Electronic Supplementary Information

Visible-Light Responsive Hydrogen-Bonded Supramolecular Polymers Based on *ortho*-Tetrafluorinated Azobenzene

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Compound 3. The solution of CF₃COOEt (1.15 g, 8.07 mmol) in 30 mL CH₂Cl₂ was added dropwise to the solution of compound 2 (0.589 g, 7.96 mmol) in 30 mL CH₂Cl₂ via 1 hours at 0 °C. The resulting mixture was further stirred at room temperature until the reaction was completed. The solvent was evaporated under vacuum and the residue was dissolved in 60 mL CH₂Cl₂, to which 6 mL of CH₂Cl₂ solution that containing Boc₂O (1.77 g, 8.10 mmol) was added dropwise through a dropping funnel, and the resulting mixture was further stirred at room temperature for another 1 hours. After the reaction was completed (monitored by TLC), 50 mL ethyl acetate was added to quench the reaction. The reaction solution was first washed by saturated sodium bicarbonate, and then extracted with ethyl acetate (30 mL \times 3), the organic phase was combined and washed by brine and dried with anhydrous Na₂SO₄. The solution was concentrated after removing the desiccant, and the residue was purified by flash column chromatography with an eluent of $CH_2Cl_2/CH_3OH = 10/1$, compound 3 was obtained as white solid (1.50 g, 69%). ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm): 7.98/6.76 (s, 1H), 3.49 (s, 2H), 3.48 (s, 2H), 2.90 (s, 3H), 1.46 (s, 9H). MS (ESI) m/z: 271.1 [M+H]+.

Compound 4. Compound **3** (1.00 g, 3.70 mmol) was dissolved in 14.4 mL CH₃OH, to which 1.60 mL H₂O and K₂CO₃ (0.326 g, 2.36 mmol) were added successively. The resulting mixture was refluxed for 4 hours. Cooling down and the solvent was evaporated and the residue was further extracted with CH₂Cl₂ (20 mL × 3), the combined organic phase was washed by water and brine successively, and then dried with anhydrous Na₂SO₄. After removing of solvent and desiccant, the residue was purified by flash column chromatography with an eluent of CH₂Cl₂/CH₃OH = 20/1. Compound **4** can be isolated as red oil (0.257 g, 40%). ¹H NMR (600 MHz, CDCl₃, 298K) δ (ppm): 3.23 (br, 2H), 2.84 (br, 3H), 2.78 (t, *J* = 6.6 Hz, 2H), 1.41 (s, 9H). MS (ESI) *m/z*: 175.1 [M+H]⁺.

Compound 6. Compound 4 (0.170 g, 0.977 mmol) and 5 (0.267 g, 0.882 mmol) were

dissolved in 3 mL CHCl₃, the resulting solution was stirred at room temperature for 4 hours. Then 10 mL CHCl₃ was added to quench the reaction, and the resulting mixture was washed successively by 10 mL diluted HCl (1M), saturated sodium bicarbonate and brine, and the organic phase was dried with anhydrous Na₂SO₄. After removing the solvent and desiccant, the residue was stirred in CH₃OH for 20 min, the mixture was filtrated and the precipitate was collected, which was further purified by flash column chromatography with an eluent of CH₂Cl₂/CH₃OH = 80/1. Compound **6** can be isolated as a white solid (0.217 g, 60%). ¹H NMR (400 MHz, CDCl₃, 298K) δ (ppm): 13.17 (s, 1H), 11.95/11.92 (s, 1H), 10.35/10.30 (s, 1H), 5.77 (s, 1H), 3.40 (br, 4H), 2.89 (s, 3H), 2.32-2.20 (m, 1H), 1.69-1.47 (m, 3H), 1.40 (s, 9H), 1.33-1.18 (m, 4H), 0.89-0.83 (m, 6H). ¹³C NMR (150 MHz, CDCl₃, 298K) δ (ppm): 173.0, 156.9, 155.7, 155.4, 154.8, 106.4, 106.2, 79.3, 79.1, 48.1, 48.0, 45.4, 37.9, 37.8, 35.1, 34.5, 32.9, 29.3, 28.3, 26.6, 22.5, 13.9, 11.7. MS (ESI) *m/z*: 410.3 [M+H]⁺. HRMS (ESI) Calcd For C₂₀H₃₆N₅O₄ [M+H]⁺: 410.2762, Found: 410.2748.

Compound 7. Compound **6** (0.142 g, 0.347 mmol) was dissolved in 5 mL CH₂Cl₂, to which 2 mL CF₃COOH was added and the resulting mixture was stirred at room temperature for 1.5 hours. After the reaction was completed, the solvent was evaporated under vacuum and the residue was dissolved in 10 mL CH₂Cl₂, washed by sodium bicarbonate and brine, and then dried over anhydrous Na₂SO₄. After removing the solvent and desiccant, compound **7** can be obtained as a white solid (0.073 g, 68%). ¹H NMR (600 MHz, CDCl₃, 298K) δ (ppm): 13.05 (br, 1H), 11.95 (s, 1H), 10.19 (br, 1H), 5.80 (s, 1H), 3.48 (q, *J* = 5.4 Hz, 2H), 2.99 (br, 2H), 2.57 (s, 3H), 2.34-2.25 (m, 1H), 1.71-1.50 (m, 4H), 1.36-1.20 (m, 4H), 0.96-0.85 (m, 6H). ¹³C NMR (150 MHz, CDCl₃, 298K) δ (ppm): 173.4, 157.0, 155.8, 154.4, 106.2, 50.0, 45.4, 38.7, 35.1, 32.9, 29.3, 26.6, 22.5, 13.9, 11.7. MS (ESI) *m/z*: 310.3 [M+H]⁺. HRMS (ESI) Calcd For C₁₅H₂₈N₅O₂ [M+H]⁺: 310.2238, Found: 310.2234.

Compound 1. Compound **8** (0.034 g, 0.099 mmol), **PyBOP** (0.104 mg, 0.200 mmol) and 0.5 mL **DIPEA** were dissolved in 5 mL DMF, the resulting mixture was stirred at

room temperature for 10 min. Compound 7 (0.071 g, 0.230 mmol) was added and the reaction solution was further stirred for another 4 hours. After quenching by ethyl acetate, the reaction solution was washed by brine (30 mL \times 3) and the organic phase was dried over anhydrous Na₂SO₄. After removing the desiccant and concentrated, the residue was further purified by flash column chromatography with an eluent of $CH_2Cl_2/CH_3OH = 80/1$. The crude compound 1 was collected and washed with hot CH_3OH for twice, the pure compound 1 could be obtained as orange solid (0.046 g, 50%). After filtrating, compound 1 was obtained as an orange solid (0.046 g, 50%). ¹H NMR (600 MHz, DMSO-*d*₆, 298K) δ (ppm): 11.64 (s, 1H), 11.36 (s, 1H), 10.10 (s, 1H), 9.93 (s, 1H), 7.44-7.20 (m, 6H), 5.75 (s, 1H), 5.71 (s, 1H), 3.64-3.58 (m, 2H), 3.50-3.44 (br, 2H), 3.42-3.39 (br, 2H), 3.34-3.30 (br, 2H), 2.27-2.17 (br, 2H), 1.57-1.39 (m, 8H), 1.26-1.05 (m, 8H), 0.81-0.72 (m, 12H). ¹⁹F NMR (564 MHz, DMSO-*d*₆, 298K) δ (ppm): -120.0 (d), -120.2 (d). ¹³C NMR (150 MHz, DMSO-*d*₆, 298K) δ (ppm): 171.3 (br), 167.8, 167.6, 161.4 (br), 155.8, 155.2 (br), 154.1, 152.1 (br), 141.6 (br), 131.2 (t, J = 9.0 Hz), 131.0 (t, J = 9.0 Hz), 112.1 (dd, J = 21.6, 4.5 Hz), 105.7 (br), 50.4, 48.4 (br), 47.2, 37.8, 37.4, 37.0, 33.5, 32.9, 29.5, 29.4, 27.0, 22.6, 14.23, 12.2, 12.1. MS (ESI) *m/z*: 925.5 [M+H]⁺. HRMS (ESI) Calcd For C₄₄H₅₇F₄N₁₂O₆⁺ [M+H]⁺: 925.4455, Found: 925.4446.



Fig. S1 ¹H NMR spectra (600 MHz, DMSO- d_6 /CDCl₃ = 4/1, 2.5 mM, 298K) of a) the mixture solution of 0.1 mL blue light (410 nm)-irradiated CDCl₃ solution of 1 (12.5 mM) and 0.4 mL DMSO- d_6 , and b) the mixture solution of 0.1 mL yellow light ($\lambda > 500$ nm)-irradiated CDCl₃ solution of 1 (2.5 mM) and 0.4 mL DMSO- d_6 .



Fig. S2 ¹H NMR spectra (600 MHz, DMSO- d_6 /CDCl₃ = 4/1, 10 mM, 298K) of a) the mixture solution of 0.1 mL blue light (410 nm)-irradiated CDCl₃ solution of **1** (50 mM) and 0.4 mL DMSO- d_6 , and b) the mixture solution of 0.1 mL yellow light ($\lambda > 500$ nm)-irradiated CDCl₃ solution of **1** (50 mM) and 0.4 mL DMSO- d_6 .



Fig. S3 (a) UV/Vis absorption spectra and (b) plot of corresponding absorption at 461 nm of 1 (0.1 mM in CHCl₃) upon the alternating irradiation by a blue light ($\lambda = 410$ nm, 23 W/m²) for 10 min, and a yellow light ($\lambda > 500$ nm, 221 W/m²) for 20 min at room temperature.



Fig. S4 (a) Time lapse absorption spectra of light ($\lambda > 500 \text{ nm}$)-irradiated **1** (0.1 mM) in CHCl₃ at room temperature under dark; (b) plot of change in absorption A_{417 nm} versus the recording time.



Fig. S5 The high-resolution ESI-MS spectrum of (Z)-1 dimer.



Fig. S6 The dilution ¹H NMR spectra (600 MHz, CDCl₃, 298K) of 1: a) 3.2 mM; b) 12.5 mM; c) 25 mM; and d) 50 mM. The solution was irradiated with blue light ($\lambda = 410$ nm, 23 W/m²) for 20 min before submitting to the NMR spectrometer.



Fig. S7 The dilution ¹H NMR spectra (600 MHz, CDCl₃, 298K) of 1: a) 3.2 mM; b) 12.5 mM; c) 25 mM; and d) 50 mM. The solution was irradiated with yellow light ($\lambda > 500$ nm, 221 W/m²) for 50 min before submitting to the NMR spectrometer.



Fig. S8 ¹H NMR (400 MHz, CDCl₃) spectrum of compound 6.



Fig. S9¹³C NMR (150 MHz, CDCl₃) spectrum of compound 6.



Fig. S11 ¹³C NMR (150 MHz, CDCl₃) spectrum of compound 7.



Fig. S12 ¹H NMR (600 MHz, DMSO-*d*₆) spectrum of compound (*E*)-1. The solution of (*E*)-1 was obtained after the blue light ($\lambda = 410$ nm) irradiated solution of 1 was heated at 65 °C in dark for 3 days.





Fig. S13 ¹⁹F NMR (564 MHz, DMSO- d_6) spectrum of compound (*E*)-1.



Fig. S14 ¹³C NMR (150 MHz, DMSO- d_6) spectrum of compound (*E*)-1.