Aging of the Reaction Mixture as a Tool to Modulate the Crystallite Size of UiO-66 into the Low Nanometer Range

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ELECTRONIC SUPPLEMENTARY INFORMATION

Chemicals.

$ZrCl_4$ and N,N-dimethylformamide (DMF) were purchased from Alfa Aesar. Glacial acetic acid was purchased from VWR. Terephthalic acid (H_2bdc) was purchased from Sigm-Aldrich. $ZrOCl_2 \cdot 8H_2O$ was purchased from Merck Millipore.

Samples preparation:

$ZrCl_4$ (0.35 g, 1.5 mmol) was dissolved in 15 mL of DMF inside a 20 mL glass vial. H_2O and/or AcOH were then added according to Table S1 and the mixture was sonicated until complete dissolution of $ZrCl_4$. The solution was either used fresh or aged for one or two days at room temperature prior to addition of 5 mL of a 0.3 M stock solution of H_2bdc in DMF, so that in the resulting solution [Zr] = [bdc] = 0.1 M. The vial was sealed and placed in an oven at 120 °C for 24 h. The product was centrifuged, washed with DMF (20 mL) and soaked overnight in DMF (20 mL). It was successively centrifuged again, washed with acetone (20 mL), soaked overnight in acetone (20 mL) and finally dried at 70 °C under vacuum.

The relative yields were calculated considering the weight of the desolvated and dehydroxylated compounds, of formula $Zr_6O_6(bdc)_6$, obtained by subtracting the weight loss at 400 °C during thermogravimetric analysis from the crude mass yield.

Analytical procedures.

Powder X-ray diffraction (PXRD) patterns were collected in the 4-40º 2θ range with a Bruker D8 Advance diffractometer equipped with a LYNXEYE XE detector, using the Cu Kα radiation. The X-ray tube was operated at 40 W and 40 mA.

Nitrogen sorption isotherms at 77 K were measured on a Micromeritics Tristar II analyzer. The samples (about 30 mg) were activated overnight under vacuum at 150 ºC prior to analysis. The BET numbers were calculated in the 0.010-0.070 P/P_0 range.

Scanning electron microscopy (SEM) images were collected on a Gemini 1530 (Zeiss) instrument at 1 kV (UiO-66).

Transmission electron microscopy (TEM) samples were prepared by dispersing the material in ethanol and putting some drops of this suspension onto the TEM grid (C-foil on Cu grid). TEM was performed on a Tecnai F30 (FEI, USA) microscope operated at 300 kV (field emission gun; SuperTwin lens with a point resolution of ca. 2 Angstrom).

Thermal gravimetric analysis (TGA) was performed on a Mettler-Toledo instrument at a 5 ºC min^{-1} heating rate up to 700 ºC under 80:20 nitrogen/oxygen atmosphere.

Table S1. Results and characterization of all the experiments performed in this work.

Sample	Water [eq]	AcOH [eq]	Aging	Yield	FWHM (111) [°]	Approximate Crystallite Size [nm]	BET Number (Micropore-External) [$m^2\ g^{-1}$]	Micropore Volume [$cm^3\ g^{-1}$]
1a(3)	24	30	fresh	90%	0.17	100	1351 (1215-136)	0.46
1b(2)	24	30	1 d	92%	0.25	50	1240 (1056-184)	0.41
1c(1)	24	30	2 d	91%	0.27	50	1220 (1044-176)	0.40
2a(47)	12	15	fresh	91%	0.18	100	1524 (1340-184)	0.50
2b(46)	12	15	1 d	86%	0.36	25	1227 (966-261)	0.37
2c(59)	12	15	2 d	86%	0.61	10	1181 (730-451)	0.29
3a(51)	24	15	fresh	95%	0.22	75	1467 (1238-230)	0.47
3b(50)	24	15	1 d	99%	0.34	30	1145 (910-235)	0.35
3c(61)	24	15	2 d	88%	0.49	15	1138 (793-345)	0.31
4a(49)	12	30	fresh	93%	0.16	125	1606 (1458-148)	0.55
4b(48)	12	30	1 d	90%	0.23	75	1390 (1182-208)	0.45
4c(60)	12	30	2 d	95%	0.21	75	1200 (1008-192)	0.39
5a(23)	0	30	fresh	19%	0.11	> 300	1185 (1077-108)	0.41
5b(22)	0	30	1 d	61%	0.11	> 300	1100 (985-115)	0.38
5c(21)	0	30	2 d	73%	0.11	> 300	1232 (1117-115)	0.43
6a(13)	24	0	fresh	93%	0.28	50	1454 (1146-307)	0.44
6b(12)	24	0	1 d	71%	0.69	10	999 (591-408)	0.23
6c(11)	24	0	2 d	80%	1.55	n.d.	697 (482-215)	0.19

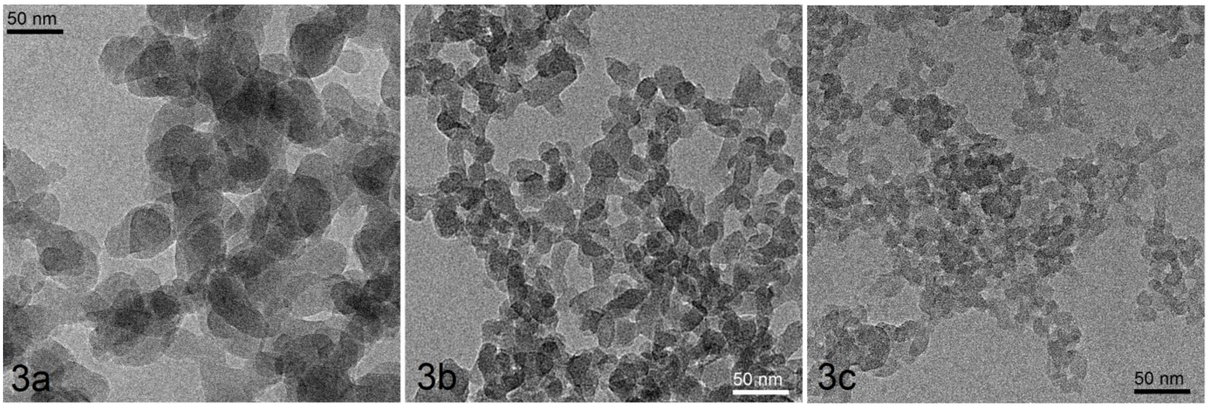

Figure S1. TEM micrographs of samples **3a** (left), **3b** (center) and **3c** (right).

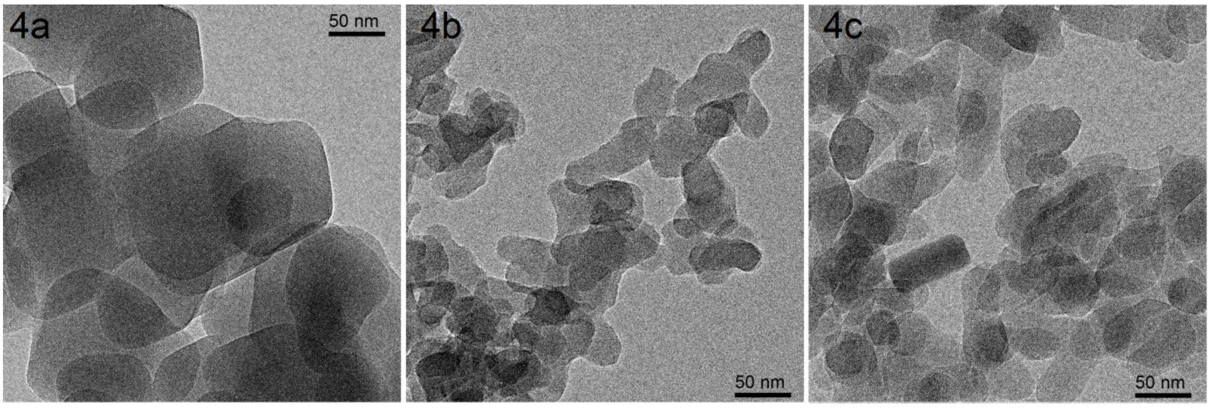

Figure S2. TEM micrographs of samples **4a** (left), **4b** (center) and **4c** (right).

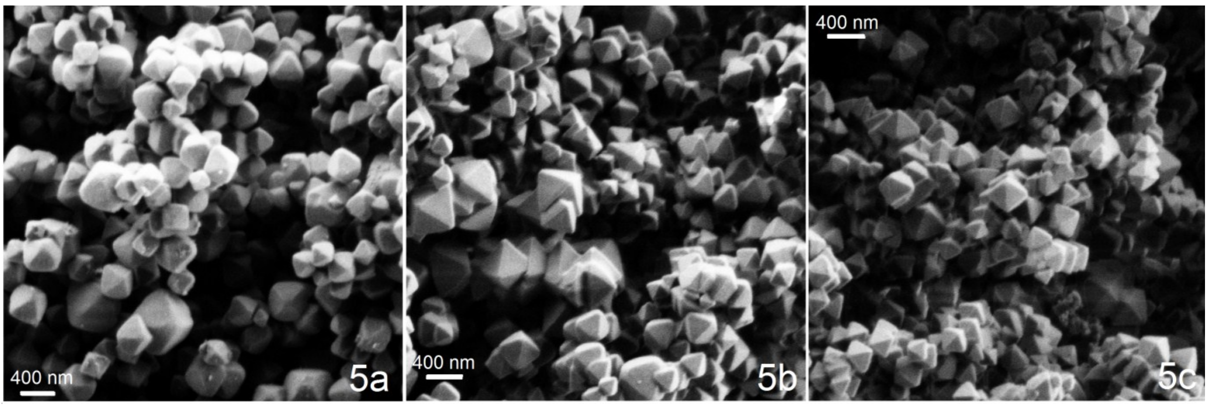

Figure S3. SEM micrographs of samples **5a** (left), **5b** (center) and **5c** (right).

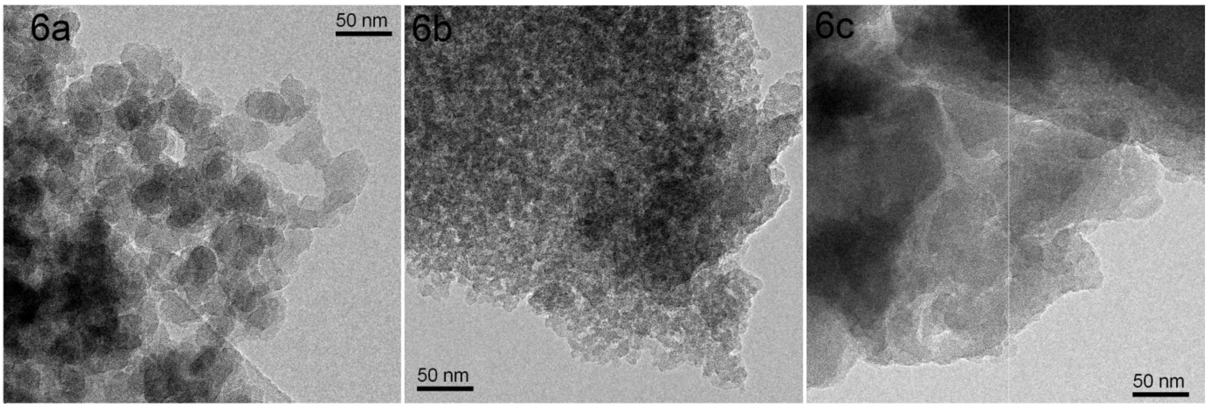

Figure S4. TEM micrographs of samples **6a** (left), **6b** (center) and **6c** (right).

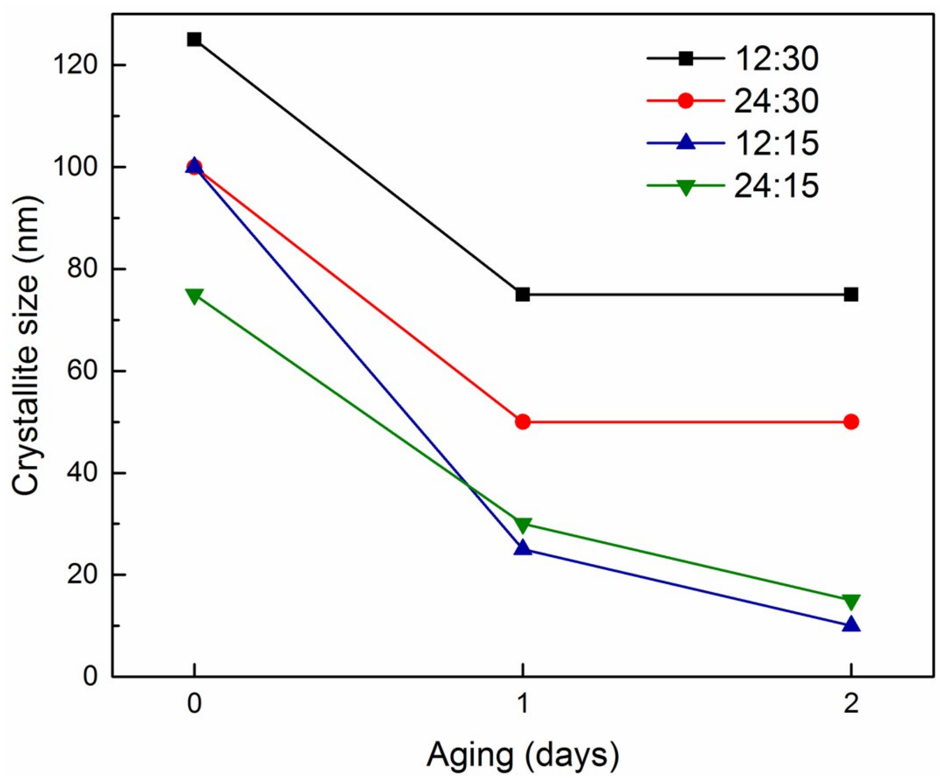

Figure S5. Effect of aging on crystallite size at different acetic acid/water ratios.

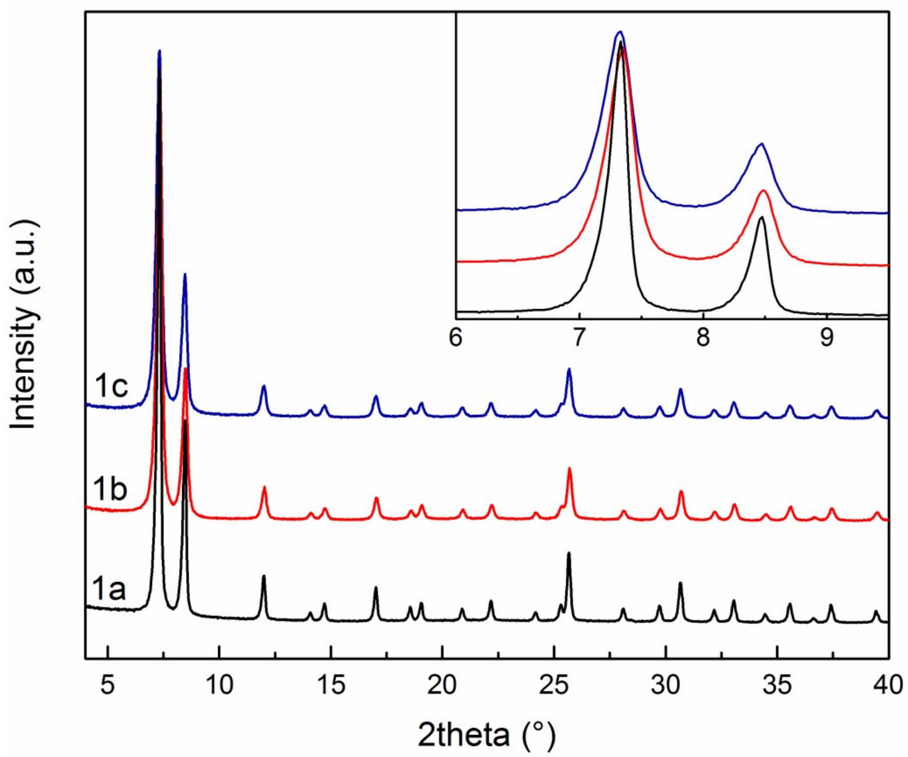

Figure S6. PXRD patterns of samples **1a**, **1b** and **1c**.

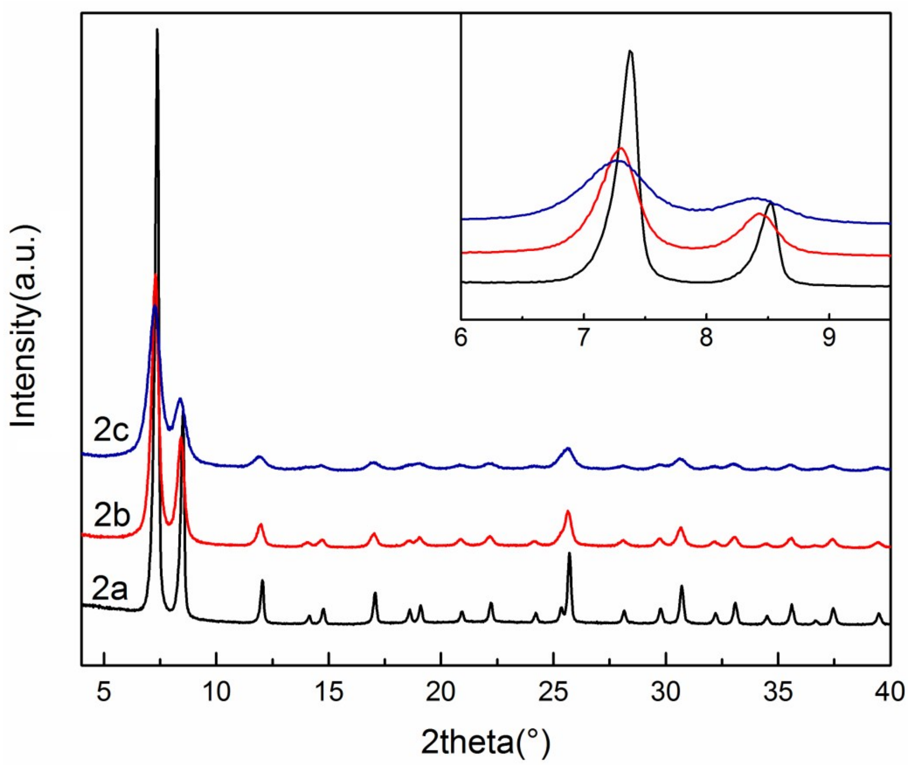

Figure S7. PXRD patterns of samples **2a**, **2b** and **2c**. The shift of the pattern of **2a** is due to sample displacement.

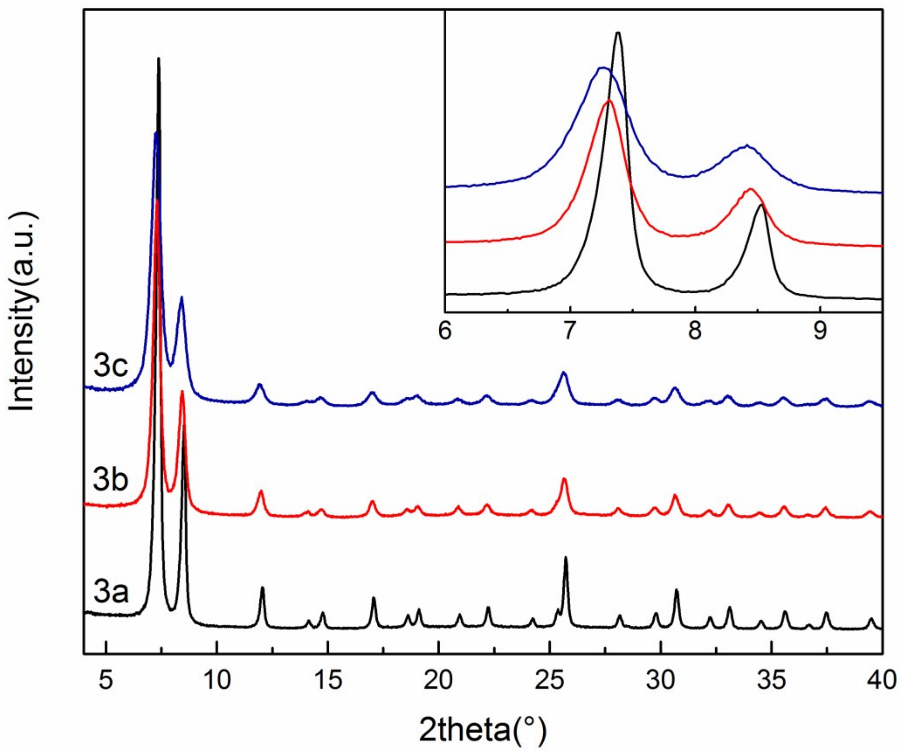

Figure S8. PXRD patterns of samples **3a**, **3b** and **3c**. The shift of the pattern of **3a** is due to sample displacement.

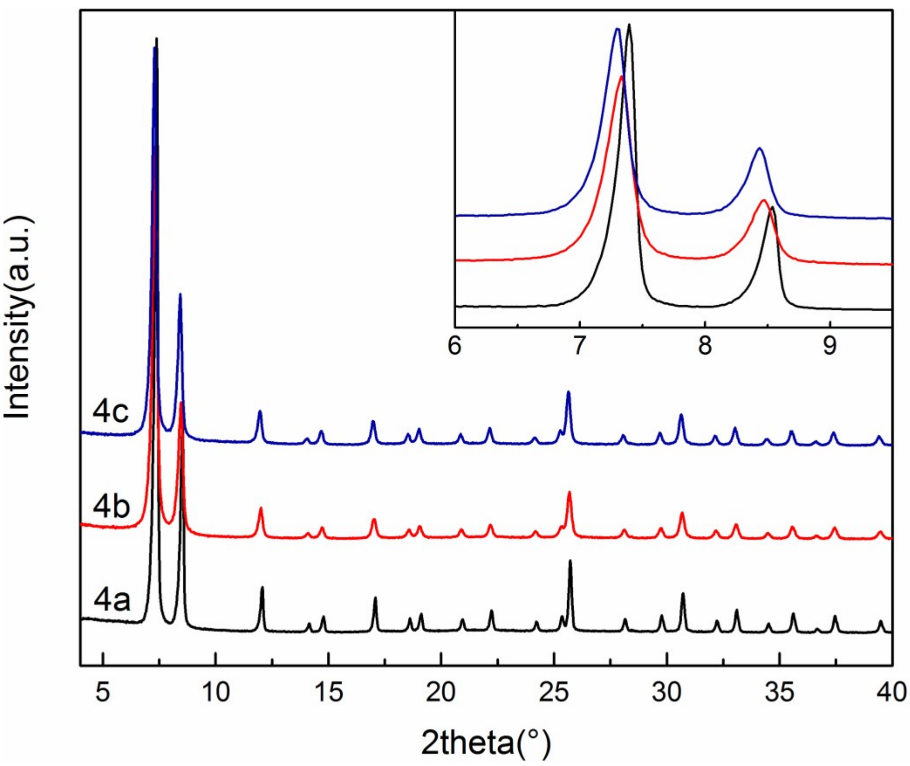

Figure S9. PXRD patterns of samples **4a**, **4b** and **4c**. The shift of the pattern of **4a** is due to sample displacement.

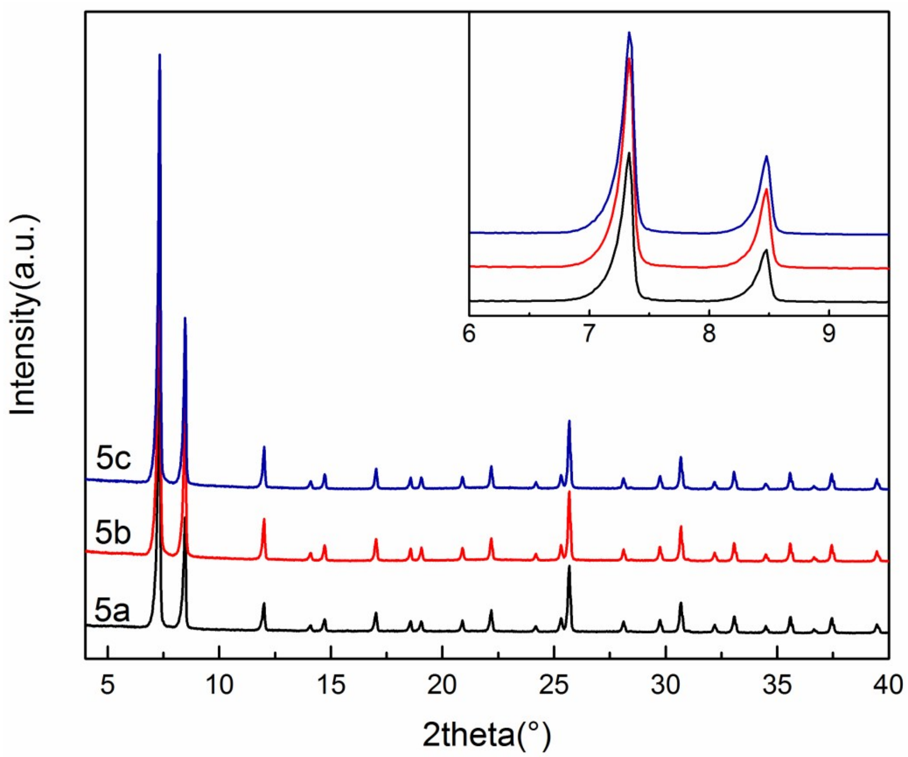

Figure S10. PXRD patterns of samples **5a**, **5b** and **5c**.

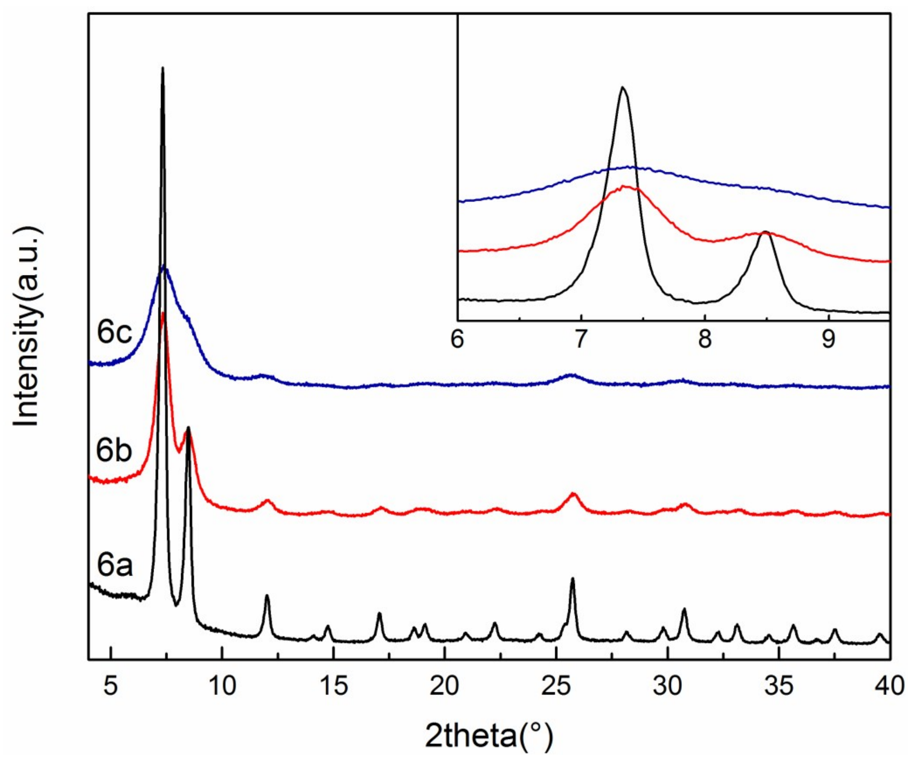

Figure S11. PXRD patterns of samples **6a**, **6b** and **6c**.

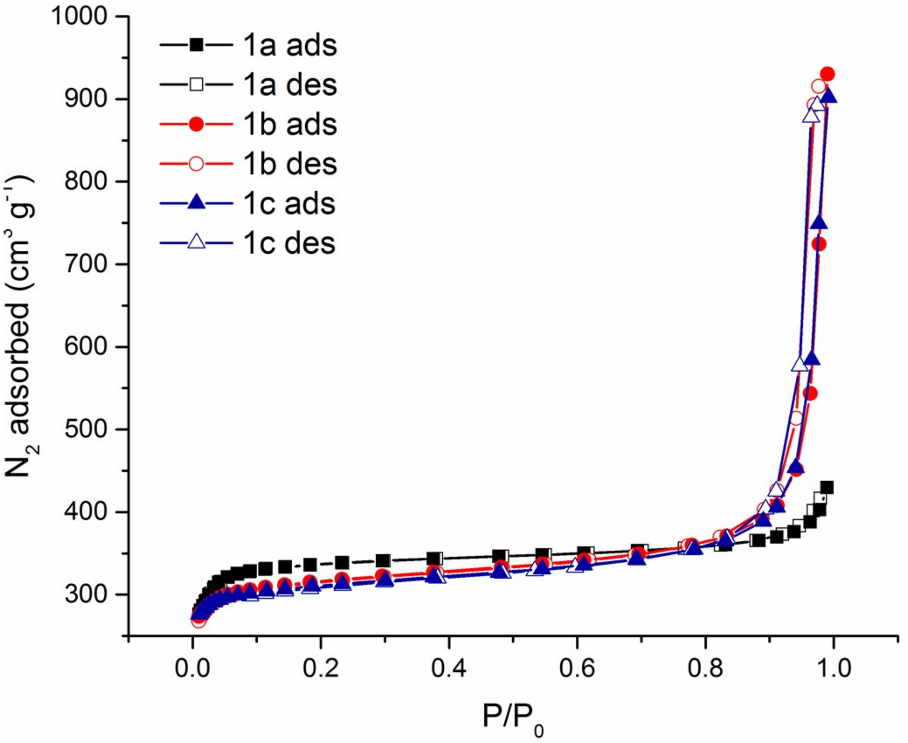

Figure S12. Nitrogen sorption isotherms of samples **1a**, **1b** and **1c**.

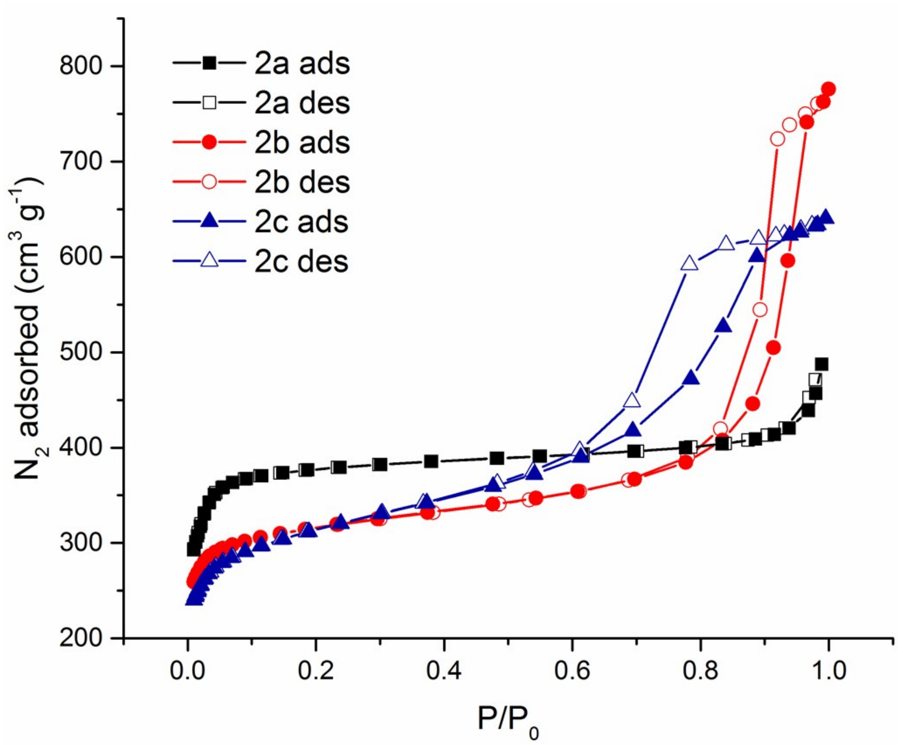

Figure S13. Nitrogen sorption isotherms of samples **2a**, **2b** and **2c**.

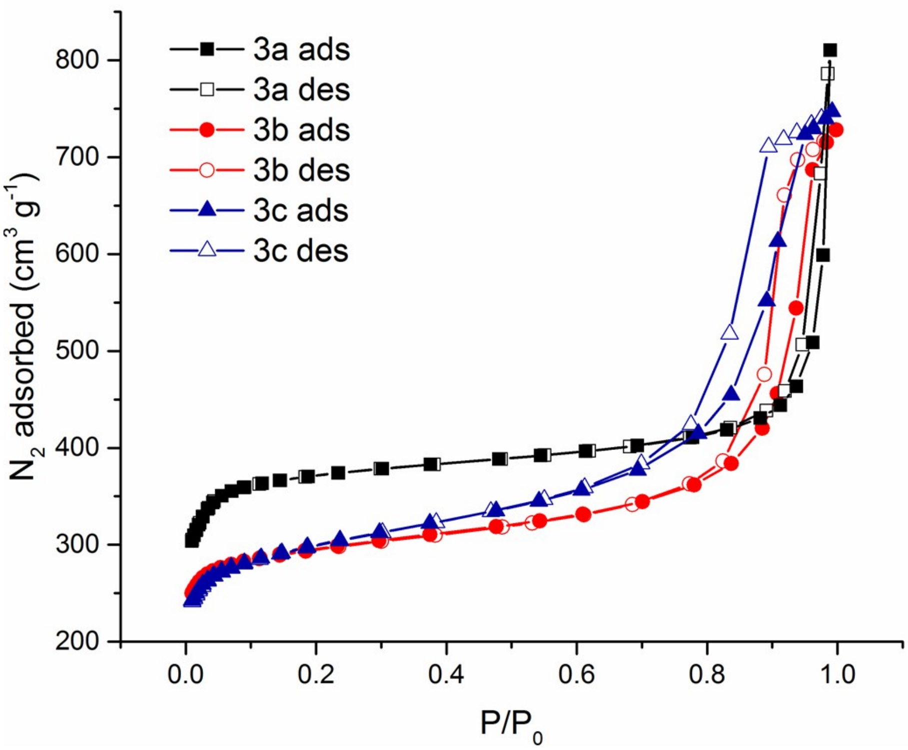

Figure S14. Nitrogen sorption isotherms of samples **3a**, **3b** and **3c**.

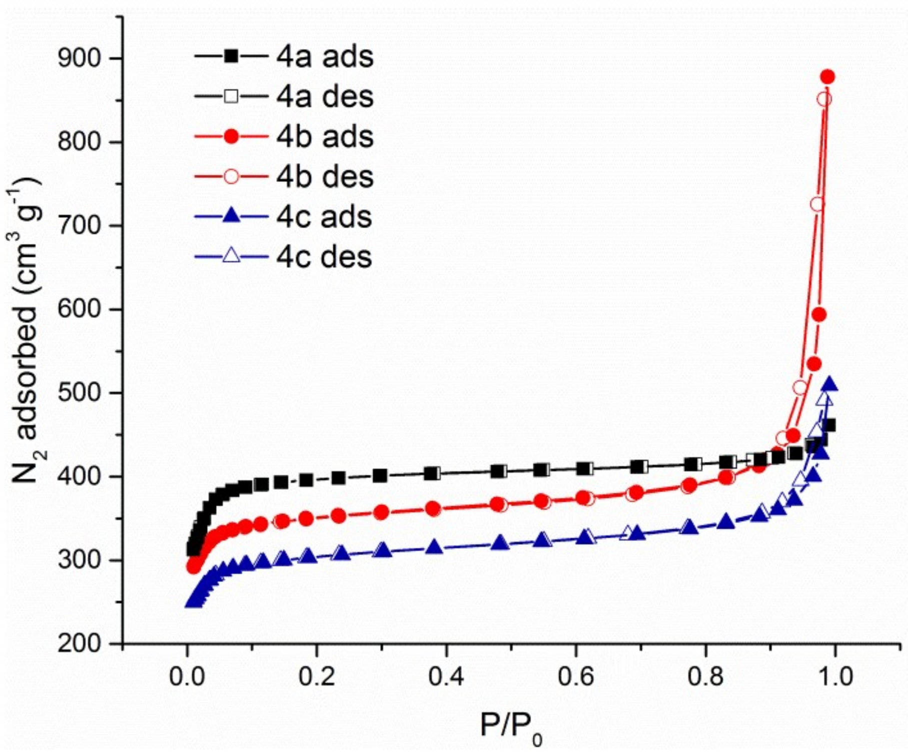

Figure S15. Nitrogen sorption isotherms of samples **4a**, **4b** and **4c**.

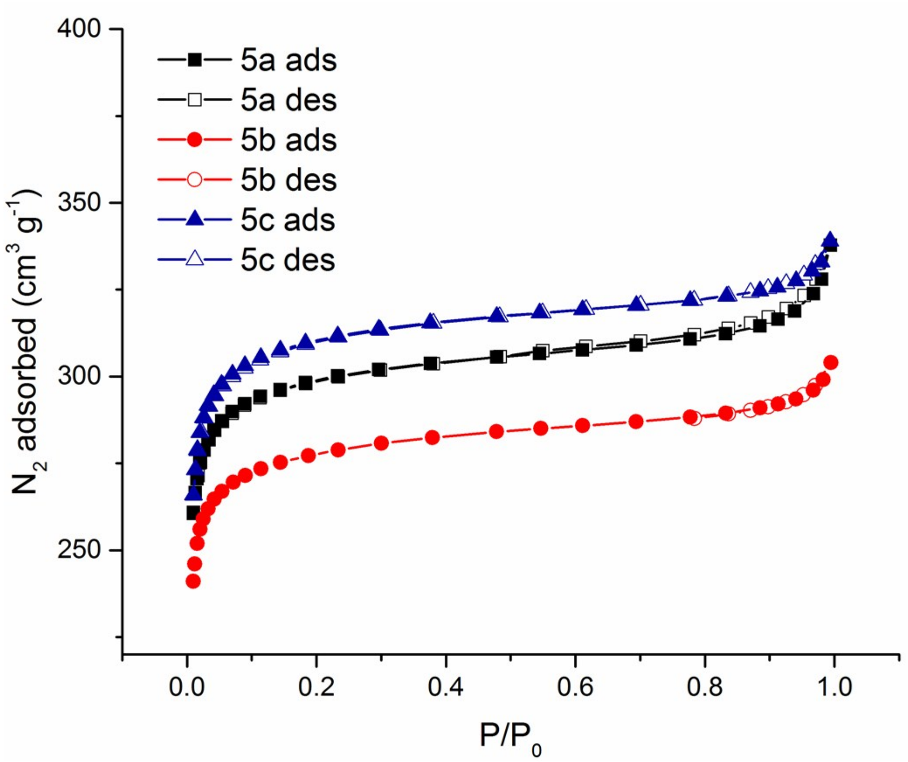

Figure S16. Nitrogen sorption isotherms of samples **5a**, **5b** and **5c**.

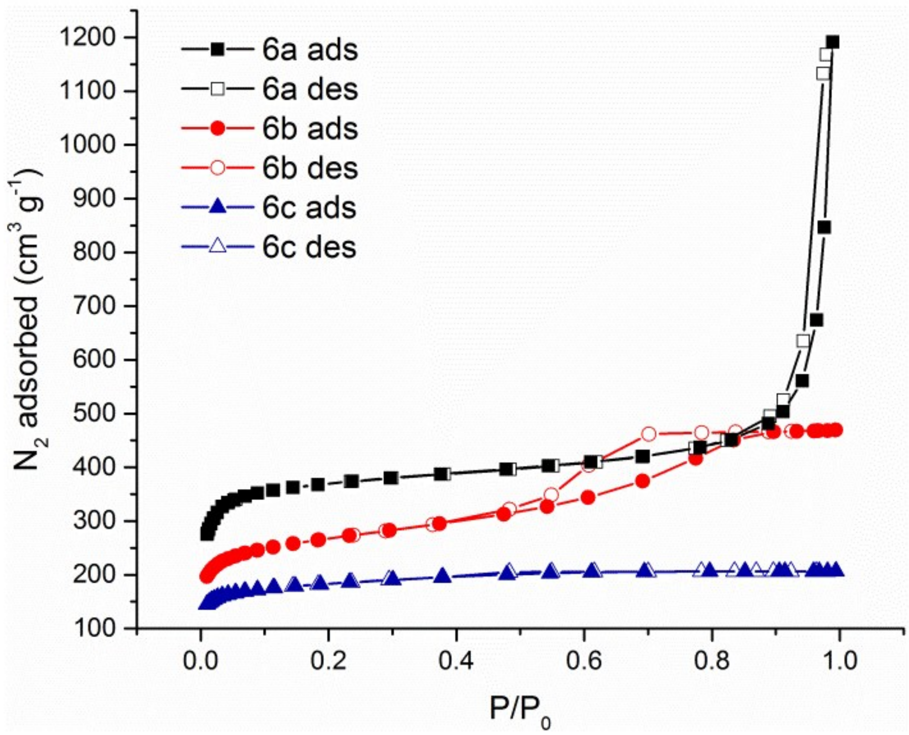

Figure S17. Nitrogen sorption isotherms of samples **6a**, **6b** and **6c**.

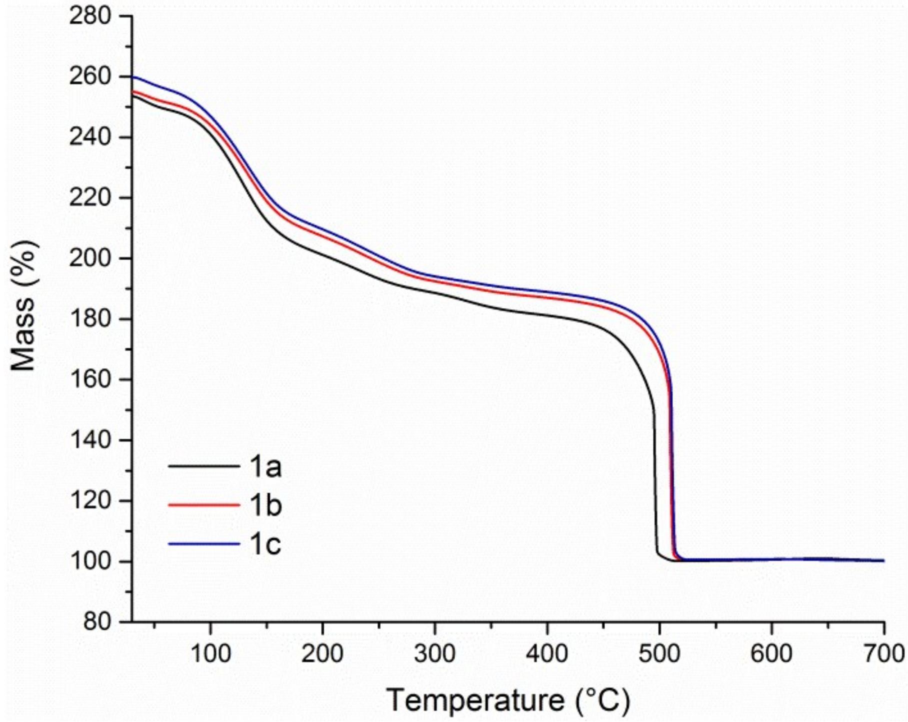

Figure S18. Thermogravimetric curves of samples **1a**, **1b** and **1c**.

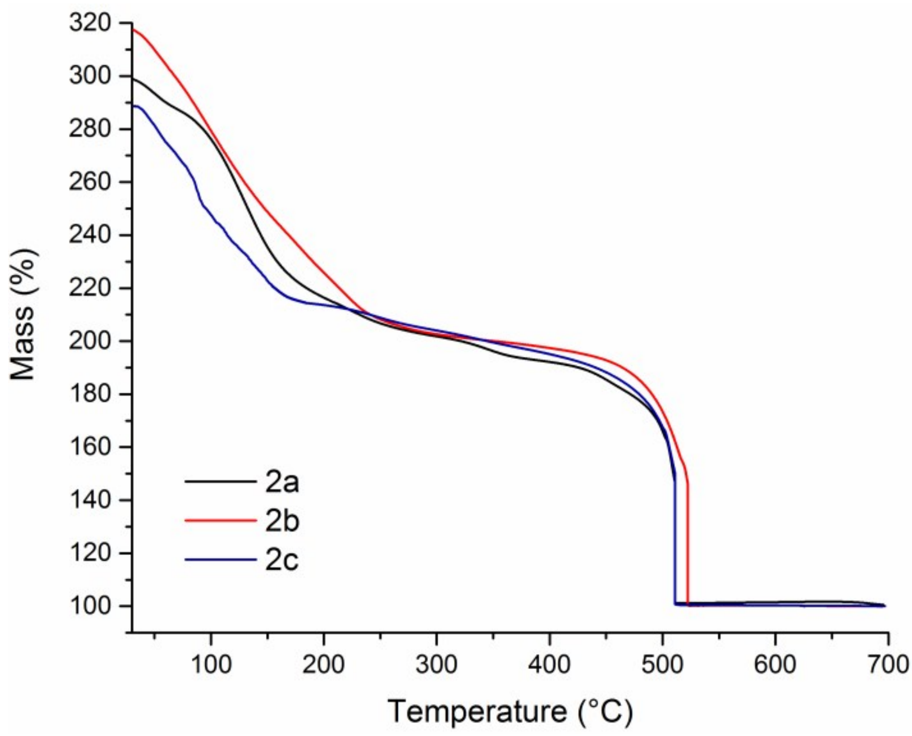

Figure S19. Thermogravimetric curves of samples **2a**, **2b** and **2c**.

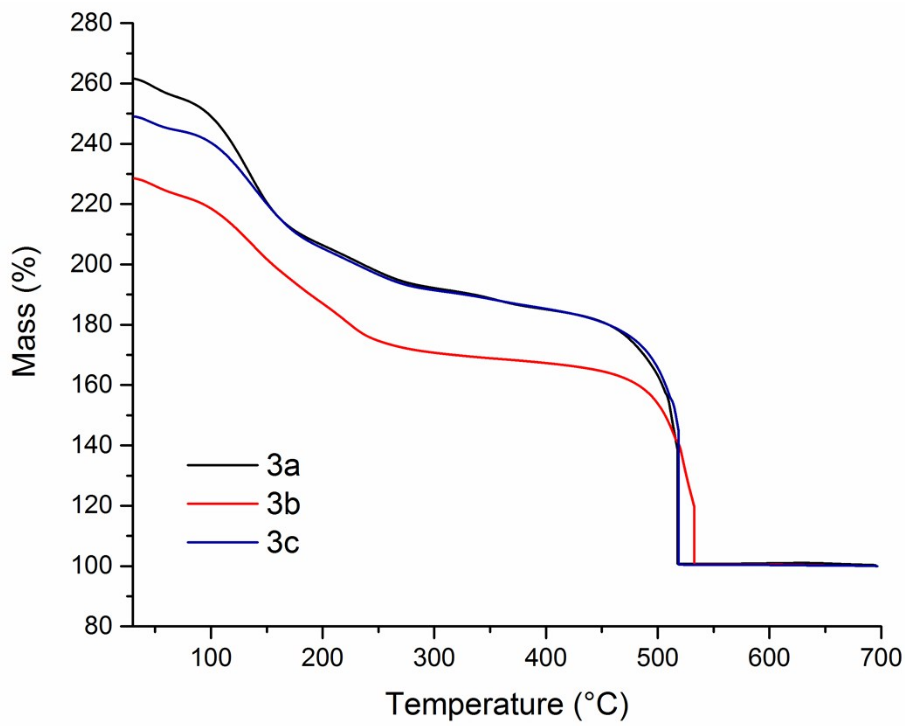

Figure S20. Thermogravimetric curves of samples **3a**, **3b** and **3c**.

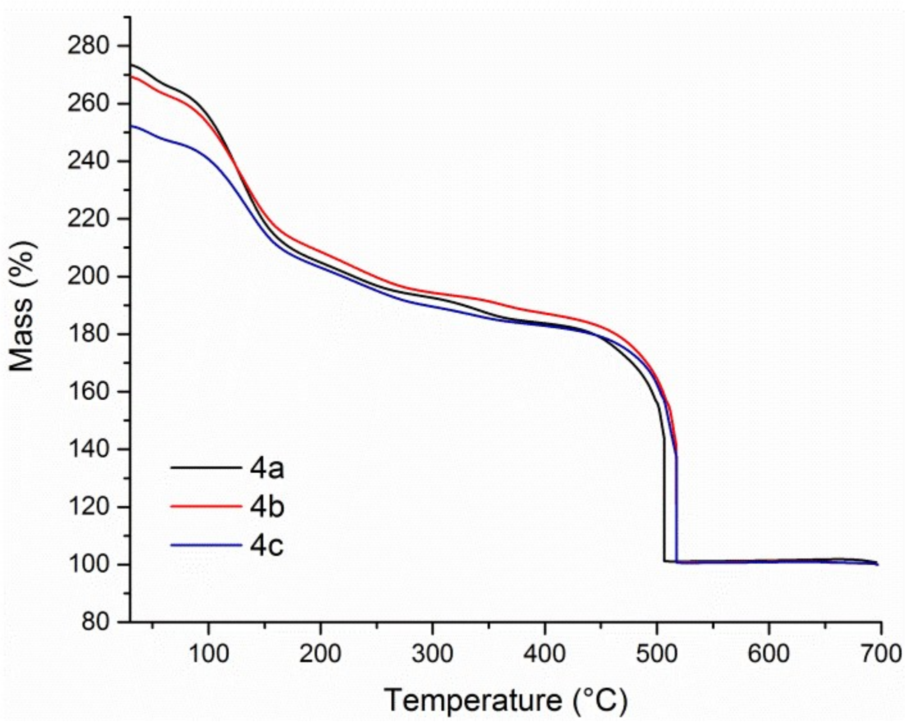

Figure S21. Thermogravimetric curves of samples **4a**, **4b** and **4c**.

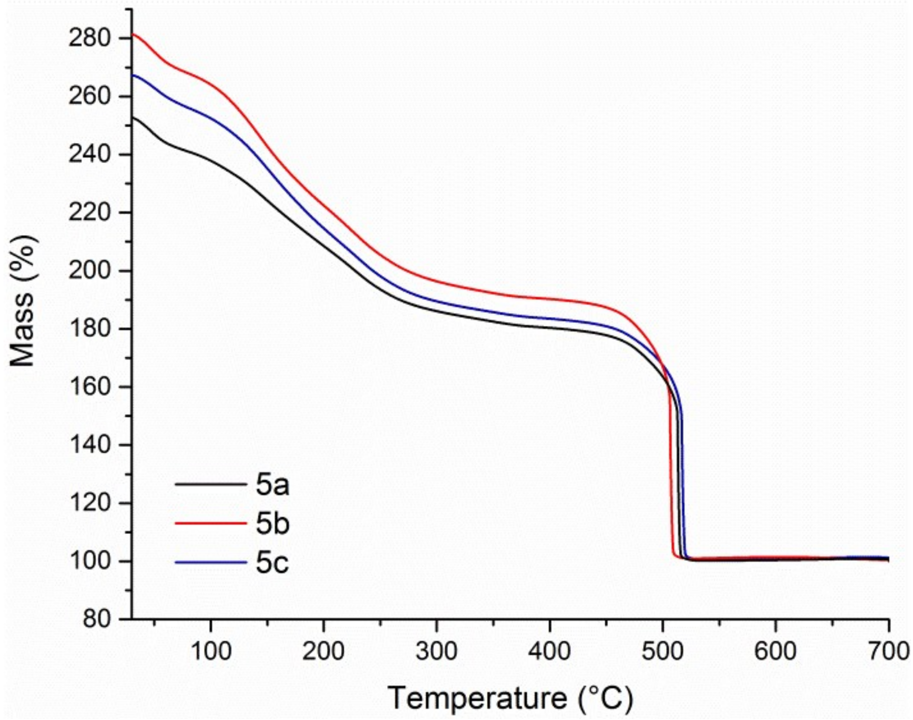

Figure S22. Thermogravimetric curves of samples **5a**, **5b** and **5c**.

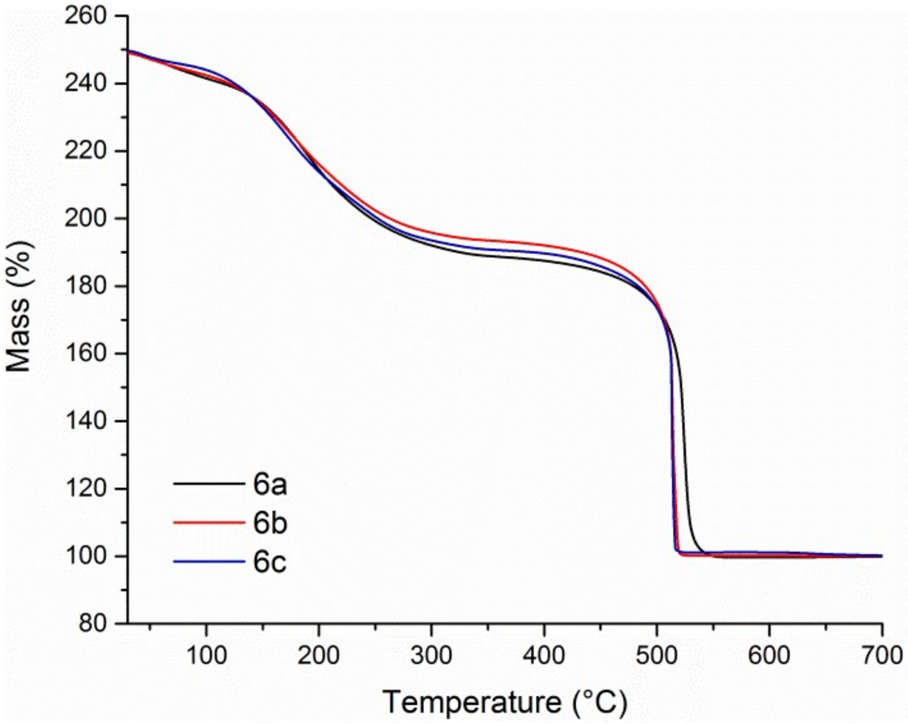

Figure S23. Thermogravimetric curves of samples **6a**, **6b** and **6c**.