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A novel synthetic protocol for poly(fluorenylenevinylene)s: a cascade Suzuki–Heck reaction

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Abstract—This article reports the use of a cascade Suzuki–Heck reaction for the polymerization of suitable aryldibromides with potassium vinyltrifluoroborate resulting in the synthesis of a series of poly(fluorenylenevinylene)s. The protocol is characterized by a great versatility, deriving from the use of easily attainable substrates, and yields polymers with low percentages of structural 1,1-diarylenevinylene defects.

Since the discovery of electroluminescence from poly(phenylenevinylene) (PPV),[1] continuous research efforts have been devoted to the synthesis of differently structured PPV derivatives, which today can be considered the most promising organic materials to be used in light-emitting diodes (LEDs). Chemical modification of the basic PPV structure permits fine colour tunability and lowering of operating voltages, which greatly attract the interest of the scientific and industrial communities. Three major synthetic approaches are followed for the synthesis of poly(phenylenevinylene)s: the Wessling route,[2] the Wittig condensation[3] and the widely preferred Gilch reaction.[4] After the report on the synthesis of PPVs from aryldibromides and ethylene,[5] the Heck reaction has been successfully employed for their obtainment from aryldihalides and the appropriate bisvinylderivative.[6] In order to minimize the amount of 1,1-diarylenevinylene defects and to avoid tedious manipulations of commercially available substrates for the synthesis of bisvinylderivatives, an interesting alternative to the use of ethylene, consisting in the poly-Heck reaction of vinyltriethoxysilane with arenediazonium salts was proposed.[7] However, the synthesis of arenediazonium salts is challenging even for the most common PPV precursors.

Intrigued by its easy preparation and stability as well as by its high reactivity with respect to vinyl boronic acid and esters in Suzuki couplings,[8] we have investigated the use of potassium vinyltrifluoroborate as a new ethylene equivalent for the synthesis of poly(fluorenylenevinylene)s (PFVs). This class of materials has recently attracted considerable interest as active layers in LED.[9] Here we present the first cascade Suzuki–Heck reaction for the obtainment of the PFVs **P1**–**3** reported in Scheme 1.

The commercially available 2,7-dibromofluorene was easily converted into 2,7-dibromo-9,9-bis(3,7-dimethyloctyl)fluorene (**1**)[10] and the latter reacted with 1 equiv of potassium vinyltrifluoroborate (**2**) in the presence of K_2CO_3 (3 equiv with respect to **2**) and $Pd(PPh_3)_4$ as catalyst (5% mol/mol with respect to **2**). We have chosen this catalytic system, because it is the commonest for both Suzuki and Heck couplings. On the other hand, promotion of the cascade Suzuki–Heck reaction leading to **P1** required the fine tuning of its conditions. In particular, a careful choice of the reaction medium proved to be crucial: using methanol, ethanol, THF/methanol (5/1) and a biphasic toluene/water (3/2) mixture did not promote the polymerization although all these media are suitable for both Suzuki and Heck couplings. On the contrary, a satisfactory 77% yield in **P1** was obtained after one day reaction in dioxane at reflux.[11]

Aiming at the obtainment of π-conjugated macromolecules with potentially tunable optical properties, we

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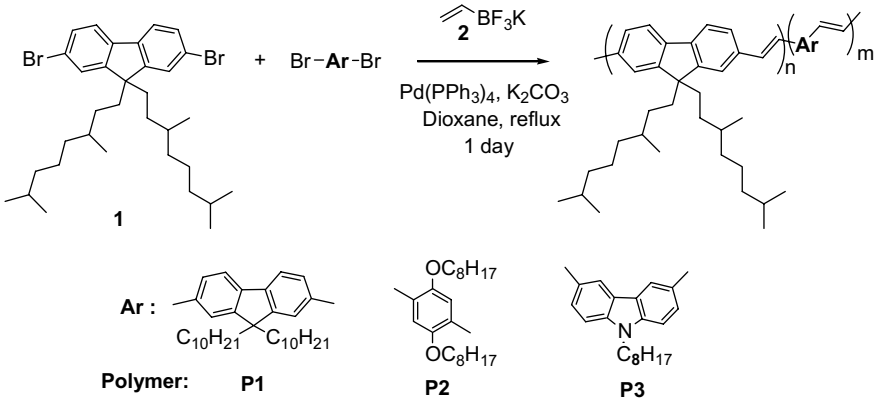

Scheme 1. Synthesis of polymers.

extended the protocol to the synthesis of random copolymers obtained reacting potassium vinyltrifluoroborate with **1** and 2,5-dioctyloxy-1,4-dibromobenzene (**P2**, obtained in 73% yield[12]) or 3,6-dibromo-*N*-octylcarbazole (**P3**, obtained in 72% yield[13]) in 2/1/1 molar ratios (Scheme 1).

All polymers were isolated by precipitation in methanol, washed with acetone in a Soxhlet apparatus in order to remove traces of oligomers and catalyst, and finally extracted with chloroform.

Comparison of the integral areas of the protons at ca. 2 ppm, with those of the dioctyloxybenzene moiety in **P2** or those of carbazole moiety in **P3** at ca. 4 ppm (Fig. 1), allowed the determination of the relative amount of arylene comonomers in the polymer that was found to be exactly equimolar. The presence of electron-donating groups in both comonomers as well as the steric effects exerted by the *ortho*-dioctyloxy groups do not seem to affect the validity of the synthetic protocol.

The presence of the vinylene functionality was unambiguously confirmed by the appearance of medium FTIR bands attributable to the out-of-plane CH bending of *trans*-vinylene at 957–963 cm^{-1}. The corresponding ^1H NMR signals fall in the region of aromatic protons and could not be assigned.

Molecular weights and distributions for **P1** (M_w = 19,000 Da, M_w/M_n = 2.3), **P2** (M_w = 14,000 Da, M_w/M_n = 2.1) and **P3** (M_w = 11,000 Da, M_w/M_n = 2.2) were measured by GPC using THF as eluent and polystyrene standards. In the case of **P1** and **P2**, the molecular mass data are in accordance with those reported for analogous polymers synthesized by Heck or Wittig polycondensation,[14,15] but lower then those obtained by the Gilch route[9a] or by molybdenum catalyzed metathesis.[16]

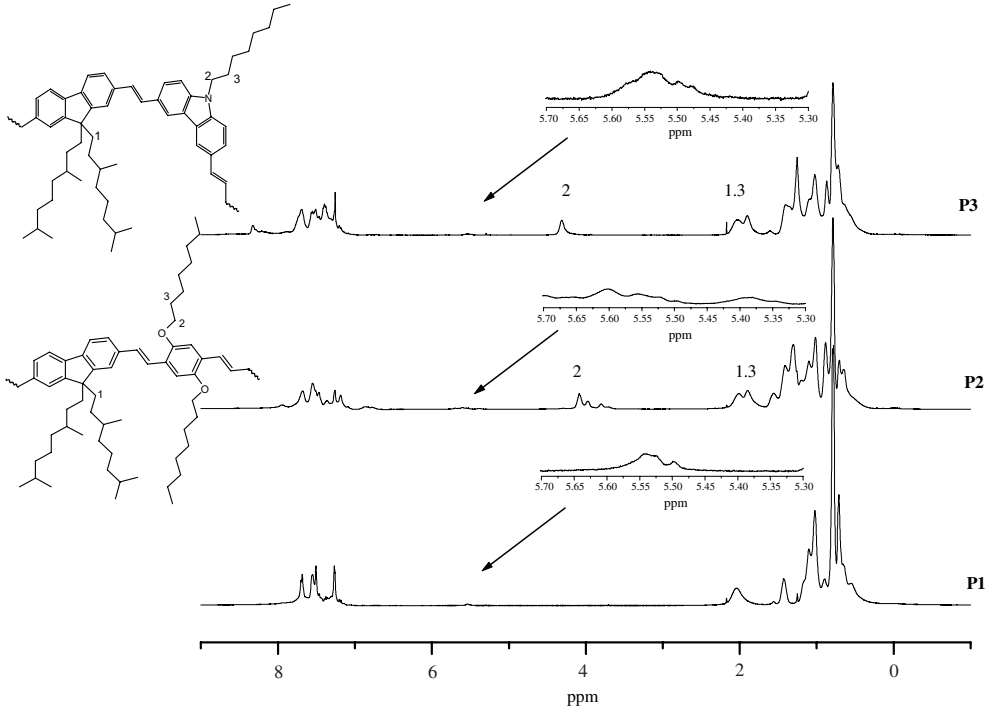

Figure 1. ^1H NMR (400 MHz, $CDCl_3$) of **P1**–**3**. The insets show the signals attributable to the 1,1-diarylenevinylene protons.

Conversely, no comparison can be done for **P3**, because it represents the first example of a poly(arylenevinylene) based on fluorene and carbazole moieties.

In order to gain insight into the reaction course we carried out the reaction of **1** with an excess (2.2 equiv) of **2**. The obtained 50% yield in the expected Suzuki product (the 2,7-divinyl-fluorene derivative) is remarkably low with respect to similar couplings of vinyltrifluoroborate with bromoaryls[8a] because of concomitant Heck coupling, leading to the formation of low molecular weight oligo(fluorenylenevinylene)s. This result suggests that, under our reaction conditions, the Suzuki coupling and the Heck reaction proceed with comparable rates. It can therefore be assumed that the Suzuki coupling is the first step occurring during the reaction and that the produced vinylaryl derivatives react in a subsequent Heck reaction as soon as formed, generating a polymer by a cascade Suzuki–Heck reaction.

Next, the amount of 1,1-diarylenevinylene defects into the polymer chain was estimated. These defects can be generated during the Heck reaction step, causing a π-conjugation interruption, which causes the drop of the quantum efficiencies of the PPV-like materials in LEDs. For example, the 1,1-diarylenevinylene defects incorporated in PPVs obtained by reaction between ethylene and aryldibromides may be up to 20%.[17] In our case, **P1** contained only 4% of such defects, as evaluated by ^{1}H NMR spectroscopy comparing the integral of the signal attributable to the 1,1-diarylenevinylene protons at 5.5–5.6 ppm (evidenced in Fig. 1) with that attributable to the methylene protons at 2 ppm. Also for **P2** and **P3** the amount of structural defects is low (10% and 5%, respectively).

The absorption and photoluminescence spectra in $CHCl_3$ solutions of the polymers are reported in Figure 2. Polymer **P1** shows an absorption maximum at 422 nm with a shoulder at 443 nm and its emission spectrum is characterized by a vibronic structure in the blue-green region (λ_{max} 465 nm).

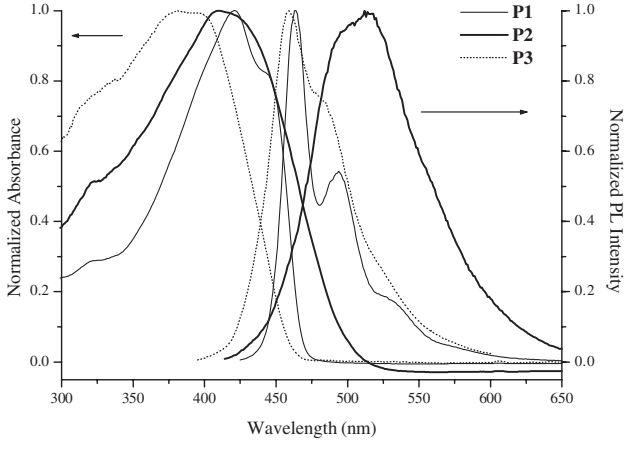

Figure 2. Absorption and photoluminescence spectra of the polymers recorded in chloroform.

Polymer **P2** absorbs at 410 nm and its emission falls in the green region (λ_{max} 513 nm). On the other hand, the introduction of carbazolylene units causes a blue shift in the UV–vis absorption of **P3** (λ_{max} 390 nm) with respect to **P1**, whereas the photoluminescence maximum (λ_{max} 460 nm) does not exhibit any substantial change.

In conclusion, poly(fluorenylenevinylene)s can be synthesized by a one-pot cascade Suzuki–Heck reaction. Differently from the known syntheses of PFVs, which require a multistep approach for the synthesis of the monomers, inevitably leading to unsatisfactory overall yields, the most important advantage of this method stands in the great versatility deriving from the use of easily attainable substrates and potassium vinyltrifluoroborate as ethylene equivalent in a high-yield reaction. Moreover, the obtained materials are characterized by a low percentage of structural 1,1-diarylenevinylene defects, which make them suitable for potential application in LEDs.

Acknowledgements

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11. *Poly[9,9-bis(3,7-dimethyloctyl)-2,7-fluorenylenevinylene]* (**P1**). A 25 mL two-necked round bottom flask was charged with **1** (1.200 g, 2.00 mmol), **2** (0.270 g,

2.00 mmol), $Pd(PPh_3)_4$ (0.110 g, 0.10 mmol), K_2CO_3 (0.800 g, 6.00 mmol) and dioxane (10 mL). The reaction mixture was refluxed for 1 d. After cooling to room temperature, the solution was poured into methanol (100 mL). The solid was filtered off and dissolved in the minimum amount of chloroform for reprecipitation in methanol. Then the polymer was washed in a Soxhlet apparatus with acetone and extracted with chloroform to yield **P1** (0.750 g, 77%) as a yellow-orange powder. ^1H NMR (400 MHz, $CDCl_3$): δ 0.54–0.97 (br m, 24H), 1.02–1.27 (br m, 12H), 1.40–1.52 (br m, 2H), 1.99–2.15 (br m, 4H), 7.27 (br s, 2H), 7.48–7.59 (br m, 4H), 7.65–7.73 (br d, 2H). IR (KBr): ν (cm^{-1}) 3020, 2975, 2931, 2868, 1598, 1464, 1356, 957 (*trans* HC=CH), 817, 734.

12. *Poly[9,9-bis(3,7-dimethyloctyl)-2,7-fluorenylenevinylene-co-2,5-dioctyloxy-1,4-phenylenevinylene]* (**P2**). A 25 mL two-necked round bottom flask was charged with **1** (0.600 g, 1.00 mmol), 2,5-dioctyloxy-1,4-dibromobenzene (0.492 g, 1.00 mmol), **2** (0.270 g, 2.00 mmol), $Pd(PPh_3)_4$ (0.110 g, 0.10 mmol), K_2CO_3 (0.800 g, 6.00 mmol) and dioxane (10 mL). The reaction mixture was refluxed for 1 d. After cooling to room temperature, the solution was poured into methanol (100 mL). The solid was filtered off and dissolved in the minimum amount of chloroform for reprecipitation in methanol. Then the polymer was washed in a Soxhlet apparatus with acetone and extracted with chloroform to yield **P2** (0.600 g, 73%) as a dark red powder. ^1H NMR (400 MHz, $CDCl_3$): δ 0.40–1.49 (br m, 64H), 1.71–2.17 (br m, 8H), 3.64–4.15 (br m, 4H), 6.70–7.85 (br m, 12H). IR (KBr): ν (cm^{-1}) 3027, 2957, 2924, 2853, 1601, 1498, 1465, 1419, 1380, 1260, 1200, 1092, 1026, 963 (*trans* HC=CH), 805, 692.

13. *Poly[9,9-bis(3,7-dimethyloctyl)-2,7-fluorenylenevinylene-co-N-octyl-3,6-carbazolylenevinylene]* (**P3**). A 25 mL two-necked round bottom flask was charged with **1** (0.600 g, 1.00 mmol), 3,6-dibromo-*N*-octylcarbazole (0.440 g, 1.00 mmol), **2** (0.270 g, 2.00 mmol), $Pd(PPh_3)_4$ (0.110 g, 0.10 mmol), K_2CO_3 (0.800 g, 6.00 mmol) and dioxane (10 mL). The reaction mixture was refluxed for 1 d. After cooling to room temperature, the solution was poured into methanol (100 mL). The solid was filtered off and dissolved in the minimum amount of chloroform for reprecipitation in methanol. Then the polymer was washed in a Soxhlet apparatus with acetone and extracted with chloroform to yield **P3** (0.560 g, 72%) as a dark green powder. ^1H NMR (400 MHz, $CDCl_3$): δ 0.40–1.49 (br m, 51H), 1.87–2.16 (br m, 6H), 4.22–4.37 (br s, 2H), 7.16–7.60 (br m, 10H), 7.61–7.81 (br m, 4H), 8.25–8.36 (br m, 2H). IR (KBr): ν (cm^{-1}) 3029, 2954, 2933, 2858, 1587, 1490, 1463, 1346, 1085, 962 (*trans* HC=CH), 797, 686.

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