Electronic Supplementary Information

# A new polymerisation route to conjugated polymers: Regio- and stereoselective synthesis of linear and hyperbranched poly(arylene chlorovinylene)s by decarbonylative polyaddition of aroyl chlorides and alkynes

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### **Experimental section**

### **General information**

Toluene and tetrahydrofuran (THF) were distilled in an atmosphere of nitrogen from sodium benzophenone ketyl immediately prior to use. *o*-Xylene was dried over anhydrous magnesium sulphate. Dichloromethane (DCM) was distilled under nitrogen over calcium hydride. The rhodium complexes  $[Rh(cod)Cl]_{2,1}$   $[Rh(nbd)Cl]_{2,2}$  and  $[RhCp*Cl_{2}]_{2,3}$  were prepared according to the published procedures. Monomers 2 and 4,  $[Rh(cod)(PPh_{3})_{2}]^{+}PF_{6}^{-}$ ,  $[Rh(cod)(PPh_{2})(CH_{2})_{4}(PPh_{2})]^{+}BF_{4}^{-}$ , and other chemicals and reagents were all purchased from Aldrich and used as received without further purification.

 $M_{n,r}$ ,  $M_{w,r}$ , and PDI ( $M_{w,r}/M_{n,r}$ ) values of the polymers were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a Waters 515 HPLC pump, a set of Styragel columns (HT3, HT4, and HT6; molecular weight range  $10^2-10^7$ ), a column temperature controller, a Waters 486 wavelength-tunable UV-vis detector, a Waters 2414 differential refractometer, and a Waters 2475 fluorescence detector. The polymers were dissolved in THF (~2 mg/mL) and filtered through 0.45 µm PTFE syringe-type filters before being injected into the GPC system. THF was used as eluent at a flow rate of 1.0 mL/min. The column temperature was maintained at 40 °C, and the working wavelength of the UV-vis detector was set at 254 nm. A set of monodisperse polystyrene standards (Waters) covering the molecular weight range of  $10^3-10^7$  were used for the molecular weight calibration.  $M_{W,a}$  values of the polymers were determined on a LLS spectrometer (ALV/DLS/SLS-5022F) equipped with a multi- $\tau$  digital time correlator (ALV5000) and a cylindrical 22 mW He–Ne laser ( $\lambda_0 = 632$  nm, Uniphase) as light source. The dn/dC value at 632.8 nm was measured on a Jianke differential refractometer to be 0.244 mL/g in THF at 25 °C.

X-ray diffraction intensity data of the monomer were collected at 173 K on a Bruker-Nonius Smart Apex CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation. The data were processed using the SAINT and SADABS routines, and the structure solution and refinement were carried out by the SHELXTL suite of X-ray programs (version 6.10) (Table S1). IR spectra were recorded on a Perkin-Elmer 16 PC FTIR spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on Bruker ARX 300 or 400 NMR spectrometers using chloroform-*d* as solvent. Optical absorption spectra were measured on a Milton Ray Spectronic 3000 array spectrophotometer. High resolution mass spectra (HRMS) were recorded on a GCT Premier CAB 048 mass spectrometer operating in an electronionization (EI) mode. Thermal gravimetric (TGA) analyses were conducted under nitrogen on a Perkin-Elmer TGA 7 analyzer at a heating rate of 10 °C/min. The thermal transitions were investigated by differential scanning colorimeter (DSC) using a TA Instruments DSC Q1000 at a heating rate of 10 °C/min. Cyclic Voltammetry (CV) measurement of the samples were performed in a three-electrode cell using a CHI-600D Electrochemical Workstation with 0.1 M tetra-*n*-butylammonium  $\frac{2}{2}$ 

hexafluorophosphate  $([n-Bu_4N]^+[PF_6]^-)$  in DCM as electrolyte at a scan rate of 100 mV/s under room temperature by purging Nitrogen before and between the measurement. A platinum wire was used as the counter electrode and a saturated calomel electrode (Hg/HgCl<sub>2</sub>/KCl) (SCE) was used as the reference electrode. The concentrations of the samples are 0.4 mg/mL in DCM. The HOMO energy levels were derived from the onset oxidation potentials (E<sub>onset-ox</sub>) according to the equation: HOMO =  $-(E_{onset-ox} + 4.4)$  eV, which is based on the energy level of SCE of -4.4 eV relative to vacuum.

## Monomer synthesis

Monomers  $\mathbf{1a}^4$  and  $\mathbf{1b}^5$  were prepared according to the literatures. Monomer  $\mathbf{1c}$  was synthesized according to the synthetic route shown in Scheme S1.

Synthesis of 1,2-bis(4-bromophenyl)-1,2-diphenylethene ( $Br_2TPE$ ).<sup>6</sup> In a two-necked flask equipped with a magnetic stirrer were added 4-bromobenzophenone (5 g, 19.2 mmol), zinc powder (2.5 g, 38.3 mmol), and 60 mL of THF. After the mixture was cooled to -78 °C, TiCl<sub>4</sub> (2.1 mL, 19.2 mmol) was slowly added by a syringe. The mixture was warmed to room temperature and stirred for 0.5 h and then heated to reflux for overnight. After cooled to room temperature, the reaction mixture was quenched with hydrochloric acid aqueous solution and then extracted with DCM. The organic layer was collected and concentrated. The crude product was purified by silica-gel column chromatography to give a white solid in a yield of 90%.

#### Scheme S1 Synthetic route to monomer 1c



Synthesis of 1,2-bis(4-iodophenyl)-1,2-diphenylethene ( $I_2TPE$ ). n-Butyllithium (1.6 M in hexane, 9.2 mL, 14.7 mmol) was added dropwise into a THF solution (50 mL) of Br<sub>2</sub>TPE (3 g, 6.1 mmol) at -78 °C. After the solution was stirred for 2 h, iodine (4.7 g, 18.4 mmol) was added into the solution in three

portions. After warmed to room temperature and stirred for 2 h, the mixture was poured into water and extracted with DCM. The organic layer was washed by saturated sodium thiosulfate solution and water, and dried over magnesium sulfate. After filtration and solvent evaporation, the crude product  $I_2$ TPE was obtained in a yield of 92%.

Synthesis of 1,2-bis{4-[(1-hydroxy-1-methyl)ethylethynyl]phenyl}-1,2-diphenylethene (HO<sub>2</sub>TPE). In a 250 mL two-necked round-bottom flask was dissolved I<sub>2</sub>TPE (3 g, 5.1 mmol) in 50 mL of triethylamine at room temperature. After addition of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (180 mg, 0.26 mmol), triphenylphosphine (135 mg, 0.51 mmol), CuI (98 mg, 0.51 mmol), and 2-methylbut-3-yn-2-ol (2.6 g, 30.8 mmol), the mixture was heated to reflux for 12 h under nitrogen. The solvent was removed by rotary evaporation and the residue was extracted with DCM and water. The combined organic phases were dried over anhydrous MgSO<sub>4</sub> and concentrated using a rotary evaporator. The crude product was purified by silica-gel column chromatography to afford 2.2 g of white powder in an 87% yield.

*Characterization Data of HO*<sub>2</sub>*TPE*. White solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ (ppm): 7.15–7.09 (m, 10H), 6.99–6.93 (m, 8H), 1.81 (s, 2H), 1.59 (s, 12H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>), δ(ppm): 144.39, 144.32, 143.70, 141.54, 131.99, 131.93, 131.81, 131.70, 128.58, 128.44, 127.52, 127.45, 121.45, 121.32, 94.80, 94.69, 82.86, 66.30, 32.15. HRMS (MALDI-TOF): *m/z* 496.2411 [M<sup>+</sup>, calcd 496.2402].

Synthesis of 1,2-bis(4-ethynylphenyl)-1,2-diphenylethene (1c). In a 100 mL two-necked round-bottom flask were added HO<sub>2</sub>TPE (2 g, 4.0 mmol), potassium hydroxide (1.6 g, 40.3 mmol), and 50 mL THF/methanol (1/1 v/v) under nitrogen atmosphere. The mixture was heated to reflux for 6 h. The solvent was removed by rotary evaporation and the residue was extracted with dichloromethane and water. The combined organic phases were dried over anhydrous MgSO<sub>4</sub> and concentrated using a rotary evaporator. The residue was purified by silica-gel column chromatography to afford 1.15 g of 1c as a white powder in a yield of 76%.

*Characterization Data of Ic*. White solid; E/Z = 45/55. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.23 (m, 4H), 7.14–7.07 (m, 6H), 7.02–6.94 (m, 8H), 3.04 (s, 0.9H, HC=C from *E*-isomer), 3.02 (s, 1.1H, HC=C from *Z*-isomer). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 144.15, 144.04, 142.92, 142.83, 140.89, 131.62, 131.48, 131.25, 131.23, 131.21, 127.93, 127.77, 126.90, 126.80, 120.19, 120.04, 83.69, 83.62, 77.50, 77.37. HRMS (MALDI-TOF): m/z 380.1559 (M<sup>+</sup>, calcd 380.1565).

# **Polymer synthesis**

All the polymerisation reactions were carried out under nitrogen using standard Schlenk technique in a vacuum line system or an inert atmosphere glovebox. A typical experimental procedure for the polymerisation of the monomers **1a** and **2** using C**1** as catalyst is described below.

To a 15 mL Schlenk tube with a three-way stopcock on the sidearm was placed 8.9 mg (0.018 mmol) of C1, 9.5 mg (0.036 mmol) of PPh<sub>3</sub>, 78.1 mg of 1a, and 60.9 mg of 2 under nitrogen in a glovebox. Freshly dried *o*-xylene (3 mL) was then injected into the tube using a hypodermic syringe. The resultant mixture was stirred at 140 °C under nitrogen for 12 h. The polymerisation was quenched by the addition of a small amount of methanol. The solution was then added dropwise to 500 mL of hexane via a cotton filter under stirring. The precipitate was allowed to stand overnight and then collected by filtration. The polymer was washed with hexane and dried under vacuum at room temperature to a constant weight. Yellow-brown powder of *l*-**3a** was obtained in 91.5% yield.  $M_{w,r}$  14800; PDI 2.6 (Table 2, no. 1). IR (thin film),  $\nu$  (cm<sup>-1</sup>): 1596 (C=C stretching). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 8.20–7.20 (aromatic protons), 7.08 (broad, newly formed *Z*-vinylene protons CH=CCl), 0.59 (broad, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 140.0–139.0, 134.9–125.1, –2.5. Other polymers were prepared using similar procedures.

*Characerization Data of l-3c*. Yellow-brown powder; yield 85.6%.  $M_{w,r}$  9300; PDI 2.8 (Table 2, no. 5). IR (thin film), v (cm<sup>-1</sup>): 1599 (C=C stretching). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 8.20–7.20 (aromatic protons), 7.08 (newly formed *Z*-vinylene protons CH=CCl). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 146.0–139.7, 136.5–134.0, 133.0–125.8.

*Characerization Data of hb-5a*. Yellow-brown powder; yield 71.3%.  $M_{w,r}$  10300; PDI 3.0 (Table 3, no. 3). IR (thin film),  $\nu$  (cm<sup>-1</sup>): 3297 (=C–H stretching), 1757 (C=O stretching), 1592 (C=C stretching). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 8.50–8.25 (aromatic protons ortho to COCl), 8.06 (1,3,5-benzene protons), 7.80–7.30 (aromatic protons), 7.12 (newly formed *Z*-vinylene protons CH=CCl), 0.58 (CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 168.2, 142.5–124.2, 83.6, 77.9, –2.6.

#### **Model reactions**

To confirm the occurrence of the decarbonylative polymerisations and gain insights to the chemical structures of the PACVs, three model reactions were performed as shown in Scheme 5. Commercially available benzoyl chloride (6), terephthaloyl dichloride (2), and benzene-1,3,5-tricarbonyl tricholoride (4) were reacted with phenylacetylene in the presence of C1 to afford sole (*Z*)-1-chloro-1,2-diphenylethene (7), (*Z*,*Z*)-1,4-bis(2-chloro-2-phenylvinyl)benzene (8), and (*Z*,*Z*,*Z*)-1,3,5-tris(2-chloro-2-phenylvinyl)benzene (9), showing high regio- and stereoselectivities. The structures of model compounds 7–9 were characterized by standard spectroscopic techniques, from which satisfactory analysis data corresponding to their expected molecular structures were obtained. The model molecules 8 and 9 were further confirmed by single crystal X-ray diffraction technique. All these results verify the hypothesis of decarbonylative *cis*-addition of aroyl chloride to triple bond in a regioselective manner.

Interestingly, the two chlorine atoms in 8 are arranged in a syn conformation.

(Z)-1-Chloro-1,2-diphenylethene (7). Into a 15 mL Schlenk tube with a three-way stopcock on the sidearm were added 4.9 mg (0.01 mmol) of [Rh(cod)Cl]<sub>2</sub> and 5.2 mg (0.02 mmol) of PPh<sub>3</sub> under nitrogen. 4 mL *o*-xylene solution of benzoyl chloride **6** (281.1 mg, 2 mmol) and phenylacetylene (306.9 mg, 3 mmol) was then injected into the tube using a hypodermic syringe. The resulting mixture was stirred at 140 °C for 24 h. The white solid product **7** was purified in a yield of 83.4% by a silica gel column using hexane as eluent. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.70 (d, *J* = 11.6 Hz, 2H), 7.67 (d, *J* = 6.0 Hz, 2H), 7.38–7.22 (m, 6H), 7.04 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 139.2, 135.2, 132.0, 129.4, 128.7, 128.3, 128.2, 127.9, 126.6, 126.0. HRMS (EI): *m/z* 214.0546 (M<sup>+</sup>, calcd. 214.0549).

(Z,Z)-1,4-Bis(2-chloro-2-phenylvinyl)benzene (8). The compound was synthesized by a reaction of terephthaloy dichloride (2) with phenylacetylene using procedures described above. White solid; yield 63.2%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 7.81 (s, 4H), 7.72 (d, J = 8.0 Hz, 4H), 7.45–7.34 (m, 6H), 7.08 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 139.3, 134.9, 132.5, 129.4, 128.8, 128.4, 126.7, 125.6. HRMS (EI): m/z 350.0630 (M<sup>+</sup>, calcd. 350.0629).

(Z,Z,Z)-1,3,5-*Tris*(2-chloro-2-phenylviny)benzene (9). Reaction of benzene-1,3,5-tricarbonyl trichloride (4) with phenylacetylene gave 9. Colorless solid; yield 38.7%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 8.06 (s, 3H), 7.72 (d, J = 8.0 Hz, 6H), 7.45–7.34 (m, 9H), 7.11 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 139.1, 135.3, 132.9, 129.9, 128.9, 128.4, 126.8, 125.6. HRMS (EI): m/z 486.0708 (M<sup>+</sup>, calcd. 486.0709).

Empirical formula	C22 H16 Cl2	
Formula weight	351.25	
Temperature	173.0 K	
Wavelength	1.5418 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 6.24573(8)  Å	$\alpha = 90^{\circ}$ .
	b = 7.28740(10)  Å	$\beta = 90^{\circ}$ .
	c = 37.2516(5)  Å	$\gamma = 90^{\circ}$ .
Volume	1695.51(4) Å <sup>3</sup>	
Ζ	4	
Density (calculated)	1.376 Mg/m <sup>3</sup>	
Absorption coefficient	3.413 mm <sup>-1</sup>	
F(000)	728	
Crystal size	0.4 x 0.35 x 0.1 mm <sup>3</sup>	
Theta range for data collection	9.39 to 67.48°.	
Index ranges	-7<=h<=5, -8<=k<=7, -40<=l<=44	
Reflections collected	5408	
Independent reflections	3017 [R(int) = 0.0164]	
Completeness to theta = $66.50^{\circ}$	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0 and 0.56208	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	3017 / 0 / 217	
Goodness-of-fit on F <sup>2</sup>	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0258, wR2 = 0.0713	
R indices (all data)	R1 = 0.0264, wR2 = 0.0717	
Absolute structure parameter	0.001(12)	
Largest diff. peak and hole	0.220 and -0.177 e.Å <sup>-3</sup>	

<b>Table SI</b> Crystal data and structure refinement for model compound
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Empirical formula	C30 H21 Cl3	
Formula weight	487.82	
Temperature	173.0 K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	R3c	
Unit cell dimensions	a = 24.8014(16)  Å	$\alpha = 90^{\circ}$ .
	b = 24.8014(16)  Å	$\beta = 90^{\circ}$ .
	c = 6.8350(9)  Å	$\gamma = 120^{\circ}$ .
Volume	3641.0(6) Å <sup>3</sup>	
Z	6	
Density (calculated)	1.335 Mg/m <sup>3</sup>	
Absorption coefficient	0.394 mm <sup>-1</sup>	
F(000)	1512	
Crystal size	0.25 x 0.08 x 0.06 mm <sup>3</sup>	
Theta range for data collection	1.64 to 26.98°.	
Index ranges	-31<=h<=30, -29<=k<=31, -8<=l<=7	
Reflections collected	6926	
Independent reflections	1603 [R(int) = 0.0254]	
Completeness to theta = $25.00^{\circ}$	98.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.916220	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	1603 / 1 / 100	
Goodness-of-fit on F <sup>2</sup>	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0344, wR2 = 0.0828	
R indices (all data)	R1 = 0.0357, wR2 = 0.0834	
Absolute structure parameter	0.03(6)	
Largest diff. peak and hole	0.293 and -0.172 e.Å <sup>-3</sup>	

Table S2 Crystal data and structure refinement for model compound 9



**Fig. S1** Scattering vector dependence of Rayleigh ratio  $[KC/R_{vv}(q)]$  of *hb*-**5a** in THF. Concentration:  $\sim 1.0 \times 10^{-4}$  g/mL.



**Fig. S2** IR spectra of monomers (A) **1a** and (B) **4** and (C) hyperbranched polymer *hb*-**5a** (sample taken from Table 3, no. 3).



**Fig. S3** <sup>13</sup>C NMR spectra of monomers (A) **1a** and (B) **2**, model compound **9** (C), and (D) hyperbranched polymer *hb*-**5a** (sample taken from Table 3, no. 3). The solvent peaks (CDCl<sub>3</sub> and *o*-xylene) are marked with asterisks.



**Fig. S4** Normalized absorption spectra of (A) *l*-**3a** and *hb*-**5a** and (B) *l*-**3c** in THF solutions and their thin casting films. Concentrations:  $10^{-5}$  M.



**Fig. S5** Cyclic voltammograms of (A) model compounds **8**, **9** and (B) polymers *l*-**3a**, *hb*-**5a** recorded in 0.1 M tetra-*n*-butylammonium hexafluorophosphate in DCM at a scan rate of 100 mV/s. Voltage values are reported versus SCE. The concentrations of the samples are 0.4 mg/mL.

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