

## *Supporting Information*

### Bridging of poly(acetylene)s and PEG-modified poly(olefin)s through ring-opening metathesis copolymerization (ROMCP)

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## Experimental Section

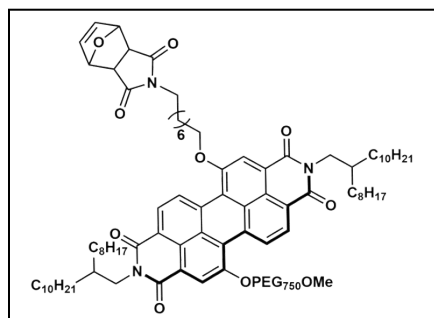
### General Remarks

All manipulations were performed in oven- or flame-dried glassware and teflon coated stir bars under an argon atmosphere using standard Schlenk techniques or in a glovebox unless specified otherwise. Solvents were dried according to the reported methods,<sup>1</sup> particularly deuterated solvent was distilled from appropriate drying agents and stored over molecular sieves (4Å) under argon. All starting materials were purchased from Sigma-Aldrich or Alfa Assar and were used without further purification. Synthesized products were purified using flash chromatography on silica gel (pore size 60Å, particle size 230-400 mesh) received from Sigma Aldrich. Celite (Supleco R566) was used for filtration. Reactions were controlled with TLC on Merck Silica Gel 60Å F-254 precoated plates (0.25 mm thickness), and components were visualized under ultraviolet light (254 and 365 nm).

NMR spectra were recorded on a Bruker Avance II 400 (<sup>1</sup>H: 400 MHz, <sup>13</sup>C: 100 MHz, <sup>19</sup>F: 376 MHz) and Bruker Avance II 600 (<sup>1</sup>H: 600 MHz, <sup>13</sup>C: 150 MHz) spectrometers using CDCl<sub>3</sub> as indicated solvent and are listed in parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard for <sup>1</sup>H and <sup>13</sup>C NMR. Number-average molecular weight ( $M_n$ ) and polydispersity index ( $\mathcal{D}$ ) values of the polymer samples were determined by size-exclusion chromatography (SEC). Analyses were performed on an Agilent Technologies 1200 series system composed of GPC equipped with a set of PL mixed B columns in series using chlorobenzene as an eluent at a flow rate of 1.0 mL min<sup>-1</sup> at 85 °C. The column system was calibrated with polystyrene standards. Prior to injection, samples were diluted to a concentration of 5 mg mL<sup>-1</sup> and filtered through 0.22 μm PTFE syringe filters. Thermal properties of the polymers were analyzed using PerkinElmer Jade DSC Differential Scanning Calorimeter at a heating rate of 5 °C/min.

UV-Vis spectra were recorded on a PerkinElmer Lambda 1050 UV-Vis spectrometer. The spectral baseline was corrected using Cary Win UV software. Fluorescence emission spectra were recorded on a SCINCO FS-2 spectrofluorometer. IR spectra were recorded on PerkinElmer Spectrum One FT-IR spectrometer using ATR technology and the mass spectra were recorded on Triple Quad LC/MS 6420 (Agilent Technologies) spectrometer. A Bruker Dimension Icon Atomic Force Microscopy (AFM) with Nanoscope V controller was used to collect height and phase images of the samples. The images were collected at 2×2 μm area using the tapping method and a Bruker Tespa V2 probe. The scan rate was 0.8 Hz, and the amplitude setpoint was 11.8 nm. Thermo Fisher Apreo S Field Emission Scanning Electron Microscope

was used for the SEM analysis and Kratos AXIS Ultra DLD X-ray Photoelectron Spectroscopy was used for XPS analysis.



**Synthesis of M2:** Monomer **M2** was synthesized following a modified procedure reported previously.<sup>2,3</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  9.75 (br. d,  $J = 8.5$  Hz, 1H), 9.64 (br. d,  $J = 8.5$  Hz, 1H), 8.58 (br. t,  $J = 7.0$  Hz, 2H), 8.49 (br. d,  $J = 7.0$  Hz, 2H), 6.50 (s, 2H), 5.26 (s, 2H), 4.63 (br, 2H), 4.48 (t,  $J = 6.6$  Hz, 2H), 4.15 (d,  $J = 7.1$  Hz), 4.10 (t,  $J = 4.6$  Hz, 2H), 3.86 (m, 2H), 3.79 (m, 2H), 3.63 (br. s, 65H),

3.51 (brs, 8H), 3.38 (s, 3H), 2.06 (m, 4H), 1.20 (brs, 72H), 0.83 (br, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  176.4, 171.0, 164.1, 164.09, 164.02, 163.9, 156.9, 156.4, 136.6, 134.1, 134.0, 133.8, 129.2, 128.6, 123.84, 123.60, 123.36, 123.30, 121.89, 121.44, 117.4, 81.0, 70.6, 59.1, 47.5, 44.8, 39.0, 37.9, 36.8, 32.0, 31.9, 30.2, 29.7, 29.4, 27.6, 26.7, 26.3, 22.8, 14.2.

**General Polymerization Procedure:** All polymerizations were carried out in a Glovebox under an argon atmosphere.

**(a) Homopolymerization:** A solution of trifluoroacetate modified Hoveyda-Grubbs type 2<sup>nd</sup> generation catalyst (1 mol%) in CHCl<sub>3</sub> (2 mL) was added to monomer **M2** (0.020 mmol) in the same solvent (5 mL) and the reaction solution was stirred at RT for 1-2 hours depends on the complete consumption of monomer to polymer. Then, ethyl vinyl ether (2 mL) was added to the reaction mixture and stirred for another 20 min. The solvent was removed in vacuum under reduced pressure, after that to the concentrated polymer solution, 10 mL of *n*-pentane was added dropwise to precipitate the polymer. The solvent was filtered off and polymer material was dried in vacuo yielding dark red solids.

**(b) Di- or Tri-Block Copolymerization:** A solution of trifluoroacetate modified Hoveyda-Grubbs type 2<sup>nd</sup> generation catalyst (2 mol%) in CHCl<sub>3</sub> (3 mL) was added to monomer **M1** (0.020 mmol) in the same solvent (3 mL) and the reaction solution was stirred at RT for 2 hours. After the complete consumption of monomer **M2**, analyzed by <sup>1</sup>H NMR experiment, PEG<sub>750</sub>-PDI-derived monomer **M2** (0.020 mmol) was added to the polymerization reaction solution and allowed to polymerize at RT for another 5 hours. After the complete consumption of **M2** analyzed <sup>1</sup>H NMR experiment, N-alkyl substituted oxa-norbornene imide

monomer **M3** (0.020 mmol) was added to the growing polymer solution of propagating polymer **P2** and the polymerization reaction mixture was stirred at RT for another 6 hours. After the complete consumption of monomer **M3** analyzed <sup>1</sup>H NMR experiment, ethyl vinyl ether (2 mL) was added to terminate the polymerization. The solvent was removed in vacuum under reduced pressure, after that to the concentrated polymer solution, 10 mL of *n*-pentane was added dropwise to precipitate the polymer. The solvent was filtered off and triblock polymer **P4** was dried in vacuo yielding dark red solids.

In the case of the synthesis of regular diblock polymer **P3**, ethyl vinyl ether (2 mL) was used to terminate the polymerization after the complete consumption of **M2** and after the reprecipitation of the concentrated polymer solution in *n*-pentane yielding diblock polymer **P3** as dark red solids.

**(c) Random Binary- or Ternary-Block Copolymerization:** A solution of trifluoroacetate modified Hoveyda-Grubbs type 2<sup>nd</sup> generation catalyst (2 mol%) in CHCl<sub>3</sub> (3 mL) was added to monomers **M1** and **M2** (0.020 mmol each) in the same solvent (3 mL) and the reaction solution was stirred at RT for 6 hours. After the complete consumption of monomers, ethyl vinyl ether (2 mL) was added to terminate the polymerization. The solvent was removed in vacuum under reduced pressure, after that the concentrated polymer solution, 10 mL of *n*-pentane was added dropwise to precipitate the polymer. The solvent was filtered off and random binary copolymer **P5** was dried in vacuo yielding dark red solids. In the case of the synthesis of random ternary copolymer **P6**, monomers **M1**, **M2**, and **M3** (0.020 mmol each) were added to the initiator solution and stirred at RT for 12 hours. After the complete consumption of monomers, ethyl vinyl ether (2 mL) was added to terminate the polymerization, and after the reprecipitation of the concentrated polymer solution in *n*-pentane yielding random ternary copolymer **P6** was isolated as dark red solids.

**Homopolymer P2:** PEG<sub>750</sub>-PDI-derived **P2** were synthesized and well characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV-Vis, Emission as well as IR (ATR) spectroscopic analysis.

**Diblock Polymer P3:** Isolated as dark red solid in 98% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298K): δ 9.47 (m, 1.8H, ArH), 8.44 (brm, 4H, ArH), 6.92-6.68 (brm combined with brs, 4.5H, =CH of poly(ene) and poly(olefin)), 6.16 (brs, 1.7H), 5.87 (brs, 0.5H), 4.56 (brs, 4.4H), 4.21 (brs, 17H), 3.64 (brs, 63H), 2.22 (m, 15.7H), 1.25 (m, 116.8H), 0.82 (brs, 13H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298K): δ 172.1, 137.0, 130.3, 128.8, 128.0, 123.2, 73.7, 72.0, 70.6, 62.0, 59.4,

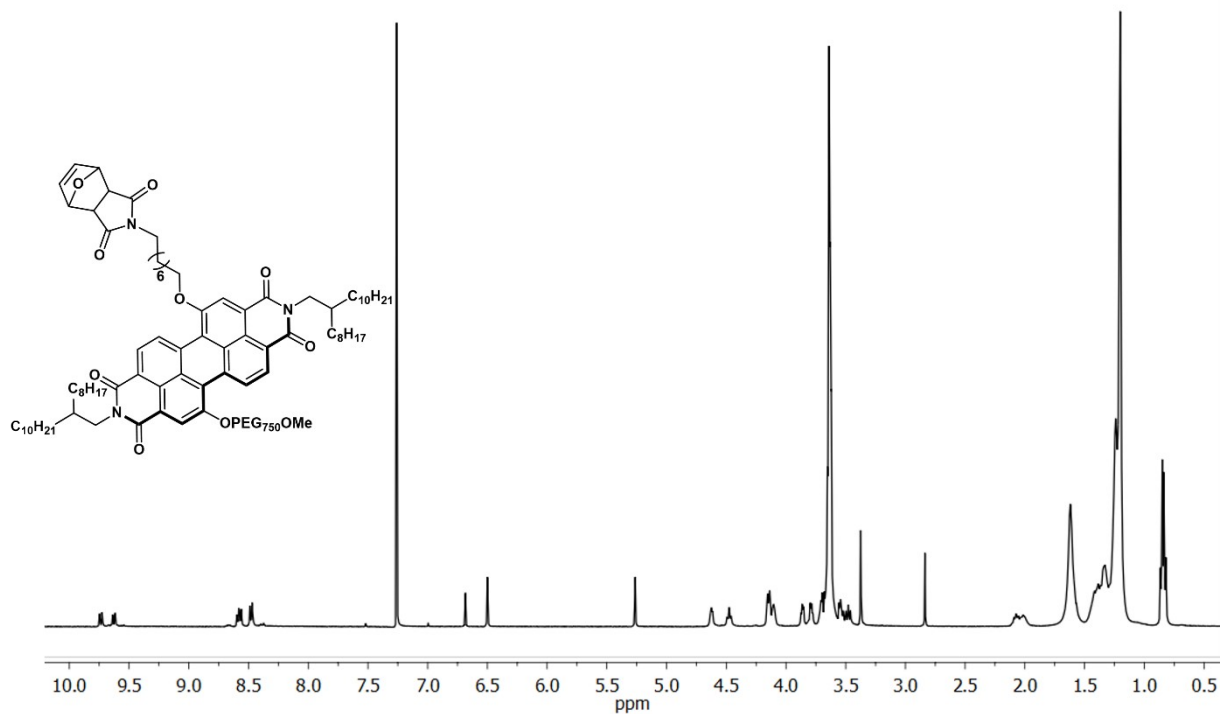
57.3, 52.2, 41.5, 38.1, 36.8, 32.0, 31.3, 30.2, 29.8, 29.4, 26.7, 22.7, 21.3, 17.1, 15.5, 14.2; UV-Vis (chloroform): 527 nm (solution) and 513 nm (film casted from the same solvent); Emission (chloroform): 600 nm (solution), 700 nm (film casted from the same solvent); IR (ATR mode): 2925 (s), 2854 (s), 1727 (s), 1653 (s), 1595, 1263 (s), 1072 (w)  $\text{cm}^{-1}$ ; SEC analysis in chlorobenzene as an eluent:  $M_n = 62.0$  kDa,  $D = 1.5$

**Triblock Polymer P4.** Isolated as dark red solid in 96% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  9.64 (m, 1.6H, ArH), 8.44 (brm, 4H, ArH), 6.93-6.68 (brm combined with brs, 4.4H, =CH of poly(ene) and poly(olefin)), 6.68 (brs, 2.4H, =CH of poly(olefin)), 6.16 (brs, 1.3H), 6.60 (2.4H), 5.79 (brs, 1.3H), 4.97 (brs, 1.5H), 4.34 (m, 30H), 3.63 (brs, 66.7H), 2.15 (m, 15.5H), 1.31 (brm, 140H), 0.86 (18H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  175.9, 175.6, 172.0, 137.0, 132.0, 131.0, 123.2, 81.14, 72.1, 70.6, 62.0, 59.0, 57.3, 53.5, 52.4, 41.5, 39.0, 32.0, 29.8, 29.6 (t), 29.4 (m), 29.3, 29.2, 27.8, 27.0, 26.9, 26.7, 22.8, 14.2; UV-Vis (chloroform): 527 nm (solution) and 553 nm (film casted from the same solvent); Emission (chloroform): 600 nm (solution), 700 nm (film casted from the same solvent); IR (ATR mode): 2924 (s), 2854 (s), 1699 (s), 1657 (s), 1247 (s), 1159 (w), 1261 (s), 1096 (vs)  $\text{cm}^{-1}$ ; SEC analysis in chlorobenzene as an eluent:  $M_n = 79.0$  kDa,  $D = 2.1$ .

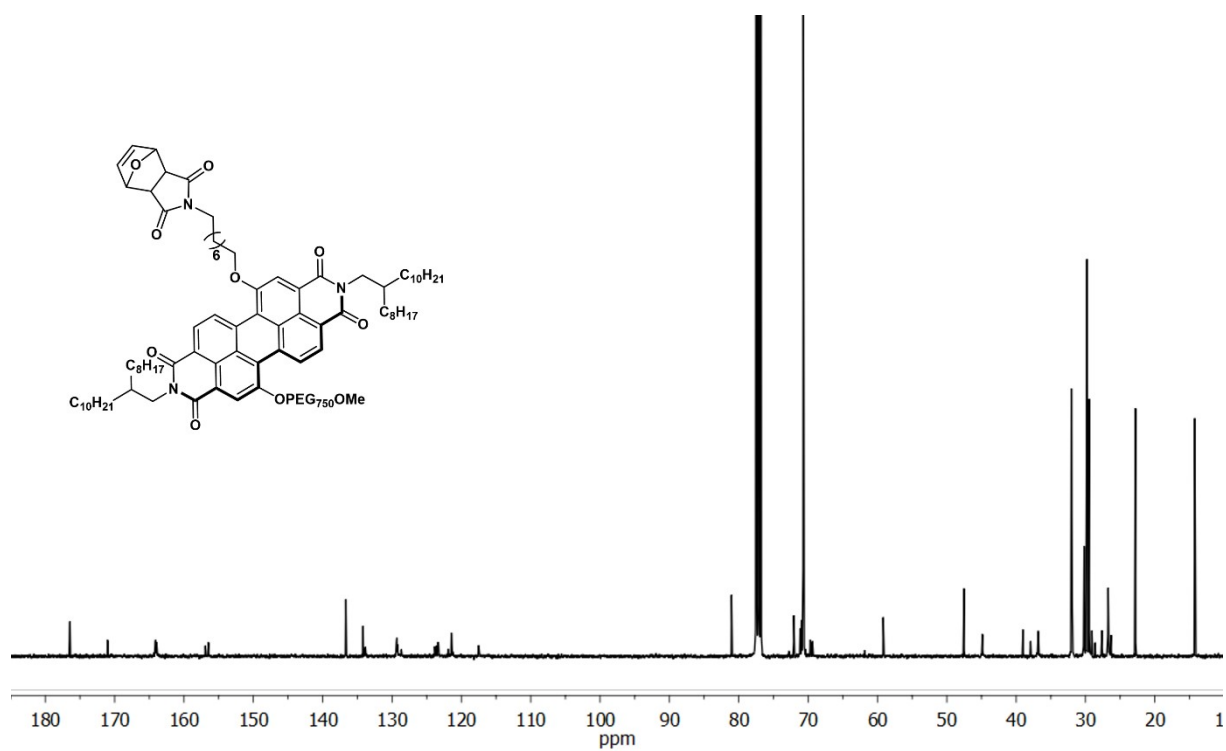
**Random Binary Copolymer P5.** Isolated as dark red solid in 95% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  9.61 (brm, 1.2, ArH), 8.38 (brm, 2.6H, ArH), 6.93 (brs, 2H, =CH), 6.63 (brs, 1.8H, =CH), 6.10 (brs, 1.7H), 5.71 (brs, 1.5H), 4.54 (brs, 5H), 4.15 (m, 12H), 3.63 (brs, 30.2H), 2.25 (brm, 8.4H), 1.34 (brs, 98H), 0.85 (brs, 13H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  172.1, 171.7, 164.1, 156.9, 155.6, 137.0, 135.0, 134.1, 130.1, 129.4, 128.7, 128.0, 123.2, 72.0, 70.9, 62.0, 59.1, 57.3, 44.8, 41.5, 36.7, 32.0, 31.9, 30.2, 29.7, 29.4, 26.7, 22.7, 22.3, 21.2, 14.2; UV-Vis (chloroform): 534 nm (solution) and 510 nm (film casted from the same solvent); IR (ATR mode): 2925 (s), 2852 (s), 1691 (s), 1653 (s), 1245 (s), 1159 (w), 1263 (s), 1091 (vs)  $\text{cm}^{-1}$ ; SEC analysis in chlorobenzene as an eluent:  $M_n = 74.3$  kDa,  $D = 1.9$ .

**Random Ternary Copolymer P6.** Isolated as dark violet solid in 97% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  9.60 (brm, 1.5H, ArH), 8.40 (brm, 4H, ArH), 6.97 (brs, 2.5H, =CH), 6.66 (brs, 2.8H, =CH), 6.14 (brs, 1H, =CH), 5.81 (brs, 1H), 4.54 (m, 4.4H), 4.12 (brm, 16H), 3.63 (brs, 55H), 2.22 (m, 11.2H), 1.38 (brm, 102H), 0.83 (brs, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  175.6, 171.9, 171.8, 171.6, 136.9, 134.9, 130.0, 129.0, 128.5, 126.2, 123.2, 82.6, 80.9, 71.9, 70.6, 61.9, 57.6, 56.7, 53.5, 52.7, 41.3, 39.1, 31.9, 30.1, 29.7, 29.6, 29.5, 29.4,

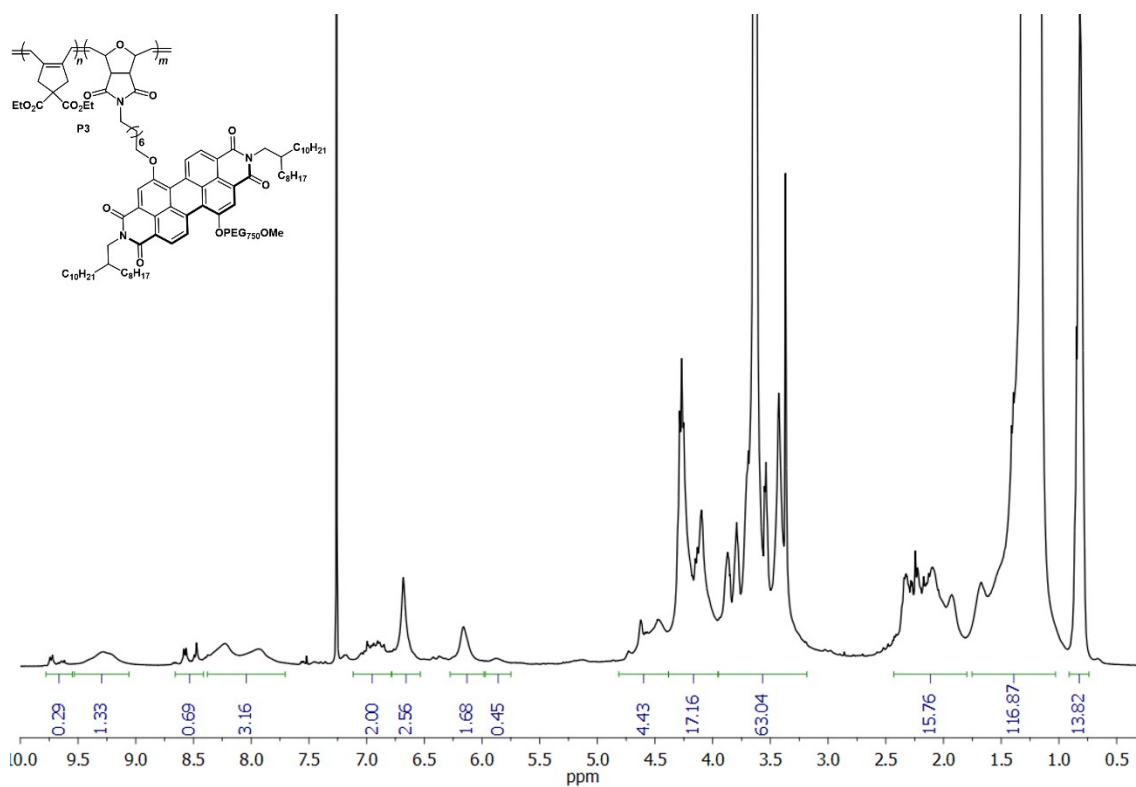
29.3, 27.7, 26.8, 26.6, 22.7, 14.7; UV-Vis (chloroform): 534 nm (solution) and 510 nm (film casted from the same solvent); IR (ATR mode): 2921 (s), 2858 (s), 1692 (s), 1654 (s), 1246 (s), 1157 (w), 1261 (s), 1094 (vs)  $\text{cm}^{-1}$ ; SEC analysis in chlorobenzene as an eluent:  $M_n = 88.3$  kDa,  $D = 2.4$ .



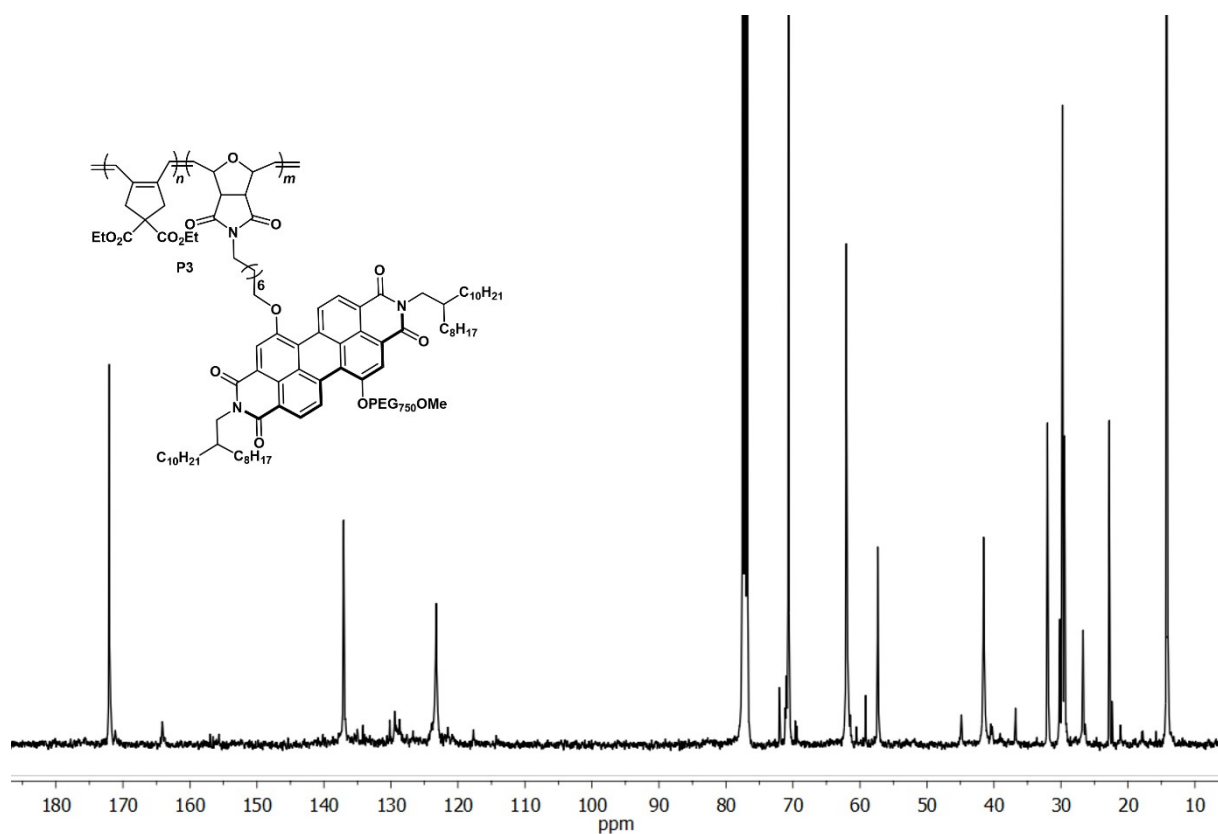
**Figure S1.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K) spectrum of monomer **M2**.



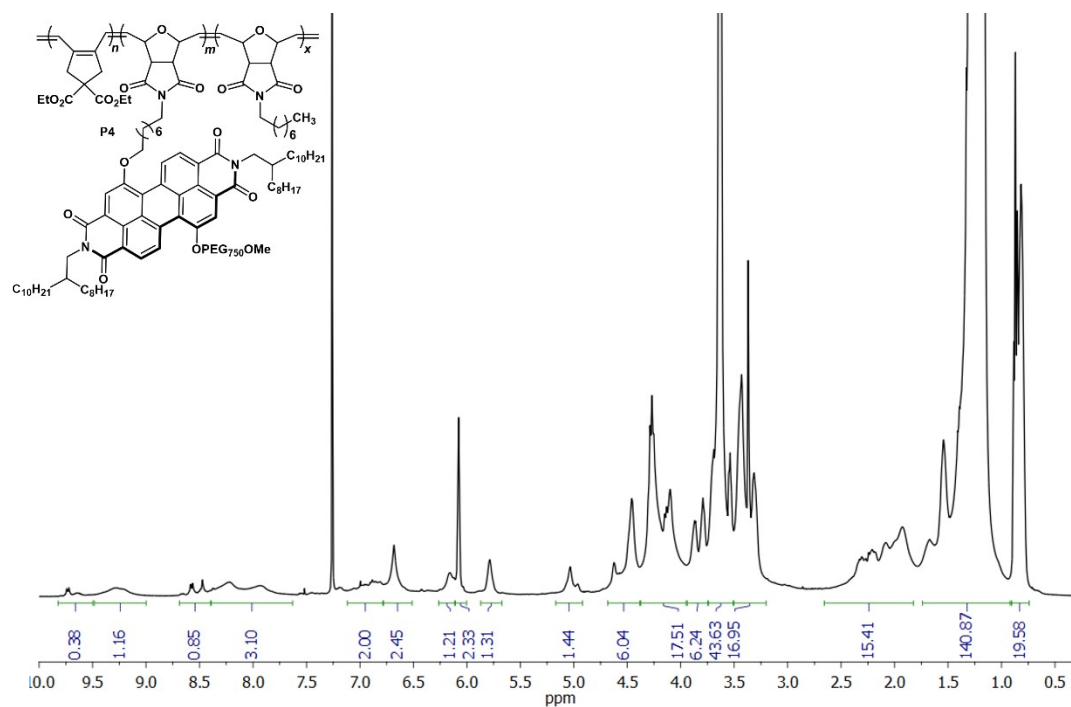
**Figure S2.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298K) spectrum of monomer **M2**.



**Figure S3.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K) spectrum of diblock polymer **P3**.

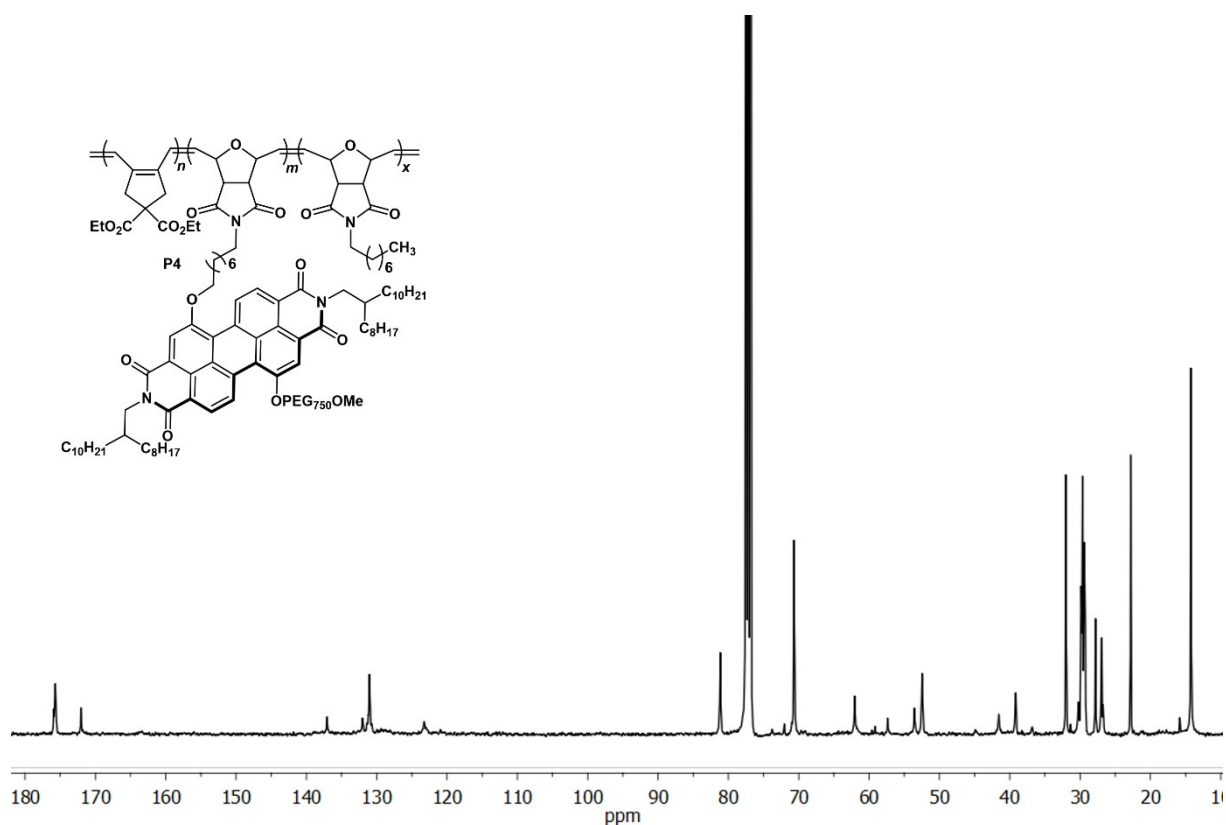


**Figure S4.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298K) spectrum of diblock polymer **P3**.

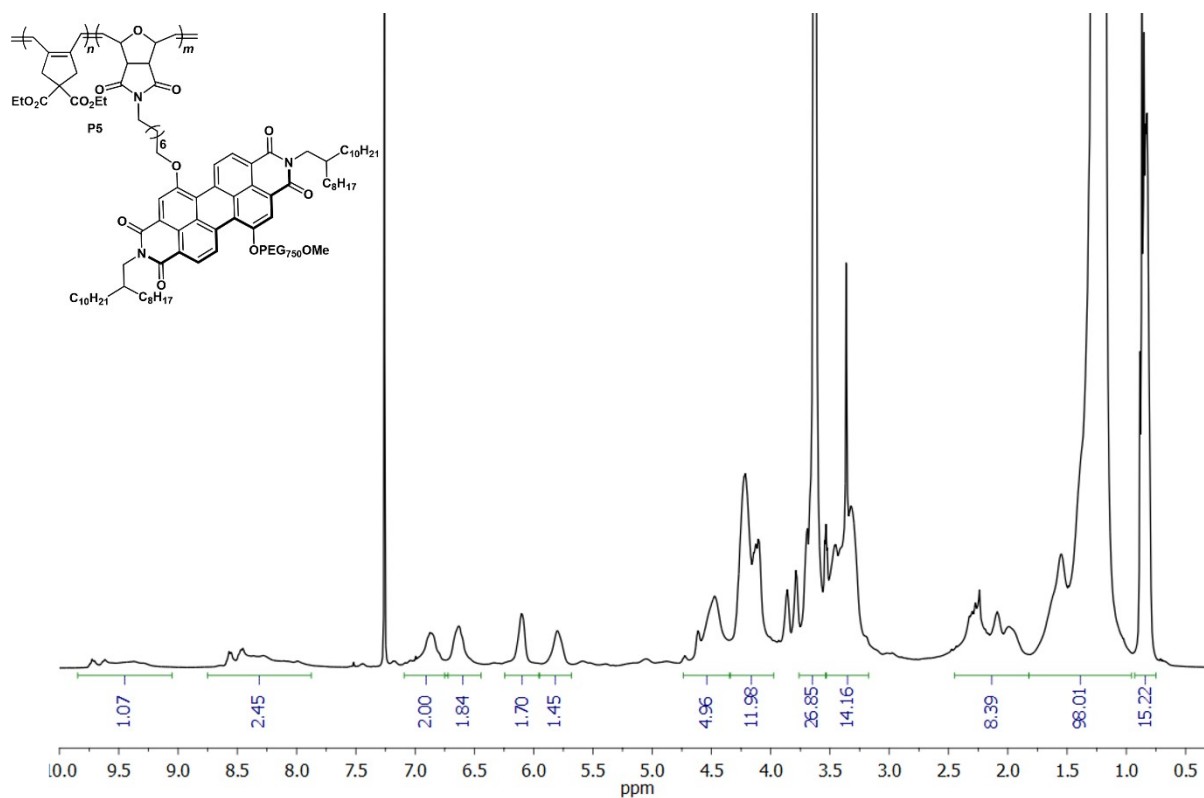


**Figure S5.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K) spectrum of triblock polymer **P4**.

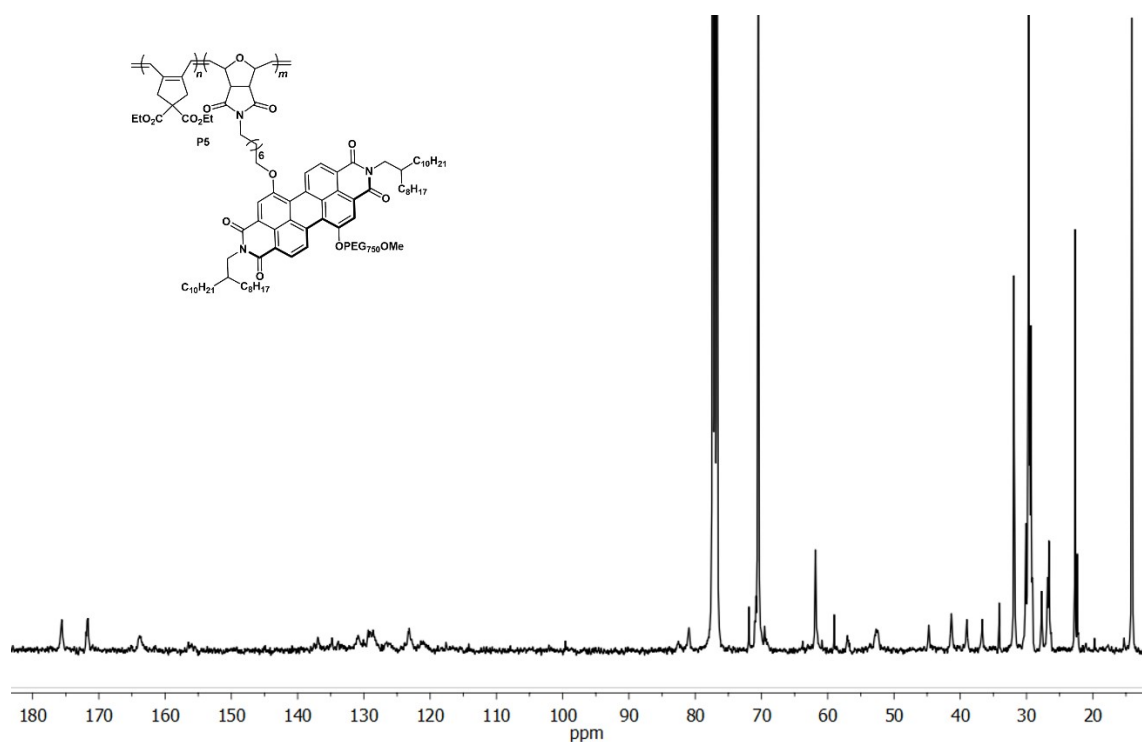




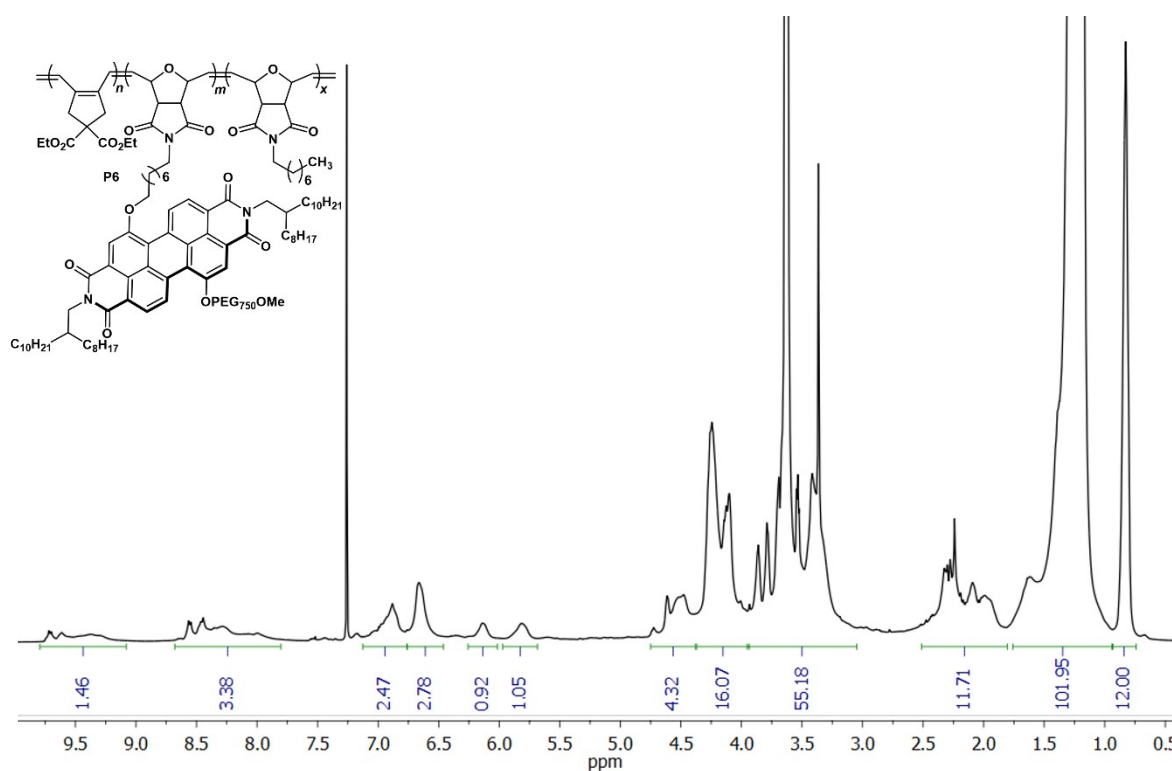
**Figure S6.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298K) spectrum triblock polymer **P4**.



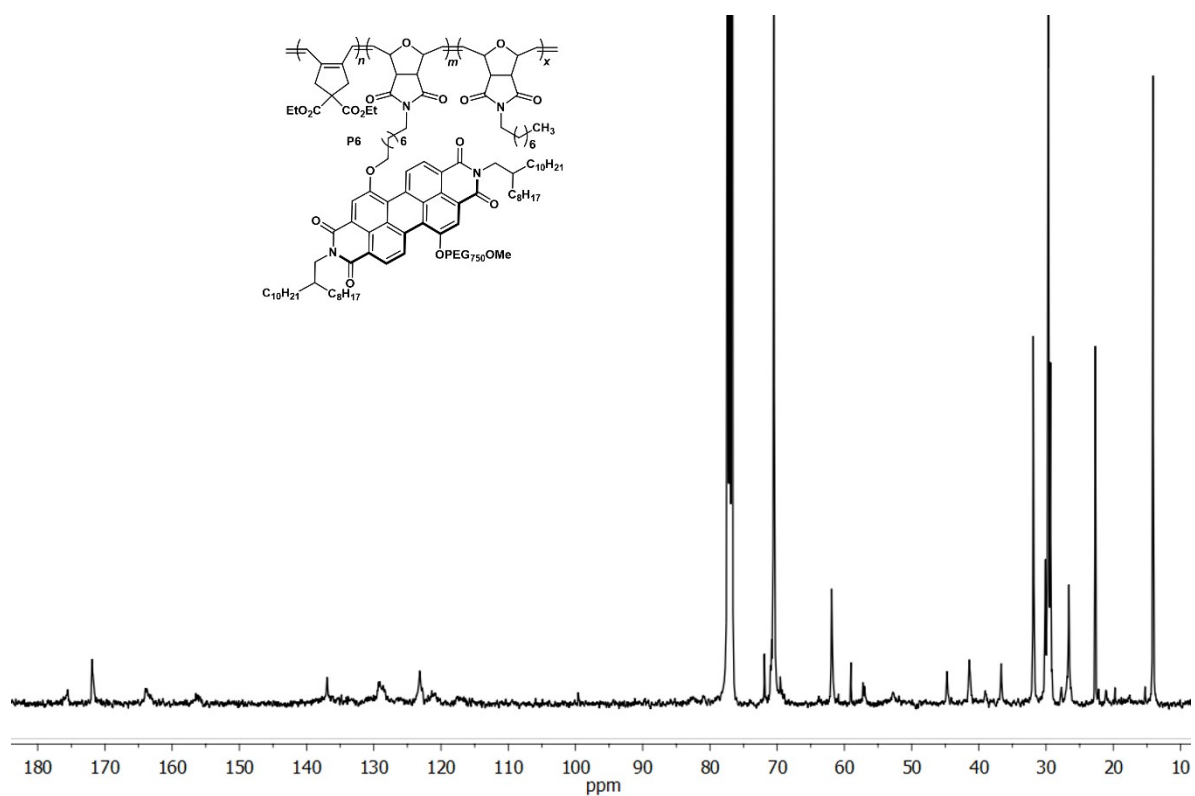
**Figure S7.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K) spectrum of random binary copolymer **P5**.



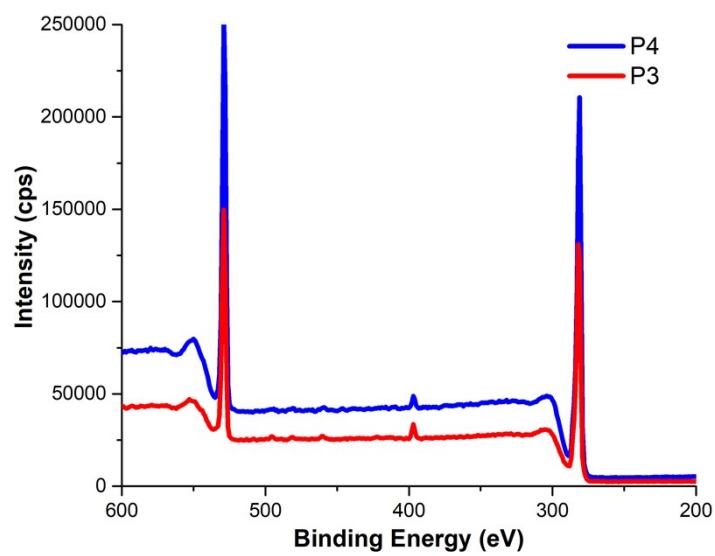
**Figure S8.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298K) spectrum of random binary copolymer **P5**.



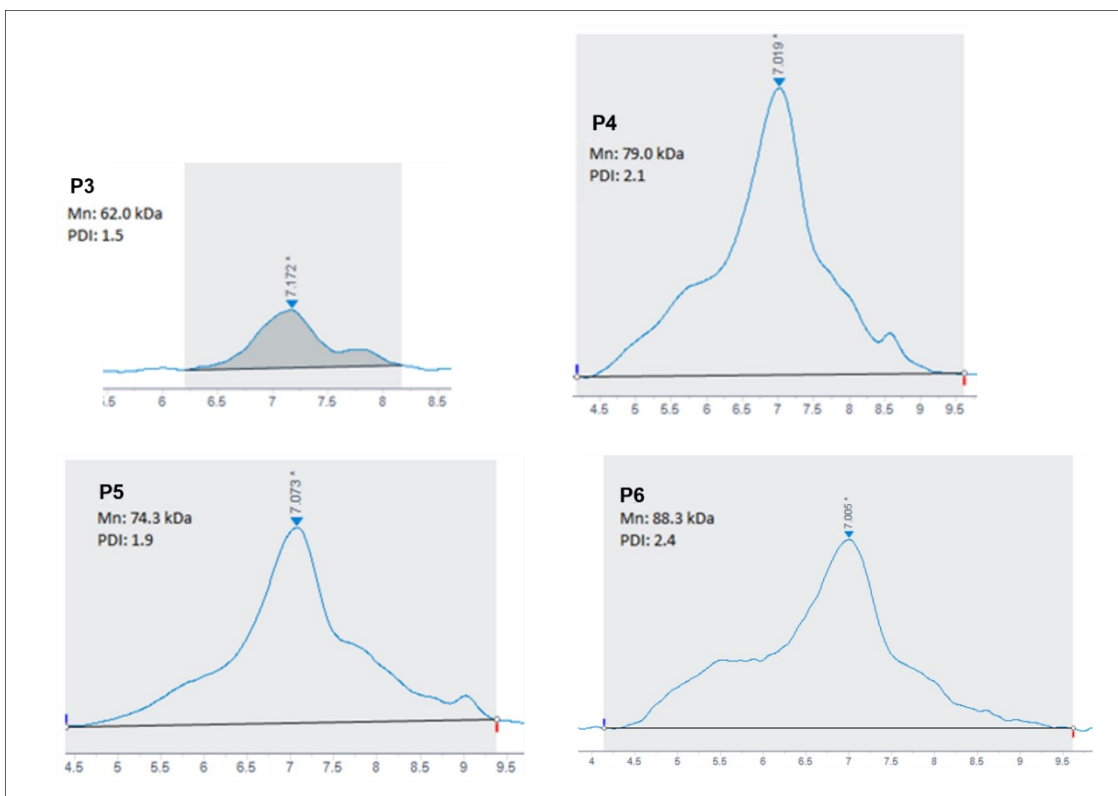
**Figure S9.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298K) spectrum of random ternary copolymer **P6**.



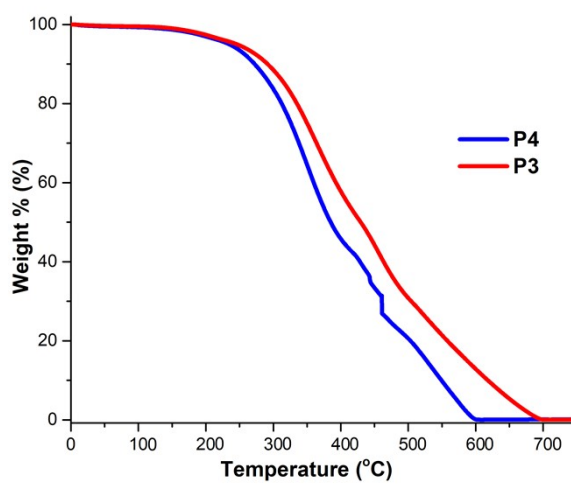
**Figure S10.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298K) spectrum of random ternary copolymer **P6**.



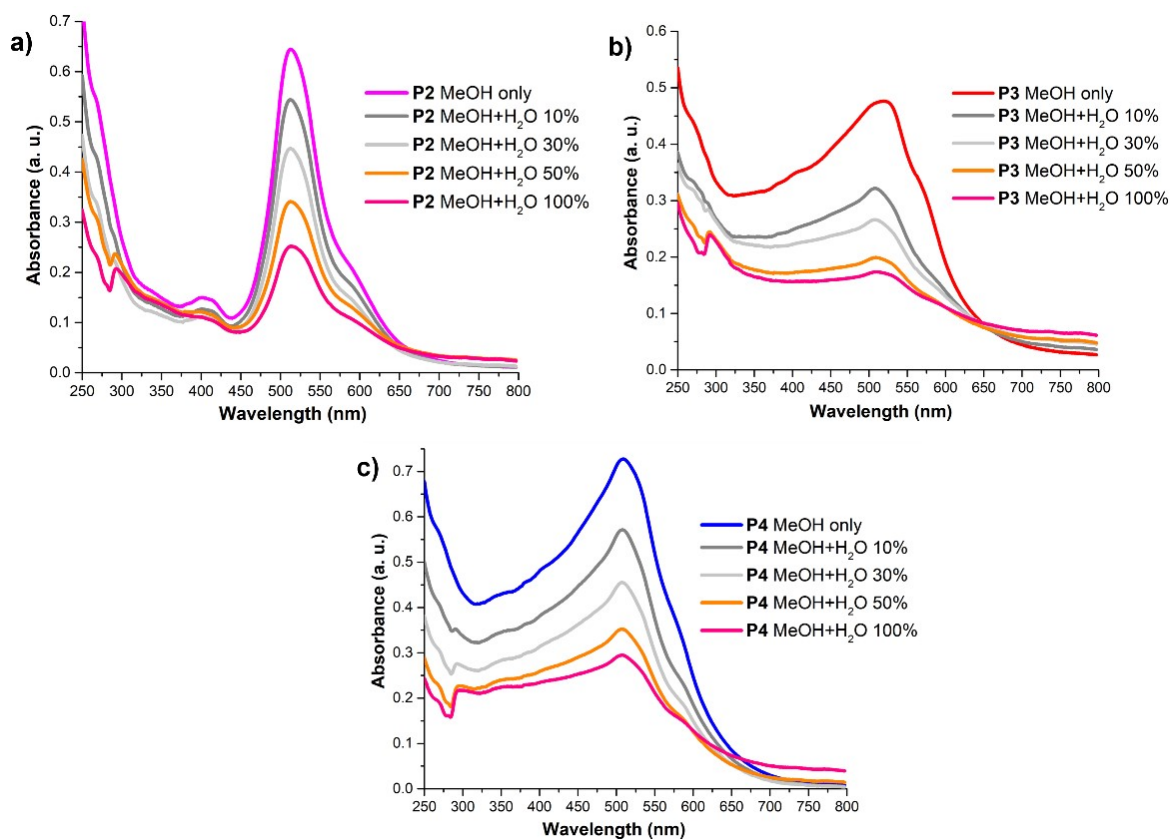
**Figure S11.** XPS Analysis of block copolymers **P3** and **P4**.



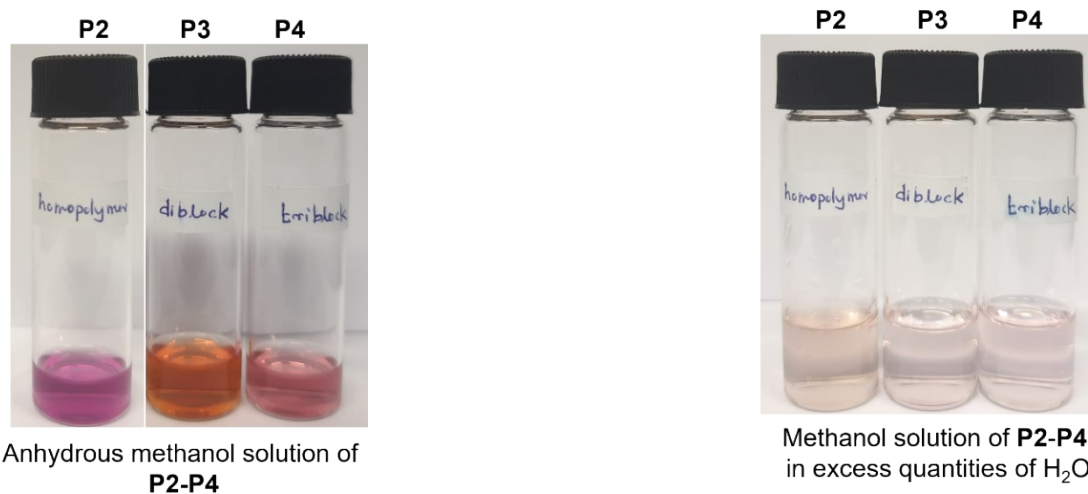
**Figure S12.** SEC traces of block copolymers **P3-P6**.



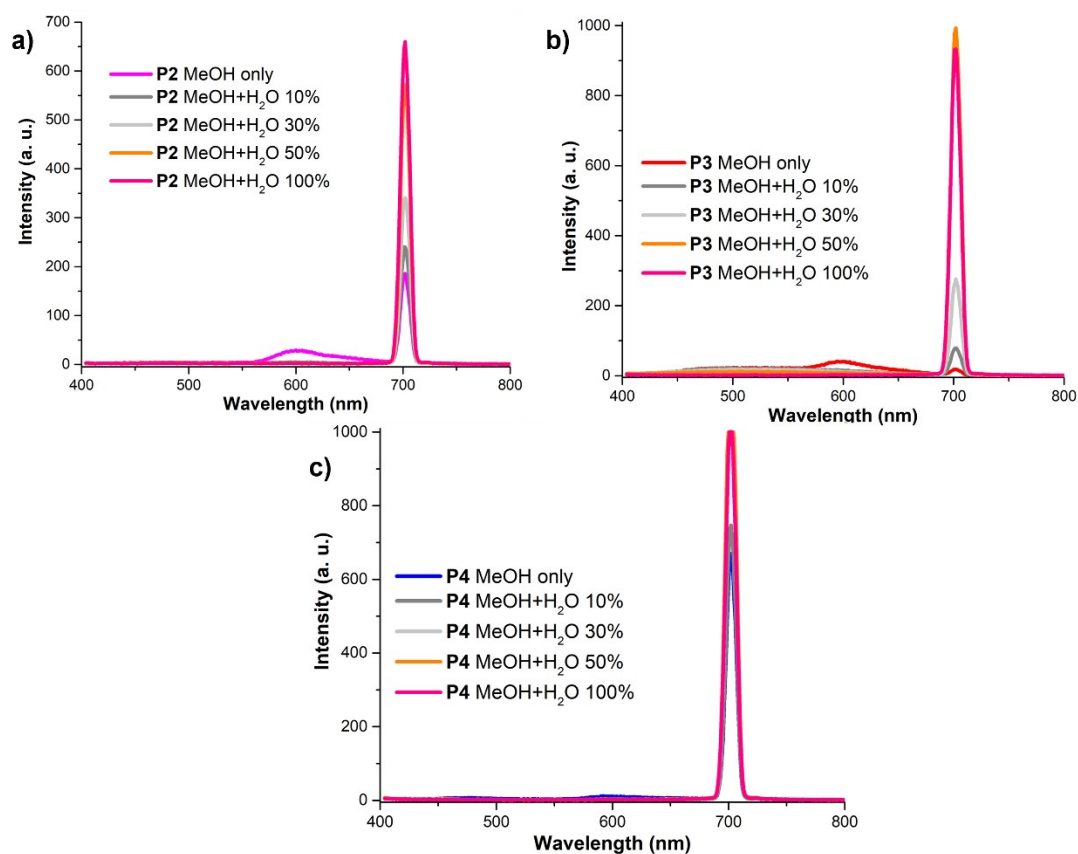
**Figure S13.** TGA traces of block copolymers **P3** and **P4**.



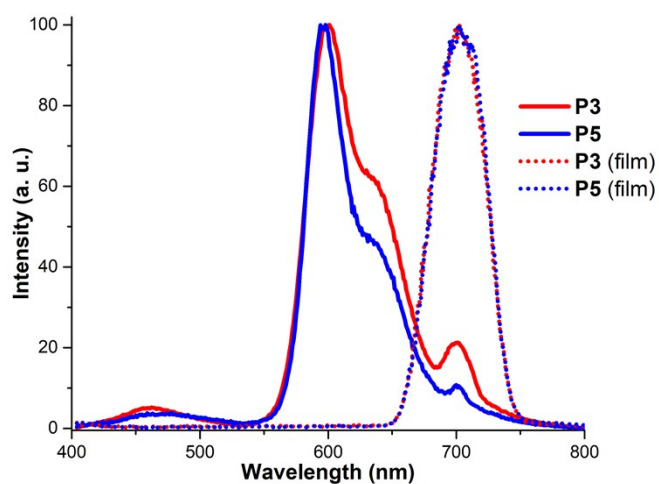
**Figure S14.** UV-Vis absorption spectra of **a)** diblock copolymer **P3** in MeOH and combination of MeOH/water, and **b)** triblock copolymer **P4** in MeOH and combination of MeOH/water.



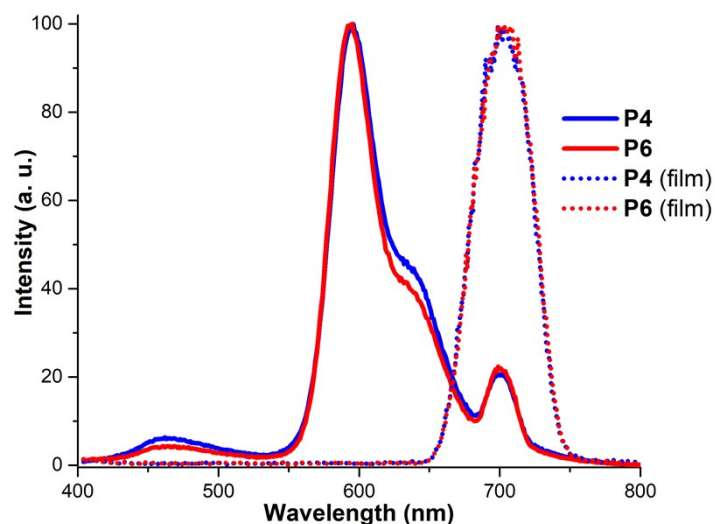
**Figure S15.** Solutions of Homopolymer **P2**, diblock copolymer **P3** and triblock copolymer **P4** in anhydrous MeOH (left) and in binary MeOH/water system (right).



**Figure S16.** Emission spectra of a) homopolymer **P2** in MeOH and combination of MeOH/water, b) diblock copolymer **P3** in MeOH and combination of MeOH/water, and c) triblock copolymer **P4** in MeOH and combination of MeOH/water.



**Figure S17.** Emission spectra of diblock copolymer **P3** (red solid line) and random binary copolymer **P5** (blue solid line) in chloroform and their thin film state of **P3** (red dotted line) and **P5** (blue dotted line) casted in the same solvent.



**Figure S18.** Emission spectra of triblock copolymer **P4** (blue solid line) and random ternary copolymer **P6** (red solid line) in chloroform and their thin film state of **P4** (blue dotted line) and **P6** (red dotted line) casted in the same solvent.

## References

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- [3] X. Wang, T. Zeng, M. Nourrein, B.-H. Lai, K. Shen, C.-L. Wang, B. Sun, M. Zhu, *RSC advances* **2017**, *7*, 26074-26081.