

## Supporting Information to

### Controlled/Living Polymerization Towards Functional Poly(*p*-phenylene vinylene) Materials

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A supporting information is added to the review as the data for Figure 5 had been reproduced following previously published procedures in order to obtain graphics with sufficient resolution. The polymers for which distributions are given have been synthesized following the procedures described and published in literature.<sup>2</sup> SEC analysis on the precursor polymer showed a bimodal distribution with  $M_n = 43\,500\text{ g}\cdot\text{mol}^{-1}$ ,  $\mathcal{D} = 2.7$  for the radical product and  $M_n = 850\text{ g}\cdot\text{mol}^{-1}$ ,  $\mathcal{D} = 1.6$  for the anionic product.

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## S1. Experimental Section

### 1.1. Materials

All materials and reagents were purchased from Acros or Sigma Aldrich and were used without further purification.

### 1.2. Analysis

Analytical Size Exclusion Chromatography (SEC) was performed on a Tosoh EcoSEC HLC-8320GPC, comprising an autosampler, a Polymer Standard Service guard column Styrene Divinyl Benzene (50 × 7.5 mm), followed by three PSS SDV analytical linear XL (5 μm, 300 × 7.5 mm) columns thermostatted at 40 °C (column molecular weight range:  $1 \times 10^2$ – $1 \times 10^6$  g·mol<sup>-1</sup>), and a differential refractive index detector using THF as the eluent at a flow rate of 1 mL·min<sup>-1</sup>. Toluene was used as a flow marker. Calibration was performed using linear narrow polystyrene (PS) standards from PSS Laboratories in the range of 470– $7.5 \times 10^6$  g·mol<sup>-1</sup>. The following Mark Houwink parameters for plain precursor MDMO-PPV were used:  $\alpha = 0.67605$  and  $k = 0.000142$  mL·g<sup>-1</sup>.<sup>1</sup>

### 1.3. Monomer Synthesis

Synthesis of 1-(chloromethyl)-5-((3,7-dimethyloctyl)oxy)-2-methoxy-4-((octylsulfinyl)methyl) benzene (MDMO-sulfinyl) premonomer was performed according to a known literature procedure.<sup>1</sup>

## References

- <sup>1</sup> N. Zaquen, J. Vandenbergh, M. Schneider-Baumann, L. Lutsen, D. Vanderzande, T. Junkers, *Polymers*, 2015, **7**, 418.
- <sup>2</sup> I. Cosemans, L. Hontis, D. Van Den Berghe, A. Palmaerts, J. Wouters, T. Cleij, L. Lutsen, W. Maes, T. Junkers, D. Vanderzande, *Macromolecules*, 2011, **44**, 7610.