

**Supplementary Information**

**Reduced Excimer Formation in Polyfluorenes by  
Introducing Coil-Like Poly[penta(ethylene glycol) methyl ether  
methacrylate] Block Segments**

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## **1. Synthesis of Hydroxyl End-Functionalized Oligofluorene 1 and its $^1\text{H}$ NMR data**

**(Figure S1) (\*:  $\text{CDCl}_3$ ).**

$\text{Ni}(\text{COD})_2$ , COD, bipyridine and anhydrous DMF were mixed with stirring at  $70^\circ\text{C}$  for 30 min under dry  $\text{N}_2$  gas. 2,7-dibromo-9,9-didodecylfluorene and 4-bromobenzyl alcohol in anhydrous toluene were added *via* a syringe. The reaction was allowed to continue with stirring at  $85^\circ\text{C}$  in the absence of light for an additional 2 days. After the reaction, the mixture was cooled to room temperature and diluted with THF and an aqueous hydrazine solution. The mixture solution was stirred overnight. The organic layer of the mixture solution was separated, filtered, concentrated and poured into methanol. The precipitated powder product was purified by extraction with methanol, and reprecipitated into methanol.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 7.65-7.86 (br, fluorene aromatic protons), 7.59, 7.49 (2d, phenyl end group), 4.78 (s,  $\text{PhCH}_2\text{O}-$ ), 2.10 (br,  $-\text{CH}_2\text{C}_{11}\text{H}_{23}$ ), 1.25-0.84 (m,  $-\text{CH}_2\text{C}_{11}\text{H}_{25}$ ).

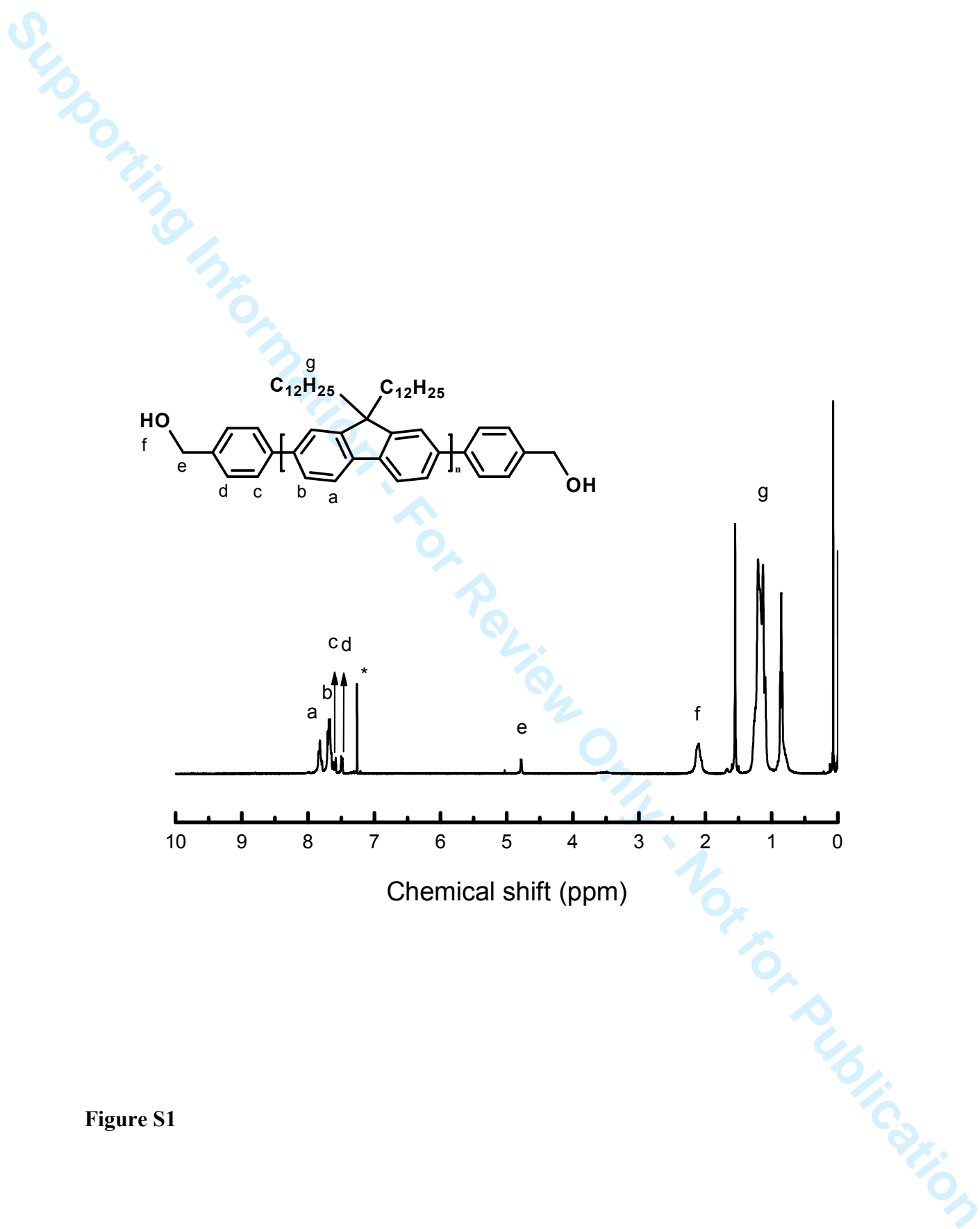


Figure S1

## **2. Synthesis of Polyfluorene Macroinitiator 2 and its $^1\text{H}$ NMR data (Figure S2) (\*:**

**$\text{CDCl}_3$** ).

Compound 1, triethylamine, anhydrous methylene chloride, purified with  $\text{CaH}_2$ , was placed in a round-bottom flask and the mixture was cooled to  $0^\circ\text{C}$ . BIB was added to the mixture dropwise *via* a syringe under dry  $\text{N}_2$  gas. The solution was stirred overnight at  $20^\circ\text{C}$ . The resulting solution was extracted with water, dried with sodium sulfate, concentrated and precipitated into methanol. The obtained, yellow powder was filtered, rinsed with methanol and passed through a short silica column (using toluene as the eluant) for purification.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  7.65-7.86 (br, fluorene aromatic protons), 7.59, 7.49 (2d, phenyl end group), 5.31 (s,  $\text{PhCH}_2\text{O-}$ ), 2.13 (br,  $-\text{CH}_2\text{C}_{11}\text{H}_{23}$ ), 2.0 (s,  $\text{C}(\text{CH}_3)_2\text{Br}$ ), 1.25-0.81 (m,  $-\text{CH}_2\text{C}_{11}\text{H}_{23}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 151.8, 151.7, 140.5, 140.0, 128.5, 127.4, 126.1, 125.7, 121.5, 120.0, 119.9, 67.4, 55.7, 55.3, 45.7, 40.4, 31.9, 30.8, 30.0, 29.6, 29.4, 29.3, 23.9, 22.7, 14.1.

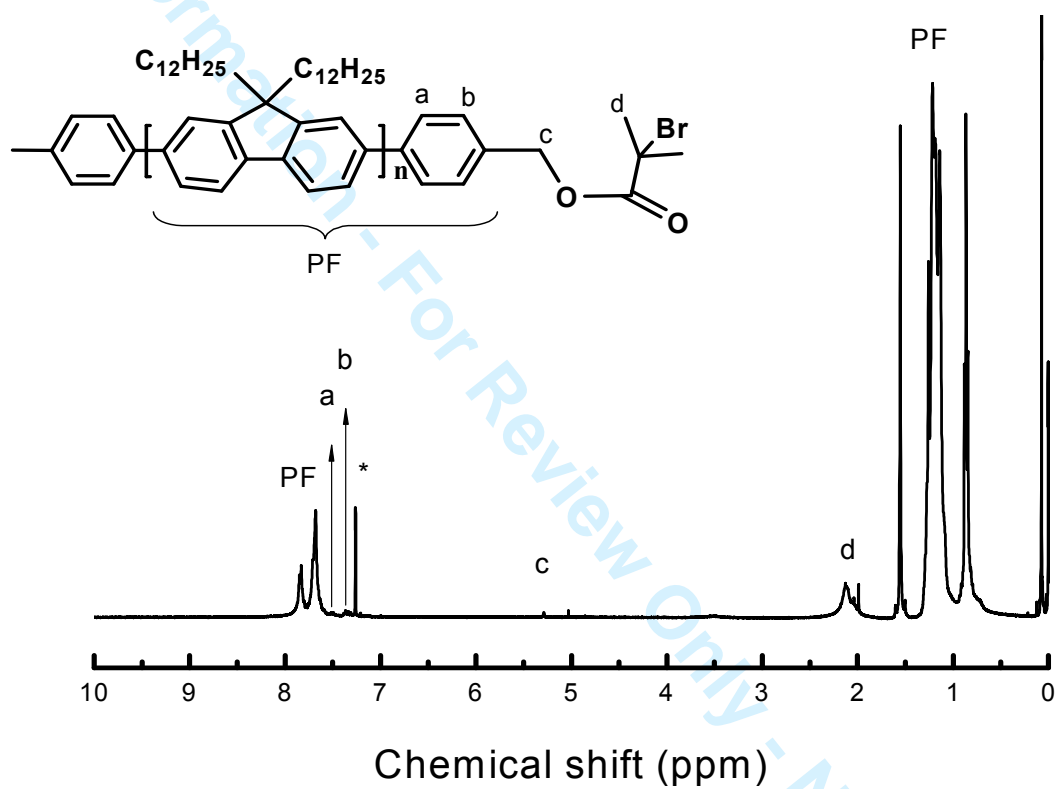


Figure S2

### **3. Synthesis of PEGMA-*b*-PF-*b*-PEGMA 3 and its $^1\text{H}$ NMR data (Figure S3) (\*:**

**$\text{CDCl}_3$** ).

Compound 2, EGMA, PMDETA, and xylene were placed in a flask and degassed by three vacuum-nitrogen cycles. After stirring the mixture at room temperature for 1 hr, CuBr was added to initiate the reaction and the mixture was transferred to an oil bath at 70 °C. After stirring for 24 hrs, the reaction was finally terminated by opening the flask and exposing the catalyst to air. The reacted mixture was diluted with methylene chloride and passed through an activated (neutral) alumina column to remove the catalyst. The unreacted monomers were removed by precipitation with methanol and the resulting product was dried under vacuum.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , ppm):  $\delta$  7.65-7.86 (br, fluorene aromatic protons), 7.59, 7.49 (2d, phenyl end group), 4.69 (s,  $-\text{PhCH}_2\text{OCO}-$ ), 4.14-4.04 (Br,  $-\text{COOCH}_2\text{CH}_2\text{O}-$ ), 3.7-3.54 (m,  $\text{O}-\text{CH}_2\text{CH}_2-\text{O}$ ), 3.38 (s,  $-\text{OCH}_3$ ) 2.16-1.77 (m,  $-\text{CH}_2(\text{CH}_3-$ ,  $-\text{CH}_2\text{C}_{11}\text{H}_{23}$  and  $-\text{COC}(\text{CH}_3)_2\text{CH}_2-$ ), 1.25-0.81 (m,  $-\text{CH}_2\text{C}_{11}\text{H}_{23}$  and  $-\text{CH}_2\text{C}(\text{CH}_3)-$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ ): 151.7, 140.5, 139.9, 126.1, 121.4, 119.9, 71.9, 70.5, 68.5, 63.9, 59.0, 55.3, 45.1, 44.7, 40.3, 31.9, 30.0, 29.6, 29.3, 23.9, 22.6, 14.0.

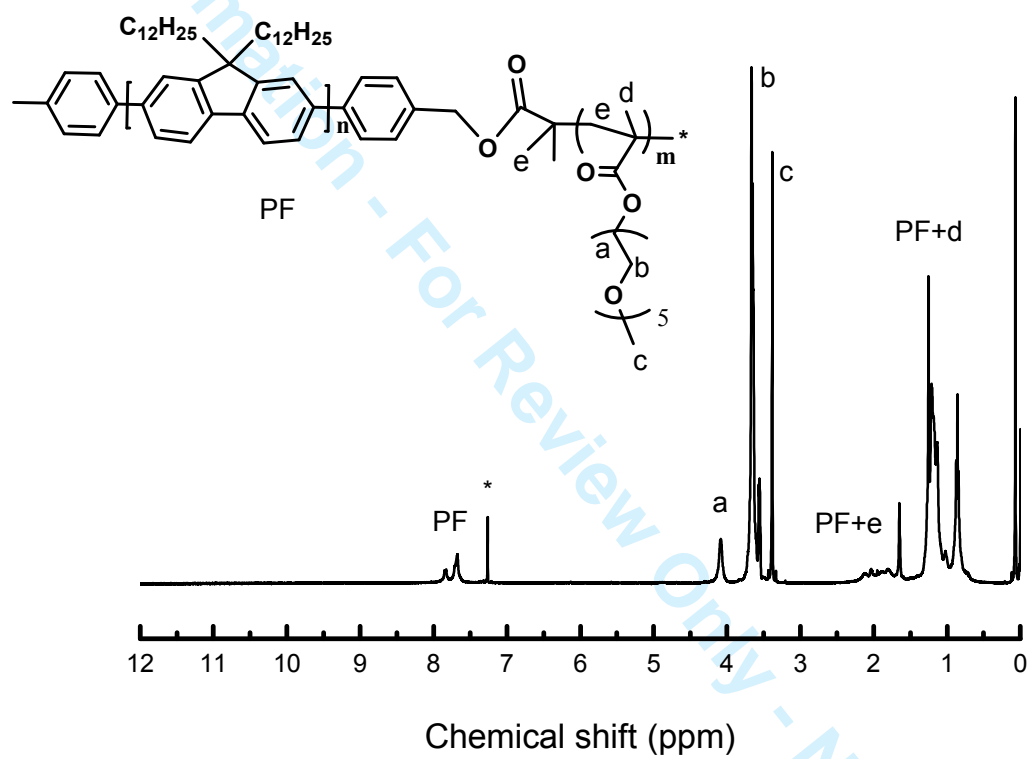


Figure S3

#### 4. $^{13}\text{C}$ NMR data of PF macroinitiator **2** (\*: $\text{CDCl}_3$ ).

The absence of fluorenone defects was confirmed by the  $^{13}\text{C}$ -NMR data of the compound **2**, showing that the peak of a carbonyl carbon at  $\delta = 194$  ppm was absent, indicating that the formation of the fluorenone defects was prevented during the reaction.

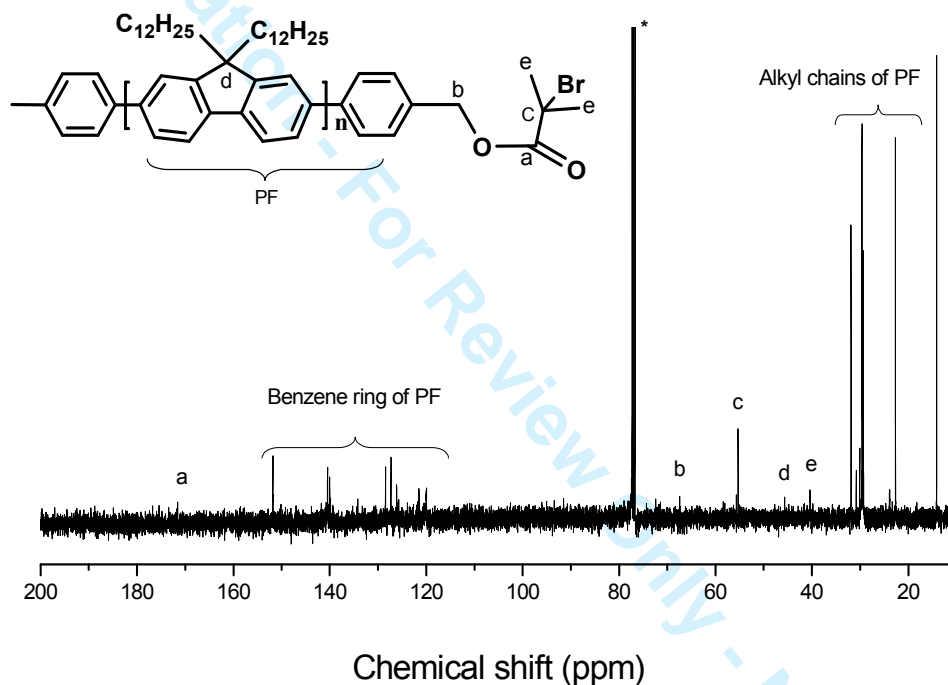
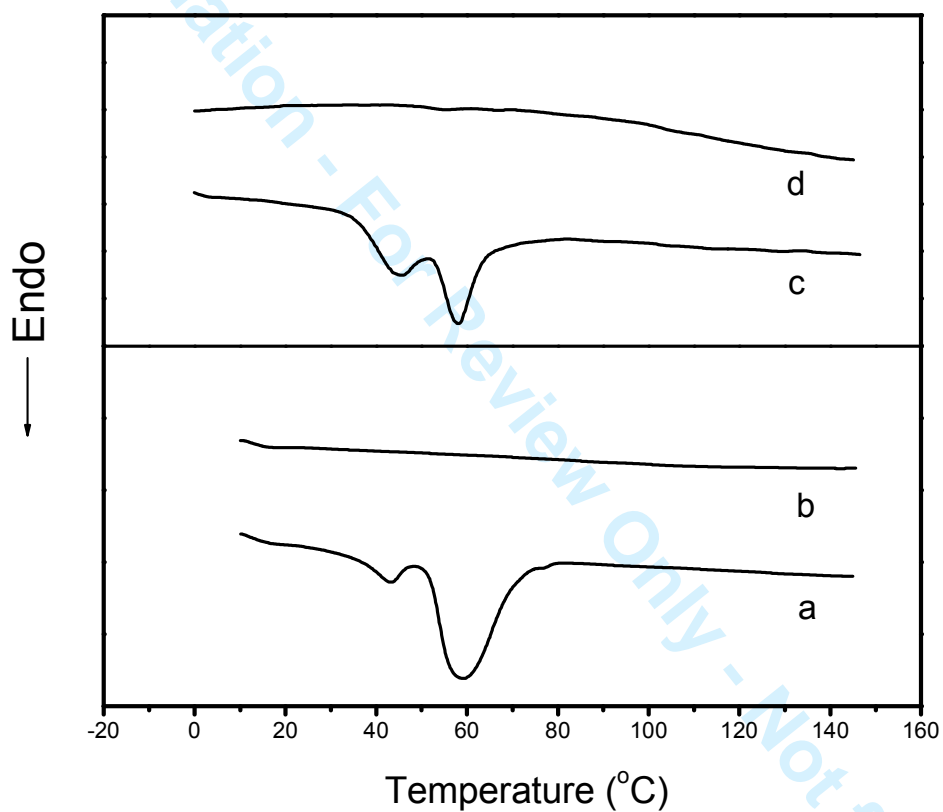


Figure S4



### 5. DSC scans of PF macroinitiator 2 and PEGMA-*b*-PF-*b*-PEGMA 3.

Figure S5 shows (a) the first and (b) second DSC heating scans of PF macroinitiator 2; and (c) the first and (d) second heating of PEGMA-*b*-PF-*b*-PEGMA 3.



**Figure S5**