

## Supporting Information:

PPPX was characterized as describe above<sup>4</sup>:

Poly(2-phenyl-*p*-xylylene) (PPPX): 2,5-bis(bromomethyl) biphenyl (1.28 g; 3.76 mmol) was electrolyzed at a mercury pool cathode in Et<sub>4</sub>NBr (0.1 mol L<sup>-1</sup>)-DMF solution (50 mL) at -1.5 V (*vs.* Ag/AgBr) in a divided cell using a graphite rode as anode. The cathode compartment was continually flushed with a slow stream of dry nitrogen. A dark yellow precipitate formed during electrolysis. After ca. 2.1 F mol<sup>-1</sup> had passed, the cell current dropped close to the background value. The precipitate was filtered and washed several times with water to remove DMF and Et<sub>4</sub>NBr, and dried in vacuo. Water was added to the filtrate and another crop of polymer was obtained (DMF-soluble fraction), which was also washed and dried. Yield: 66 mg (0.37 mmol; 10%) of insoluble fraction and 510 mg (2.83 mmol; 75%) of DMF-soluble fraction. <sup>1</sup>H NMR: 2.32 (m, 4H), 7.10 (m, 8H). FTIR (cm<sup>-1</sup>): 3054 (CH, aromatic), 2925, 2860 (CH aliphatic), 1602, 1485 (C=C, aromatic), 1443, 1341 (CH aliphatic), 825 (CH aromatic). TG: 140 °C (Δm=-2%); 300 °C (Δm=-25%); 630 °C (Δm= -92%); SEC: Mw=9.1×10<sup>2</sup> g mol<sup>-1</sup>, Mn=5.9×10<sup>2</sup> g mol<sup>-1</sup>, Mw/Mn=1.5.