# Visible Light Enabled para-Fluoro-Thiol Ligation

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# Supporting Information

# 1. Experimental Details

## 1.1. DMAC-SEC

The SEC measurements were conducted on a PSS SECurity system consisting of a PSS SECurity Degasser, PSS SECurity TCC6000 Column Oven (60 °C), PSS GRAM Column Set (8x150 mm 10  $\mu$ m Precolumn, 8x300 mm 10  $\mu$ m Analytical Columns, 1000 Å, 1000 Å and 30 Å) and an Agilent 1260 Infinity Isocratic Pump, Agilent 1260 Infinity Standard Autosampler, Agilent 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 25415 nm, B: 360 nm), Agilent 1260 Infinity Refractive Index Detector (35 °C). HPLC grade DMAc, 0.01 M LiBr, is used as eluent at a flow rate of 1 mL·min<sup>-1</sup>. Narrow disperse linear poly(styrene) (Mn: 202 g·mol<sup>-1</sup> to 2.2×106 g·mol<sup>-1</sup>) standards (PSS ReadyCal) were used as calibrants. All samples were passed over 0.22  $\mu$ m PTFE membrane filters. Molecular weight and dispersity analysis were performed in PSS WinGPC UniChrom software (version 8.2).

## **1.2.**<sup>1</sup>H NMR Measurements

NMR spectra were recorded on a Bruker Avance III 600 MHz with a 5 mm broadband autotunable probe with Z-gradients at 293 K. Chemical shifts are reported as  $\delta$  in parts per million (ppm) and referenced to the chemical shift of the residual solvent resonances (CDCl<sub>3</sub>  $\delta$  = 7.26 ppm), couplings are shown as s: singlet, d: doublet, t: triplet, m: multiplet. Polymer samples were prepared at a concentration of 10 mg mL<sup>-1</sup>. In most spectra traces of water appears as a broad singlet at around 1.5-2.5 ppm. NMR spectra were processed using MestReNova software.

## **1.3.** Mass Spectrometry

Test compounds were infused directly into the MS via a kdScientific infusion pump at a static flow rate of 650  $\mu$ L/h. MS setup was as followed: Agilent 6220 TOF MS system (Santa Clara, CA, USA) with a multimode dual nebuliser ESI/APCI source. The MS was operated in positive or negative mode using the following conditions: nebulizer pressure 35 psi, gas flowrate 8 L/min, gas temperature 300°C, capillary voltage 2500/-2500 V, fragmentor 150 and skimmer 65 V. The instrument was operated in the extended dynamic range mode with data collected in m/z range 100–3200.

## 1.4. UV-VIS Spectroscopy

UV/vis spectra were recorded on a *Shimadzu* UV-2700 spectrophotometer equipped with a CPS-100 electronic temperature control cell positioner. Samples were prepared in THF and measured in *Hellma Analytics* quartz high precision cells with a path length of 10 mm at ambient temperature.

### **1.5.** Rheology Analysis

Rheological experiments were studied using an Anton Paar rheometer (MRC302) with a plateplate configuration. The lower plate is made of quartz and the upper plate is made of stainless steel with a diameter of 25 mm. The LED light source (420 nm, I = 20 mW) was placed underneath the quartz plate. In a typical experiment, 50 µL of a solution of polymer solution (10 mM) in THF was placed on the lower plate and the upper plate was brought to a measurement gap of 0.5 mm. The test was started by applying a 0.1% strain with the frequency of 1.5 Hz on the sample, and the light was turned at predetermined interval.

# 2. Synthetic procedures

### 2.1. General Considerations

Solvents ( $CH_2CI_2$ , diethyl ether, petroleum ether, acetone, tetrahydrofuran, and methanol) were purchased from VWR in HPLC grade and used directly. Monomers (styrene and pentafluorostyrene) were passed through a column of silica gel to remove the inhibitors prior to synthesis. AIBN was recrystallized in toluene and stored in the freezer before use. All other chemicals were purchased from Sigma-Aldrich and used as received.

Thin-layer chromatography (TLC) was performed on silica gel 60 F254 alumina sheets (Merck) and visualized by UV light or potassium permanganate solution. Column chromatography was run on silica gel 60 (0.04-0.06 mm, 230-400 mesh ASTM, Merck).

### Scheme S1. Synthesis of thioxanthone-DBU



### 2.2. Synthesis of thioxanthone-DBU

**Thioxanthone-DBU** was synthesized following a previously published procedure<sup>[1]</sup> with modifications in certain steps as described below. After each step the formation of the intermediates were confirmed by comparing NMR spectral data with the published report.

*3-Nitrophthalic anhydride.* Aqueous ammonia solution 28% (20 mL) was added to 3nitrophthalic anhydride (10 g, 0.05 mol) and the mixture was heated at 85 °C until a clear solution was obtained. The solution was then slowly heated to 290 °C under an air condenser, during that time a yellow solid was formed. The solid was cooled to ambient temperature and used directly in the next synthesis.

2-(1,3-Dioxoisoindolin-4-ylthio)benzoic acid. Thiosalicylic acid (4.5 g, 0.03 mol) was dissolved in warm NaOH solution 1 M (50 mL) and the solution was stirred at 70 °C for 30 min under open air. Ethanol (100 mL) was added to the mixture and the white solid was filtered and dried in a vacuum oven (40 °C) for 5 h. The resultant solid was dissolved in DMF and 3-nitrophthalic anhydride (0.025 mmol) was added. The solution was stirred at 80 °C for 14 h and cooled to ambient temperature. To this solution was added HCl 2 M (100 mL) and the yellow precipitate was filtered, recrystallized from dioxane to give yellow needle product (yield 87%).

*Thiochromeno[2,3-e]isoindole-1,3,6(2H)-trione.* The above product (3 g, 0.01 mol) was suspended in poly(phosphoric acid) (50 g) and the solution was stirred using a mechanical stirred at 150 °C for 2 h. Ice water (200 mL) was then added to the mixture, and the yellow filtrate was collected, washed with excess amount of water and dried in a vacuum oven (40 °C) overnight (yield 91%).

1H-Thioxantheno[4,3-c]furan-1,3,6-trione. The above product (1 g, 3.6 mmol) was suspended in NaOH solution 0.1 M (100 mL) and the mixture was heated at 120 °C under refluxing condition for 2 h. The solution was acidified with concentrated HCl solution (35%) and stirred at 120 °C under refluxing condition for 18 h. After cooling to ambient temperature, the yellow solid was filtered, washed with copious amount of water and dried in a vacuum oven (40 °C) overnight. This product was suspended in a solution of acetic anhydride (20 mL) and xylene (80 mL) and the solution was heated at 150 °C for 2 h. After cooling to ambient temperature, the yellow precipitate was filtered and rinsed with pentane (20 mL x 3), and dried *in vacuo* to give product as yellow powder (yield: 89%).

4-((1,3,6-Trioxothiochromeno[2,3-e]isoindol-2(1H,3H,6H)-yl)-methyl)cyclohexanecarboxylic acid. The above product (0.7 g, 2.5 mmol) and trans-4-(aminomethyl)-cyclohexanecarboxylic acid (0.39 g, 2.5 mmol) were dissolved in acetic acid (20 mL) and the solution was heated at 120 °C under refluxing condition for 3 h. The reaction mixture was cooled to ambient temperature and poured into ice-cooled water (100 mL). The yellow crystalline product was filtered, washed with water (100 mL x 2) and dried in vacuo to give product was yellow crystal (yield 93%).

*Thioxanthone-DBU*. The above product (0.84 mg, 2 mmol) was dissolved in dioxane (10 mL) and a solution of DBU (5 mmol) in dioxane (10 mL) was added dropwise. The solution was stirred for 24 h and dioxane was concentrated in vacuo. The residue was purified by column chromatography running on ethylacetate to give product as yellow powder (yield 96%). <sup>1</sup>H NMR (600M Hz, CD<sub>3</sub>OD,  $\delta$ /ppm): 8.81-8.82 (d, 7.86), 8.47-8.49 (d, 7.88), 7.8-7.82 (d, 7.89), 7.74-7.76 (m), 7.56-7.59 (m), 3.61-3.63 (d, 9.59), 3.54-3.56 (m), 3.35-3.37 (t, 5.73), 2.68-2.7 (d, 10.37), 2.03-2.13 (m), 1.95-2 (dd, 3.52, 10.52), 1.71-1.84 (m), 1.41-1.45 (m), 1.08-1.11 (m). ESI-MS (negative mode, M<sup>-</sup>) measured: 420.0905, calculated: 420.0911; (positive mode, M + H<sup>+</sup>) measured: 153.138, calculated: 153.14).



Figure S1 <sup>1</sup>H NMR spectrum of thioxanthone-DBU (CD<sub>3</sub>OD, 600 MHz)

 $hv (\lambda = 420 \text{ nm})$ 



Before irradiation in THF (0.1 mM), pH ~ 8



After irradiation in THF (0.1 mM), pH ~ 11

**Figure S2.** Set up for the photo-uncaging of thioxanthone-DBU, after photoirradiation of the solution, pH was found to increase from 8 to 11. The release of the  $CO_2$  was also observed and caused a decrease in the pH (from 7 to 5) of the aqueous solution on the right side.



**Figure S3.** <sup>1</sup>H NMR spectra of thioxanthone-DBU before (**a**) and after (**b**) irradiation with blue light (420 nm), and **c)** pure DBU (CD<sub>3</sub>OD, 600 MHz).



Figure S4. UV-Vis absorption spectra of DBU and thioxanthone-DBU post-irradiation.



**Figure S5.** Mass spectrometry of the thioxanthone-DBU solution after blue light (420 nm) irradiation, showing the presence of the DBU peak.

### 2.3 General procedure for the light-induced PFTR of small molecules.

Thiol compounds (1.05 mmol), thioxanthone-DBU (1.1 mmol) and pentafluorobenzyl precursors (1 mmol) were dissolved in THF (10 mL) and the solution was irradiated with blue light (420 nm) for 2 h under stirring and at ambient temperature. The solution was then concentrated *in vacuo* and purified by flash column chromatography, eluting with  $CH_2CI_2$  to give product.



Figure S6. <sup>1</sup>H NMR spectrum of ligated product S1 (CDCl<sub>3</sub>, 600 MHz).



Figure S7. <sup>19</sup>F NMR spectrum of ligated product S1 (CDCl<sub>3</sub>, 600 MHz).



Figure S8. <sup>1</sup>H NMR spectrum of ligated product S2 (CDCl<sub>3</sub>, 600 MHz).



Figure S9. <sup>19</sup>F NMR spectrum of ligated product S2 (CDCl<sub>3</sub>, 600 MHz)



Figure S10. <sup>1</sup>H NMR spectrum of ligated product S3 (CDCl<sub>3</sub>, 600 MHz)



Figure S11. <sup>19</sup>F NMR spectrum of ligated product S3 (CDCl<sub>3</sub>, 600 MHz)



**Figure S12.** <sup>1</sup>H NMR spectrum of ligated product **S4** (CDCl<sub>3</sub>, 600 MHz, contains trace of MeOH)



Figure S13. <sup>19</sup>F NMR spectrum of ligated product S3 (CDCI<sub>3</sub>, 600 MHz)



Figure S14. <sup>1</sup>H NMR of the salt by-product extracted from the photo-induced PFTR.  $(D_2O, 600 \text{ MHz}).$ 



Figure S15. <sup>19</sup>H NMR of the salt by-product extracted from the photo-induced PFTR.  $(D_2O, 600 \text{ MHz}).$ 

### 2.4 Synthesis of copolymer and light-induced grafting



Styrene (1 g, 10 mmol) and pentafluorostyrene (1.94 g, 10 mmol) were dissolved in dioxane (5 mL), followed by the addition of AIBN (0.2 mmol). The solution was purged with Ar gas for 15 min and heated at 65 °C for 18 h. The solution was cooled to ambient temperature and precipitated three times into methanol to give product as white powder (yield 78%).



Figure S16. <sup>1</sup>H NMR spectrum of polymer P1 (CDCl<sub>3</sub>, 600 MHz)



Figure S17. <sup>19</sup>F NMR spectrum of polymer P1 (CDCl<sub>3</sub>, 600 MHz)

## General procedure for polymer grafting

Copolymer **P2** (200 mg, 0.3 mmol of pentafluobenzyl group) was dissolved in THF (10 mL). To this solution was added thioxanthone-DBU (0.5 mmol) and thiol compounds

(1 mmol). The solution was irradiated with blue light for 2 h under stirring and at ambient temperature. The solution was then precipitated twice in methanol to give product as pale yellow powder (yield 96%).



Figure S18. <sup>1</sup>H NMR spectrum of polymer P2 (CDCl<sub>3</sub>, 600 MHz)



Figure S19. <sup>19</sup>F NMR spectrum of ligated product P2 (CDCI<sub>3</sub>, 600 MHz)

Copolymer **P3**. The polymer product was purified by first precipitation into MeOH/HCl mixture (v/v = 10/0.5), subsequent precipitation was carried out into pure methanol to give product as white powder (yield 93%).



Figure S20. <sup>1</sup>H NMR spectrum of polymer P3 (CDCl<sub>3</sub>, 600 MHz)



Figure S21. <sup>19</sup>F NMR spectrum of ligated product P3 (CDCI<sub>3</sub>, 600 MHz)

Copolymer **P4**. The polymer product was purified by dialysis against MeOH using a diaslysis tubing with the MWCO of 3.5 kDa, followed by in vacuo solvent evaporation to give product as white powder (yield 95%).



Figure S22. <sup>1</sup>H NMR spectrum of polymer P4 (DMSO-d<sub>6</sub>, 600 MHz)



**Figure S23.** <sup>19</sup>F NMR spectrum of ligated product **P4** (CDCl<sub>3</sub>, 600 MHz) \*; nonligated PFB groups.

Table S1	
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	P1	P2	P3	P4
M <sub>n</sub> (10 <sup>3</sup> g mol <sup>-1</sup> ) <sup>a</sup>	120.6	161.4	195.1	224.7
Ð	2.00	2.05	2.72	8.76

<sup>a</sup>MW was determined using Poly(styrene) standard.



Figure S24. SEC traces of P1 and mixture of P1, thioxanthone-DBU and n-dodecanthiol in the dark for 6 days.







Figure S26. SEC traces of P1 and P2 synthesized by either LED light or sunlight irradiation.



**Figure S27**. Rheology assessment of PFR between polymer P1 and 1-dodecanthiol in the presence of thioxanthone-DBU and light irradiation.

## **Reference:**

[1] M. He, G. Chen, X. Huang, R. Xu, Z. Zeng and J. Yang, *Polymer Chemistry* **2014**, *5*, 2951-2960.