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New PIM-1 copolymers containing 2,3,6,7-anthracenetetrayl moiety and their use as gas separation membranes

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Experimental section

Materials

5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI, 97%) was obtained from TCI (Europe), 2,3,5,6,-tetrafluoroterephthalonitrile (TFTPN, 99%) P&M (Moscow, Russia). K_2CO_3 (Acrus, K_2CO_3, >99.5%) was dried overnight at 160 °C. Dimethyl sulfoxide (DMSO, ≥99%), tetrahydrofuran (THF, ≥99.0%), methanol (≥99.0%), chloroform ($CHCl_3$, 99.0%), veratrole, *p*-fluorobenzaldehyde, HPA - 12-Tungstophosphate hydrate ($H_3PW_{12}O_{40}$), were purchased from Sigma-Aldrich and were used as received.

Synthesis of 2,3,6,7-tetrahydroxy-9,10-di(p-fluorophenyl)anthracene ***6***

a) Veratrole 8.28 g (0.06 mol), *p*-fluorobenzaldehyde 2.48 g (0.02 mol), 12-Tungstophosphate hydrate 3.5 g were reacted during 5 min under microwaves of 120 W in microwave oven.

b) Next portion of *p*-fluorobenzaldehyde 4.96 g (0.04 mol), 12-Tungstophosphate hydrate 0.8 g, 10 ml of Ac_2O were added into reaction mixture which was then heated 2 h at 90 °C. After cooling 200 ml of $CHCl_3$ was added into the reaction and insoluble HPA was filtered. 100 ml of $CHCl_3$ were evaporated at room T during 2 days and 10.5 g (~70%) of the **4**+**5** -70/30 by mol. The products were separated by filtration.

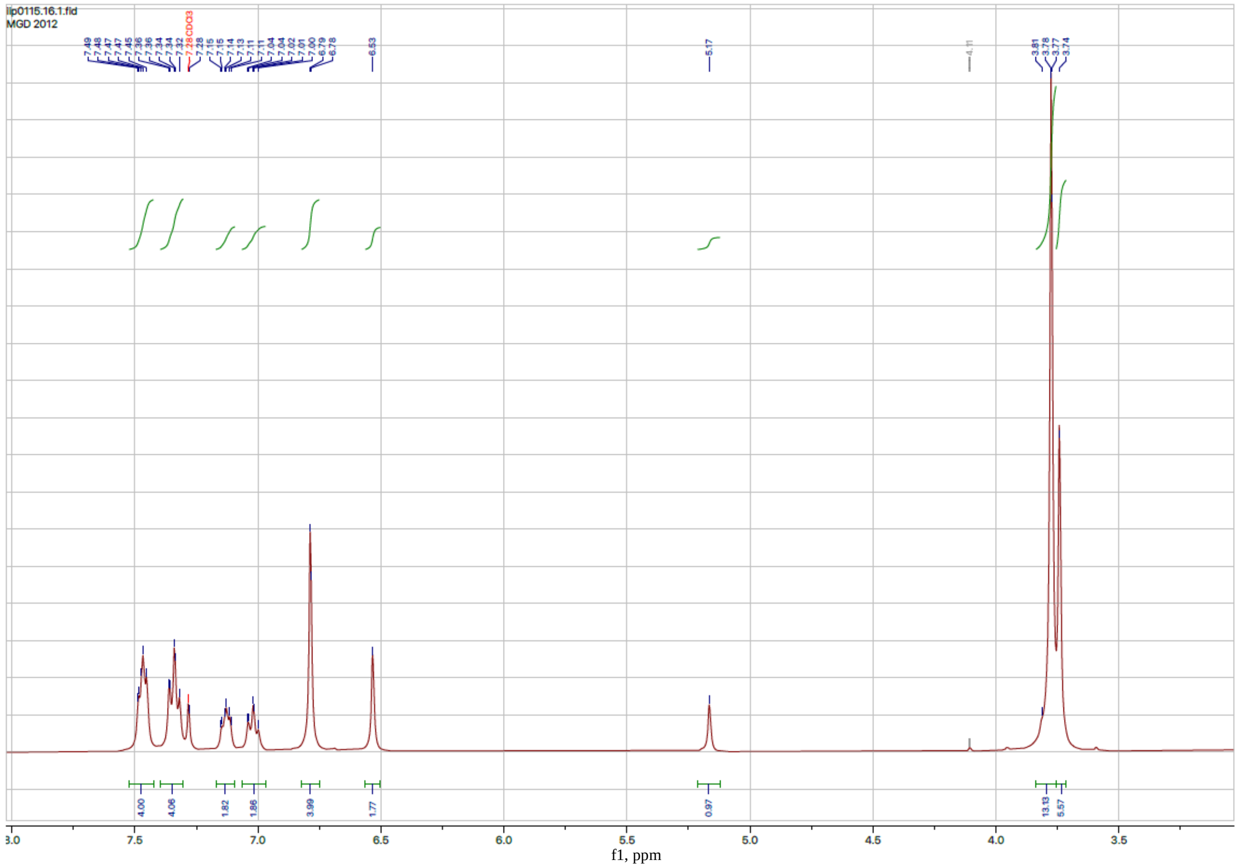

Figure S1 ^{1}H NMR spectrum of the mixture of intermediate compounds, respectively **4:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.49 (m, 4H), 7.06 – 6.97 (m, 4H), 6.53 (s, 4H), 5.17 (s, 2H), 3.74 (s, 12H) and **5:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 – 7.15 (m, 4H), 7.38 – 7.30 (m, 4H), 6.79 (s, 4H), 3.77 (s, 12H).

c) Solution of 10 g of compound **5** in 50 ml of boiling AcOH was treated by 30 ml of 48% HBr during 6 h under reflux. After cooling 8 g (~90%) of compound **6** were separated by filtration. M.P.=329-331 °C. Elemental analysis $C_{26}H_{16}F_2O_4$: C-72.56; H-3.75; F-8.83. Found C-72.61; H-3.83; F- 8.73. M-430.41

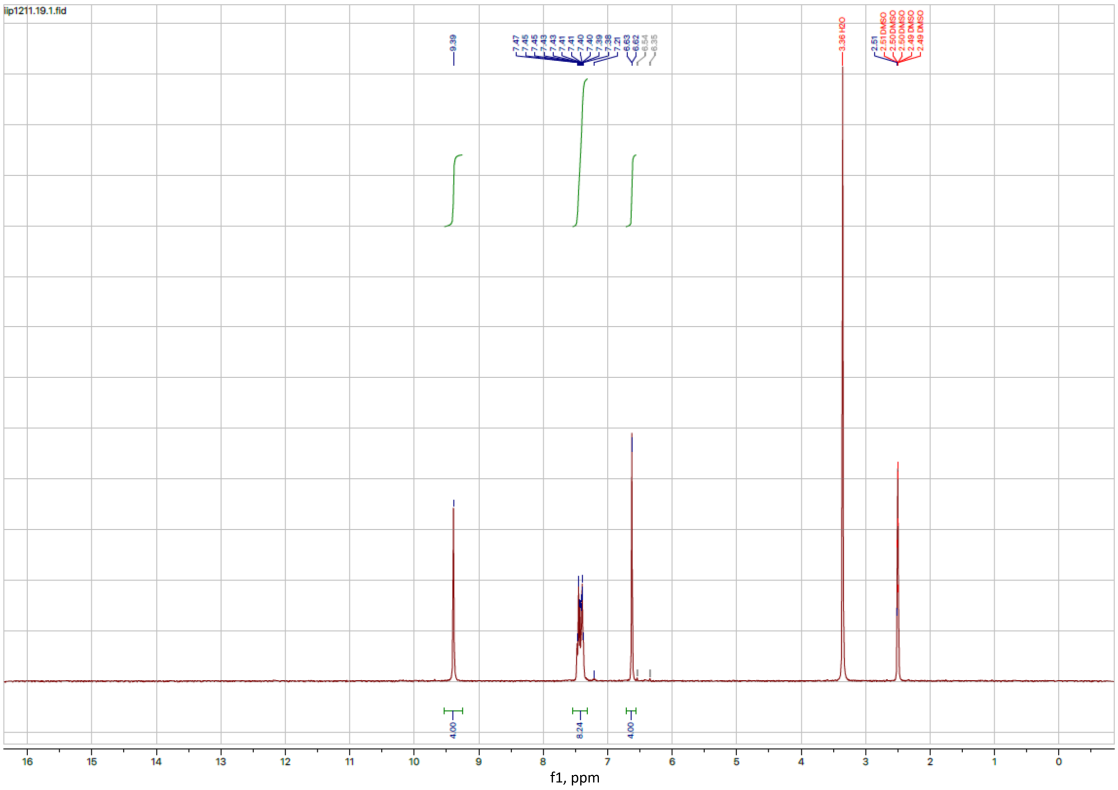

Figure S2 ^{1}H NMR of monomer **6** (400 MHz, DMSO) δ 9.39 (s, 2H), 7.59 – 7.29 (m, 4H), 6.72 – 6.54 (m, 2H).

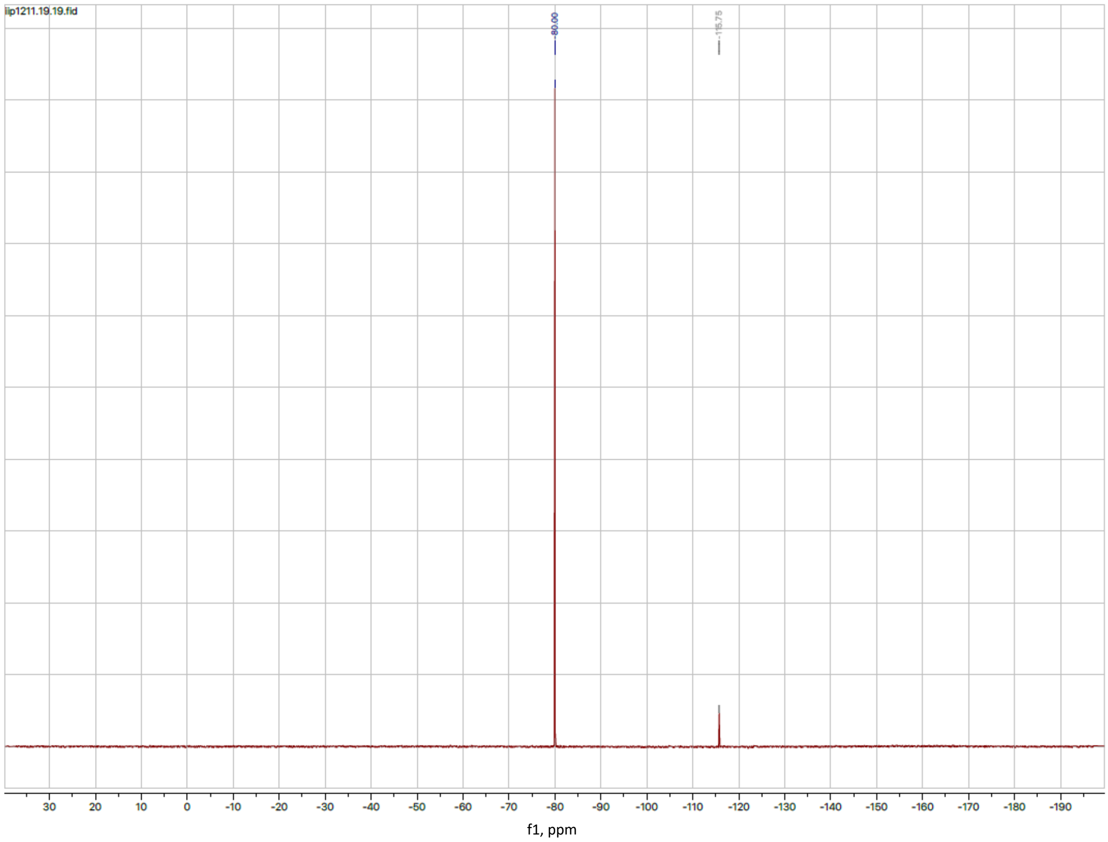

Figure S3 ^{19}F NMR of monomer **6** (400 MHz, DMSO) δ -80.00.

*Synthesis of 9,10-bis(4-fluorophenyl)-2,3,6,7-tetrakis[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenoxy]anthracene **7***

0.861 g (2 mmol) of *2*,3,6,7-tetrahydroxy-9,10-di(p-fluorophenyl)anthracene **6**, 1.9 g (8 mmol) of octafluorotoluene, 1.1 g (8 mmol) of K_2CO_3, 8 ml of DMSO and 2 ml of toluene were charged into a flask under argon flow at room temperature. The stirred mixture was placed into ultrasonic bath (Elmasonic S10H) pre-heated to 80 °C with non-stop sonification at 37 kHz for 5 h. Then 30 mL of DI water was added into reaction mixture and the heating continued under sonification for 30 min to eliminate all inorganics. After filtration and drying 2.0 g (77%) of white crystals was obtained. After crystallization from acetone 1.77 g of pure compound **7** was recovered. M.P.=256-259 °C. Elemental analysis $C_{54}H_{12}F_{30}O_4$:: C-50.10; H-0.93; F-44.02. Found C-50.5; H-0.83; F-43.93. M-1294.6

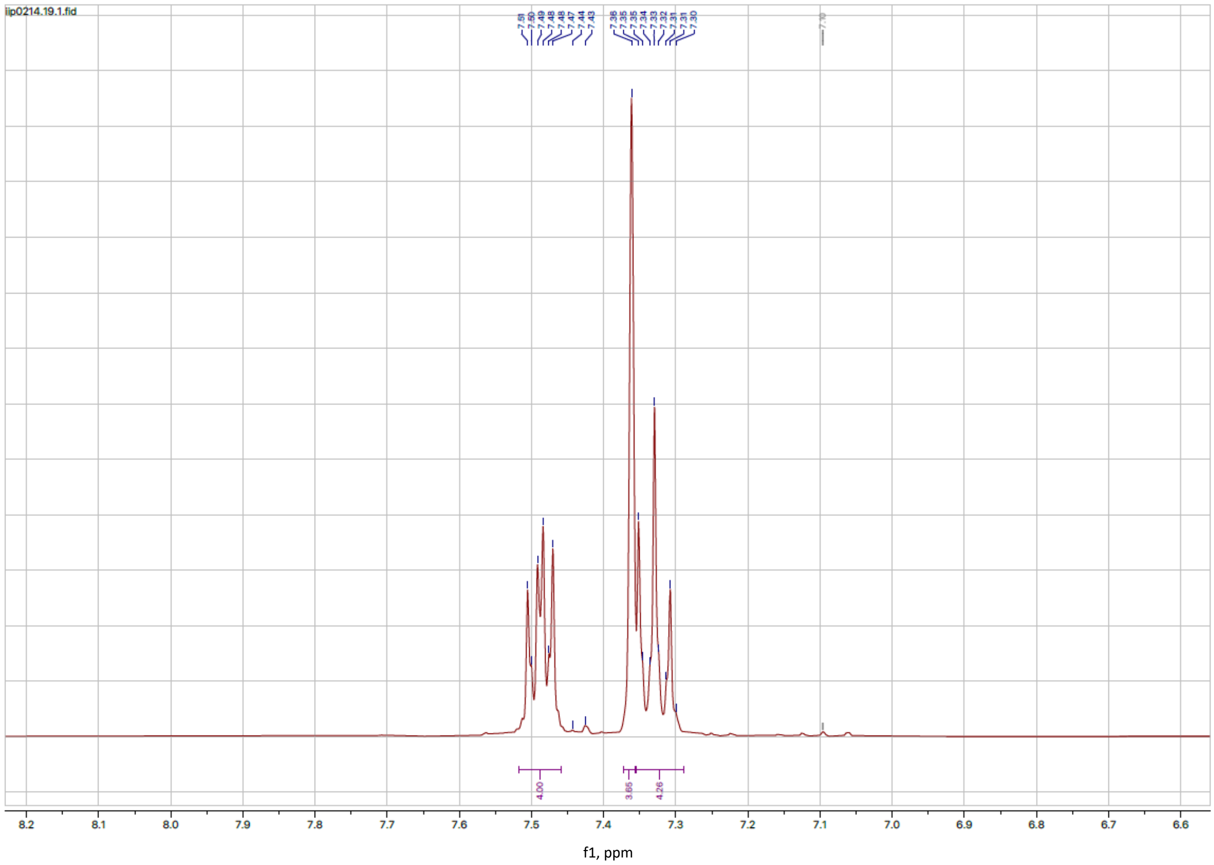

Figure S4 ^{1}H NMR of the model reaction product **7** (400 MHz, Acetone-d_6) δ 7.52 – 7.46 (m, 4H), 7.36 (s, 4H), 7.35 – 7.29 (m, 4H).

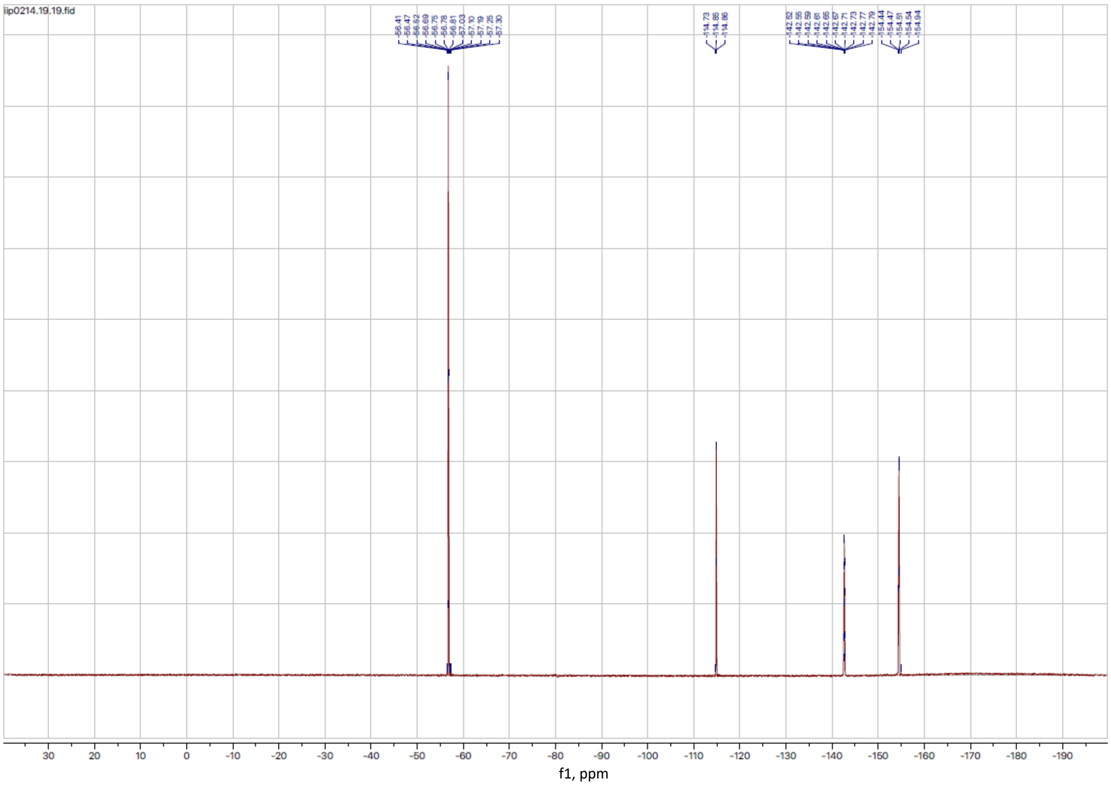

Figure S5 ^{19}F NMR of the model reaction product **7** (376 MHz, Acetone-d_6) δ -56.75, -114.85, -142.66, -154.45.

*Synthesis of PIM-1 as well as its copolymers **2** and **3a–e** in DMSO*

1.0210 g (3 mmol) of TTSBI (or its mixture with monomer **6** 0.95/0.05; 0.9/0.1; 0.85/0.15; 0.8/0.2), 0.6003 g (3 mmol) of TFTPN, 1.24 g (9 mmol) or 1.60 g (12 mmol) of K_2CO_3, 8 or 12 ml of DMSO and 2 ml of toluene were charged into a flask under argon flow and room temperature. The stirred mixture was placed into ultrasonic bath (Elmasonic S10H) pre-heated to 80 °C with non-stop sonification at 37 kHz for 5 h. Then 30 ml of DI water was added into reaction mixture and the heating continued under sonification for 30 min. Very thin yellow polymer powder was isolated by filtration. The rests of inorganic salts and DMSO were eliminated by subsequent extraction of PIM-1 powder in Soxhlet's apparatus with EtOH/water mixture 1:1 v:v. After vacuum drying the yield of PIM-1 (or copolymers) was almost quantitative, 99%.

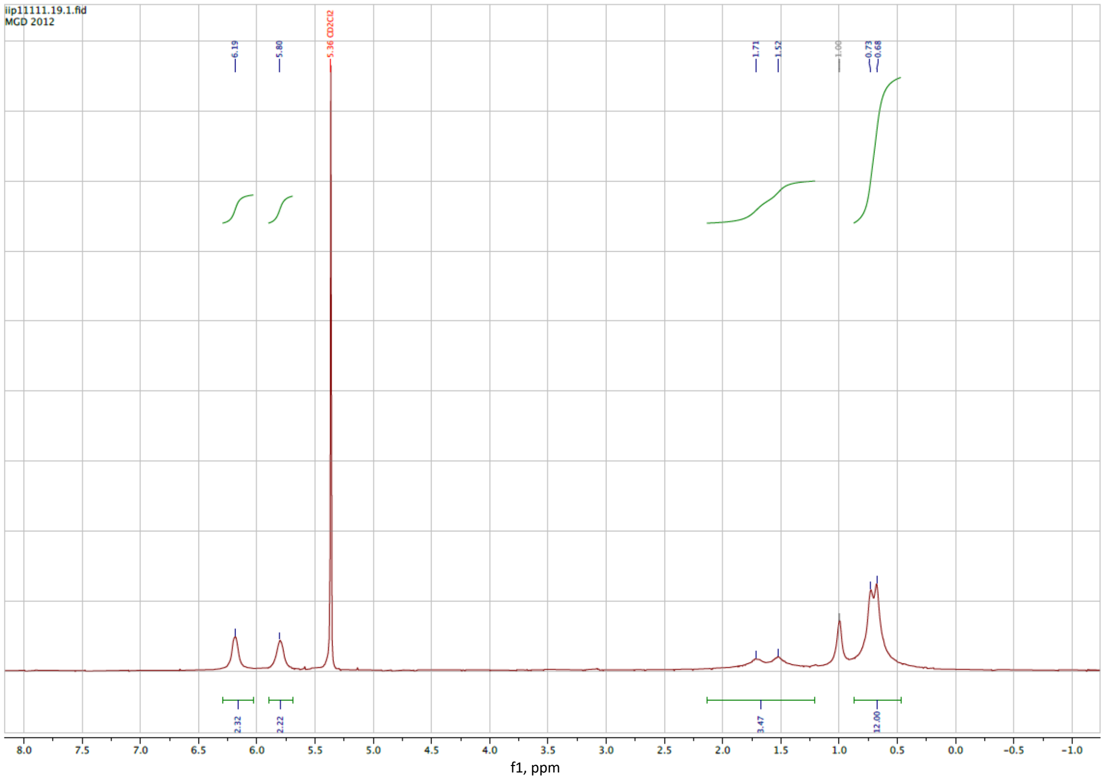

Figure S6 PIM-1 ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.19 (s, 2H), 5.80 (s, 2H), 1.61 (d, *J* = 77.6 Hz, 4H), 0.70 (m, 12H).

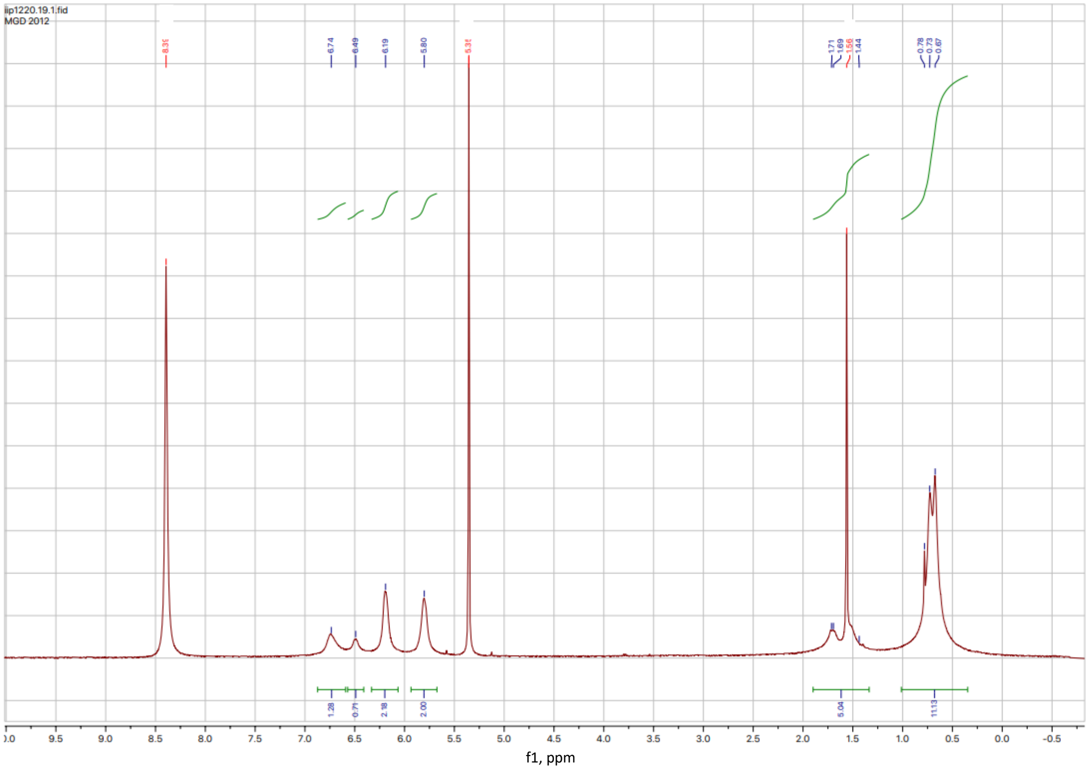

Figure S7 Copolymer **3d** (80/20) ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOD$) δ PIM-1 moiety 6.19 (s, 2H), 5.80 (s, 2H), 1.61 (d, *J* = 77.6 Hz, 4H), 0.73 (m, 12H). Monomer **6** moiety 6.74 (m, 8H), 6.69 (s, 4H).

Adsorption and desorption isotherms for polymers PIM-1, 2 and 3a-d

Nitrogen adsorption and desorption isotherms for the samples were obtained at 77 K with Surface Area and Pore Size Analyzer System 3P Micro 200 (3P Instruments GmbH & Co. KG, Germany). The calculations were performed using BET and BJH methods. T-method was applied for micropore surface area calculations. Software Surface Area & Pore Size Analyzer System, version 10 (3P Instruments) was applied for calculations of specific surface areas, specific volumes and size pore distribution plots. For higher precision, BET equation was applied to the beginning part of the isotherms precisely limited by p/p_0 values, found as p/p_0 value at maximum in Rouquerol plot of $V(1-p/p_0)$ vs. p/p_0. [J. Rouquerol, P. Llewellyn and F. Rouquerol, Stud. Surf. Sci. Catal., 2007, 160, 49.]

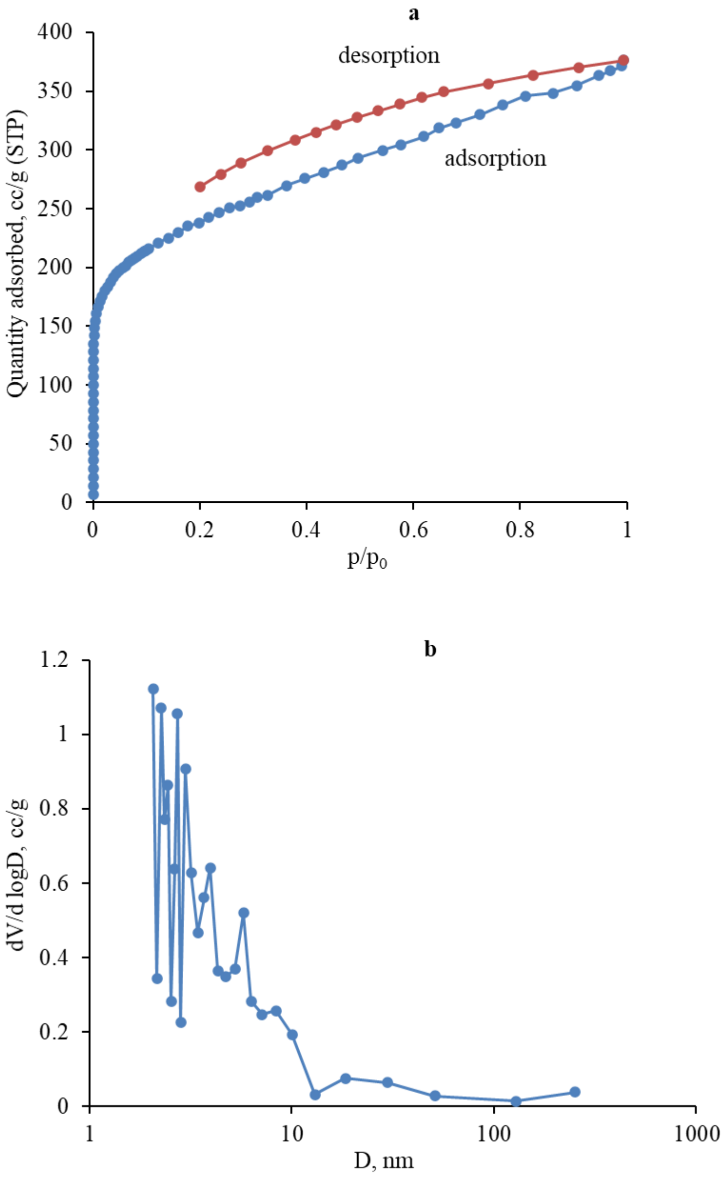

Figure S8 Adsorption and desorption isotherms (a) and BJH pore-size distribution (b) for PIM-1 (100/0).

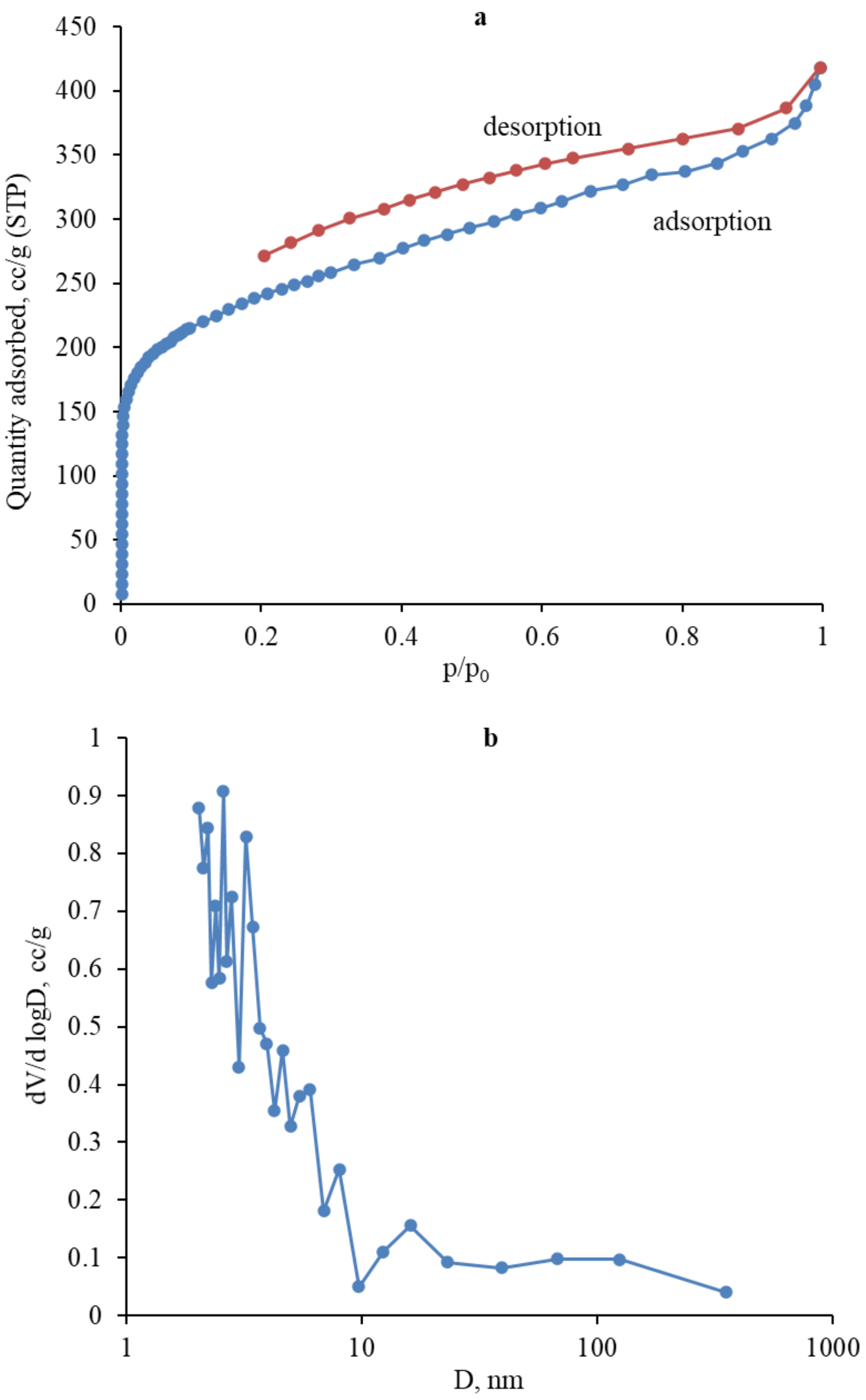

Figure S9. Adsorption and desorption isotherms (a) and BJH pore-size distribution (b) for copolymer **3a** (95/5).

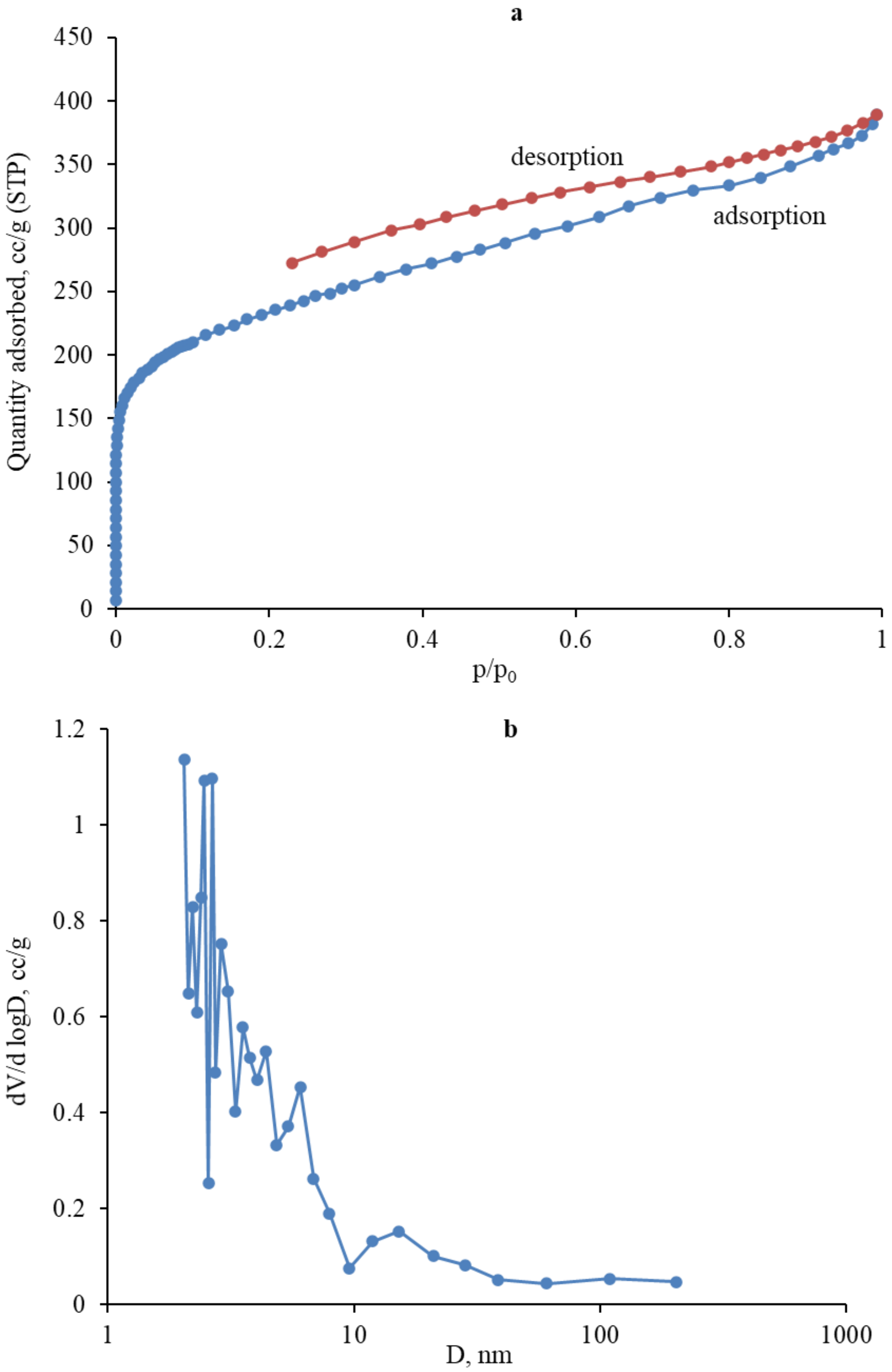

Figure S10. Adsorption and desorption isotherms (a) and BJH pore-size distribution (b) for copolymer **3b** (90/10).

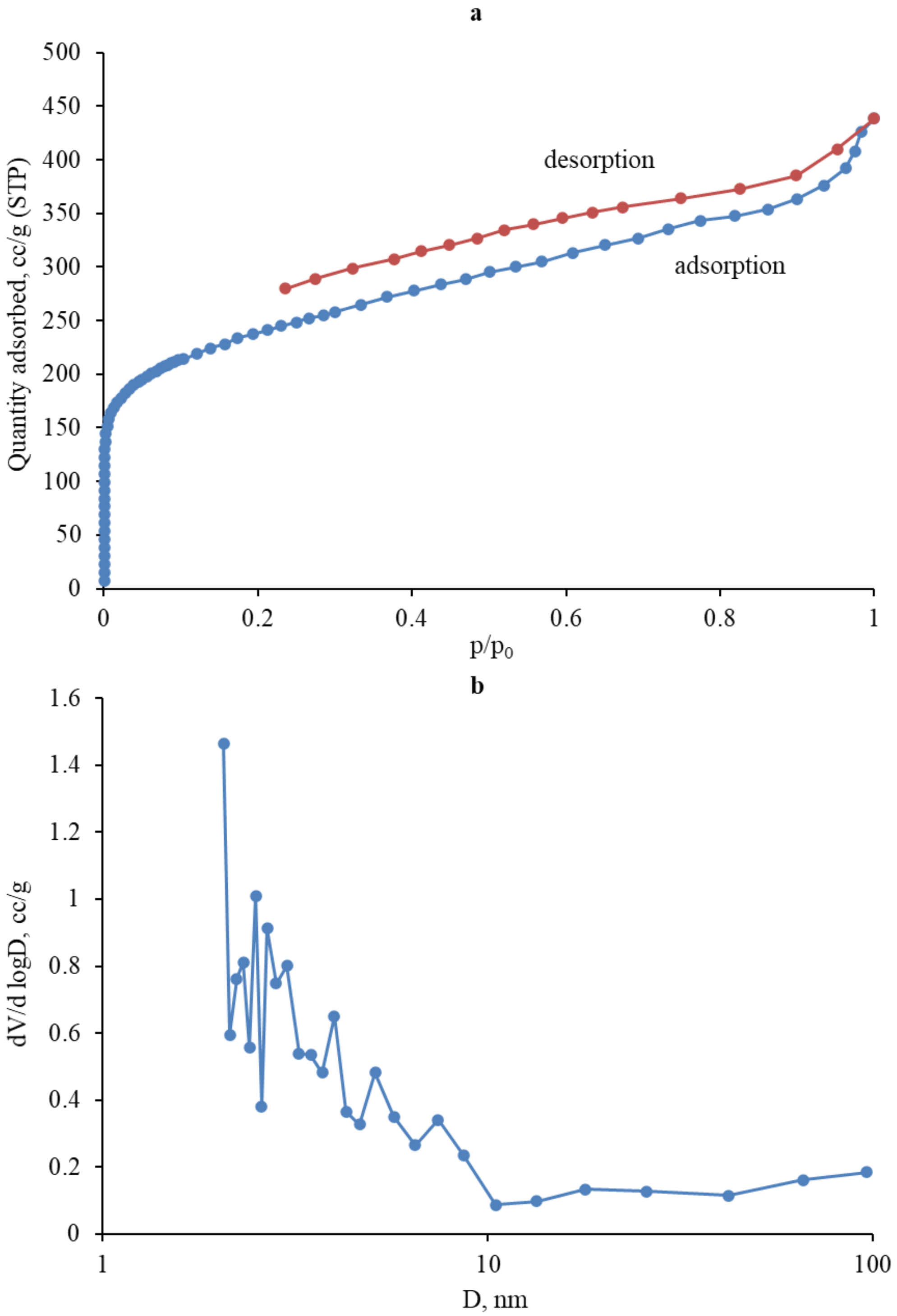

Figure S11. Adsorption and desorption isotherms (a) and BJH pore-size distribution (b) for copolymer **3c** (85/15).

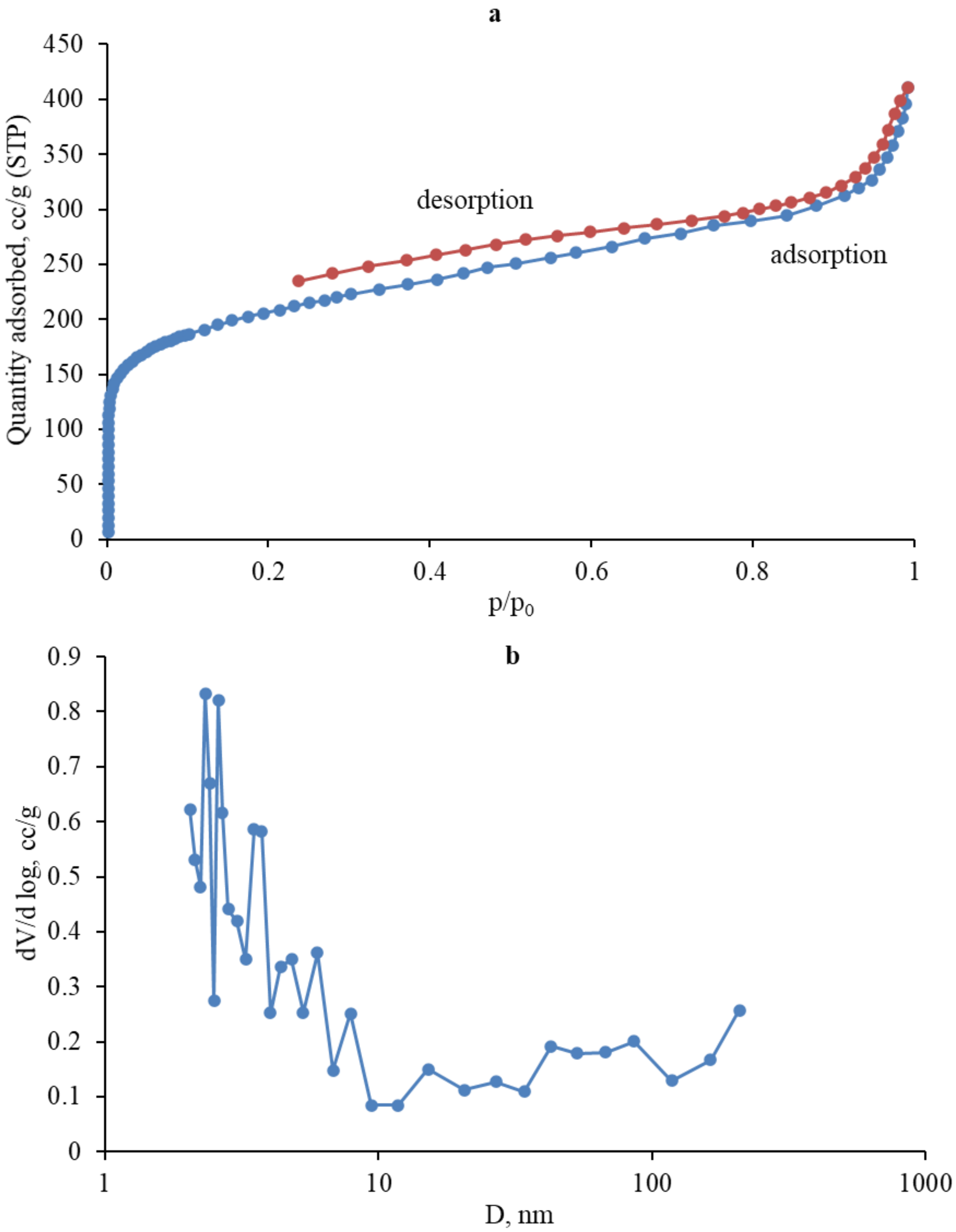

Figure S12. Adsorption and desorption isotherms (a) and BJH pore-size distribution (b) for copolymer **3d** (80/20).