

## Supporting Information

### On-Demand Acid-Gated Fluorescence Switch-On in Photo-Generated Nanospheres

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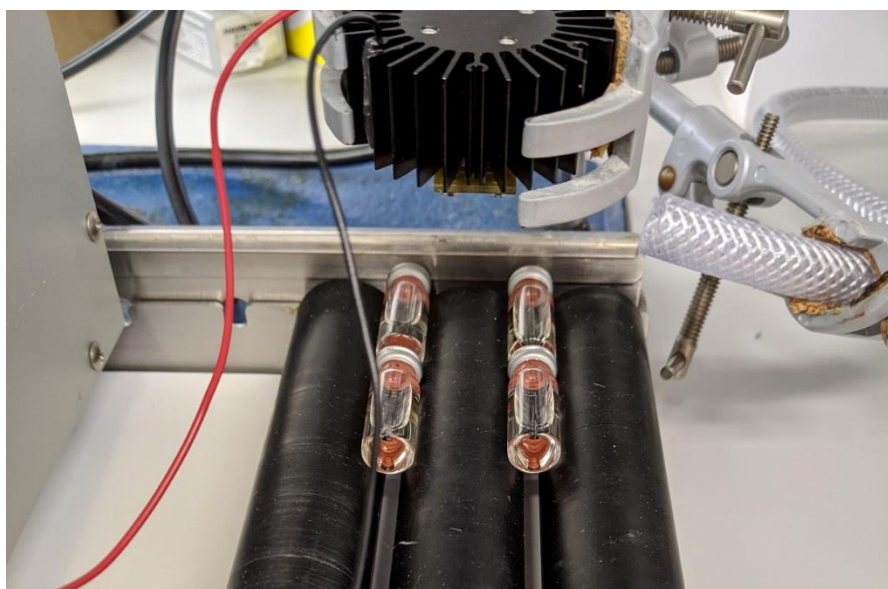
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## 1. Materials

All materials were reagent grade and used as received, unless stated otherwise. Styrene and chloromethylstyrene were deinhibited by passing over a column of activated basic alumina (Ajax) immediately prior to use. To remove acid traces, acetonitrile/THF could be passed over activated basic alumina (Ajax). Acrylic acid, 1-aminopyrene, p-anisidine, 2-bromoethanol, (1-bromoethyl)benzene, copper powder, 2-fluoro-6-methylbenzaldehyde, 3-mercaptopropionic acid, 4-methylbenzenesulfonohydrazide, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), potassium carbonate, pyridine, styrene and triphosgene were purchased from Sigma Aldrich. Cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>), chloromethylstyrene (CMS), 4-formylbenzoic acid, hydrochloric acid (32%), sodium nitrite and triethylamine were purchased from Thermo Fisher Scientific. Acetonitrile (ACN), cyclohexane, dichloromethane (DCM), dimethylformamide (DMF), ethanol, ethyl acetate, methanol, tetrahydrofuran (THF) and toluene were purchased from Thermo Fisher Scientific. Acetonitrile-d<sub>3</sub>, Chloroform-d<sub>1</sub> and dimethylsulfoxide-d<sub>6</sub> were purchased from Sigma-Aldrich.

## 2. Instrumentation



**Figure S1:** Photoreactor setup used for all experiments, consisting of vials placed on a bottle roller at 2 rpm, irradiated from above by an LED at a path length of 8 cm. See Methods for more information on reaction setup.

*Nuclear Magnetic Resonance (NMR) Spectrometry:* <sup>1</sup>H and <sup>13</sup>C-NMR spectra were recorded on a Bruker System 600 Ascend LH, equipped with a BBO-Probe (5 mm) with z-gradient (<sup>1</sup>H: 600.13 MHz, <sup>13</sup>C 150.90 MHz), or a Bruker AVANCE III 850 spectrometer. The  $\delta$ -scale was normalized relative to the solvent signal of CHCl<sub>3</sub>, DMSO or CH<sub>3</sub>CN for <sup>1</sup>H spectra and for <sup>13</sup>C spectra on the middle signal of CHCl<sub>3</sub> triplet, the DMSO quintet or the acetonitrile septet. The multiplicities were reported using the following abbreviations: s for singlet, d for doublet, t for triplet, q for quartet, p for pentet, m for multiplet and br for broad signal.

*THF Size Exclusion Chromatography (SEC):* The SEC measurements were conducted on a PSS SECurity<sup>2</sup> system consisting of a PSS SECurity Degasser, PSS SECurity TCC6000 Column Oven (35 °C), PSS SDV Column Set (8x150 mm 5  $\mu$ m Precolumn, 8x300 mm 5  $\mu$ m 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, was used as eluent at a flow rate of 1 mL·min<sup>-1</sup>. Narrow disperse linear *p*(styrene) ( $M_n$ : 266 g·mol<sup>-1</sup> to 2.52x10<sup>6</sup> g·mol<sup>-1</sup>) and *p*(methyl methacrylate) ( $M_n$ : 202 g·mol<sup>-1</sup> to 2.2x10<sup>6</sup> g·mol<sup>-1</sup>) standards (PSS ReadyCal) were used as calibrants. All samples were passed over 0.22 μm PTFE membrane filters. Molecular weight and dispersity analyses were performed in PSS WinGPC UniChrom software (v 8.2).

*Flash Column Chromatography*: Flash chromatography was performed on a Interchim XS420+ flash chromatography system consisting of a SP-in-line filter 20-μm, an UV-Vis detector (200-800 nm) and a SofTA Model 400 ELSD (55 °C diff tube temperature, 25 °C spray chamber temperature, filter 5, EDR gain mode) connected via a flow splitter (Interchim Split ELSD F04590). The separations were performed using an Interchim dry load column and an Interchim Puriflash 30 μm Silica HP column.

*UV-visible Spectroscopy*: UV-Vis spectra were recorded on a Shimadzu UV-2700 spectrophotometer equipped with a CPS-100 electronic temperature control cell positioner. Kinetic samples were prepared by diluting 100 μL of the centrifuged reaction mixture in 3 mL of acetonitrile. Measurements were performed at ambient temperature in Helma Analytics quartz high precision cells with a path length of 10 mm.

*Fluorescence Spectroscopy*: The fluorescence spectra and kinetics were measured using a Cary Eclipse Fluorescence Spectrophotometer from Agilent Technologies. The experimental parameters were set to 330 nm excitation wavelength, excitation and emission slit 5 mm and detector voltage 400 V. Samples were prepared in 10mm quartz fluorescence cuvettes with septum cap and measured at ambient temperature. Baseline measurements were performed on each of the relevant solvents and subtracted from the absorbance and fluorescence intensities.

*Centrifuge*: The particles were isolated by centrifugation using a Sigma 3-16L centrifuge, at 5000 rpm for 4 minutes.

*Scanning Electron Microscopy*: SEM images were captured using a Tescan MIRA3 SEM at 2 or 5 kV using an SE detector. Samples were prepared by dispersing the particles in THF and drop casting onto an SEM stub. Samples were coated with a 10 nm layer of gold. Analysis was done in ImageJ, with particle sizing and dispersity calculations based on counting a minimum of 100 particles, using the following equations:

$$D_n = \frac{\sum N_i D_i}{\sum N_i} \quad D_w = \frac{\sum N_i D_i^4}{\sum N_i D_i^3}$$

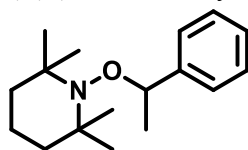
Where  $D_n$  is the number-average diameter,  $D_w$  is the weight-average diameter,  $N_i$  is the number of particles measured, and  $D_i$  is the diameter of the measured particle. The dispersity  $\mathcal{D}$  can then be calculated as

$$\mathcal{D} = \frac{D_w}{D_n}$$

### 3. Small Molecule Synthesis

*NMP Initiator (3):*

*2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine (3)*

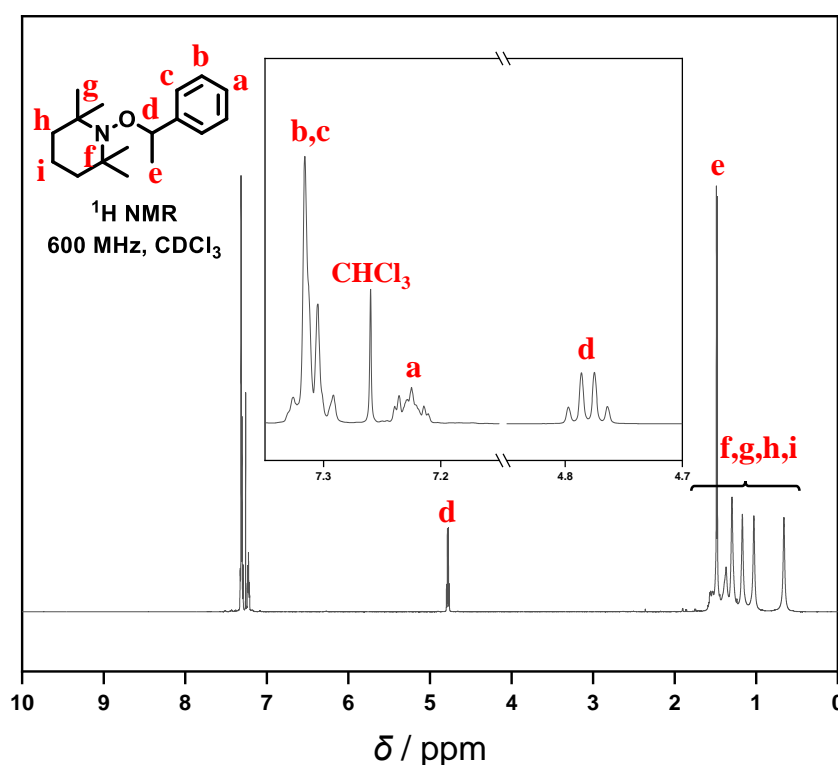


**3** was synthesised according to a modified literature procedure:

S. Harrisson, P. Couvreur, J. Nicolas. *Polym. Chem.* **2011**, 2, 1859.

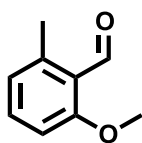
(1-bromoethyl)benzene (2.00 mL, 14.7 mmol, 1 eq) and 2,2,6,6-tetramethyl-1- piperidinyloxy (TEMPO) (2.562 g, 16.40 mmol, 1.1 eq) were dissolved in dry acetonitrile (10 mL). Copper powder (0.469 g, 7.38 mmol, 0.5 eq) was added, and the solution was degassed by bubbling with argon for 10 min. *N,N,N',N''*-Pentamethyldiethylenetriamine (PMDETA) (1.85 mL, 8.9 mmol, 0.6 eq) was added by syringe. The reaction was stirred overnight at room temperature. The product was isolated by column chromatography on basic aluminium oxide with toluene as eluent. Solvent was removed *in vacuo*, yielding **3** (3.312 g, 87 %) as a white, crystalline solid.

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 600 MHz)  $\delta$  = 7.34-7.30 (4H, m, CH), 7.24-7.22 (1H, m, CH), 4.79 (1H, q, *J* = 6.7 Hz, CH), 1.50-1.04 (18H, m, CH<sub>3</sub>/CH<sub>2</sub>), 0.67 ppm (3H, s, CH<sub>3</sub>). **<sup>13</sup>C-NMR** (CDCl<sub>3</sub>, 150 MHz)  $\delta$  = 146.0, 128.1, 126.9, 126.7, 83.3, 59.8, 40.5, 34.6, 34.3, 23.7, 20.5, 17.4 ppm.



**Figure S2.** <sup>1</sup>H-NMR spectrum of 2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine (**3**) recorded in CDCl<sub>3</sub>.

**2-methoxy-6-methylbenzaldehyde (2)**

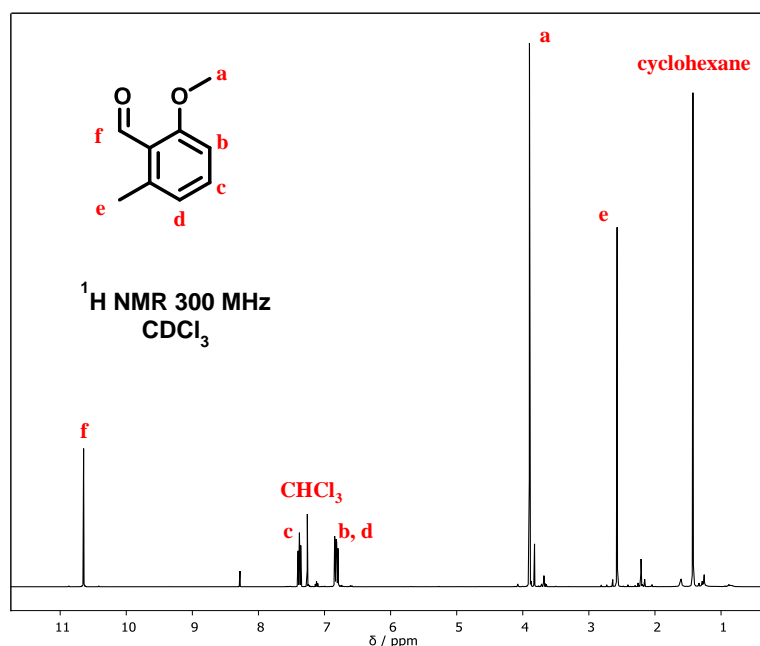


**2** was synthesised according to a modified literature procedure:

1. F. M. Hauser, S. R. Ellenberger, *Synthesis* **1987**, 1987, 723-724. 2. A. Senthilmurugan, I. S. Aidhen, *Eur. J. Org. Chem.* **2010**, 2010, 555-564.

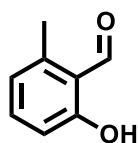
2,3-Dimethyl anisole (7.03 g, 51.6 mmol, 1.00 eq), copper sulfate pentahydrate (13.11 g, 52.5 mmol, 1.02 eq) and potassium peroxodisulfate (41.85 g, 154.8 mmol, 3.00 eq) were added to a mixture of acetonitrile/water (1:1, 500 mL). The vigorously stirred suspension was placed in a thermostatted oil bath at 90 °C until TLC showed no starting material remaining. After, the reaction mixture was cooled to ambient temperature and the undissolved copper salt removed by filtration. DCM (150 mL) was added and the phases were separated. The aqueous phase was extracted two times with DCM (100 mL) and the combined organic layers were dried over magnesium sulfate, dried *in vacuo* and purified *via* column chromatography on silica gel (5:1 CH:EA) to yield the product as a yellow solid.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 10.64 (s, 1H, CHO), 7.38 (t,  $J$  = 7.97 Hz, 1H, Ar H), 6.81 (t,  $J$  = 7.97 Hz, 2H, Ar), 3.89 (s, 3H, OCH<sub>3</sub>), 2.57 (s, 3H, CH<sub>3</sub>) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.42, 163.29, 142.16, 134.55, 124.22, 123.48, 109.17, 77.16, 55.90, 21.60. **MS** (ESI)  $m/z$ : [M + H]<sup>+</sup> calcd for C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>, 151.0754; found 151.0754.



**Figure S3.**  $^1\text{H NMR}$  spectrum of 2-methoxy-6-methylbenzaldehyde (**2**) recorded in  $\text{CDCl}_3$ .

**2-hydroxy-6-methylbenzaldehyde (1)**

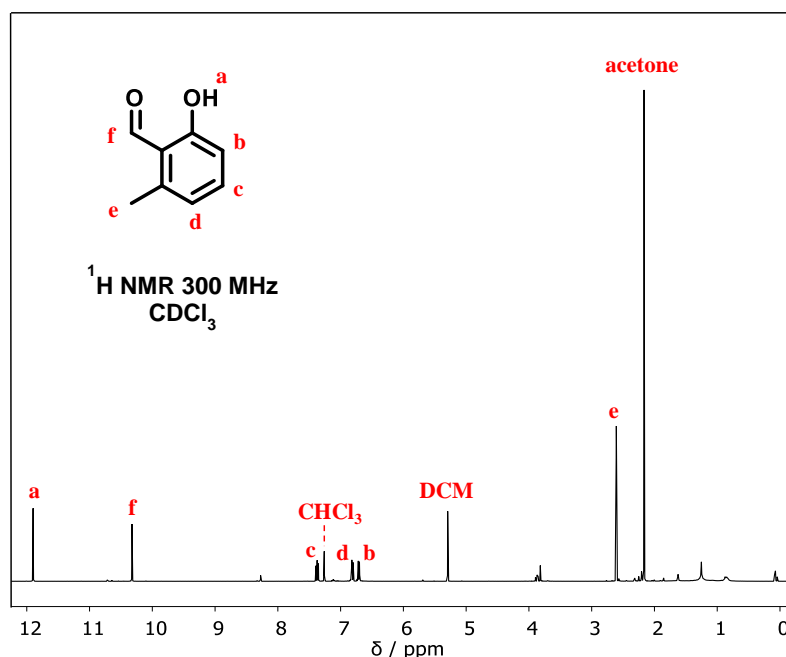


**1** was synthesised according to a modified literature procedure:

T. Pauloehrl, G. Delaittre, V. Winkler, A. Welle, M. Bruns, H. G. Börner, A. M. Greiner, M. Bastmeyer, C. Barner-Kowollik, *Angew. Chem., Int. Ed.* **2012**, *51*, 1071-1074.

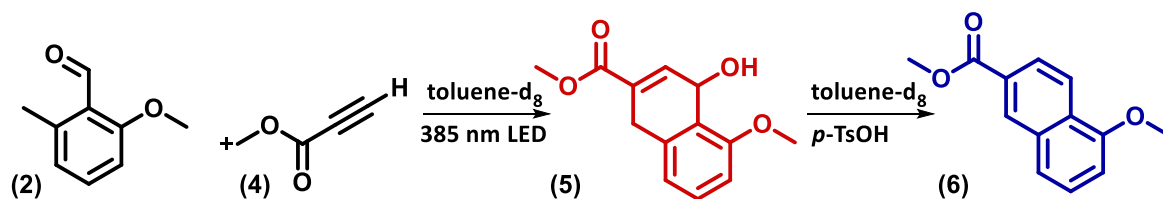
2-Methoxy-6-methylbenzaldehyde **2** (4.10 g, 27.3 mmol, 1.00 eq) was dissolved in dry DCM (60 mL) and cooled to 0 °C. AlCl<sub>3</sub> (10.9 g, 81.9 mmol, 3.00 eq) was added and the mixture was stirred at ambient temperature overnight. For quenching, the reaction mixture was poured dropwise into an ice-bath (80 mL) and the phases were separated. The aqueous layer was extracted three times with DCM (80 mL). The combined organic layers were dried over magnesium sulfate and the solvent was evaporated. The final purification was carried out by column chromatography (silica gel, solid deposit from Celite, CH/EA 2:1) yielding 3.9 g (82 %) of a yellow solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 11.91 (s, 1H, OH), 10.32 (s, 1H, CHO), 7.37 (dd, J = 8.4, 7.4 Hz, 1H, Ar H), 6.81 (d, J = 8.2 Hz, 1H, Ar H), 6.71 (d, J = 7.5 Hz, 1H, Ar H), 2.60 (s, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 195.33, 163.15, 142.15, 137.38, 118.52, 116.04, 77.16, 18.03 ppm. MS (ESI) m/z: [M + H]<sup>+</sup> calcd for C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>, 137.0597; found 137.0597.

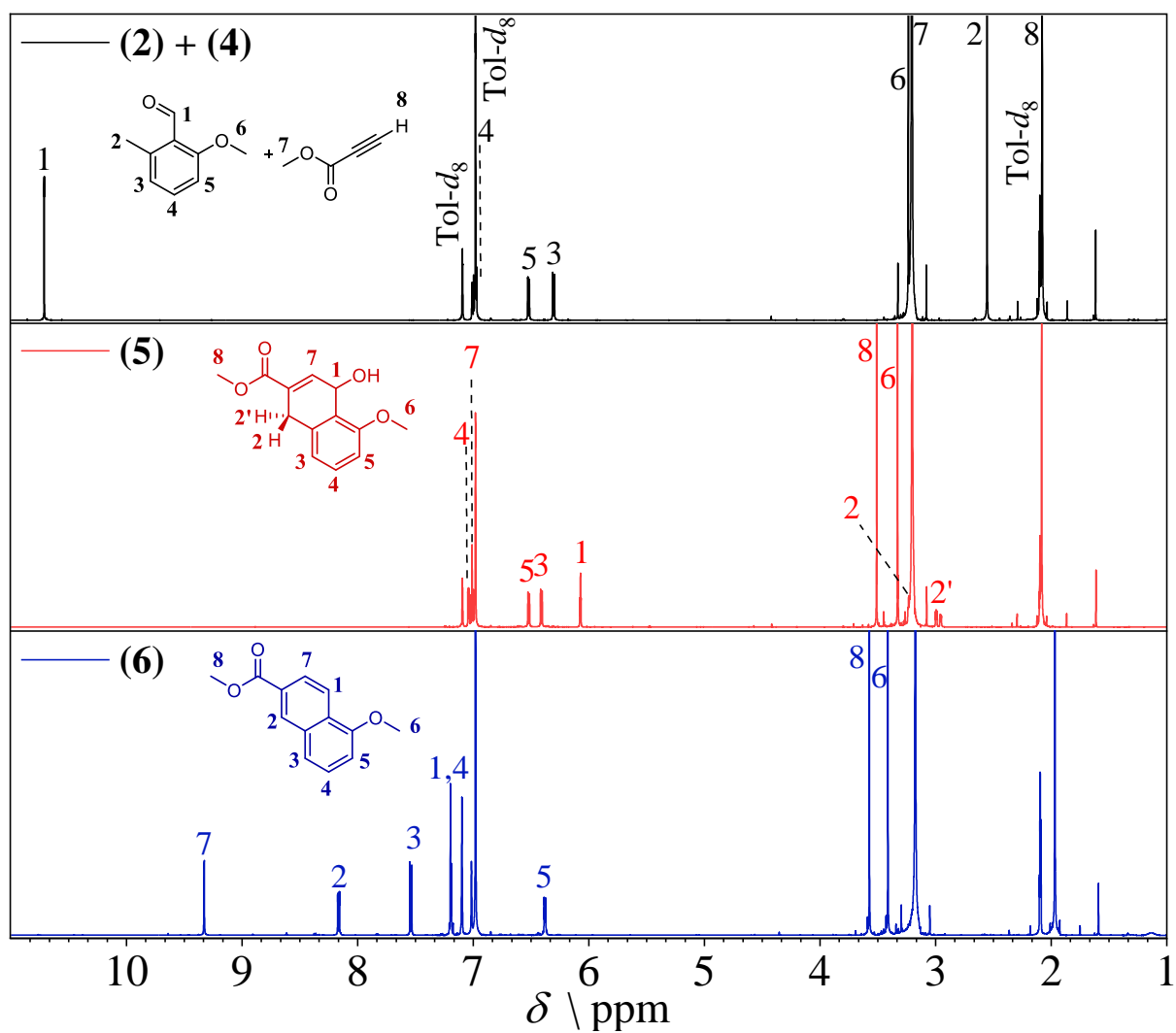


**Figure S4.** <sup>1</sup>H NMR spectrum of 2-hydroxy-6-methylbenzaldehyde (**1**) recorded in CDCl<sub>3</sub>.

#### 4. Analysis of the photo-induced Diels-Alder reaction of *o*-MBA and terminal alkynes

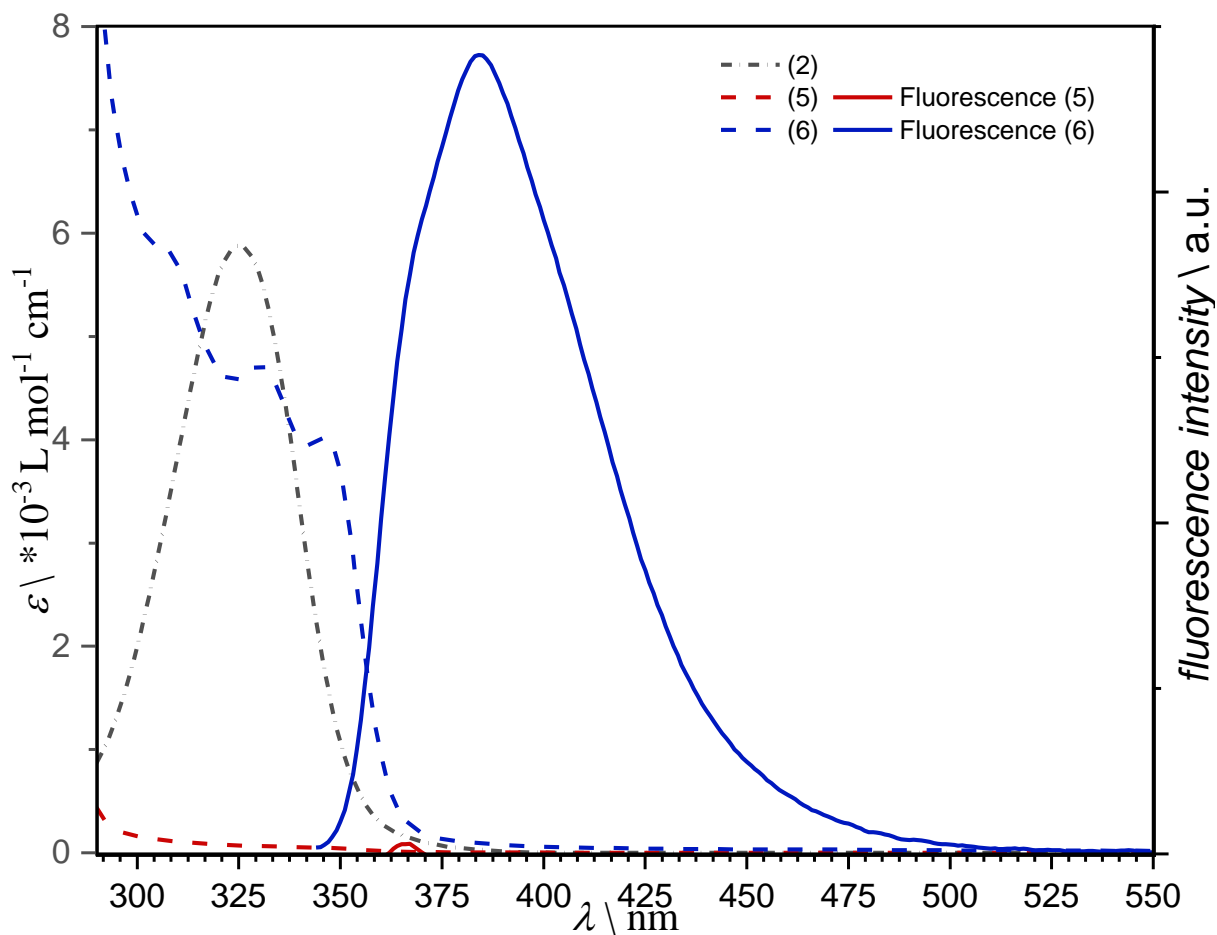


6-methyl-2-methoxybenzaldehyde (3.75 mg, 0.025 mmol, 1.00 eq.  $c = 50 \text{ mmol L}^{-1}$ ) and 22.24  $\mu\text{L}$  methyl propiolate (21.02 mg, 0.25 mmol, 10.00 eq.  $c = 500 \text{ mmol L}^{-1}$ ) were dissolved in 0.5 mL  $\text{toluene-d}_8$ , filled in an NMR tube. A  $^1\text{H-NMR}$  spectrum was recorded (refer to Fig. S14, top). Afterwards the solution was degassed by passing through  $\text{N}_2$  and irradiated (385 nm LED, 0.25 A, XX V, 4 cm distance) for 120 min. Afterwards, a  $^1\text{H-NMR}$  spectrum was recorded (refer to Fig. S14, middle). From this solution, the extinction coefficient of naphthol (5) was determined by transferring 50  $\mu\text{L}$  of the solution into 10 mL toluene and subsequent UV-VIS measurement (refer to Fig. S15). Finally, 100  $\mu\text{L}$  of a para-toluenesulfonic acid solution (0.1 mg in 0.5 mL  $\text{toluene-d}_8$ ) was added and the mixture was kept at room temperature for 12 h. Subsequently, another  $^1\text{H-NMR}$  spectrum was recorded (refer to Fig. S14, bottom). The extinction coefficient of naphthalene (6) was determined from the previously prepared solution after addition of one crystal para-toluenesulfonic acid and storage for 12h (refer to Fig. S15).



**Figure S5:** <sup>1</sup>H-NMR spectra the reaction between 6-methyl-2-methoxybenzaldehyde (2) and methyl propiolate (4) to form cycloadduct (5) under irradiation with 385 nm LED. Top: Starting materials before irradiation; middle: cycloadduct (5), bottom: naphthalene (6) formed after the addition of *p*-toluenesulfonic acid.

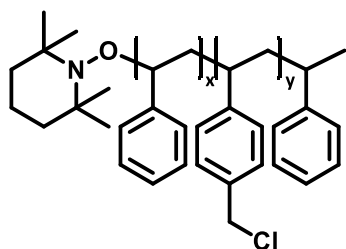




**Figure S6:** Molar attenuation coefficients (dashed lines) and fluorescence emission (full lines) of 6-methyl-2-methoxybenzaldehyde (**2**), cycloadduct (**5**) and naphthalene (**6**). methyl propiolate (**4**) Does not exhibit a significant extinction coefficient in the relevant region. The attenuation coefficients of cycloadduct (**5**) and naphthalene (**6**) are determined from a sample of the reaction mixture described above.

## 5. Polymer Synthesis and Functionalisation

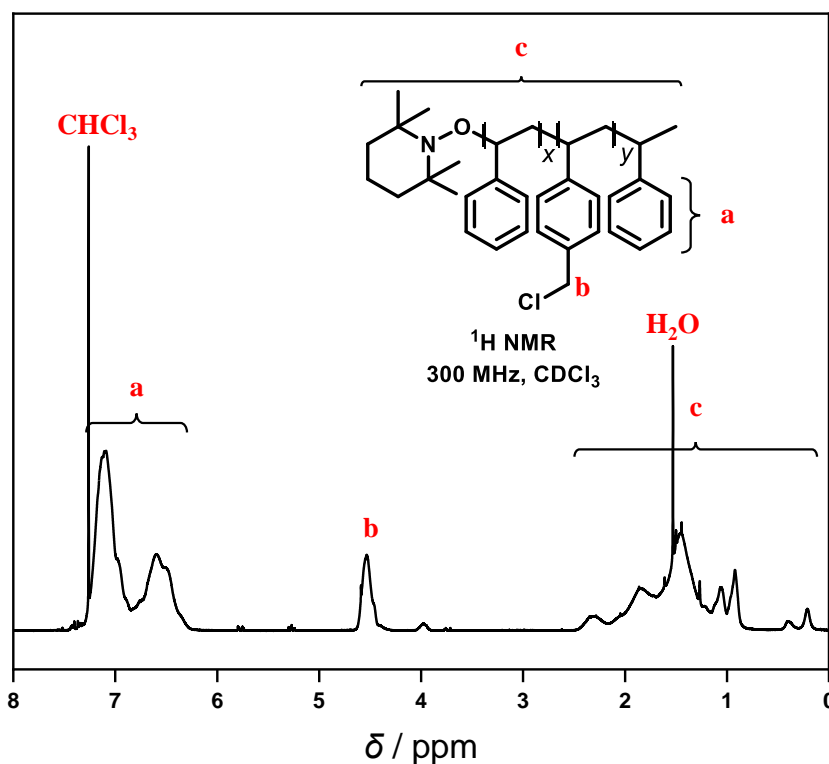
### *Poly(styrene-co-chloromethylstyrene) (P1)*



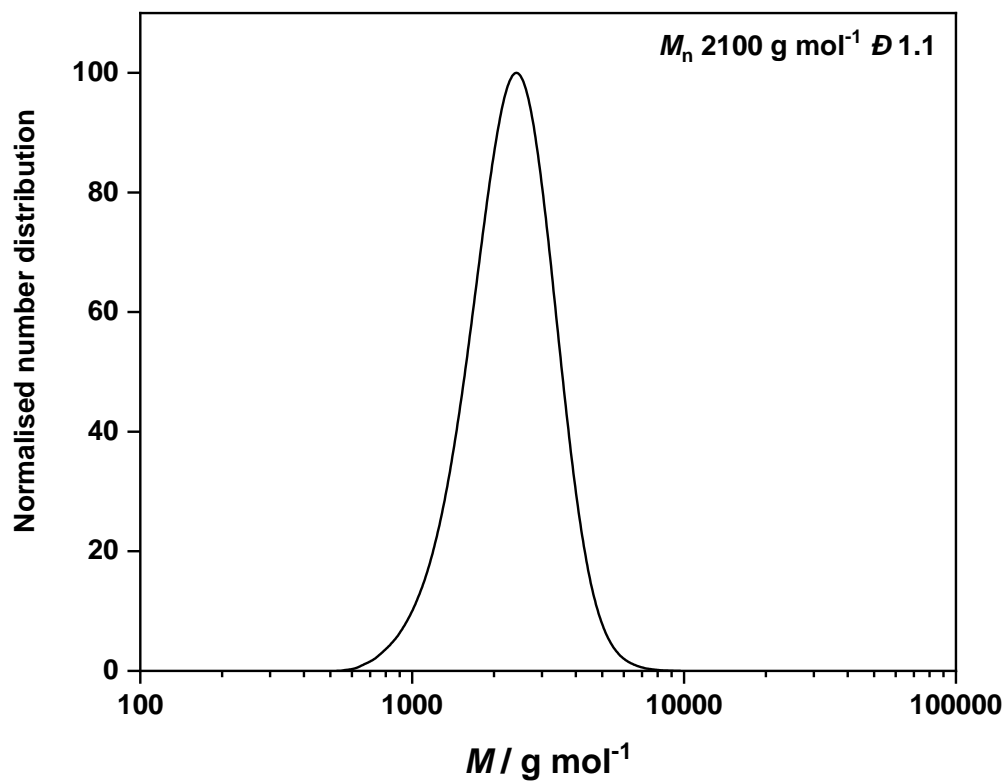
Initiator **3** (0.5195 g) was added to a crimp vial and dissolved in styrene (7 mL) and chloromethylstyrene (2 mL). The reaction mixture was degassed by bubbling with argon for 30 min, then heated to 120 °C. After 60 min the reaction was stopped by cooling the flask in liquid nitrogen. The crude mixture was dissolved in a small amount of THF (2 mL) and added dropwise to a solution of cold methanol. The precipitate was collected by filtration and dried under vacuum, yielding the product (**P1**) as a white solid (1.2461 g).

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  = 7.30 – 6.20 (m, ArH), 4.65 – 4.30 (s, br,  $\text{CH}_2\text{Cl}$ ), 2.50 – 0.84 ppm (m, aliphatic H).

SEC (PS cal.): 2100  $\text{g}\cdot\text{mol}^{-1}$ ,  $D$  1.1.

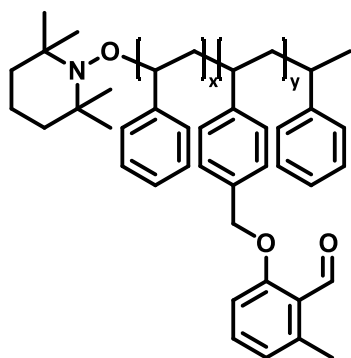


**Figure S7.**  $^1\text{H-NMR}$  spectrum of poly(styrene-co-chloromethylstyrene) **P1** recorded in chloroform-*d*.



**Figure S8.** Normalised SEC chromatogram of poly(styrene-*co*-chloromethylstyrene) (**P1**) in THF using a polystyrene calibration.

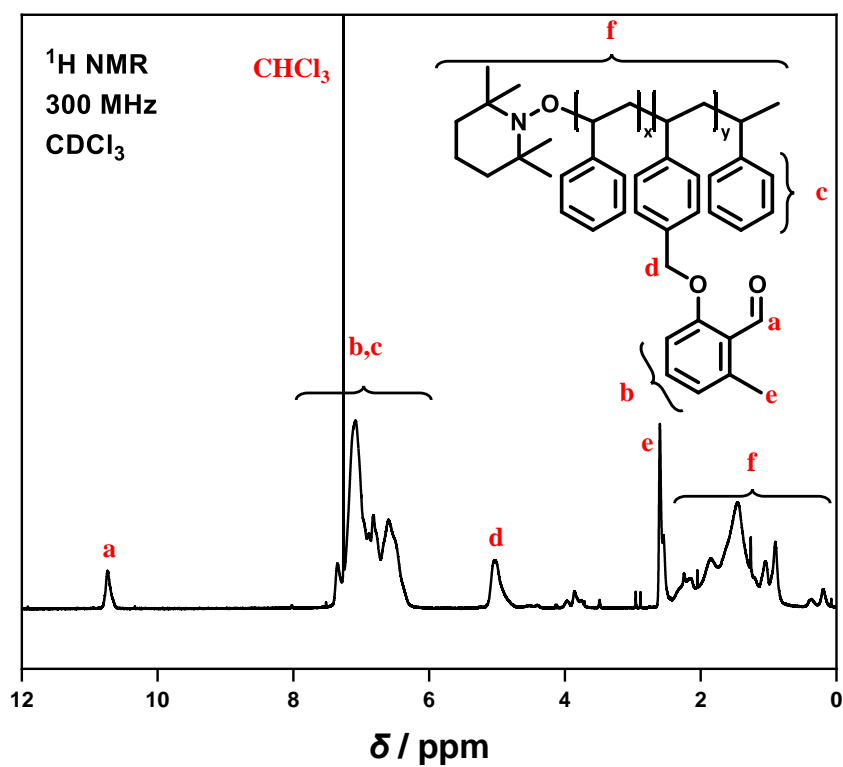
*Poly(styrene-co-photoenol) (P2)*



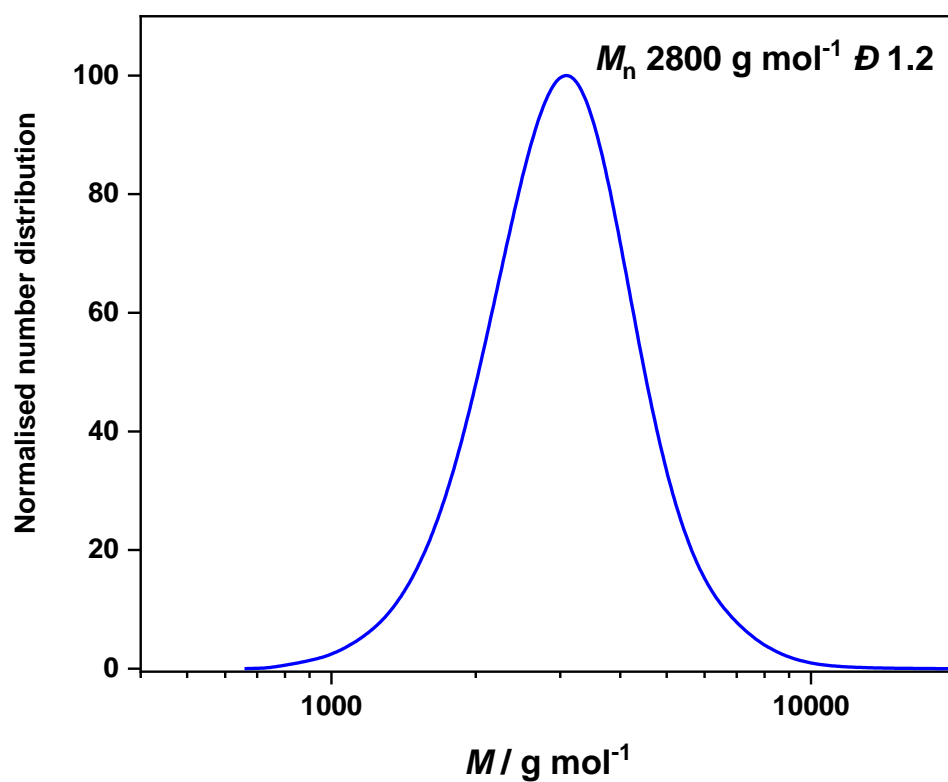
Poly(styrene-*co*-chloromethylstyrene) **P1** (0.4078 g), 2-hydroxy-6-methylbenzaldehyde **1** (0.203 g, 0.9 mmol) and Cs<sub>2</sub>CO<sub>3</sub> (0.95 g, 2.9 mmol) were dissolved in DMF, and stirred at 40 °C for 48 h. Subsequently, DMF was removed under reduced pressure and the reaction mixture diluted with EtOAc (100 mL), washed twice with water (50 mL) and then twice with brine (50 mL). The organic phase was dried with MgSO<sub>4</sub>, and the solvent removed under reduced pressure. The residue was dissolved in a minimum amount of THF and precipitated into cold methanol (50 mL). The precipitate was filtered under vacuum and washed with cold methanol, yielding the product **P2** (0.4027 g) as a brown solid.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz) δ = 10.66 (s, br, CH=O), 7.50 – 5.75 (m, ArH), 5.40 – 4.80 (m, CH<sub>2</sub>O), 2.60 (s, br, CH<sub>3</sub>), 2.50 – 0.75 ppm (m, aliphatic H).

SEC (PS cal.): 2800 g·mol<sup>-1</sup>, *D* 1.2.

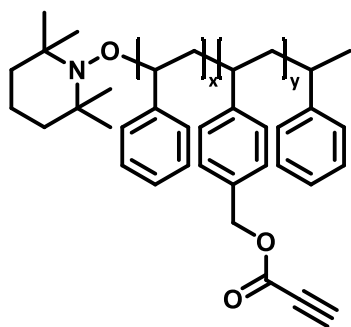


**Figure S9.**  $^1\text{H}$ -NMR spectrum of poly(styrene-*co*-photoenol) **P2** recorded in chloroform-*d*.



**Figure S10.** Normalised SEC chromatogram of poly(styrene-*co*-photoenol) (**P2**) in THF using a polystyrene calibration.

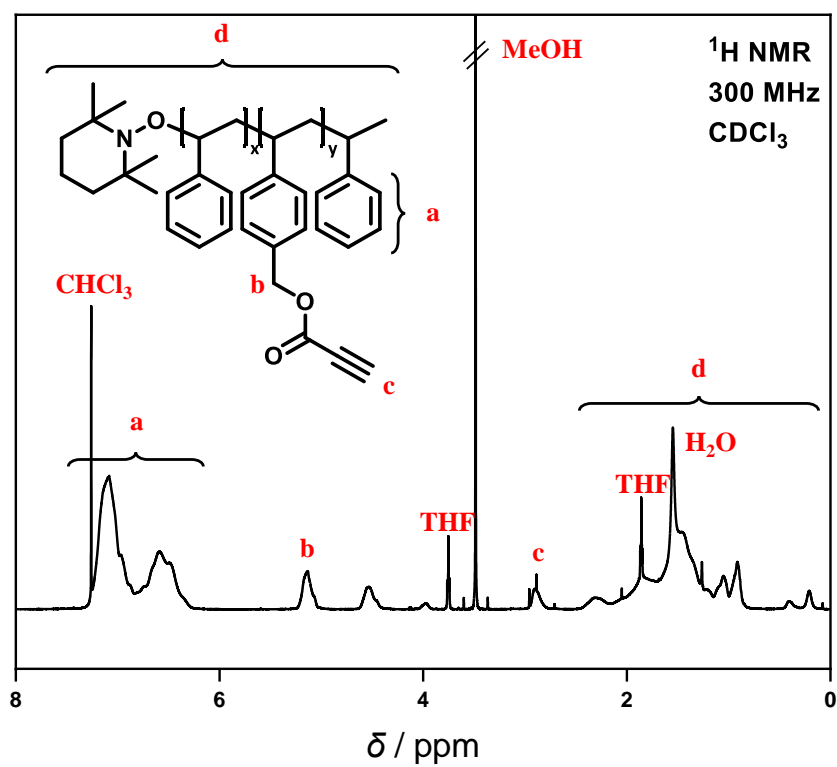
*Poly(styrene-co-propiolate) (P3)*



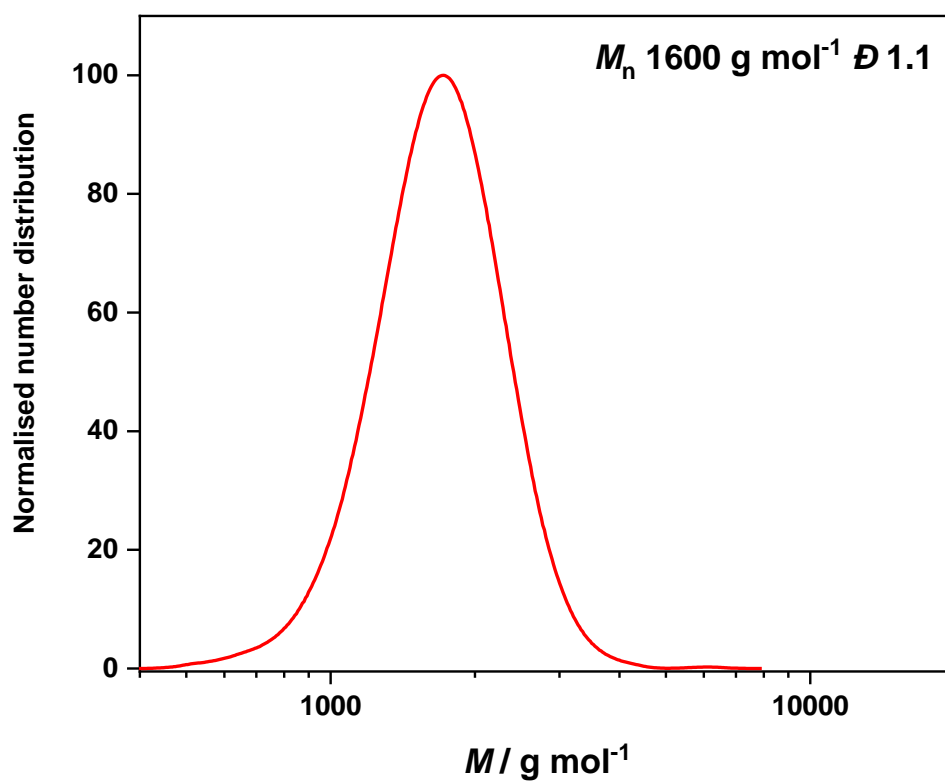
Poly(styrene-*co*-chloromethylstyrene) **P1** (0.4201 g, 1 eq), propiolic acid (0.5 mL, 5 eq) and Cs<sub>2</sub>CO<sub>3</sub> (0.93 g, 2.5 eq) were dissolved in DMF (50 mL), and stirred at room temperature for 72 h. Subsequently, DMF was removed under reduced pressure and the reaction mixture diluted with ethyl acetate (50 mL), washed twice with water (50 mL) and then twice with brine (50 mL). The organic phase was dried with MgSO<sub>4</sub>, and the solvent removed under reduced pressure. The residue was dissolved in THF and precipitated into cold methanol. The precipitate was collected by filtration and dried under vacuum, yielding the product **P3** as a white solid (0.2130 g).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz) δ = 7.30 – 6.20 (m, ArH), 5.30 – 5.00 (s, br, CH<sub>2</sub>O), 3.00 – 2.80 (s, br, C=CH), 2.50 – 0.75 ppm (m, aliphatic H).

SEC (PS cal.): 1600 g.mol<sup>-1</sup>, *D* 1.1.



**Figure S11.** <sup>1</sup>H-NMR spectrum of poly(styrene-*co*-propiolate) **P3** recorded in chloroform-*d*.



**Figure S12.** Normalised SEC chromatogram of poly(styrene-*co*-propiolate) (**P3**) in THF using a polystyrene calibration.

## Particle Synthesis

For a typical reaction, a solution of **P2** and **P3** was prepared at a concentration of 3 mg mL<sup>-1</sup> in 90:10% acetonitrile:tetrahydrofuran. The reaction solution was then filtered through a 0.22 µm PTFE syringe filter into an unused glass crimp vial, sealed and then degassed for 2 min with nitrogen. Reactions were then placed on a bottle roller at 2 rpm and irradiated with an LED ( $\lambda_{em} = 365 \text{ nm}$ ,  $I = 1.5 \text{ A}$ ;  $U = 14.55\text{V}$ ) for 2 h. The resulting cloudy dispersion was then centrifuged at 5000 rpm for 5 min, and the sediment twice redispersed in THF followed by centrifugation to yield the isolated microspheres.

To minimise re-aromatisation of the intermediate during particle synthesis, solvents were passed over basic alumina, and reaction vials washed to remove trace amounts of acid, prior to their use in the reaction.



## 6. Analysis of Copolymer Functionality and Composition

The percentage of functional monomer in copolymer **P1** was calculated from the <sup>1</sup>H-NMR spectrum using the ratio of the CH<sub>2</sub>-group and compared to the total aromatic protons. Overlap of the photo-enol peaks in **P2** with both the CH<sub>2</sub> and aromatic peaks makes post-functionalisation quantification difficult. Contribution to the aromatic integral from the initiator is considered to be negligible.

Chemical shifts (δ) used in calculations:

$$\int(\text{CH}_2) \text{ P1 } \delta (^1\text{H}) = 4.3 - 4.7$$

$$\int(\text{Ph-H}) \text{ P1 } \delta (^1\text{H}) = 6.2 - 7.25$$

**P1:**

$$\frac{5}{2 \cdot \frac{\int(\text{Ph-H})}{\int(\text{CH}_2)} + 1}$$
$$\frac{5}{2 \cdot \frac{14.6}{2} + 1} = \mathbf{32\%}$$

### Calculation of functional monomer per polymer chain

Using the percentages obtained above from the <sup>1</sup>H-NMR spectra and the  $M_n$  determined by SEC, the average number of units of functional monomer per polymer chain were approximated for **P1** as follows:

$$n(\text{CMS}) = n(\text{monomers}) \cdot X(\text{CMS})$$

Where  $n(\text{monomers})$  is the average number of monomers per polymer chain.

$X(\text{CMS})$  is the fraction of CMS in the copolymer

$$n(\text{monomers}) = \frac{M_n(\text{Polymer}) - M(\text{NMPgroup})}{M_{\text{Average}}(\text{monomer})}$$

Where  $M_n(\text{polymer})$  is the number-average molar mass of the copolymer determined by SEC.

$M(\text{NMPgroup})$  is the molar mass of the NMP initiator present in each polymer chain.

$M_{\text{Average}}(\text{monomer})$  is the combined average monomer mass:

$$M_{\text{Average}} = X(\text{CMS}) \cdot M(\text{CMS}) + X(\text{Styrene}) \cdot M(\text{Styrene})$$

Where  $M(\text{CMS})$  is the molar mass of CMS.

$X(\text{Styrene})$  is the fraction of Styrene in the copolymer.

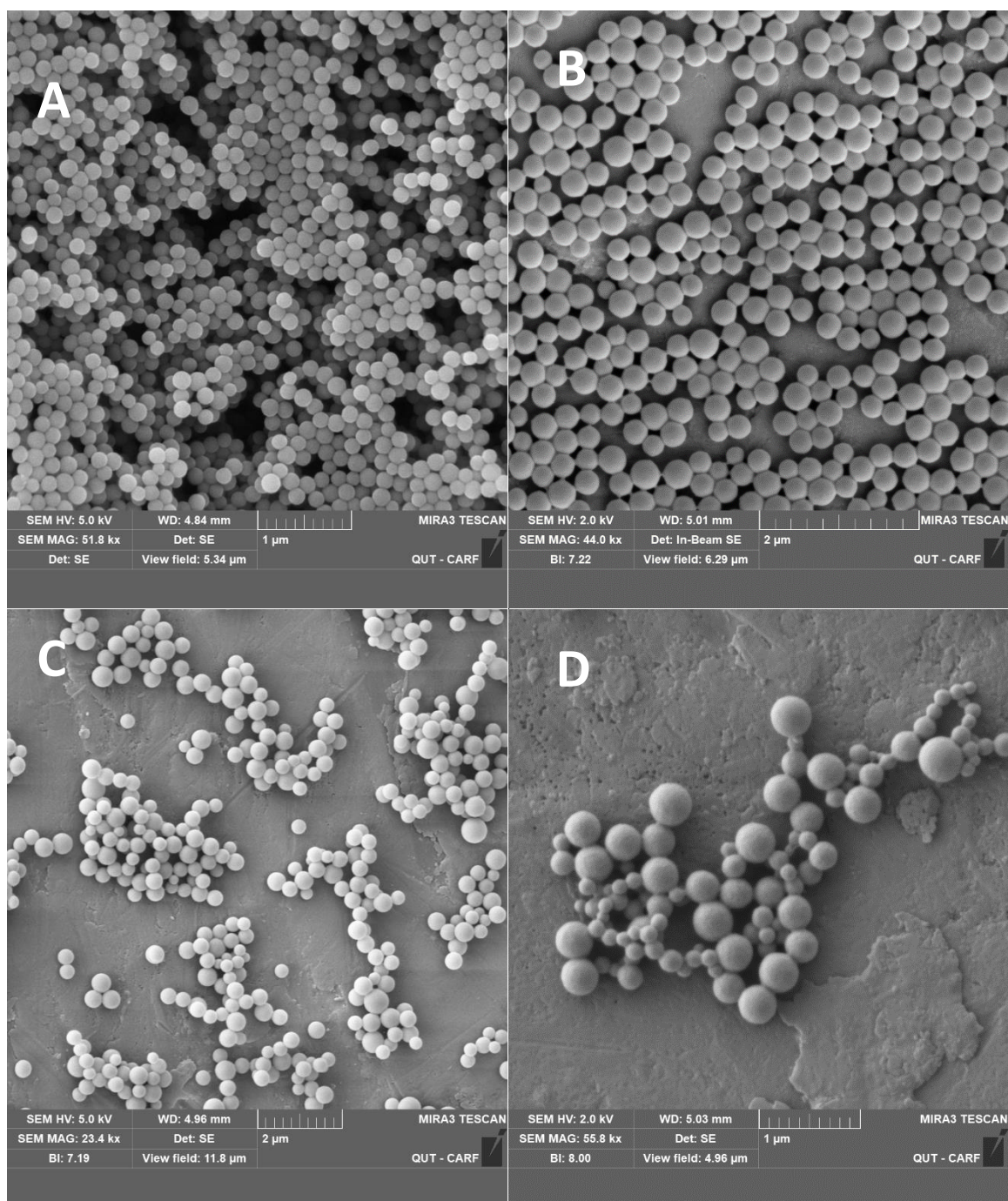
$M(\text{Styrene})$  is the molar mass of Styrene.

Combining for the number of CMS monomer units ( $n(\text{CMS})$ ):

$$\begin{aligned}n(\text{CMS}) &= \frac{M_n(\text{Polymer}) - M(\text{NMPgroup})}{X(\text{CMS}) \cdot M(\text{CMS}) + X(\text{Styrene}) \cdot M(\text{Styrene})} \cdot X(\text{CMS}) \\ &= \left( \frac{2100 \text{ g} \cdot \text{mol}^{-1} - 261 \text{ g} \cdot \text{mol}^{-1}}{0.32 \cdot 152 \text{ g} \cdot \text{mol}^{-1} + 0.68 \cdot 104 \text{ g} \cdot \text{mol}^{-1}} \right) \cdot 0.32 = 5\end{aligned}$$

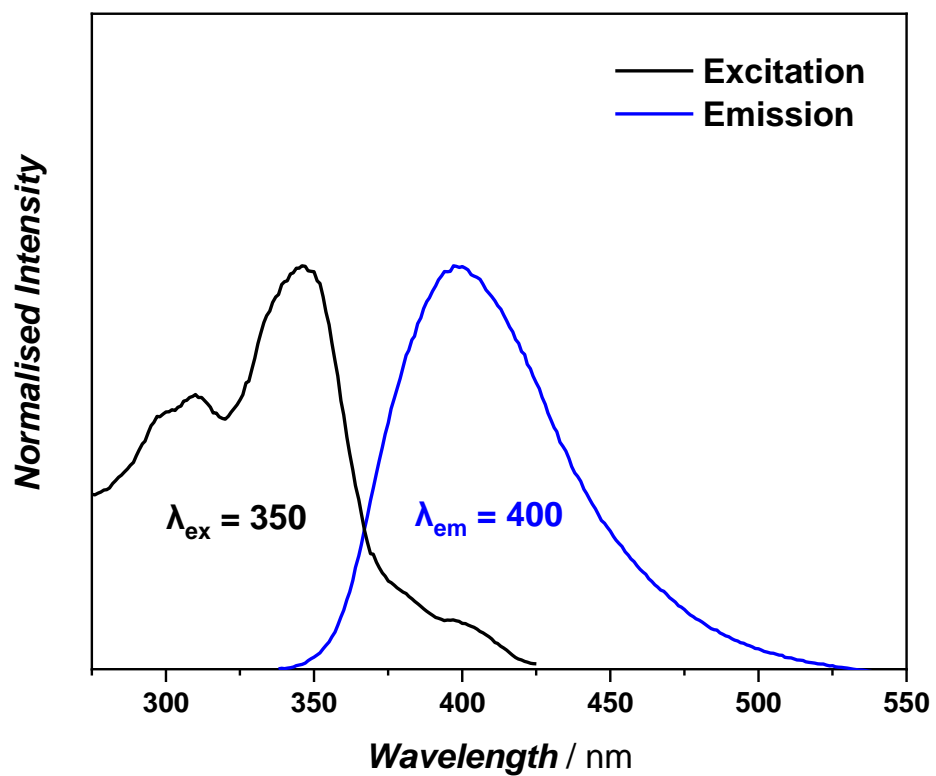
$$\begin{aligned}n(\text{Styrene}) &= \frac{M_n(\text{Polymer}) - M(\text{NMPgroup})}{X(\text{CMS}) \cdot M(\text{CMS}) + X(\text{Styrene}) \cdot M(\text{Styrene})} \cdot X(\text{Styrene}) \\ &= \left( \frac{2100 \text{ g} \cdot \text{mol}^{-1} - 261 \text{ g} \cdot \text{mol}^{-1}}{0.32 \cdot 152 \text{ g} \cdot \text{mol}^{-1} + 0.68 \cdot 104 \text{ g} \cdot \text{mol}^{-1}} \right) \cdot 0.68 = 10\end{aligned}$$

## 7. SEM Analysis of Microspheres



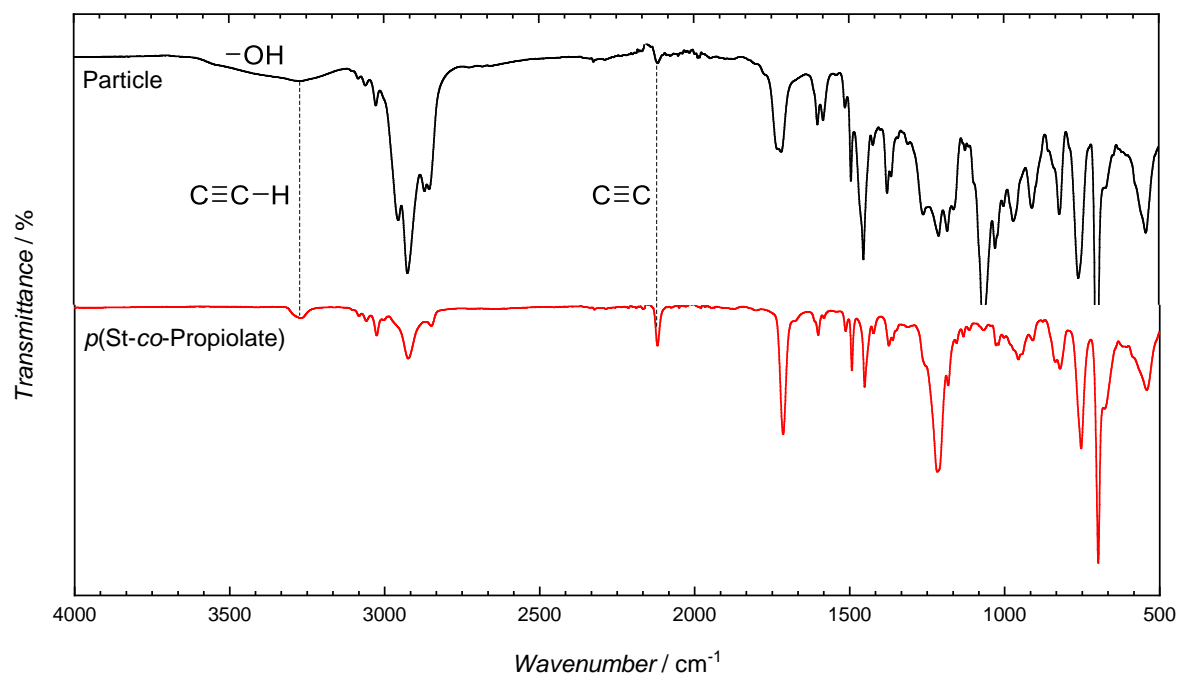
**Figure S13.** Particle Synthesis reactions of **P2** and **P3** under different conditions. (A)  $c = 2 \text{ mg mL}^{-1}$ , 100:0 ACN:THF; (B)  $c = 3 \text{ mg mL}^{-1}$ , 90:10 ACN:THF; (C)  $c = 3 \text{ mg mL}^{-1}$ , 80:20 ACN:THF; (D)  $c = 3 \text{ mg mL}^{-1}$ , 70:30 ACN:THF.

## 8. Particle Emission/Absorption Spectra via Fluorescence Spectroscopy



**Figure S14.** Fluorescence excitation and emission spectra of the microspheres, dispersed in THF.

## 9. IR Spectroscopy



**Figure S15:** IR spectroscopy of *p*(St-co-Propiolate) P3 and the synthesised particles, highlighting the stretching vibrations of the terminal alkyne.