

*Supplementary Information*

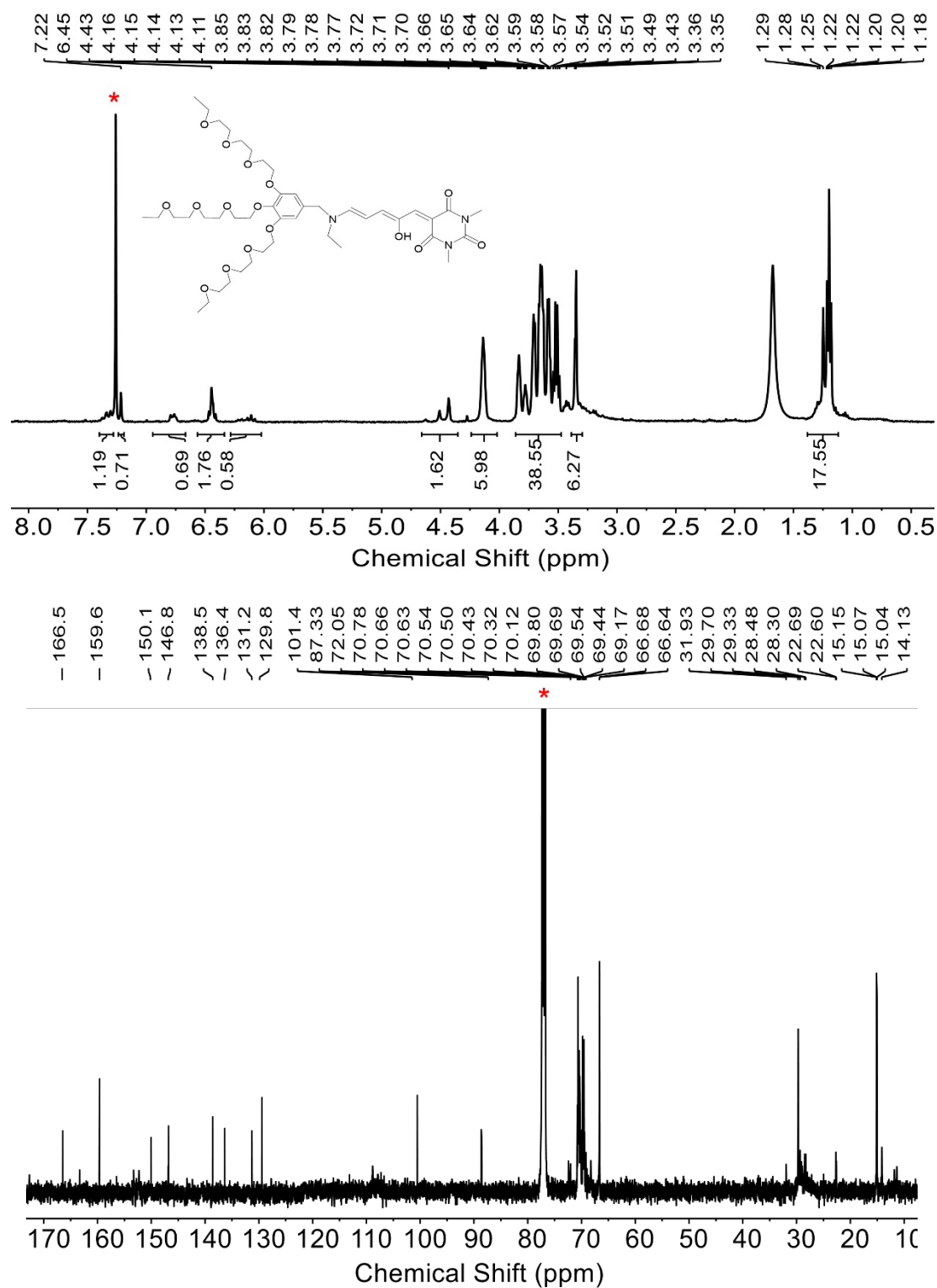
**Crowding for Confinement: Reversible Isomerization of First-Generation Donor-Acceptor Stenhouse Adduct Derivatives in Water Modulated by Thermoresponsive Dendritic Macromolecules**

Jiaxing Zhang, Qinqin Ma, Huan Wang, Peinan Zhang, Xinyan Su,<sup>\*</sup> Afang Zhang,<sup>\*</sup> and Wen Li<sup>\*</sup>

International Joint Laboratory of Biomimetic and Smart Polymers, School of Materials Science and Engineering, Shanghai University, Mailbox 152, Shangda Rd. 99, Shanghai 200444, China.  
Tel: +86-21-66138053. Fax: +86-21-66138039. Emails: [wli@shu.edu.cn](mailto:wli@shu.edu.cn) (W.L.), [xysu@shu.edu.cn](mailto:xysu@shu.edu.cn) (X.S.), and [azhang@shu.edu.cn](mailto:azhang@shu.edu.cn) (A.Z.)

## Table of Contents

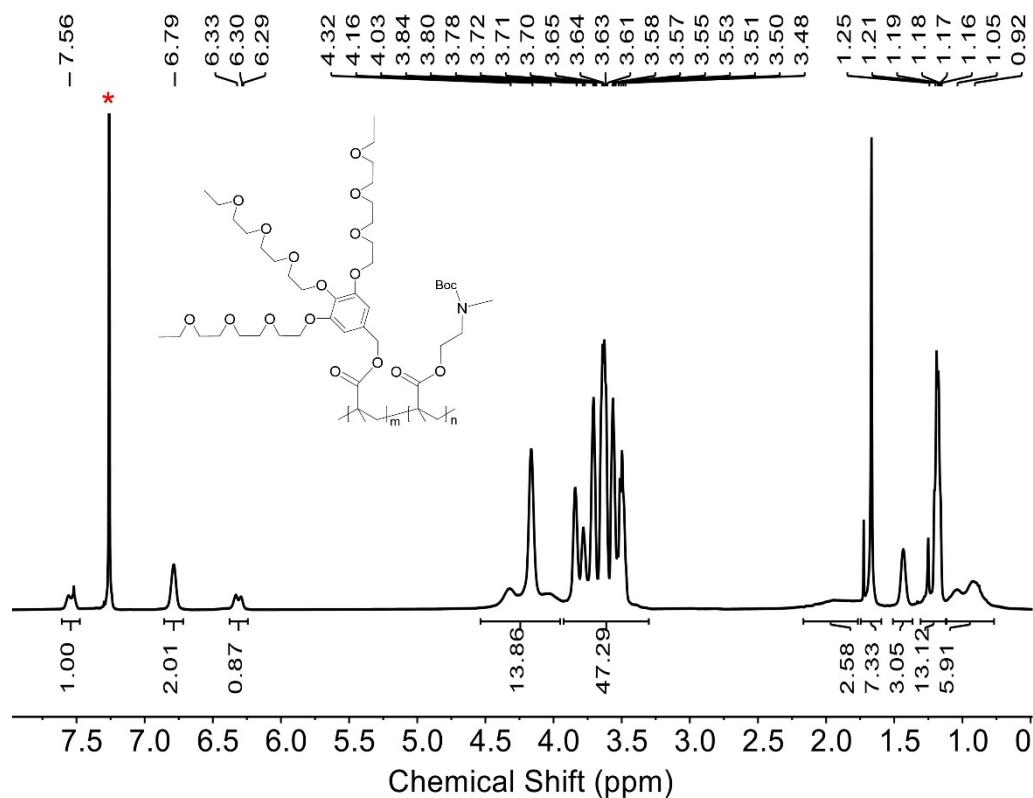
<b>Figure S1.</b> $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of <b>Et-Dm</b> in $\text{CDCl}_3$ .....	S3
<b>Figure S2.</b> $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of <b>Me-Do</b> in $\text{CDCl}_3$ .....	S4
<b>Figure S3.</b> $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of <b>Et-Do</b> in $\text{CDCl}_3$ .....	S5
<b>Figure S4.</b> $^1\text{H}$ spectra of <b>Poly(G1Et<sub>20</sub>-co-Boc<sub>1</sub>)</b> in $\text{CDCl}_3$ .....	S6
<b>Figure S5.</b> $^1\text{H}$ spectra of <b>Poly(G1Me<sub>20</sub>-co-Boc<sub>1</sub>)</b> in $\text{CDCl}_3$ .....	S6
<b>Figure S6.</b> $^1\text{H}$ spectra of <b>Poly(G1Et<sub>20</sub>-co-H<sub>1</sub>)</b> in $\text{CDCl}_3$ .....	S7
<b>Figure S7.</b> $^1\text{H}$ spectra of <b>Poly(G1Me<sub>20</sub>-co-H<sub>1</sub>)</b> in $\text{CDCl}_3$ .....	S7
<b>Figure S8.</b> $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of <b>Poly(G1Et<sub>20</sub>-co-Dm<sub>1</sub>)</b> in $\text{CDCl}_3$ .....	S8
<b>Figure S9.</b> $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of <b>Poly(G1Me<sub>20</sub>-co-Do<sub>1</sub>)</b> in $\text{CDCl}_3$ .....	S9
<b>Figure S10.</b> $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of <b>Poly(G1Et<sub>20</sub>-co-Do<sub>1</sub>)</b> in $\text{CDCl}_3$ .....	S10
<b>Figure S11.</b> HR-MS spectrum of compound <b>Et-Dm</b> .....	S11
<b>Figure S12.</b> HR-MS spectrum of compound <b>Me-Do</b> .....	S11
<b>Figure S13.</b> HR-MS spectrum of compound <b>Et-Do</b> .....	S11
<b>Table S1.</b> Conditions for and results from the copolymerization of <b>G1Me</b> or <b>G1Et</b> with <b>Dm</b> or <b>Do</b> .....	S12
<b>Figure S14.</b> Optical micrographs of the aqueous solutions from dendronized DASAs (a) and the corresponding dendronized copolymethacrylates (b) below and above their $T_{\text{cps}}$ .....	S12
<b>Figure S15.</b> UV/vis spectra of dendronized DASAs in aqueous solutions with a concentration of $0.25 \text{ mg}\cdot\text{mL}^{-1}$ (a), as well as these from <b>Et-Dm</b> (b), <b>Me-Do</b> (c), and <b>Et-Do</b> (d) in aqueous solutions with different concentrations.....	S13
<b>Figure S16.</b> Plots of time-dependent absorbance at $\lambda_{\text{max}}$ for <b>Et-Dm</b> (a), <b>Me-Do</b> (b), and <b>Et-Do</b> (c) in aqueous solutions with different concentrations in dark.....	S14
<b>Figure S17.</b> UV/vis spectra of <b>Et-Dm</b> (a), <b>Me-Do</b> (b), and <b>Et-Do</b> (c) in aqueous solutions at different temperatures in dark.....	S14
<b>Figure S18.</b> UV/vis spectra of <b>Et-Dm</b> (concentration = $0.25 \text{ mg}\cdot\text{mL}^{-1}$ ) photoisomerization (a), light-sheltered heating at $25^\circ\text{C}$ (b), $45^\circ\text{C}$ (c), and $65^\circ\text{C}$ (d).....	S15
<b>Figure S19.</b> UV/vis spectra of <b>Me-Do</b> (concentration = $0.25 \text{ mg}\cdot\text{mL}^{-1}$ ) photoisomerization (a), light-sheltered heating at $25^\circ\text{C}$ (b), $45^\circ\text{C}$ (c), and $65^\circ\text{C}$ (d).....	S15
<b>Figure S20.</b> UV/vis spectra of <b>Et-Do</b> (concentration = $0.25 \text{ mg}\cdot\text{mL}^{-1}$ ) photoisomerization (a), light-sheltered heating at $25^\circ\text{C}$ (b), $45^\circ\text{C}$ (c), and $65^\circ\text{C}$ (d).....	S16
<b>Figure S21.</b> Plots of $R_{\text{h}}$ vs temperature for <b>Et-Dm</b> , <b>Me-Do</b> , and <b>Et-Do</b> at different temperatures (a), and plots of $R_{\text{h}}$ vs temperature for <b>Me-Do</b> and <b>Et-Do</b> in aqueous solutions after repeated photo-irradiation and heating (b). Concentration = $0.25 \text{ mg}\cdot\text{mL}^{-1}$ .....	S16
<b>Figure S22.</b> Plots of absorbance at $\lambda_{\text{max}}$ for <b>Et-Dm</b> (a), <b>Me-Do</b> (b), and <b>Et-Do</b> (c) with different concentrations against time after photo-irradiation and followed by annealing at $65^\circ\text{C}$ .....	S17
<b>Figure S23.</b> UV/vis spectra of <b>Poly(G1Et<sub>20</sub>-co-Dm<sub>1</sub>)</b> , <b>Poly(G1Me<sub>20</sub>-co-Do<sub>1</sub>)</b> , and <b>Poly(G1Et<sub>20</sub>-co-Do<sub>1</sub>)</b> (c) in aqueous solutions with different concentrations.....	S17
<b>Figure S24.</b> UV/vis spectra of <b>Poly(G1Et<sub>20</sub>-co-Dm<sub>1</sub>)</b> (a), <b>Poly(G1Me<sub>20</sub>-co-Do<sub>1</sub>)</b> (b), and <b>Poly(G1Et<sub>20</sub>-co-Do<sub>1</sub>)</b> (c) in aqueous solutions at different temperatures in dark.....	S18
<b>Figure S25.</b> UV/vis spectra of <b>Poly(G1Et<sub>20</sub>-co-Dm<sub>1</sub>)</b> in aqueous solutions (concentration = $0.25 \text{ mg}\cdot\text{mL}^{-1}$ ) through photo-irradiation (a), and followed by thermal annealing at $25^\circ\text{C}$ (b), $45^\circ\text{C}$ (c), and $65^\circ\text{C}$ (d) in dark.....	S18
<b>Figure S26.</b> UV/vis spectra of <b>Poly(G1Me<sub>20</sub>-co-Do<sub>1</sub>)</b> in aqueous solutions (concentration = $0.25 \text{ mg}\cdot\text{mL}^{-1}$ ) through photo-irradiation (a), and followed by thermal annealing at $25^\circ\text{C}$ (b), $45^\circ\text{C}$ (c), and $65^\circ\text{C}$ (d) in dark.....	S19
<b>Figure S27.</b> UV/vis spectra of <b>Poly(G1Et<sub>20</sub>-co-Do<sub>1</sub>)</b> in aqueous solutions (concentration = $0.25 \text{ mg}\cdot\text{mL}^{-1}$ ) through photo-irradiation (a), and followed by thermal annealing at $25^\circ\text{C}$ (b), $45^\circ\text{C}$ (c), and $65^\circ\text{C}$ (d) in dark.....	S19



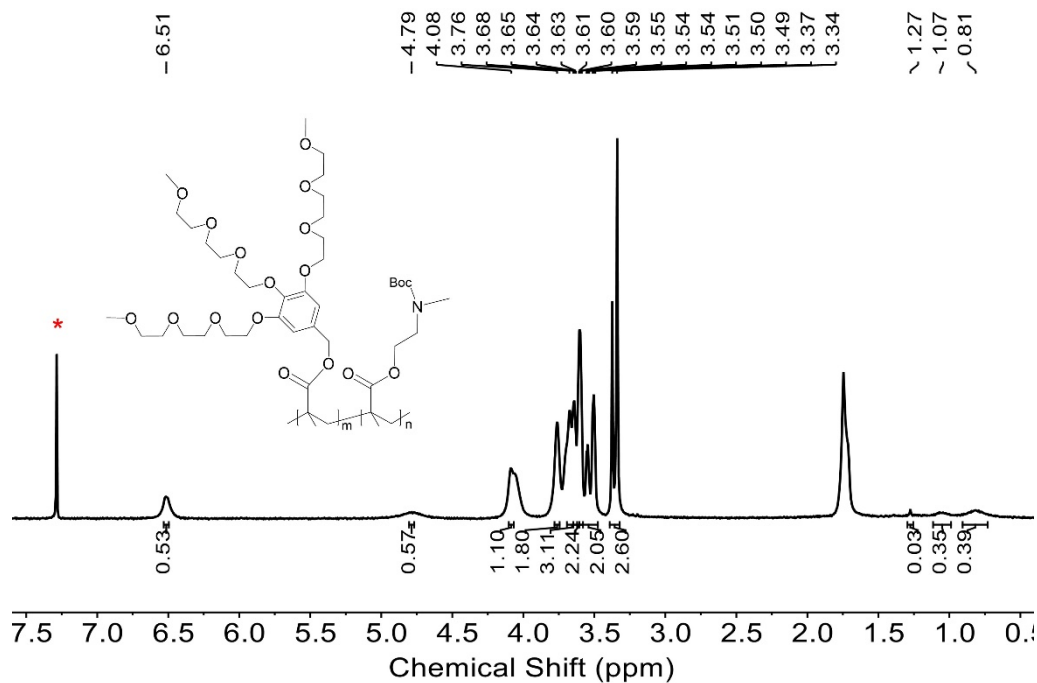
**Figure S1.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **Et-Dm** in CDCl<sub>3</sub>. Solvent peaks and water peaks marked as \*.



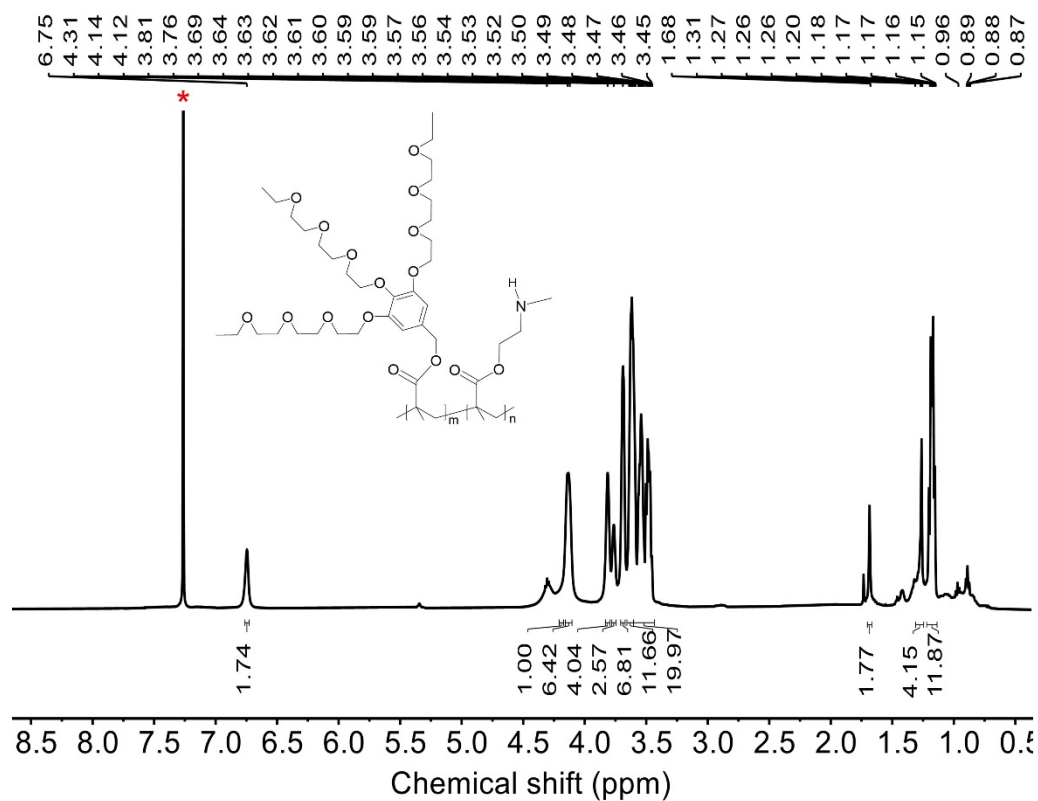




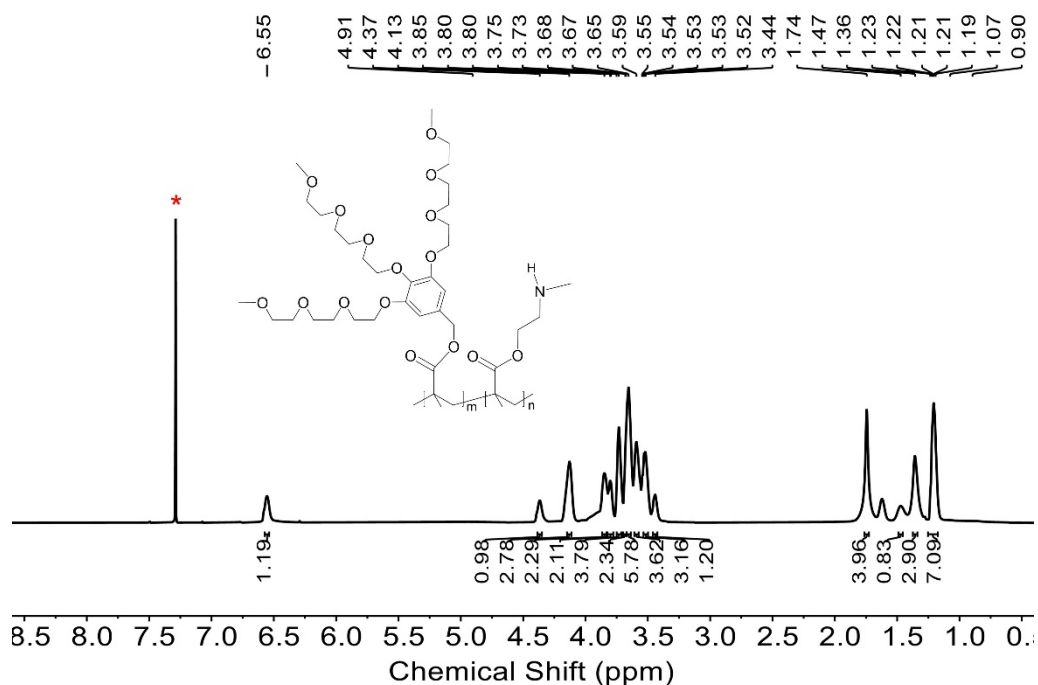
**Figure S4.** <sup>1</sup>H spectra of Poly(G1Et<sub>20</sub>-co-Boc<sub>1</sub>) in CDCl<sub>3</sub>. Solvent peaks and water peaks are marked as \*.



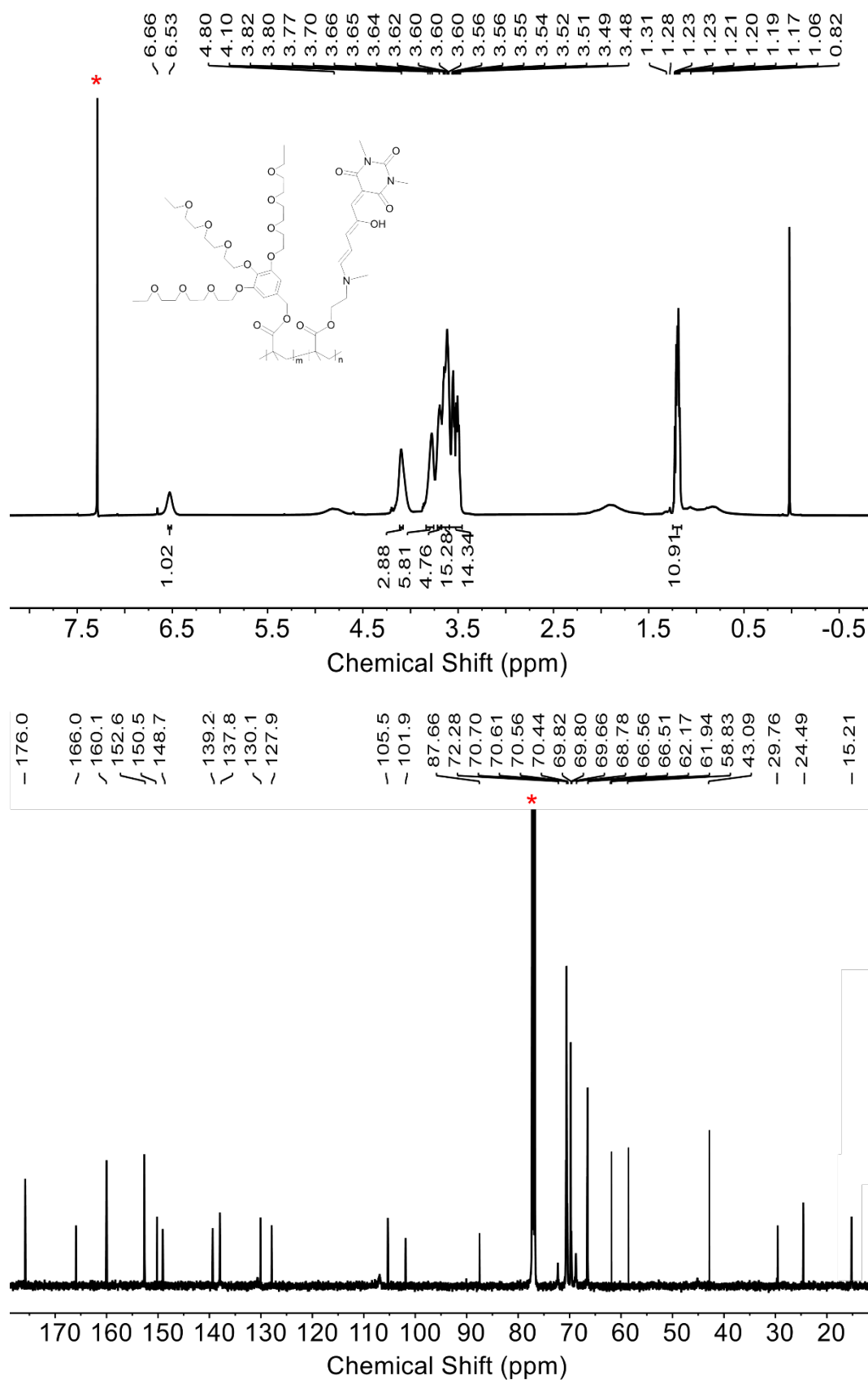
**Figure S5.** <sup>1</sup>H spectra of Poly(G1Me<sub>20</sub>-co-Boc<sub>1</sub>) in CDCl<sub>3</sub>. Solvent peaks and water peaks are marked as \*.



**Figure S6.**  $^1\text{H}$  spectra of **Poly(G1Et<sub>20</sub>-co-H<sub>1</sub>)** in  $\text{CDCl}_3$ . Solvent peaks and water peaks are marked as \*.

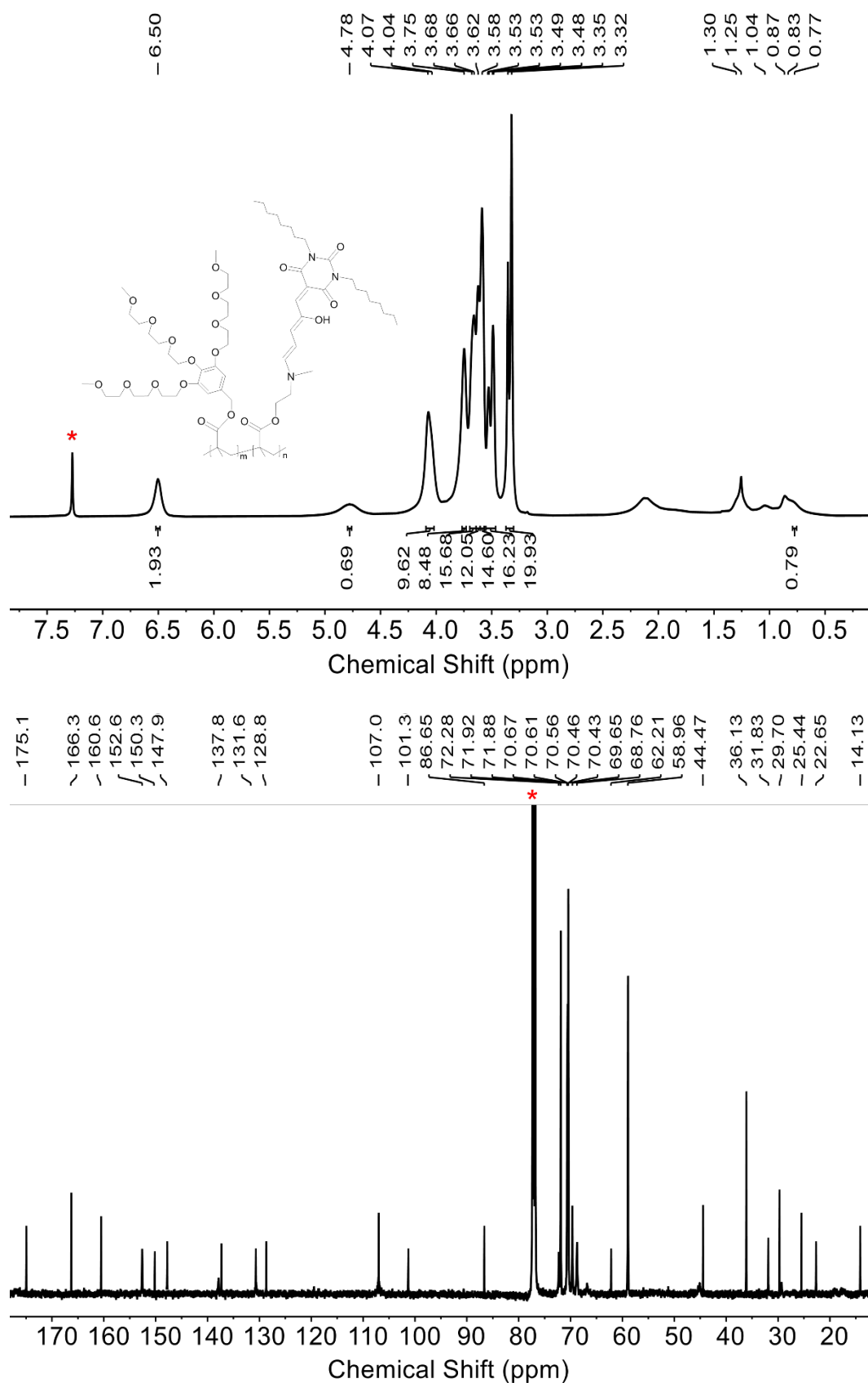


**Figure S7.**  $^1\text{H}$  spectra of **Poly(G1Me<sub>20</sub>-co-H<sub>1</sub>)** in  $\text{CDCl}_3$ . Solvent peaks and water peaks are marked as \*.

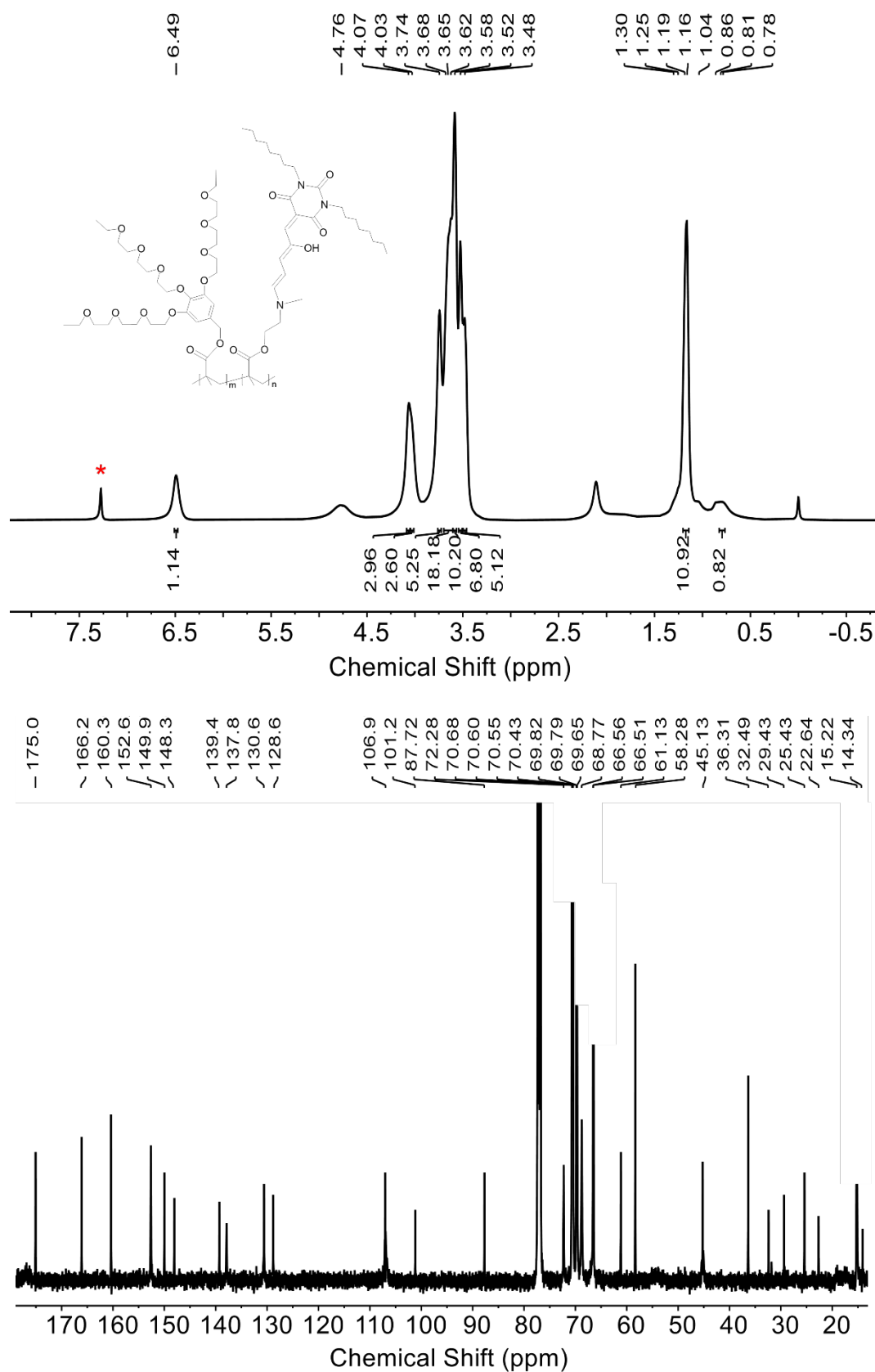


**Figure S8.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of Poly(G1Et<sub>20</sub>-co-Dm<sub>1</sub>) in CDCl<sub>3</sub>. Solvent peaks and water peaks are marked as \*.

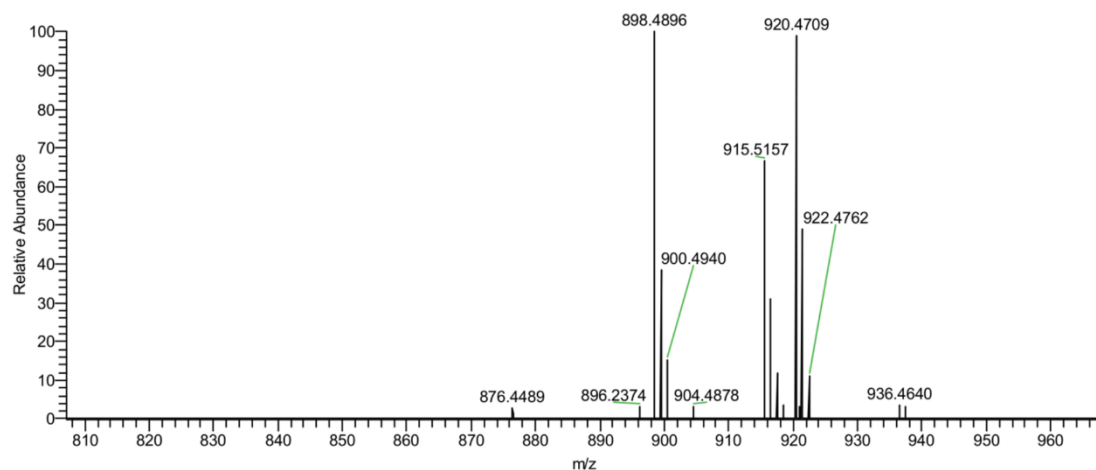




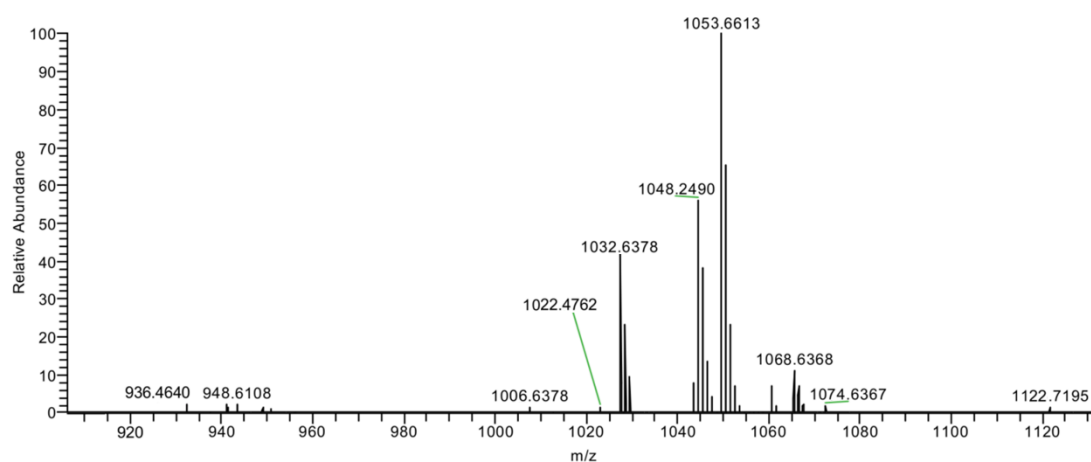
**Figure S9.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **Poly(G1Me<sub>20</sub>-co-Do<sub>1</sub>)** in CDCl<sub>3</sub>. Solvent peaks and water peaks are marked as \*.



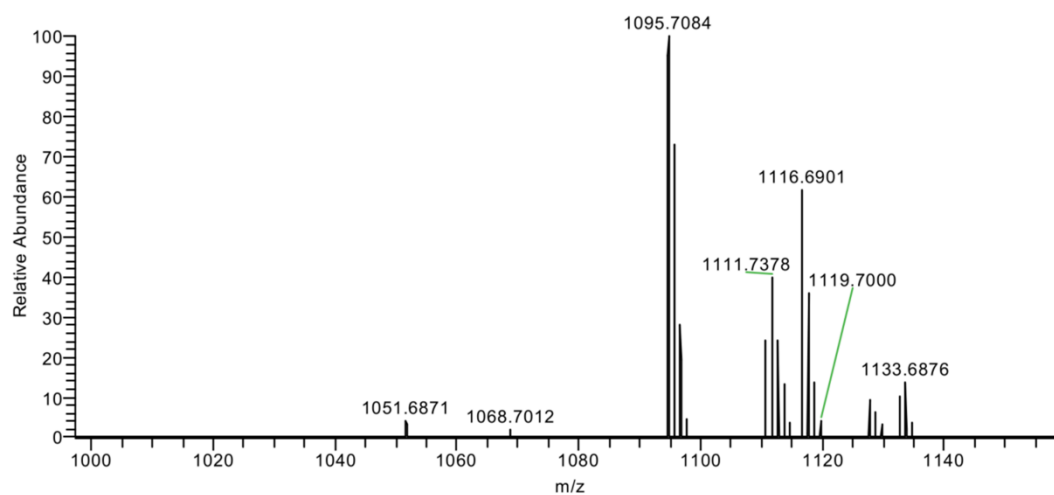
**Figure S10.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of **Poly(G1Et<sub>20</sub>-co-Do<sub>1</sub>)** in CDCl<sub>3</sub>. Solvent peaks and water peaks are marked as \*.



**Figure S11.** HR-MS spectrum of compound **Et-Dm**.



**Figure S12.** HR-MS spectrum of compound **Me-Do**.

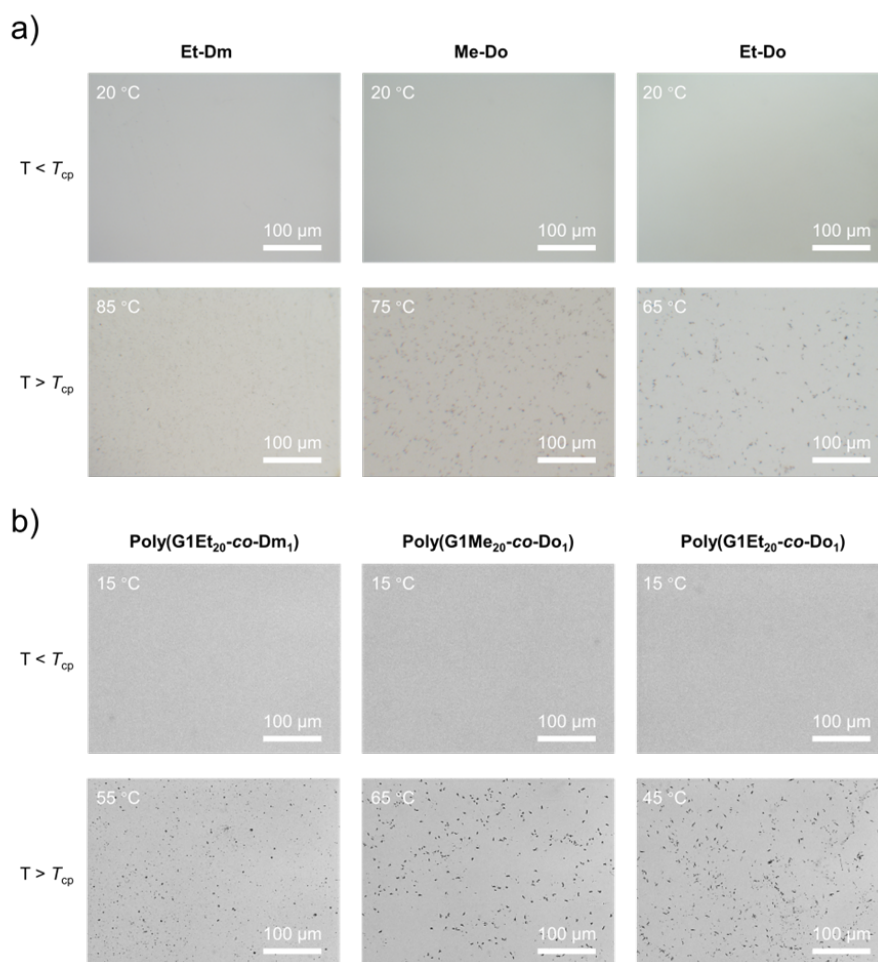


**Figure S13.** HR-MS spectrum of compound **Et-Do**.

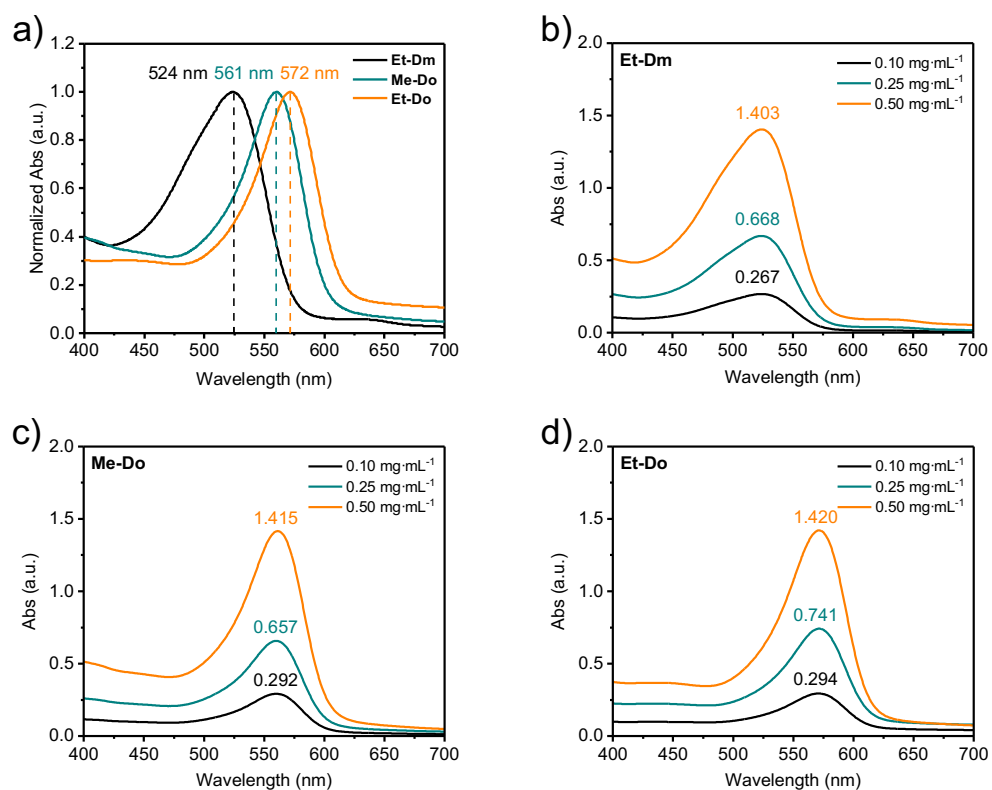
**Table S1.** Conditions for and results from the copolymerization of **G1Me** or **G1Et** with **Dm** or **Do**.

Sample names	Feed ratio <sup>a</sup>	Actual ratio <sup>b</sup>	GPC result <sup>c</sup>	
			$M_n (\times 10^{-5})$	$\bar{D}$
<b>Poly(G1Et<sub>20-co</sub>-Dm<sub>1</sub>)</b>	20:1	20:1	1.1	2.5
<b>Poly(G1Me<sub>20-co</sub>-Do<sub>1</sub>)</b>	20:1	22:1	1.3	2.7
<b>Poly(G1Et<sub>20-co</sub>-Do<sub>1</sub>)</b>	20:1	21:1	1.0	3.1

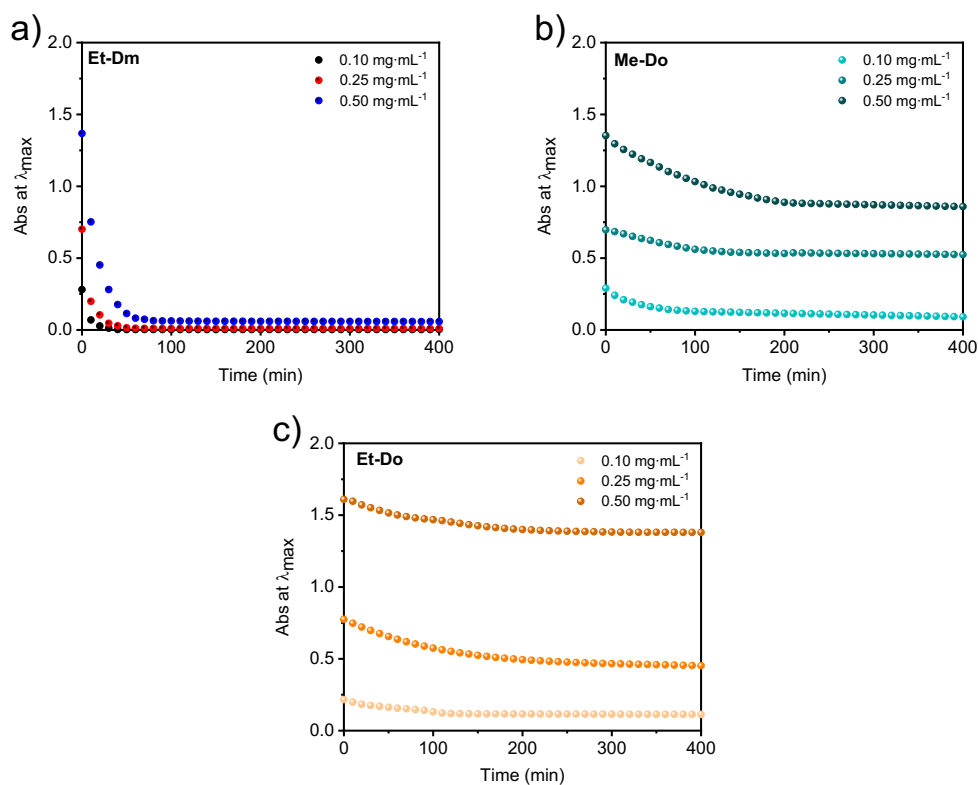
<sup>a</sup> Feed ratio of monomer **G1Me** or **G1Et** to monomer **Dm** or **Do**. <sup>b</sup> Obtained from the proton integral ratios of <sup>1</sup>H NMR spectra. <sup>c</sup> Determined by GPC with DMF as eluent containing 1.00 mg·mL<sup>-1</sup> of LiBr.  $M_n$  and  $\bar{D}$  represent number-average molecular weight and polydispersity of the polymers, respectively.



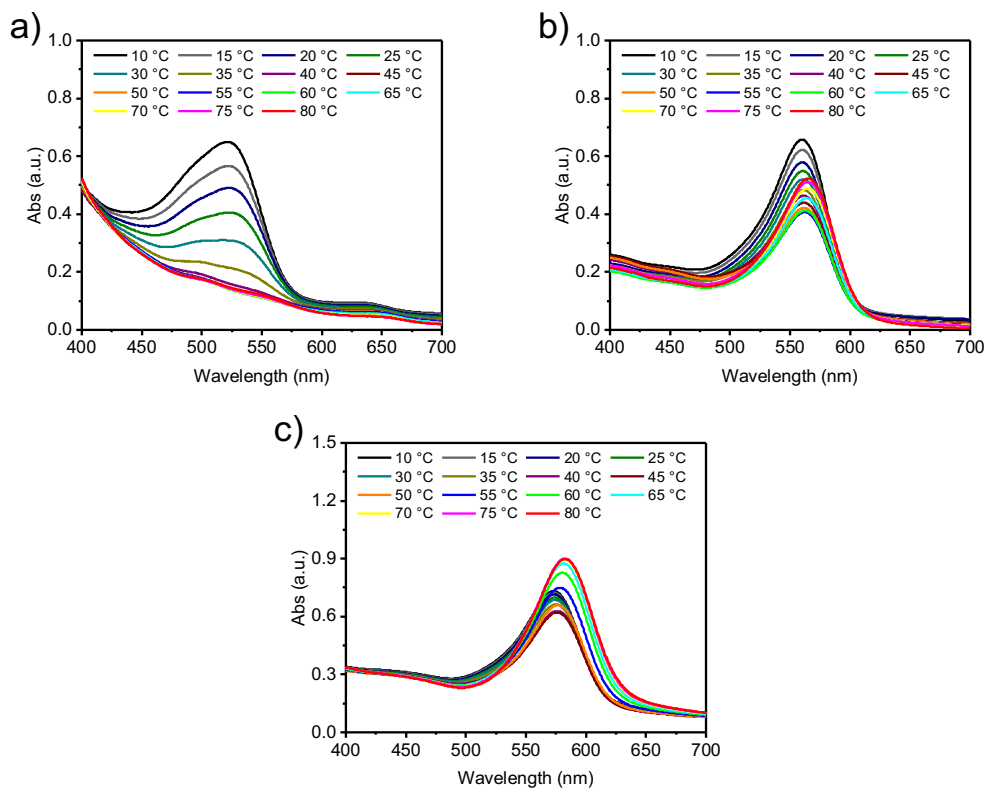
**Figure S14.** Optical micrographs of the aqueous solutions from dendronized DASAs (a) and the corresponding dendronized copolymethacrylates (b) below and above their  $T_{cps}$ . Concentration = 0.50 mg·mL<sup>-1</sup>.



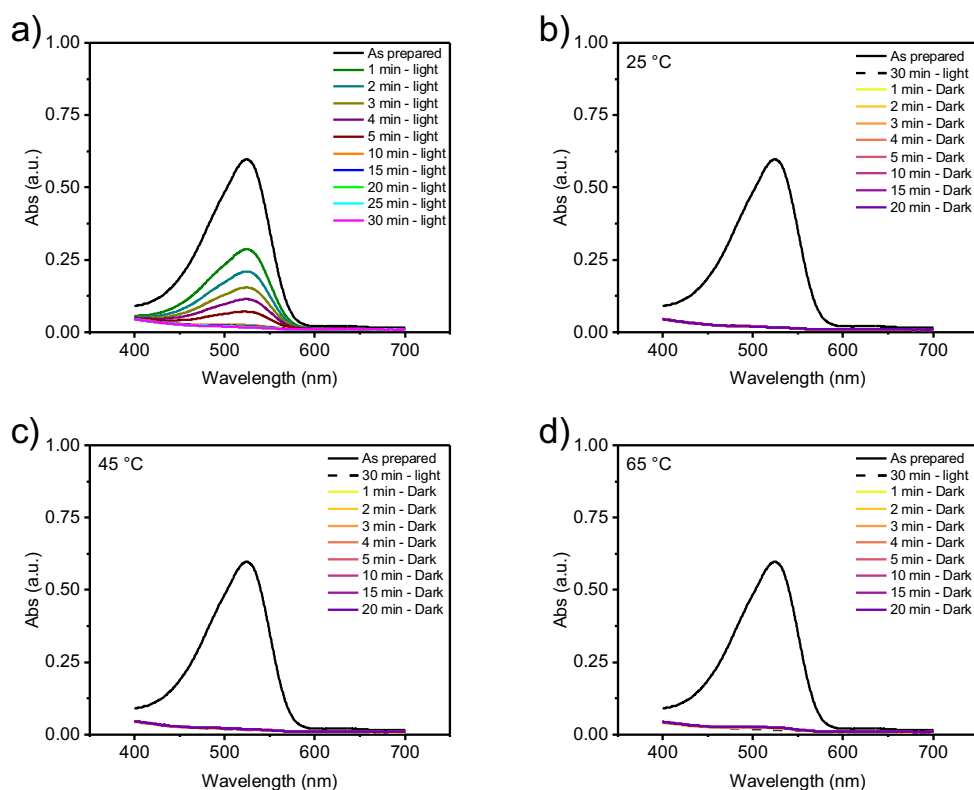
**Figure S15.** UV/vis spectra of the dendronized DASAs in aqueous solutions with a concentration of 0.25 mg·mL<sup>-1</sup> (a), as well as these from **Et-Dm** (b), **Me-Do** (c), and **Et-Do** (d) in aqueous solutions with different concentrations. Temperature was set to 25.0 °C for all measurements.



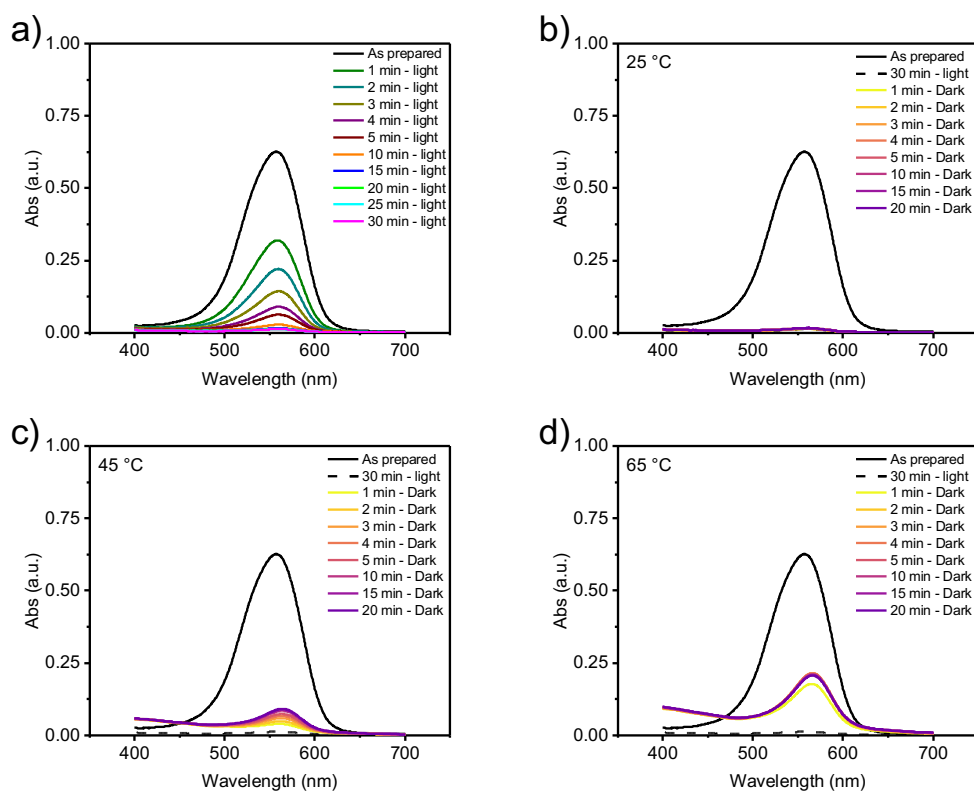
**Figure S16.** Plots of time-dependent absorbance at  $\lambda_{\max}$  for **Et-Dm** (a), **Me-Do** (b), and **Et-Do** (c) in aqueous solutions with different concentrations in dark.



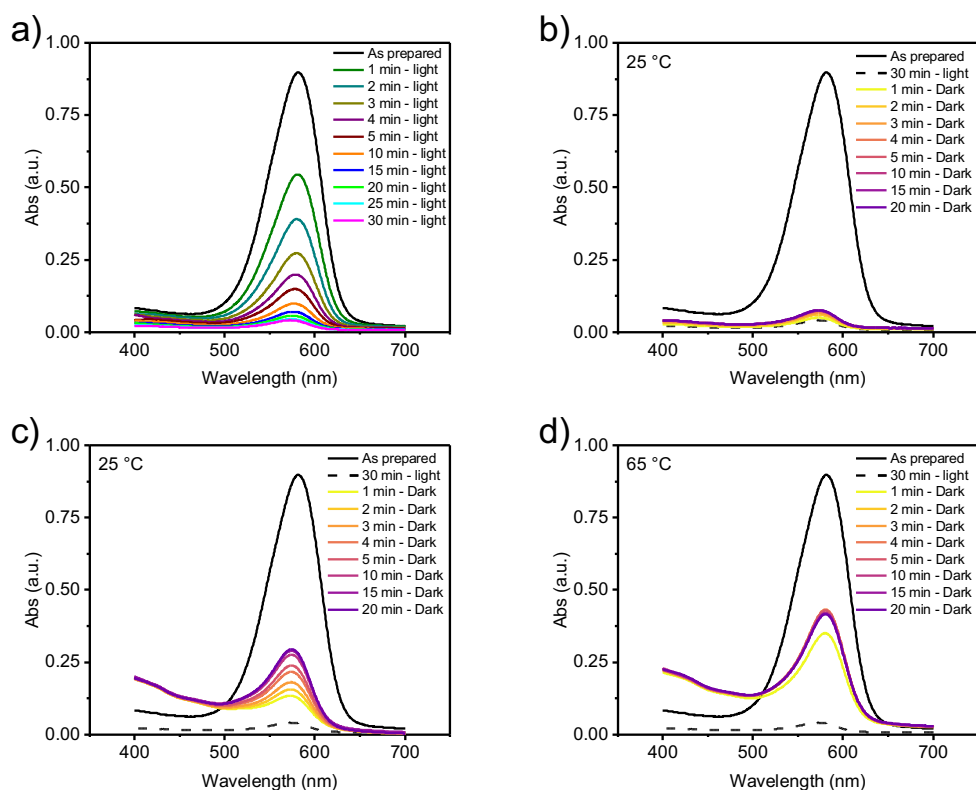
**Figure S17.** UV/vis spectra of **Et-Dm** (a), **Me-Do** (b), and **Et-Do** (c) in aqueous solutions at different temperatures in dark. Concentration = 0.25 mg·mL<sup>-1</sup>.



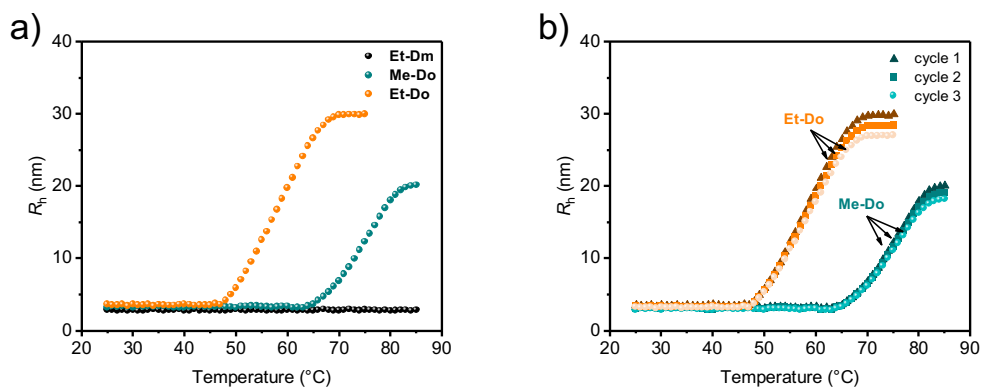
**Figure S18.** UV/vis spectra of **Et-Dm** (concentration = 0.25 mg·mL<sup>-1</sup>) photoisomerization (a), light-sheltered heating at 25 °C (b), 45 °C (c), and 65 °C (d).



**Figure S19.** UV/vis spectra of **Me-Do** (concentration = 0.25 mg·mL<sup>-1</sup>) photoisomerization (a), light-sheltered heating at 25 °C (b), 45 °C (c), and 65 °C (d).

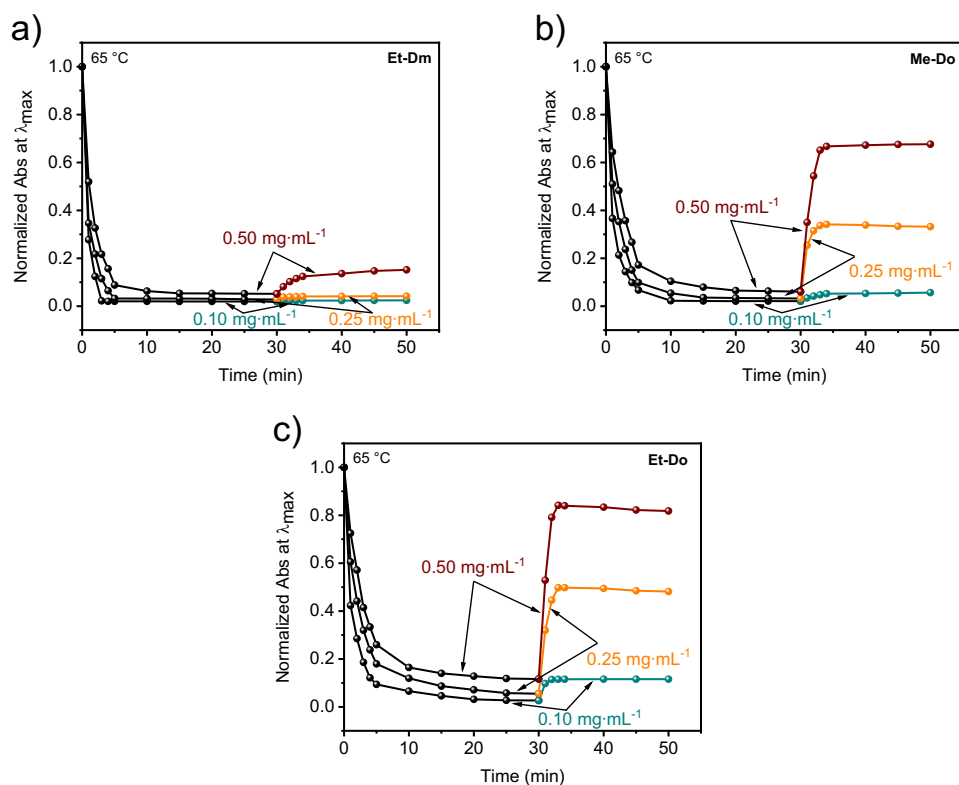


**Figure S20.** UV/vis spectra of **Et-Do** (concentration =  $0.25 \text{ mg}\cdot\text{mL}^{-1}$ ) photoisomerization (a), light-sheltered heating at 25 °C (b), 45 °C (c), and 65 °C (d).

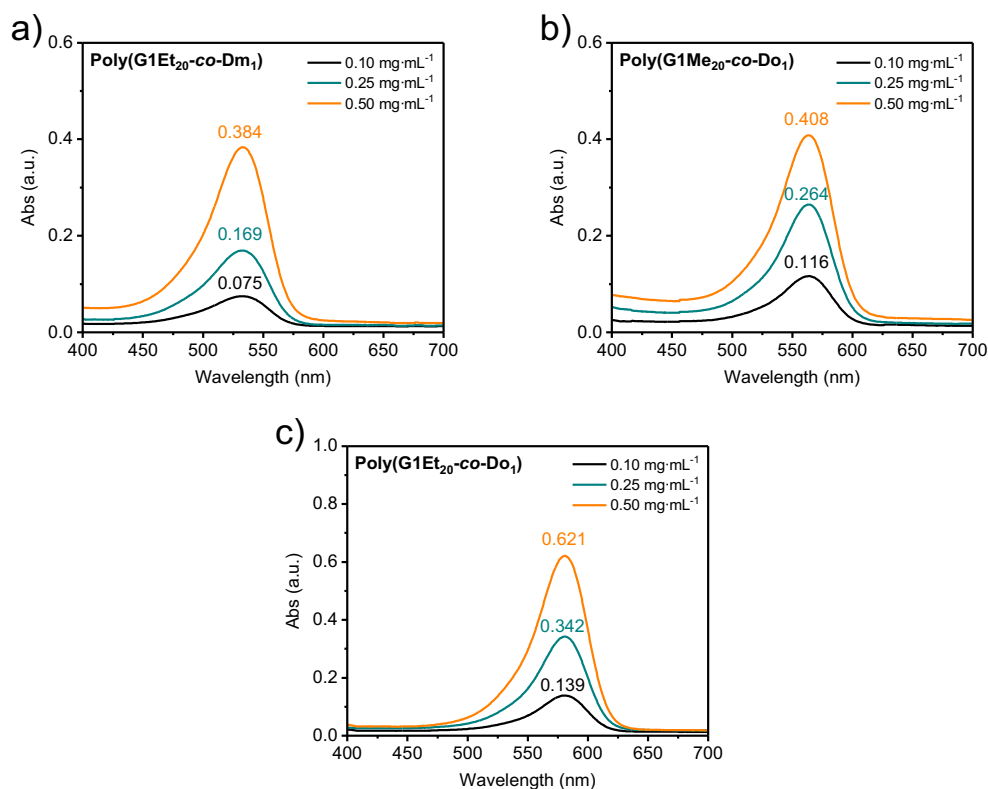


**Figure S21.** Plots of  $R_h$  vs temperature for **Et-Dm**, **Me-Do**, and **Et-Do** at different temperatures (a), and plots of  $R_h$  vs temperature for **Me-Do** and **Et-Do** in aqueous solutions after repeated photo-irradiation and heating (b). Concentration =  $0.25 \text{ mg}\cdot\text{mL}^{-1}$ .

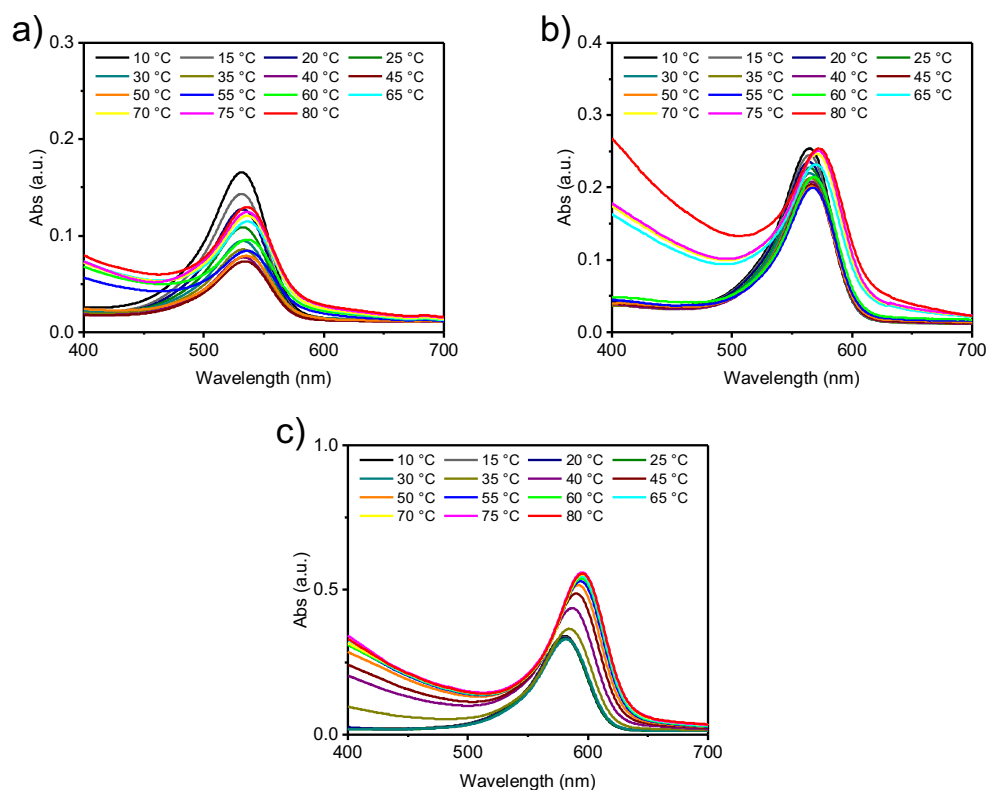




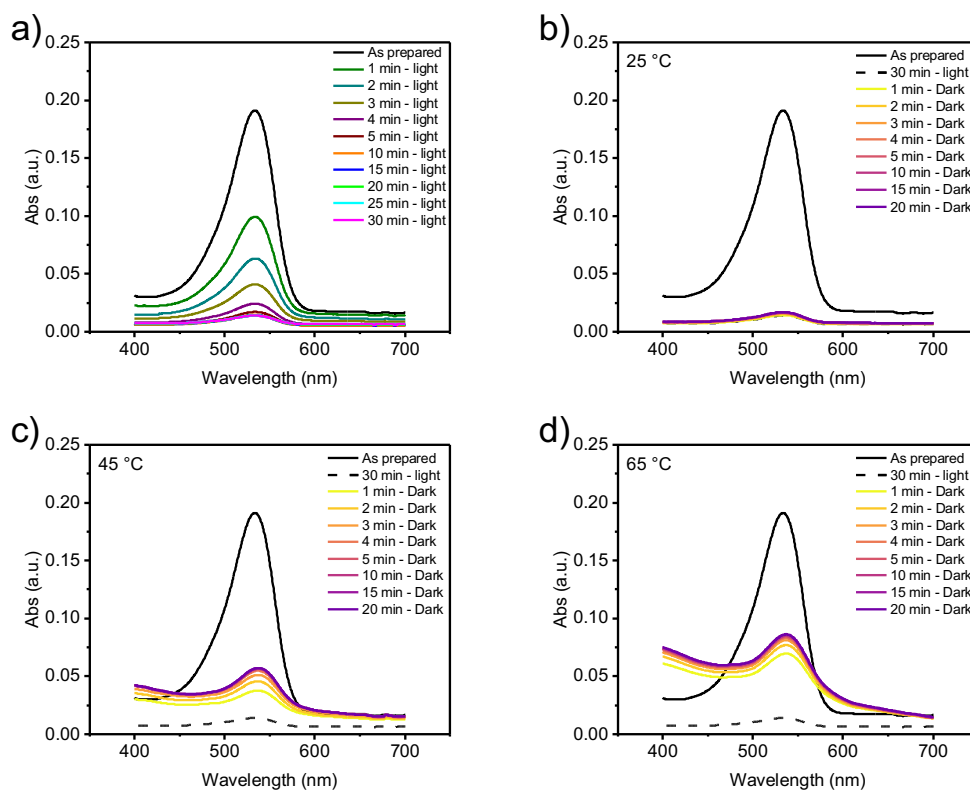
**Figure S22.** Plots of absorbance at  $\lambda_{\max}$  for **Et-Dm** (a), **Me-Do** (b), and **Et-Do** (c) with different concentrations against time after photo-irradiation and followed by annealing at 65 °C. The absorbance was normalized.



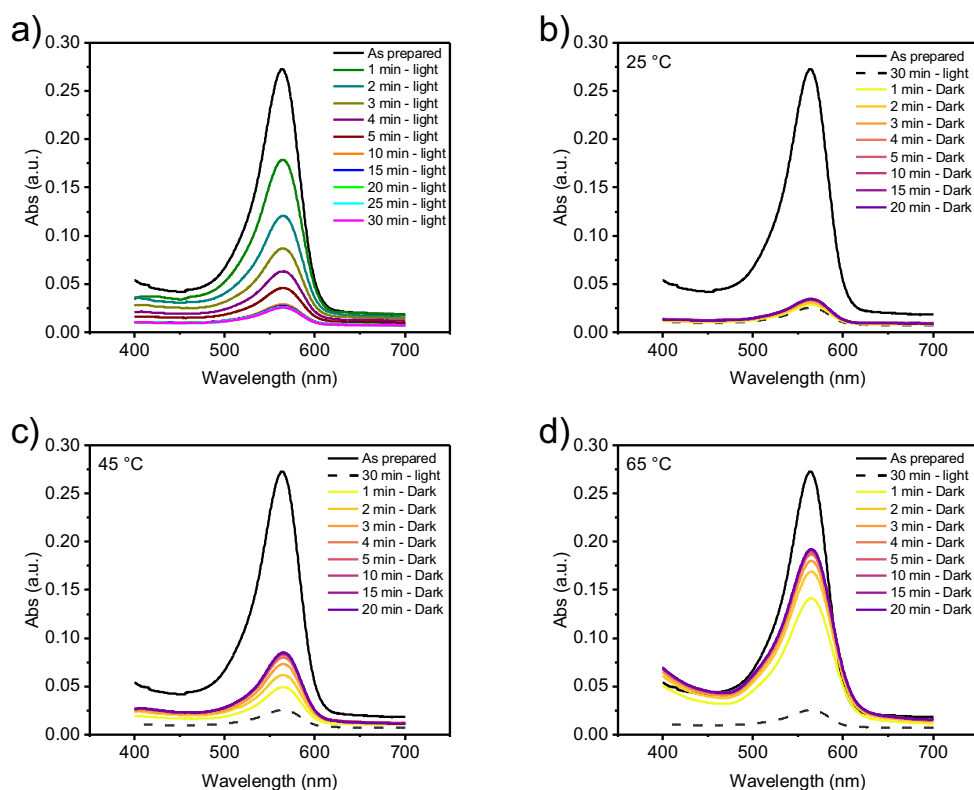
**Figure S23.** UV/vis spectra of **Poly(G1Et<sub>20</sub>-co-Dm<sub>1</sub>)** (a), **Poly(G1Me<sub>20</sub>-co-Do<sub>1</sub>)** (b), and **Poly(G1Et<sub>20</sub>-co-Do<sub>1</sub>)** (c) in aqueous solutions with different concentrations. Temperature was set to 25.0 °C for all measurements.



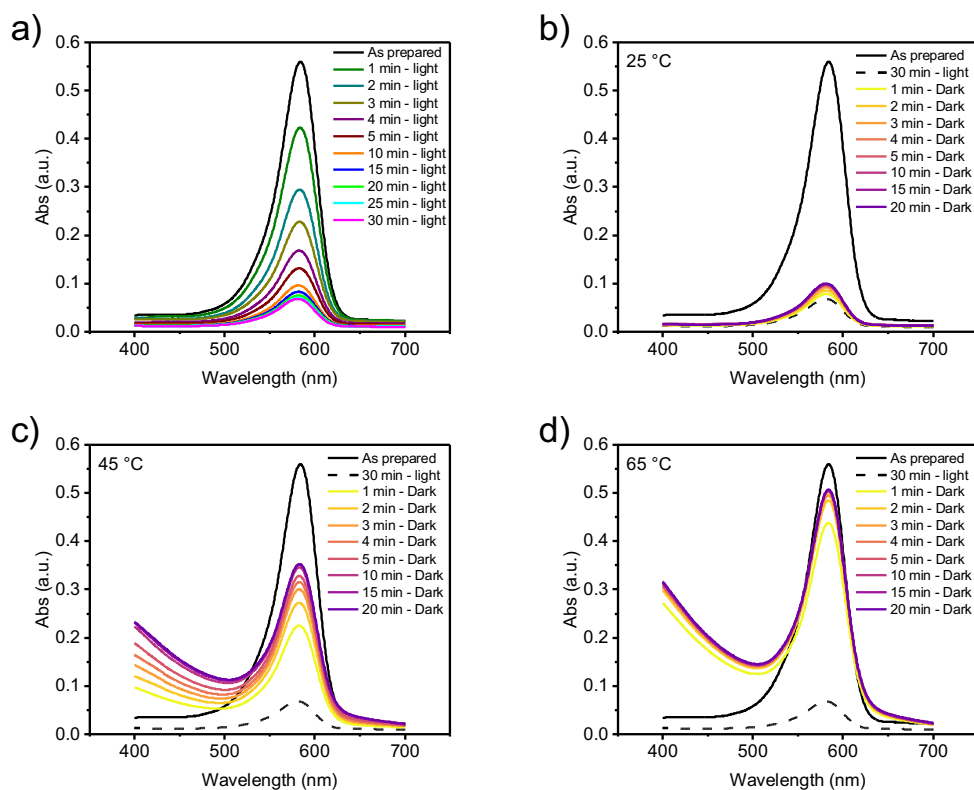
**Figure S24.** UV/vis spectra of **Poly(G1Et<sub>20</sub>-co-Dm<sub>1</sub>)** (a), **Poly(G1Me<sub>20</sub>-co-Dm<sub>1</sub>)** (b), and **Poly(G1Et<sub>20</sub>-co-Dm<sub>1</sub>)** (c) in aqueous solutions at different temperatures in dark. Concentration = 0.25 mg·mL<sup>-1</sup>.



**Figure S25.** UV/vis spectra of **Poly(G1Et<sub>20</sub>-co-Dm<sub>1</sub>)** in aqueous solutions (concentration = 0.25 mg·mL<sup>-1</sup>) through photo-irradiation (a), and followed by thermal annealing at 25 °C (b), 45 °C (c), and 65 °C (d) in dark.



**Figure S26.** UV/vis spectra of **Poly(G1Me<sub>20</sub>-co-Do<sub>1</sub>)** in aqueous solutions (concentration = 0.25 mg·mL<sup>-1</sup>) through photo-irradiation (a), and followed by thermal annealing at 25 °C (b), 45 °C (c), and 65 °C (d) in dark.



**Figure S27.** UV/vis spectra of **Poly(G1Et<sub>20</sub>-co-Do<sub>1</sub>)** in aqueous solutions (concentration = 0.25 mg·mL<sup>-1</sup>) through photo-irradiation (a), and followed by thermal annealing at 25 °C (b), 45 °C (c), and 65 °C (d) in dark.