FTMS + p ESI Full ms [200.00-1200.00]
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Figure S18. HR-ESI-MS spectrum of monomer (*E*)-**1**.

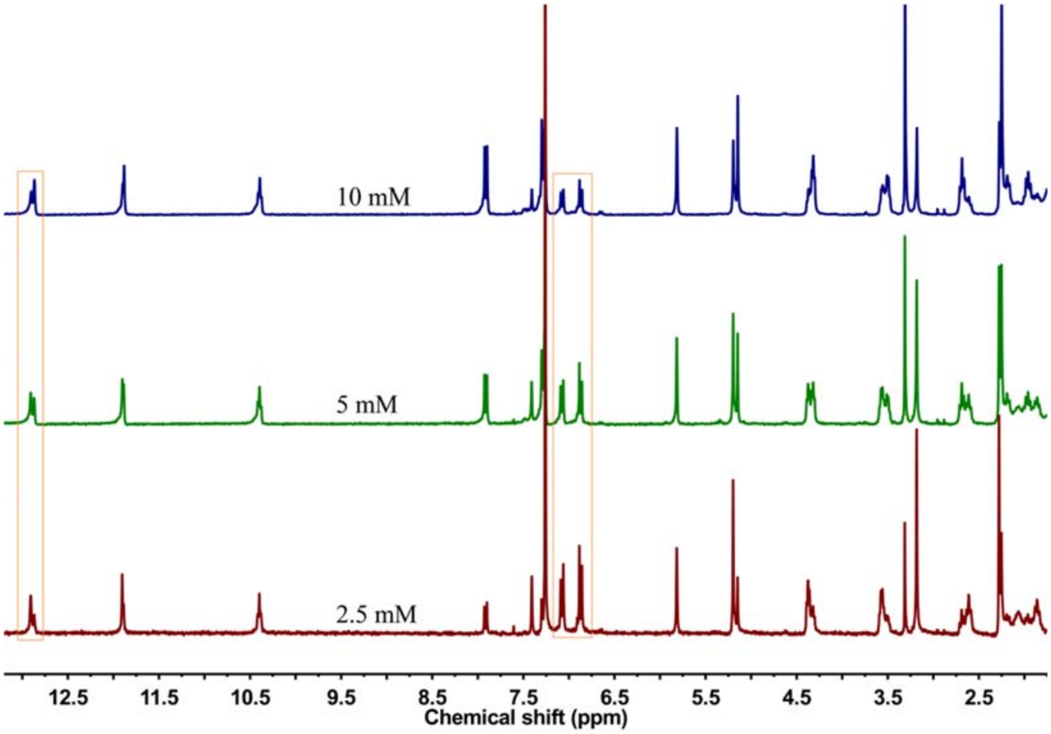

Figure S19. ^{1}H NMR spectra of (*E*)-**1** in $CDCl_3$ with different concentrations after irradiated with 380 nm UV light for 3 min.

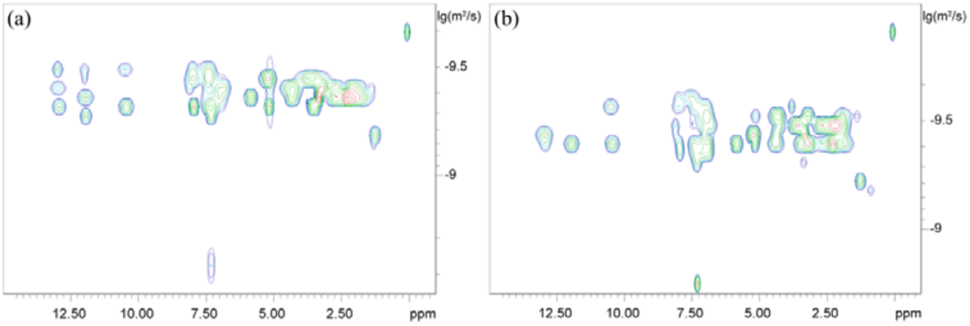

Figure S20. DOSY spectra of (a) solution (*E*)-**1** (20 mM) and (b) the solution of (*E*)-**1** (20 mM) after irradiated with 380 nm UV light for 20 min.

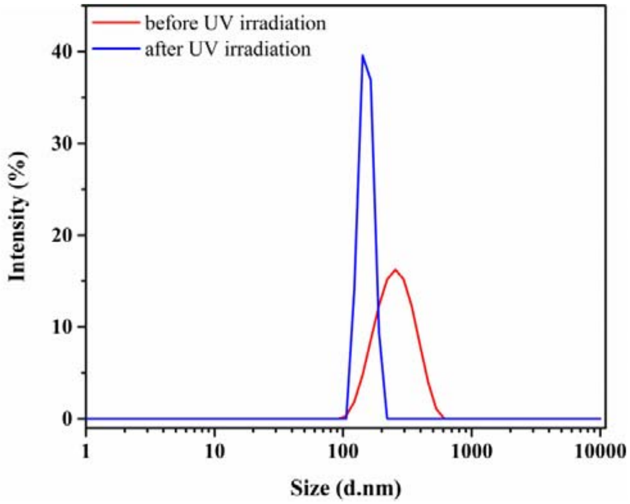

Figure S21. DLS plots of (*E*)-**1** in chloroform (2.5 mM) and after irradiated with 380 nm UV light for 30 min.

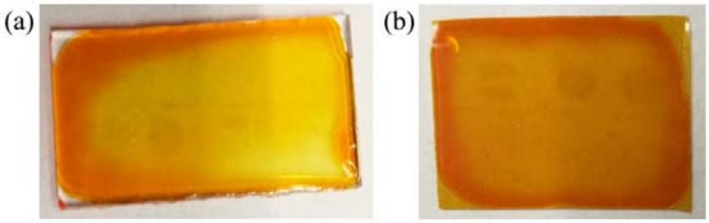

Figure S22. Photographs of supramolecular polymer films on (a) the glass slide and (b) polyimide film.

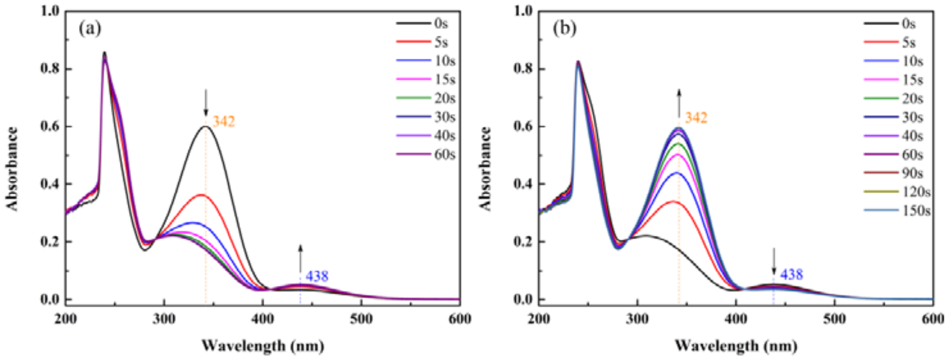

Figure S23. UV-vis spectral changes in dependence of time for the solution of (*E*)-**1** in chloroform (50 μM) at 25 ^{o}C: (a) upon irradiation with 380 nm UV light and (b) upon irradiating the solution at the photostationary state with 450 nm visible light.

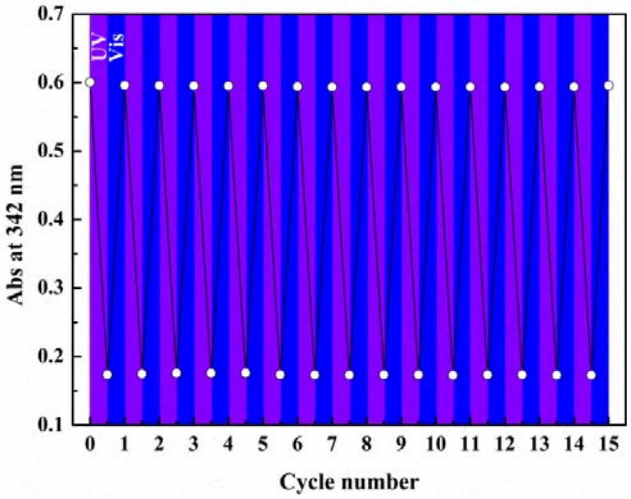

Figure S24. Absorption changes under alternating UV irradiation (380 nm, 40s) and subsequent visible light irradiation (450 nm, 90s).

References:

1. Wong CH, Chow HF, Hui SK, and Sze KH. *Org. Lett.* 2006, **8**, 1811-1814.

2. Feldman KE, Kade MJ, de Greef TFA, Meijer EW, Kramer EJ, and Hawker CJ. *Macromolecules* 2008, **41**, 4694-4700.