# Supporting Information

**A Sequential ROMP Strategy to Donor-Acceptor Di-, Tri- and Tetra Arylenevinylene Block Copolymers**

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## CONTENTS

**General experimental details for synthesis:**

Nuclear magnetic resonance (NMR) spectra were obtained on either 400 MHz or 500 MHz Bruker spectrometers. Chemical shifts are reported in ppm relative to the indicated residual solvent (^{1}H NMR spectroscopy; 7.23 ppm for chloroform-$d$ and 5.23 ppm for dichloromethane-$d_2$, and ^{13}C NMR spectroscopy; 77.16 ppm for chloroform-$d$). The longitudinal relaxation time constant (T1) for the paracyclophanediene monomers **M1**-**M3**, and **G3** catalyst were determined by inversion-recovery with a maximum T1 of 3 s, so relaxation delay of 15 s was used in all of the experiments. The following abbreviations are used to indicate the multiplicity of the signals; s = singlet, d = doublet, m = multiplet, brm = broad multiplet. The molecular weight of polymers were analysed using gel permeation chromatography (GPC) in THF solution (~1 mg/mL) using a ViscotekGPCmax VE3580 solvent/sample module with 2 × PL gel 10 μm MIXED-B + 1 × PL gel 500A columns, a Viscotek VE3580 RI detector and a VE 3240 UV-Vis multichannel detector as well as an Agilent 1260 Infinity II system equipped with 2 × PL gel 10 μm mixed-B columns and refractive index detector. The flow

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rate was 1 mL min$^{-1}$ and the system was calibrated with narrow PDI polystyrene standards in the range of 0.2 – 1,800 kg mol$^{-1}$ from Polymer Laboratories. The analysed samples contained *n*-dodecane as a flow marker. UV-Vis absorption spectra and optical densities were recorded on a Varian Cary 5000 UV-Vis-NIR spectrophotometer and photoluminescence spectra were recorded on Cary Eclipse Fluorescence Spectrophotometer. Fluorescence quantum yields for all the polymers were measured in dilute chloroform solutions on HAMAMATSU Absolute PL Quantum Yield Spectrometer C11347 using integration sphere method.

Anhydrous THF used for all the polymerization reactions was purchased from Sigma-Aldrich and degassed by freeze-pump-thaw technique (three times). All other anhydrous solvents and reagents were purchased from Sigma-Aldrich, Fisher Scientific, Alfa Aesar or Acros and used as received. Column chromatography was performed using silica gel (60 Å, 230−400 mesh). Petroleum ether refers to the fraction obtained at 40-60 ˚C. All reactions were carried out using standard Schlenk techniques under argon, unless stated otherwise.

**DFT Calculations:** The electronic structures and properties of the trimer of *cis/trans* and all *trans* D-A diblock copolymer 2 were calculated using density functional theory (DFT) calculations, carried out with Gaussian 09W package software, and GaussView 5.0.8 molecular visualization program, employing the B3LYP (Becke three-parameter hybrid correlation functional combined with Lee–Yang–Parr correlation functional). The geometry optimization and electronic structure calculations were performed using a B3LYP/6-311G(d,p) basis set.

**Sequential ROMP of monomers M1 and M3 with G3 catalyst; *in-situ* ¹H NMR experiments**

General experimental procedure: Monomer **M1**[1] (30 mg, 0.065 mmol, 100 mol%) and **G3** catalyst (5.7 mg, 0.006 mmol, 10 mol%) were added into separate vials and transferred into an argon filled glovebox. **G3** catalyst was dissolved in tetrahydrofuran-$d_8$ ([**M**] = 100 mM) and the solution was transferred to the vial containing **M1** and mixed until the solution becomes homogeneous. The solution was transferred into a Young's NMR tube, sealed, removed from the glovebox and kept in an ice bath. The first ¹H NMR spectrum for t=0 was recorded at 25 °C. Then the spectrometer probe was set at 40 °C and the NMR spectra were recorded at every 7 min intervals throughout the ROMP. Once the signals corresponding to the monomer **M1** disappeared the NMR tube was cooled down to 25 °C, transferred back into the glove box and a solution of monomer **M3**[2] (31.6 mg, 0.065 mmol, 100 mol%) in THF-$d_8$ (0.3 mL) was added. The NMR tube was shaken well and removed from glove box and kept in an ice bath. The first ¹H NMR spectrum for t=0 was recorded at 25 °C. The spectrometer probe was then set at 55 °C and the NMR spectra were recorded at every 7 min intervals until the consumption of monomer **M3** was observed. The reaction mixture was cooled to room temperature and

quenched with excess of deoxygenated ethyl vinyl ether (0.15 mL, 1.56 mmol, 2500 mol%) in a vial and stirred at room temperature for 6 h. The crude reaction mixture was purified *via* precipitation into methanol/celite plug followed by extraction of the polymer with chloroform. The chloroform layer was evaporated under reduced pressure to give poly(*p*-(di-2-ethylhexyloxyphenyl)pheneylenevinylene)-*block*-poly(*p*-(di-*n*-octylphenylene)benzothiadiazole vinylene) diblock copolymer **2** (50 mg, 81% yield) as a brown amorphous film.
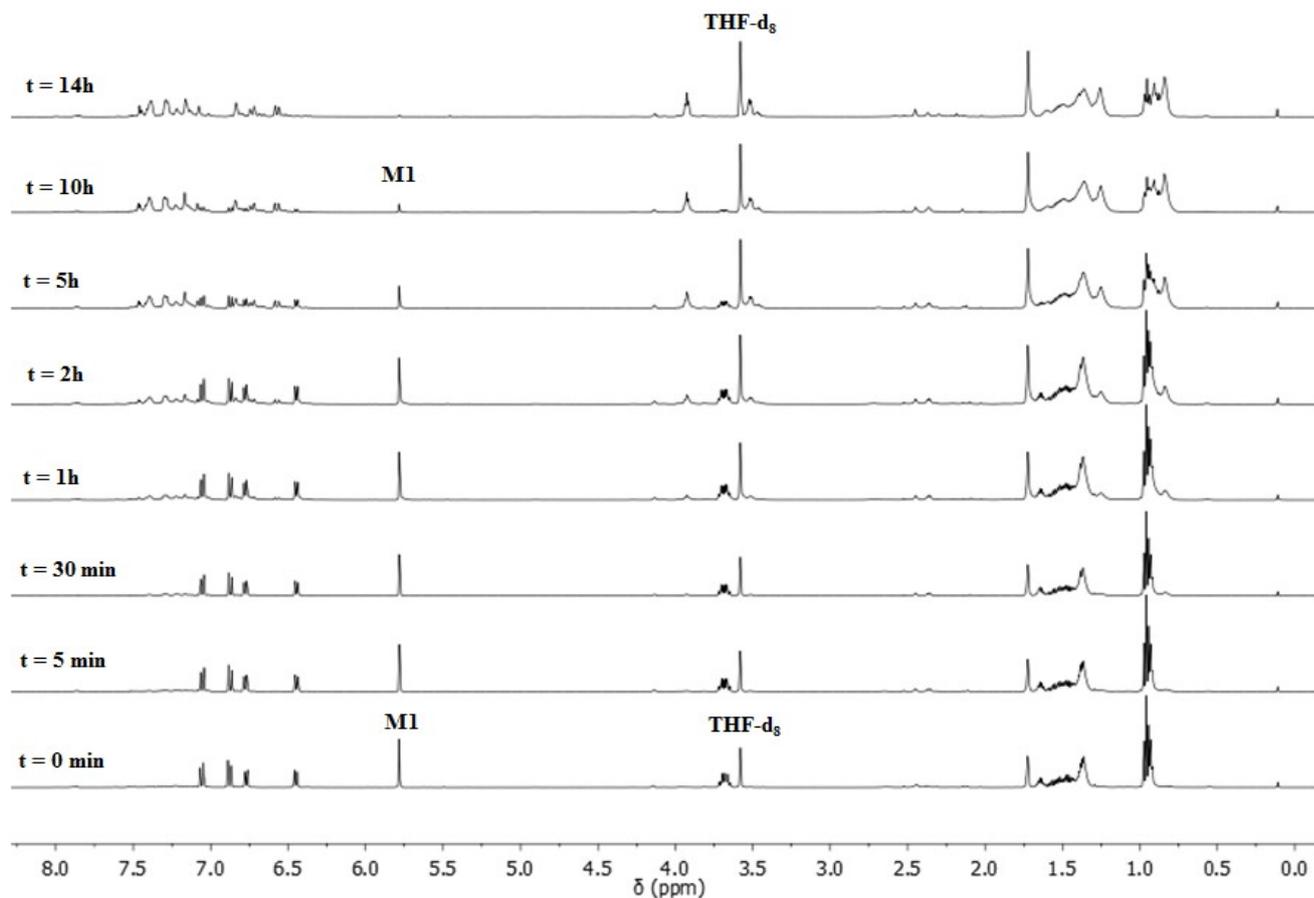


**Figure S1.** Consumption of monomer **M1** in the sequential ROMP of monomers **M1** and **M3** with **G3** catalyst; *in-situ* $^1$H NMR experiment in THF-$d_8$ at 40 °C (t= 0 at 25 °C)
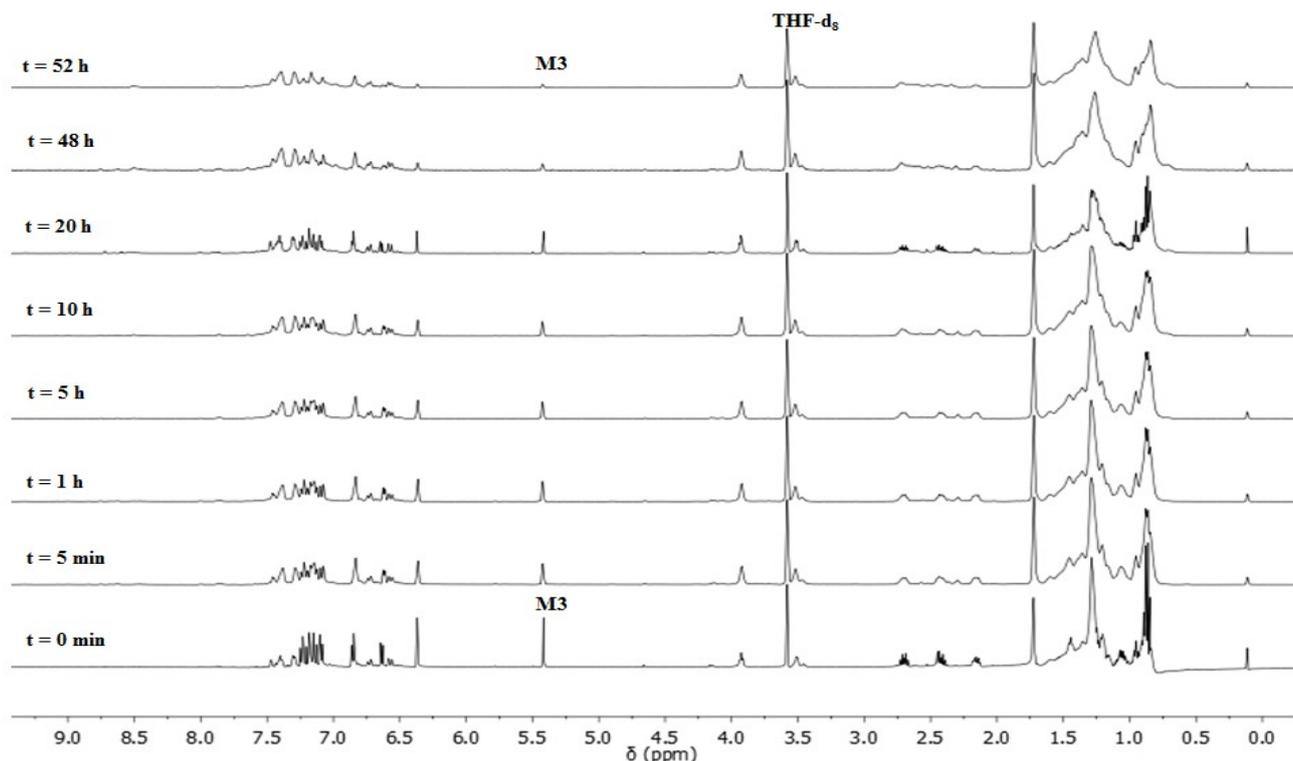
**Figure S2.** Consumption of monomer **M3** in the sequential ROMP of monomers **M1** and **M3** with **G3** catalyst; *in-situ* ^{1}H NMR experiment in THF-$d_8$ at 55 °C (t= 0 at 25 °C)

**Sequential ROMP of monomers M1, M2 and M3 with G3 catalyst-synthesis of fully conjugated donor-acceptor di-, tri- and tetrablock copolymers 2-5**

Representative experimental procedure for the synthesis of diblock BCP **2**: In an argon filled glovebox a solution of **G3** catalyst (5.7 mg, 0.006 mmol, 10 mol%) in anhydrous, degassed THF (0.65 mL, [**M**] = 100 mM) was added into a vial containing cyclophanediene monomer **M1**(30.0 mg, 0.065mmol, 100 mol%). The vial was sealed, wrapped in aluminium foil and mixed at room temperature for 5 minutes. The reaction was placed in a preheated Drysyn aluminium block at 40 °C and stirred for 3.5 h until consumption of the monomer was observed (GPC and TLC). The reaction mixture was cooled to rt and added a solution of the second monomer **M3** (31.6 mg, 0.065 mmol, 100 mol%) in THF (0.3 mL). The reaction mixture was stirred at 60 °C for 16 h until the consumption of the monomer **M3** (GPC and TLC) and excess of deoxygenated ethyl vinyl ether (0.15 mL, 1.32 mmol, 2500 mol%) was added followed by stirring at room temperature for 6 hours. The crude was precipitated into a short methanol/Celite column, washed with methanol and the polymer was extracted with chloroform. The chloroform layer was evaporated under reduced pressure and dried to obtain desired diblock copolymer **2** (53 mg, 88% yield) as a brown amorphous film.
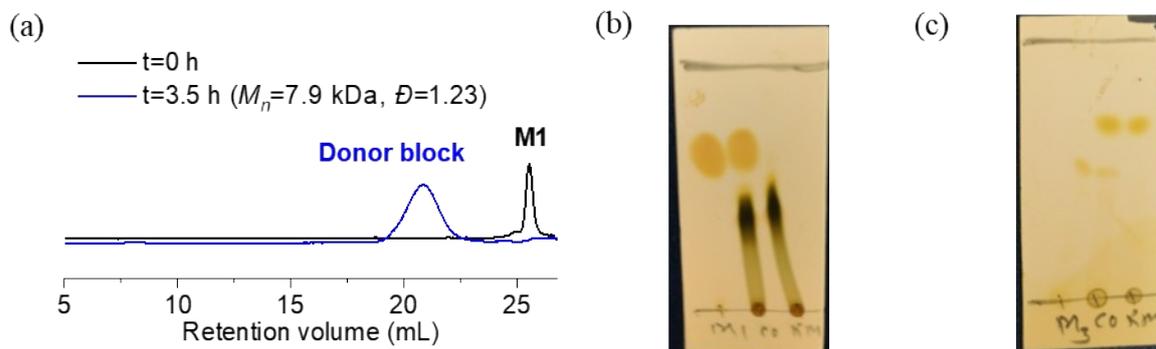
**Figure S3.** Consumption of monomers **M1-M3** in the synthesis BCPs **2** (a) consumption of **M1**-GPC profile after 3.5 h at 40 °C, (b) consumption of **M1**-TLC analysis after 3.5 h (5%EA/PE) and (c) consumption of **M3** at 60 °C-TLC analysis after 16 h (5%EA/PE).

**Table S1**: Sequential ROMP of monomers **M1, M2** and **M3**-Synthesis of BCPs **2-5**

| Entry | BCP | Monomer ratio | t (h) | GPC data purified[a] | | | $M_{n(calc.)}$ (kD) (¹H NMR) | %Yield |
| | | | | $M_{n(calc.)}$ (kD) | $M_{n(obs.)}$ (kD) | $Đ_m$ | | |
|---|---|---|---|---|---|---|---|---|
| 1 | **2** | [M1]/[M3]=10/10 | 19.5 | 9.5 | 15.2 | 1.37 | 9.5 | 88 |
| 2 | **3** | [M1]/[M2]=10/20 | 23.5 | 14.1 | 24.2 | 1.51 | 14.1 | 91 |
| 3 | **4** | [M1]/[M2]/[M3]=10/10/10 | 33.5 | 14.7 | 22.5 | 1.56 | 14.7 | 85 |
| 4 | **5** | [M1]/[M3]=20/20 | 46.5 | 18.9 | 26.2 | 1.69 | 17.1 | 76 |

a. $M_{n(calc.)}$ was calculated from [monomer]/[catalyst] ratio and $M_{n(obs.)}$ was calculated against polystyrene standards



**2** (R=2-ethylhexyl, R'= *n*-octyl)

**3** (R=2-ethylhexyl, R'= *n*-octyl)

**4** (R=2-ethylhexyl, R'= *n*-octyl)

**5** (R=2-ethylhexyl, R'= *n*-octyl)
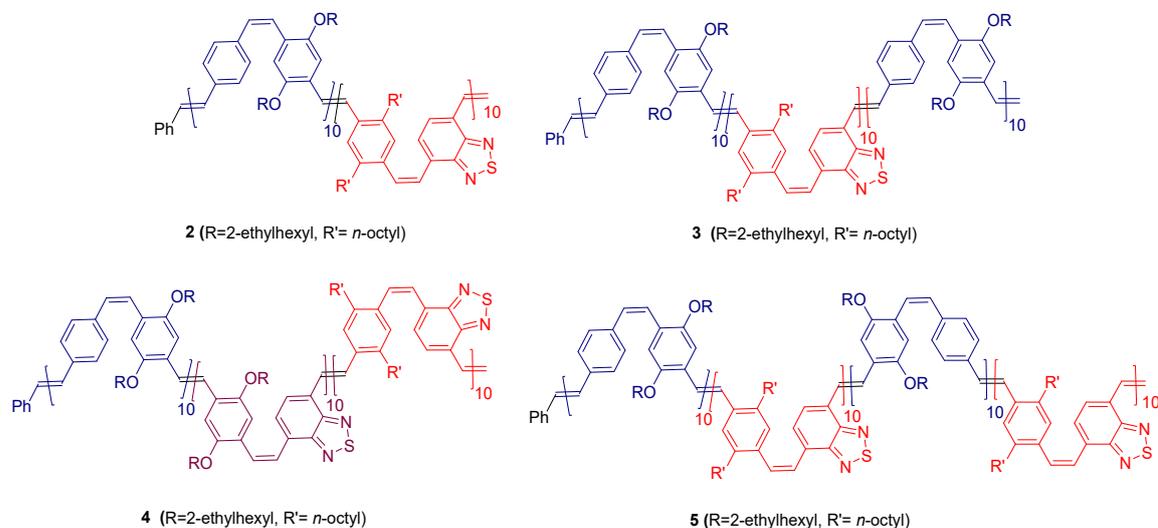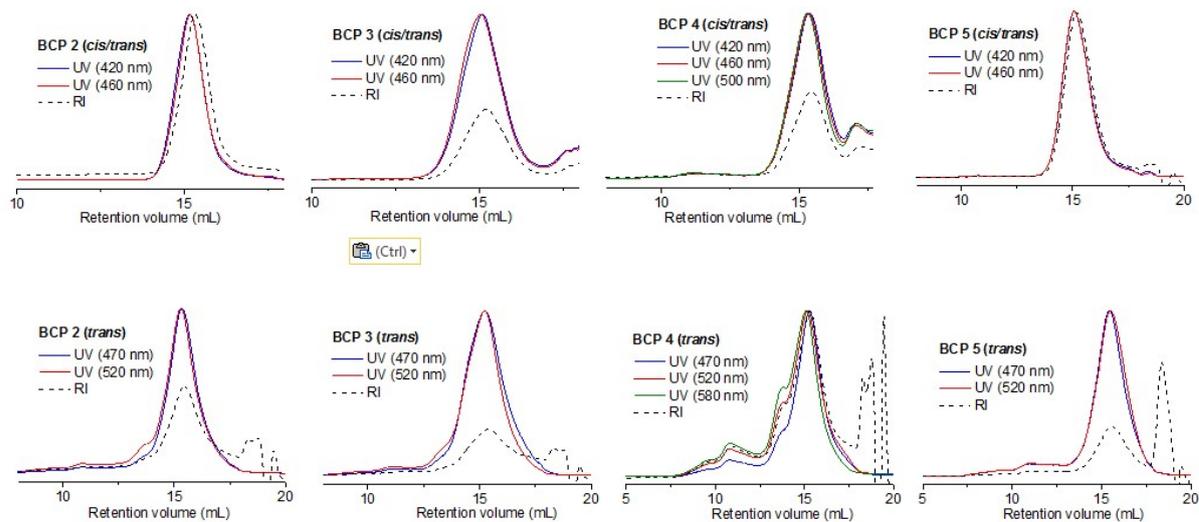
**Figure S4.** GPC traces (UV and RI) of *cis/trans* and *all-trans* BCPs **2-5**.
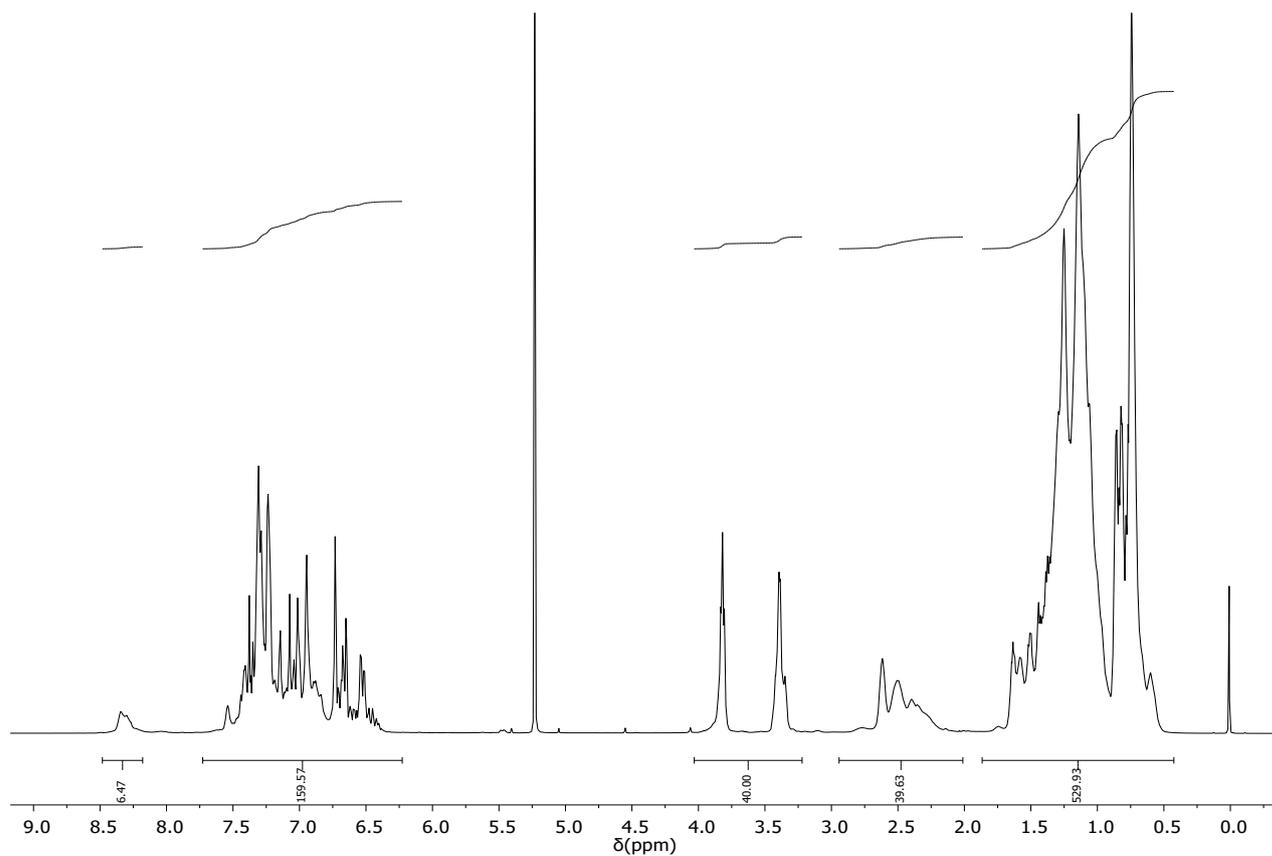


**Figure S5.** ¹H NMR spectrum of BCP **2** in DCM-*d₂*
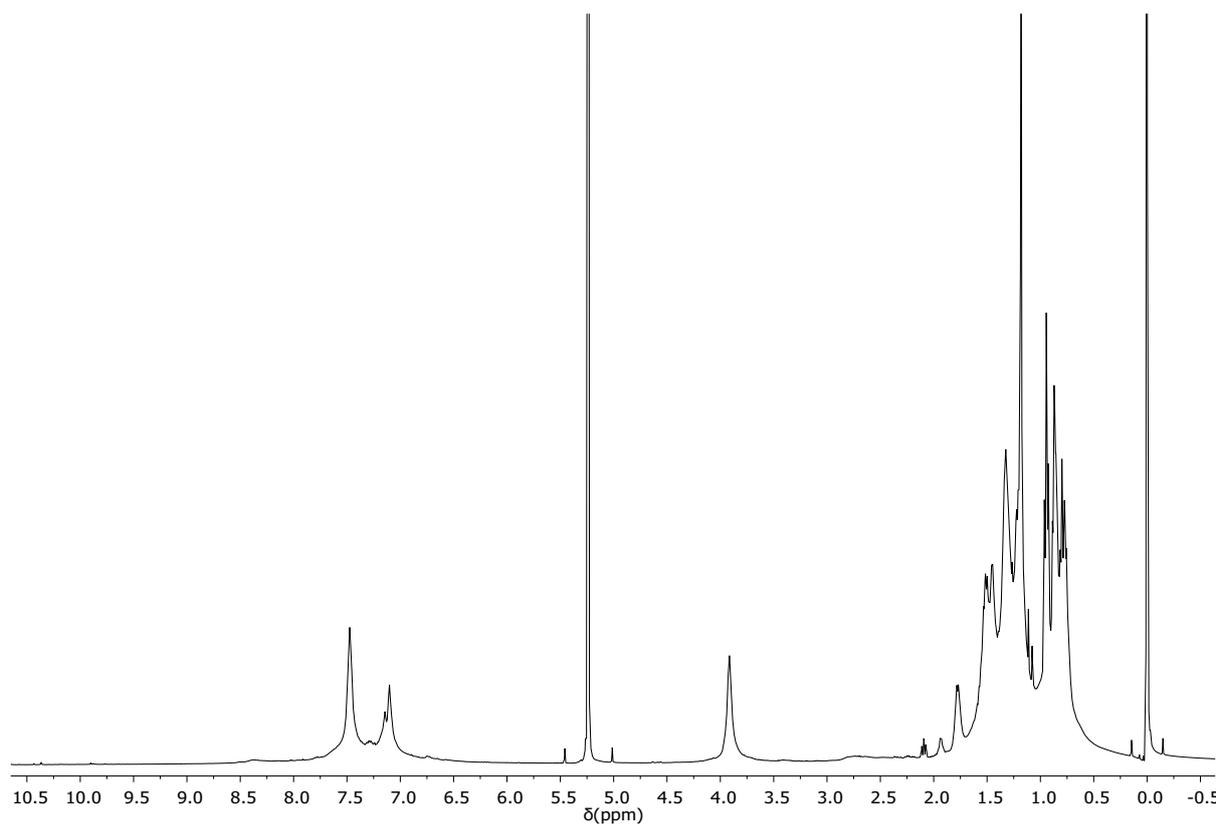
**Figure S6.** $^1$H NMR spectrum of *trans*-**2** in DCM-$d_2$
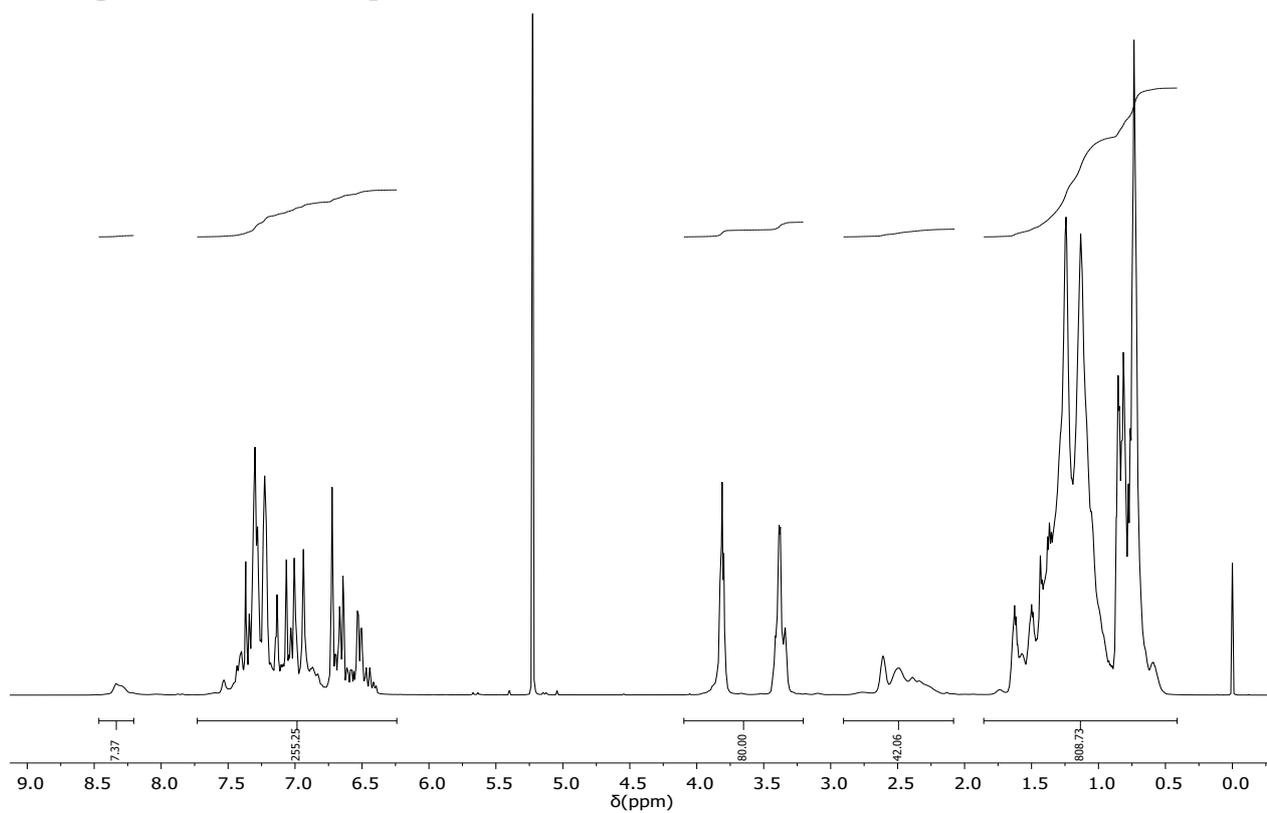


**Figure S7.** $^1$H NMR spectrum of BCP **3** DCM-$d_2$
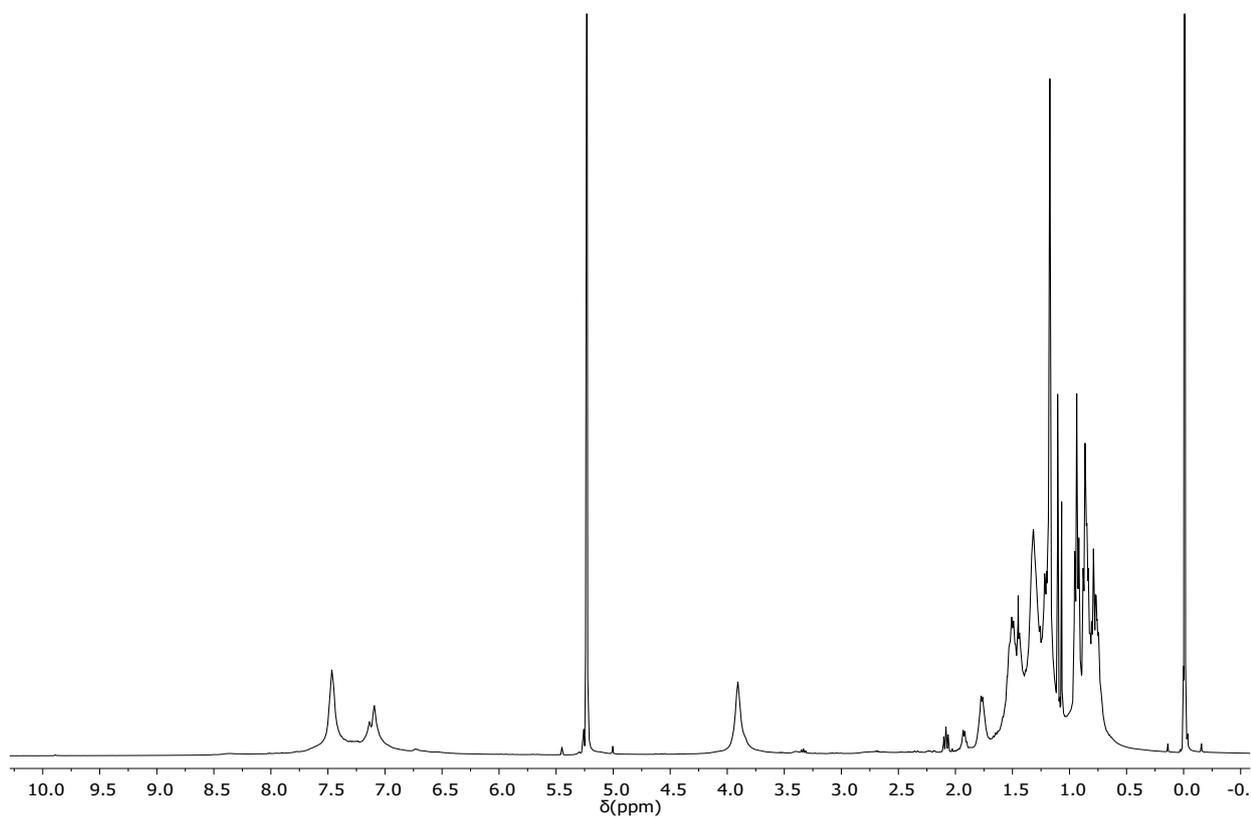
**Figure S8.** $^1$H NMR spectrum of *trans*-**3** in DCM-$d_2$
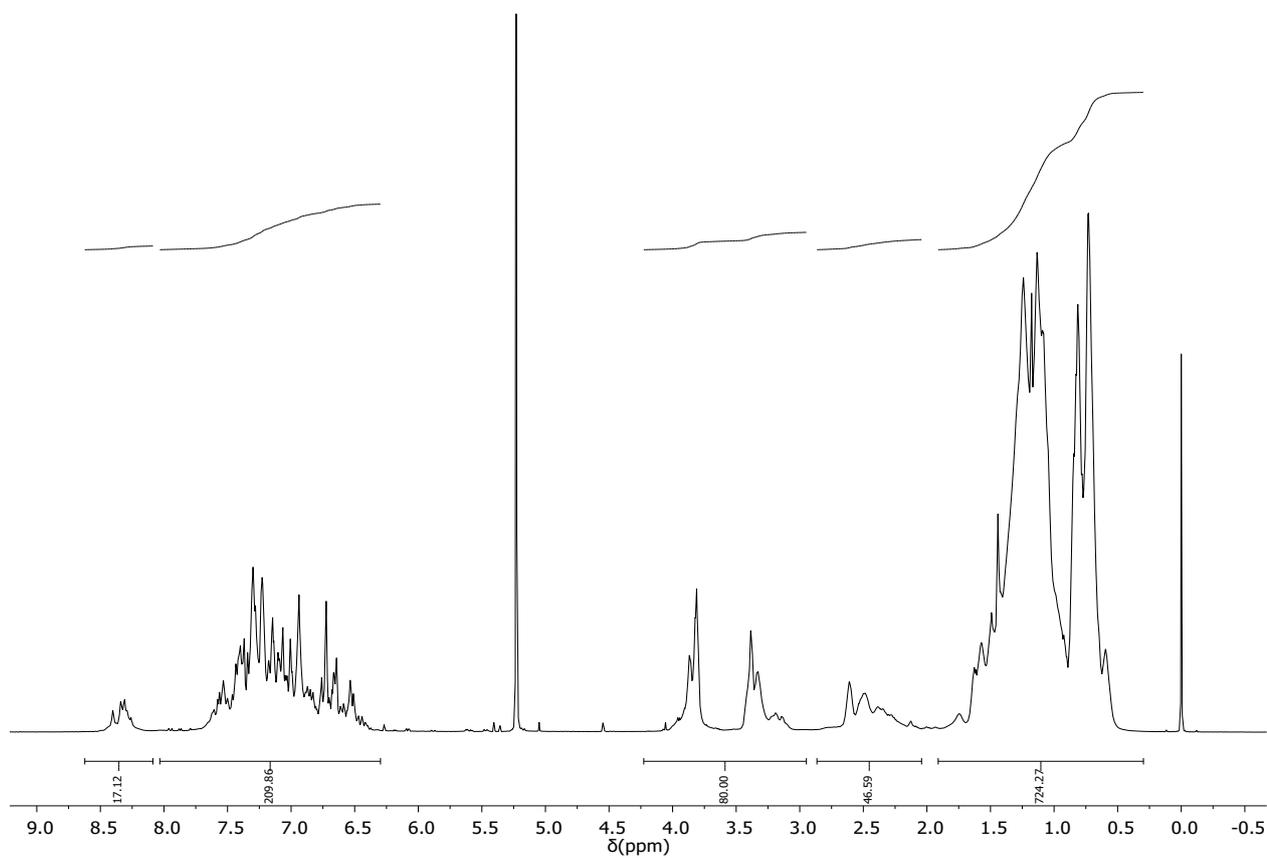


**Figure S9.** $^1$H NMR spectrum of BCP **4** in DCM-$d_2$
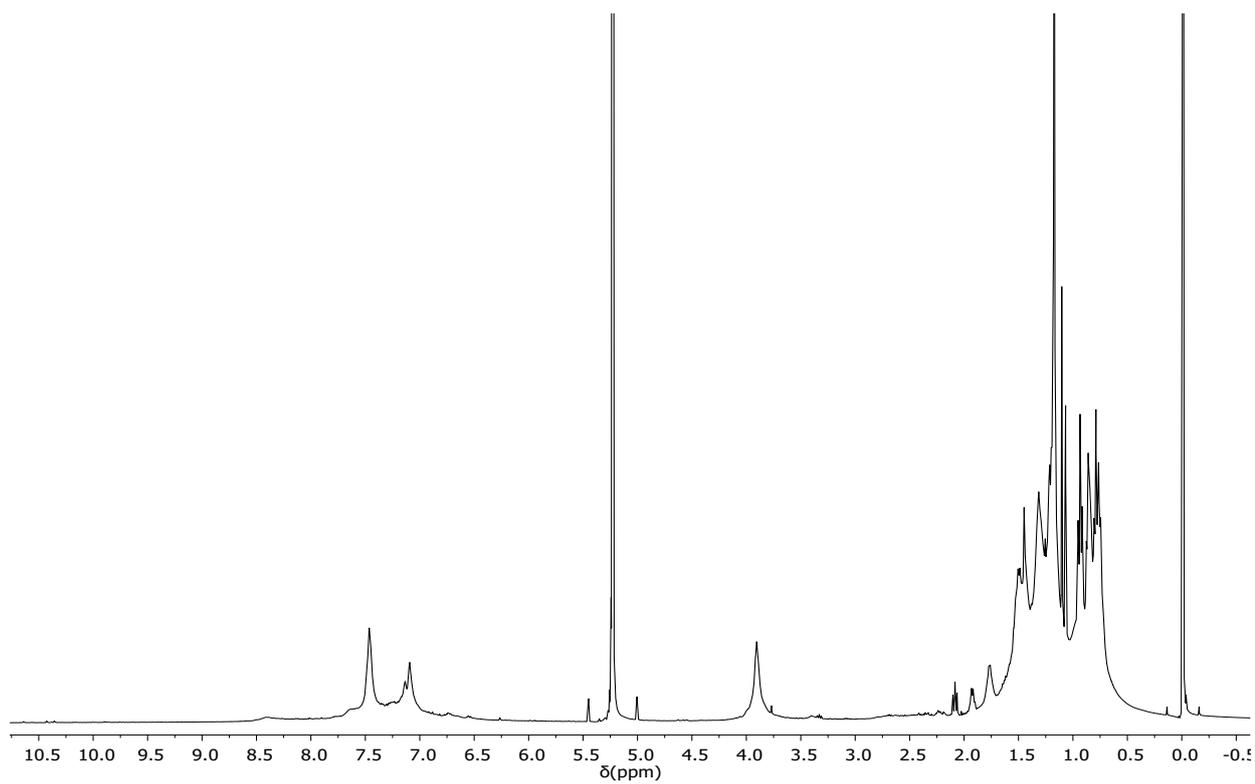
**Figure S10.** $^1$H NMR spectrum of *trans*-**4** in DCM-$d_2$
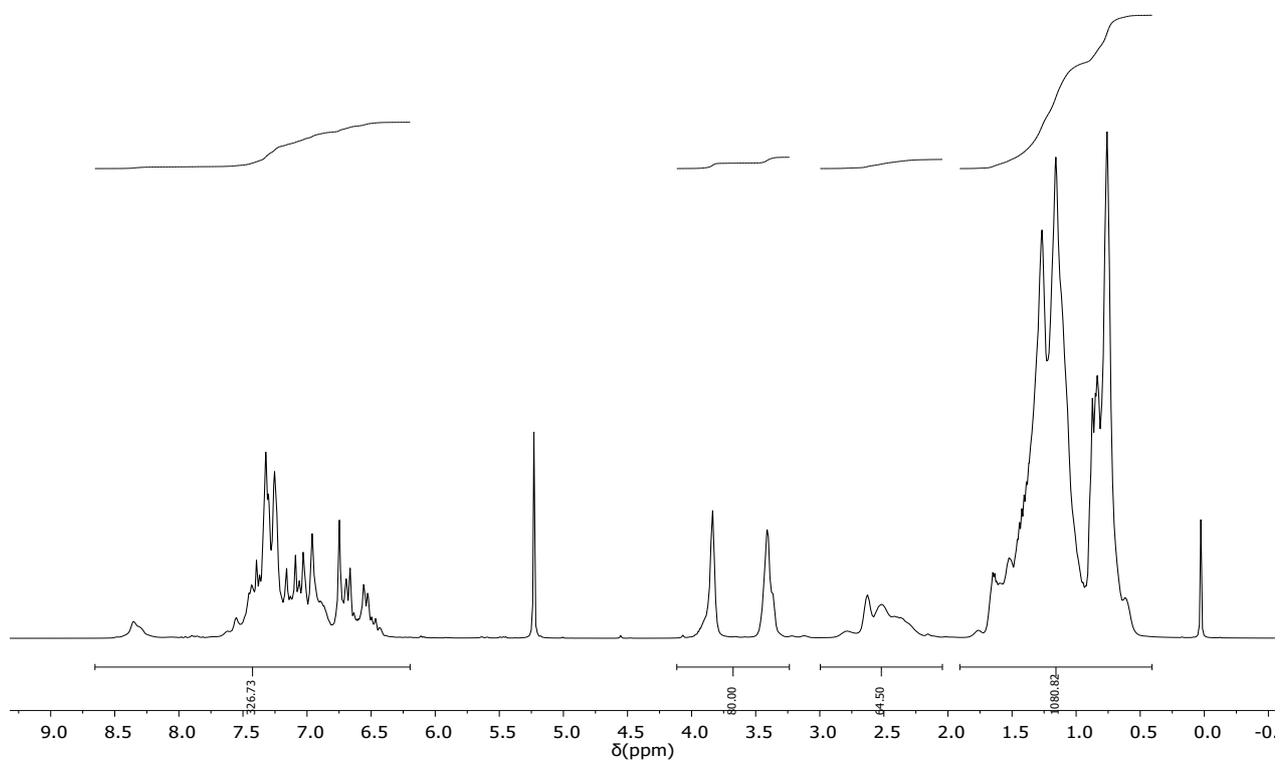


**Figure S11.** $^1$H NMR spectrum of BCP **5** in DCM-$d_2$
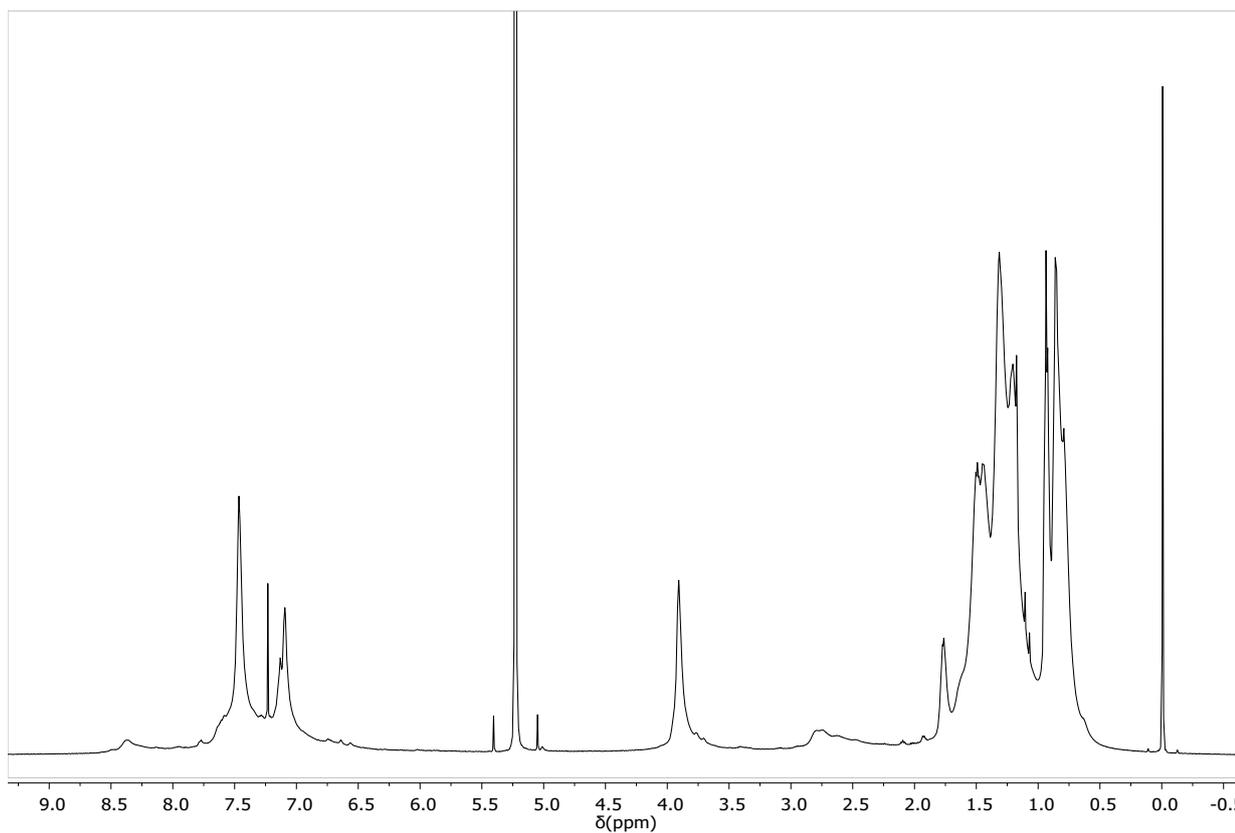
**Figure S12.** $^1$H NMR spectrum of *trans*-**5** in DCM-$d_2$

## Optical properties of block copolymers 2-5:
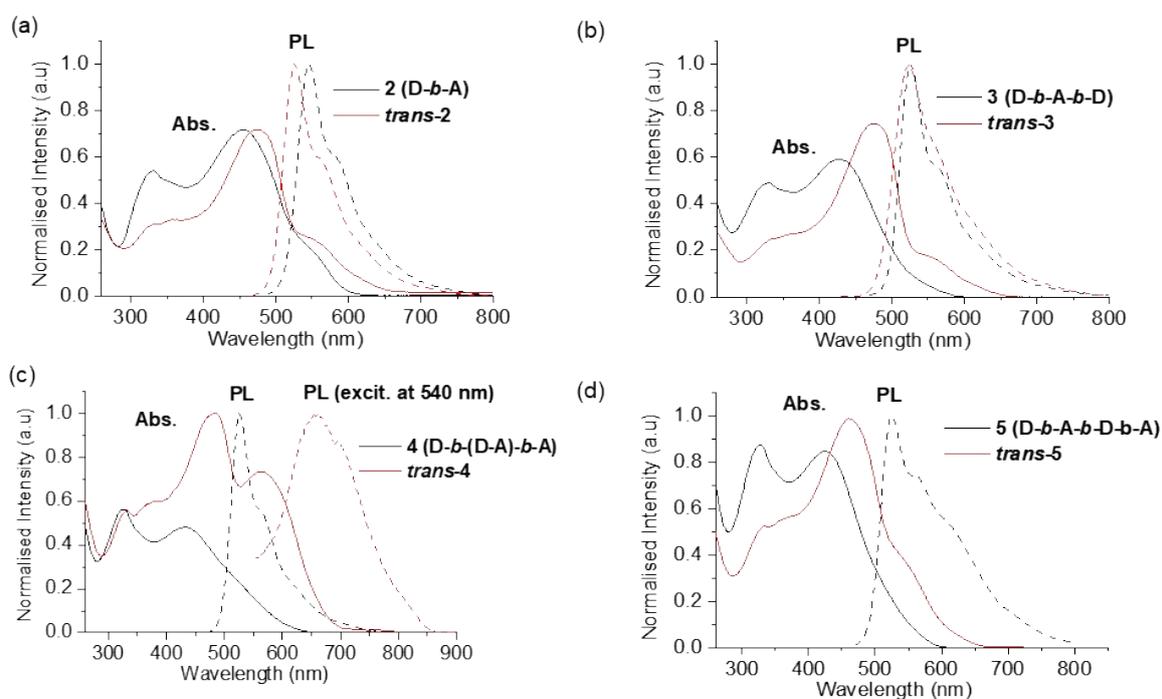


**Figure S13**. Absorption and emission profiles of *cis/trans* and all-*trans* block copolymers (a) **2**, (b) **3**, (c) **4** and (d) **5** in CHCl$_3$
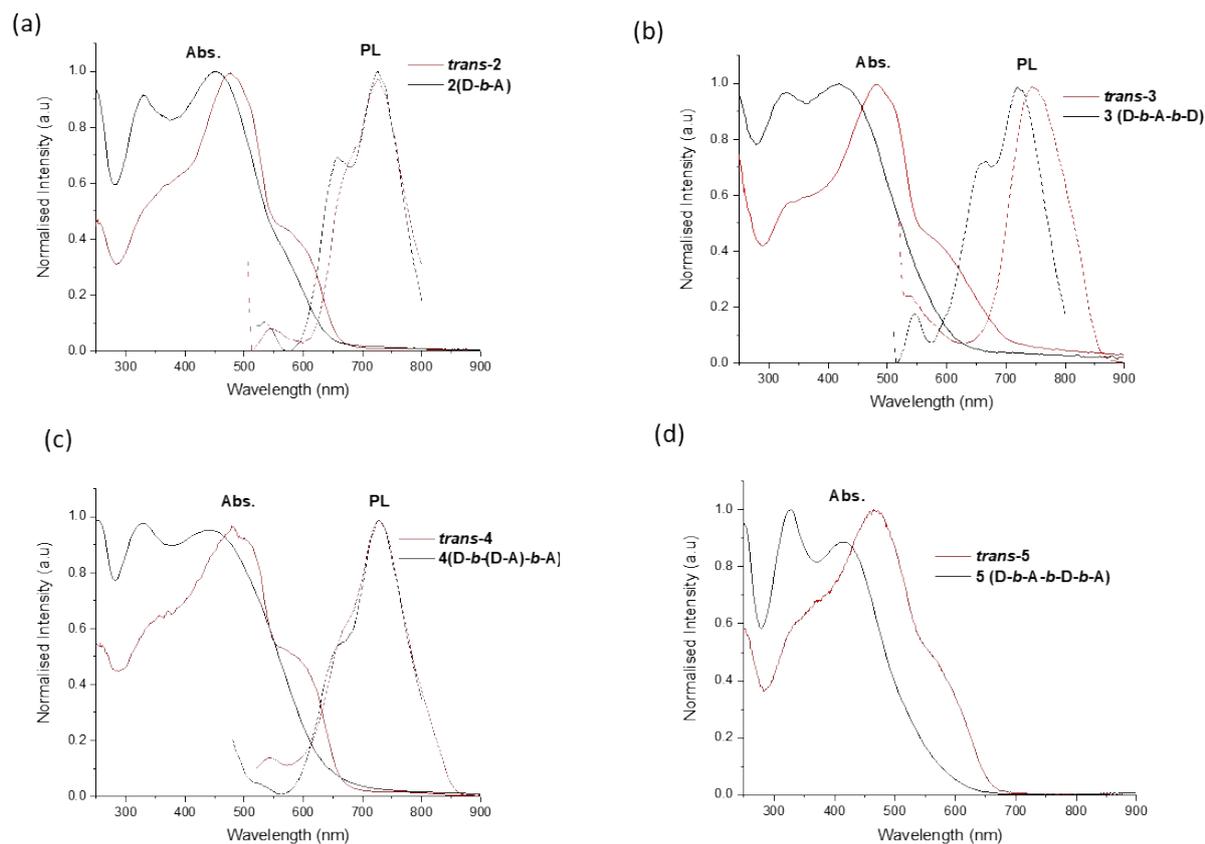
**Figure S14**. Absorption and emission profiles of block copolymers (a) **2**, (b) **3**, (c) **4** and (d) **5** in thin film

**Table S2**: UV-vis and PL data of BCPs **2-5** in chloroform solution and in solid state

| BCP | $\lambda_{\max(abs.)}$ (solution) | $\lambda_{\max(abs.)}$ (thin film) | $\lambda_{(excit.)}$ | $\lambda_{\max(PL)}$ (solution) | $\lambda_{\max(PL)}$ (thin film) | $\emptyset_{PL}(\%)$ | $\lambda_{onset}$ | $E_g$ (eV)[a] |
|---|---|---|---|---|---|---|---|---|
| **2** | 330, 455 | 451 | 440 | 526 (567) | 725 | 16 | 614 | 2.02 |
| *trans-2* | 330, 476 | 476 | 460 | 524 (569) | 725 | 20 | 663 | 1.87 |
| **3** | 330, 430 | 418 | 420 | 525 (566) | 719 | 22 | 593 | 2.09 |
| *trans-3* | 330, 477 (555) | 482 | 460 | 524 (568) | 744 | 30 | 660 | 1.88 |
| **4** | 325, 434 | 427 | 420 | 525 (566) | 727 | 9.3 | 649 | 1.91 |
| *trans-4* | 481 (560) | 483 (560) | 460 | 525 (569) | 727 | 13.3 | 738 | 1.68 |
|  |  |  | 540 | 667 (720) |  |  |  |  |
| **5** | 326, 425 | 327, 416 | 420 | 525 (564) | - | 16 | 605 | 2.05 |
| *trans-5* | 460 | 467 | 450 | 527 (560) | - | 31.5 | 626 | 1.98 |

a. The optical gap ($E_g$) was calculated from the onset of absorption (i.e. $E_g = 1240/\lambda_{onset}$)

**Table S3**: Electrochemical properties of BCPs **2-5** in solid state

| BCP | $[O]_{onset}$ (V) | $[R]_{onset}$ (V) | HOMO (eV)[a] | LUMO (eV)[a] | $E_g$ (eV)[b] |
|---|---|---|---|---|---|
| **2** | 0.63 | 1.28 | -5.36 | -3.45 | 1.91 |
| ***trans*-2** | 0.62 | 1.21 | -5.34 | -3.50 | 1.83 |
| **3** | 0.65 | 1.27 | -5.36 | -3.44 | 1.92 |
| ***trans*-3** | 0.51 | 1.21 | -5.22 | -3.51 | 1.72 |
| **4** | 0.64 | 1.29 | -5.36 | -3.43 | 1.93 |
| ***trans*-4** | 0.57 | 1.18 | -5.29 | -3.54 | 1.75 |
| **5** | 0.67 | 1.23 | -5.36 | -3.49 | 1.87 |
| ***trans*-5** | 0.61 | 1.25 | -5.32 | -3.46 | 1.86 |

a. HOMO= $(E_{ox}{}^{onset} - Fc_{ox}) + 4.8$, LUMO= $(E_{red}{}^{onset} - Fc_{ox}) + 4.8$, b. $E_{g\ (ec.)}$= HOMO-LUMO
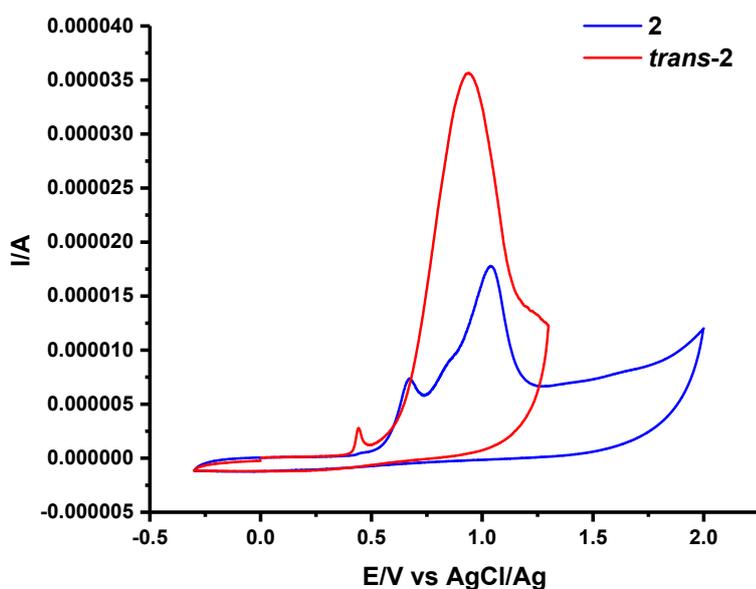


**Figure S15**: Cyclic voltammograms of irreversible oxidation **2** and *trans*-**2** on a Pt electrode in an acetonitrile solution containing 0.1 M n-Bu$_4$NPF
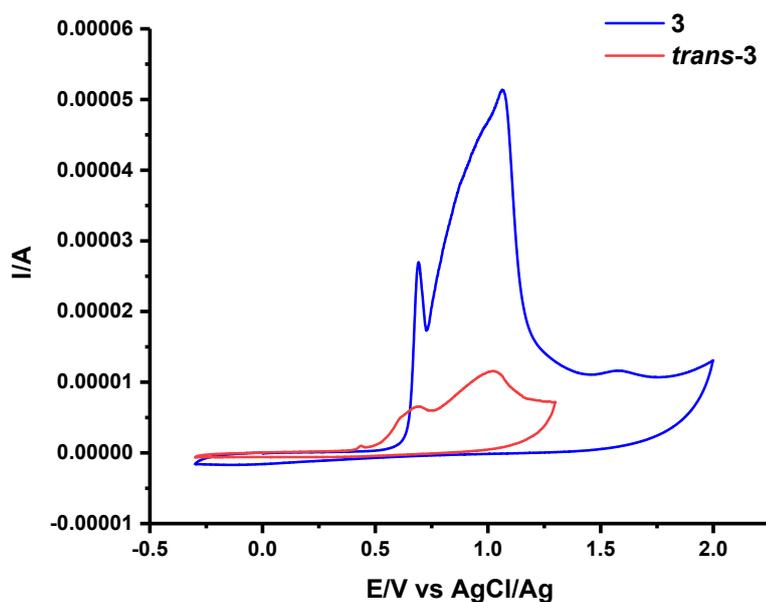
**Figure S16**: Cyclic voltammograms of irreversible oxidation **3** and *trans*-**3** on a Pt electrode in an acetonitrile solution containing 0.1 M n-Bu$_4$NPF
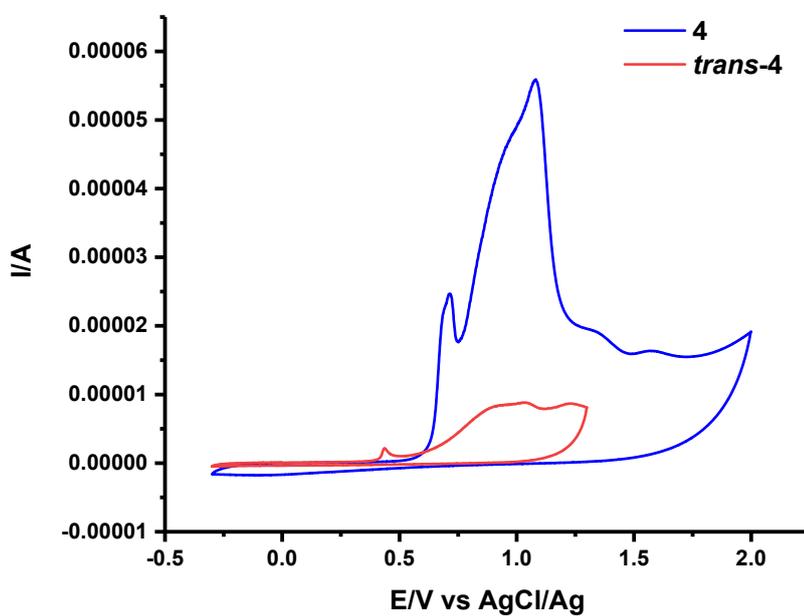


**Figure S17**: Cyclic voltammograms of irreversible oxidation **4** and *trans*-**4** on a Pt electrode in an acetonitrile solution containing 0.1 M n-Bu$_4$NPF
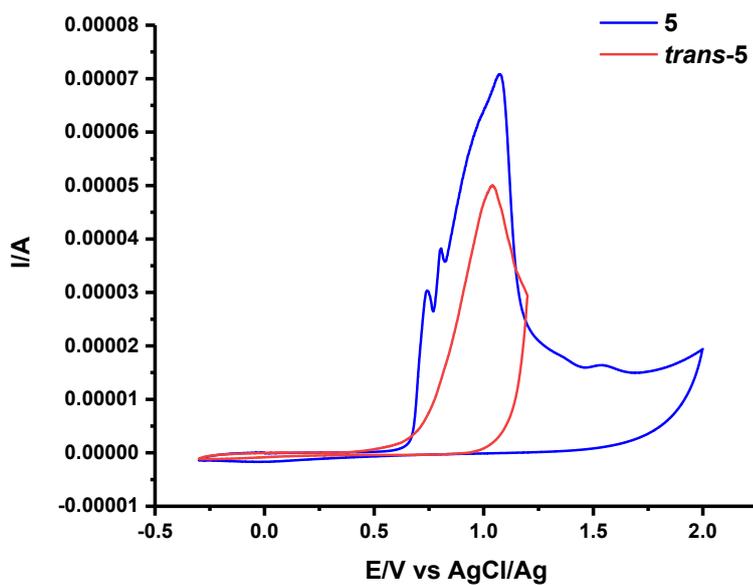
**Figure S18**: Cyclic voltammograms of irreversible oxidation **5** and *trans*-**5** on a Pt electrode in an acetonitrile solution containing 0.1 M n-Bu₄NPF
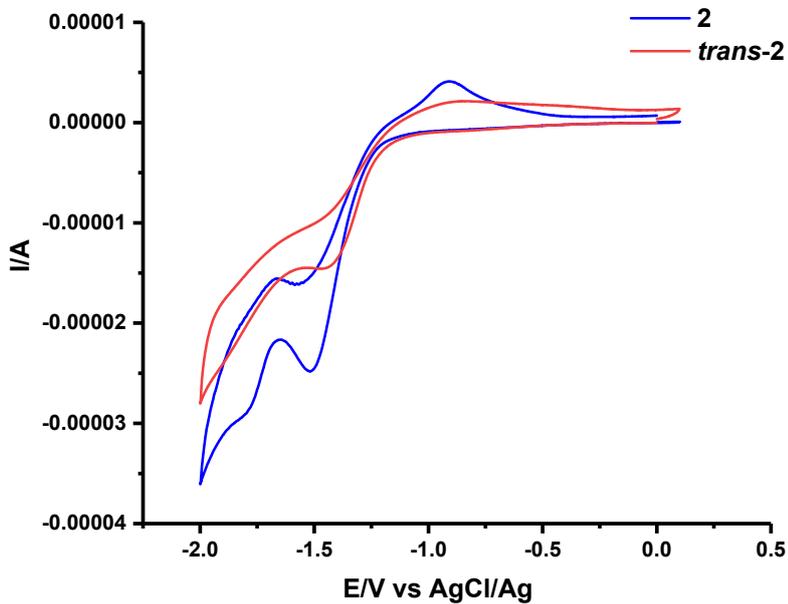


**Figure S19**: Cyclic voltammograms of reversible reduction **2** and *trans*-**2** on a Pt electrode in an acetonitrile solution containing 0.1 M n-Bu₄NPF
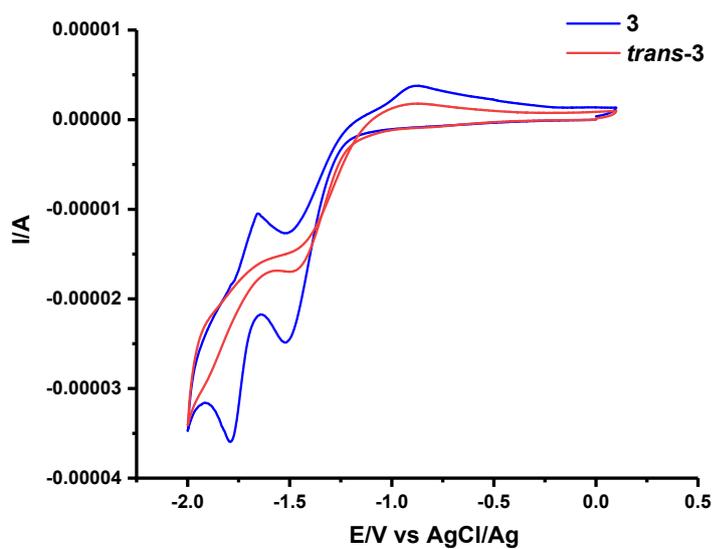
**Figure S20**: Cyclic voltammograms of reversible reduction **3** and *trans*-**3** on a Pt electrode in an acetonitrile solution containing 0.1 M n-Bu$_4$NPF
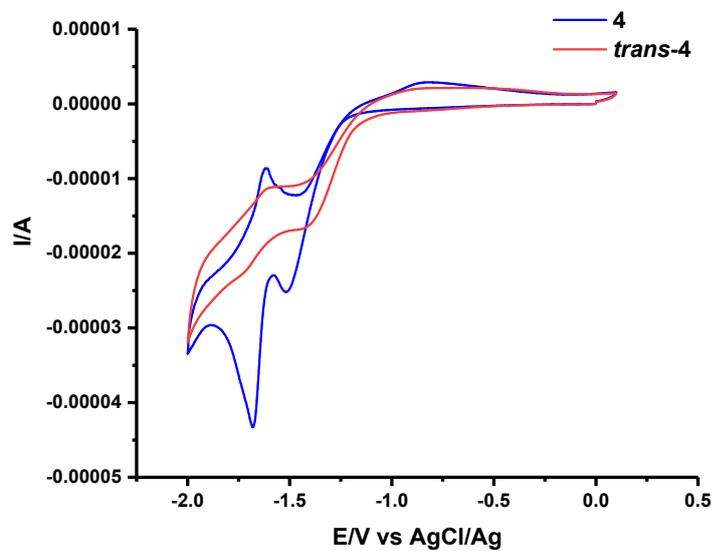


**Figure S21**: Cyclic voltammograms of reversible reduction **4** and *trans*-**4** on a Pt electrode in an acetonitrile solution containing 0.1 M n-Bu$_4$NPF
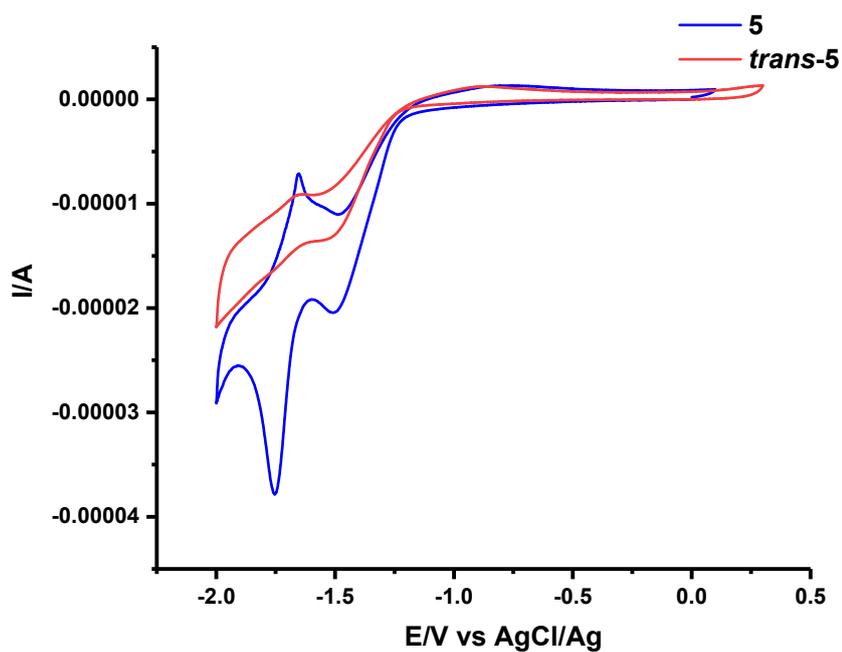
**Figure S22**: Cyclic voltammograms of reversible reduction **5** and *trans*-**5** on a Pt electrode in an acetonitrile solution containing 0.1 M n-Bu$_4$NPF

## References:

[1]     B. J. Lidster, J. M. Behrendt, M. L. Turner, *Chem. Commun.* **2014**, *50*, 11867-11870.

[2]     V. Komanduri, D. J. Tate, R. Marcial-Hernandez, D. R. Kumar, M. L. Turner, *Macromolecules* **2019**, *52*, 7137-7144.