Supporting Information

Thermoresponsive Helical Poly(phenylacetylene)s

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Table of Contents

Experimental Section

The first generation dendritic monomer **MA-G1** [S1] and compound **6** [S2] were prepared according to previous reports.

Compound **7**. Compound **6** (3.18 g, 19.00 mmol) was dissolved in excess pyrrole (38.52 g, 57.40 mmol). A catalytic amount of TFA (0.22 g, 1.9 mmol) was added, and the mixture was stirred for 22 h at room temperature. The excess of pyrrole was evaporated off, and the residue was purified with chromatograph using hexane/DCM (50:1) as eluent to afford **7** as black solids (2.16 g, 41%). ^{1}H NMR ($CDCl_3$): δ = 3.93-3.95 (m, 2H, CH_2), 4.05-4.07 (m, 2H, CH_2), 5.43 (s, H, CH), 5.89-5.91 (m, 2H, pyrrole-H), 6.15 (dd, J = 2.8, 6.0 Hz, 2H, pyrrole-H), 6.68-6.69 (m, 2H, pyrrole-H), 6.85-6.88 (m, 2H, Ar-H), 7.12-7.14 (m, 2H, Ar-H), 7.98 (br, 2H, NH).

Compound **8**. DCM solution (10 mL) of *p*-chloranil (1.44 g, 6.00 mmol) was added dropwise to DCM solution (15 mL) of compound **7** (1.61 g, 5.71 mmol) at 0 ^{o}C. The reaction mixture was stirred at 0 ^{o}C for 3 h and then was raised to room temperature. The mixture was stirred at room temperature for another 18 h before DIPEA (8.10 g, 62.8 mmol) and $BF_3{\cdot}OEt_2$ (12.20 g, 85.70 mmol) were added. The solution was stirred at room temperature for 48 h before partitioned between brine and DCM. The organic phase was dried over $MgSO_4$. After filtration, the solvent was evaporated *in vacuo*. The residue was purified with chromatograph using hexane/DCM (10:1) as eluent to afford compound **8** as yellow solids (0.67 g, 36%).^{1}H NMR ($CDCl_3$): δ = 4.03- 4.04 (m, 2H, CH_2), 4.18-4.20 (m, 2H, CH_2), 6.55 (d, J = 2.8 Hz, 2H, pyrrole-H), 6.97 (d, J = 3.9 Hz, 2H, pyrrole-H), 7.08 (d, J = 8.6 Hz, 2H, Ar-H), 7.56 (d, J = 8.6 Hz, 2H, Ar-H), 7.92 (s, 2H, pyrrole-H).

Monomer **MA-BDY**. Methacryloyl chloride (0.19 g, 1.80 mmol) in DCM (5 mL) was added dropwise to a solution of **8** (0.30 g, 0.90 mmol), DMAP (0.06 g, 0.18 mmol) and triethylamine (0.27 g, 2.70 mmol) in DCM (20 mL) at 0 ^{o}C. The mixture was stirred at room temperature for 13 h before adding methanol to quench the reaction. The mixture solution was concentrated before partitioned between saturated sodium bicarbonate solution and DCM. The organic phase was dried over $MgSO_4$. It was purified with chromatograph by

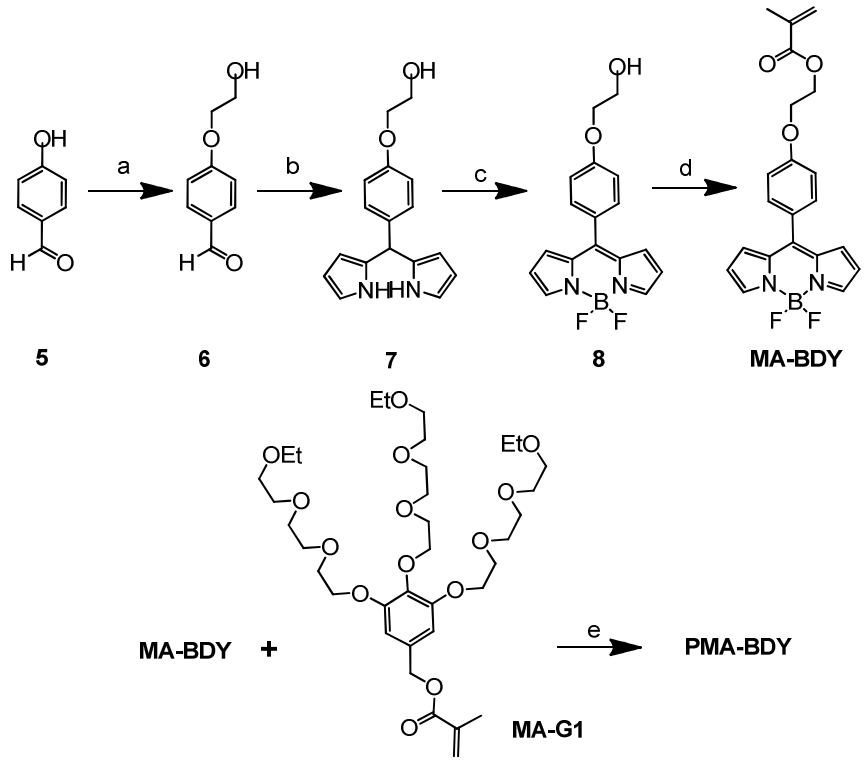
using DCM/MeOH (100:1) as eluent to afford monomer **MA-BDY** as yellow solids (0.21 g, 59%). ^{1}H NMR ($CDCl_3$): δ = 1.96-1.97 (m, 3H, CH_3), 4.32-4.34 (m, 2H, CH_2), 4.55-4.56 (m, 2H, CH_2), 5.61-5.62 (m, 1H, CH_2), 6.16-6.17 (m, 1H, CH_2), 6.54 (dd, J = 1.2, 3.8 Hz, 2H, pyrrole-H), 6.96 (d, J = 4.1 Hz, 2H, pyrrole-H), 7.06-7.08 (m, 2H, Ar-H), 7.54-7.55 (m, 2H, Ar-H), 7.92 (br, 2H, pyrrole-H). ^{13}C NMR ($CDCl_3$), **δ** = 18.30, 62.84, 66.16, 114.69, 118.37, 126.24, 126.60, 126.63, 131.36, 132.44, 134.76, 135.91, 143.45, 147.22, 161.07, 167.23. HRMS (ESI): m/z calcd for $C_{21}H_{19}BF_2N_2$ $[M+H]^+$: 395.1493, found: 395.1496.

Polymer **PMA-BDY**. Monomer **MA-G1** (0.20 g, 0.28 mmol), **MA-BDY** (0.22 mg, 0.58 mol), and AIBN (3 mg) were dissolved in dry DMF (0.10 mL) inside a Schlenk tube. The solution was thoroughly deoxygenated by several freeze-pump-thaw cycles and then stirred at 70 ^{o}C for 25 h. After cooling to rt, the polymer was dissolved in DCM, and purified with chromatograph by using DCM as eluent to afford the product as a viscous yellow liquid (0.11 g, 55%). ^{1}H NMR ($CDCl_3$, 50 ^{o}C): δ = 0.82-1.05 (br, 3H, CH_3), 1.14-1.19 (m, 9H, CH_3), 3.47-3.74 (m, 36H, CH_2+CH_3), 4.04-4.07 (br, 6H, CH_2), 4.77 (br, 2H, CH_2), 6.51 (br, 2H, Ar-H).

References

[S1] Li, W.; Zhang, A.; Schlüter, A. D. *Chem. Commun*. **2008**, 5523–5525.

[S2] Jackson, A. W.; Stakes, C.; Fulton, D. A. *Polym. Chem*. **2011**, *2*, 2500–2511.



Scheme S1. Reagents and reaction conditions: (a) **5**, 2-bromoethanol, DMF, K_2CO_3, 150 ^oC, 24 h (47%); (b) **6**, TFA, pyrrole, rt, 21 h (41%); (c) **7**, *p*-chloranil, DCM, 0 ^oC - rt, 12 h; (d) DIPEA, $BF_3{\cdot}OEt_2$, rt, 52 h (36%, two steps); (e) **8**, MAC, TEA, 0 ^oC - rt, 12 h (59%); (f) **MA-G1**, **MA-BDY**, AIBN, DMF, 70 ^oC, 25 h, (55%). DMF = dimethylformamide, DIPEA = diisopropylethylamine, AIBN = azobis(isobutyronitrile), MAC = methacryloyl chloride, TFA = trifluoroacetic acid.

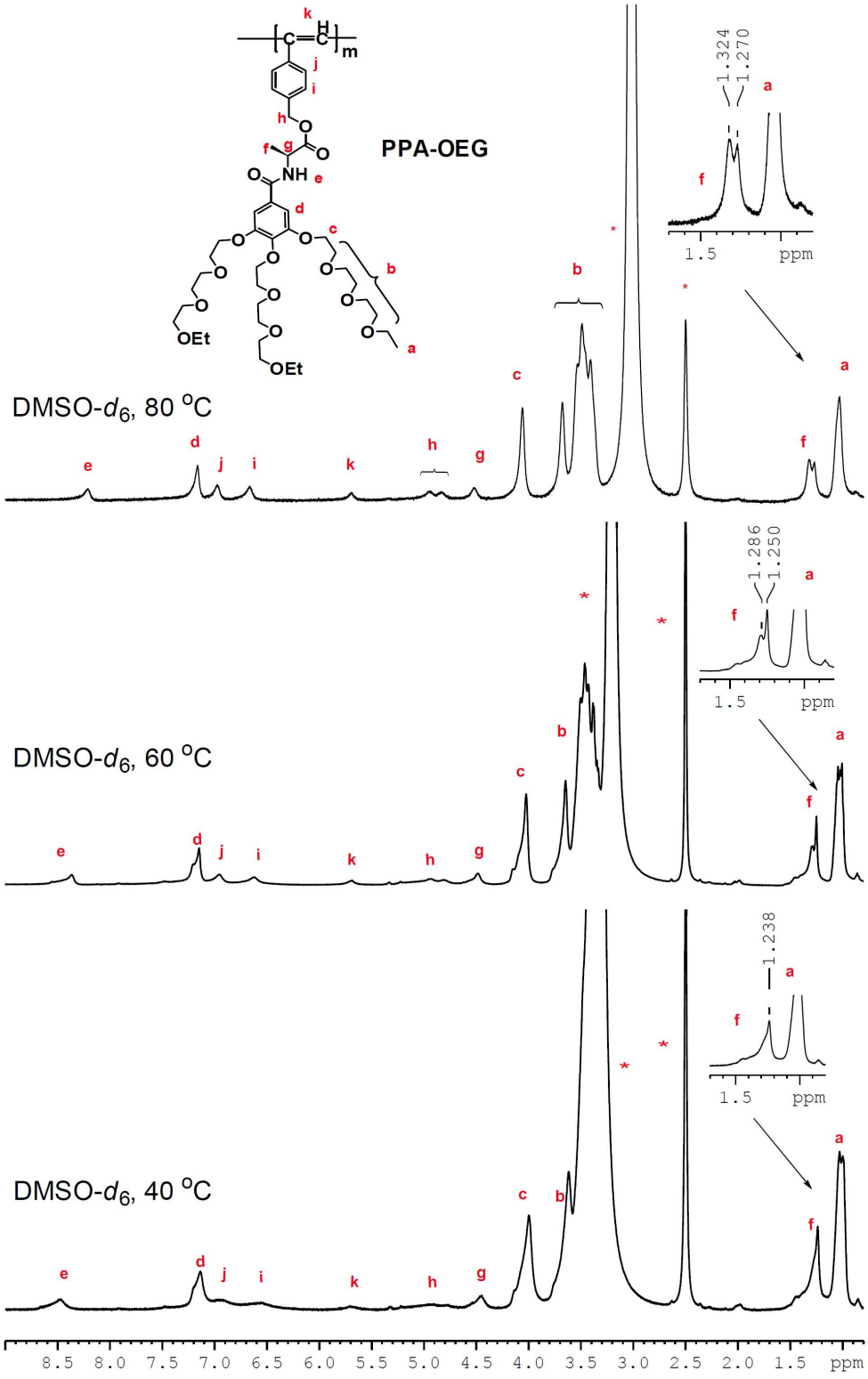


Figure S1. ^{1}H NMR spectra of **PPA-OEG** in DMSO-d_6 at 40, 60 and 80 °C, respectively.

The solvent peaks are marked with asterisks.

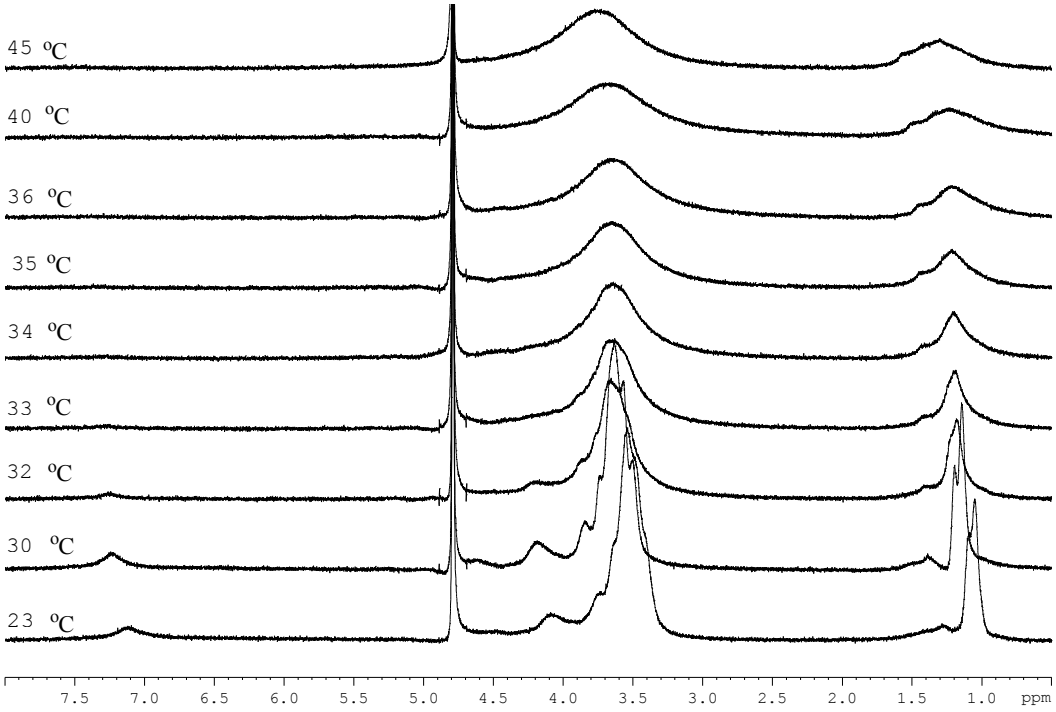


Figure S2. Temperature-varied ^{1}H NMR spectra of **PPA-BDY** (0.31 wt %) in D_2O (T_{cp} = 33.9 °C).

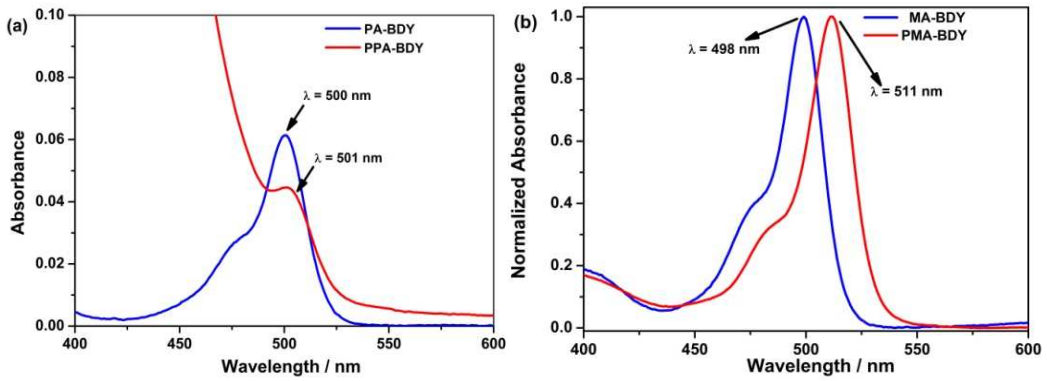


Figure S3. (a) Absorption spectra of **PA-BDY** (1.13×10^{-6} mol·L^{-1}) and **PPA-BDY** (0.56 mg·mL^{-1}) in methanol at 25 °C. (b) Normalized absorption spectra of aliphatic monomer **MA-BDY** (2.09×10^{-5} mol·L^{-1}) and **PMA-BDY** (0.50 mg·mL^{-1}) in DCM at 25 °C

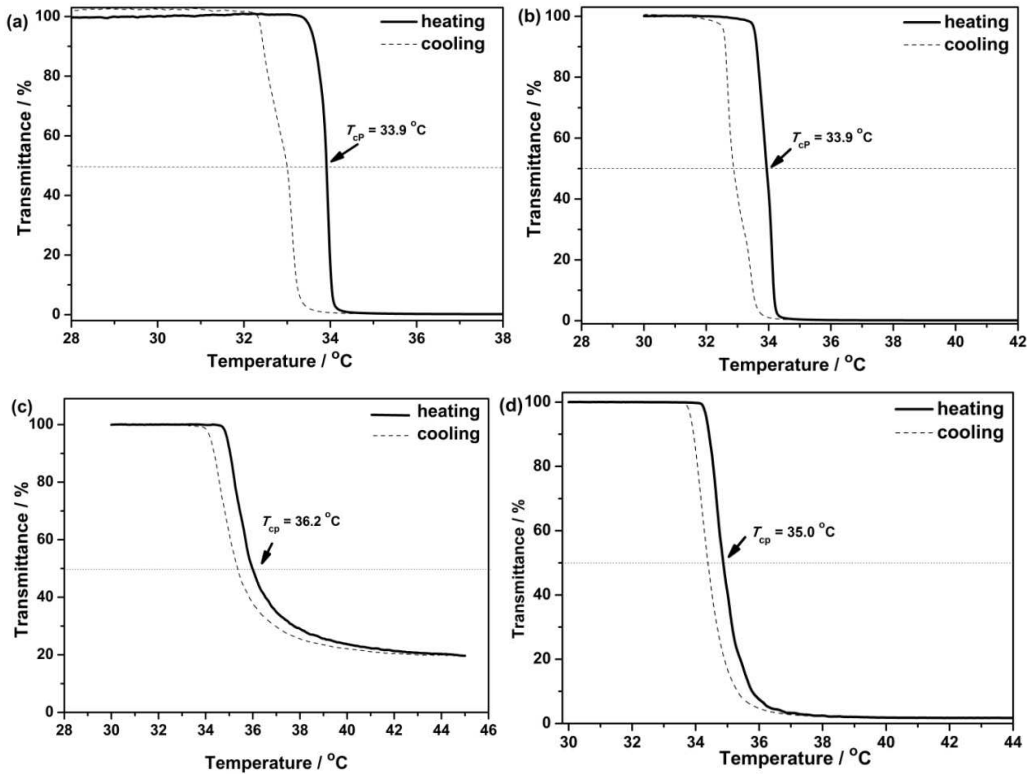


Figure S4. Turbidity curves for **PPA-OEG** (a, 0.40 wt %) and **PPA-BDY** (b, 0.31 wt %) in D_2O, and for **PPA-BDY** (c, 0.025 wt %) and **PMA-BDY** (d, 0.10 wt %) in H_2O.

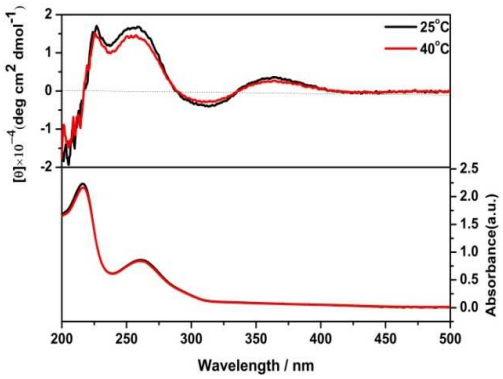


Figure S5. CD and UV/vis spectra for **PPA-OEG** (0.060 wt %) in methanol at 25 °C and 40 °C, respectively.

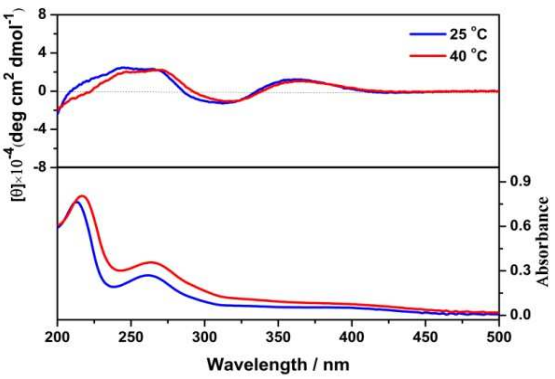


Figure S6. CD and UV/vis spectra for **PPA-OEG** (0.025 wt %) aqueous solution at 25 °C and 40 °C. The sample was kept at room temperature for 3 days before measurements.

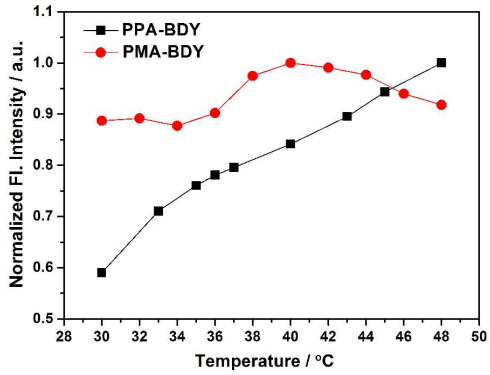


Figure S7. Plots of normalized fluorescence intensity for **PPA-BDY** at 522 nm and **PMA-BDY** at 524 nm versus temperature.

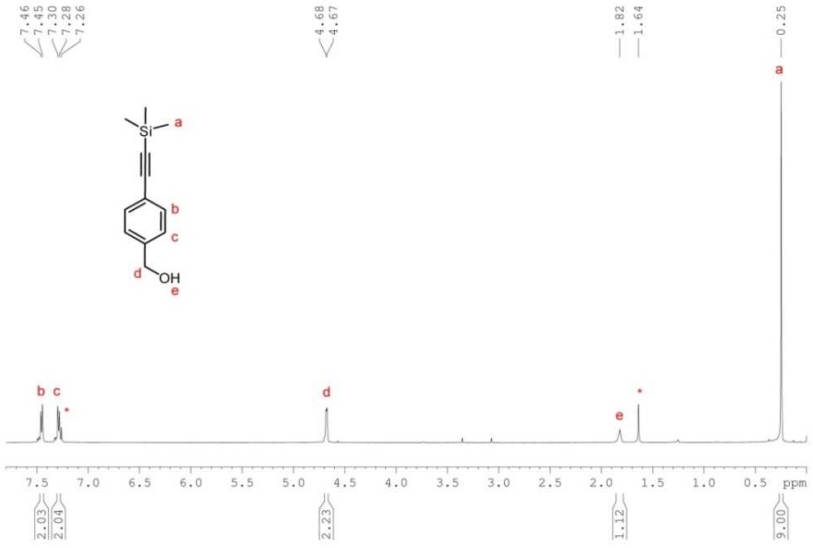


Figure S8. ^{1}H NMR spectrum of compound **2** in $CDCl_3$. The solvent peaks are marked with asterisk (*).

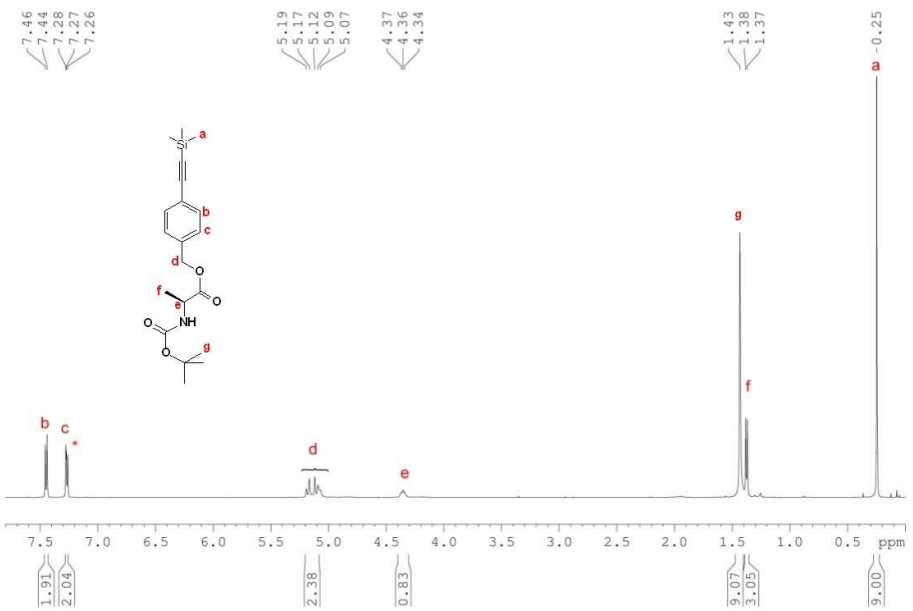


Figure S9. ^{1}H NMR spectrum of compound **3** in $CDCl_3$. The solvent peak is marked with asterisk (*).

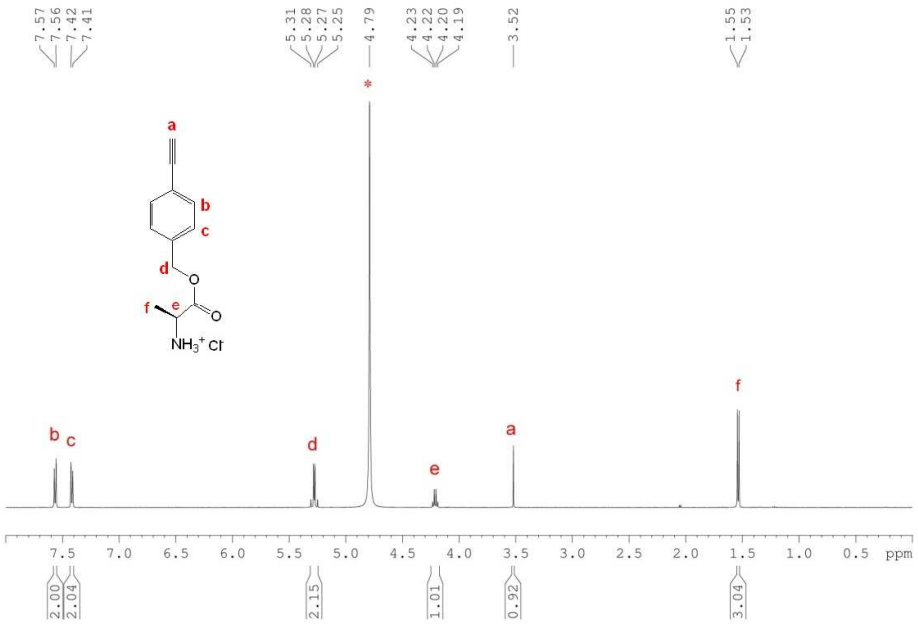


Figure S10. ^{1}H NMR spectrum of compound **4** in D_2O. The solvent peak is marked with asterisk (*).

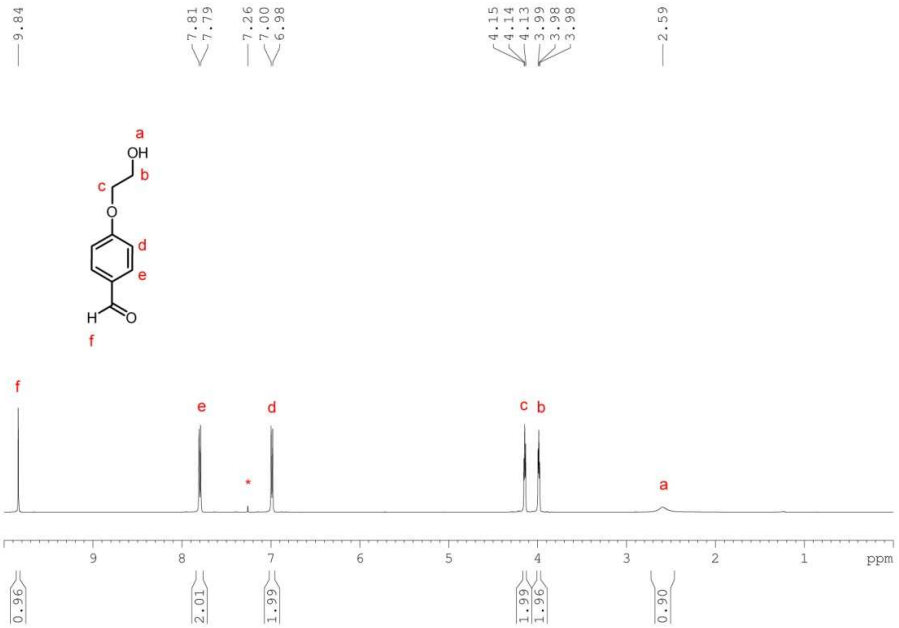


Figure S11. ^{1}H NMR spectrum of compound **6** in $CDCl_3$. The solvent peak is marked with asterisk (*).

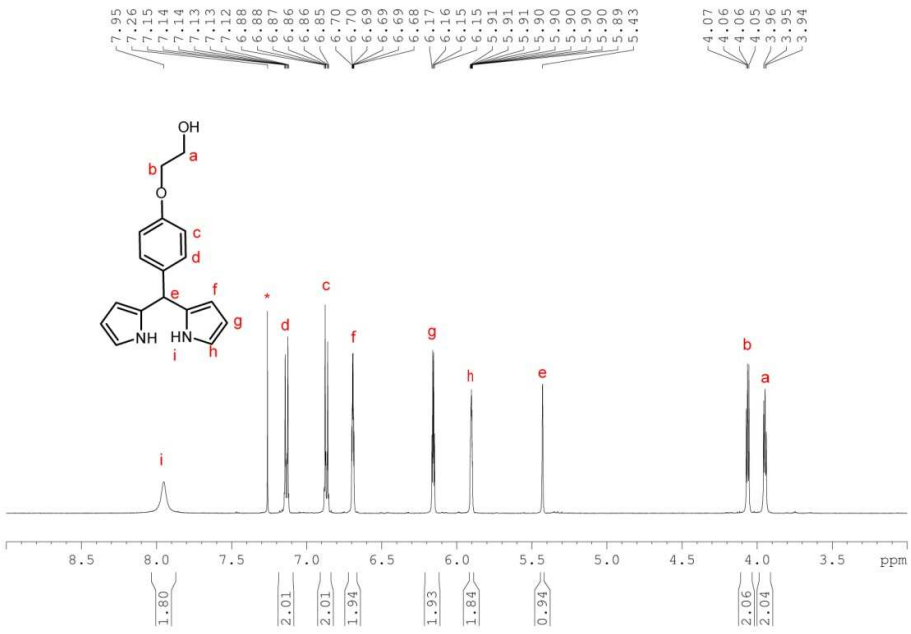


Figure S12. ^{1}H NMR spectrum of compound **7** in $CDCl_3$. The solvent peak is marked with asterisk (*).

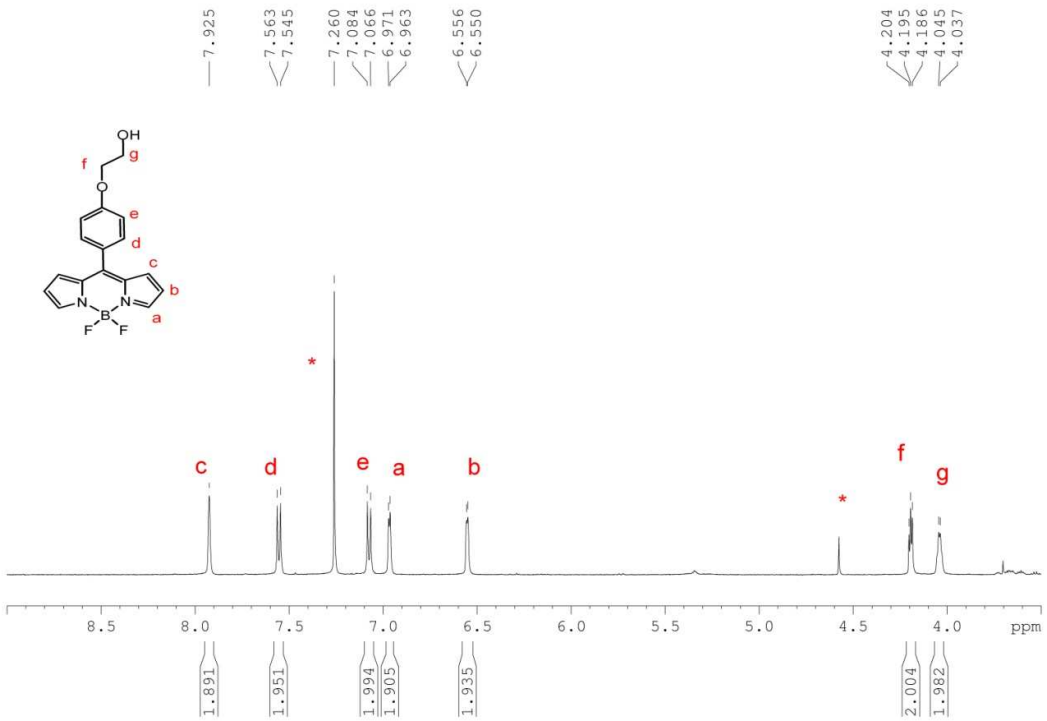


Figure S13. ^{1}H NMR spectrum of compound **8** in $CDCl_3$. The solvent peaks are marked with asterisk (*).

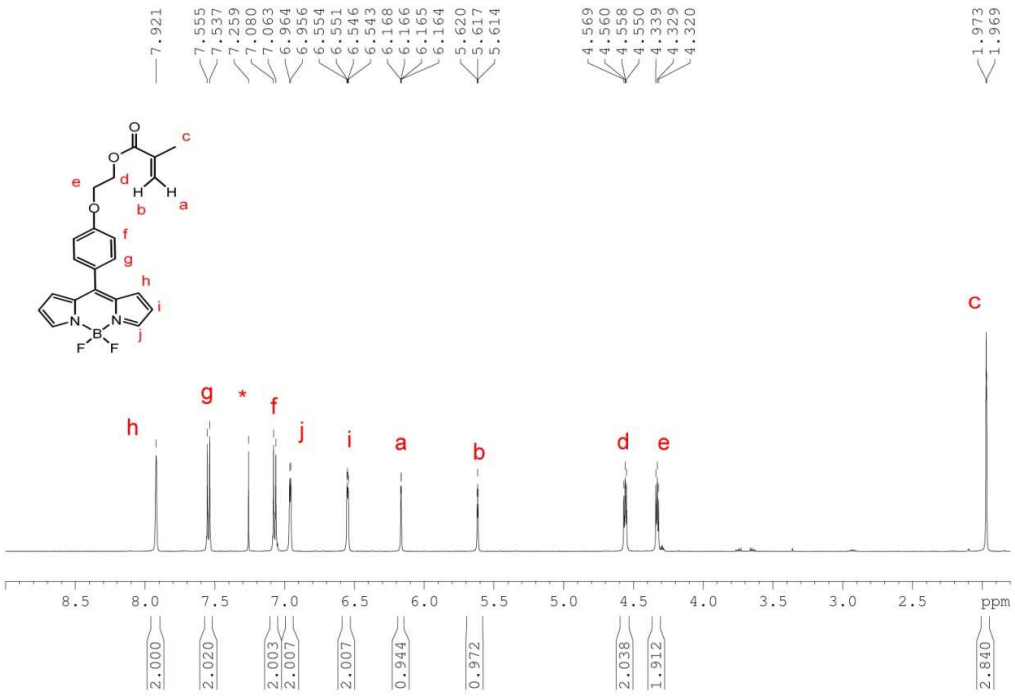


Figure S14. ^{1}H NMR spectrum of monomer **MA-BDY** in $CDCl_3$. The solvent peak is marked with asterisk (*).

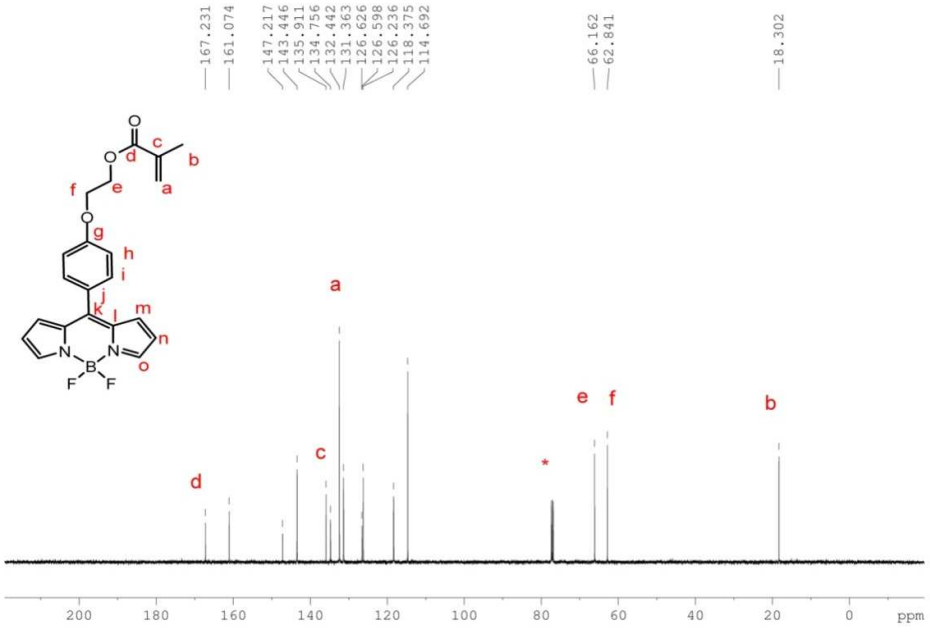


Figure S15. ^{13}C NMR spectrum of monomer **MA-BDY** in $CDCl_3$. The solvents peak is marked with asterisk (*). The aromatic peaks are not assigned in this spectrum.

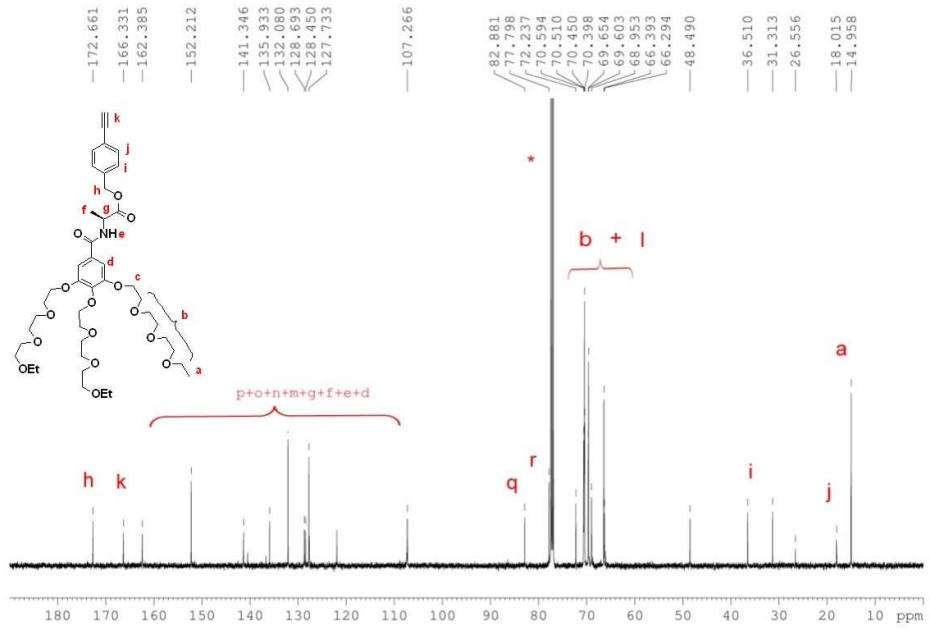


Figure S16. ^{13}C NMR spectrum of **PA-OEG** in $CDCl_3$. The solvent peak is marked with asterisk (*).

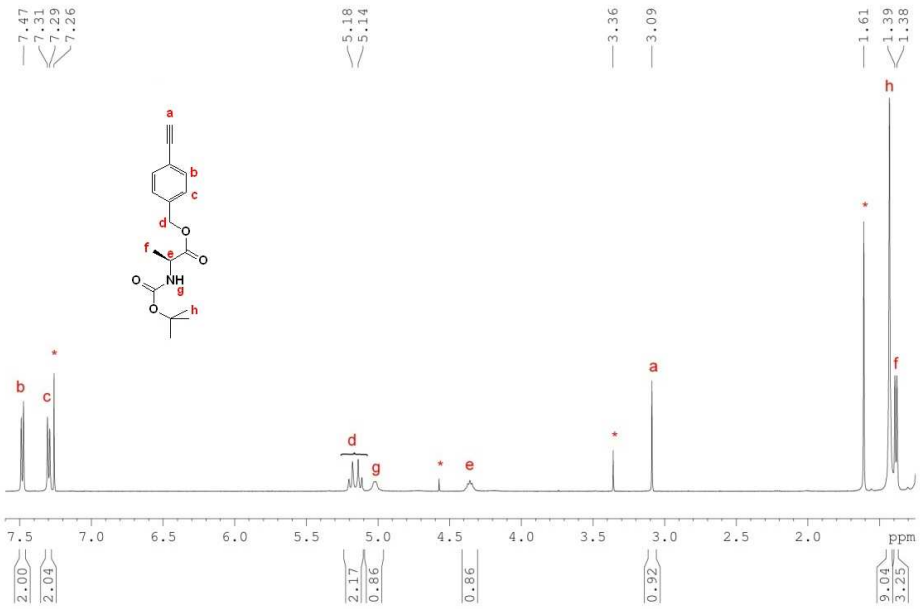


Figure S17. ^{1}H NMR spectrum of **PA-Boc** in $CDCl_3$. The solvent peaks are marked with asterisk (*).

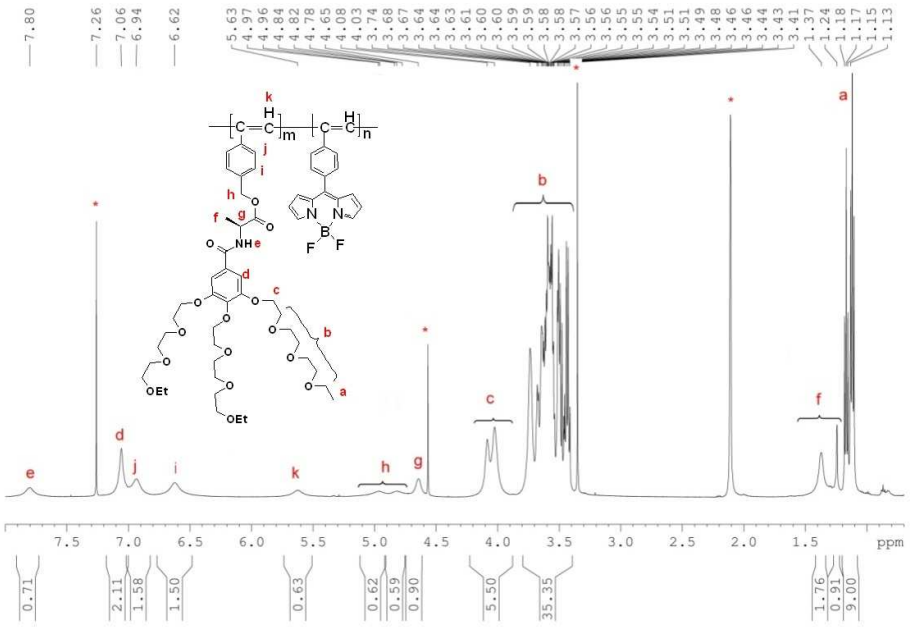


Figure S18. ^{1}H NMR spectrum of **PPA-BDY** in $CDCl_3$ at 50 ^{o}C. The solvent peaks are marked with asterisk (*).

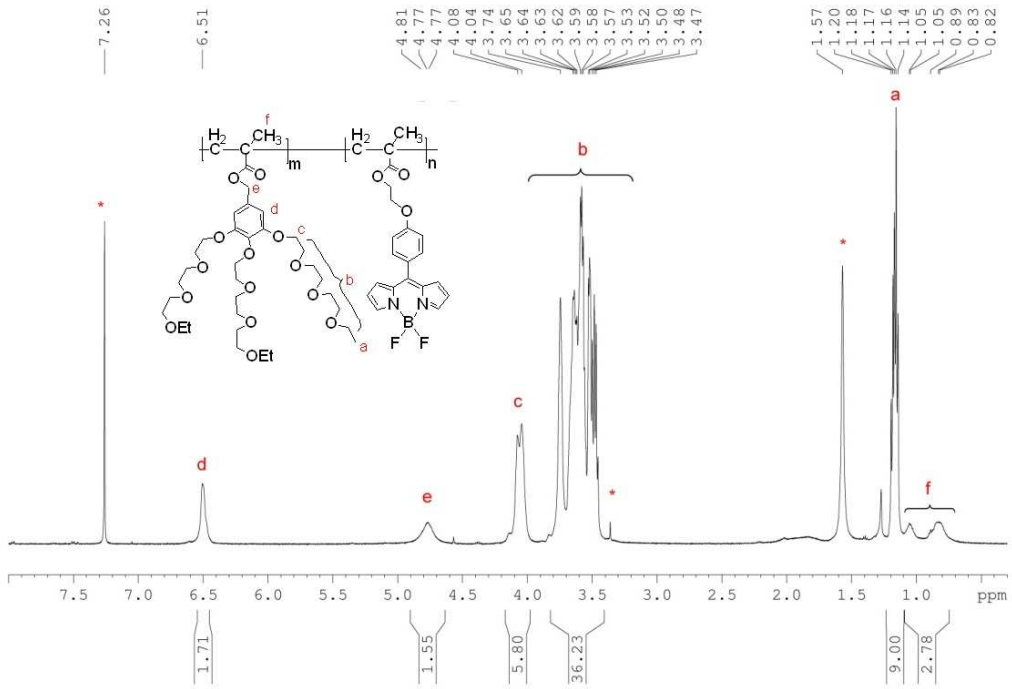


Figure S19. ^{1}H NMR spectrum of **PMA-BDY** in $CDCl_3$ at 50 ^{o}C. The solvent peaks are marked with asterisk (*).