

## Electronic Supplementary Information

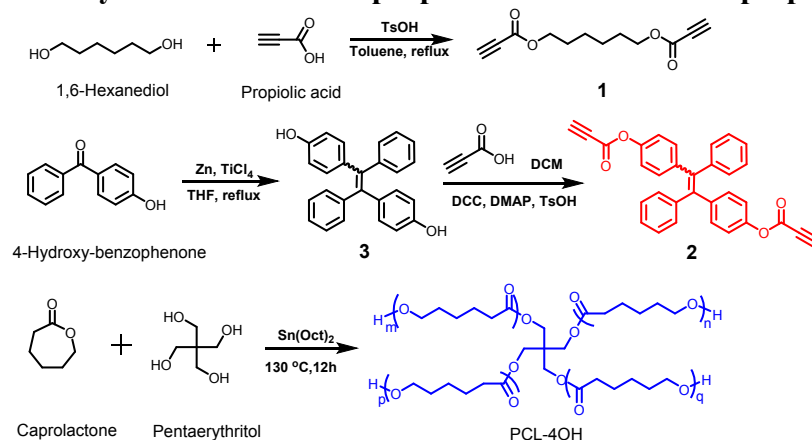
### **Luminescent two-way reversible shape memory polymers prepared by the hydroxyl-yne click polymerization**

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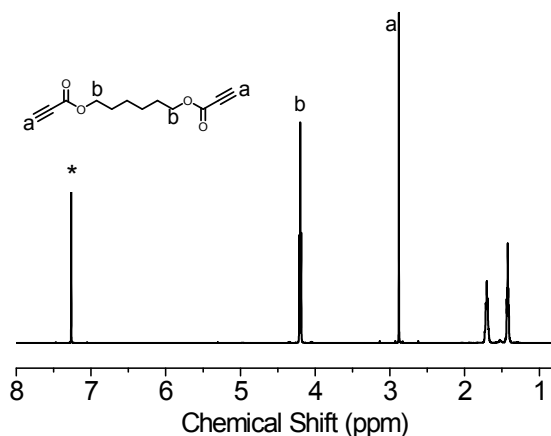
### Scheme S1. Synthetic routes to dipropiolates and PCL-4OH prepolymers



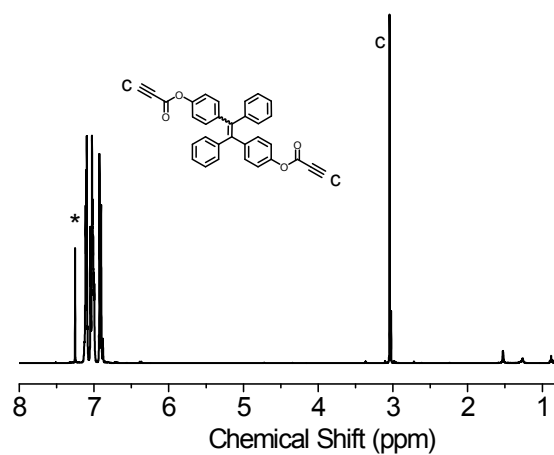
**Table S1. Molecular weights and thermal properties of PCL-4OH prepolymers**

$M_{n,\text{NMR}}^a$ (g/mol)	$M_{n,\text{SEC}}^b$ (g/mol)	$D^b$	$T_c^c$ (°C)	$T_m^c$ (°C)	$\Delta H_c^c$ (J/g)	$\Delta H_m^c$ (J/g)
2200	3800	1.45	10.3	35.7 (44.2)	71.6	68.5
3600	5700	1.21	21.5	42.9 (46.8)	77.2	79.1
4500	7100	1.25	20.3	45.8 (50.0)	71.9	76.9
5800	8000	1.29	24.5	48.3	74.9	79.3

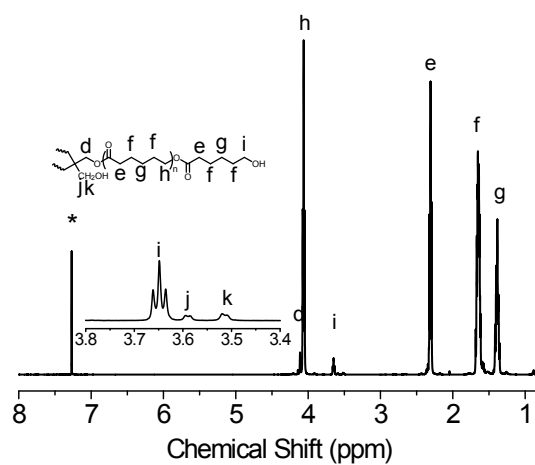
<sup>a</sup> Calculated from the ratio of <sup>1</sup>H NMR signal integral;  $M_n$  = number-average molecular weight. <sup>b</sup> Estimated by SEC in THF on the basis of a polystyrene (PS) calibration;  $D$  = polydispersity index ( $M_w/M_n$ ,  $M_w$  = weight-average molecular weight). <sup>c</sup> Measured by DSC. Defined by crystallization ( $T_c$ ) and melting temperatures ( $T_m$ ).



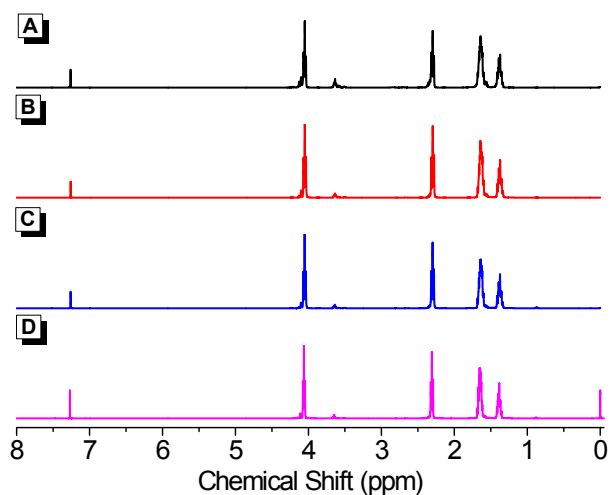
**Figure S1.** <sup>1</sup>H NMR spectrum of dipropiolate **1** in CDCl<sub>3</sub>. The solvent peak is marked with an asterisk.



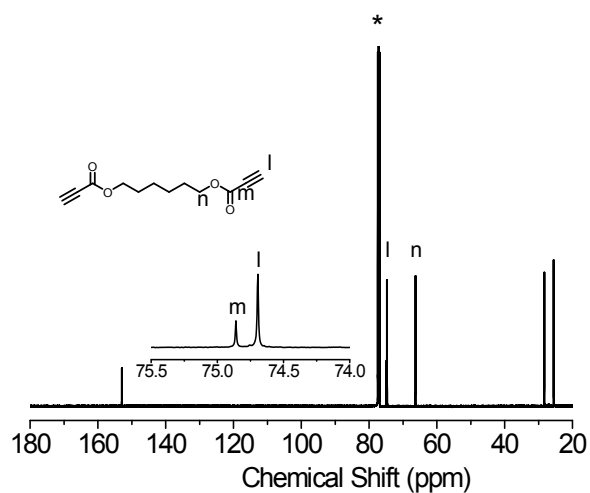
**Figure S2.**  $^1\text{H}$  NMR spectrum of TPE-containing dipropiolate **2** in  $\text{CDCl}_3$ . The solvent peak is marked with an asterisk.



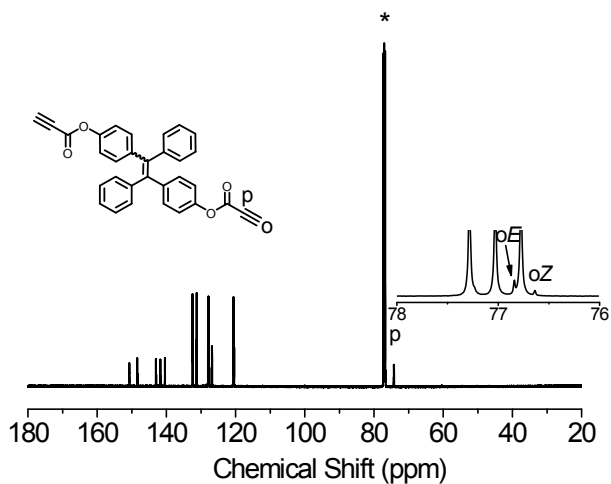
**Figure S3.**  $^1\text{H}$  NMR spectrum of  $\text{PCL}_{3600}\text{-4OH}$  in  $\text{CDCl}_3$ . The solvent peak is marked with an asterisk.



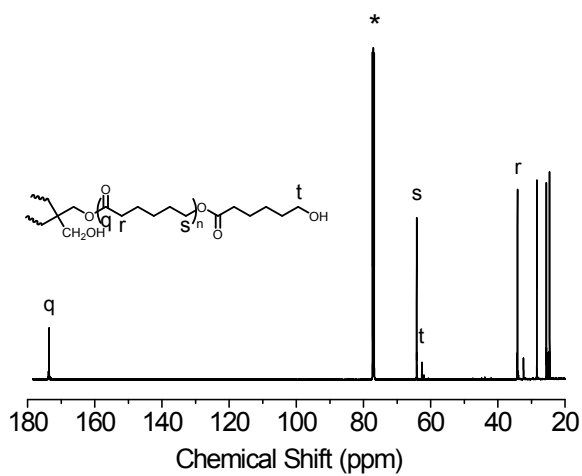
**Figure S4.**  $^1\text{H}$  NMR spectra of PCL<sub>2200</sub>-OH (A), PCL<sub>3600</sub>-OH (B), PCL<sub>4500</sub>-OH (C), and PCL<sub>5800</sub>-4OH (D) in  $\text{CDCl}_3$ . The solvent peaks are marked with asterisks.



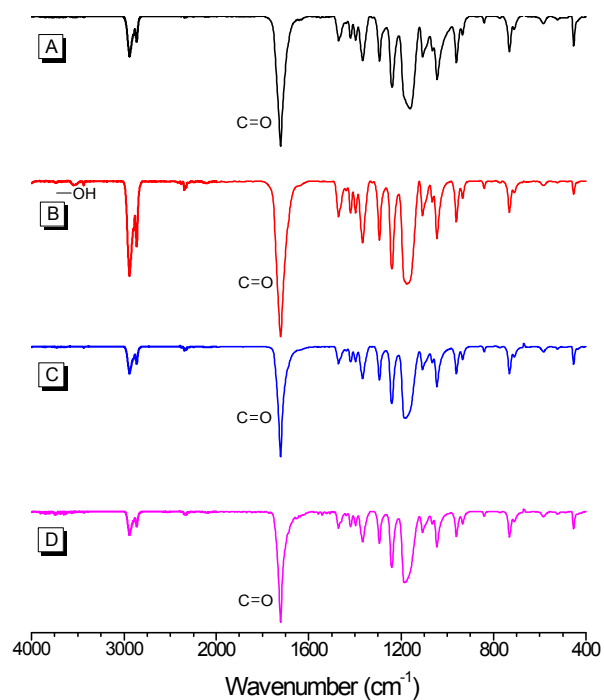
**Figure S5.**  $^{13}\text{C}$  NMR spectrum of dipropiolate **1** in  $\text{CDCl}_3$ . The solvent peak is marked with an asterisk.



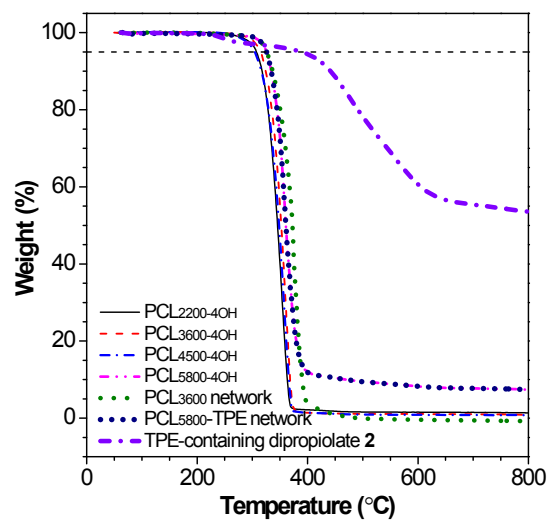
**Figure S6.**  $^{13}\text{C}$  NMR spectrum of TPE-containing dipropiolate **2** in  $\text{CDCl}_3$ . The solvent peak is marked with an asterisk.



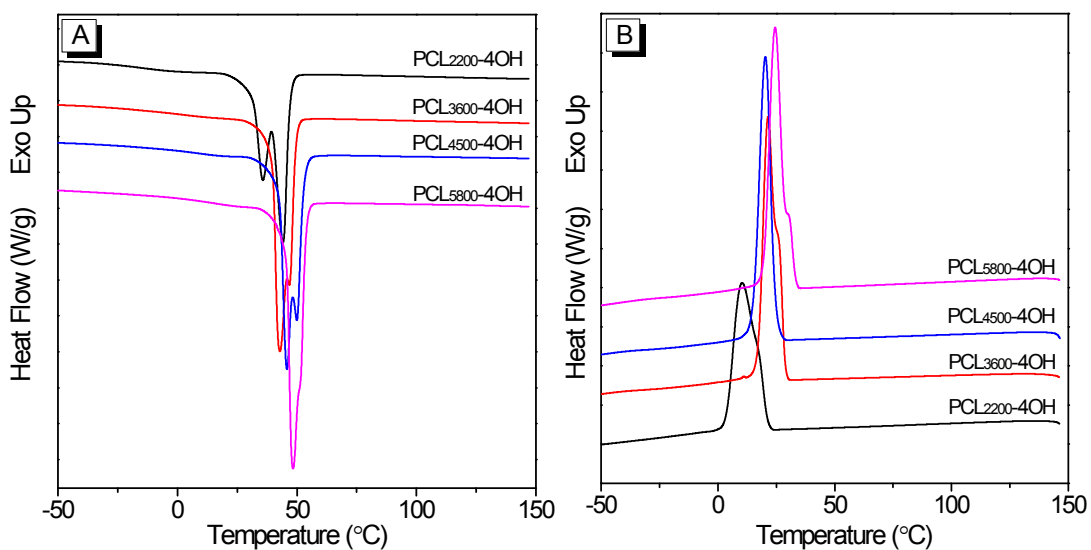
**Figure S7.**  $^{13}\text{C}$  NMR spectrum of  $\text{PCL}_{3600}\text{-4OH}$  in  $\text{CDCl}_3$ . The solvent peak is marked with an asterisk.



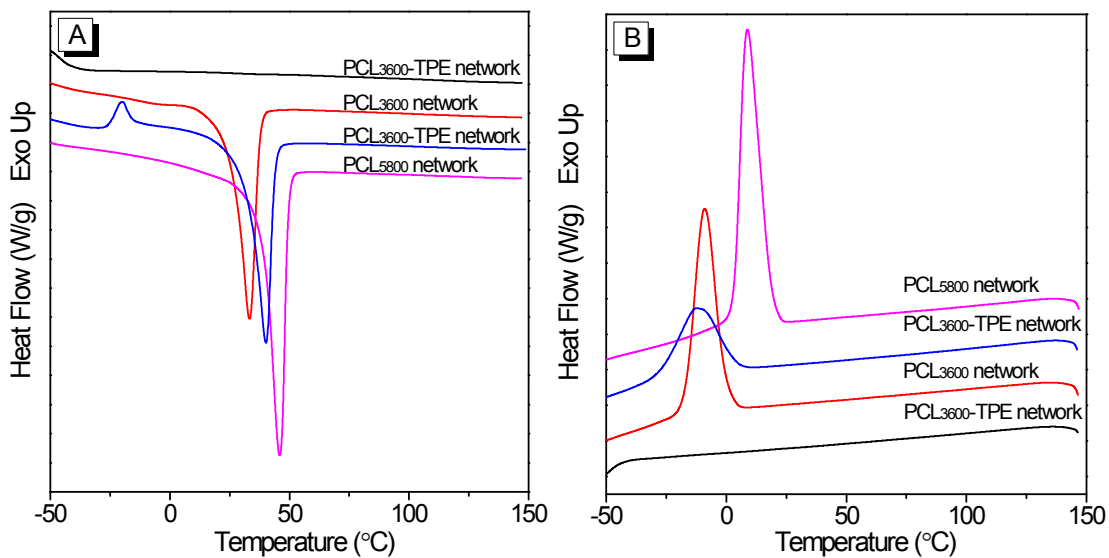
**Figure S8.** FT-IR spectra of PCL<sub>2200</sub>-OH (A), PCL<sub>3600</sub>-OH (B), PCL<sub>4500</sub>-OH (C), and PCL<sub>5800</sub>-4OH (D).



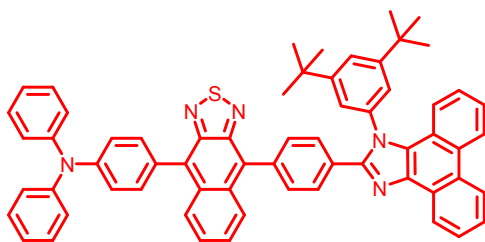
**Figure S9.** TGA curves of PCL-4OH prepolymers, PCL-based networks, and TPE-containing dipropiolate **2**.



**Figure S10.** DSC heating (A) and cooling (B) curves of PCL-4OH prepolymers.



**Figure S11.** DSC curves of heating (A) and cooling (B) processes of PCL-based networks.



**Figure S12.** Chemical structure of the AIEgen with red emission.