

Supporting Information

General Information

^1H NMR and ^{13}C NMR spectra were recorded on BRUKER 500 (500 MHz) spectrometers for CDCl_3 using tetramethylsilane (TMS) as an internal standard. Data for ^1H NMR spectra are reported as follows: chemical shift δ (ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), integration, coupling constant (Hz). ^{13}C NMR spectra were reported as chemical shifts in ppm and multiplicity where appropriate. FT-IR spectra were recorded on a JASCO FT-IR 469 plus spectrometer. Melting points were recorded on a Yanaco MP-500P micro melting point apparatus. High-resolution mass spectra (FAB+) were obtained using a JEOL JMS700 mass spectrometer.

UV-Vis spectra were recorded on a JASCO V-670 UV-Vis spectrophotometer. Fluorescence spectra were recorded on a JASCO FP-6500 spectrofluorometer. Quantum yields were measured by a Hamamatsu Photonics Quantaurus QY apparatus. Fluorescence lifetime was measured by a Hamamatsu Photonics Quantaurus τ apparatus.

Gel permeation chromatography (GPC) was performed with a JASCO UV-2070 detector and a JASCO RI-2031 detector (TOSOH TSK-gel GMH-HR column) using tetrahydrofuran (THF) as the eluent after the instrument was calibrated with standard polystyrenes.

The morphology of the substrate was examined with a scanning electron microscope (SEM) (VE-9800, Keyence Corp.).

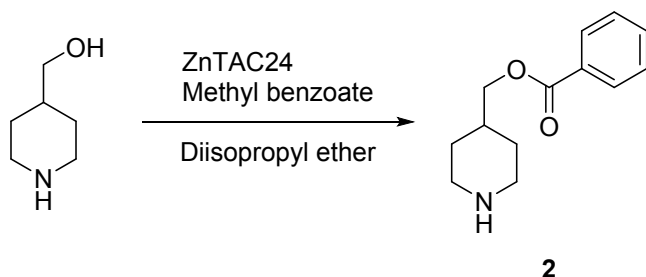
To elucidate the glass transition of polymers and mixtures, DSC measurements were conducted using a PerkinElmer DSC 8500. The samples were melted at 200°C and cooled to 50°C and subsequently heated to 200°C to measure the thermograms. The sample weight ranged from 8 to 10 mg and the scanning rate applied was $20^\circ\text{C min}^{-1}$.

Materials

Unless otherwise noted, all reagents and chemicals were used as received without further purification. 9,10-dibromoanthracene, sodium *tert*-butoxide, ZnTAC24[®], 4-piperidinemethanol, methyl benzoate, diisopropyl ether, triphosgene, 2,2-(4-hydroxyphenyl)propane, and 1,6-hexanediol were obtained from TCI (Tokyo, Japan). Poly(bisphenol A carbonate) and PEPSI[™]-IPr catalyst were purchased from Sigma-Aldrich Japan (Tokyo, Japan). Sodium hydroxide was purchased from Wako Pure Chemicals (Tokyo, Japan). Dry 1,4-dioxane, dry pyridine, dry dichloromethane and silica gel 60 N (spherical, neutral) (63-210 μm) were obtained from Kanto Chem (Tokyo, Japan). Magnesium sulfate and spectrograde THF were purchased from Nacalai Tesque (Kyoto, Japan).

Experiment Procedure

Piperidine-4-ylmethyl benzoate (**2**)



All apparatus underwent flame drying before use. Methyl benzoate (3.8 mL, 30 mmol) was added dropwise to a stirred solution of 4-piperidinemethanol (4.2 g, 37 mmol), ZnTAC24 (0.36 g, 0.38 mmol) in deaerated and dehydrated diisopropyl ether (100 mL) at 60°C. The reaction mixture was stirred at 90°C for 18 hours. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate and the organic layer was washed with water and brine. The organic layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using ethyl acetate and subsequently ethyl acetate: methanol = 5 : 1 (v/v) with 5% triethylamine as eluent to afford **piperidin-4-ylmethyl benzoate (2)** (4.1 g) as a yellow oil. Yield: 58 %; ¹H NMR (500 MHz, CDCl₃): δ 8.07-8.03 (m, 2H, ArH), 7.58-7.54 (m, 1H, ArH), 7.47-7.41 (m, 2H, ArH), 4.18 (d, 2H, OCH₂), 3.15-3.09 (m, 2H, NCH₂), 2.68-2.61 (m, 2H, NCH₂), 1.99-1.87 (m 1H CH(CH₃)₃), 1.82-1.75 (m, 2H, CH₂), 1.58 (br s, 1H, NH), 1.35-1.24 (m, 2H, CH₂) ppm (**Figure S1**).

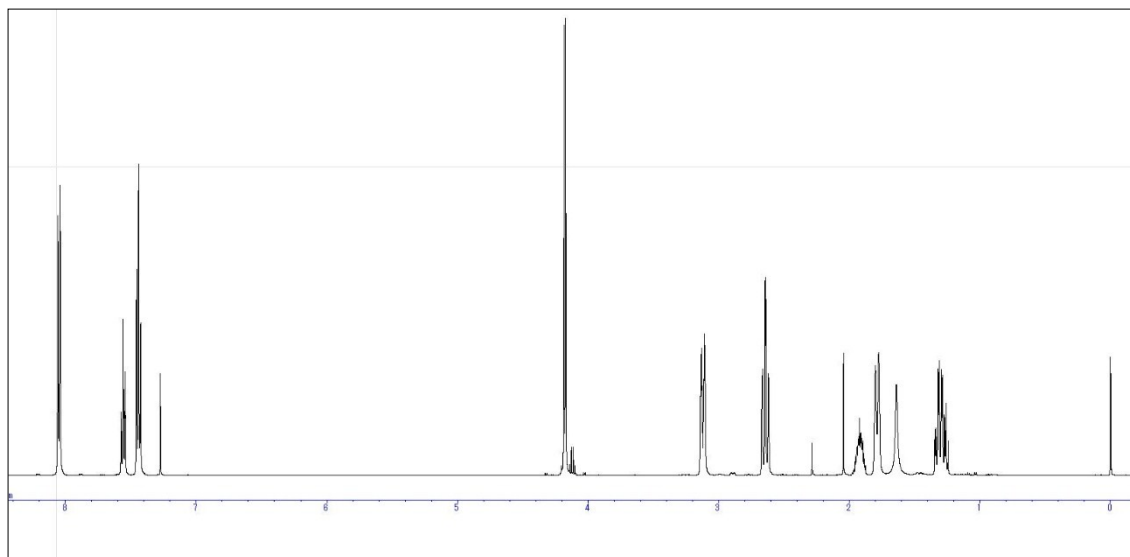
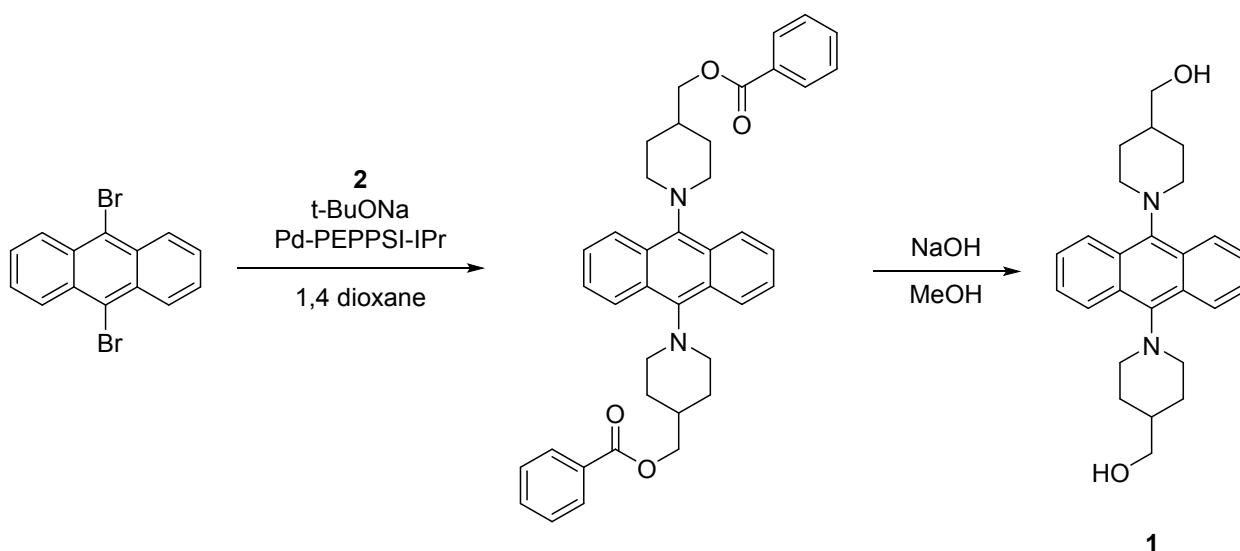


Figure S1. ¹H-NMR spectrum of **piperidin-4-ylmethyl benzoate** (500 MHz, CDCl₃).

9,10-bis(4-(hydroxymethyl)piperidyl)anthracene (9,10-BHMPA) (1)



All apparatus underwent flame drying before use. Piperidin-4-yl methyl benzoate (1.7 g, 7.4 mmol) was added to a solution of 9,10 dibromoanthracene (1.0 g, 2.9 mmol), sodium *tert*-butoxide (0.71 g, 7.4 mmol), $\text{Pd-PEPPSI}^{\text{TM}}\text{-IPr}$ catalyst (0.12 g, 0.18 mmol), in dry 1,4-dioxane (50 mL) at room temperature. The reaction mixture was then stirred at 100°C for 2 days. After cooling to room temperature, sodium hydroxide (1.0 g, 25 mmol) in methanol (20 mL) was added to the mixture. The reaction mixture was stirred for another 1 hour at room temperature. The reaction mixture was then extracted with dichloromethane and the organic layer was washed with water and brine. The organic layer was dried over magnesium sulfate and solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using dichloromethane : ethyl acetate = 3 : 1 (v/v) as eluent to afford **9,10-bis(4-(hydroxymethyl)piperidyl)anthracene** (0.49 g) as a yellow solid. Yield: 41 %. $^1\text{H NMR}$ (500 MHz, CDCl_3) : δ 8.74-8.63 (m, 2H, ArH), 8.27-8.19 (m, 2H, ArH), 7.51-7.38 (m, 4H, ArH), 3.77-3.67 (m, 8H, NCH_2 and OCH_2), 3.31-3.25 (m, 4H, NCH_2), 1.95-1.82 (m, 6H, CH_2 and $\text{CH}(\text{CH}_2)_3$), 1.73-1.63 (m, 4H, CH_2), 1.42 (t, 2H, OH) ($^3J = 12.5$ Hz) ppm (**Figure S2**). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) : δ 143.3 (*Ar*), 131.5 (*Ar*), 131.5 (*Ar*), 131.3 (*Ar*), 131.2 (*Ar*), 126.0 (*Ar*), 125.9 (*Ar*), 125.4 (*Ar*), 125.1 (*Ar*), 125.0 (*Ar*), 124.7 (*Ar*), 124.4 (*Ar*), 123.8 (*Ar*), 68.5 (OCH_2), 51.9 (NCH_2), 39.2 ($\text{CH}(\text{CH}_2)_3$), 30.5 (CH_2) ppm (**Figure S3**).; HRMS (FAB+) exact mass calculated for $[\text{M}]^+$ ($\text{C}_{26}\text{H}_{32}\text{N}_2\text{O}_2$) requires m/z 404.2464, found m/z 404.2468; FT-IR (KBr): 3250 (O-H stretch), 2934 (C-H stretch), 1398 (N-Ar stretch), 1248 (N-C stretch) cm^{-1} (**Figure S4**).

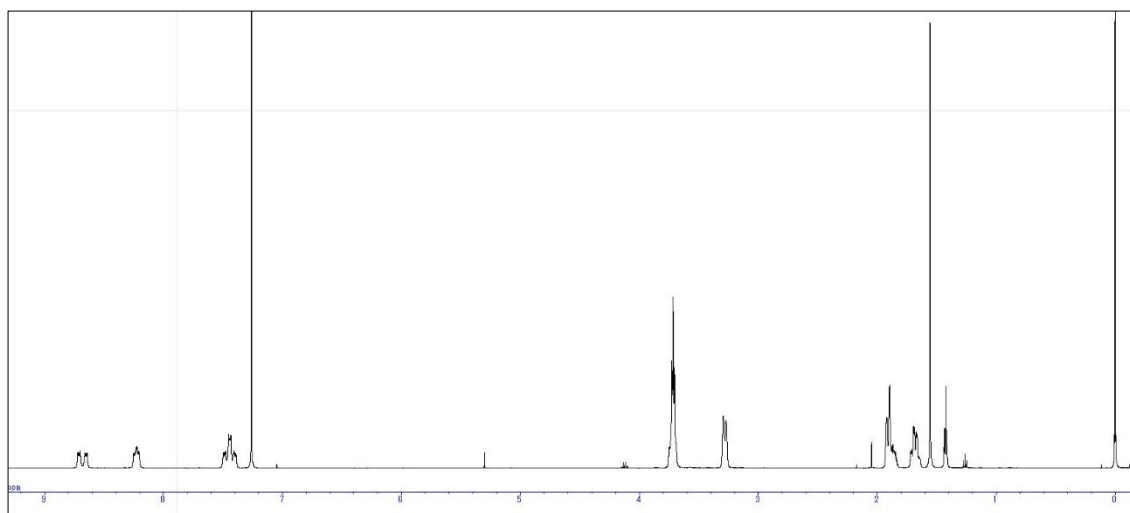


Figure S2. ¹H-NMR spectrum of **9,10-bis(4-(hydroxymethyl)piperidyl)anthracene (9,10-BHMPA)** (500 MHz, CDCl₃).

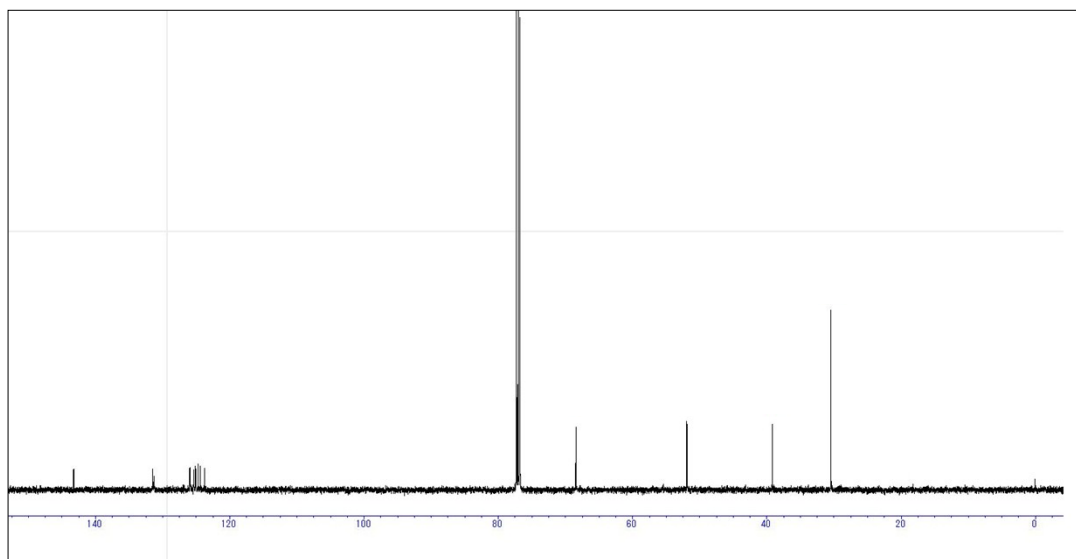


Figure S3. ¹³C-NMR spectrum of **9,10-bis(4-(hydroxymethyl)piperidyl)anthracene (9,10-BHMPA)** (125 MHz, CDCl₃).

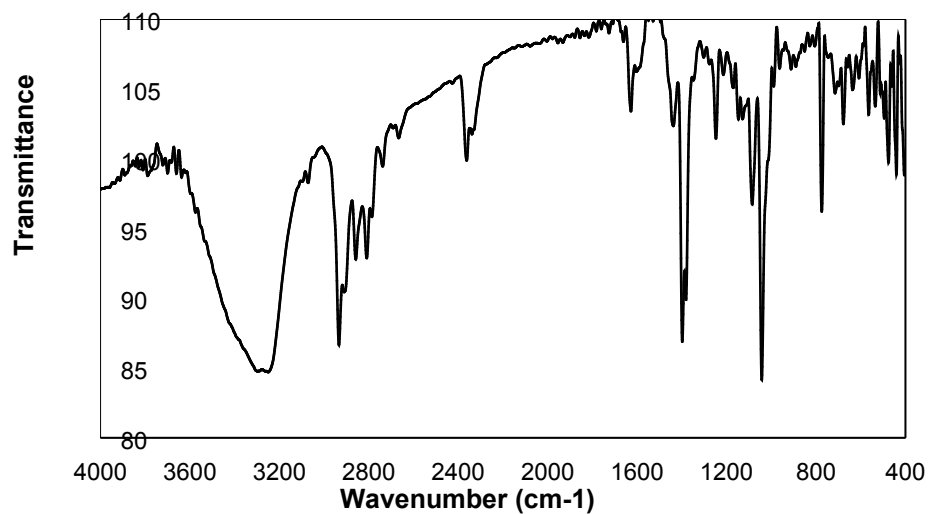
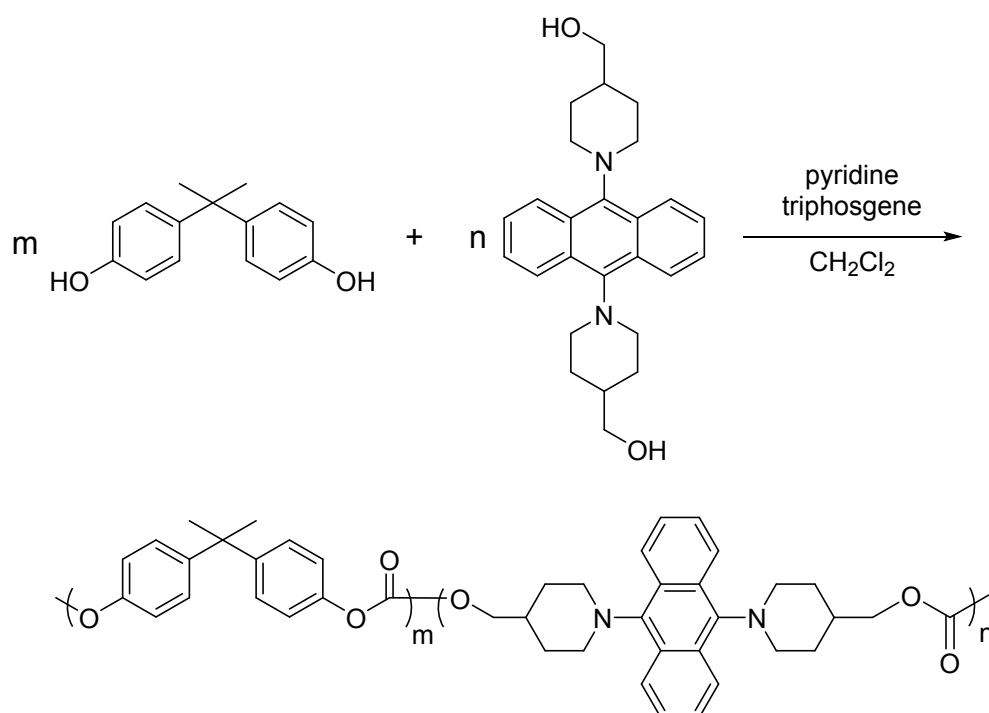


Figure S4. FT-IR spectra of **9,10-bis(4-(hydroxymethyl)piperidyl)anthracene (9,10-BHMPA)**.

PolyBP series (PolyBP5, PolyBP10, PolyBP20)



PolyBP5

Triphosgene (0.29 g, 0.99 mmol) in dichloromethane (2.5 mL) was added dropwise to a solution of 2,2-bis(hydroxyphenyl)propane (0.54 g, 2.3 mmol) and 9,10-bis(4-(hydroxymethyl)piperidyl)anthracene (0.050 g, 0.12 mmol) in pyridine (2.5 mL). The mixture was stirred at 0°C for 30 minutes, then at room temperature for another 30 minutes. The reaction mixture was then added dropwise into methanol, and the precipitate was filtered. The obtained polymer was washed with methanol and dried to afford **PolyBP5** (0.60 g) as a yellow solid. Yield: 92 %. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.28-7.22 (m, 4H, ArH), 7.19-7.12 (m, 4H, ArH), 1.68 (s, 6H, CH_3) ppm (bisphenol A), δ 8.73-8.62 (m, 2H, ArH), 8.25-8.19 m, 2H, ArH), 7.53-7.38 (m, 4H, ArH), 4.31 (d, 2H, OCH_2), 4.26 (d, 2H, OCH_2), 3.78-3.70 (m 4H NCH_2), 3.33-3.26 (m, 4H, NCH_2), 2.20-2.08 (m, 4H, CH), 1.99-1.93 (m 4H CH_2), 1.80-1.64 (m 4H CH_2) ppm (9,10-BHMPA) (**Figure S5**); FT-IR (KBr): 2968 (C-H stretch), 1775 (C=O stretch), 1227 (C-O stretch), 1193 (C-O stretch) cm^{-1} (**Figure S6**).

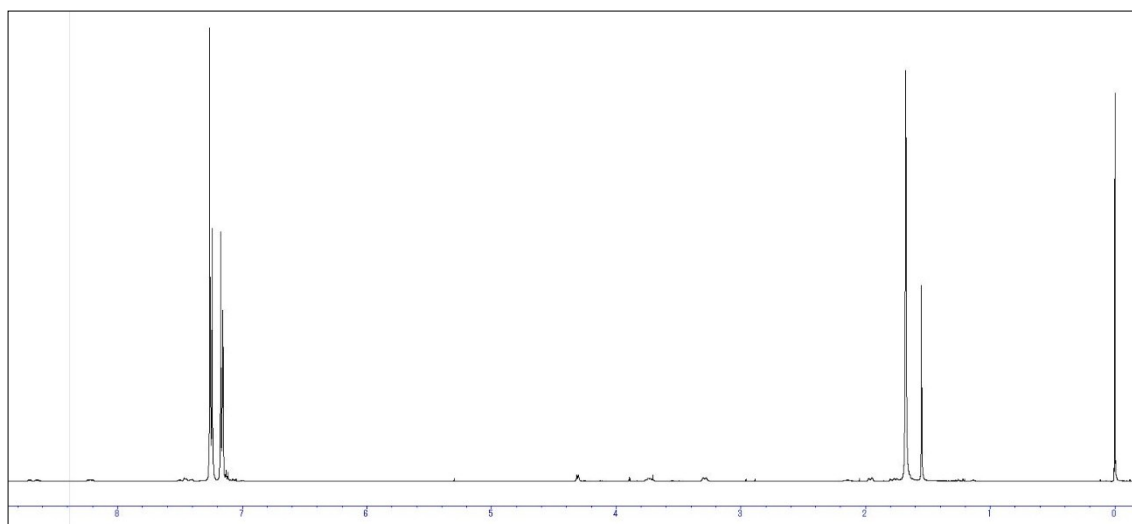


Figure S5. ^1H -NMR spectrum of **PolyBP5** (500 MHz, CDCl_3).

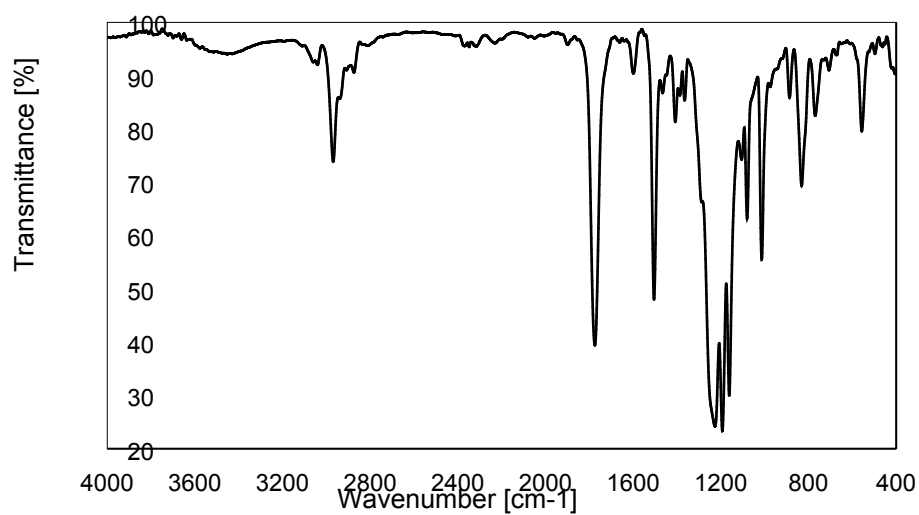


Figure S6. FT-IR spectrum of **PolyBP5**.

PolyBP10

Triphosgene (0.30 g, 1.0 mmol) in dichloromethane (2.5 mL) was added dropwise to a solution of 2,2-bis(hydroxyphenyl)propane (0.51 g, 2.3 mmol) and 9,10-bis(4-(hydroxymethyl)piperidyl)anthracene (0.10 g, 0.25 mmol) in pyridine (2.5 mL). The mixture was stirred at 0°C for 30 minutes, then at room temperature for another 30 minutes. After completion of the polymerization reaction, dichloromethane was added to dissolve the precipitate formed. The reaction mixture was then added dropwise into methanol, and the precipitate was filtered. The obtained polymer was washed with methanol and dried to afford **PolyBP10** (0.49 g) as a yellow solid. Yield: 72 %. ¹H NMR (500 MHz, CDCl₃): δ 7.28-7.22 (m, 4H, ArH), 7.19-7.12 (m, 4H, ArH), 1.68 (s, 6H, CH₃) ppm (bisphenol A), δ 8.73-8.62 (m, 2H, ArH), 8.26-8.18 (m, 2H, ArH), 7.53-7.38 (m, 4H, ArH), 4.31 (d, 2H, OCH₂), 4.26 (d, 2H, OCH₂), 3.78-3.69 (m 4H NCH₂), 3.33-3.25 (m, 4H, NCH₂), 2.20-2.09 (m, 4H, CH₂), 1.99-1.92 (m 4H CH₂) 1.82-1.70 (m 4H CH₂) ppm (9,10-BHMPA)(Figure S7).

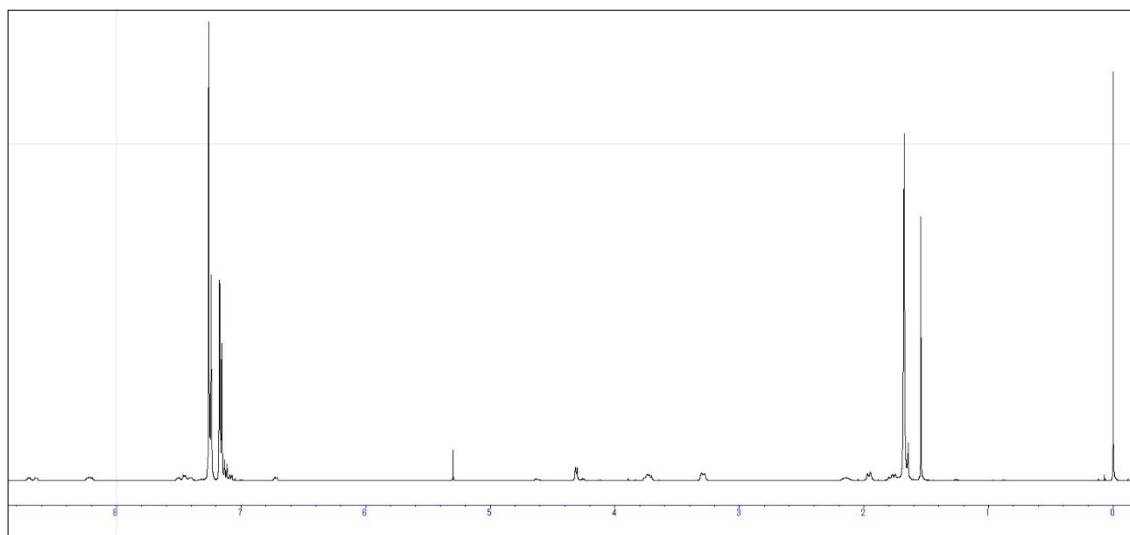


Figure S7. ¹H-NMR spectrum of **PolyBP10** (500 MHz, CDCl₃).

PolyBP20

Triphosgene (0.29 g, 0.99 mmol) in dichloromethane (0.62 mL) was added dropwise to a solution of 2,2-bis(hydroxyphenyl)propane (0.050 g, 0.12 mmol) and 9,10-bis(4-(hydroxymethyl)piperidyl)anthracene (0.11 g, 0.49 mmol) in pyridine (0.62 mL). The mixture was stirred at 0°C for 30 minutes, then at room temperature for another 30 minutes. After completion of the polymerization reaction, dichloromethane was added to dissolve the precipitate formed. The reaction mixture was then added dropwise into methanol, and the precipitate was filtered. The obtained polymer was washed with methanol and dried to afford **PolyBP20** (0.0852 g) as a yellow solid. Yield: 48%. ^1H NMR (500 MHz, CDCl_3) : δ 7.28-7.22 (m, 4H, ArH), 7.19-7.12 (m, 4H, ArH), 1.68 (s, 6H, CH_3) ppm (bisphenol A), δ 8.73-8.62 (m, 2H, ArH), 8.25-8.19 m, 2H, ArH), 7.53-7.38 (m, 4H, ArH), 4.31 (d, 2H, OCH_2), 4.26 (d, 2H, OCH_2), 4.26 (d, 2H, OCH_2), 3.78-3.70 (m, 4H NCH_2), 3.33-3.26 (m, 4H, NCH_2), 2.20-2.08 (m, 4H, CH), 1.99-1.93 (m 4H CH_2), 1.80-1.64 (m 4H CH_2) ppm (9,10-BHMPA) (**Figure S8**).

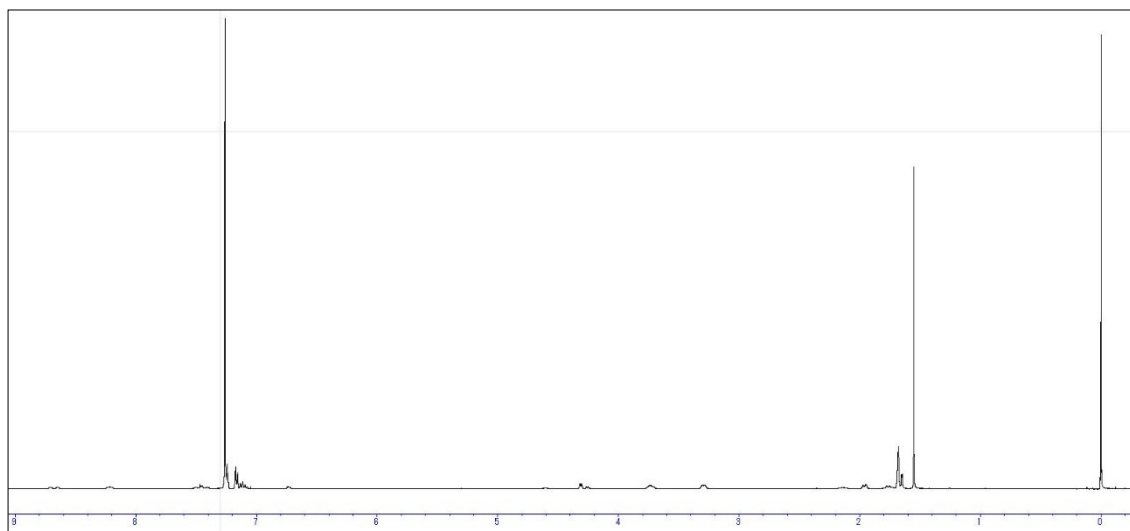
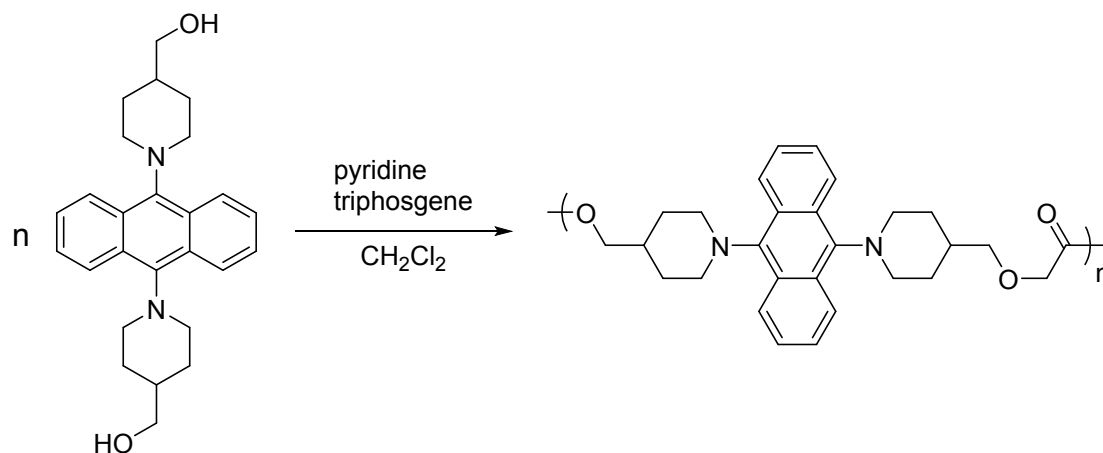


Figure S8. ^1H -NMR spectrum of **PolyBP20** (500 MHz, CDCl_3).

PolyBHMPA



Triphosgene (0.045 g, 0.15 mmol) in dichloromethane (0.15 mL) was added dropwise to a solution of 9,10-bis(4-(hydroxymethyl)piperidyl)anthracene (0.060 g, 0.15 mmol) in pyridine (0.15 mL). The mixture was reacted at 0°C for 30 minutes, then at room temperature for another 30 minutes. After completion of the polymerization reaction, dichloromethane was added to dissolve the precipitate formed. The reaction mixture was then added dropwise into methanol, and the precipitate was filtered. The obtained polymer was washed with methanol and dried to afford **PolyBHMPA** (0.019 g) as a yellow solid. Yield :30 %; ^1H NMR (500 MHz, CDCl_3) : δ 8.73-8.63 (m, 2H, ArH), 8.26-8.18 (m, 2H, ArH), 7.53-7.38 (m, 4H, ArH), 4.26 (d, 2H, OCH_2), 3.77-3.68 (m 4H NCH_2), 3.32-3.25 (m, 4H, NCH_2), 2.16-2.07 (m, 4H, CH), 1.98-1.88 (m 4H CH_2), 1.79-1.64 (m 4H CH_2) ppm (**Figure S9**).

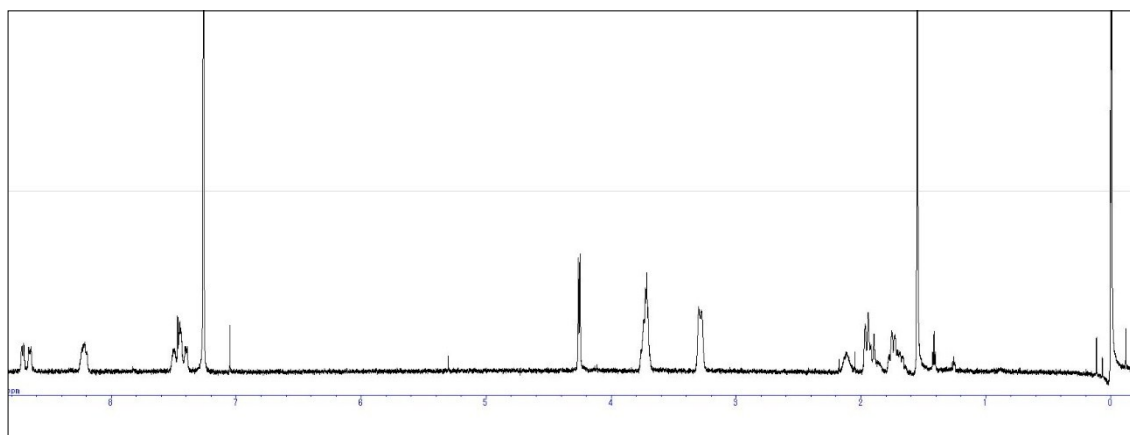
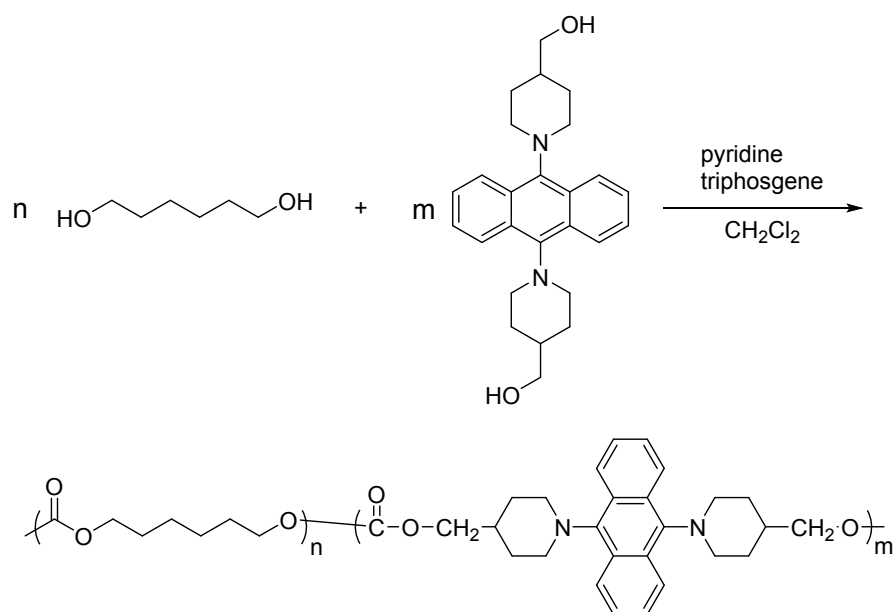


Figure S9. ^1H -NMR spectrum of **PolyBHMPA** (500 MHz, CDCl_3).

PolyHD10



Triphosgene (0.30 g, 1.0 mmol) in dichloromethane (2.5 mL) was added dropwise to a solution of 1,6-hexanediol (0.27 g, 2.3 mmol) and 9,10-bis(4-(hydroxymethyl)piperidyl)anthracene (0.10 g, 0.25 mmol) in pyridine (2.5 mL). The mixture was reacted at 0°C for 30 minutes, then at room temperature for another 30 minutes. The obtained polymer was extracted with dichloromethane and the organic layer was washed with water and brine. The organic layer was dried over magnesium sulfate and solvent was removed *in vacuo* to afford **PolyHD10** as a yellow solid. Yield : 72 % ; $^1\text{H-NMR}$ (500 MHz, CDCl_3) : δ 8.73-8.61 (m, 2H, ArH), 8.24-8.16 (m, 2H, ArH), 7.52-7.38 (m, 4H, ArH), 4.21-4.16 (m, 2H, OCH_2), 3.76-3.67 (m, 4H NCH_2), 3.32-3.24 (m, 4H, NCH_2), 2.12-2.00 (m, 4H, CH), 1.95-1.88 (m, 4H CH_2)ppm. (**Figure S10**)

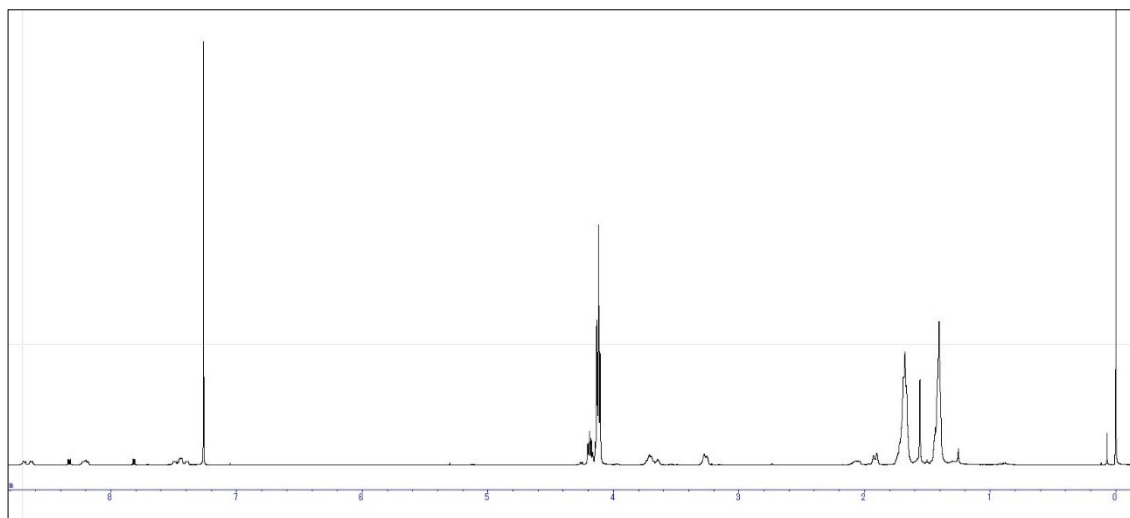


Figure S10. $^1\text{H-NMR}$ spectrum of **PolyHD10** (500 MHz, CDCl_3).

Spectral Data

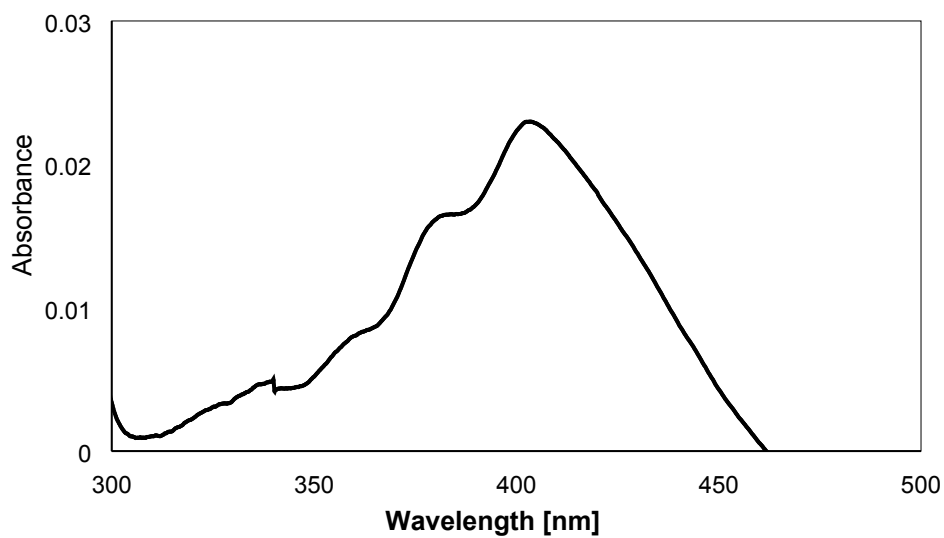


Figure S11. Absorbance spectrum of 9,10-BHMPA and Ba-PC dispersion (ratio of 9,10-BHMPA to Ba-PC = 0.05:99.5 (w/w)).

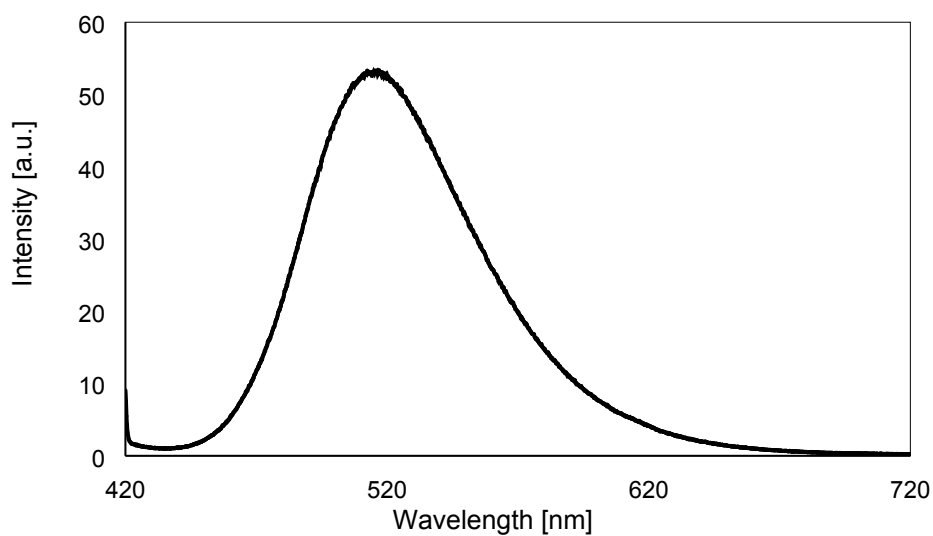


Figure S12. Fluorescence spectrum of 9,10-BHMPA and Ba-PC dispersion (ratio of 9,10-BHMPA to Ba-PC = 0.05:99.5 (w/w)).

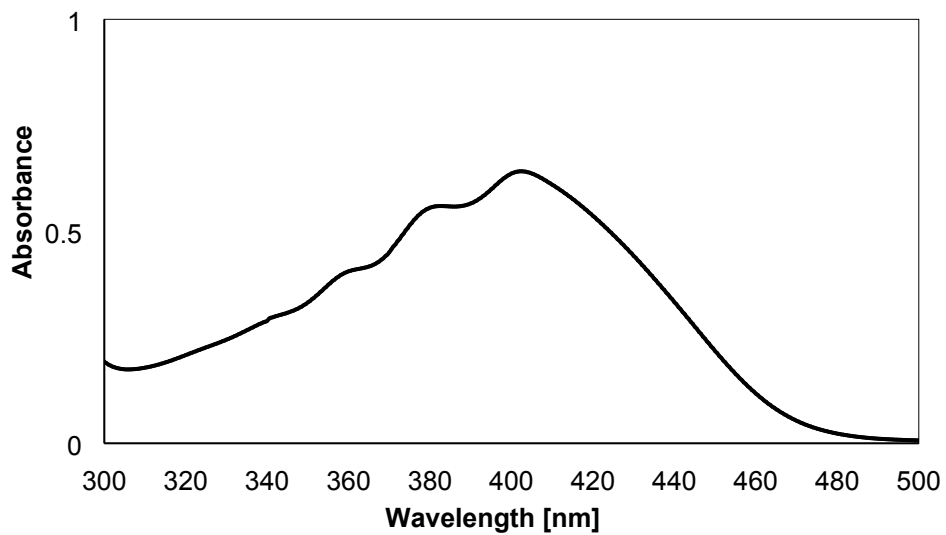


Figure S13. Absorbance spectrum of PolyBP5 film.

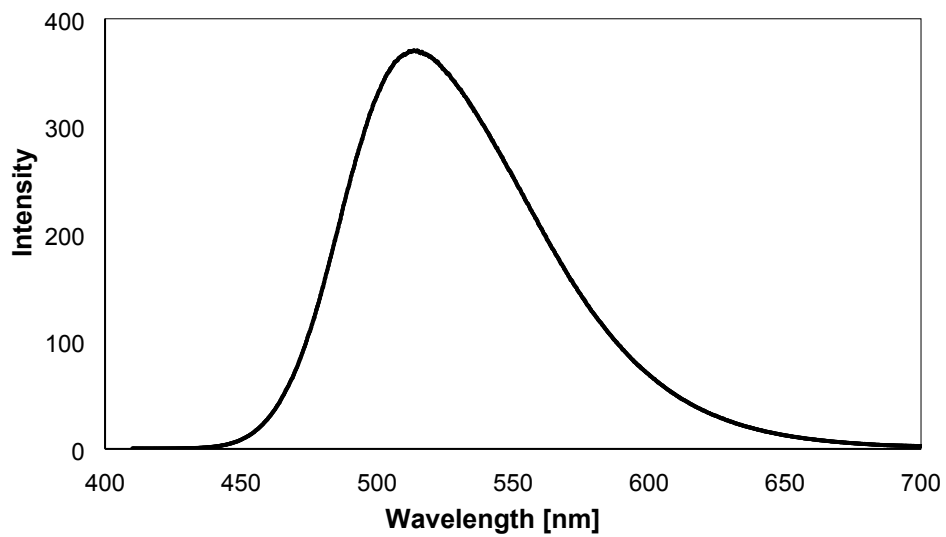


Figure S14. Fluorescence spectrum of PolyBP5 film.

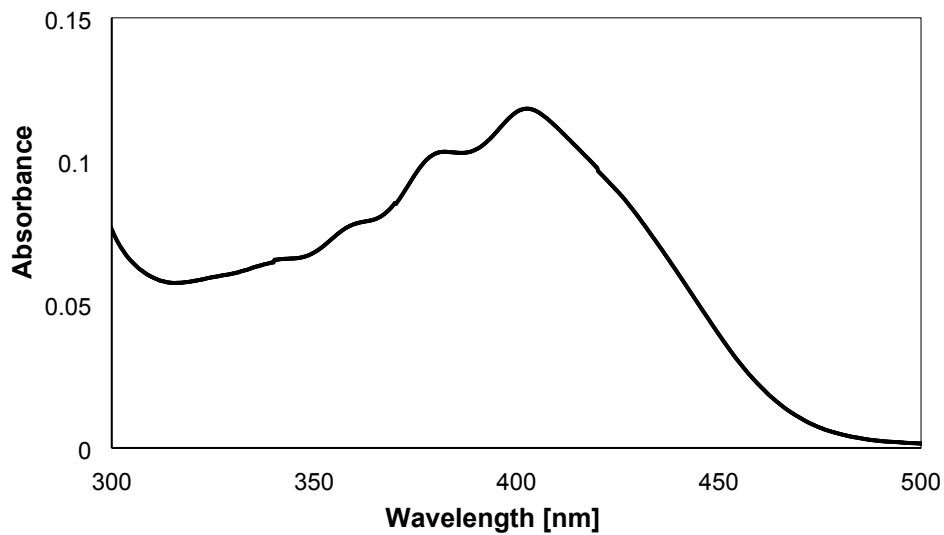


Figure S15. Absorbance spectrum of polycarbonate blend film of **PolyBP5** and Ba-PC (ratio: 1:1 (w/w)).

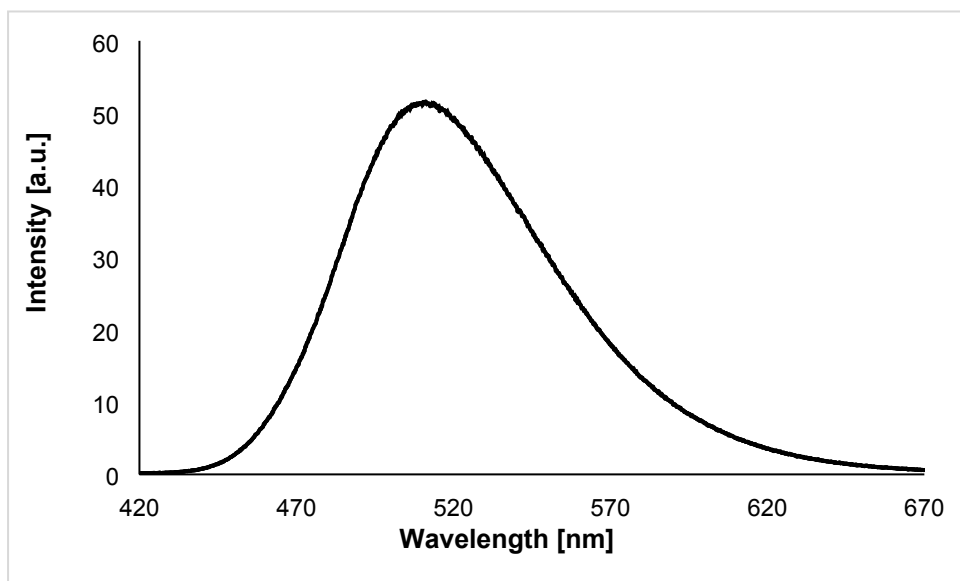


Figure S16. Fluorescence spectrum of polycarbonate blend film of **PolyBP5** and Ba-PC (ratio: 1:1 (w/w)).

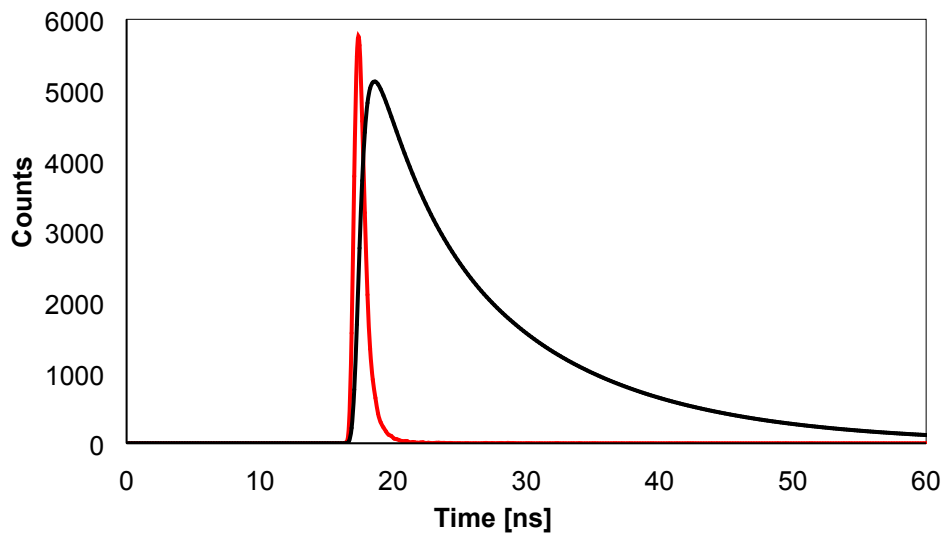
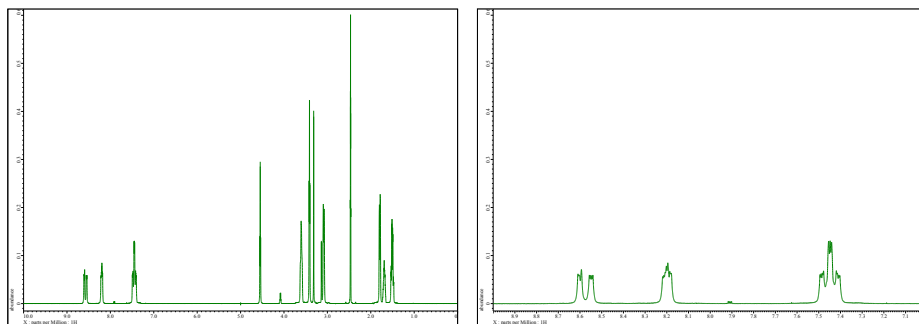


Figure S17. Fluorescence lifetime measurement of polycarbonate blend film **PolyBP5** and Ba-PC (ratio: 1:1 (w/w)).

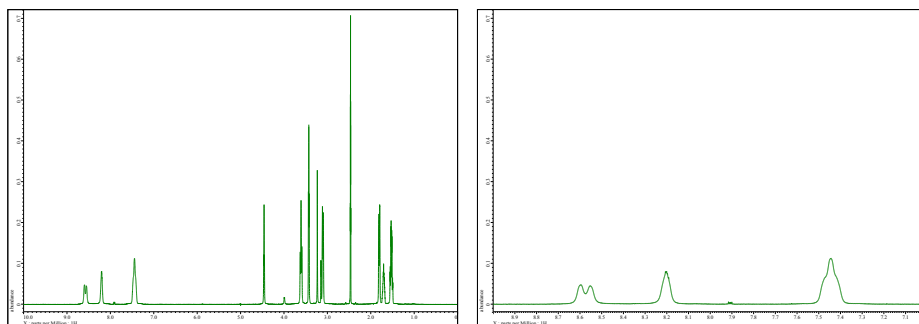
NMR data for 1 (Figure S18)

^1H NMR (600 MHz, $\text{DMSO-}d_6$) [JEOL JNM-LA600]

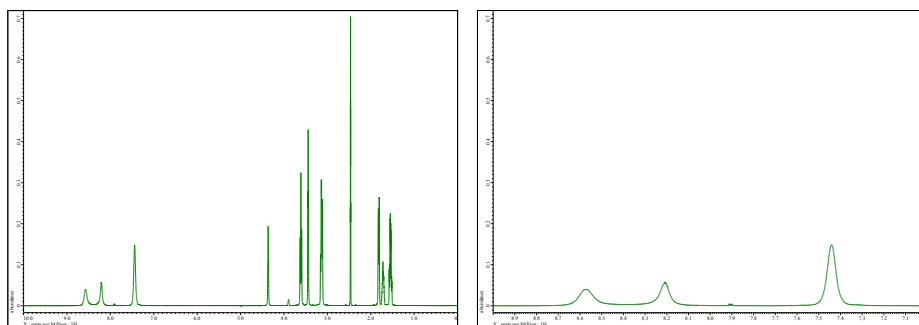
rt (20.5 °C)



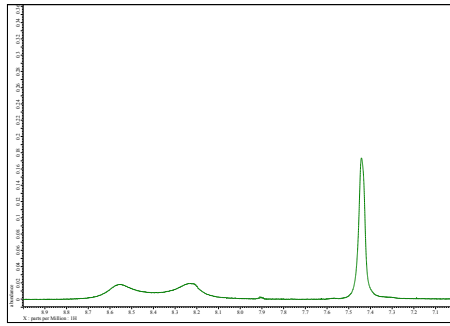
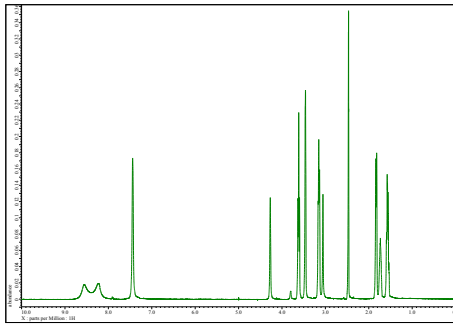
40 °C



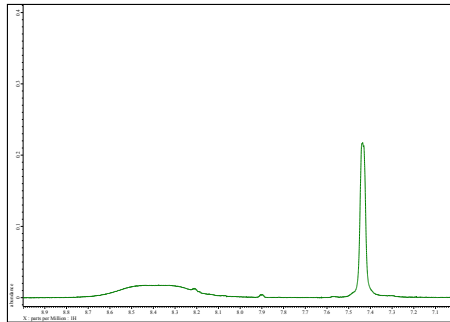
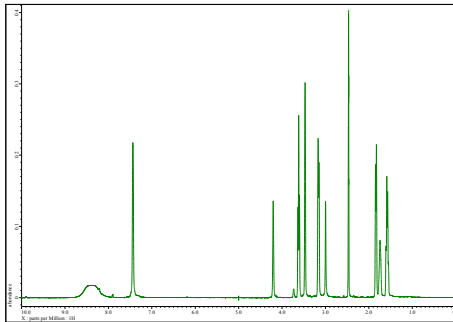
60 °C



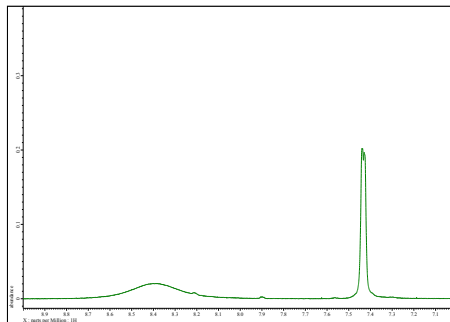
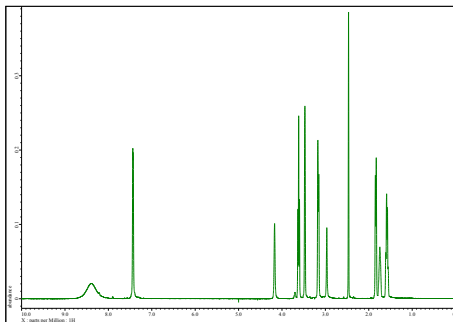
80 °C



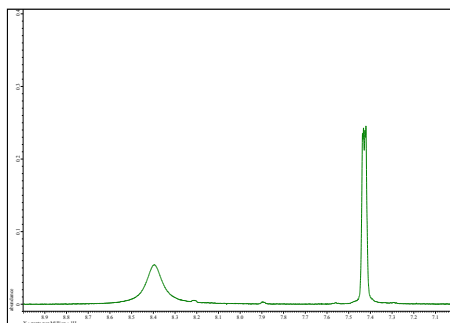
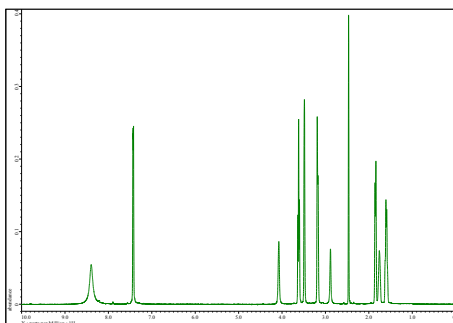
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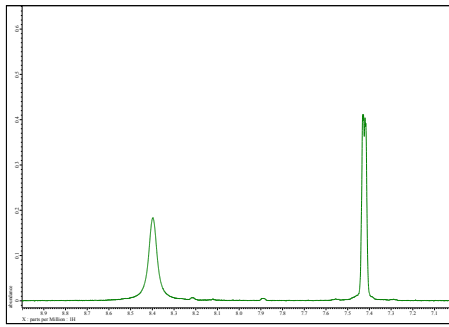
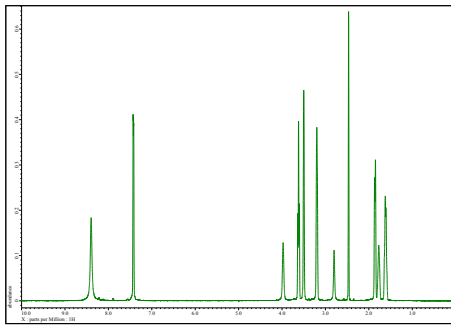
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120 °C

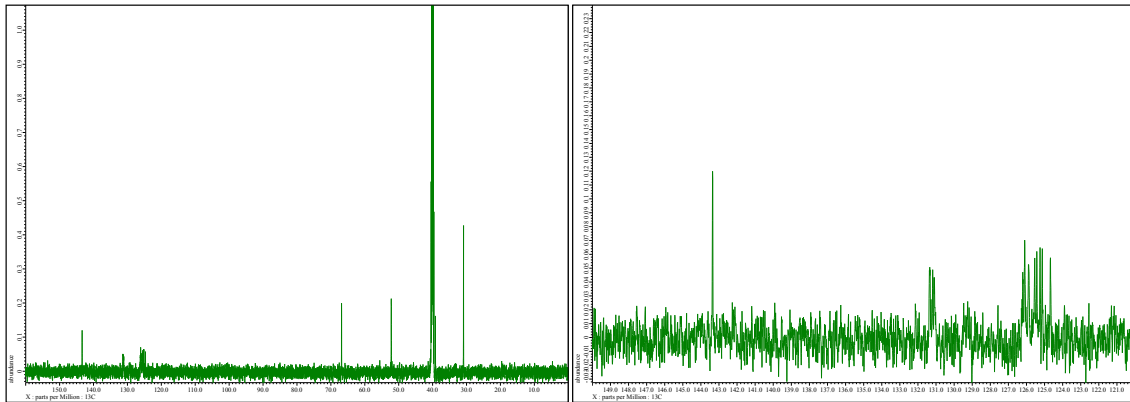


140 °C

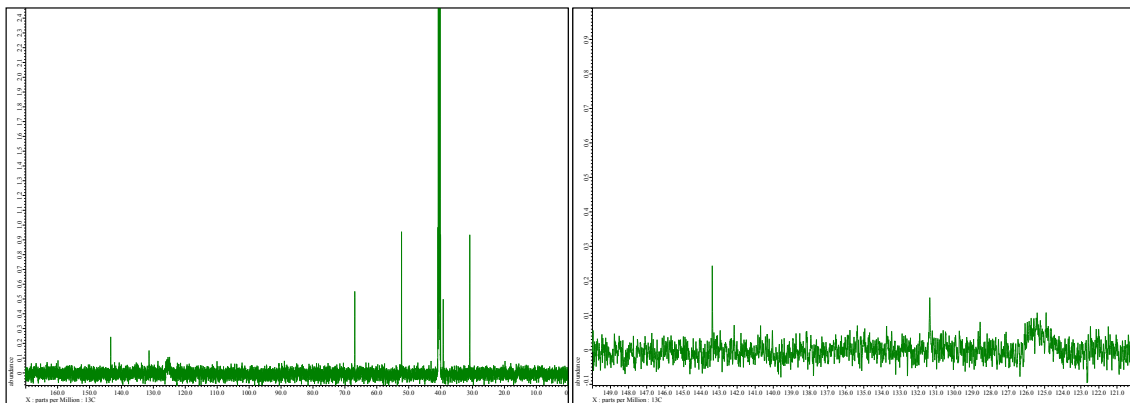


^{13}C NMR (125 MHz, $\text{DMSO-}d_6$) [JEOL JNM-LA600]

rt (20.5 °C)



80 °C



140 °C

