

## Electronic supplementary information (ESI)

**Experimental details.** Unless otherwise indicated, all reagents were obtained from commercial suppliers and were used without further purification. The solvents used were of commercial p.a. quality. The reactions were carried out under argon with the use of standard and Schlenk techniques. Solution  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data of the monomers were recorded on a Bruker ARX 400-spectrometer. Thermogravimetric analyses were performed at a Mettler Toledo TGA Star<sup>e</sup> System. Elemental analyses were obtained on a Perkin Elmer 240 B. Mass spectrometry analysis was performed on a time-of-flight mass spectrometer (Bruker Daltonics MicrOTOF) equipped with a homemade multi purpose ion source (MPIS) [20].

**Nitrogen sorption measurements.** The nitrogen sorption measurements were performed at a QUANTACHROME Autosorb-1 or a BELSORP Max. The surface areas were calculated using the BET model in the pressure range  $p/p_0$  from 0.05 – 0.25. The total pore volume was determined at a relative pressure of 0.95.

**Solid-State NMR Methods.** All  $^{13}\text{C}$ -CPMAS spectra were recorded at 125.77 MHz using a Bruker Avance 500 machine and a commercially available Bruker 2.5 mm double-resonance MAS probe at a spinning frequency of 25 kHz, typical  $\pi/2$ -pulse lengths of 2.5  $\mu\text{s}$  and recycle delays of 4-20 s. The  $^{13}\text{C}$  NMR spectra were referenced with respect to tetramethyl silane (TMS) using solid L-alanine as secondary standard (carbonyl peak at 177.9 ppm). If not stated otherwise, all spectra were collected at room temperature, acquiring 16384 or 4096 scans, respectively, with TPPM15 proton decoupling at an approximate rf-field of 100 kHz.

**Treatment (washing) with supercritical carbon dioxide.** Prior to the supercritical drying process all samples were soaked with absolute ethanol (72 h). The drying procedure was performed in a supercritical point dryer from Tousimis<sup>TM</sup> (Samdri – 795) with liquid  $\text{CO}_2$  (Messer) as carbon dioxide source. The dry samples were obtained after four drying cycles:

The ethanol-containing samples were placed inside the dryer and the ethanol was exchanged by rinsing with liquid  $\text{CO}_{2(l)}$  over a period of 1 hour. After that the chamber was sealed and the temperature was raised to 40°C resulting in a chamber pressure of around 1300 psi well above the critical point of  $\text{CO}_2$ . The chamber was held above the critical point for 1 hour. This procedure was repeated for additional three times with the following modifications: second run: 5 min purging, 1 h supercritical conditions, third run: 5 min purging, 2.5 hr supercritical conditions; last run 5 min purging, 14 h supercritical conditions.

## Monomer synthesis

### General procedure for monomers **G** and **H**

14.79 mmol (5.0 g) 3,6-dibromofluorenone, 40.13 mmol of the N-methyl- or N-phenyl-substituted aniline, 42.0 mmol (4.0 g) sodium-*tert*-butoxide, 0.20 mmol (45 mg) palladium(II) acetate and 0.40 mmol (81 mg) tri-*tert*-butylphosphine in 100 mL of dry toluene were introduced into a Schlenk tube under inert atmosphere and exclusion of light. The reaction mixture was heated up to 100°C for 18 h. The mixture was then filtered through celite and washed with several portions of hot ethyl acetate. After evaporation of the solvent the remaining residue was purified by column chromatography on silica (eluent: hexane/tetrahydrofurane: 96 /4 v/v).

### 3,6-Bis(N,N-diphenylamino)fluorenone (**G**)

Yield: 82% orange solid

<sup>1</sup>H NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 400 MHz): δ [ppm] = 7.44 (d, J=8.2, 2H), 7.30 (m, 8H), 7.12 (m, 12H), 7.03 (s, 2H), 6.77 (d, J=8.2, 2H).

<sup>13</sup>C NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 100 MHz): δ [ppm] = 191.1, 153.7, 146.8, 145.4, 129.9, 128.6, 125.9, 125.4, 124.8, 121.4, 113.5.

Mass: m/z (calc) = 514.19 (514.62).

Anal. Calcd. for C<sub>37</sub>H<sub>26</sub>N<sub>2</sub>O: C, 86.35; H 5.09; N, 5.44; O, 3.11; Found: C, 86.44; H, 5.18; N, 5.30.

### 3,6-Bis(N-phenyl-N-methylamino)fluorenone (**H**)

Yield: 65 % orange solid

<sup>1</sup>H NMR (THF-d<sub>8</sub>, 400 MHz): δ [ppm] = 7.40 – 7.34 (m, 6H), 7.24 (d, J = 1.2, J = 8.7 Hz, 4H), 7.18 – 7.14 (m, 2H), 7.03 (d, J = 2.1 Hz, 2H), 6.63 (dd, J = 2.2, J = 8.3 Hz, 2H), 3.40 (s, 6H)

<sup>13</sup>C NMR (THF-d<sub>8</sub>, 100 MHz): δ [ppm] = 190.0, 154.6, 148.9, 146.4, 130.3, 127.3, 126.0, 125.5, 124.9, 115.4, 107.7, 40.7.

Mass: m/z (calc) = 390.16 (390.48)

Anal. Calcd. for C<sub>27</sub>H<sub>22</sub>N<sub>2</sub>O: C, 83.05; H, 5.68; N, 7.17; O, 4.10; Found: C, 82.81; H, 5.62; N, 7.14.

### *General procedure for monomers I and J*

In a 30 mL microwave vial 3.46 mmol (1.00 g) 4-(diphenylamino)phenylboronic acid, 1.73 mmol (0.584 g) 3,6-dibromofluorenone, (80 mg, 0.069 mmol, 2.0 mol %) tetrakis(triphenylphosphino)palladium(0), 3.5 ml of a 40% aqueous solution of triton B, and 15 mL of tetraline were irradiated with microwaves under an inert atmosphere for 12 min (120°C, 300 W) in a Biotage Microwave apparatus. The mixture was diluted with 300 mL of chloroform and washed with aqueous 2N HCl, water, and brine. The organic phase was dried with magnesium sulfate and the chloroform removed at reduced pressure. The product was crystallized from tetraline to yield red-orange coloured solids.

#### 3,6-Bis[4-(N,N-diphenylamino) phenyl]fluorenone (**I**)

Yield: 53%, orange solid

<sup>1</sup>H NMR (THF-d<sub>8</sub>, 400 MHz): δ [ppm] = 8.04 (s, 2H), 7.68 – 7.64 (m, 6H), 7.60 (dd, J = 1.4, J = 7.7 Hz, 2H), 7.30 – 7.25 (m, 8H), 7.16 – 7.10 (m, 12H), 7.06 – 7.01 (m, 4H).

<sup>13</sup>C NMR (THF-d<sub>8</sub>, 100 MHz): δ [ppm] = 195.8, 153.0, 152.1, 151.4, 149.5, 138.3, 137.7, 133.8, 132.4, 131.4, 129.1, 128.5, 127.8, 127.7, 123.0.

Mass: m/z (calc) = 666.23 (666,81)

Anal. Calc for C<sub>49</sub>H<sub>34</sub>N<sub>2</sub>O: C, 88.26; H, 5.14; N, 4.20; O, 2.40. Found: C, 87.78; H, 4.96; N, 4.01.

#### 3,6-Bis[4-(N-phenyl-N-methylamino)phenyl]fluorenone (**J**)

Yield: 60% red solid

<sup>1</sup>H NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 400 MHz): δ [ppm] = 7.75 (s, 2H), 7.66 (d, J=7.5 Hz, 2H), 7.56 (d, J= 8.3 Hz, 4H), 7.48 (d, J=7.2 Hz, 2H), 7.36 (dd, J=7.2 Hz, J=7.5 Hz, 4H), 7.16 (d, J=7.5 Hz, 4H), 7.07 (dd, J=7.2 Hz, J=7.2 Hz, 2H), 7.01 (d, J=7.9 Hz, 4H), 3.36 (s, 6H).

<sup>13</sup>C NMR (C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> 100 MHz): δ [ppm] = 192.1, 149.1, 148.4, 147.8, 145.1, 133.0, 131.0, 129.8, 128.2, 127.1, 124.9, 123.5, 123.4, 118.4, 118.2, 40.5

Mass: m/z (calc) = 542.21 (542,67)

Anal. Calc for C<sub>39</sub>H<sub>30</sub>N<sub>2</sub>O: C, 86.32; H, 5.57; N, 5.16; O, 2.95. Found: C, 85.78; H, 5.25; N, 4.92

## Polymer synthesis

### *General Procedure for Polymerisation*

2.5 mmol of the mono- or bisarylamino-fluorenone and 35.0 mmol of methane sulfonic acid in 20 ml of *o*-dichlorobenzene were heated up to 140°C for 18 h. The crude product was filtered off from the hot reaction mixture and carefully extracted with water, ethanol, acetone, and chloroform to remove reagents, solvents and possible low molecular weight by-products. The product was vacuum dried at 180°C for 3 days. The MPNs were obtained in quantitative yields as reddish brown colored, powdery solids.

#### *Polymer A (from monomer A)*

Yield: quantitatively

Elemental Analysis: Calc.: N, 5.66; Found: N, 5.26.

TGA: first decomposition step, maximum: 318°C (weight loss: 3.7 %)

#### *Polymer B (from monomer B)*

Yield: quantitatively

Elemental Analysis: Calc.: N, 7.52; Found: N, 7.31.

TGA: first decomposition step, maximum: 353°C (weight loss: 8.4 %)

#### *Polymer A/B (from monomers A/B)*

Yield: quantitatively

Elemental Analysis: Calc.: N, 6.46; Found: N, 5.74.

TGA: first decomposition step, maximum: 390°C (weight loss: 4.2%)

#### *Polymer C (from monomer C)*

Yield: quantitatively

Elemental Analysis: Calc.: N, 4.25; Found: N, 4.33;

TGA: first decomposition step, maximum: 310°C (weight loss: 9.0 %)

#### *Polymer A/C (from monomers A/C)*

Yield: quantitatively

Elemental Analysis: Calc.: N, 4.95; Found N, 4.53

TGA: first decomposition step, maximum: 343°C (weight loss: 4.6 %)

*Polymer B/C (from monomers B/C)*

Yield: quantitatively

Elemental Analysis: Calc.: N, 5.88. Found: N, 5.48.

TGA: first decomposition step, maximum: 338°C (weight loss: 4.86 %)

*Polymer D (from monomer D)*

Yield: quantitative

Elemental Analysis: Calc.: N, 4.33. Found: N, 4.15.

TGA: first decomposition step, maximum: 335°C (weight loss: 2.8 %)

*Polymer D/F (from monomers D/F)*

Yield: quantitative

Elemental Analysis: Calc.: N, 3.89. Found: N, 3.23.

TGA: first decomposition step, maximum: 363°C (weight loss: 3.4 %)

*Polymer F (from monomer F)*

Yield: quantitative

Elemental Analysis: Calc.: N, 3.46; Found: N, 2.91.

TGA: first decomposition step, maximum: 347°C (weight loss: 2.6 %)

*Polymer E (from monomer E)*

Yield: quantitative

Elemental Analysis: Calc.: N, 5.34. Found: N, 4.93.

TGA: first decomposition step, maximum: 400°C (weight loss: 10.4 %)

*Polymer E/F (from monomers E/F)*

Yield: quantitative

Elemental Analysis: Calc.: N, 4.28; Found: N, 3.94;

TGA: first decomposition step, maximum: 373°C (weight loss: 13.9 %)

*Polymer D/E (from monomers D/E)*

Yield: quantitative

Elemental Analysis: Calc.: N, 4.83; Found N, 4.55;

TGA: first decomposition step, maximum: 298°C (weight loss: 14.8 %)

*Polymer G (from monomer G)*

Yield: quantitative

Elemental Analysis: Calc.: N, 5.66; Found: N, 5.26

TGA: first decomposition step, maximum: 299°C (weight loss: 1.4 %)

*Polymer H (from monomer H)*

Yield: quantitative

Elemental Analysis: Calc.: N, 7.52; Found: 7.14;

TGA: first decomposition step, maximum: 382°C (weight loss: 10.8 %)

*Polymer G/H (from monomers G/H)*

Yield: quantitative

Elemental Analysis: Calc.: N, 6.46 Found: 6.51

TGA: first decomposition step, maximum: 262°C (weight loss: 2.9 %)

*Polymer I (from monomer I)*

Yield: quantitative

Elemental Analysis: Calc.: N, 4.33. Found: 4.28.

TGA: first decomposition step, maximum: 301°C (weight loss: 3.9 %)

*Polymer J (from monomer J)*

Yield: quantitative

Elemental Analysis: Calc.: N, 4.33. Found: 4.14

TGA: first decomposition step, maximum 336°C (weight loss 4.03%)

*Polymer I/J (from monomers I/J)*

Yield: quantitative

Elemental Analysis: Calc.: N, 4.83; Found N, 4.86

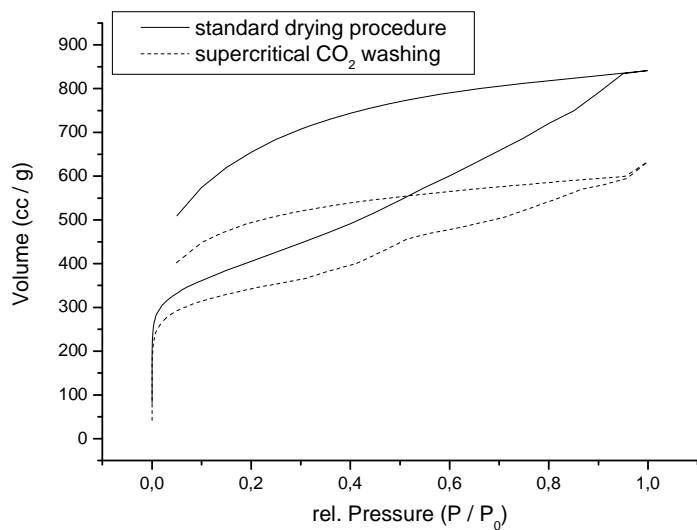
TGA: first decomposition step, maximum 300°C (weight loss 6,11%)

*Polymer A/D (from monomers A/D)*

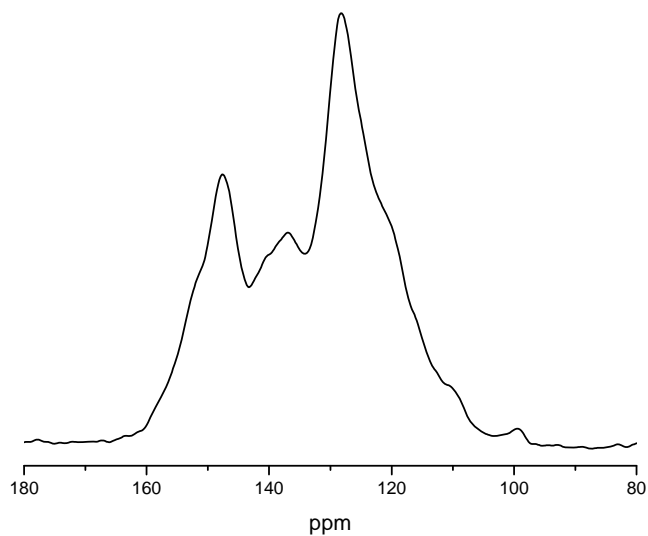
Yield: quantitative

Elemental Analysis: Calc.: N, 4.99; Found N, 4.50

TGA: first decomposition step, maximum 367°C (weight loss 1.52%)



*Figure S1: Nitrogen physisorption isotherm of the MPN generated from monomer A (Entry 1) before and after supercritical carbon dioxide washing.*



*Figure S2: Solid State <sup>13</sup>C NMR (MAS) spectrum of the MPN generated from monomer A (Entry 1).*

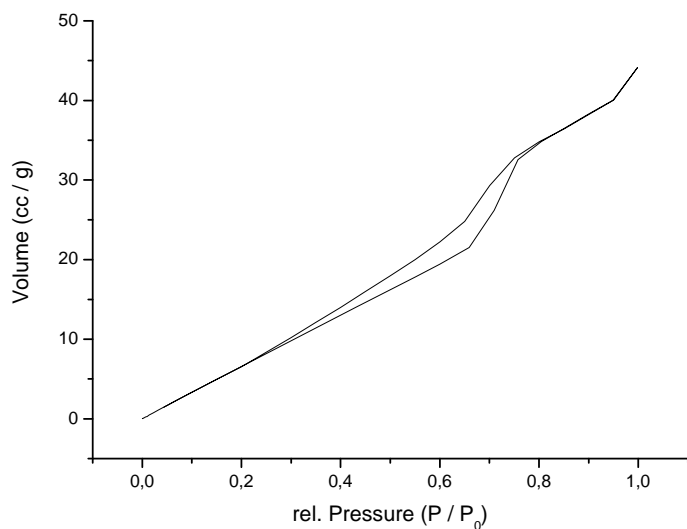


Figure S3: Nitrogen physisorption isotherm of the MPN generated from monomer **B** (Entry 2).

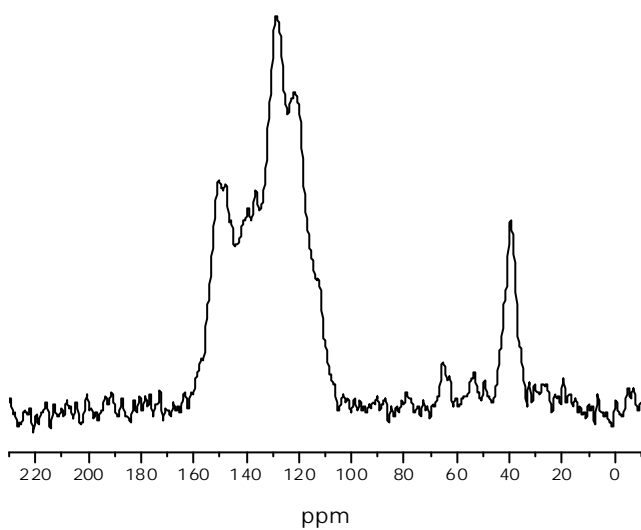
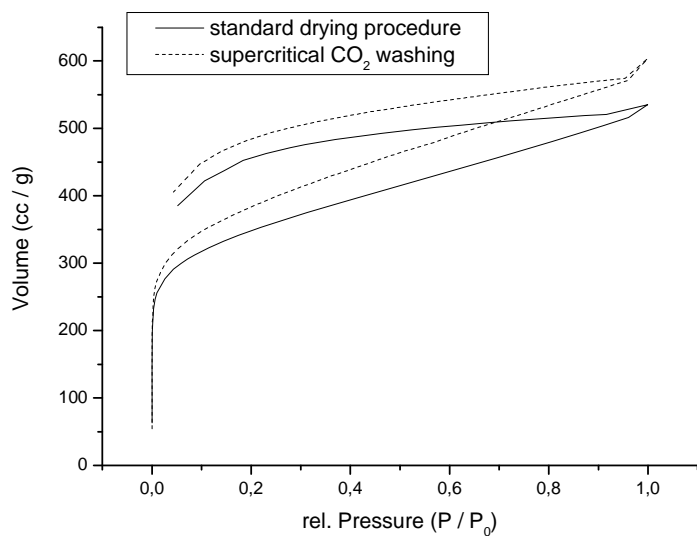
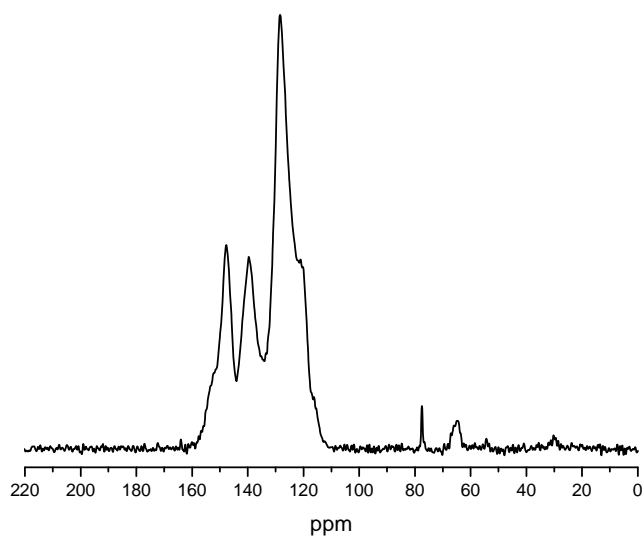


Figure S4: Solid State  $^{13}\text{C}$  NMR (MAS) spectrum of the MPN generated from monomer **B** (Entry 2).





*Figure S5: Nitrogen physisorption isotherm of the MPN generated from monomer **D** (Entry 3) before and after supercritical carbon dioxide washing.*



*Figure S6: Solid State <sup>13</sup>C NMR (MAS) spectrum of the MPN generated from monomer **D** (Entry 3).*

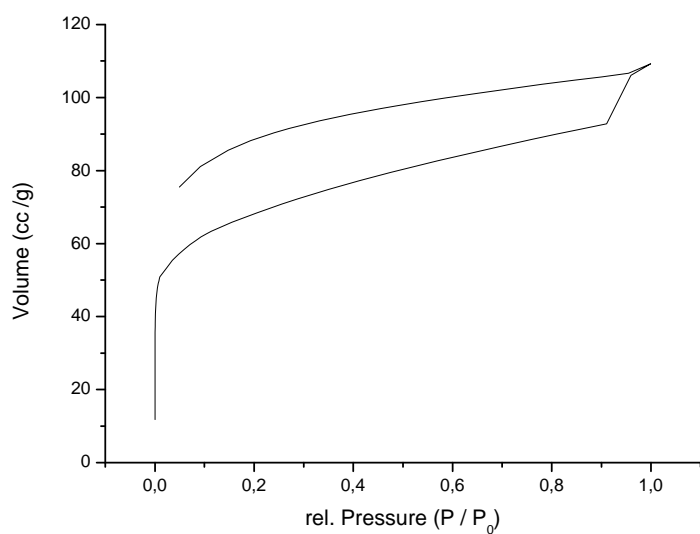


Figure S7: Nitrogen physisorption isotherm of the MPN generated from monomer C (Entry 4).

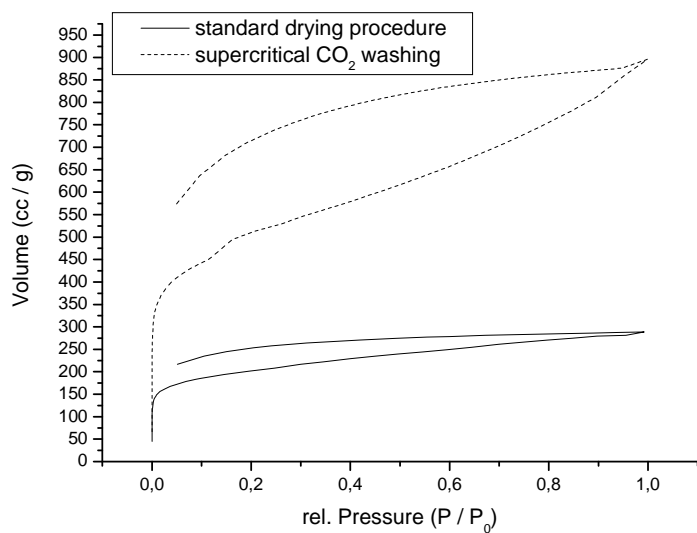
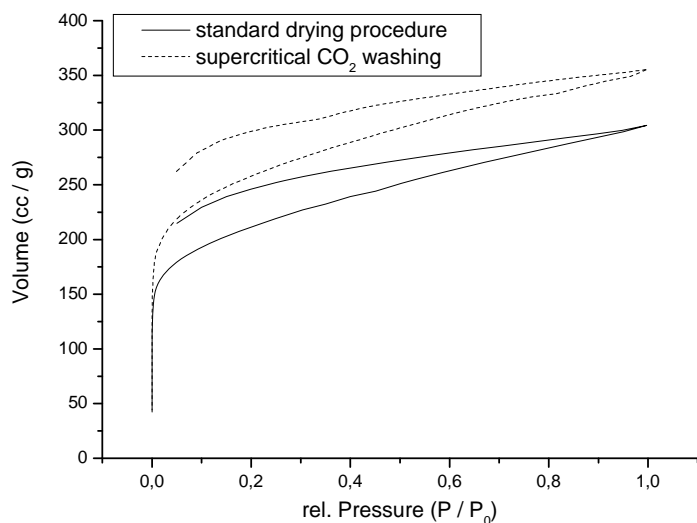
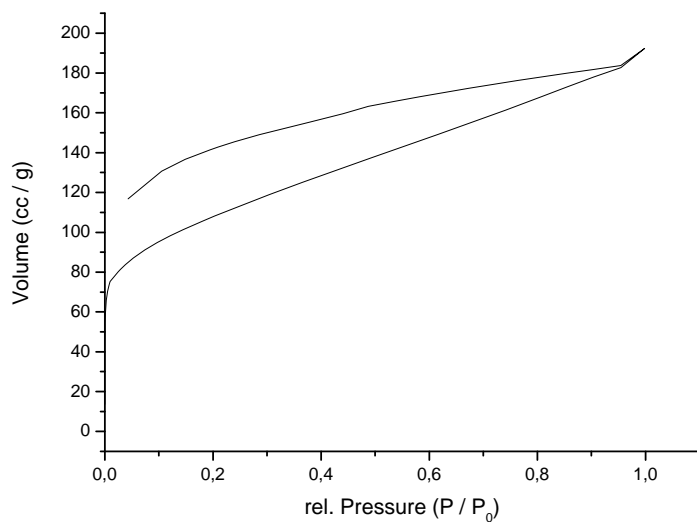


Figure S8: Nitrogen physisorption isotherm of the MPN generated from monomers A/C (Entry 5) before and after supercritical carbon dioxide washing.



*Figure S9: Nitrogen physisorption isotherm of the MPN generated from monomer F (Entry 9) before and after supercritical carbon dioxide washing.*



*Figure S10: Nitrogen physisorption isotherm of the MPN generated from monomers D/F (Entry 11).*

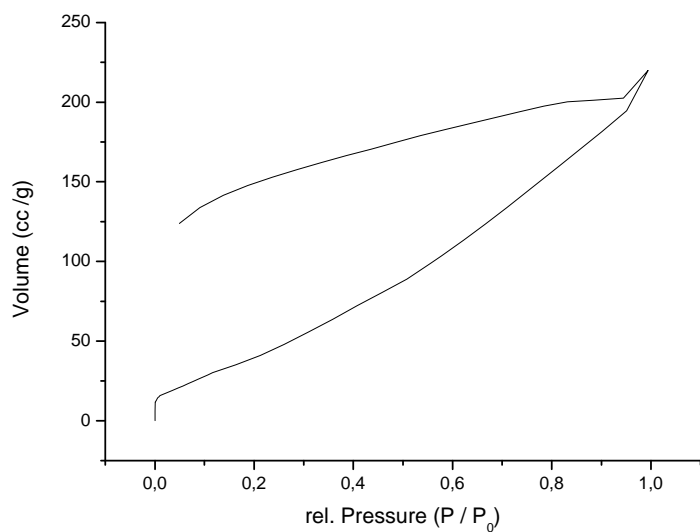


Figure S11: Nitrogen physisorption isotherm of the MPN generated from monomer **J** (Entry 17).

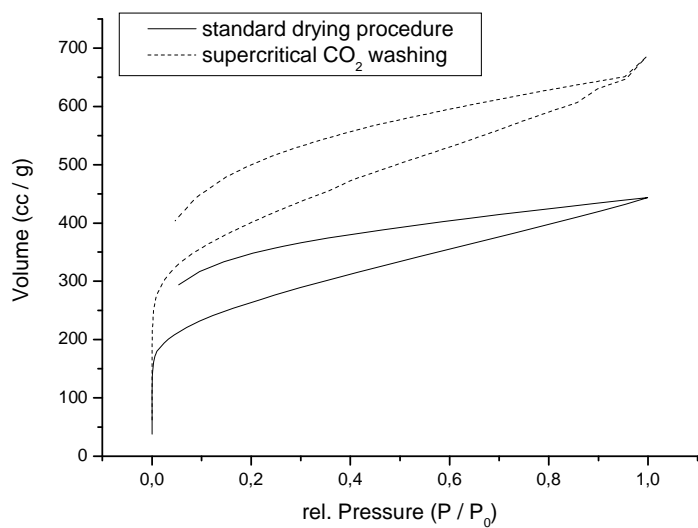
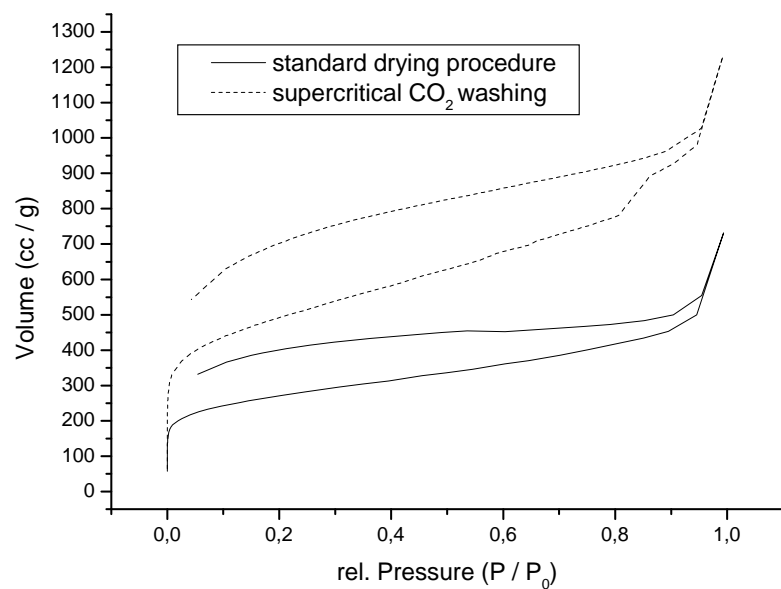


Figure S12: Nitrogen physisorption isotherm of the MPN generated from monomers **I/J** (Entry 18) before and after supercritical carbon dioxide washing.



*Figure S13: Nitrogen physisorption isotherms of the MPN generated from monomers A/D (Entry 19) before and after supercritical carbon dioxide washing.*