

Synthesis of pyrrole-based poly(arylenevinylene)s *via* Co-catalyzed hydroarylation of alkynes

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Polyaddition *via* the Co-catalyzed hydroarylation of 1-(2-pyrimidinyl)pyrrole with aromatic diynes affords poly(arylenevinylene)s under mild conditions. This reaction avoids production of stoichiometric amounts of by-products. While structural analysis of the obtained polymers revealed the presence of 1,1-vinylidene unit, switching the counter anion of the Co catalyst and steric hindrance of the diyne monomers improved the regioselectivity of the polymers. When a catalyst with bulky counter anions is used for the reaction of less hindered diyne monomers, 1,2-vinylene linkages are formed dominantly over 1,1-vinylidene linkages (93:7). The effect of the regioselectivity of the polymer on the optical and semiconducting properties is also evaluated.

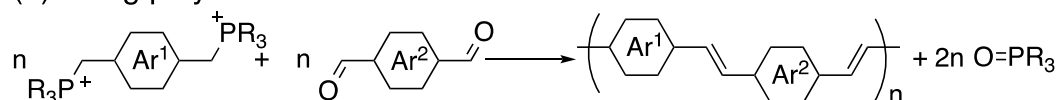
1. Introduction

π -Conjugated polymers are promising semiconducting materials for use in organic optoelectronic devices such as organic photovoltaic cells (OPVs), organic field-effect transistors (OFETs), and organic light-emitting diodes (OLEDs).^[1–4] Poly(arylenevinylene)s (PAVs) are an attractive family of π -conjugated polymers, for which a large number of applications have been reported.^[5–9] PAVs have generally been prepared by polycondensation^[10] based on the Gilch reaction,^[11,12] Wittig reaction,^[13–15] Knoevenagel reaction,^[16,17] olefin metathesis,^[18–24] Suzuki-Miyaura cross-coupling,^[25] Migita-Kosugi-Stille cross-coupling,^[26] and Mizoroki-Heck reaction.^[27–29] However, these polycondensation reactions also produce stoichiometric amounts of by-products derived from the reactive functional groups of the monomers (**Scheme 1a**), thereby necessitating tedious purification steps. The synthesis of PAVs *via* direct alkenylation has also been demonstrated (**Scheme 1b**).^[30–32] While this strategy allowed the straightforward C-H/C-H cross-coupling of arenes with alkenes, the use of a stoichiometric amount of oxidant led to the formation of an equivalent amount of reductant. In contrast to polycondensation reactions, polyaddition *via* hydroarylation of alkynes is a desirable synthetic target because it can help circumvent the formation of stoichiometric amounts of by-products, thus providing straightforward access to PAVs. However, examples of such polyaddition reactions are limited. The synthesis of PAVs *via* Rh-catalyzed hydroarylation of internal diynes has been reported (**Scheme 1c**),^[33] whereas hydroarylation of terminal diynes has not been conducted. Alternatively, Au-catalyzed hydroarylation polyaddition of terminal diynes provided aromatic polymers with 1,1-vinylidene units (**Scheme 1d**).^[34] The difference is associated with the orientation of alkyne coordination and insertion to the metal catalysts. Therefore, control of regioselectivity is a key issue in the synthesis of π -conjugated PAVs *via* hydroarylation polyaddition.^[35] This work focuses on the Co-catalyzed hydroarylation of terminal alkynes.^[36,37] As opposed to other transition-metal catalysts, a Cp*Co(III)-catalyst would be compatible with terminal alkynes in C-H activation

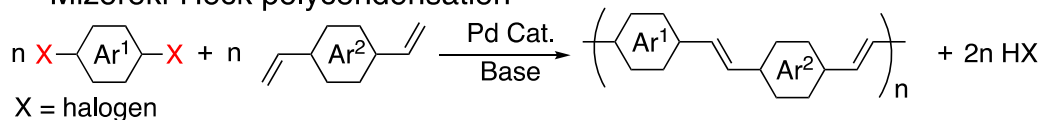
systems. The use of a pyrrole monomer bearing directing groups could also induce *ortho*-metalation and accelerate the site-selective C-H functionalization.^[30,36–38] We herein report polyaddition *via* the Co-catalyzed hydroarylation of 1-(2-pyrimidinyl)pyrrole **1a** with aromatic diynes to produce the corresponding PAVs (**Scheme 1e**). The appropriate reaction conditions for the regiocontrol of the polymers were explored. The effect of the regioselectivity of the polymers on the optical and semiconducting properties was also evaluated.

Previous work

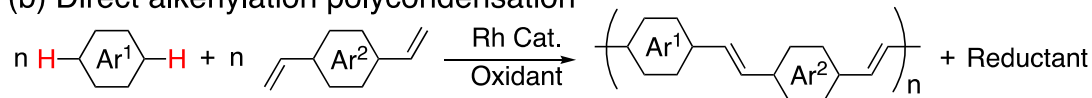
(a) Wittig polycondensation



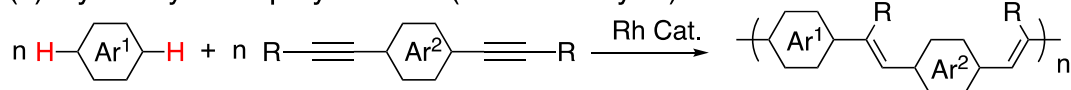
Mizoroki-Heck polycondensation



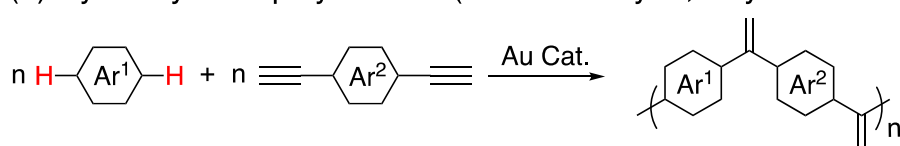
(b) Direct alkenylation polycondensation



(c) Hydroarylation polyaddition (Internal alkyne)

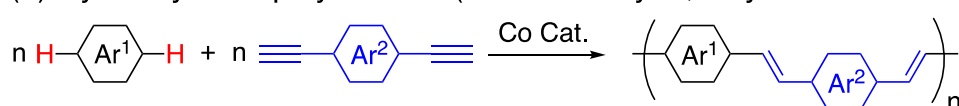


(d) Hydroarylation polyaddition (Terminal alkyne, vinylidene main chain)



This work

(e) Hydroarylation polyaddition (Terminal alkyne, vinylene main chain)

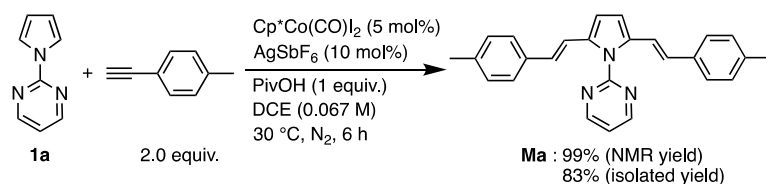


Scheme 1. Synthesis of poly(arylenevinylene)s.

2. Results and Discussion

2.1. Model reaction

For smooth hydroarylation polyaddition, we first attempted the model reaction of **1a** with 2.0 equivalent of 4-ethynyltoluene according to a previous report.^[36] The reaction proceeded smoothly in the presence of Cp*Co(CO)I₂ (5 mol%), AgSbF₆ (10 mol%), and pivalic acid (PivOH, 1 equiv.) at 30 °C for 6 h under N₂ atmosphere to give the corresponding dialkenylated compound (**Ma**) in good yield (**Scheme 2**), which was isolated as an *E,E*-isomer. The results for optimizing the reaction conditions are summarized in Tables S1 and S2. To determine the effect of the 2-pyrimidinyl substituent on the reaction, 1-phenylpyrrole was tested under the same conditions; the control experiment did not give the corresponding dialkenylated compound (Scheme S1). The reaction of **1a** was also attempted in the absence of 4-ethynyltoluene under the same conditions (Scheme S2); the control experiment did not lead to the homocoupling of **1a**. These results were consistent with the trend observed in a previous report on Rh-catalyzed direct alkenylation polycondensation.^[30]



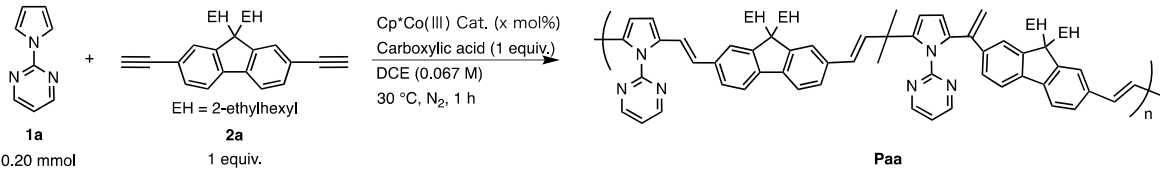
Scheme 2. Model reaction of **1a** with 4-ethynyltoluene.

2.2. Polyaddition reaction

Subsequently, to determine the appropriate polymerization conditions, the polyaddition of **1a** with 2,7-diethynyl-9,9-bis(2-ethylhexyl)fluorene **2a** was carried out under various conditions. **Table 1** summarizes the polymerization results. The polyaddition with Cp*Co(CO)I₂ (5 mol%), AgSbF₆ (10 mol%), and PivOH (1 equiv.) in 1,2-dichloroethane (DCE) proceeded smoothly at 30 °C and gave the corresponding polymeric product (**Paa**) in a

moderate yield after 6 h (Entry 1). The main signals in the ^1H NMR spectrum and MALDI-TOF MS of **Paa** (Figures S5 and S6) agreed with those for **Paa** obtained by Rh-catalyzed direct alkenylation polycondensation.^[30] However, structural analysis of the polymeric product from Entry 1 revealed the presence of the 1,1-vinylidene unit. The integral ratio between the minor unit and the recurring unit in the ^1H NMR spectrum indicated that the polymer included 20% of the 1,1-vinylidene unit. Switching the Co catalyst $[\text{Cp}^*\text{Co}(\text{CH}_3\text{CN})_3](\text{SbF}_6)_2$,^[39,40] which could eliminate the addition of AgSbF_6 in the catalytic system, improved the catalytic activity, resulting in a shorter reaction time and increased yield and molecular weight of **Paa** (Entry 2). The use of neodecanoic acid (NDA) resulted in a lower amount of Co catalyst loading (Entry 4)^[41-43]; however, the degree of regioselectivity of the polymer was preserved.

Table 1. Hydroarylation polyaddition of **1a** with **2a**



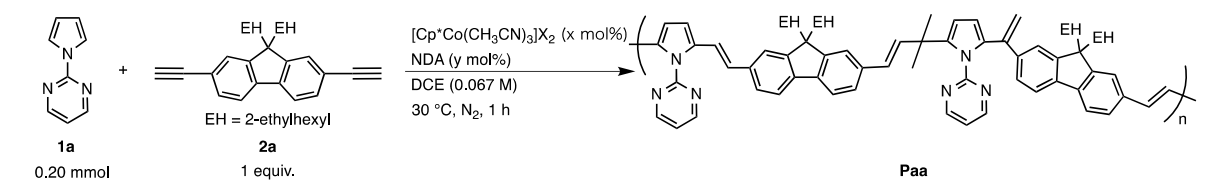
Entry	Cp*Co(III) Cat.	x [mol%]	Carboxylic acid	Yield ^d [%]	M_n^e ($\times 10^4$)	PDI ^e	Regioselectivity ^f [%]	
							1,2- vinylene	1,1- vinylidene
1 ^a	$\text{Cp}^*\text{Co}(\text{CO})\text{I}_2/\text{AgSbF}_6^b$	5	PivOH	67	1.5	2.1	80	20
2	$[\text{Cp}^*\text{Co}(\text{CH}_3\text{CN})_3](\text{SbF}_6)_2$	5	PivOH	82	4.7	2.5	79	21
3	$[\text{Cp}^*\text{Co}(\text{CH}_3\text{CN})_3](\text{SbF}_6)_2$	5	NDA	83	4.5	2.2	80	20
4	$[\text{Cp}^*\text{Co}(\text{CH}_3\text{CN})_3](\text{SbF}_6)_2$	2	NDA ^c	84	2.9	2.2	80	20

DCE = 1,2-dichloroethane, PivOH = pivalic acid, NDA = neodecanoic acid. ^aThe reaction was carried out for 6 h.

^b $[\text{Co}]/[\text{Ag}] = 0.5$. ^c NDA = 30 mol%. ^e The products were obtained by reprecipitation from DCE – CH_3OH and insoluble in hexane. ^d Estimated by GPC calibrated on polystyrene standards using DMF solution of LiCl (0.01 M) at 40 °C. ^e Determined by ^1H NMR analysis of a polymer.

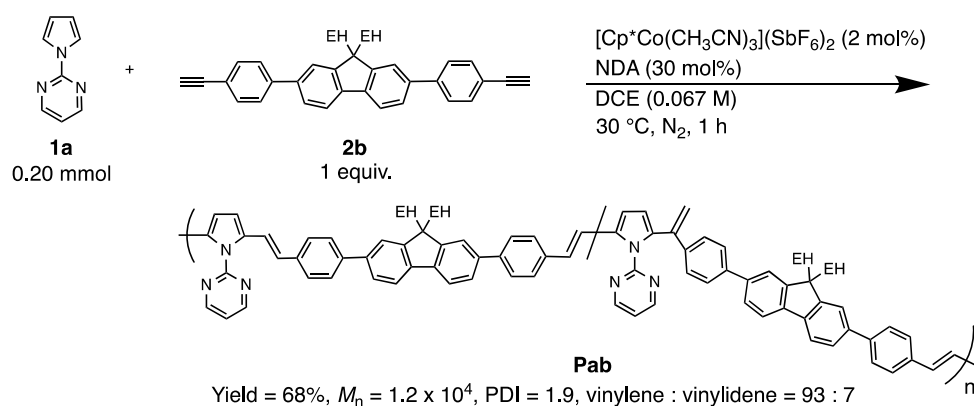
To improve the regioselectivity of the polymer, we attempted to switch the counter anion of the Co catalyst. We envisioned that the use of a bulky counter anion would strengthen the cationic nature of the Co catalyst and promote the 2,1-insertion of alkyne.^[44] The reactions under the appropriate conditions gave **Paa** in good yields. The results of the polymerization are shown in

Table 2. The use of a bulky counter anion, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BARF⁻), increased the regioselectivity of the polymer (Entry 2), whereas the use of BF₄⁻ and TfO⁻ decreased the regioselectivity of the polymer (Entries 3 and 4). Alternatively, the chemical structure of diyne monomer **2** was changed because the model reaction of **1a** with 4-ethynyltoluene did not produce the corresponding 1,1-vinylidene by-product (Scheme 2). As expected, the introduction of a phenylene unit into diyne monomer **2b** improved the regioselectivity of the polymer, **Pab** (Scheme 3). However, even by using **2b**, 1,1-vinylidene unit cannot be perfectly eliminated because of the steric effect of adjacent dialkylfluorene unit. Since the cationic strength of the Co-catalyst and the steric hindrance of the alkyne moiety of the monomer have a strong influence on the regioselectivity, further investigation of these factors will improve the regioselectivity. On the other hand, the reaction with 2,5-bis(2-ethylhexyloxy)-1,4-diethynylbenzene **2c** did not furnish a polymeric product, presumably due to the presence of bulky alkoxy groups (Table S4). The effect of the directing group was also examined; polyaddition of 1-(2-pyridyl)pyrrole **1b** with **2a,b** gave the corresponding polymers, **Pba** and **Pbb** (Table S5). Compound **1b** showed considerably higher reactivity than did **1a**, and **Pbb** was obtained in 10 min; however, changing the directing group did not improve the regioselectivity of the polymer.

Table 2. Optimization of counter anion of Cp*Co(III) catalyst


Entry	X ⁻	x [mol%]	y [mol%]	Yield ^a [%]	M _n ^b (x10 ⁴)	PDI ^b	Regioselectivity ^c [%]	
							1,2-vinylene	1,1-vinylidene
1	SbF ₆ ⁻	2	30	84	2.9	2.2	80	20
2	BArF ⁻	2	30	77	2.5	4.3	86	14
3	BF ₄ ⁻	5	100	68	1.9	1.6	77	23
4	OTf ⁻	5	100	84	1.6	1.6	77	23

DCE = 1,2-dichloroethane, NDA = neodecanoic acid. ^a The products were obtained by reprecipitation from DCE – CH₃OH and insoluble in hexane. ^b Estimated by GPC calibrated on polystyrene standards using DMF solution of LiCl (0.01 M) at 40 °C. ^c Determined by ¹H NMR analysis of a polymer.



Scheme 3. Hydroarylation polyaddition of **1a** with **2b**.

2.3. Optical and electronic properties

To evaluate the effect of 1,1-vinylidene units on the physical properties of **Paa**, its optical properties (20% of the 1,1-vinylidene unit, Table 1, Entry 4) were compared with those of **Paa** without the 1,1-vinylidene unit, which was prepared by direct alkenylation polycondensation previously.^[30] The optical data for the polymer samples are summarized in **Table 3**. The presence of the 1,1-vinylidene units slightly increased the bandgap (E_g) of the polymer samples (Figure S15), which could be attributed to a decrease in the effective conjugation length. The 1,1-vinylidene units also affected the electronic properties of the

polymer samples (Table 3). While both samples showed p-type semiconducting characteristics in the corresponding OFET devices, the presence of the 1,1-vinylidene units decreased the hole mobility (μ_h) by one order of magnitude (Figure S17a and Table 3), indicating that the 1,1-vinylidene units suppressed carrier mobility through the polymer chain. The absorption of **Pab** was somewhat blue-shifted as compared to that of **Paa** (Table 3 and Figure S16); the introduction of a phenylene unit probably reduced coplanarity along the polymer chain. **Pab** also showed p-type semiconducting characteristics, with a μ_h of $1.0 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the corresponding OFET devices (Figure S17b and Table 3).

Table 3. Optical and electronic properties of polymers

Polymer (1,2-vinylene : 1,1-vinylidene)	$\lambda_{\text{max}}^{\text{a}}$ [nm]	E_{g}^{b} [eV]	$E_{\text{HOMO}}^{\text{c}}$ [eV]	$E_{\text{LUMO}}^{\text{d}}$ [eV]	$\mu_{\text{h}}^{\text{e}}$ [$\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$]
Paa (100 : 0) ^f	475	2.30	-5.42	-3.12	$7.5 \pm 0.7 \times 10^{-5}$
Paa (80 : 20)	461	2.32	-5.39	-3.07	$3 \pm 2 \times 10^{-6}$
Pab (93 : 7)	436	2.48	-5.47	-2.99	$1.0 \pm 0.4 \times 10^{-6}$

^a Absorption peak in the film state. ^b Optical bandgap from the absorption edge. ^c The value of was obtained from the ionization potential. ^d $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}$. ^e The average value with standard deviation were calculated from the results of six OFET samples. OFET configuration; Glass/Au gate electrode/Parylene-C insulator/Polymer/Au source–drain electrodes. ^f Synthesized by direct alkenylation polycondensation; reported in ref. 30.

3. Conclusion

In summary, polyaddition *via* Co-catalyzed hydroarylation of the pyrrole monomer bearing a directing group with aromatic diynes was demonstrated. Currently, the synthetic examples are very specific, and a small amount of 1,1-vinylidene unit remains in the polymers, which serves as a defect in the electronic devices. However, the hydroarylation polyaddition did not produce a stoichiometric amount of by-products, and the obtained polymers showed p-type semiconducting properties in OFETs. Therefore, this synthetic methodology is a promising tool for the synthesis of π -conjugated PAVs with good atom and step economy. Further studies aimed at minimizing the 1,1-vinylidene units and extending this protocol to other aromatic monomers are underway.

4. Experimental Section

Materials: All reagents from commercial sources were used without further purification, unless otherwise noted. Carbonyldiiodo(pentamethylcyclopentadienyl)cobalt(III) ((Cp*Co(CO)I₂)) and anhydrous solvents were purchased from Kanto Chemical. 4-Ethynyltoluene, silver hexafluoroantimonate(V) (AgSbF₆), pivalic acid (PivOH) were purchased from Tokyo Chemical Industry. Neodecanoic acid (NDA) was purchased from Wako Pure Chemical Industries. The other reagents were also purchased from Kanto Chemical, Tokyo Chemical Industry, and Sigma Aldrich. Silver tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (AgBARF) was prepared according to the literature method.^[42]

General methods: ¹H, ¹⁹F, and ¹³C{¹H} NMR spectra were recorded on Bruker AVANCE-400 or AVANCE-600 NMR spectrometers. ¹H, ¹⁹F and ¹³C{¹H} NMR spectra were measured with TMS (0.00 ppm for ¹H NMR), CHD₂CN (1.94 ppm for ¹H NMR), C₂HDCl₄ (6.00 ppm for ¹H NMR), C₆F₆ (-162.9 ppm for ¹⁹F NMR), and CDCl₃ (77.0 ppm for ¹³C NMR) as an internal reference. Gel permeation chromatography (GPC) measurements were carried out on a SHIMADZU prominence GPC system equipped with polystyrene gel columns, using DMF solution of LiCl (0.01 M) as an eluent after calibration with polystyrene standards. The absorption spectra were recorded on a JASCO V-630 spectrometer. MALDI-TOF-MS spectra were recorded on an AB SCIEX MALDI TOF/TOF 5800 using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN Elemental Analyzer.

*Synthesis of [Cp*Co(CH₃CN)₃](BARF)₂*^[45]: To a stirred solution of AgBARF in CH₃CN (2.4 mL) was added Cp*Co(CO)I₂ (38.1 mg, 0.080 mmol). The reaction mixture was stirred for 1 h at room temperature under light shielding. The precipitate was filtered off through celite

and rinsed with CH₃CN. The filtrate was evaporated and dispersed in a mixture of hexane and dichloromethane (v/v = 1:1). Subsequently, the turbid liquid was shaken for 5 min under ultra sound condition. The precipitate was collected by filtration and washed with a mixture of hexane and dichloromethane (v/v = 1:1). [Cp*Co(CH₃CN)₃](BArF)₂ was obtained as a purple solid (112 mg, 69%). ¹H NMR (400 MHz, CD₃CN): δ 7.69 (s, 16H), 7.66 (s, 8H), 1.96 (s, 9H), 1.38 (s, 15H). ¹⁹F NMR (376 MHz, CD₃CN): δ -61.69. Anal. calcd. for C₈₀H₄₈B₂CoF₄₈N₃: C 47.02, H 2.37, N 2.06; found: C 47.06, H 2.39, N 2.07.

General procedure for Co-catalyzed hydroarylation polyaddition of alkynes: A mixture of a Cp*Co(III) catalyst (0.0040 mmol), a pyrrole monomer (0.20 mmol), an alkyne monomer (0.20 mmol), and NDA (11.4 μL, 0.06 mmol) was stirred in anhydrous DCE (3.0 mL) for a prescribed time at a prescribed temperature under nitrogen atmosphere in the dark. Then the reaction mixture was diluted with DCE (50 mL) and poured into 28% aqueous solution of NH₃ (50 mL). The organic layer was washed with 28% aqueous solution of NH₃ (50 mL) and distilled water (100 mL x 2). The organic layer was dried over sodium sulfate and filtered through a Celite plug. The solution of DCE was concentrated and reprecipitated into methanol. The precipitate was washed with hexane and a polymeric product was obtained.

Synthesis of Paa (Table 1, Entry 4): 1-(2-Pyrimidinyl)pyrrole (**1a**) (29.0 mg, 0.20 mmol) and 2,7-diethynyl-9,9-bis(2-ethylhexyl)fluorene (**2a**) (87.7 mg, 0.20 mmol) were used as the monomers. The reaction was carried out at 30 ° C for 1 h, giving **Paa** as an orange solid in 84% yield (98.5 mg, *M_n* = 2.9 x 10⁴, PDI = 2.2). ¹H NMR (600 MHz, C₂D₂Cl₄, 373 K): δ 8.96 (d, *J* = 4.4 Hz, 2H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.39-7.34 (m, 5H), 7.19 (d, *J* = 15.8 Hz, 2H), 6.97 (d, *J* = 15.8 Hz, 2H), 6.78 (s, 2H), 2.00 (s, 4H), 1.06-0.57 (m, 30H). Minor signal corresponding for the 1,1-vinylidene unit: δ 8.68 (d, *J* = 4.8 Hz), 7.50 (d, *J* = 7.0 Hz), 7.44 (s), 7.27-7.26 (br

m), 7.08 (br s), 7.02 (d, $J = 17.2$ Hz), 6.74 (s), 6.38 (s), 5.38-5.34 (br m), 5.12-5.06 (br m). Anal. calcd. for $C_{41}H_{49}N_3$: C 84.34, H 8.46, N 7.20; found: C 84.00, H 8.37, N 6.68.

Synthesis of Pab (Scheme 3): 1-(2-Pyrimidinyl)pyrrole (**1a**) (29.0 mg, 0.20 mmol) and 2,7-di(4-ethynylphenyl)-9,9-bis(2-ethylhexyl)fluorene (**2b**) (118.2 mg, 0.20 mmol) were used as the monomers. The reaction was carried out at 30 ° C for 1 h, giving **Pab** as a yellow solid in 68% yield (99.8 mg, $M_n = 1.2 \times 10^4$, PDI = 1.9). 1H NMR (600 MHz, $C_2D_2Cl_4$, 373 K): δ 9.00 (d, $J = 4.4$ Hz, 2H), 7.80 (d, $J = 7.7$ Hz, 2H), 7.65-7.62 (br m, 8H), 7.49 (d, $J = 7.3$ Hz, 4H), 7.41 (t, $J = 4.6$ Hz, 1H), 7.25 (d, $J = 15.8$ Hz, 2H), 6.96 (d, $J = 15.8$ Hz, 2H), 6.81 (s, 2H), 2.15 (br s, 4H), 0.98-0.62 (m, 30H). Minor signal corresponding for the 1,1-vinylidene unit: δ 8.63 (d, $J = 4.0$ Hz), 7.34 (d, $J = 7.7$ Hz), 6.57 (s), 5.47 (br s), 5.41 (br s). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 158.5, 157.3, 151.1, 140.2, 138.8, 136.5, 134.5, 132.3, 126.9, 126.7, 126.3, 125.6, 122.2, 119.7, 118.9, 118.3, 109.7, 54.8, 44.3, 34.5, 33.6, 28.0, 26.9, 22.5, 13.7, 10.1. Anal. calcd. for $C_{53}H_{57}N_3$: C 86.49, H 7.81, N 5.71; found: C 85.52, H 7.67, N 4.88.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Polyaddition *via* the Co-catalyzed hydroarylation of 1-(2-pyrimidinyl)pyrrole with aromatic diynes affords poly(arylenevinylene)s without production of stoichiometric amounts of by-products. The counter anion of the Co catalyst and steric hindrance of the diyne monomers affect the regioselectivity of the polymers. The effect of the regioselectivity on the optical and semiconducting properties is also evaluated.

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Synthesis of pyrrole-based poly(arylenevinylene)s *via* Co-catalyzed hydroarylation of alkynes

