

Supporting Information for

**Self-assembly of BODIPY based pH-sensitive near-infrared
polymeric micelles for drug controlled delivery and
fluorescent imaging applications†**

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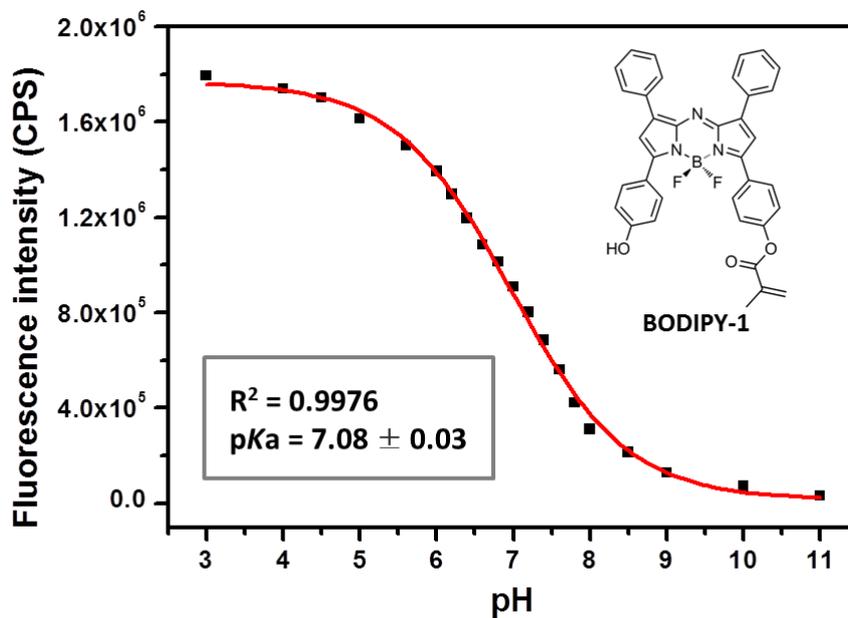


Figure S1. The pH calibration curve of **BODIPY-1** based on fluorescence emission, observed in the emission maximum at $\lambda_{em} = 706$ nm.

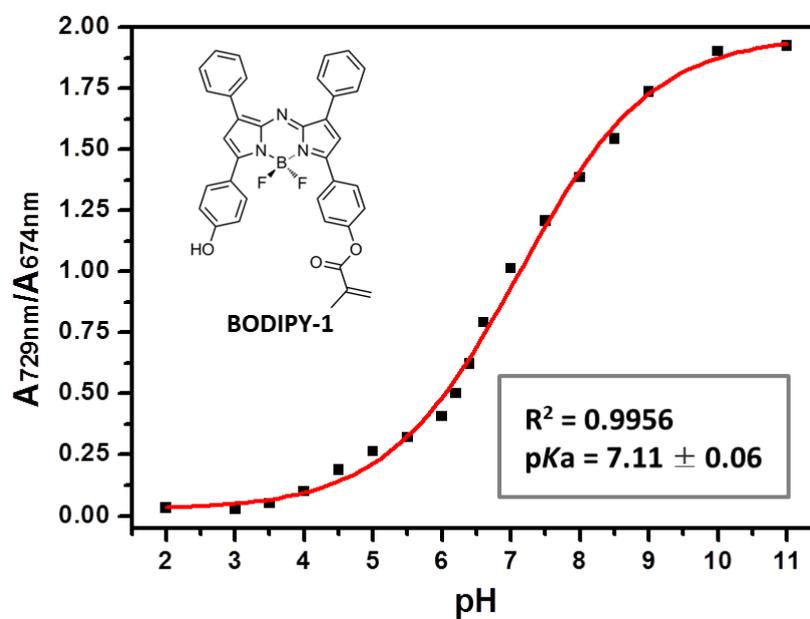


Figure S2. The pH calibration curve of **BODIPY-1** based on absorption, observed in the the absorbance ratios $A_{729\text{ nm}}/A_{674\text{ nm}}$.

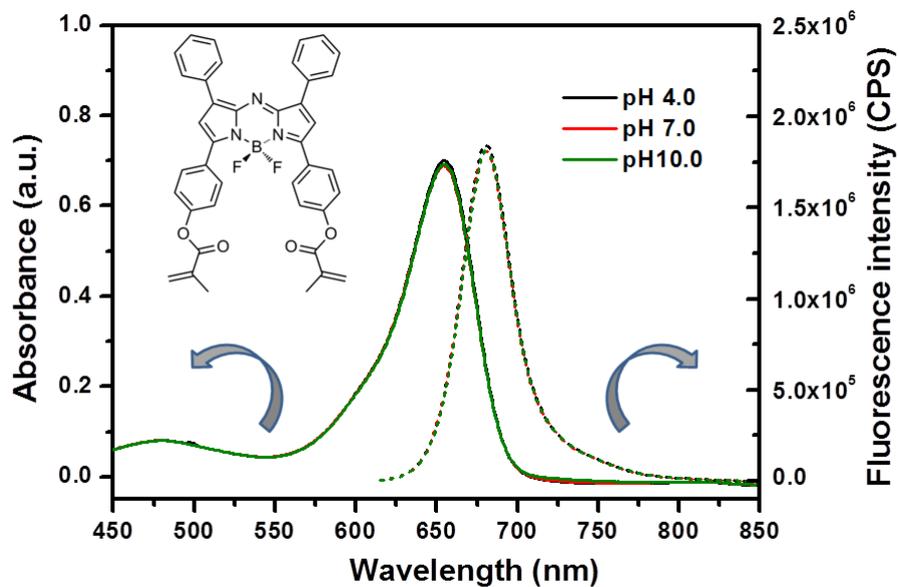


Figure S3. Absorption (solid lines) and emission (dashed lines, $\lambda_{\text{ex}} = 600 \text{ nm}$) spectra of **BODIPY-2**.

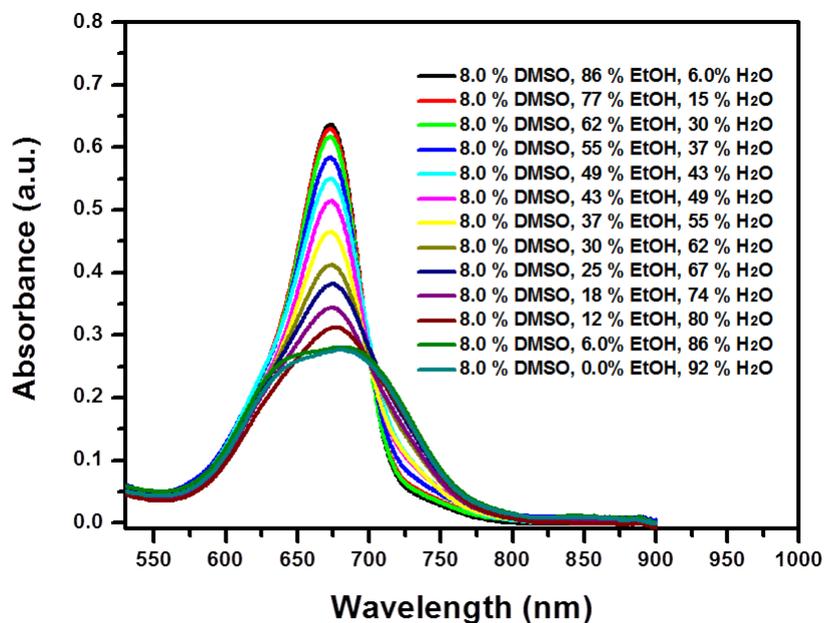


Figure S4. Absorbance spectra of **BODIPY-1** ($10 \mu\text{M}$) in co-solvent mixtures (mixed with DMSO, EtOH and water in different volume ratios) under acidic condition (pH 4.0).

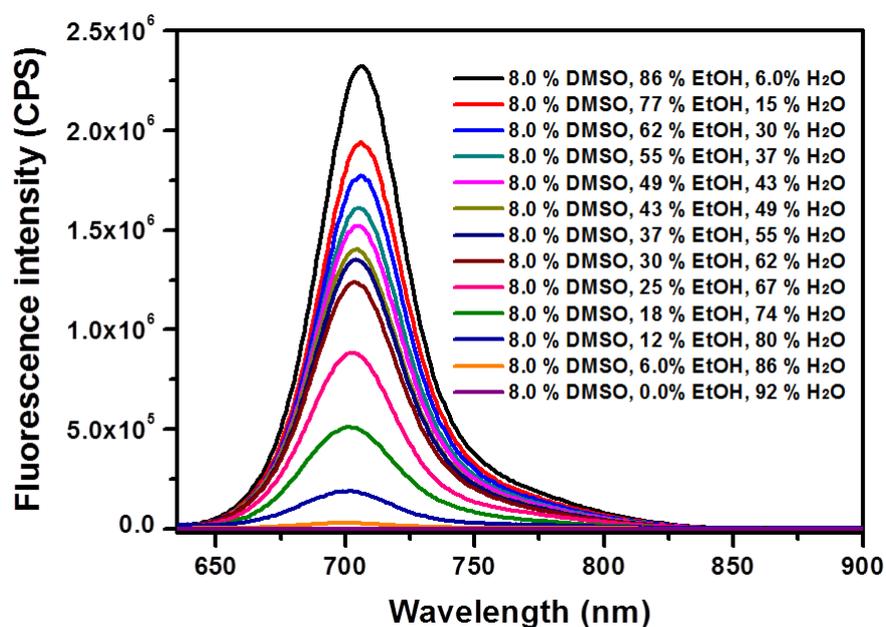


Figure S5. Fluorescence spectra of **BODIPY-1** (10 μM) in co-solvent mixtures (mixed with DMSO, EtOH and water in different volume ratios) under acidic condition (pH 4.0).

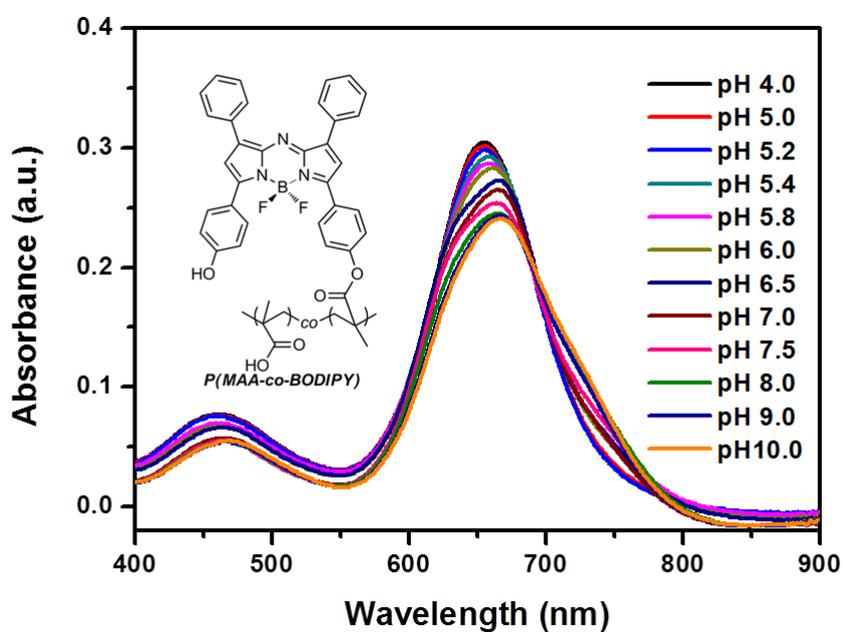


Figure S6. Absorption spectra of P(MAA-co-BODIPY) (0.10 mg/mL) under different pH in Na₂HPO₄-citric acid buffer solution.

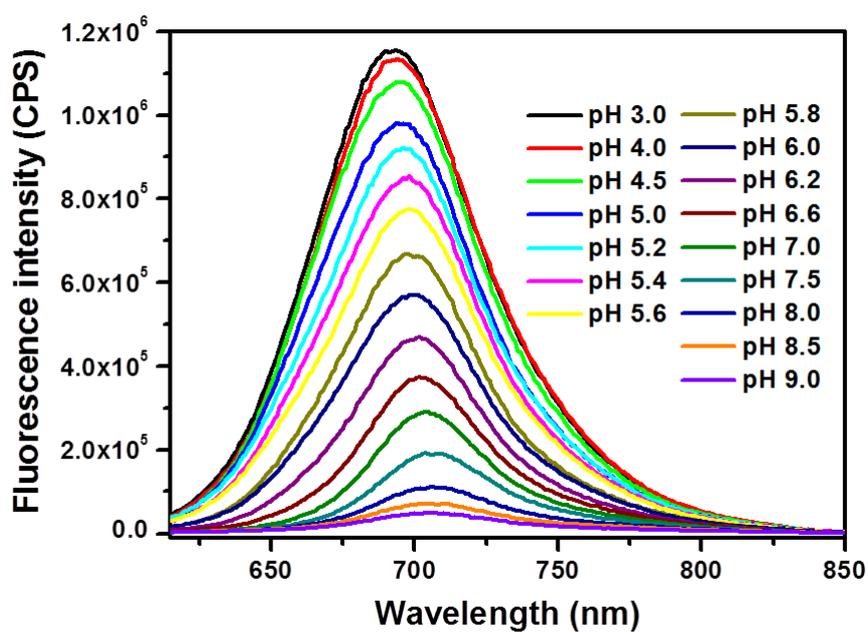


Figure S7. Fluorescence spectra of P(MAA-co-BODIPY) (0.10 mg/mL) under different pH in Na₂HPO₄-citric acid buffer solution, $\lambda_{\text{ex}} = 600$ nm.

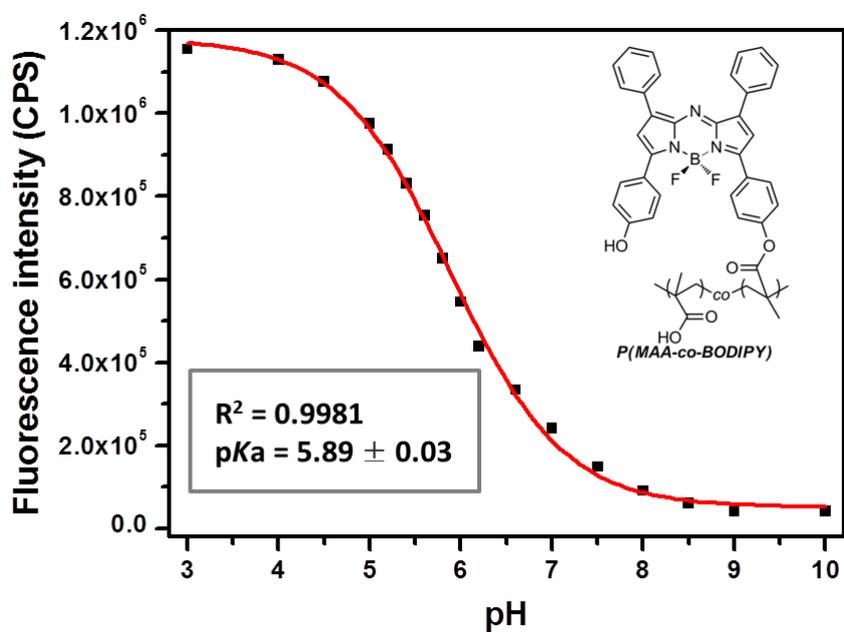


Figure S8. The pH calibration curve of P(MAA-co-BODIPY) based on fluorescence emission, observed in the emission maximum at $\lambda_{\text{em}} = 694$ nm.

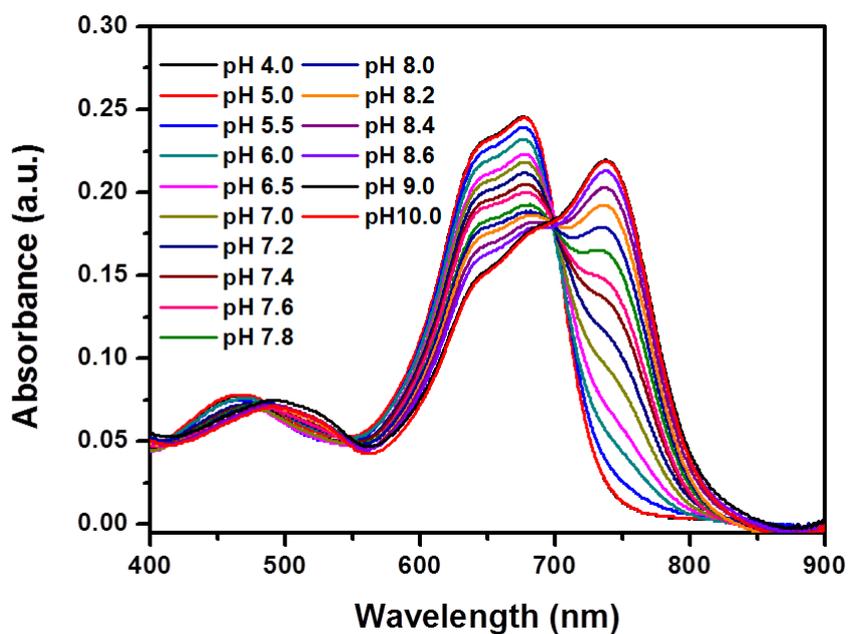


Figure S9. Absorption spectra of P(PEGMA-*co*-BODIPY) (0.10 mg/mL) under different pH in Na₂HPO₄-citric acid buffer solution.

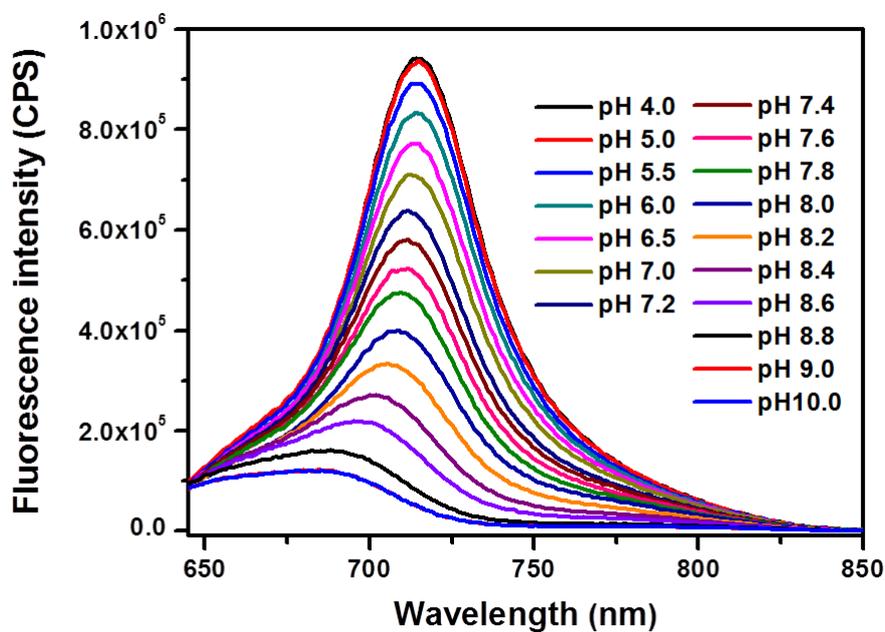


Figure S10. Fluorescence spectra of P(PEGMA-*co*-BODIPY) (0.10 mg/mL) under different pH in Na₂HPO₄-citric acid buffer solution, $\lambda_{\text{ex}} = 620$ nm.

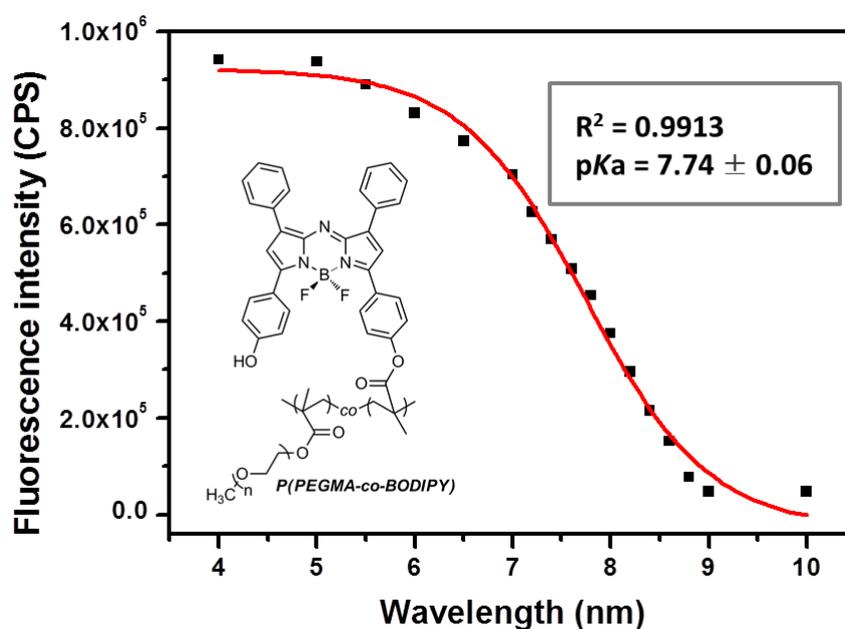


Figure S11. The pH calibration curve of P(PEGMA-co-BODIPY) based on fluorescence emission, observed in the emission maximum at $\lambda_{em} = 715$ nm.

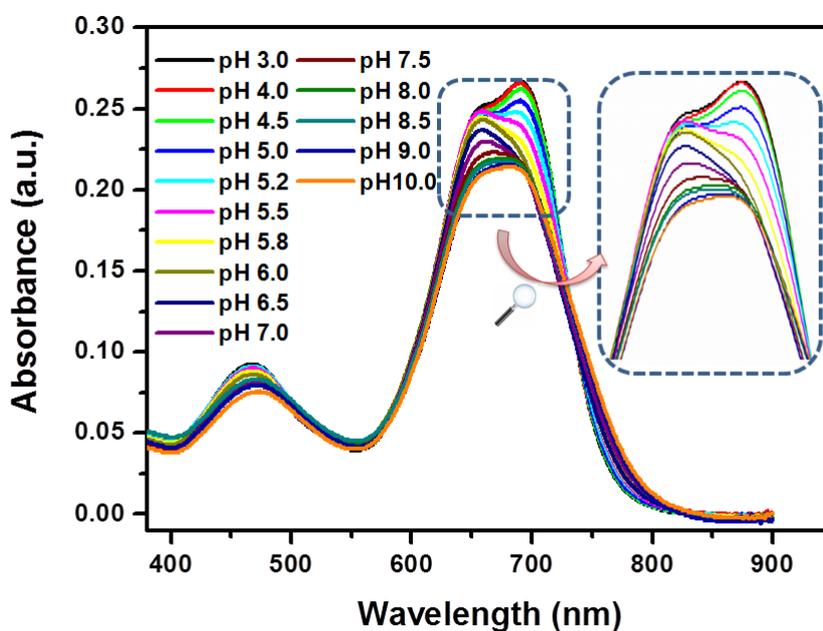


Figure S12. Absorption spectra of P(PEGMA-co-MAA-co-BODIPY) (0.25 mg/mL) under different pH in Na_2HPO_4 -citric acid buffer solution.

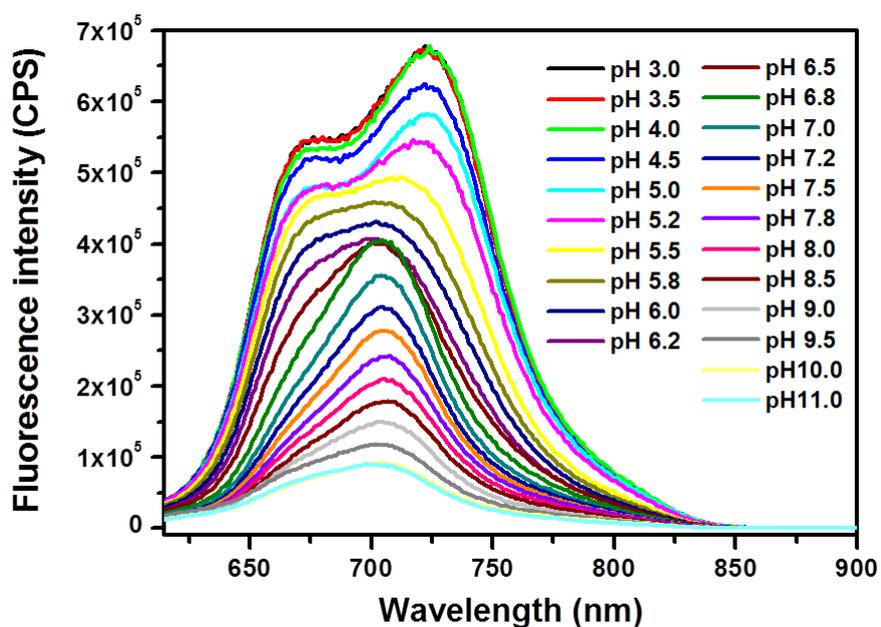


Figure S13. Fluorescence spectra of P(PEGMA-*co*-MAA-*co*-BODIPY) (0.25 mg/mL) under different pH in Na₂HPO₄-citric acid buffer solution, $\lambda_{\text{ex}} = 600$ nm.

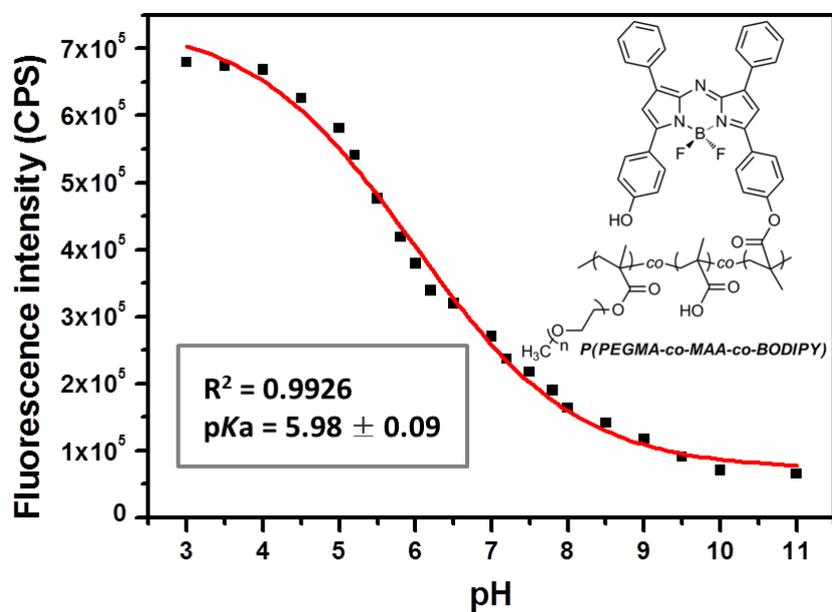


Figure S14. The pH calibration curve of P(PEGMA-*co*-MAA-*co*-BODIPY) based on fluorescence emission, observed in the emission maximum at $\lambda_{\text{em}} = 722$ nm.

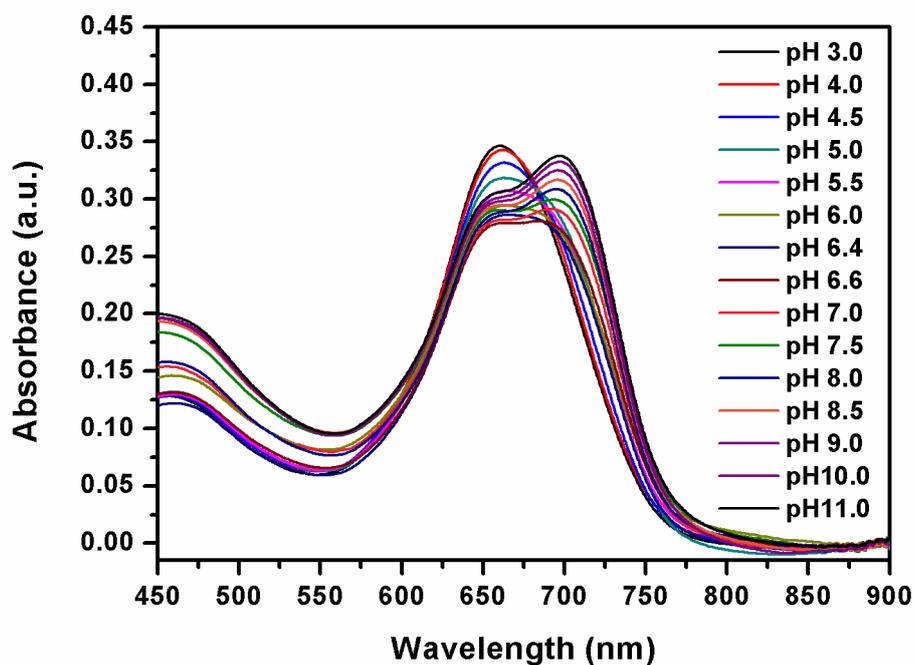


Figure S15. Absorption spectra of PPEGMA-*b*-P(MAA-*co*-BODIPY) (0.25 mg/mL) under different pH in Na₂HPO₄-citric acid buffer solution.

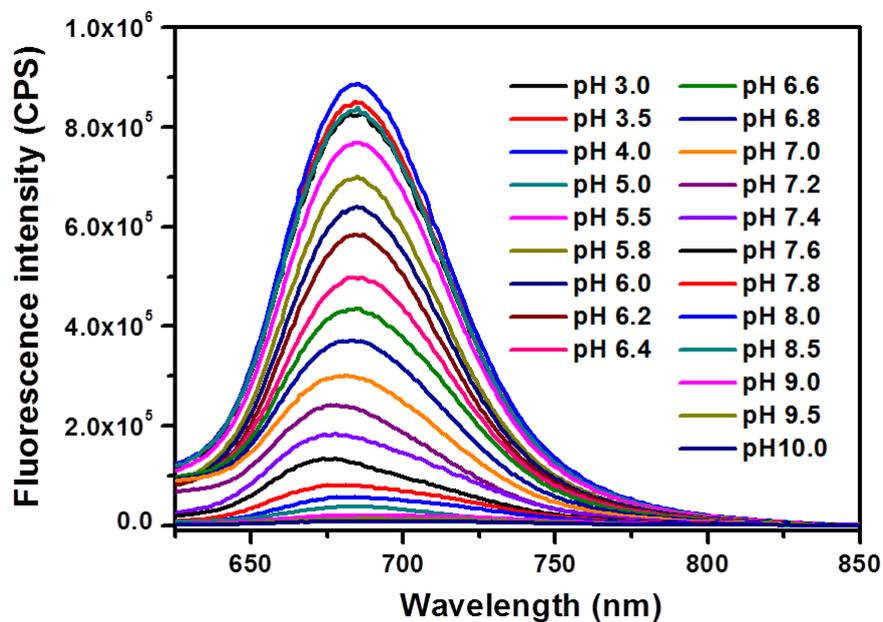


Figure S16. Fluorescence spectra of PPEGMA-*b*-P(MAA-*co*-BODIPY) (0.25 mg/mL) under different pH in Na₂HPO₄-citric acid buffer solution, $\lambda_{\text{ex}} = 600$ nm.

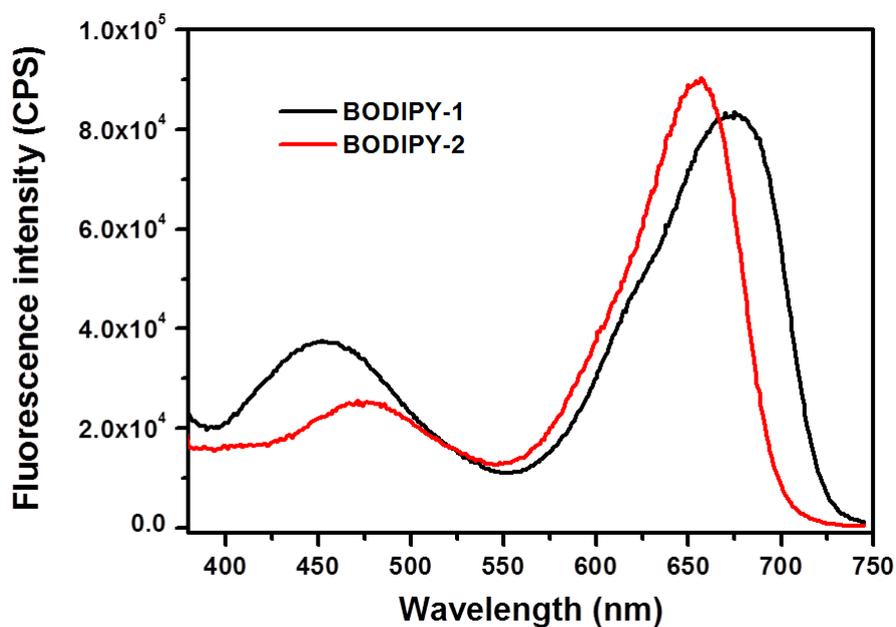


Figure S17. Excitation spectra of **BODIPY-1** (10 μM) and **BODIPY-2** (10 μM). Conditions: DMSO–ethanol– Na_2HPO_4 –citric acid buffer solution (50 mM, 8/62/30 %, v/v/v, pH 4.0, rt), $\lambda_{\text{em}} = 750$ nm.

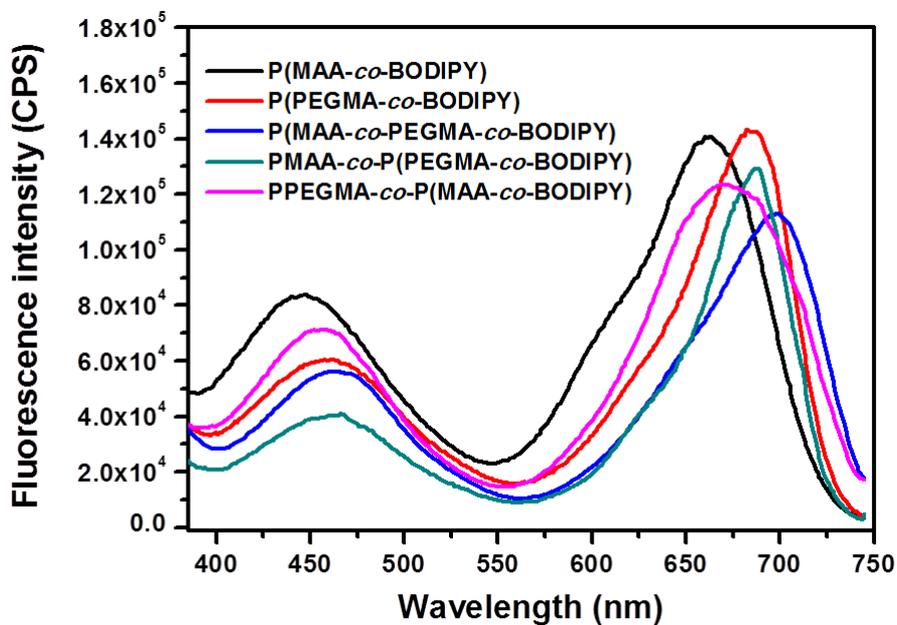


Figure S18. Excitation spectra of polymers in Na_2HPO_4 –citric acid buffer solution (50 mM, pH 4.0, rt), $\lambda_{\text{em}} = 750$ nm.

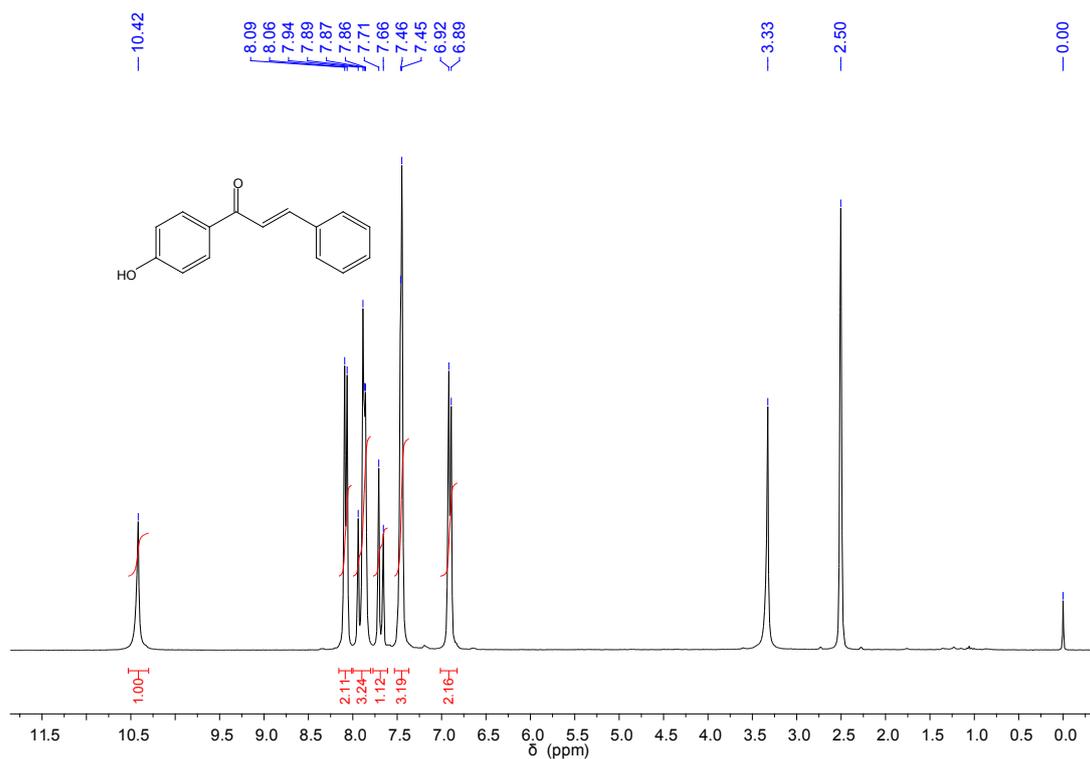


Figure S19. ^1H NMR spectrum of compound **1** in $\text{DMSO-}d_6$.

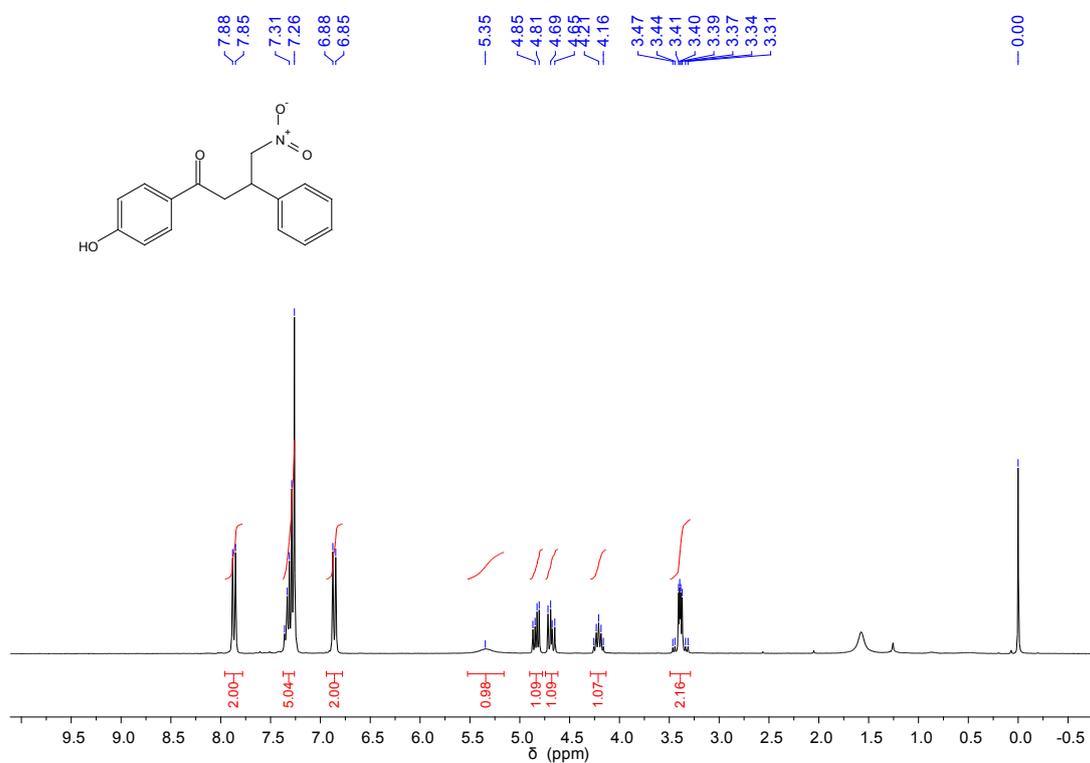


Figure S20. ^1H NMR spectrum of compound **2** in $\text{DMSO-}d_6$.

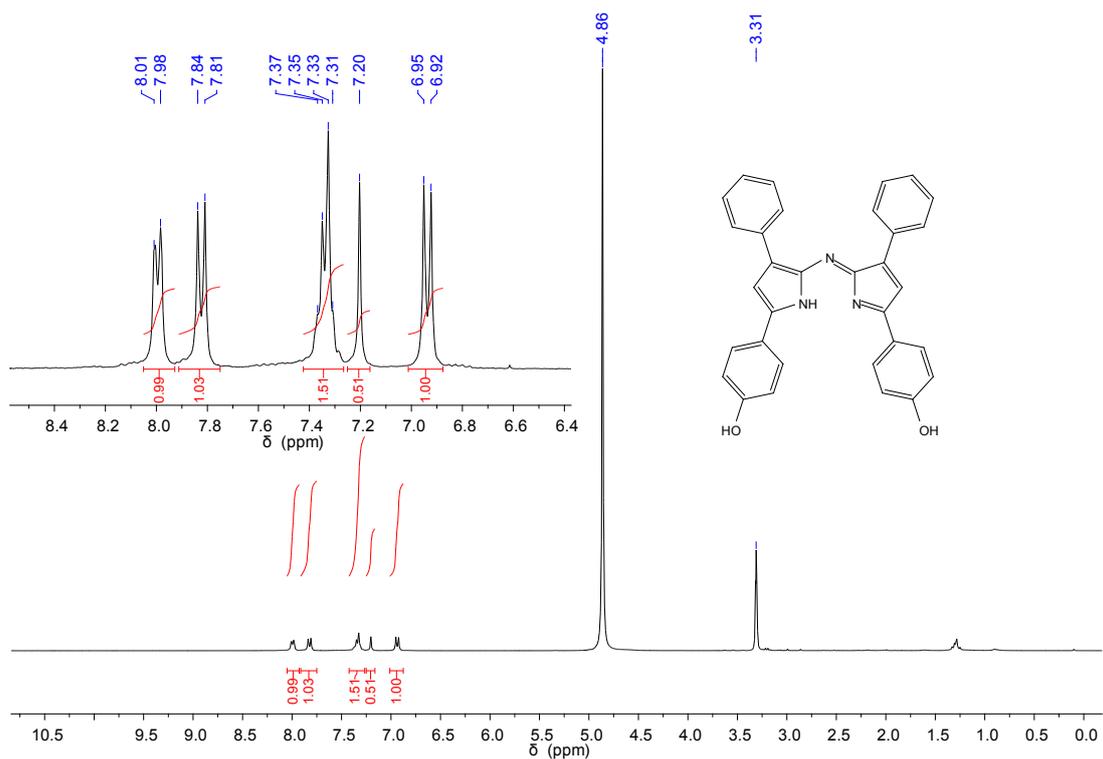


Figure S21. ^1H NMR spectrum of compound **3** in CD_3OD .

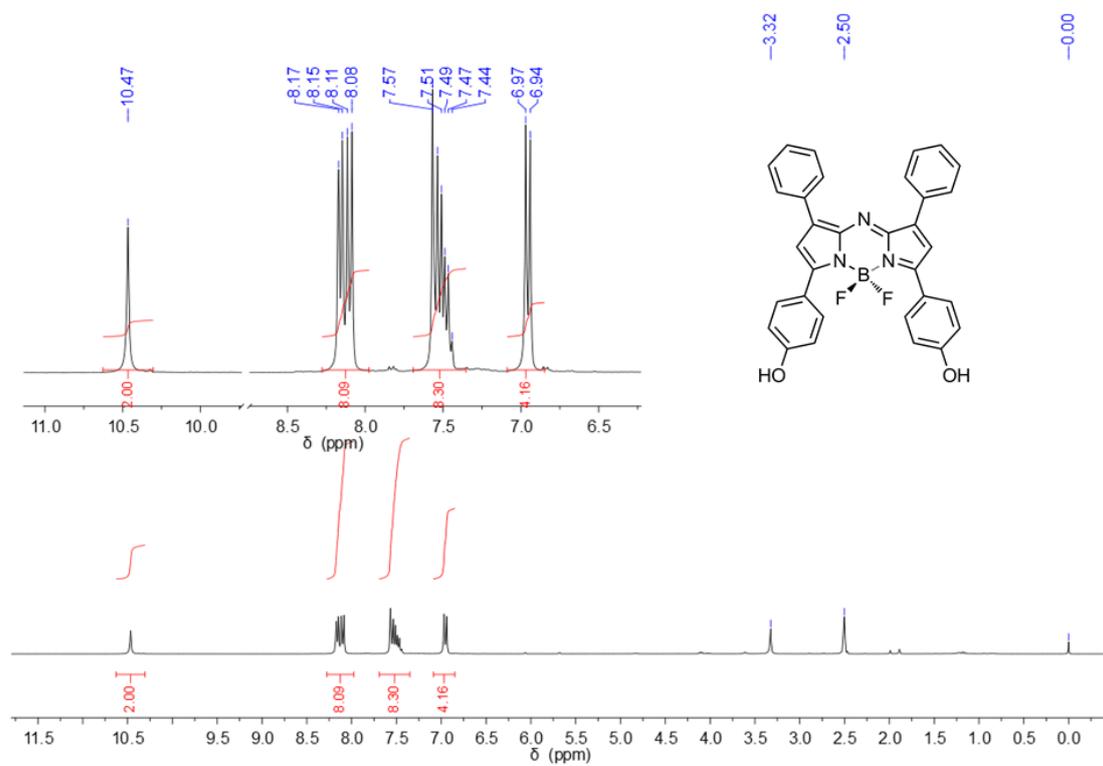


Figure S22. ^1H NMR spectra of compound **4** in $\text{DMSO}-d_6$.

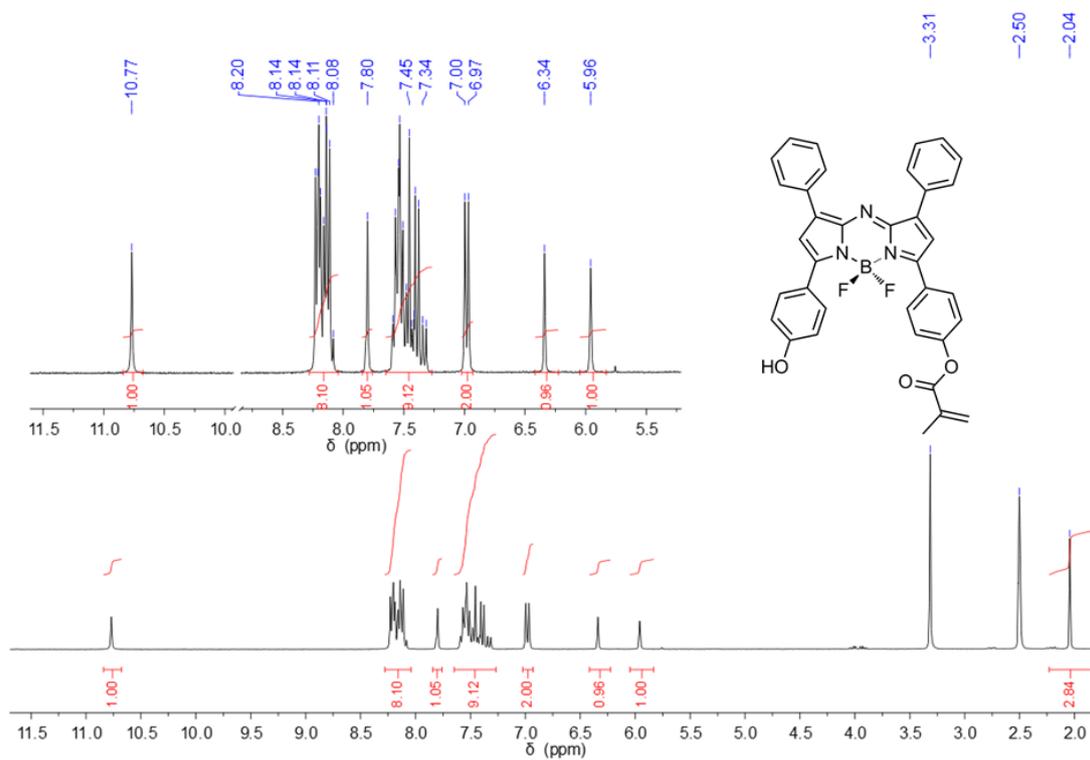


Figure S23. ^1H NMR spectrum of **BODIPY-1** in $\text{DMSO-}d_6$.

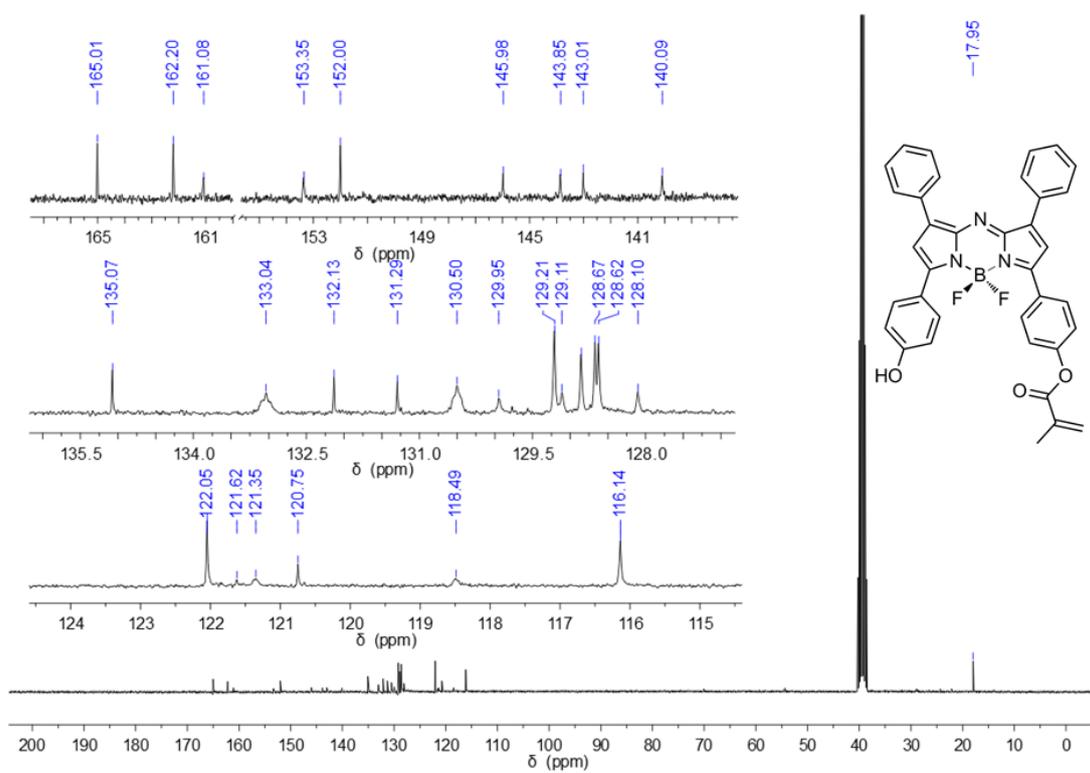


Figure S24. ^{13}C NMR spectrum of **BODIPY-1** in $\text{DMSO-}d_6$.

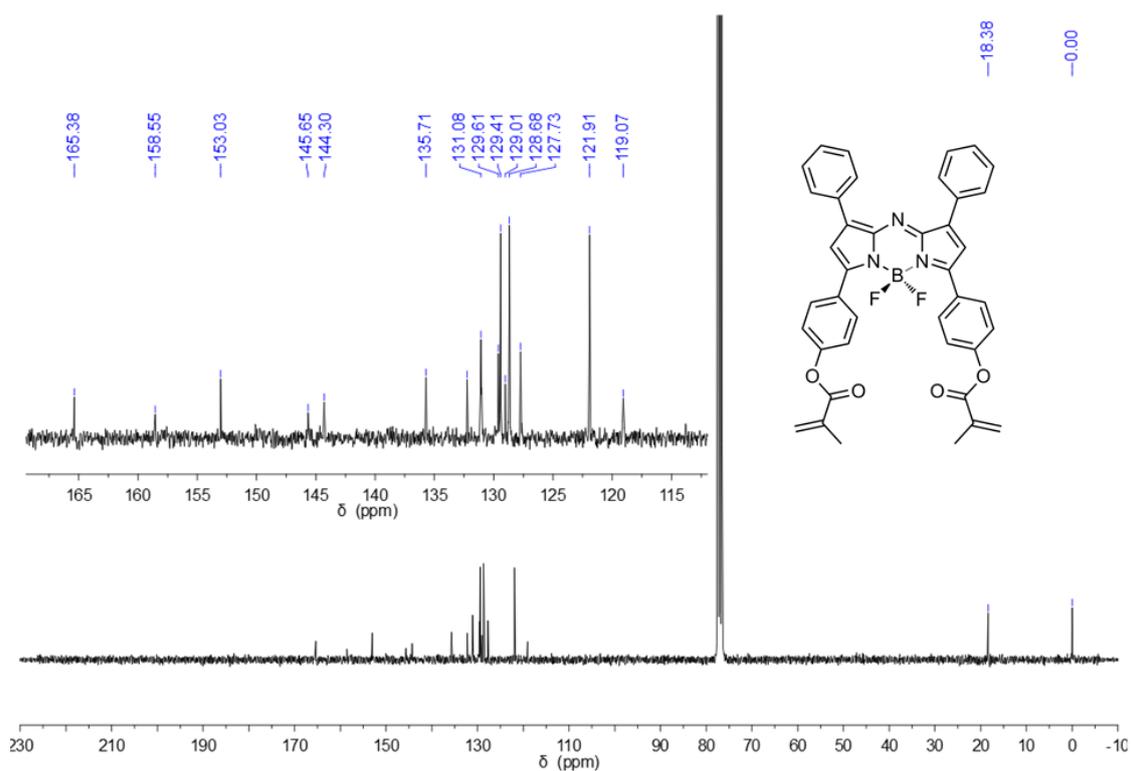


Figure S27. ^{13}C NMR spectrum of **BODIPY-2** in CDCl_3 .

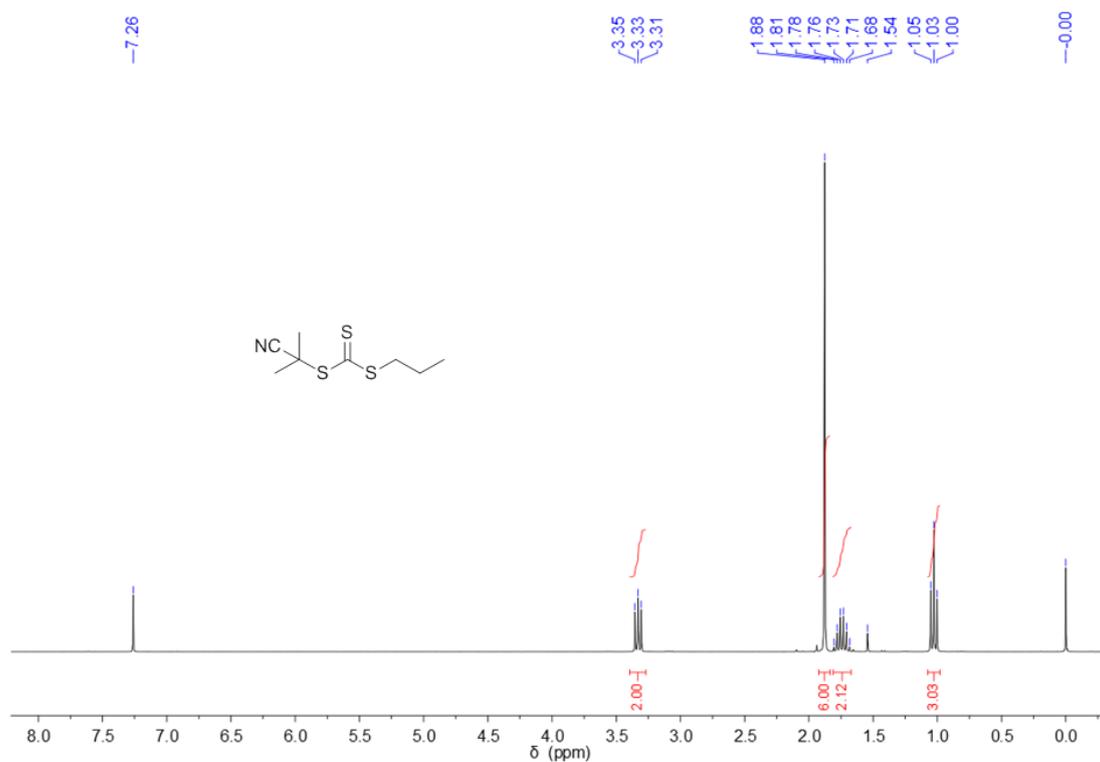


Figure S28. ^1H NMR spectrum of **CPPTC** in CDCl_3 .

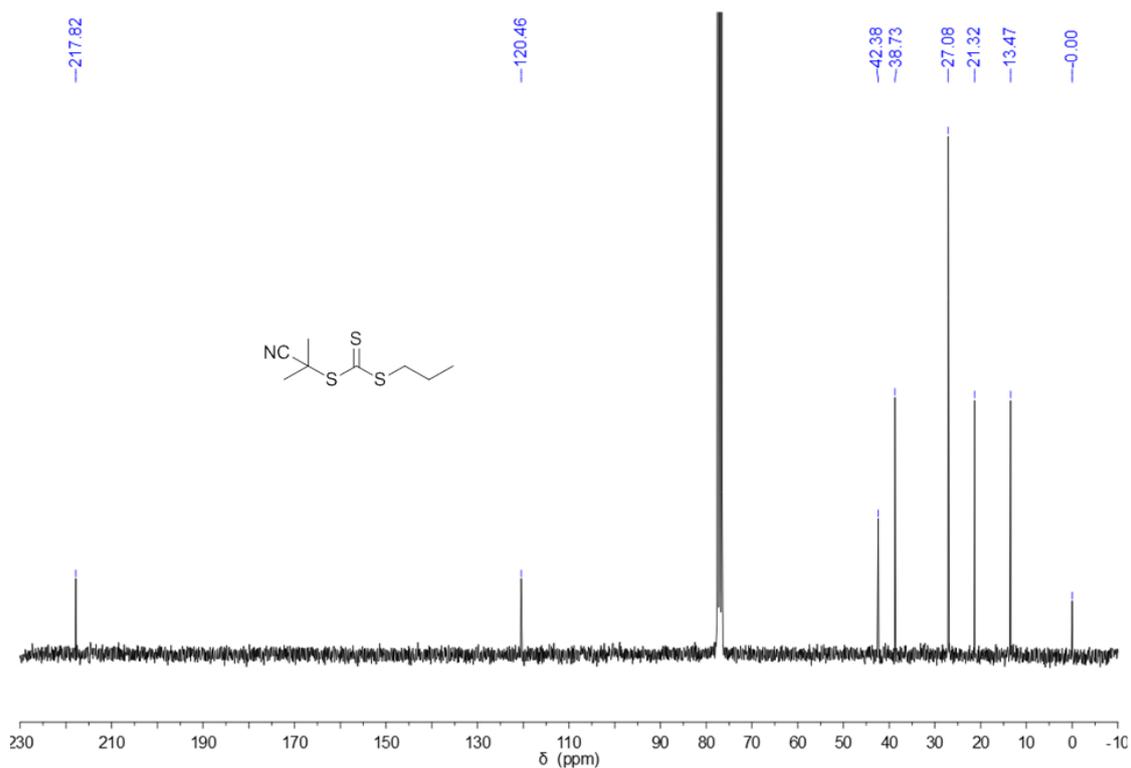
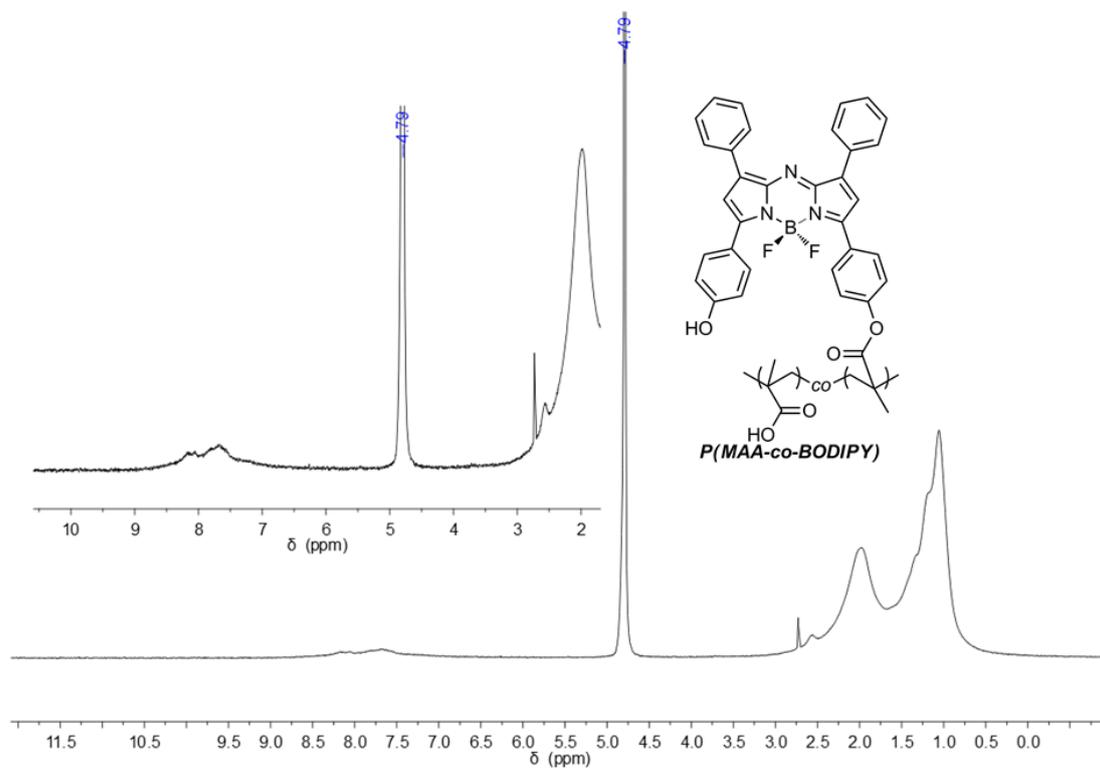


Figure S29. ^{13}C NMR spectrum of CPPTC in CDCl_3 .



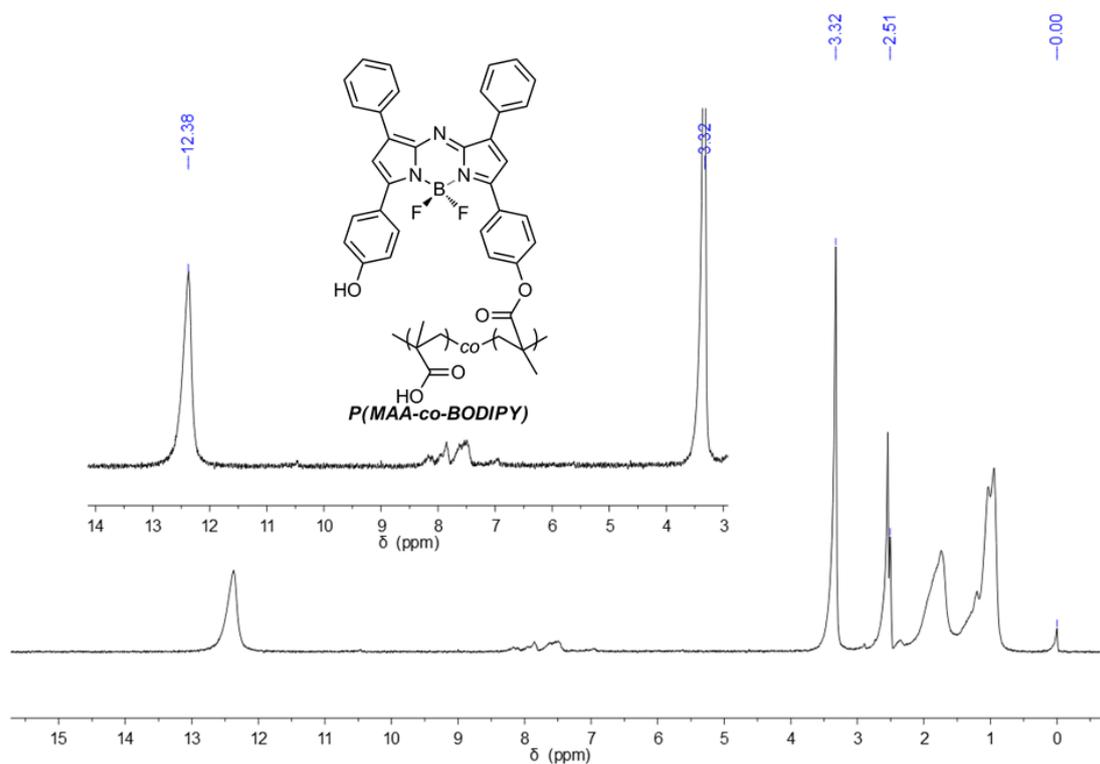


Figure S31. ¹H NMR spectrum of polymer P(MAA-co-BODIPY) in DMSO-d₆.

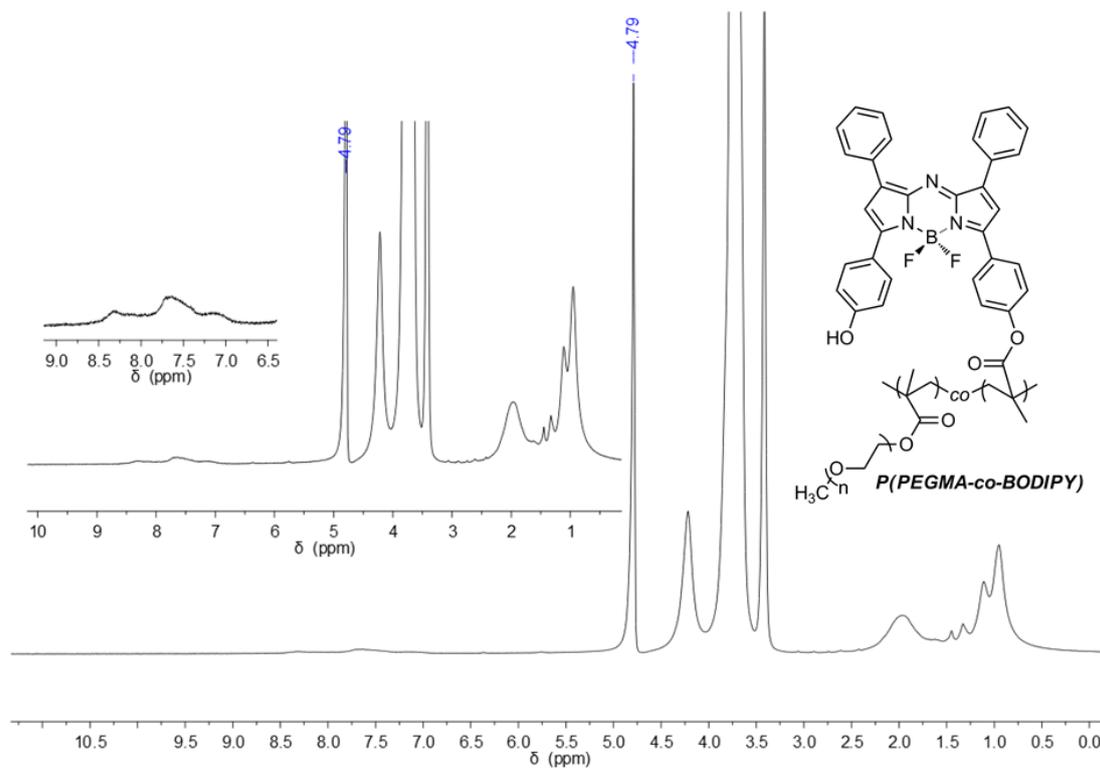


Figure S32. ¹H NMR spectrum of polymer P(PEGMA-co-BODIPY) in D₂O.

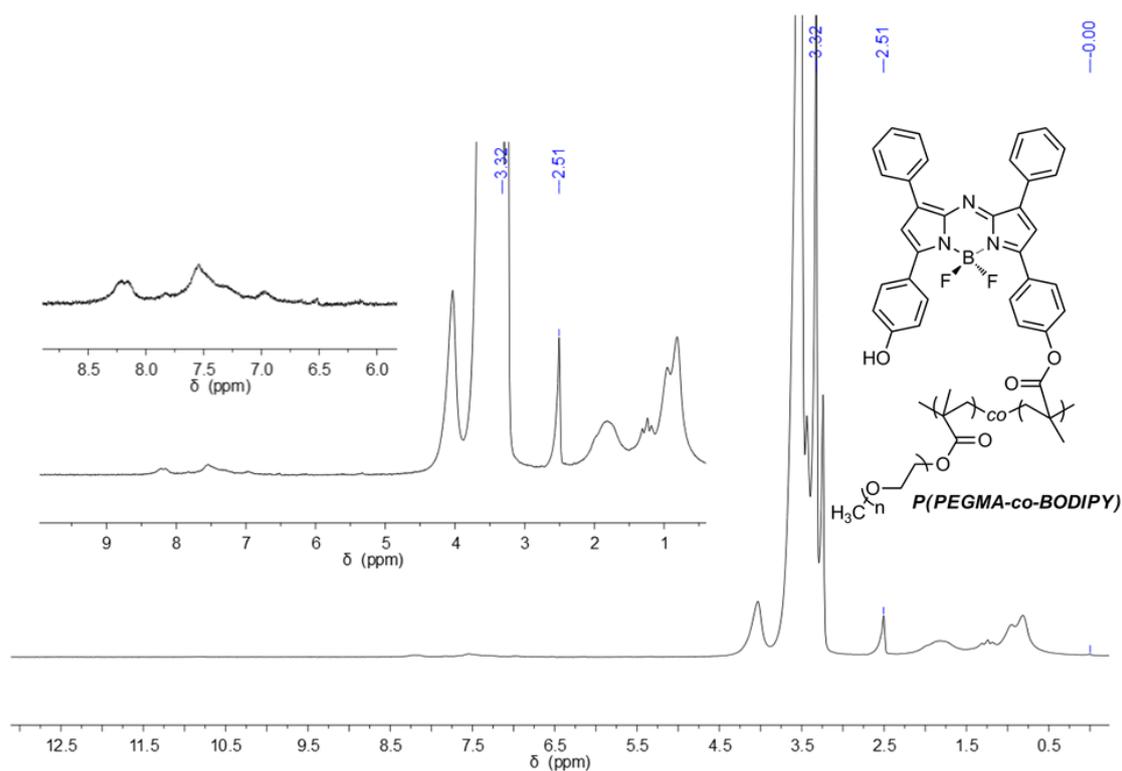


Figure S33. ^1H NMR spectrum of polymer $\text{P}(\text{PEGMA-co-BODIPY})$ in $\text{DMSO-}d_6$.

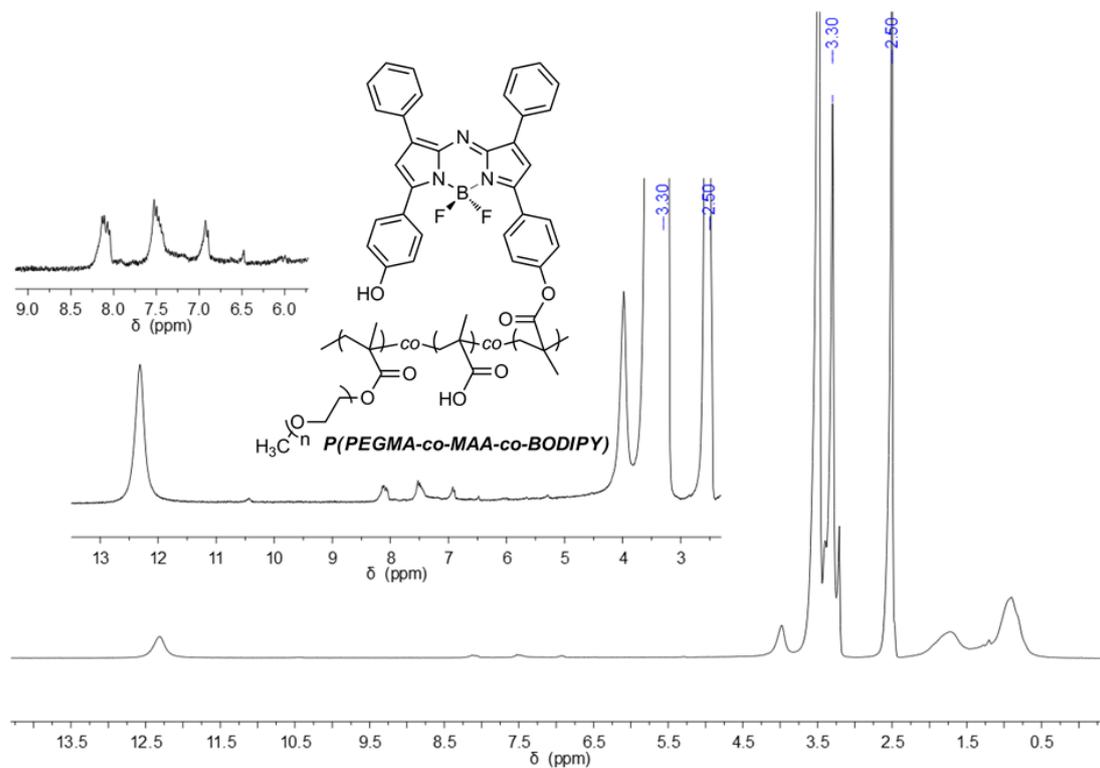


Figure S34. ^1H NMR spectrum of $\text{P}(\text{PEGMA-co-MAA-co-BODIPY})$ in $\text{DMSO-}d_6$.

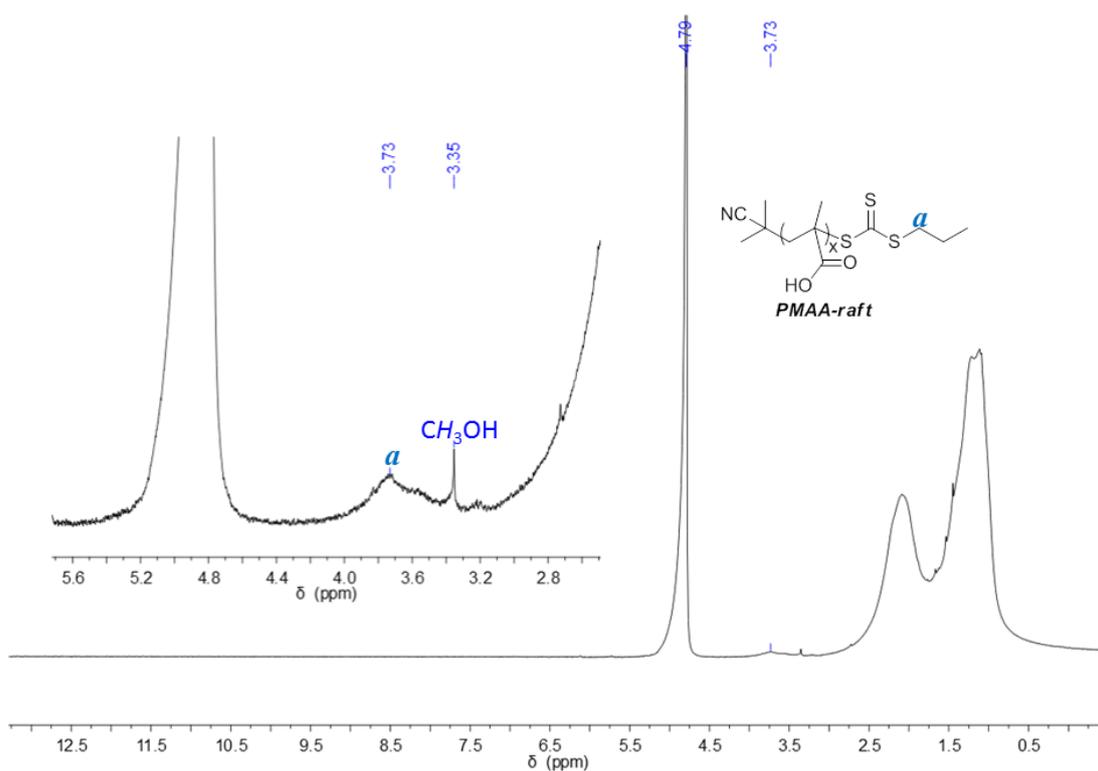


Figure S35. ^1H NMR spectrum of polymer **PMAA-raft** in D_2O .

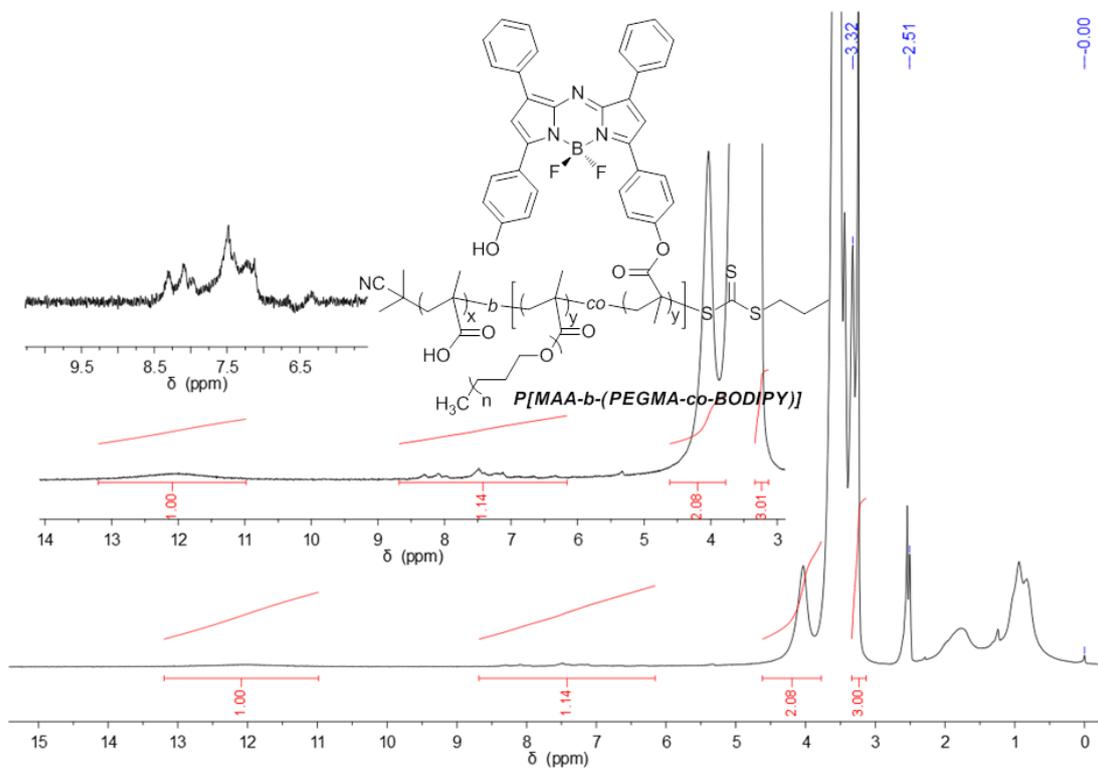


Figure S36. ^1H NMR spectrum of PMAA-*b*-P(PEGMA-*co*-BODIPY) in $\text{DMSO-}d_6$.

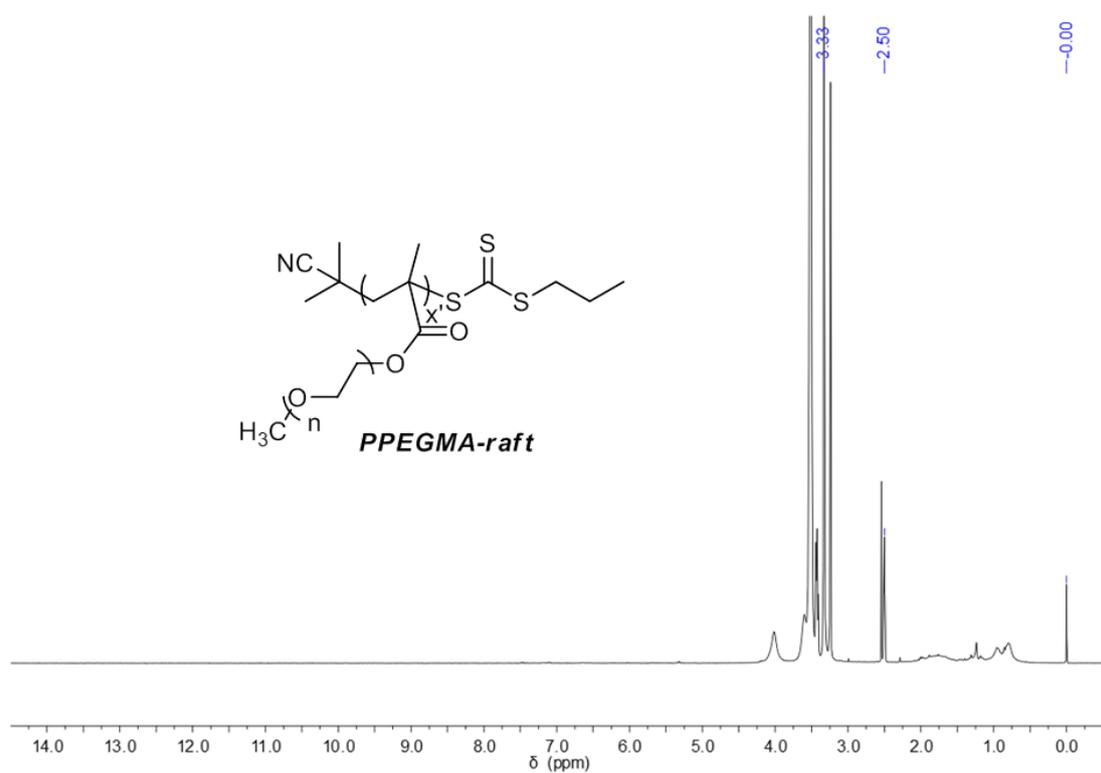


Figure S37. ^1H NMR spectrum of polymer **PPEGMA-raft** in $\text{DMSO}-d_6$.

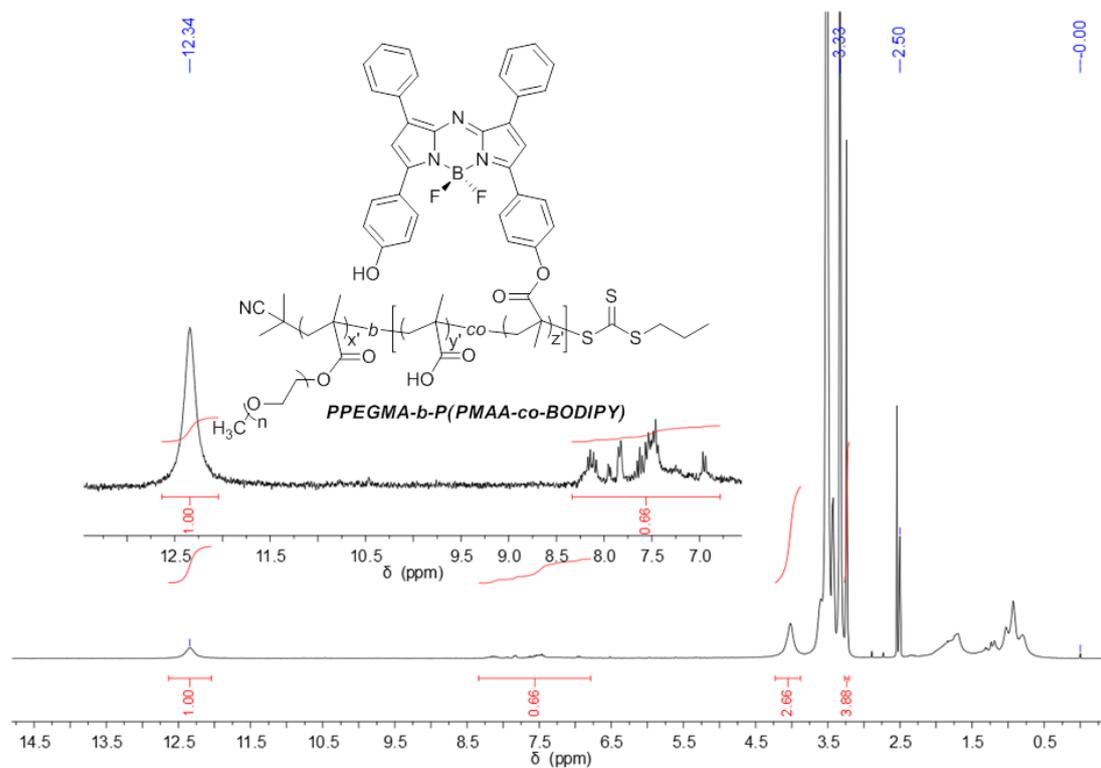


Figure S38. ^1H NMR spectrum of **PPEGMA-*b*-P(MAA-*co*-BODIPY)** in $\text{DMSO}-d_6$.

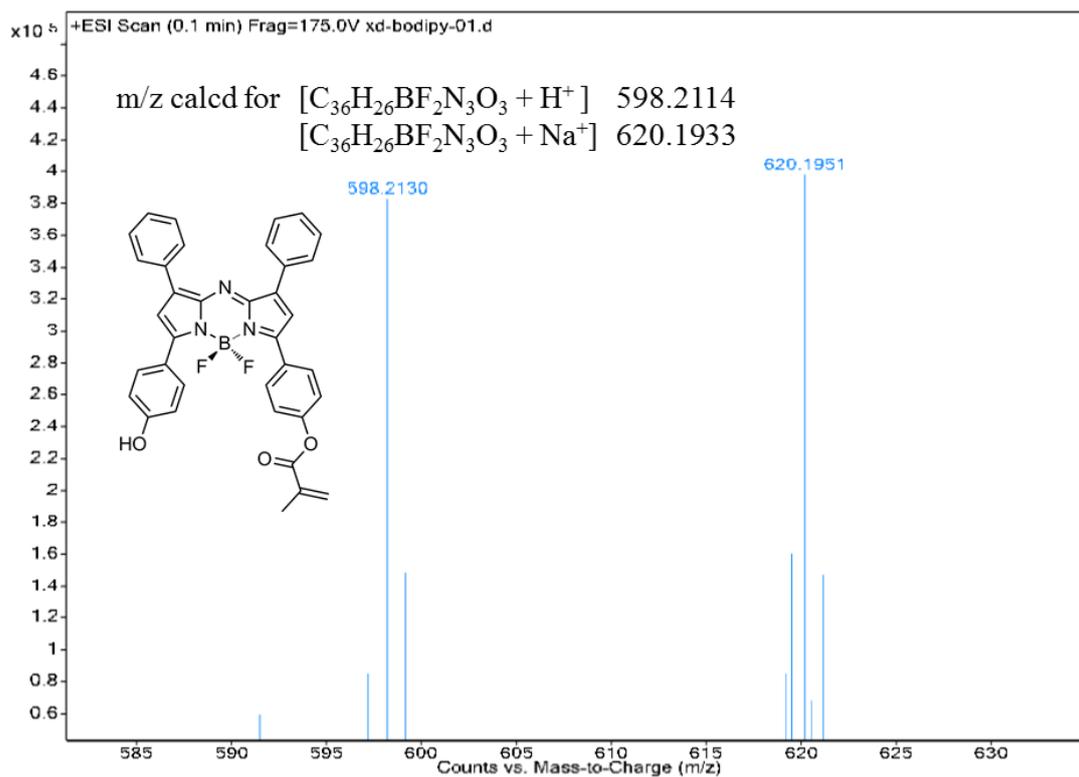


Figure S39. High resolution mass spectrum of **BODIPY-1**.

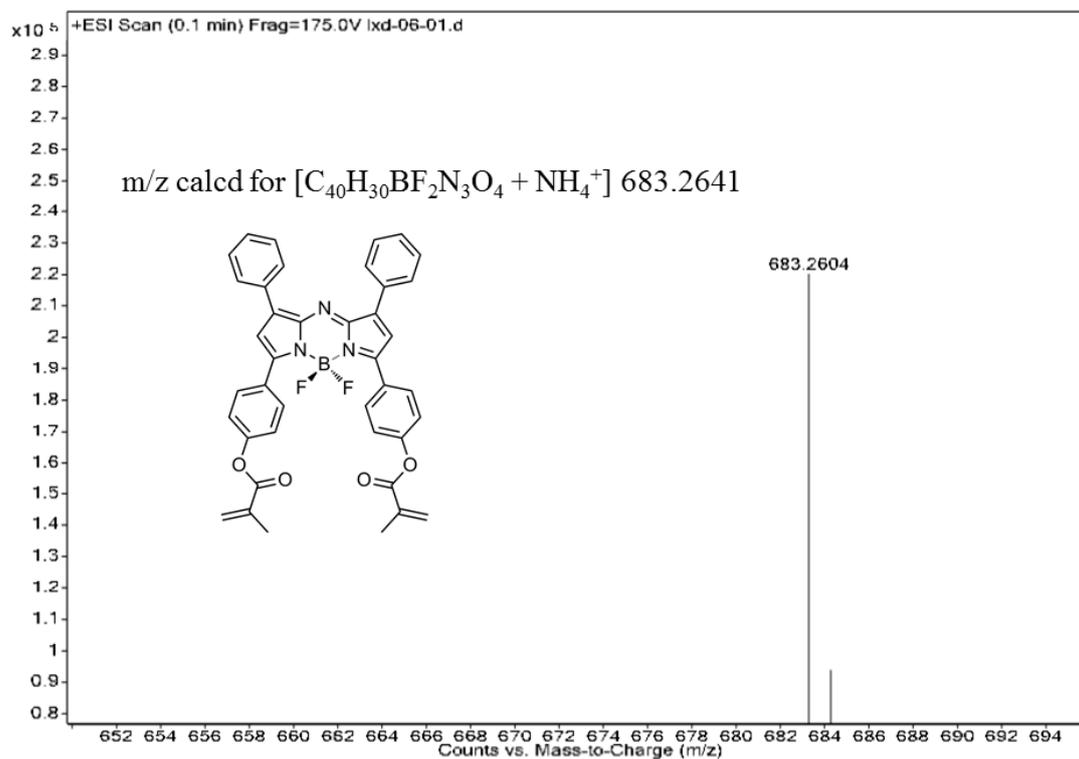


Figure S40. High resolution mass spectrum of **BODIPY-2**.

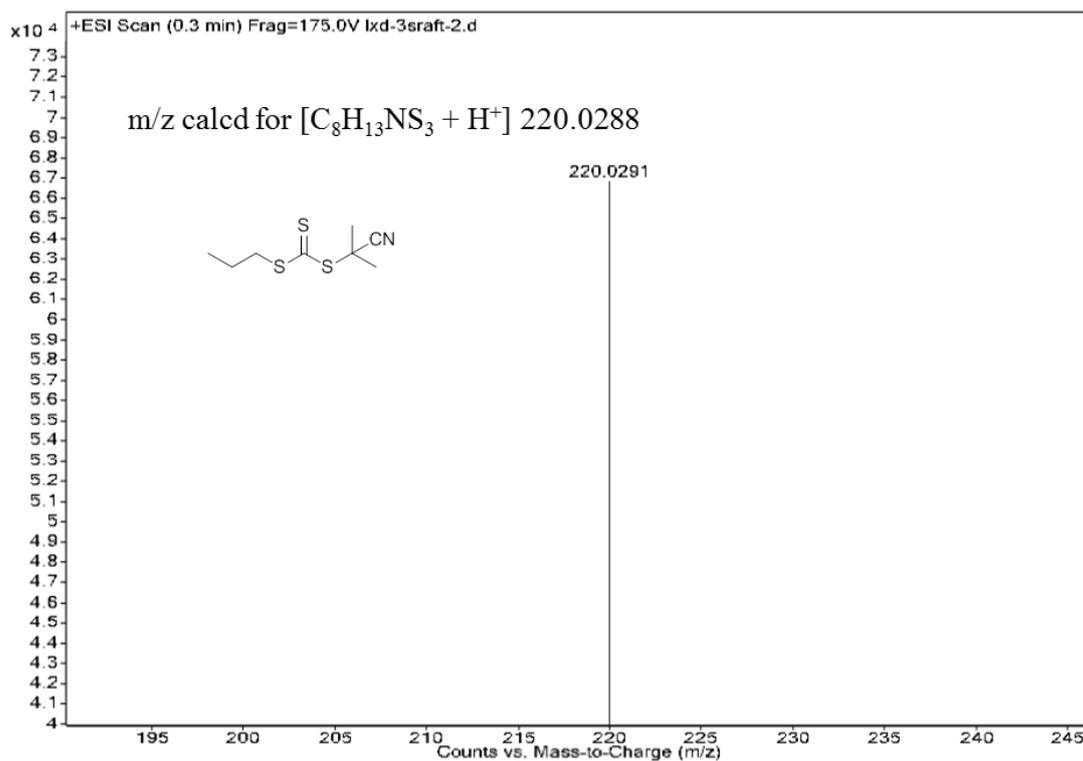


Figure S41. High resolution mass spectrum of CPPTC.

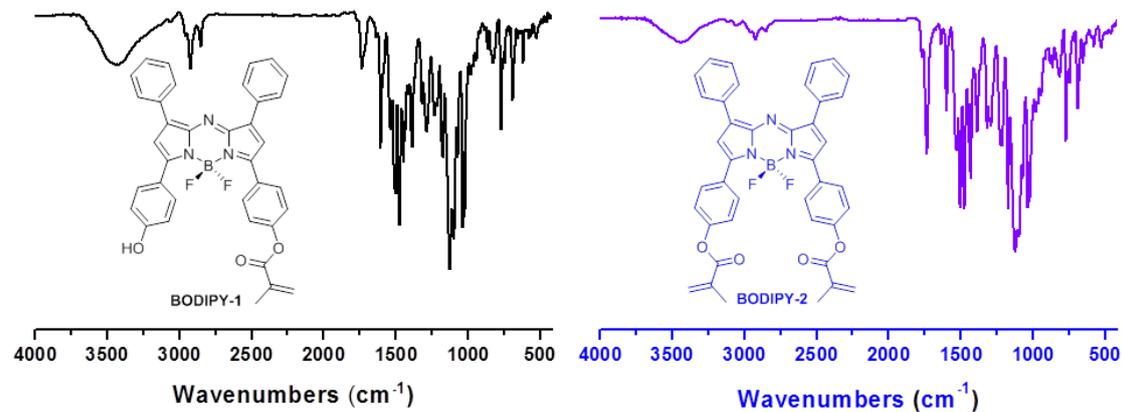


Figure S42. FT-IR spectra of BODIPY-1 and BODIPY-2.

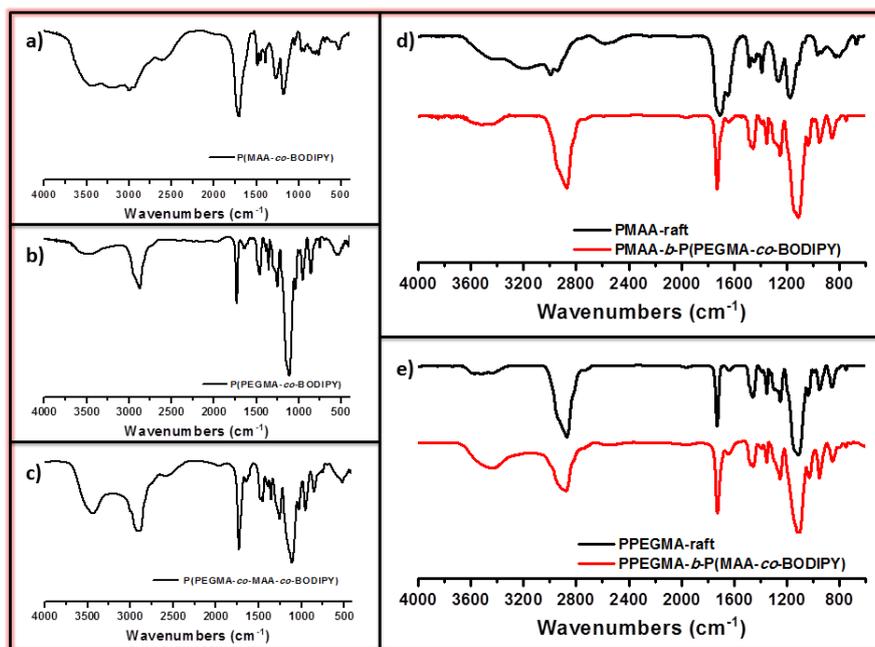


Figure S43. FT-IR spectra of (a) P(MAA-co-BODIPY), (b) P(PEGMA-co-BODIPY), (c) P(PEGMA-co-MAA-co-BODIPY), (d) PMAA-raft and PMAA-*b*-P(PEGMA-co-BODIPY), (e) PPEGMA-raft and PPEGMA-*b*-P(MAA-co-BODIPY).

Table S1 Concentrations of DOX-coordinated complexes ($[DOX]/[COOH] = 0.75$) and corresponding DOX concentrations in the medium.

RUN	P(MAA-co-PEGMA-co-BODIPY)		RUN	PMAA- <i>b</i> -P(PEGMA-co-BODIPY)	
	Sample polymer Concentration	DOX Concentration		Sample polymer Concentration	DOX Concentration
1	4.949 $\mu\text{g/mL}$	3 $\mu\text{g/mL}$	1'	7.770 $\mu\text{g/mL}$	3 $\mu\text{g/mL}$
2	9.897 $\mu\text{g/mL}$	6 $\mu\text{g/mL}$	2'	15.54 $\mu\text{g/mL}$	6 $\mu\text{g/mL}$
3	16.50 $\mu\text{g/mL}$	10 $\mu\text{g/mL}$	3'	25.90 $\mu\text{g/mL}$	10 $\mu\text{g/mL}$
4	24.74 $\mu\text{g/mL}$	15 $\mu\text{g/mL}$	4'	38.85 $\mu\text{g/mL}$	15 $\mu\text{g/mL}$
5	32.99 $\mu\text{g/mL}$	20 $\mu\text{g/mL}$	5'	51.80 $\mu\text{g/mL}$	20 $\mu\text{g/mL}$
6	39.59 $\mu\text{g/mL}$	24 $\mu\text{g/mL}$	6'	62.16 $\mu\text{g/mL}$	24 $\mu\text{g/mL}$
7	46.19 $\mu\text{g/mL}$	28 $\mu\text{g/mL}$	7'	72.52 $\mu\text{g/mL}$	28 $\mu\text{g/mL}$
8	52.78 $\mu\text{g/mL}$	32 $\mu\text{g/mL}$	8'	82.88 $\mu\text{g/mL}$	32 $\mu\text{g/mL}$
9	59.38 $\mu\text{g/mL}$	36 $\mu\text{g/mL}$	9'	93.24 $\mu\text{g/mL}$	36 $\mu\text{g/mL}$
10	65.98 $\mu\text{g/mL}$	40 $\mu\text{g/mL}$	10'	103.6 $\mu\text{g/mL}$	40 $\mu\text{g/mL}$