



## A white emitting poly(phenylenevinylene)



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### ABSTRACT

A white emitting copolymer with the polyphenylenevinylene (PPV) structure is obtained via the Stille cross-coupling reaction. Substitution of hydrogen atoms with fluorine atoms on the vinylene units of poly(1,4-dialkoxyphenylenevinylene) shifts the emission from orange-red to blue. White emission is obtained by combining dialkoxyphenylenedifluorovinylene and dialkoxyphenylenevinylene units in proper ratio. The two complementary emitters are obtained separately by Stille polymerization reaction. Then, the two reaction mixtures are combined without purification in different ratios and further reacted in similar experimental conditions. A white luminescent material is obtained using 99/1 mixing ratio. OLED devices fabricated with this copolymer shows near-white emission with CIE (0.30, 0.40) and excellent stability in the range 10–200 cd/m<sup>2</sup>.

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### 1. Introduction

White polymeric light-emitting diodes (WPLEDs) [1–12] have been the subject of intense research activity over the last years in both academic and industrial laboratories. Their manifold applications include low-cost back-lighting in liquid-crystal displays, full-colour displays and especially new generation solid state lighting sources. The most efficient WPLEDs outperform incandescent lamps and equal fluorescent lamps [13,14], and are considered as possible energy-effective substitutes of traditional lighting sources [15,16].

White light can be obtained by simultaneous emission of light of the three primary colours (red, green and blue, RGB) [17–21], or of two complementary colours (e.g. blue and orange) [6,22–27]. Combination of emitters of different colours requires proper control of energy transfer processes [28] which funnel the excitation to the lowest energy emitters [29,30].

Several approaches to white electroluminescence with organic emitters have been reported so far; the simplest way consists in

blending fundamental or complementary colours emitting molecules or polymers [31,32]. However, WPLEDs based on emitters blends often suffer from colour instability mainly caused by phase separation of emitting components with different chemical structures. Moreover, colour-aging effects due to differential degradation processes of the single emitters [33] and undesired dependence of the emission spectrum on the driving voltage are often observed [6,26].

A convenient approach to overcome these issues, obtaining at the same time simple device architectures by solution processing, consists in the use of white emitting single copolymers. White-emitting copolymers can be synthesized either by wiring emitters of the fundamental colours in the main polymer backbone or incorporating complementary colour (e.g. orange) emitting units into the main chain of a blue emitting polymer. A fine control of the energy transfer and charge trapping processes is necessary to maintain simultaneous and balanced emission from all the components [29,30].

The blue emitter is the essential and major component in white organic electroluminescent copolymers, and therefore it is critical for colour purity, efficiency and device stability. The most common blue emitters are polyfluorene derivatives [34], which have been optimized to achieve high photoluminescence quantum yields, chemical-, thermal- and photostability [35] and good solubility in the most common organic solvents. Only a small concentration of the complementary dyes (e.g. orange or yellow/green) is required

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to obtain white light and various classes of emitters have been used as co-monomers or side groups in blue emitting polymers such as, for example, phosphorescent iridium complexes [36–43], phenothiazine units [44], 2,1,3-benzothiadiazole [45–51] and thiophene derivatives [52]. In many cases, the structures of the resulting polymers are very complex and the synthetic procedures are not suitable for industrial scale-up. Actually, structurally simple, cost-effective and stable materials are necessary to make the WPLED technology scalable.

In the context of our studies on fluorinated conjugated polymers for organic optoelectronics [53–63], we have recently reported a blue electroluminescent polymer based on the PPV structure, poly(2-methoxy-5-[(2-ethylhexyl)oxy]-1,4-phenylenedifluorovinylene) (**MEH-PPDFV**) [64–67], which is the difluorovinylene analogue of **MEH-PPV**, one of the most widely used red-orange electroluminescent polymers.

Fluorination of the double bonds in **MEH-PPDFV** causes enlargement of the HOMO-LUMO gap compared to **MEH-PPV**. This shifts the emission from the orange (**MEH-PPV**) to the blue (**MEH-PPDFV**) region of the visible spectrum and, at the same time, improves resistance to oxidation and affects charge transport properties [68].

Here we demonstrate white (electro)luminescence from a simple PPV polymer resulting from the combination of **MEH-PPDFV** with **MEH-PPV** units.

## 2. Experimental

### 2.1. Materials and methods

All chemicals were purchased from Aldrich, Alfa Aesar and Acros and used without further purification. THF was distilled from sodium and benzophenone under a nitrogen atmosphere. DMF was distilled from 4Å molecular sieves under a nitrogen atmosphere. All solvents were freshly distilled immediately prior to use. 1-(2-Ethylhexyloxy)-2,5-diiodo-4-methoxybenzene, (E)-(1,2-difluoro-1,2-ethenediyl)bis[tributylstannane] and (E)-(1,2-ethenediyl)bis[tributylstannane] were prepared as reported in the literature [64].

Merck Silica gel 60 F<sub>254</sub> aluminium sheets were used for analytical TLC. FT-IR spectra were measured on a Perkin–Elmer 1710 spectrophotometer using dry KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker AM 500 spectrometer at 500 MHz and 125 MHz, respectively. The residual CHCl<sub>3</sub> signal at δ = 7.24 ppm and the CDCl<sub>3</sub> signal at δ = 77.0 ppm were used as the standards for <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra, respectively. Elemental analyses were done by a Carlo Erba CHNS-O EA1108-Elemental Analyzer. UV–vis spectra were recorded on a Shimadzu UV-2401 PC spectrophotometer. Emission spectra were recorded with a Varian Cary Eclipse Fluorimeter. Molecular weights were determined by SEC with a Hewlett–Packard HP 1050 liquid chromatograph instrument equipped with a Plgel 5 μ Mixed-D300 × 7.5 mm column, using THF as a solvent and polystyrene standard calibration.

Differential scanning calorimetry (DSC) measurements were performed with a Perkin–Elmer Pyris1 instrument. Samples were heated from –50 °C to 200 °C with a scan rate of 20 °C min<sup>-1</sup> in the first heating and at 40 °C in the second under a helium flow (30 mL min<sup>-1</sup>).

### 2.2. Synthetic protocols

#### 2.2.1. Synthesis of poly(2-methoxy-5-[(2-ethylhexyl)oxy]-1,4-phenylenedifluorovinylene) (**2d-MEH-PPDFV**)

A mixture of 2,5-diiodo-4-[(2-ethylhexyl)oxy]methoxybenzene **1** (1.00 g, 2.05 mmol), (E)-(1,2-difluoro-1,2-ethenediyl)bis

[tributylstannane] **2** (1.32 g, 2.05 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.12 g, 0.10 mmol) and CuI (0.39 g, 2.05 mmol) in dry THF (30 mL) and dry DMF (30 mL) was stirred at room temperature in a nitrogen atmosphere for two days. The reaction mixture quickly turned to a dark solution and, after two days, to a dark green solution.

#### 2.2.2. Synthesis of poly(2-methoxy-5-[(2-ethylhexyl)oxy]-1,4-phenylenevinylene) (**2d-MEH-PPV**)

A mixture of 2,5-diiodo-4-[(2-ethylhexyl)oxy]methoxybenzene **1** (0.1 g, 0.205 mmol), (E)-(1,2-ethenediyl)bis[tributylstannane] **3** (0.125 g, 0.205 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.012 g, 0.01 mmol) and CuI (0.039 g, 0.205 mmol) in dry THF (5 mL) and dry DMF (5 mL) was stirred at 100 °C in a nitrogen atmosphere for two days. The reaction mixture quickly turned to a dark solution and, after two days, to an orange solution.

#### 2.2.3. General procedure. Synthesis of **CP1**

55 mL of **2d-MEH-PPDFV** and 0.93 mL of **2d-MEH-PPV** reaction mixtures (after two days reaction time) were mixed under a nitrogen atmosphere in a three-necked bottom flask. Pd(PPh<sub>3</sub>)<sub>4</sub> (0.104 g, 0.09 mmol) and CuI (0.36 g, 1.9 mmol) were added to the resulting mixture and then refluxed in a nitrogen atmosphere for further 4 day. Subsequently, the stannyl end groups of the living copolymer chains were end-capped with iodobenzene (0.21 mL, 1.90 mmol) and the reaction was carried out for one additional day. After cooling to room temperature, the solvent was evaporated at reduced pressure and the crude copolymer was purified by extraction in a Soxhlet apparatus with hexane (24 h), methanol (24 h) and chloroform (12 h). The copolymer was recovered, after evaporation of chloroform, as a dark green powder (0.309 g, yield 55%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.23–6.70 (br. s, 2H), 4.10–3.52 (br. s, 5H), 1.84–1.66 (br. s, 1H), 1.65–1.14 (br. s, 8H), 1.04–0.70 (br. s, 6H) ppm.

#### 2.2.4. Synthesis of **CP2**

Following the same procedure reported above, 55 mL of **2d-MEH-PPDFV** and 0.46 mL of **2d-MEH-PPV** reaction mixtures were mixed. After work-up as for **CP1** the copolymer was recovered as a dark green powder (0.325 g, yield 58%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.24–6.70 (br. s, 2H), 4.10–3.52 (br. s, 5H), 1.86–1.66 (br. s, 1H), 1.65–1.14 (br. s, 8H), 1.04–0.70 (br. s, 6H) ppm.

#### 2.2.5. Synthesis of **CP3**

Following the same procedure reported above, 55 mL of **2d-MEH-PPDFV** and 0.09 mL of **2d-MEH-PPV** reaction mixtures were mixed. After work-up as for **CP1** the copolymer was recovered as a dark green powder (0.334 g, yield 60%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 7.24–6.70 (br. s, 2H), 4.10–3.60 (br. s, 5H), 1.84–1.68 (br. s, 1H), 1.66–1.16 (br. s, 8H), 1.05–0.78 (br. s, 6H) ppm.

All the copolymers showed similar <sup>1</sup>H NMR spectra and elemental analysis results. For example, **CP1**: Anal. Calc.: C, 68.98; H, 7.50. Found: C, 68.74; H, 7.37, (**MEH-PPDFV**: Anal. Calc.: C, 68.90; H, 7.48. Found: C, 68.61; H, 7.38 [64]). Due to their very low percentage in the final copolymers, the **MEH-PPV** units were difficult to be detected by <sup>1</sup>H NMR and elemental analysis.

### 2.3. Optical measurements

Photoluminescence (PL) and electroluminescence (EL) were obtained with monochromator equipped with a CCD detector, by exciting with a monochromated Xenon lamp, or by applying a constant bias, respectively. Solid-state PL quantum yields (QY) were obtained by using a home-made integrating sphere [69]. Current density–Luminance–voltage (*J–L–V*) characteristics were recorded with a Keithley 2602 source meter and a calibrated photodiode.

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