Supplementary Information

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General

1. 1D NMR Spectroscopy Measurements

¹H- and ¹³C-spectra were recorded on a *Bruker* Avance III HD 600 MHz spectrometer, equipped with a BBO-Probe (5 mm) with z-gradient (¹H 600.13 MHz, ¹³C: 150.90 MHz). All measurements were carried out in deuterated solvents. The chemical shift (δ) is reported in parts per million (ppm) relative to the residual solvent protons. The measured coupling constants were calculated in Hertz (Hz). MESTRENOVA 11.0 software was used to analyze the spectra. The signals were designated as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, q=quartet and m = multiplet.

2. UV-Vis Spectroscopy

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

3. Size Exclusion Chromatography

The SEC conducted a PSS SECurity² system measurements were on consisting of a PSS SECurity Degasser, PSS SECurity TCC6000 Column Oven (35 °C), PSS SDV Column Set (8x150 mm 5 μm Precolumn, 8x300 mm 5 μm Analytical Columns, 100000 Å, 1000 Å and 100 Å) and an Agilent 1260 Infinity Isocratic Pump, Agilent 1260 Infinity Standard Autosampler, Agilent 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), Agilent 1260 Infinity Refractive Index Detector (35 °C). HPLC grade THF, stabilized with BHT, is used as eluent at a flow rate of 1 mL·min⁻¹. Narrow disperse linear poly(styrene) (M_n: 266 g·mol⁻¹ to 2.52x10⁶ g·mol⁻¹) and poly(methyl methacrylate) (M_n : 202 g·mol⁻¹ to 2.2x10⁶ g·mol⁻¹) standards (*PSS* ReadyCal) were used as calibrants. All samples were passed over 0.22 µm PTFE membrane filters. Molecular weight and dispersity analysis was performed in PSS WinGPC UniChrom software (version 8.2).

4. LC-MS Measurements

LC-MS measurements were performed on an UltiMate 3000 UHPLC system (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SZ, autosampler WPS 3000TSL) and a temperature-controlled column compartment (TCC 3000). Separation was performed on a C18 HPLC-column (Phenomenex Luna 5µm, 100 Å,250 × 2.0 mm) operating at 40 °C. A gradient of ACN:H2O 10:90 \rightarrow 80:20 v/v (additive 10 mmol L⁻¹ NH₄CH₃CO₂) at a flow rate of 0.20 mL min⁻¹ during 15 min was used as the eluent. The flow was split in a 9:1 ratio, where 90 % (0.18 mL min⁻¹) of the eluent was directed through the UV-detector (VWD 3400, Dionex, detector wavelengths 215, 254, 280, 360 nm) and 10 % (0.02 mL min⁻¹) was infused into the electrospray source. Spectra were recorded on a LTQ Orbitrap Elite mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the m/z range 74-1822 using premixed calibration

solutions (Thermo Scientific). A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 5 and 2 were applied, respectively. The capillary temperature was set to 300 °C, the S-lens RF level was set to 68, and the aux gas heater temperature was set to 125 °C.

5. SEC-ESI-MS

Spectra were recorded on a Q Exactive Plus (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe. The instrument was calibrated in the m/z range 74-1822 using premixed calibration solutions (Thermo Scientific) and for the high mass mode in the m/z range of 600-8000 using ammonium hexafluorophosphate solution. A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 10 and 0 were applied, respectively. The capillary temperature was set to 320 °C, the S-lens RF level was set to 150, and the aux gas heater temperature was set to 125 °C. The Q Exactive was coupled to an UltiMate 3000 UHPLC System (Dionex, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SD), autosampler (WPS 3000TSL), and a temperature-controlled column compartment (TCC 3000). Separation was performed on two mixed bed size exclusion chromatography columns (Agilent, Mesopore 250 × 4.6 mm, particle diameter 3 μ m) with a precolumn (Mesopore 50 × 7.5 mm) operating at 30 °C. THF at a flow rate of 0.30 mL min⁻¹ was used as eluent. The mass spectrometer was coupled to the column in parallel to an UV detector (VWD 3400, Dionex), and a RI-detector (RefractoMax520, ERC, Japan) in a setup described earlier.[1] 0.27 mL min⁻¹ of the eluent was directed through the UV and RI-detector and 30 μ L·min⁻¹ was infused into the electrospray source after post-column addition of a 50 μ M solution of sodium iodide in methanol at 20 µL min⁻¹ by a micro-flow HPLC syringe pump (Teledyne ISCO, Model 100DM). A 100 µL aliquot of a polymer solution with a concentration of 2 mg mL⁻¹ was injected into the SEC system.

6. Tunable Laser Studies

All laser experiments were conducted using the apparatus shown in **Figure 1**. The light source was an Opotek Opolette 355 OPO, producing 7 ns, 20 Hz pulses. The output beam was initially passed through a beam expander (-50 mm and 100 mm lens combination) to ensure it was large enough to uniformly irradiate the entire sample volume. The beam then passed through an electronic shutter and was directed upwards using a UV silica right angle prism. Finally, the beam entered the sample, suspended in an aluminum block, from below. The laser energy deposited into the sample was measured above the aluminum block before and after experiments using a Coherent EnergyMax thermopile sensor (J-25MB-LE) to account for any power fluctuations during irradiation.



Figure 1. Schematic diagram of apparatus used for laser experiments.



Figure 2. Transmittance of the bottom of the glass vials used in this study. The transmittance values shown and used here were obtained analogously to a method reported previously.¹ The glass vials were cut at a height of 3 mm.

For laser measurements, all samples were prepared in a 0.7 mL glass crimp vials (ID 6.2 mm) capped with a rubber/PTFE septum. The wavelength dependent glass transmittance, essential for quantitative measurements, is presented in **Figure 2**. Precise photons numbers were determined from the laser pulse energy using the following relation

$$N_p = \frac{E_{pulse}\lambda f_{rep}t}{hc \left[T_\lambda/100\right]} \tag{1}$$

where E_{pulse} is the measured pulse energy above the aluminum block, λ is the wavelength of the incident radiation, f_{rep} is the laser repetition rate, t is the irradiation time, h is Planck's constant, c is the speed of light and T_{λ} is the wavelength dependent glass transmittance presented in **Figure 2**. Once an initial measurement was completed and the photon number was known, the required energies at other wavelengths can be found by rearranging Equation 1 to give



Figure 3. Wavelength dependent penetration depth, at which 99% of the incident light is absorbed. Calculated using the molar absorptivities at each wavelength investigated and a sample concentration of 1 mmol L⁻¹.



7. Emission Spectrum of 415 nm LED

Figure 4. Emission spectrum of the commercially available 415 nm LED manufactured by *ELE Doctor* used for irradiation experiments.

8. Emission Spectrum of 505 nm LED



Figure 5. Emission spectrum of the 505 nm LED manufactured by ELE Doctor and used for irradiation experiments.

9. UV-B Reactions

The samples were irradiated in a Luzchem LZC-4V photoreactor using LZC-UVB lamps (λ_{max} = 300 nm). Eight lamps were installed for side irradiation. The internal chamber was ventilated to maintain ambient temperature during the entire experiment.





10. Extraction of Kinetic Data from UV-Vis Spectra

When a sample contains multiple components, the overall absorbance of the sample at a particular wavelength is equal to the sum of the absorbance contributions of the constituting components.

Moreover, each of these contributions is defined by the Beer-Lambert law that dictates that the absorbance of a component is given by

$$A = \varepsilon c l$$

where ε and c are the molar extinction coefficient and the concentration of the component, respectively, and l is the pathlength of the light through the sample. In other words, when only **Py-chal** (C) and (**Py-chal**)₂ (C₂) are present in the sample, which is a reasonable assumption since the photodimerization proved to be a clean reaction according to ¹H-NMR and the isosbestic points in the UV-Vis reaction profiles, the overall absorbance can be written as

$$A(\lambda) = A_{\mathcal{C}}(\lambda) + A_{\mathcal{C}_{2}}(\lambda) = l\left(c_{\mathcal{C}}\varepsilon_{\mathcal{C}}(\lambda) + c_{\mathcal{C}_{2}}\varepsilon_{\mathcal{C}_{2}}(\lambda)\right)$$

When the UV-Vis spectrum is considered for wavelengths between 300 nm and 500 nm, i.e. the region containing the characteristic absorptions of both **Py-chal** and **(Py-chal)**₂, a set of equations (l = 1 cm)

$$\begin{bmatrix} A(300 nm) \\ \vdots \\ A(500 nm) \end{bmatrix} = \begin{bmatrix} \varepsilon_{\mathcal{C}}(300 nm) \varepsilon_{\mathcal{C}_{2}}(300 nm) \\ \vdots \\ \varepsilon_{\mathcal{C}}(500 nm) \varepsilon_{\mathcal{C}_{2}}(500 nm) \end{bmatrix} \begin{bmatrix} c_{\mathcal{C}} \\ c_{\mathcal{C}_{2}} \end{bmatrix}$$

is obtained from which the concentrations c_c and c_2 of **Py-chal** and **(Py-chal)**₂, respectively, can be extracted via a least squares linear regression. This concept is illustrated in **Figure 6**, showing the experimental spectrum of the reaction mixture after 90 s of irradiation with a 10 W 415 nm LED and the molar extinction coefficients of **Py-chal** and **(Py-chal)**₂ determined in the reaction solvent (**Figure 6**A). As soon as the concentrations are extracted via a least squares fit, the absorption spectra of the individual components can be calculated, while their sum is in good correspondence with the experimental spectrum (**Figure 6**B). Note that the obtained concentrations are those obtained for the UV-Vis sample and must be corrected for the dilution of the sample.

А





Figure 7. (A) The measured UV-Vis spectrum of the product mixture after irradiating Py-chal with a 415 nm LED (10 W) for 90 s. (B) The individual UV-Vis spectra of Py-chal and (Py-chal)₂ as extracted from the experimental data *via* a least squares fit and the sum of the individual spectra fitted against the experimental spectrum.

The irradiation experiments at 415 nm and subsequent UV-vis data collection were conducted as follows:

23.7mg of **Py-chal** was dissolved in 5mL DCM and degassed with argon for 10 minutes. The solution was irradiated with a blue 10W LED (λ_{max} =415 nm) and a 10 µL aliquot was retrieved from the sample at regular intervals (0, 10, 20, 30, 50, 70, 90, 120, 150, 180, 240, 300, 360, 480, 600 and 720 seconds) with a Hamilton syringe and added to 1990 µL of DCM in a cuvette, and the UV-vis spectrum measured.

The irradiation experiments with UV-B light and the subsequent UV-vis data collection were conducted as follows:

23.8 mg of (**Py-chal**)₂ was dissolved in 5 mL DCM and degassed with argon for 10 minutes. The solution was irradiated with 8 UV-B lamps (λ_{max} =300 nm) and a 10 µL aliquot was retrieved from the sample at regular intervals (0, 5, 10, 20, 30, 45, 60, 90, 120, and 180 minutes) with a Hamilton syringe and added to 1990 µL of DCM in a cuvette, and the UV-vis spectrum measured.

Pyrene Chalcone Experimental





Acetovanillone (14.4 g, 85.6 mol, 1 eq), potassium carbonate (26.3 g, 190 mol, 2.2 eq) and 3bromopropanol (17 mL, 0.12 mol, 1.2 eq) were combined in dimethylformamide (50 mL) and stirred under argon for 48 h. The reaction was poured into an ice-brine mixture (800 mL) and extracted with ethyl acetate. The organic fraction was dried over anhydrous magnesium sulfate before being dried under reduced pressure. The product (22.71 g) still contained 3-bromopropanol (the purity was calculated to be 85% from ¹H NMR) but was used without further purification in the next step (product mass=19.19 g, 98%).

¹H NMR (600 MHz, DMSO- d_6) δ =7.60 (dd, J = 8.4, 2.1 Hz, 1H), 7.43 (d, J = 2.0 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 4.11 (t, J = 6.4 Hz, 2H), 3.81 (s, 3H), 3.56 (td, J = 6.1, 5.1 Hz, 2H), 2.52 (s, 3H), 1.88 (q, J = 6.3 Hz, 2H).



Figure 8. ¹H NMR spectrum of M1 in deuterated DMSO (600 MHz)



Figure 9. Mass spectrum of M1

Symbol	m/z _{exp}	m/z _{theor}	Δ_{ppm}	composition
[M +H] ⁺	225.1101	225.1121	8.88	$C_{31}H_{27}O_5^+$
[M+Na] ⁺	247.0918	247.0941	9.31	$C_{31}H_{26}O_5Na^+$

12. M2



1-Pyrenecarboxaldehyde (5.0 g, 21.7 mmol, 1 eq) and **M1** (6.0 g, 22.8 mmol, 1.05 eq) were mixed and suspended in 60 mL ethanol with 18 mL of NaOH (3 M) added and stirred under argon for 18 hours in the dark. The reaction mixture was poured into water (1200 mL) and 10 mL of concentrated HCl was added to the suspension and stirred. The product was isolated by filtration and washed with water to yield the product as a yellow powder which was subsequently dried in a vacuum oven at 40 °C (Yield=9.1 g, 96%).

¹H NMR (600 MHz, DMSO- d_6) δ =8.89 – 8.82 (m, 2H), 8.63 (d, J = 9.4 Hz, 1H), 8.42 – 8.35 (m, 4H), 8.32 – 8.23 (m, 3H), 8.13 (t, J = 7.6 Hz, 1H), 8.02 (dd, J = 8.5, 2.1 Hz, 1H), 7.72 (d, J = 2.0 Hz, 1H), 7.16 (d, J = 8.5 Hz, 1H), 4.18 (t, J = 6.4 Hz, 2H), 3.91 (s, 3H), 3.59 (td, J = 6.2, 5.1 Hz, 2H), 1.93 (p, J = 6.3 Hz, 2H)



Figure 10. ¹H NMR spectrum of M2 in deuterated DMSO (600 MHz)





Symbol m/z_{exp} m/z_{theor} Δ_{ppm} composition	/mbol m/z _{exp}
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13. M3 – Py-chal-OCOMe



M2 (1.0 g, 2.29 mmol, 1 eq) was suspended in DCM (20 mL) and triethylamine (1 mL, 6.9 mmol, 3 eq) was added to the mixture before cooling it over an ice bath. Acetyl chloride (650µL, 9.2 mmol, 4 eq) was added to the chilled suspension and stirred overnight at room temperature. The reaction mixture was diluted to 100 mL with DCM and washed twice with 100 mL saturated aqueous sodium bicarbonate. The aqueous phase was extracted with 100 mL DCM and the combined organic fractions were finally washed with 100 mL brine. The product was then adsorbed onto celite and isolated via column chromatography with a gradient eluent of toluene/3% acetone \rightarrow toluene/5% acetone \rightarrow toluene/10% acetone. 1.02g (93%) of the target compound was obtained.

¹H NMR (600 MHz, Chloroform-d) δ =8.98 (d, J = 15.3 Hz, 1H), 8.58 (d, J = 9.3 Hz, 1H), 8.43 (d, J = 8.1 Hz, 1H), 8.28 – 8.18 (m, 4H), 8.14 (d, J = 8.8 Hz, 1H), 8.09 (d, J = 8.8 Hz, 1H), 8.05 (t, J = 7.6 Hz, 1H), 7.83 (d, J = 15.3 Hz, 1H), 7.78 (dd, J = 8.4, 2.0 Hz, 1H), 7.73 (d, J = 2.0 Hz, 1H), 6.98 (d, J = 8.3 Hz, 1H), 4.32 (t, J = 6.2 Hz, 2H), 4.22 (t, J = 6.3 Hz, 2H), 3.99 (s, 3H), 2.24 (p, J = 6.3 Hz, 2H), 2.08 (s, 3H).





Figure 12. ¹H NMR spectrum of M3 in deuterated CDCl₃ (600 MHz)



Figure 13. Mass spectrum of M3

Symbol	m/z _{exp}	m/z _{theor}	Δ_{ppm}	composition
[M +H] ⁺	479.1822	479.1853	6.47	$C_{31}H_{26}O_5H^+$

14. (Py-chal)₂



124 mg of **M3** (259 µmol) was divided over five vials to which 5mL of DCM was added. Each vial, containing a solution of approximately 10 mM of M16 was degassed with argon for 10 min and irradiated for 10min with a 10W 415nm LED. The resulting solutions were combined and evaporated on celite. The product was isolated as an off-white solid via column chromatography with acetone (0% to 10%) in toluene as eluent. (Yield = 95.6 mg, 77 %)

¹H NMR (600 MHz, Chloroform-*d*) δ =8.71 (d, J = 8.1 Hz, 1H), 8.35 (d, J = 8.1 Hz, 1H), 8.13 – 8.09 (m, 1H), 8.09 – 7.99 (m, 3H), 8.00 – 7.96 (m, 1H), 7.90 (t, J = 7.6 Hz, 1H), 7.70 (d, J = 9.4 Hz, 1H), 7.46 (dd, J = 8.5, 2.0 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H), 6.53 (d, J = 8.5 Hz, 1H), 5.44 – 5.39 (m, 1H), 5.17 – 5.13 (m, 1H), 4.14 – 4.09 (m, 2H), 3.91 (m, J = 36.7, 9.7, 6.3 Hz, 2H), 3.45 (s, 3H), 2.04 – 1.98 (m, 2H), 1.96 (s, 3H).





Figure 14. ¹H NMR Spectrum of (Py-chal)₂ in deuterated CHCl₃ (600 MHz).





Acetovanillone (16.6 g, 0.10 mol, 1 eq), potassium carbonate (30.0 g, 0.22 mol, 2.2 eq) and ethyl-4bromobutyrate (17 mL, 0.12 mol, 1.2 eq) were combined in dimethylformamide (50 mL) and stirred under Argon for 17.5 h. The reaction was poured into water (800 mL) and stirred for 24 h. The product was isolated by filtration to yield ethyl 4-(4-ethanoyl-2-methoxyphenoxy) butanoate as a white powder. (Yield = 27.5 g, 98%).

¹H NMR (600 MHz, DMSO-d6) δ =7.60 (dd, J = 8.4, 2.1 Hz, 1H), 7.44 (d, J = 2.0 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 4.06 (q, J = 7.1, 6.6 Hz, 4H), 3.82 (s, 3H), 2.52 (s, 3H), 2.46 (t, J = 7.3 Hz, 2H), 1.99 (p, J = 6.8 Hz, 2H), 1.18 (t, J = 7.1 Hz, 3H).





Figure 15.¹H NMR spectrum of M4 in deuterated DMSO (600 MHz).



Figure 16. Mass spectrum of M4.

Symbol	m/z _{exp}	m/z _{theor}	Δ_{ppm}	composition
[M +H]+	281.1388	281.1384	1.42	$C_{15}H_{30}O_5^+$
[M+Na] ⁺	303.1207	303.1203	1.32	$C_{15}H_{20}O_5Na^+$

16. M5



1-Pyrenecarboxaldehyde (5.0 g, 21.7 mmol, 1 eq) and **M4** (6.0 g, 21.7 mmol, 1 eq) were suspended in 60 mL ethanol with 18 mL of NaOH (3 M) added and stirred under argon for 18 hours in the dark. The reaction mixture was poured into water (1200 mL) and 10 mL of concentrated HCl was added to the suspension and stirred. The product was isolated by filtration to yield the product as a yellow powder which was subsequently dried in a vacuum oven at 40 °C (Yield = 9.91 g, 98%).

¹H NMR (600 MHz, DMSO-d6) δ =8.89 – 8.81 (m, 2H), 8.61 (d, J = 9.4 Hz, 1H), 8.40 – 8.32 (m, 4H), 8.30 – 8.22 (m, 3H), 8.12 (t, J = 7.6 Hz, 1H), 8.00 (dd, J = 8.5, 2.1 Hz, 1H), 7.72 (d, J = 2.0 Hz, 1H), 7.15 (d, J = 8.5 Hz, 1H), 4.13 (t, J = 6.5 Hz, 2H), 3.91 (s, 3H), 2.42 (t, J = 7.3 Hz, 2H), 2.05 – 1.96 (m, 2H).





Figure 17. ¹H NMR spectrum of M5 in deuterated DMSO (600 MHz).





M5 (1.0 g, 2.15 mmol, 1 eq) and sulfuric acid (0.21 g, 2.15mmol, 1 eq) were dissolved in 30 mL methanol and refluxed at 70 °C for two hours under inert atmosphere. The reaction mixture was then precipitated in an ice-brine mixture and stirred. The product was isolated by filtration to yield the product as a yellow powder which was subsequently dried in a vacuum oven at 40 °C (Yield = 1.03 g, 99.9%).

¹H NMR (600 MHz, DMSO-d6) δ =8.90 – 8.82 (m, 2H), 8.63 (d, J = 9.4 Hz, 1H), 8.42 – 8.34 (m, 4H), 8.32 – 8.23 (m, 3H), 8.13 (t, J = 7.6 Hz, 1H), 8.01 (dd, J = 8.5, 2.0 Hz, 1H), 7.73 (d, J = 2.0 Hz, 1H), 7.16 (dd, J = 8.5, 4.8 Hz, 1H), 4.14 (t, J = 6.4 Hz, 2H), 3.91 (s, 3H), 3.62 (s, 3H), 2.53 (s, 2H), 2.07 – 1.98 (m, 2H).



Figure 18. ¹H NMR spectrum of M6 in deuterated DMSO (600 MHz).



Figure 19. Mass spectrum of M6.





Figure 20. COSY NMR spectrum of Py-Chal in deuterated acetonitrile.

18. M7 Chalcone RAFT CTA



M2 (1.0 g, 2.29 mmol, 1.00 eq), DMAP (28 mg, 229 μ mol, 0.10 eq) and 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (0.77 g, 2.75 mmol, 1.20 eq) were dissolved in 40 mL dry DCM and stirred over an ice bath. EDC hydrochloride (0.5 g, 2.52 mmol, 1.1 eq) was added to the mixture with stirring and the mixture was allowed to slowly warm up to room temperature overnight. After 24 hours of stirring, the mixture was washed three times with water and the organic fraction was dried with anhydrous magnesium sulfate. The mixture was then filtered to remove the magnesium sulfate and dried and vacuum at 25°C.

The product was purified via column chromatography with a gradient eluent DCM \rightarrow DCM/1% MeOH \rightarrow DCM/2% MeOH \rightarrow DCM/3% MeOH. The product was then dried before characterizing with NMR and LC-MS

¹H NMR (600 MHz, DMSO-d6) δ = 8.90 – 8.80 (m, 2H), 8.62 (dd, J = 9.6, 2.0 Hz, 1H), 8.42 – 8.33 (m, 4H), 8.30 – 8.23 (m, 3H), 8.13 (t, J = 7.6 Hz, 1H), 8.01 (ddd, J = 8.3, 6.6, 2.1 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.73 (dd, J = 3.4, 2.0 Hz, 1H), 7.66 (tt, J = 7.2, 1.2 Hz, 1H), 7.49 (ddt, J = 7.4, 6.3, 1.3 Hz, 1H), 7.16 (d, J = 8.5 Hz, 1H), 4.24 (q, J = 5.5, 4.8 Hz, 1H), 4.20 (q, J = 7.4, 6.8 Hz, 2H), 3.91 (s, 3H), 2.72 – 2.61 (m, 1H), 2.56 (ddd, J = 14.0, 10.1, 5.6 Hz, 1H), 2.48 – 2.42 (m, 1H), 2.17 – 2.07 (m, 2H), 1.91 (s, 2H).



Figure 21. ¹H NMR spectrum of M7 in deuterated DMSO (600 MHz)

Symbol	m/z _{exp}	m/z _{theor}	Δ_{ppm}	composition
[M +H] ⁺	698.2093	698.2029	9.17	$C_{42}H_{36}NO_5S_2^+$

[M +K]+	736.1664	736.1588	10.32	$C_{42}H_{35}KNO_{5}S_{2}^{+}$
[M +Na] ⁺	720.1924	720.1849	10.41	$C_{42}H_{35}NNaO_5S_2^+$



Figure 22. Mass spectrum of M7

19. Synthesis of P1'



M7 (50 mg, 72µmol, 1 eq), azobisisobutyronitrile (1 mg, 7 µmol, 0.1 eq) and MMA (0.5 g, 4 mmol, 60 eq) were dissolved in 1 mL dry dioxane and the mixture was degassed. The reaction was allowed to run over 3 hours under inert atmosphere at 70°C in the dark. The reaction was quenched by cooling in liquid nitrogen and exposing to air, and the polymer was purified *via* precipitation in cold methanol.

¹H NMR (600 MHz, Acetonitrile- d_3) δ 8.94 (d, J = 15.2 Hz, 1H), 8.64 (d, J = 10.7 Hz, 3H), 8.33 (d, J = 13.3 Hz, 8H), 8.22 (dd, J = 17.0, 9.6 Hz, 5H), 8.14 – 8.03 (m, 5H), 7.92 (s, 1H), 7.75 (s, 1H), 7.12 (s, 1H), 3.55 (s, 142H), 1.35 – 1.22 (m, 72H), 0.97 (s, 52H), 0.78 (s, 82H).





Figure 23. ¹H NMR spectrum of P1' in Acetonitrile-*d*₃ (600 MHz)





The protocol outlined by Dietrich *et al.* was utilized to convert the dithioester into an alcohol functional group.² An excess of AIBN was dissolved THF and heated to 60°C with stirring under ambient conditions. The polymer was added to the heating mixture and stirred for 20 minutes. The temperature was then lowered to 40°C and an excess of triphenylphosphine was added and stirred for a further 20 minutes. The sample was concentrated under reduced pressure and precipitated in cold methanol twice. The isolated polymer was dried in a vacuum oven at 40°C overnight.



Figure 24. Size exclusion chromatogram of P1.

21. (Py-chal)₂



0.5 mg of **M6** was dissolved in 1 mL of deuterated acetonitrile and purged with a stream of argon before irradiating with a green light LED (λ_{max} =505 nm) for three days. The product mixture was then characterized via ¹H and COSY NMR spectroscopy.



Figure 25. COSY NMR spectrum of the photoproduct of Py-chal after exposure to light from an LED centered at 505 nm for 3 days in deuterated acetonitrile. An internal standard of 1,3,5-trimethoxybenzene was used for reference.

Supplementary Results



22. ¹H NMR Spectra for The Action Plot of Py-chal

Figure 26. ¹H NMR spectra of the chalcone photoproduct in deuterated acetonitrile after irradiation at each wavelength with a tunable laser (18 μ mol of photons at each wavelength).

23. UV-Vis Absorption Spectra



Figure 27. Molar extinction coefficients of Py-chal in DCM, DMF, THF and chloroform indicating no significant shift in molar absorptivity between different solvents.

24. Fluorescence Spectrum



Figure 28. The fluorescence spectrum of Py-chal measured in DCM.

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