# Supporting Information

## Photoresponsive supramolecular polymers synthesized by olefin

### metathesis polymerization from supramonomers

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1. Materials and methods

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Compound S5 was synthesized according to the literature procedure.<sup>1</sup> NMR spectra were obtained using a JOEL JNM-ECA 400 spectrometer. UV-vis spectra were measured using a HITACHI U-3010 spectrophotometer (path length 10.0 mm). Viscosity measurements were carried out with a micro-Ubbelohde dilution viscometer. The photo reactions were carried out by using a high-pressure Hg lamp (500 W). Dynamic light scattering (DLS) measurements were performed on a DynaPro NanoStar (Wyatt Technology) with a gallium-arsenide diode laser of 658 nm emission.

2. Calculation of degree of polymerization and molecular weight of supramolecular polymers

The molecular weights of supramolecular polymers were calculated from the diffusion coefficient measured by DOSY. DOSY experiment of the supramonomer (VB-UPy, 50 mM) was firstly carried out and a diffusion coefficient of  $D_A = 5.7 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$  was obtained. The average degree of polymerization (DP) of supramolecular polymers can therefore be estimated using following equation:

$$\mathrm{DP} = (D_A/D)^3$$

where D is the diffusion coefficient for the sample of supramolecular polymer measured by DOSY. The molecular weight then can be calculated from DP.

### 3. Experimental section

### Synthesis of monomer VB-UPy



Scheme S1. Synthesis of monomer VB-UPy.

A solution of S1 (0.90 g, 6.0 mmol), 1,2-dibromoethane (5.2 mL, 11.3 g, 60 mmol), and excess K<sub>2</sub>CO<sub>3</sub> in 150 mL acetone was heat at reflux for 3 days. After the reaction was completed, the solvent was evaporated under reduced press. 150 mL of CH<sub>2</sub>Cl<sub>2</sub> was added to the resulting solid and then washed with water and brine. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent under reduced pressure and the further purification was carried out by column chromatography using petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> (5/1) as eluent to afford 0.92 g of S2. Yield: 60%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  6.98 (s, 1H), 6.92 (m, 2H), 6.66 (dd, 1H, *J* = 17.6 Hz, *J* = 10.8 Hz), 5.65 (d, 1H, *J* = 17.6 Hz), 5.19 (d, 1H, *J* = 10.8 Hz), 4.33 (t, 2H, *J* = 6.8 Hz), 3.90 (s, 3H), 3.65 (t, 2H, *J* = 6.8 Hz).



A solution of S2 (0.92 g, 3.6 mmol) and potassium phthalimide (1.33 g, 7.2 mmol) in 15 mL DMF was heated at 50 °C overnight. After the reaction was completed, 120 mL of brine was added to the solution and then extracted with EtOAc (50 mL, 4 times). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent under reduced pressure and the further purification was carried out by column chromatography using CH<sub>2</sub>Cl<sub>2</sub> as eluent to afford 0.93 g of S3. Yield: 80%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.86 (m, 2H), 7.72 (m, 2H), 6.89 (m, 3H), 6.62 (dd, 1H, *J* = 17.6 Hz, *J* = 10.8 Hz), 5.61 (d, 1H, *J* = 17.6 Hz), 5.15 (d, 1H, *J* = 10.8 Hz), 4.28 (t, 2H, *J* = 6.4 Hz), 4.12 (t, 2H, *J* = 6.4 Hz), 3.78 (s, 3H).



To a solution of S3 (0.93 g, 2.9 mmol) in  $CH_2Cl_2$  (50 mL) and  $CH_3OH$  (50 mL) under Ar atmosphere, hydrazine monohydrate (2.0 mL, 2.0 g, 40 mmol) was added and the mixture was heated at 60 °C overnight. After evaporation, the mixture was dissolved in 80 mL 15% aqueous NaOH and then extracted with  $CH_2Cl_2$  (40 mL, 4 times). The combined organic phase was washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure to afford 0.50 g of S4. Yield: 90%.

To a solution of S4 (0.50 g, 2.6 mmol) in 60 mL dry CH<sub>2</sub>Cl<sub>2</sub> was added S5 (1.18 g, 3.9 mmol), then the mixture was stirred at room temperature for 5 h. After the reaction was completed, the resulting mixture was washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent under reduced pressure and further purification was carried out by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (200/1 to 200/3, v/v) as eluent to afford 0.91 g of final product as a yellow powder. Yield: 82%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  13.13 (br, 1H), 12.02 (br, 1H), 10.50 (br, 1H), 6.95 (s, 1H), 6.92 (s, 2H), 6.64 (dd, 1H, *J* = 17.6 Hz, *J* = 10.8 Hz), 5.80 (s, 1H), 5.62 (d, 1H, *J* = 17.6 Hz), 5.15 (d, 1H, *J* = 10.8 Hz), 4.19 (t, 2H, *J* = 6.4 Hz), 3.85 (s, 3H), 3.72 (q, 2H, *J* = 6.0 Hz), 2.31 (m, 1H), 1.63 (m, 4H), 1.25 (m, 4H), 0.90 (m, 6H). HR-ESI-MS: calculated for [M + Na]<sup>+</sup> C<sub>23</sub>H<sub>32</sub>N<sub>4</sub>O<sub>4</sub>Na<sup>+</sup>: 451.2321; measured: 451.2309; error: 2.7 ppm.



Olefin metathesis of supramonomer



Scheme S2. Olefin metathesis of compound VB-UPy.

The supramolecular polymer was prepared by olefin metathesis of the supramonomer (VB-UPy dimer). Typically, a  $1,2-C_2H_4Cl_2$  solution of VB-UPy (50 mM) and Hoveyda-Grubbs II catalyst (5 mol%) was heated at 55 °C under Ar atmosphere for 24 h. The supramolecular polymer was formed in situ when the reaction was completed.

4. <sup>1</sup>H NMR spectra of supramonomer at various temperatures



Figure S1. Partial  ${}^{1}$ H NMR spectra of VB-UPy (50 mM) at 298 K (down) and 333 K (up), CDCl<sub>3</sub>, 400 MHz.

5. Mass spectra of the supramonomer.



Figure S2. HR-ESI-MS of the supramonomer.

6. UV-vis spectra of ST-dUPy and ST-dUPy after UV light irradiation



Figure S3. UV-vis spectra of ST-dUPy (black) and ST-dUPy after UV light irradiation (red), concentration 5  $\mu$ M.

7. DLS measurements of *E*-ST-dUPy at different concentrations.



Figure S4. DLS measurements of *E*-ST-dUPy at 5 mM and 25 mM.

8. DLS measurements of the supramolecular polymers.



Figure S5. DLS measurements of (1) *E*-ST-dUPy (25 mM) and (2) after irradiation with UV light for 0.5 h (3) after addition of 5 mol% Hoveyda-Grubbs II catalyst for 24h.

9. DOSY spectra of the supramolecular polymers.



Figure S6. DOSY spectrum of E-ST-dUPy (25 mM). (1)



Figure S7. DOSY spectrum of (1) after irradiation with UV light for 0.5 h. (2)



Figure S8. DOSY spectrum of (2) after addition of 5 mol% Hoveyda-Grubbs II catalyst for 24h. (3)

Reference

1. H. M. Keizer, R. P. Sijbesma and E. W. Meijer, Eur. J. Org. Chem., 2004, 2553.