## **Supporting Information**

# Bidirectional ROMP of Paracylophane-1,9-dienes to Tri- and Penta-Block *p*-Phenylenevinylene Copolymers

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## General experimental details for synthesis:

Nuclear magnetic resonance (NMR) spectra were obtained on either 400 MHz or 500 MHz Brucker spectrometers. Chemical shifts are reported in ppm relative to the indicated residual solvent (<sup>1</sup>H NMR spectroscopy; 7.26 ppm for chloroform-*d* and 5.23 ppm for dichloromethane- $d_2$ . The longitudinal relaxation time constant (T1) for the paracyclophanediene monomers **M1**, **M2**, and catalyst **1** 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. <sup>13</sup>C NMR spectroscopy; 77.16 ppm for chloroform-*d*). The

following abbreviations are used to indicate the multiplicity of the signals; s = singlet, d = doublet, m = multiplet, brm = broad multiplet. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was conducted using a Shimadzu Biotech AXIMA Confidence MALDI mass spectrometer in linear (positive) mode, referencing against poly(propylene glycol),  $M_n = 4.0 \text{ kg mol}^{-1}$ . 50 µL of polymer solution (1 mg mL<sup>-1</sup> in THF) was mixed with 50 µL of a 10 mg mL<sup>-1</sup> solution of the matrix (dithranol) in THF. A drop of this solution was spotted onto a MALDI plate and the solvent allowed to evaporate at room temperature. Elemental compositions of carbon, hydrogen and sulfur atoms were measured using a Flash 2000 Organic Elemental Analyser (Thermo Scientific). Elemental composition of bromine was determined by titration against silver nitrate using an 888 Titrando (Metrohm). Nominal and high resolution electrospray mass spectrometry were carried out using SQD2 and QTOF Spectrometers (Waters). Infrared spectroscopy was conducted using a Nicolet iS5 (Thermo Scientific) with iD5 ATR accessory. Gel permeation chromatography (GPC) was conducted in THF using a ViscotekGPCmax VE2001 solvent/sample module with 2  $\times$ PL gel 10 µm MIXED-B + 1 × PL gel 500A columns, a Viscotek VE3580 RI detector and a VE 3240 UV-Vis multichannel detector. The flow rate was 1 mL min<sup>-1</sup> and the system was calibrated with narrow PDI polystyrene standards in the range of 0.2 - 1,800 kg mol<sup>-1</sup> 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 on Fluorimeter using integration sphere. Slow additions were performed using a 205S Watsons-Marlow peristaltic pump.

THF was distilled over sodium/benzophenone and all other 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. Degassed solvents were prepared either by purging with argon/nitrogen or by freeze-pump-thaw (three times) for reactions involving organometallic reagents.

#### Preparation of bifunctional Hoveyda-Grubbs catalyst 1<sup>[1]</sup>



Synthesis of 1,4-dimethoxy-2,5-divinylbenzene 3: To a stirred degassed solution of 1,4dimethoxy-2,5-dibromobenzene 2 (1010 mg, 3.38 mmol, 1.0 eq.) and *n*-tributylvinylstannane (2790)8.79 2.6 toluene (20mL) mg, mmol, eq.) in anhydrous tetrakis(triphenylphosphine)palladium(0) catalyst (195 mg, 0.168 mmol, 0.05 eq.) was added, the reaction mixture was purged with argon (5 min) and stirred at 100 °C for 12h. Upon consumption of 2 (TLC) the reaction mixture was cooled to ambient temperature, poured into a beaker containing 1N NaOH (aq.) solution and stirred for 1h. The reaction mixture was partitioned between 30% ethylacetate/petroleum ether (2x50 mL) and water (100 mL). The organic layer was washed with water (50 mL), brine (50 mL) followed by drying (anhydrous MgSO<sub>4</sub>). The solution was concentrated under reduced pressure and the crude was purified by silica gel flash column chromatography (0.5% ethyl acetate/petroleum ether) to obtain the desired product **3** (475 mg, 74% yield) as a pale yellow solid. MS (APCI):191[M+H]<sup>+</sup>, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ 7.06 (d, J=10.0 Hz, 1H), 7.02 (d, J=10.0 Hz, 1H), 7.00 (s, 2H), 5.74 (dd, J=20, 5 Hz, 2H), 5.28 (dd, J=10, 5 Hz, 2H), 3.84 (s, 6H), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 **MHz**): δ 151.3, 131.5, 127.1, 114.5, 109.5, 56.4.

Synthesis of catalyst 1: A Schlenk flask was charged with intermediate 3 (63 mg, 0.33 mmol, 1.0 eq.), G2 (510 mg, 0.60 mmol, 1.8 eq.) and HCl (0.3 mL, 2M solution in diethyl ether) in degassed anhydrous ethyl acetate (10 mL) in an argon filled glove box. The flask was taken out of glove box, covered with alumnium foil and stirred at ambient for 5h. The reaction mixture was filtered on a small Schott filter and the resulting green powder was washed with ethyl acetate (50 mL) until the filtrate was almost colourless. The precipitate was redisolved in a dichloromethane/ethyl acetate solvent mixture (35/5 mL) and slowly evaporated on rotary evaporator at ambient temperature to a lower volume (~5 mL). The precipitate was filtered, washed with methanol (50 mL) and dried to obtain the desired catalyst1 (0.142g, 40% yield) as a dark green solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ 16.02 (*s*, 2H), 6.97 (*s*, 8H), 6.23 (*s*, 2H), 4.08-3.95 (m, 16H), 3.73-3.61 (m, 12H), 2.43-2.20 (m, 36H), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ 208.5, 141.0, 138.7, 138.6, 129.4, 103.2, 58.3, 51.7, 20.8, 18.9.



Figure S1. <sup>1</sup>H NMR spectrum of catalyst 1 in DCM- $d_2$ 



Figure S2. <sup>13</sup>C NMR spectrum of catalyst 1 in DCM- $d_2$ 

#### ROMP of monomers M1 and M2 with catalyst 1- in-situ <sup>1</sup>H NMR experiments

General experimental procedure: Monomer **M** (30 mg, 0.065 mmol, 100 mol%) and Hoveyda-Grubbs bifunctional catalyst **1** (6.43 mg, 0.006 mmol, 10 mol%) were added into separate vials and transferred into an argon filled glovebox. **1** was dissolved in tetrachloroethane- $d_2$  ([**M**] = 100 mM) and the solution was transferred to the vial containing **M** and mixed until homogenous. The solution was transferred into a Young's NMR tube, sealed, removed from the glovebox and kept in an ice bath. The first <sup>1</sup>H NMR spectrum for t=0 was recorded at 25 °C. Then the spectrometer probe was set at 60 °C and the NMR spectra were recorded at every 5 min intervals throughout the ROMP. At the end of the reaction mixture was quenched with ethyl vinyl ether (0.15 mL, 1.56 mmol, 2400 mol%) in a vial and stirred at rt for 4 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 in reduced pressure to give poly(*p*-phenylenevinylene)s as orange or green amorphous films.



**Figure S3. Figure S3.** ROMP of monomer **M1** with bifunctional catalyst **1**; *In-situ*<sup>1</sup>H NMR experiment in TCE- $d_2$  at 60 °C (The carbene signals in the region of  $\delta$ 16.10-17.57 ppm were integrated against TCE-d2 at  $\delta$  5.99 ppm at t=0, 10, 300, 600 min intervals and observed >95% fidelity)



**Figure S4.** ROMP of monomer **M2** with bifunctional catalyst; *In-situ*<sup>1</sup>H NMR experiment in TCE- $d_2$  at 40 °C (The carbene signals in the region of  $\delta$ 16.07-19.55 ppm were integrated against TCE-d2 at  $\delta$  5.99 ppm at t=0, 20, 300, 600 and 1200 min intervals and observed >90% fidelity)

Entry	Monomer	Ligand	Solvent	Т	t	GPC o	GPC data purified <sup>b</sup>		
	[ <b>M</b> ]/[ <b>1</b> ]=1	а	[0.1 M]	(°C	(h)	M <sub>n(calc.)</sub>	$M_{n(obs.)}(kD)$	$\overline{\mathbf{D}}_m$	%
	0	(mol%)		)		(kD)			
1	M1	0	DCM-	25	63	4.7	5.5	1.41	89
			$d_2$						
2	M1	0	TCE- $d_2$	60	10	4.7	5.7	1.40	95
3	M2	0	DCM-	25	1.5	4.4	>79	1.82	-
			$d_2$						
4	M2	40	TCE- $d_2$	40	20	4.4	7.1	1.38	92

a. 3-BrPy was used as ligand b. Mn<sub>(calc.)</sub> was calculated from [monomer]/[catalyst] ratio and Mn<sub>(obs.)</sub> was calculated against polystyrene standards

#### ROMP of monomers M1 and M2 with catalyst 1-bulk experiments

General experimental procedure: In an argon filled glovebox a solution of catalyst 1(6.43 mg, 0.006 mmol, 10 mol%) in anhydrous, degassed TCE ([**M**] = 100 mM) was added into a vial

containing cyclophanediene M1(30 mg, 0.065 mmol, 100 mol%). The vial was sealed, removed from the glovebox, wrapped in foil and mixed at room temperature for 10 minutes. The reaction was placed in a preheated oil bath at 60 °C and stirred until complete monomer conversion was observed by GPC and TLC. The reaction was cooled to room temperature and deoxygenated ethyl vinyl ether (0.15 mL, 1.56 mmol, 2400 mol%) was added and stirred at room temperature for 4 h. The reaction was precipitated into a short methanol/Celite column, washed with methanol and the polymer extracted with chloroform. The chloroform layer was evaporated in reduced pressure to give poly(p-phenylenevinylenes) as orange or green amorphous films.

(In case of alkyl monomer **M2**, external ligand 3-BrPyr (40 mol%) was added to a solution of catalyst **1** in anhydrous dichloromethane and stirred for 15-20 min at ambient temperature before adding into a vial containing the monomer followed by stirring the reaction mixture at 40 °C.)

#### Cis-trans isomerisation of poly(p-phenylenevinylene)s

General experimental procedure: Degassed dilute solutions of *p*-phenylenevinylene polymers in DCM (1 mg/mL) were subjected to photoisomerisation by exposing to UV irradiation at 365 nm for 24-72h. Solvent evaporation by purging nitrogen followed by drying under high vacuum for 16 h gave *all trans*-polymers as orange solids in quantitative yields. <sup>1</sup>H NMR of the solids in  $CD_2Cl_2$  showed complete isomerisation of olefin double bonds to *trans* geometry.

Entry	Polymer	[Monomer]/	Ligand	Solvent	Т	t	GPC d	lata purified <sup>b</sup>		Yield
		[catalyst]	а	[0.1 M]	(°C	(h)	M <sub>n(calc.)</sub>	$M_{n(obs.)}(kD)$	$D_{\rm m}$	%
			(mol%)		)		(kD)			
1	2a	[ <b>M1</b> ]/[ <b>1</b> ]=1	0	TCE	60	8	4.7	5.2	1.35	96
		0								
2	2b	[ <b>M1</b> ]/[ <b>1</b> ]=1	0	TCE	60	12	7.1	6.9	1.37	94
		5								
3	2c	[ <b>M1</b> ]/[1]=2	0	TCE	60	16	9.3	9.2	1.46	93
		0								
4	3a	[ <b>M2</b> ]/[ <b>1</b> ]=1	40	TCE	40	8	4.4	6.6	1.41	75
		0								
5	3a	[ <b>M2</b> ]/[ <b>1</b> ]=1	40	DCM	40	8	4.4	5.4	1.48	95
		0								
6	3b	[ <b>M2</b> ]/[1]=2	40	DCM	40	12	8.7	11.4	1.58	84
		0								
7	3c	[ <b>M2</b> ]/[1]=3	40	DCM	40	12	13.0	15.2	1.59	81

Table S2: ROMP of monomers M1 and M2in bulk with catalyst 1

		0								
8°	4a	[ <b>M1</b> ]/[ <b>1</b> ]=1	0	TCE	60	8	5.3	5.8	1.34	95
		0								
9 <sup>d</sup>	5a	[ <b>M2</b> ]/[ <b>1</b> ]=1	40	DCM	40	8	4.9	6.7	1.57	98
		0								

a. 3-BrPy was used as ligand b.  $Mn_{(calc.)}$  was calculated from [monomer]/[catalyst] ratio and  $Mn_{(obs.)}$  was calculated against polystyrene standards c. f > 89% and d. f > 75%



Figure S5. <sup>1</sup>H NMR spectrum of PPV 2a in DCM- $d_2$ 



Figure S6. <sup>1</sup>H NMR spectrum of *trans*-2a in DCM- $d_2$ 



Figure S7. <sup>1</sup>H NMR spectrum of PPV **2b** in DCM- $d_2$ 



Figure S8. <sup>1</sup>H NMR spectrum of PPV *trans*-2b in DCM- $d_2$ 

trans-2b



Figure S9. <sup>1</sup>H NMR spectrum of PPV 2c in DCM- $d_2$ 



Figure S10. <sup>1</sup>H NMR spectrum of PPV *trans*-2c in DCM- $d_2$ 



Figure S11. <sup>1</sup>H NMR spectrum of PPV 3a in DCM- $d_2$ 



Figure S12. <sup>1</sup>H NMR spectrum of *trans*-3a in DCM- $d_2$ 

trans-3a



Figure S13.<sup>1</sup>H NMR spectrum of PPV 3b in DCM- $d_2$ 



Figure S14. <sup>1</sup>H NMR spectrum of PPV *trans*-3b in DCM- $d_2$ 



ure S15. <sup>1</sup>H NMR spectrum of PPV 3c in DCM- $d_2$ 





Figure S17. <sup>1</sup>H NMR spectrum of  $\alpha$ -bromoester end capped PPV 4a in DCM- $d_2$ 



Figure S18. <sup>1</sup>H NMR spectrum of  $\alpha$ -bromoester end capped PPV 5a in DCM- $d_2$ 



**Figure S19.** MALDI-TOF-MS profile of *α*-bromoester end capped PPV **5a** (TCNQ matrix)



10



Figure S20. <sup>1</sup>H NMR spectrum of  $\alpha$ -bromoester end capped BCP 10 (m=5) in DCM- $d_2$ 

## ATRP of macroinitiators 4a, 5a and 10-synthesis of *coil-rod-coil* triblock and *coil-rod-rod-coil* pentablock copolymers

General experimental procedure for the synthesis of ABA triblock copolymers 6a-c:

In an argon filled glove box,  $\alpha$ -bromoester bifunctionalised poly(*p*-phenylenevinylene-2,5diethylhexyloxy-*p*-phenylenevinylene) (**4a**, n=10) (30 mg, 5.6 µmol), CuBr (3.26 mg, 22.76 µmol, 4 eq.), methyl methacrylate (0.36 mL, 3.36mmol, 600 eq.) were dissolved into degassed toluene (0.72 mL) in a glass vial containing a magnetic stir bar. The vial was tightly sealed and placed in a preheated oil bath set at 90 °C. After 5 min, a solution of *N*-(*n*-propyl)-2-pyridylmethanimine (6.75 mg, 45.5 µmol, 8 eq.) in toluene (0.1 mL) was added into the reaction with stirring. On addition of ligand the reaction mixture turned dark brown. To obtain block copolymers with different chain lengths of MMA, aliquots were taken out from the reaction mixture at different intervals (30, 90, 180 min) and exposed to air followed by precipitation into methanol three times. The solids were redissolved in chloroform and precipitated by addition of diethyl ether. Upon filtration, PMMA-*b*-(alkoxy)PPV-*b*-PMMA triblock polymers **6a-c** were obtained as orange solids.

General experimental procedure for the synthesis of *coil-rod-coil* ABA triblock copolymers **7a-c:** In an argon filled glove box,  $\alpha$ -bromoesterbifunctionalized poly(*p*-phenylenevinylene-2,5-dioctyl*p*-phenylenevinylene) (**5a**, n=10) (30 mg, 6 µmol), CuBr (3.4 mg, 48 µmol, 4 eq.), methyl methacrylate (0.37 mL, 3.6 mmol, 600 eq.) were dissolved into degassed toluene (0.75 mL) in a glass vial containing a magnetic stir bar. The vial was tightly sealed placed on a preheated oil bath set at 90 °C. After 5 min, a solution of *N*-(n-propyl)-2-pyridylmethanimine (7.56 mg, 48 µmol, 8 eq.) in toluene (0.1 mL) was added into the reaction mixture with stirring. On the addition of ligand the reaction mixture turned dark brown. To obtain block copolymers with different chain lengths of MMA, aliquots were taken out from the reaction mixture at different intervals (30, 90, 180 min) and exposed to air followed by precipitation into methanol three times. The solids were redissolved in chloroform and precipitated by addition of diethyl ether. Upon filtration, PMMA-*b*-(alkyl)PPV-*b*-PMMA triblock polymers **7a-c** were obtained as yellow solids.

General experimental procedure for the synthesis of *coil-rod-rod-coil* ABABA and CBABC pentablock copolymers **11a-c**:

In an argon filled glove box, macroinitiator **10** (36 mg, 3.82  $\mu$ mol), CuBr (2.2 mg, 15.30  $\mu$ mol, 8 eq.), methyl methacrylate (1.0 mL, 5.72 mmol, 1200 eq.) were dissolved into degassed toluene (0.9 mL) in a glass vial containing a magnetic stir bar. The vial was tightly sealed and taken out of glove box and placed on a preheated oil bath set at 90 °C. After 5 min, a solution of *N*-(n-propyl)-2-pyridylmethanimine (4.52 mg, 30.5  $\mu$ mol, 8 eq.) in toluene (0.1 mL) was added into the reaction mixture with stirring. On the addition of ligand the reaction mixture turned dark brown. To obtain block copolymers with different chain lengths of MMA, aliquots were taken out from the reaction mixture at different intervals (60, 120, 180 min) and exposed to air followed by precipitation into methanol three times. The solids were redissolved in chloroform and precipitated by addition of diethyl ether. Upon filtration, PMMA-*b*-(alkyl)PPV-*b*-PMMA triblock polymers **13a-c** were obtained as yellow solids.

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Block copolymer	Time	$M_{n\left(\text{GPC}\right)}$	$M_{n(1\mathrm{H}\mathrm{NMR})}$	$D_m$						
	(Min)	(kD)	(kD)							
<b>4a,</b> Alkoxy PPV <sub>10</sub>	0	5.77	4.97	1.34						
<b>6a</b> , PMMA <sub>8</sub> -alkoxyPPV <sub>10</sub> -PMMA <sub>8</sub>	30	7.33	6.50	1.32						
<b>6b,</b> PMMA <sub>111</sub> -alkoxyPPV <sub>10</sub> -PMMA <sub>111</sub>	90	28.23	27.10	1.32						
<b>6c,</b> PMMA <sub>167</sub> -alkoxyPPV <sub>10</sub> -PMMA <sub>167</sub>	180	38.37	38.37	1.33						
<b>5a,</b> Alkyl PPV <sub>10</sub>	0	7.52	4.47	1.47						

Table S3: ATRP of macroinitiators 4a, 5a and 10-Synthesis of BCPs 6a-c, 7a-c and 11a-c

<b>7a</b> , PMMA <sub>43</sub> -alkyl PPV <sub>10</sub> -PMMA <sub>43</sub>	30	19.16	13.08	1.23
<b>7b,</b> PMMA <sub>147</sub> -alkyl PPV <sub>10</sub> -PMMA <sub>147</sub>	90	40.57	33.81	1.26
<b>7c,</b> PMMA <sub>168</sub> -alkyl PPV <sub>10</sub> -PMMA <sub>168</sub>	180	48.70	38.21	1.25
<b>10,</b> Alkoxy PPV <sub>5</sub> – <i>b</i> -Alkyl PPV <sub>10</sub> – <i>b</i> -Alkoxy PPV <sub>5</sub>	0	11.77	9.40	1.76
<b>11a,</b> PMMA <sub>10</sub> - <i>b</i> - Alkoxy PPV <sub>5</sub> - <i>b</i> -Alkyl PPV <sub>10</sub> - <i>b</i> -Alkoxy PPV <sub>5</sub> - <i>b</i> -PMMA <sub>10</sub>	60	20.63	11.40	1.49
<b>11b,</b> PMMA <sub>27</sub> - <i>b</i> - Alkoxy PPV <sub>5</sub> - <i>b</i> -Alkyl PPV <sub>10</sub> - <i>b</i> -Alkoxy PPV <sub>5</sub> - <i>b</i> -PMMA <sub>27</sub>	120	21.20	14.80	1.35
<b>11c,</b> PMMA <sub>102</sub> - <i>b</i> - Alkoxy PPV <sub>5</sub> - <i>b</i> -Alkyl PPV <sub>10</sub> - <i>b</i> -Alkoxy PPV <sub>5</sub> - <i>b</i> -PMMA <sub>102</sub>	180	36.53	29.80	1.25





Figure 21.GPC traces for *coil-rod-coil* triblock (**6a-c**&7**a-c**) and *coil-rod-rod-coil* pentablock copolymers (**11b-c**)



Figure S22. <sup>1</sup>H NMR spectrum of BCP 6a in DCM- $d_2$ 



Figure S23. <sup>1</sup>H NMR spectrum of BCP 6b in DCM- $d_2$ 



e S25. <sup>1</sup>H NMR spectrum of BCP 7a in DCM- $d_2$ 



Figure S26. <sup>1</sup>H NMR spectrum of BCP 7b in DCM- $d_2$ 



Figure S27. <sup>1</sup>H NMR spectrum of BCP 7c in DCM- $d_2$ 



Figure S28. <sup>1</sup>H NMR spectrum of BCP 11a in DCM- $d_2$ 



Figure S29. <sup>1</sup>H NMR spectrum of BCP 11b in DCM- $d_2$ 



Figure S30. <sup>1</sup>H NMR spectrum of BCP 11c in DCM- $d_2$ 

## Sequential ROMP of monomers M1 and M2-synthesis of fully conjugated rod type tri and pentablock copolymers

General experimental procedure: In an argon filled glovebox a solution of catalyst 1(3.2 mg, 0.003 mmol, 10 mol%) in anhydrous, degassed TCE (0.32 mL, [M] = 100 mM) was added cyclophanediene monomer M1(15 mg, 0.032mmol, 100 mol%). into a vial containing The vial was sealed, wrapped in foil and mixed at room temperature for 10 minutes. The reaction was placed in a preheated oil bath at 60 °C and stirred until consumption of the monomer was observed (GPC and TLC). The reaction mixture was cooled to rt, 3-BrPy (~1.2 µL, 40 mol%) was added and stirred for 15-20 min followed by addition of the second monomer M2 (30 mg, 0.067 mmol, 200 mol%) in TCE (0.33 mL). The reaction mixture was stirred at 40 °C until the consumption of the monomer (GPC and TLC) and deoxygenated ethyl vinyl ether (0.15 mL, 1.56 mmol, 2400 mol%) was added followed by stirring at room temperature for 4 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 to obtain desired triblock copolymer as an orange amorphous film.

BCP	Monomer	t	GPC o	lata purifi	ed <sup>c</sup>	Monomer	M <sub>n(calc.)</sub>	%Yield
	ratio	(h) b	M <sub>n(calc.)</sub>	M <sub>n(obs.)</sub>	$\mathbf{D}_m$	ratio ( <sup>1</sup> H NMR)	(kD)	
			(kD)	(kD)			( <sup>1</sup> H NMR)	
8a	[M2]/[M1]=10/10	20	8.92	9.76	1.87	[M2]/[M1]=8/10	8.04	84
8b	[M2]/[M1]=20/10	24	13.21	12.80	1.97	[M2]/[M1]=19/10	12.75	88
8c	[M2]/[M1]=30/10	32	17.45	18.02	1.87	[M2]/[M1]=26/10	15.75	80
9a <sup>a</sup>	[M1]/[M2]=10/10	22	8.92	9.51	1.87	[M2]/[M1]=10/10	8.92	96
9b <sup>a</sup>	[M1]/[M2]=15/10	24	11.23	13.05	1.35	[M2]/[M1]=14/10	10.90	97
9c <sup>a</sup>	[M1]/[M2]=20/10	26	13.53	15.28	1.38	[M2]/[M1]=19/10	13.21	93
<b>12</b> <sup>a</sup>	[M1]/[M2]=15/20	24	15.5	15.1	1.67	[M1]/[M2]=15/19	15.2	90
<b>13</b> <sup>a</sup>	[M1]/[M2]/[M3]=15/10/1	24	17.9	16.7	1.61	[M1]/[M2]/[M3]=15/10/	16.5	80
	0					8		

Table S4: Sequential ROMP of monomers M1, M2 and M3-Synthesis of BCPs 8a-c, 9a-c, 12 and 13

a.3-BrPy was used as ligand, b. The first monomer gets consumed in approximately 8 h, c. M<sub>n(calc.)</sub> was calculated from [monomer]/[catalyst]

ratio and  $M_{n(\textit{obs.})}$  was calculated against polystyrene standards





Figure S31.<sup>1</sup>H NMR spectrum of BCP 8a in DCM- $d_2$ 



Figure S32. <sup>1</sup>H NMR spectrum of *trans*-8a in DCM- $d_2$ 



Figure S33. <sup>1</sup>H NMR spectrum of BCP 8b DCM-*d*<sub>2</sub>



Figure S34. <sup>1</sup>H NMR spectrum of BCP *trans*-8b in DCM-*d*<sub>2</sub>



Figure S35. <sup>1</sup>H NMR spectrum of BCP 8c in DCM- $d_2$ 



Figure S36. <sup>1</sup>H NMR spectrum of BCP *trans*-8c in DCM-*d*<sub>2</sub>



Figure S38. <sup>1</sup>H NMR spectrum of BCP trans-9a in DCM-d<sub>2</sub>



Figure S40. <sup>1</sup>H NMR spectrum of BCP *trans*-9b in DCM-*d*<sub>2</sub>

9b



**Figure S41.** <sup>1</sup>H NMR spectrum of BCP **9c** in DCM- $d_2$ trans-9c



Figure S42. <sup>1</sup>H NMR spectrum of BCP *trans*-9c in DCM-*d*<sub>2</sub>



Figure S43. <sup>1</sup>H NMR spectrum of BCP 12 in DCM- $d_2$ 



Figure S44. <sup>1</sup>H NMR spectrum of BCP *trans*-12 in DCM-*d*<sub>2</sub>



Figure S45. <sup>1</sup>H NMR spectrum of BCP 13 in DCM- $d_2$ 



Figure S46. <sup>1</sup>H NMR spectrum of BCP *trans*-13 in DCM-*d*<sub>2</sub>



**Figure S47.** Consumption of **M1** in the synthesis ABA BCPs **8a-c** (a) GPC profile (b) TLC analysis after 8h (5%EA/PE)



**Figure S48.** Consumption of **M2** in the synthesis BAB BCPs **9a-c** (a) GPC profile (b) TLC analysis after 8h (100%PE)

Optical properties of homo (2a-c&3a-c) and block copolymers (6a-c, 7a-c, 8a-c, 9a-c, 12 and 13)



Figure S49. Absorbance and emission profiles of homopolymers (a)2a-c and (b)3a-c in CHCl<sub>3</sub>



Figure S50. Absorbance and emission profiles of block copolymers (a) 6a-c, (b)7a-c and (c)11a-c in CHCl<sub>3</sub>



**Figure S51**. Absorbance and emission profiles of triblock copolymers (a)**8a-c** and (b)**9a-c** in CHCl<sub>3</sub>



**Figure S52**. Absorbance and emission profiles of rod type pentablock copolymers (a)12 and (b)13 in CHCl<sub>3</sub>

<b>Table S5</b> : UV-vis and PL	data of homopolymers	(2a-c &3a-c) a	and BCPs (6a-c,	7a-c, 8a-c,
9a-c, 12 and 13) in chlorof	orm solution			

Polymer	$\lambda_{max(abs.)}$	$\lambda_{(excit.)}$	$\lambda_{max(PL)}$	Ø <sub>PL</sub> (%)	Eg	Polymer	$\lambda_{max(abs.)}$	$\lambda_{max(excit.)}$	$\lambda_{max(PL)}$	Ø <sub>PL</sub> (%)	Eg
					(eV) <sup>a</sup>						(eV) <sup>a</sup>
2a	423	440	526	57	2.30	MI-10	386	370	518	60	2.34
trans-2a	470	475	527	58	2.28	11a <sup>b</sup>	460	450	522	60	2.30
2b	424	440	525	63	2.30	11b	386	370	520	59	2.32
trans -2b	471	475	527	61	2.27	11c	387	370	520	57	2.32
2c	440	440	526	67	2.29	<b>8</b> a	382, 450	370, 563	524	57	2.31
trans -2c	471	475	526	62	2.27	<i>trans</i> -8a	446	440	527	68	2.30
<b>3</b> a	375	380	497	70	2.50	8b	380, 453	370, 445	524	53	2.27
trans-3a	425	435	491	76	2.46	trans-8b	440	440	522	70	2.29
3b	376	380	494	70	2.47	8c	371, 453	360, 445	522	57	2.27
trans-3b	429	435	486	75	2.43	trans-8c	431	435	518	69	2.31
3c	376	380	491	67	2.45	9a	383	370	521	58	2.33
trans-3c	428	435	490	75	2.42	<i>trans</i> -9a	447	440	524	63	2.30
MI-4a	450	430	526	65	2.53	9b	386	370	519	58	2.32
MI-5a	386	390	492	65	2.55	<i>trans</i> -9b	452	440	525	65	2.28
6a	462	460	527	58	2.33	9c	394	380	523	57	2.30
7a	389	400	491	72	2.55	trans-9c	455	440	527	61	2.26
6b	462	460	527	65	2.32	12	380	370	521	58	2.34
7b	400	400	491	74	2.52	trans-12	445	440	522	66	2.29
6c	459	460	527	65	2.31	13	384	370	523	60	2.31
7c	389	400	491	75	2.52	trans-13	446	440	521	66	2.28

a.  $E_g=1240/\lambda_{onset}$  b. partial isomerisation to the corresponding *trans* isomer



Figure S53. Absorbance and emission profiles of block copolymers (a) 6a-c, (b)7a-c and (c)11a-c in thin film



Figure S54. Absorbance and emission profiles of block copolymers (a) *trans* 8a-c, (b) *trans* 9a-c, (c) *trans*-12 and (d) *trans*-13 in thin film

BCP	$\lambda_{max(abs.)}$	$\lambda_{(excit.)}$	$\lambda_{max(PL)}$	BCP	$\lambda_{\max(abs.)}$	$\lambda_{max(excit.)}$	$\lambda_{max(PL)}$
6a	446	440	568	<i>tran</i> s-9a	451	440	547
6b	449	440	547	<i>tran</i> s-9b	457	450	547
6c	441	440	546	trans-9c	468	440	544
7a	362	360	522	11a	459 <sup>a</sup>	450	547
7b	362	360	510	11b	388	380	547
7c	380	360	514	11c	387	380	549
<b>8</b> a	381	360	566	12	-	-	-
8b	362	360	542	trans-12	458	450	546
8c	377	400	552				
trans-8a	450	440	552	13	-	-	-
trans-8b	450	440	548	trans-13	454	445	543
trans-8c	437	430	541				
9a	378	380	531				
9b	378	380	508				
9c	388	400	562				

Table S6: Solid state UV-vis and PL data of BCPs (6a-c, 7a-c, 8a-c, 9a-c, 12 and 13)

a. partial isomerisation to the corresponding *trans* isomer

Homo	[O] <sub>onset</sub>	[R] <sub>onset</sub>	HOMO	LUMO	Eg	BCP	[O] <sub>onset</sub>	[R] <sub>onset</sub>	НОМО	LUMO	$\mathrm{E}_{\mathrm{g}}$
polymer			(eV) <sup>a</sup>	(eV) <sup>a</sup>	(eV) <sup>b</sup>				(eV) <sup>a</sup>	(eV) <sup>a</sup>	(eV) <sup>b</sup>
2a	0.53	-1.94	-5.14	-2.66	2.48	8a	0.60	-1.85	-5.23	-2.77	2.46
trans-2a	0.37	-1.79	-5.01	-2.84	2.17	<i>trans</i> -8a	-	-	-	-	-
2b	0.53	-1.95	-5.13	-2.66	2.47	8b	0.48	-1.93	-5.12	-2.69	2.43
trans-2b	-	-	-	-	-	<i>trans</i> -8b	0.39	-1.92	-5.03	-2.70	2.33
2c	0.52	-1.93	-5.12	-2.64	2.48	8c	0.39	-1.77	-5.05	-2.78	2.27
trans-2c	-	-	-	-	-	<i>trans</i> -8c	-	-	-	-	-
3a	0.72	-2.04	-5.36	-2.58	2.78	9a	0.45	-1.97	-5.10	-2.67	2.43
trans-3a	0.47	-1.82	-5.10	-2.81	2.29	<i>trans</i> -9a	0.38	-1.88	-5.02	-2.75	2.27
3b	0.71	-1.89	-5.34	-2.73	2.61	9b	0.49	-1.98	-5.14	-2.66	2.48
trans-3b	-	-	-	-	-	<i>trans</i> -9b	0.41	-1.96	-5.05	-2.66	2.39
3c	0.71	-2.00	-5.34	-2.62	2.72	9c	0.49	-2.00	-5.14	-2.60	2.54
trans-3c	-	-	-	-	-	<i>trans</i> -9c	0.38	-1.92	-5.01	-2.70	2.31
						12	0.60	-1.99	-5.14	-2.64	2.50
						trans-12	0.40	-1.94	-5.04	-2.69	2.35
						13	0.48	-1.80	-5.19	-2.79	2.40
						trans-13	0.41	-1.95	-5.05	-2.67	2.38

Table S7: Electrochemical properties of homo and rod type block copolymers

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

## **References:**

[1]

K. Grudzień, M. Malinska, M. Barbasiewicz, Organometallics 2012, 31, 3636-3646.