

# SUPPORTING INFORMATION

## **Site-specific functionalization of hyperbranched polymers using “click” chemistry**

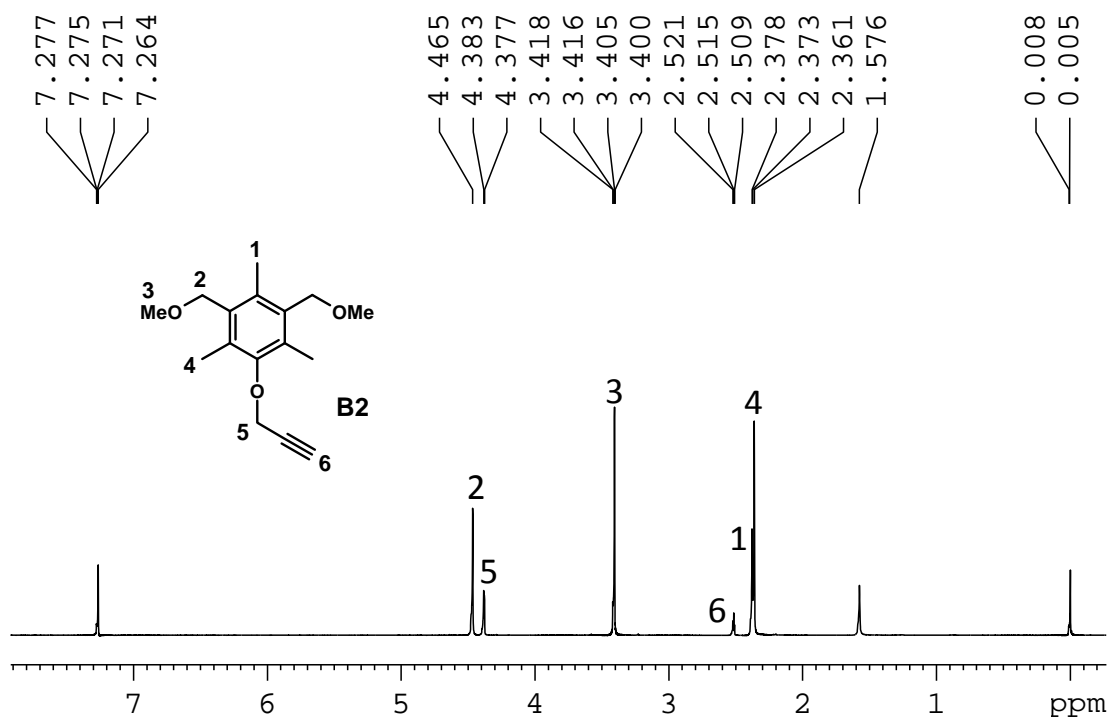
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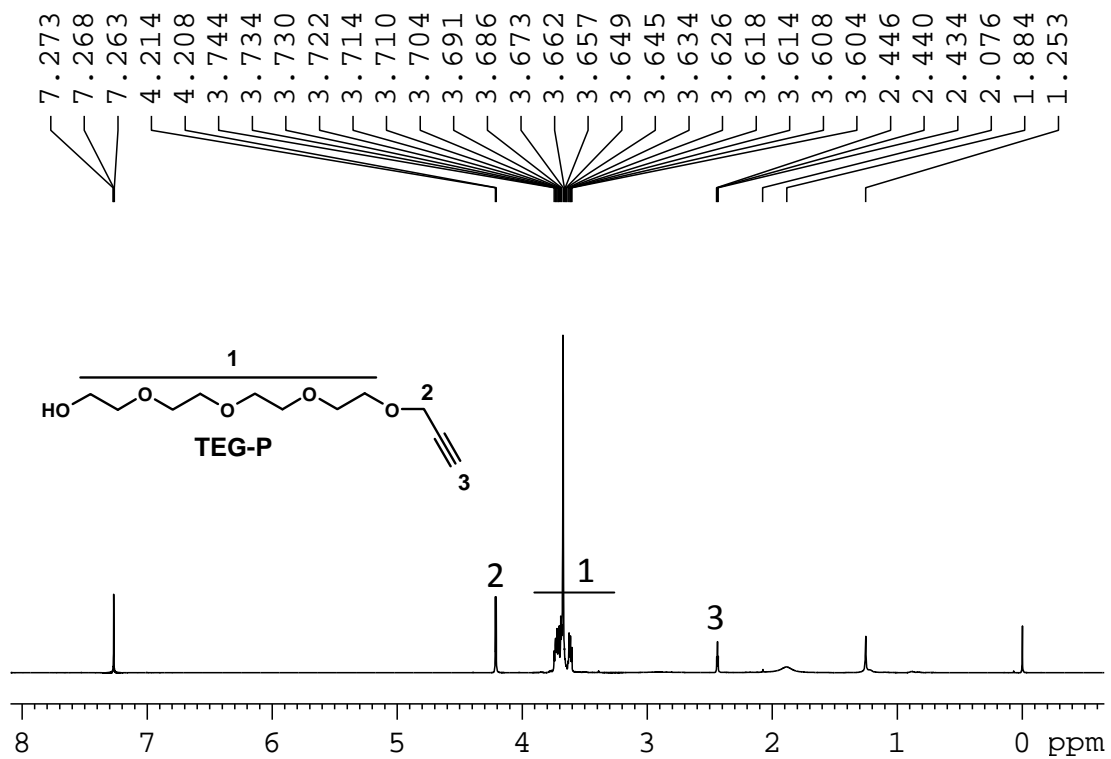
Indian Institute of Science

Bangalore-560012, India

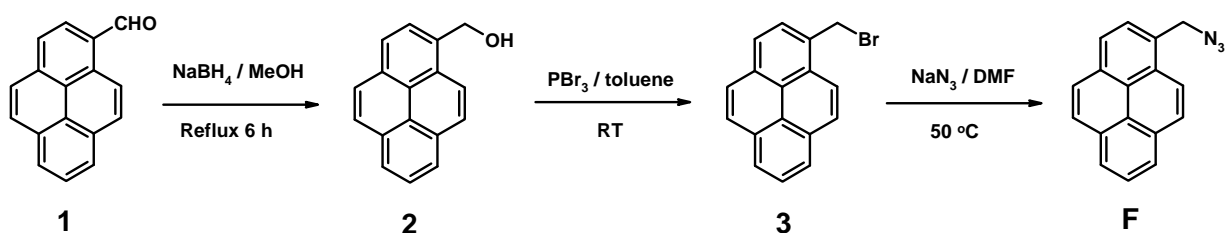
E-mail: raman@ipc.iisc.ernet.in



**Figure S1.** <sup>1</sup>H NMR spectrum of monomer **B2**.



**Figure S2.** <sup>1</sup>H NMR spectrum of monomer **TEG-P**.



**Scheme S1.** Synthesis of the azide derivative of the fluorophore.

### 1-Pyrenemethanol (2)

1-Pyrenecarboxaldehyde **1** (2.8 g, 12.2 mmol) was taken into 100 mL of dry MeOH. Then NaBH<sub>4</sub> (0.68 g, 18.1 mmol) was added to it in portions at 0 °C. The reaction mixture was stirred at room temperature for 30 min and then was refluxed for 6 h under N<sub>2</sub>. After the reaction was over, the reaction mixture was diluted with 150 mL of 5% HCl. White precipitate came out. It was filtered and extracted in EtOAc. The EtOAc layer was washed with brine, passed over Na<sub>2</sub>SO<sub>4</sub> and finally dried to get the solid product. Yield = 99 %. M.P. = 126-128 °C. <sup>1</sup>H NMR (δ, ppm, CDCl<sub>3</sub>): 5.41 (s, 2H, ArCH<sub>2</sub>); 8.05-8.38 (m, 9H, Ar-H).

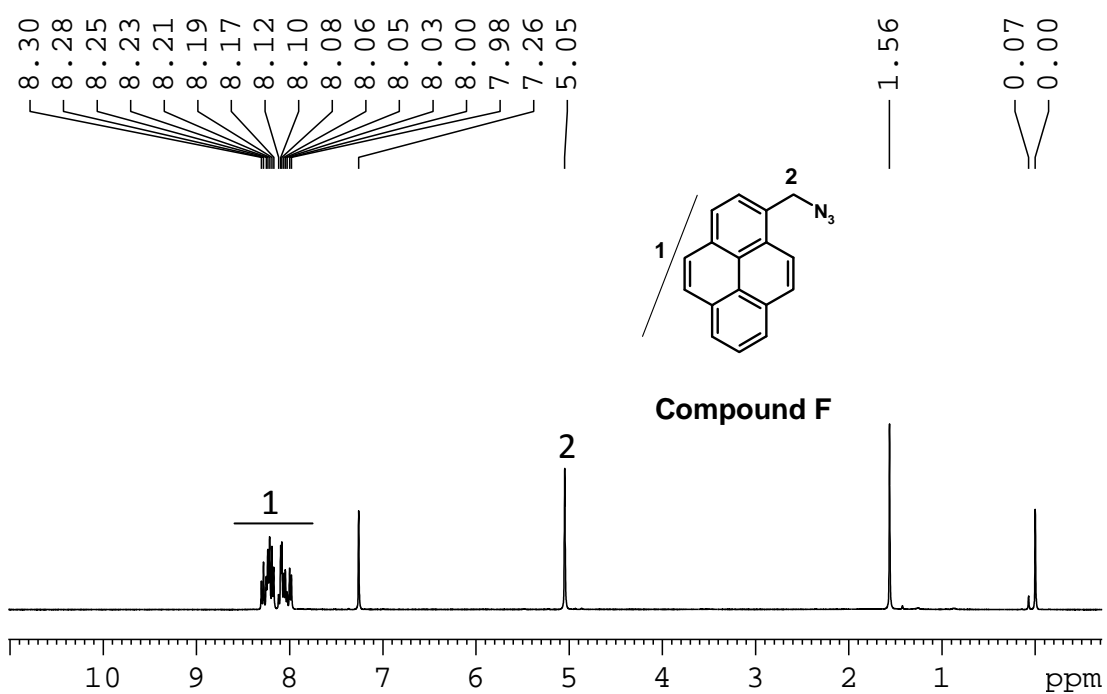
### 1-Bromomethyl pyrene (3)

Compound **2** (2.8 g, 12.1 mmol) was taken in 60 mL of toluene. This suspension was cooled to 0 °C and PBr<sub>3</sub> (1.4 mL, 14.4 mmol) was added to it drop-wise. The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 12 h. After the reaction was over, 50 mL of saturated solution of Na<sub>2</sub>CO<sub>3</sub> was added to it slowly under ice-cold condition because it was vigorous. The two phases got separated. The toluene layer was passed over Na<sub>2</sub>SO<sub>4</sub> and yellowish solid product obtained. Yield = 70 %. This product was used directly for the next step without further purification. <sup>1</sup>H NMR (δ, ppm, CDCl<sub>3</sub>): 5.26 (s, 2H, ArCH<sub>2</sub>); 8.02-8.40 (m, 9H, Ar-H).

### 1-Azidomethyl pyrene (F)

Compound **3** (2.5 g, 8.4 mmol) was dissolved in 35 mL of dry DMF. Then NaN<sub>3</sub> (2.7 g, 42.3 mmol) was added to it and the reaction mixture was stirred at 50 °C for 5 h.

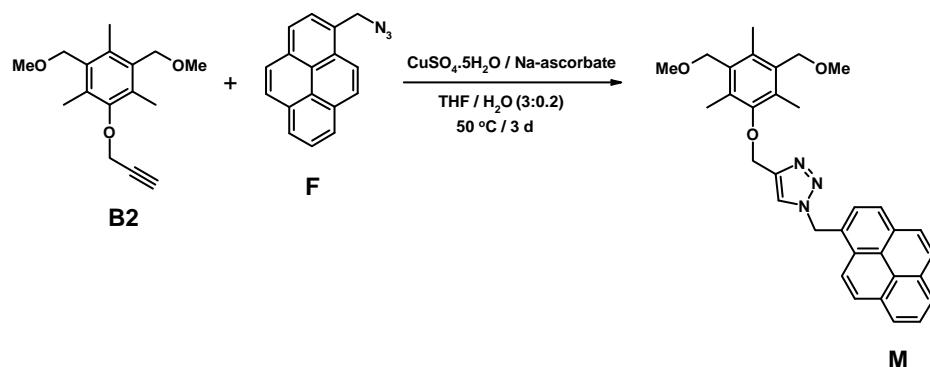
After the reaction was over, 20 mL of H<sub>2</sub>O was added to it and extracted in EtOAc. The EtOAc layer was washed with brine, passed over Na<sub>2</sub>SO<sub>4</sub> and purified by silica column using petroleum ether and EtOAc as the eluent to get the yellow solid product. Yield = 97 %. <sup>1</sup>H NMR (δ, ppm, CDCl<sub>3</sub>): 5.04 (s, 2H, ArCH<sub>2</sub>); 7.98-8.25 (m, 9H, Ar-H).



**Figure S3.** <sup>1</sup>H NMR spectrum of compound F.

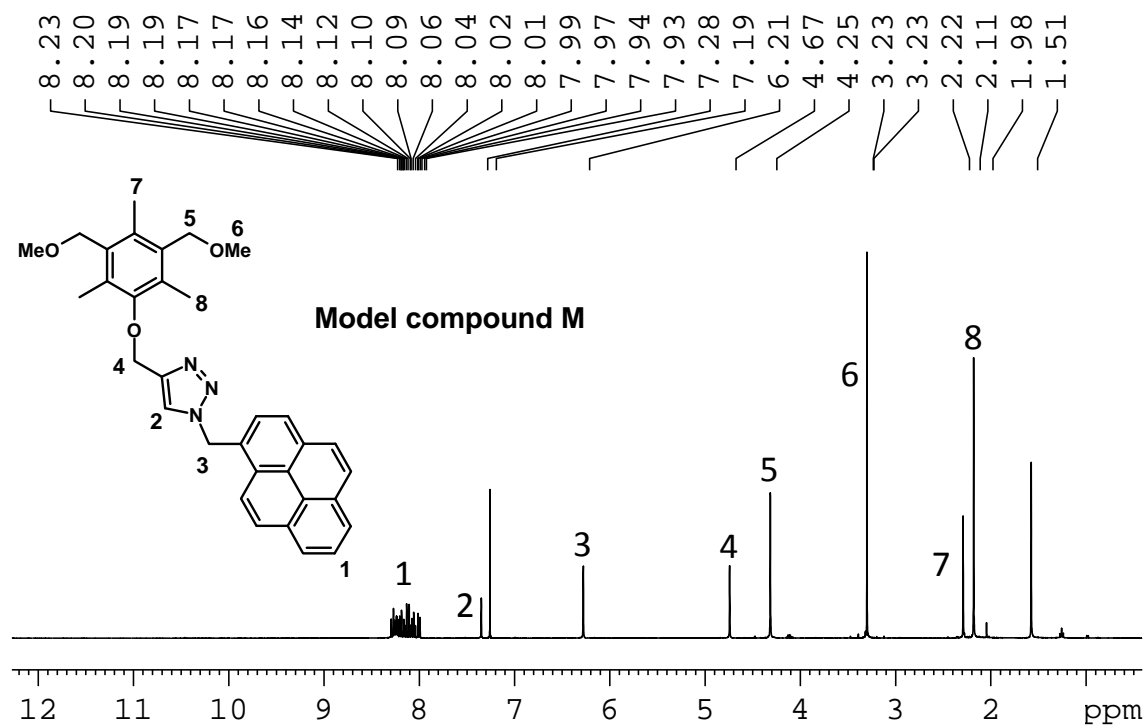
## Model click reaction

### Compound M

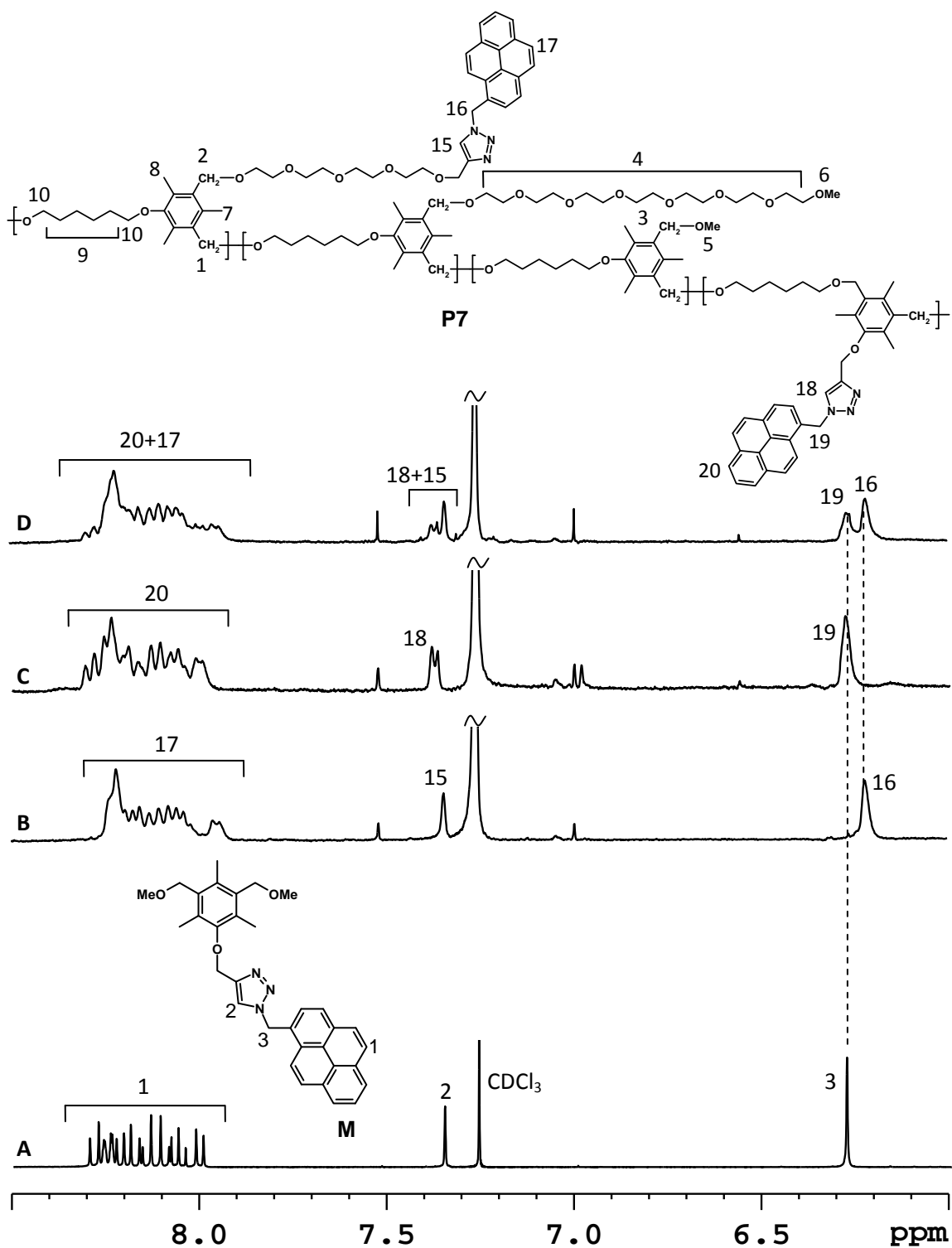


**Scheme S2.** Model click reaction.

Monomer **B2** (100 mg, 0.38 mmol) and **F** (109.2 mg, 0.419 mmol) was dissolved in 3 mL of THF. Then CuSO<sub>4</sub>·5H<sub>2</sub>O (4.7 mg, 0.019 mmol) dissolved in 0.1 mL of H<sub>2</sub>O was added to it, followed by the addition of sodium ascorbate (7.5 mg, 0.038 mmol) dissolved in 0.1 mL of H<sub>2</sub>O. Immediately, after the addition of sodium ascorbate, the reaction flask was flushed with N<sub>2</sub> and the contents were stirred for 3 days at 50 °C. Thereafter, 5 mL of H<sub>2</sub>O was added to it and was extracted in EtOAc. The EtOAc layer was passed through Na<sub>2</sub>SO<sub>4</sub> and dried. It was finally purified by silica column using petroleum ether and EtOAc as the eluent to get the yellowish solid product. Yield = 96 %. M.P. = 105 °C. <sup>1</sup>H NMR (δ, ppm, CDCl<sub>3</sub>): 2.11 (s, 6H, ArCH<sub>3</sub>); 2.22 (s, 3H, ArCH<sub>3</sub>); 3.23 (s, 6H, OCH<sub>3</sub>); 4.25 (s, 4H, ArCH<sub>2</sub>); 4.67 (s, 2H, ArOCH<sub>2</sub>); 6.21 (s, 2H, pyrene-CH<sub>2</sub>); 7.28 (s, 1H, triazole ring proton); 7.94-8.17 (m, 9H, pyrene ring protons).

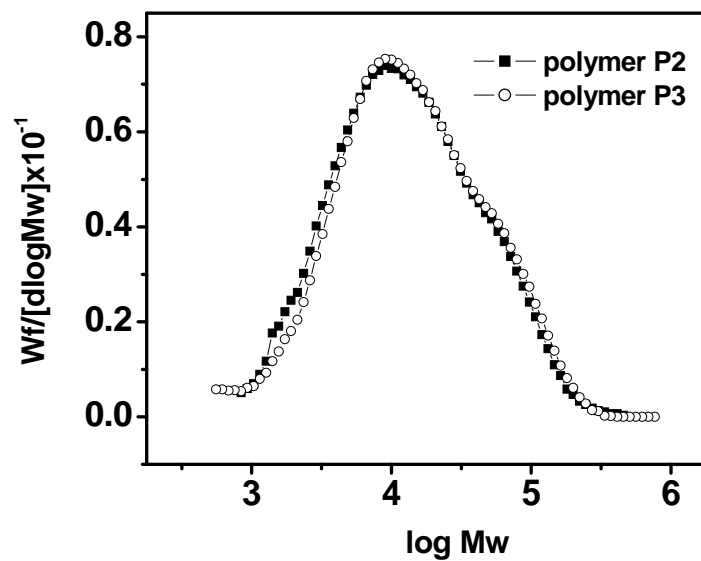


**Figure S4.**  $^1\text{H}$  NMR spectrum of model compound **M**.

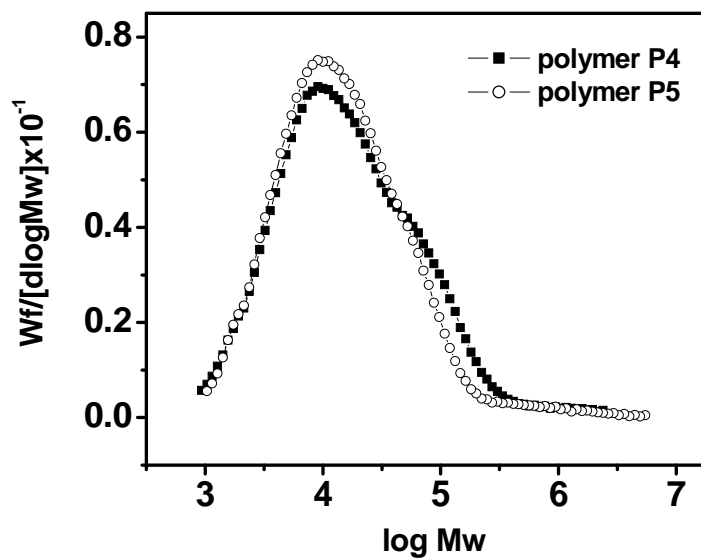


**Figure S5.** <sup>1</sup>H NMR spectra of (A) **M**, product of the model click reaction, (B) hyperbranched polymer **P3** having pyrene at the molecular periphery, (C) hyperbranched polymer **P5** having pyrene within the core, and (D) hyperbranched polymer **P7** having pyrene both at the molecular periphery as well as within the core, recorded in CDCl<sub>3</sub>.

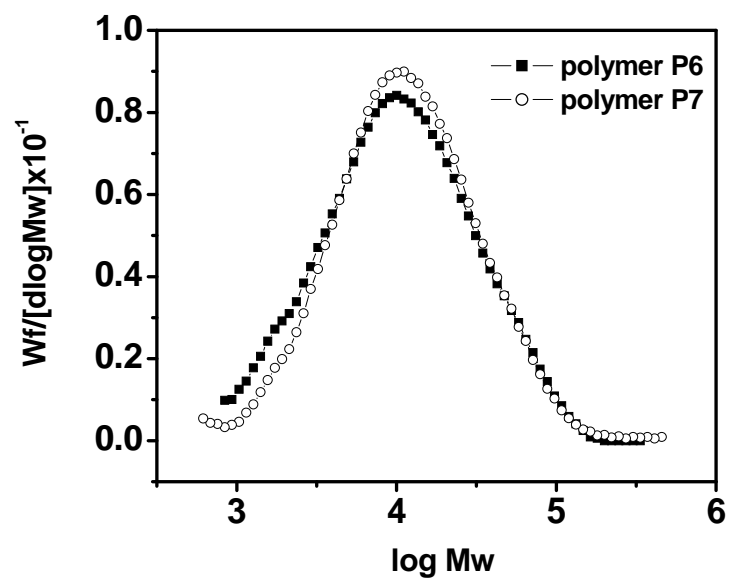




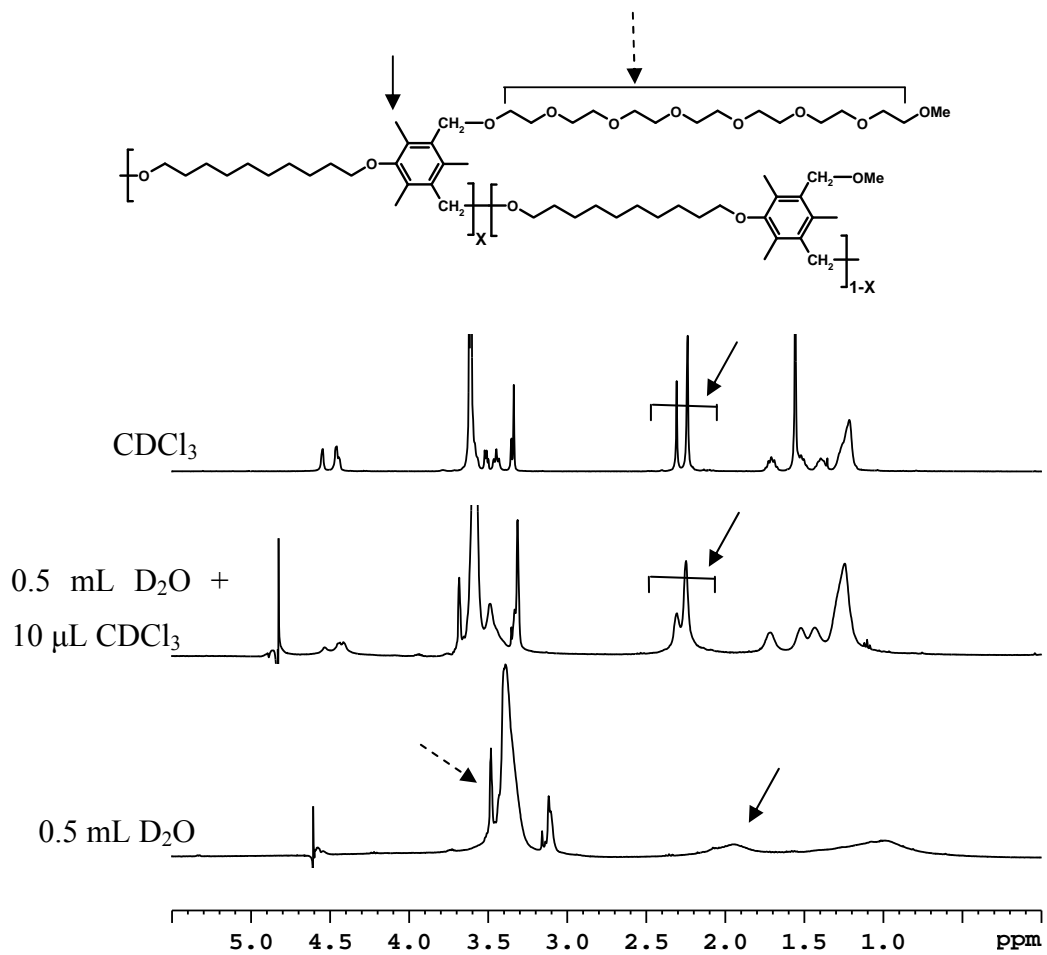
**Figure S6.** Size exclusion chromatograms of polymer **P2** (before click), and polymer **P3** (after click).



**Figure S7.** Size exclusion chromatograms of polymer **P4** (before click), and polymer **P5** (after click).



**Figure S8.** Size exclusion chromatograms of polymer **P6** (before click), and polymer **P7** (after click).



**Figure S9.**  $^1\text{H}$  NMR spectra of polymer AB2-C10-HPEG in different solvents.