Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Microwave assisted *N*-alkylation of amine functionalized crystal-like mesoporous phenylene-silica

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Table of Contents

1. Experimental - characterization

Transmission electron microscopy (TEM) images were recorded by a 200 kV Hitachi H8100 Instrument and by a 200 kV High Resolution (HR) and energy-filtered (EF) TEM JEOL 2200FS Instrument.

Powder X-ray diffraction (PXRD) data were collected with a Phillips X'Pert MPD diffractometer using Cu-Kα radiation.

Nitrogen adsorption-desorption isotherms were recorded at -196 ºC using a Gemini V 2.00 instrument model 2380. Functionalized PMO materials were dehydrated overnight at 150 ºC to an ultimate pressure of 1024 mbar and then cooled to room temperature prior to adsorption.

^{13}C, ^{29}Si and ^{15}N NMR spectra were recorded using a double resonance MAS probe on a Bruker Avance III 400 spectrometer operating at 9.4 T. ^{13}C cross-polarization magic-angle spinning (CP MAS) NMR spectra were collected using the following parameters: 4 μs ^{1}H 90º pulse; contact time (CT): 1 ms; ν_1^H: 70 kHz and ν_1^C: 78 kHz for CT pulses; MAS rate (ν_R): 8 kHz and recycle delay (RD): 4 s. TPPM decoupling during the acquisition of the ^{13}C signal was employed using a pulse length of 4.5 μs (ca. 165° pulses) for the basic unit block. ^{29}Si MAS NMR spectra were collected employing a 40º flip angle pulse; ν_R: 5 kHz; RD: 60 s. ^{29}Si CP MAS NMR spectra were acquired with a 4 μs ^{1}H 90º pulse; CT: 8 ms, ν_R: 5 kHz; RD: 5 s. ^{15}N CP MAS NMR spectra were recorded using a 4 μs ^{1}H 90º flip angle pulse; ν_1^H: 57.7 kHz and ν_1^N: 62.5 kHz for CT pulses; CT: 8 ms; ν_R: 5 kHz and RD: 5 s. In both ^{29}Si and ^{15}N NMR experiments a CW decoupling rf field strength of 53 kHz was applied during the acquisition time. In all the CPMAS experiments, the ^{1}H rf field strengths used during the CT pulse were ramped from 50% to 100% to improve CP stability.

The ^{13}C and ^{29}Si NMR spectra were quoted in ppm from trimethylsilane, while ^{15}N NMR spectra were referenced against a solid sample of natural abundance L-glycine, a secondary reference standard with respect to nitromethane.

Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 instrument with a program rate of 5 ºC min^{-1} in air.

Fourier transform infrared (FTIR) was done in a FTIR Bruker Tensor 27 instrument with a Golden Gate ATR (Attenuated Total Reflectance). Mesoporous powders were dehydrated at 100 ºC for 24 h before FTIR analysis. The FTIR spectra were recorded in transmittance mode.

Elemental analysis was carried out in C.A.C.T.I. in the Vigo University.

2. Characterization PMO materials

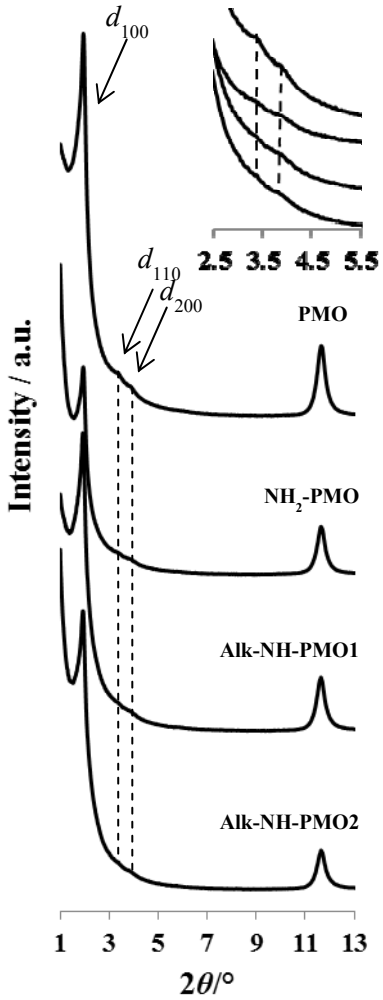

Figure S1. X-ray diffraction patterns of PMO, NH_2-PMO, Alk-NH-PMO1 and Alk-NH-PMO2. The inset displays the magnified patterns in the 2θ region from 2.5 to 5.5°.

Table S1. Physical properties of PMO, NH_2-PMO, Alk-NH-PMO1 and Alk-NH-PMO2.

Sample	d_{100} / nm	S_{BET} / m^2 g^{-1}	V_P / cm^3 g^{-1}	d_P / nm[a]	b / nm[b]
PMO	4.48	782	0.63	3.55	1.62
NH_2-PMO	4.53	719	0.51	3.55	1.68
Alk-NH-PMO1	4.53	693	0.50	3.41	1.82
Alk-NH-PMO2	4.53	698	0.53	3.41	1.82

[a]Pore width obtained from the maximum on the BJH pore size distribution calculated on the basis of adsorption data. [b]Pore wall thickness calculated as ($2d_{100}/\sqrt{3} - d_P$), where the first term is the unit cell parameter.

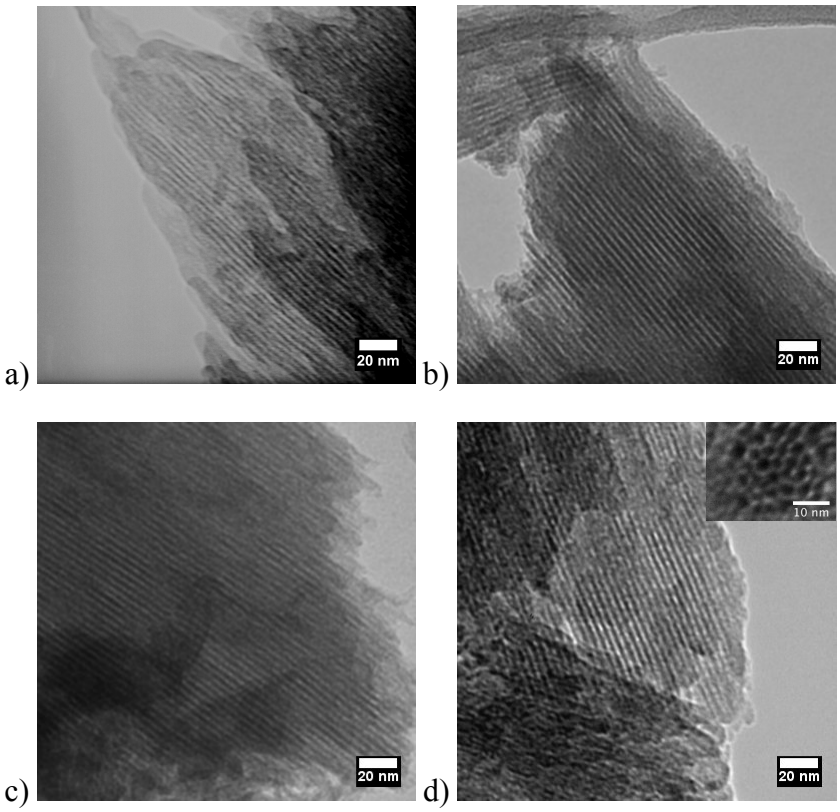

Figure S2. TEM micrographs of: a) PMO, b) NH_2-PMO, c) Alk-NH-PMO1 and d) Alk-NH-PMO2 (the inset displays a micrograph where the hexagonal arrangement of pores can be seen).

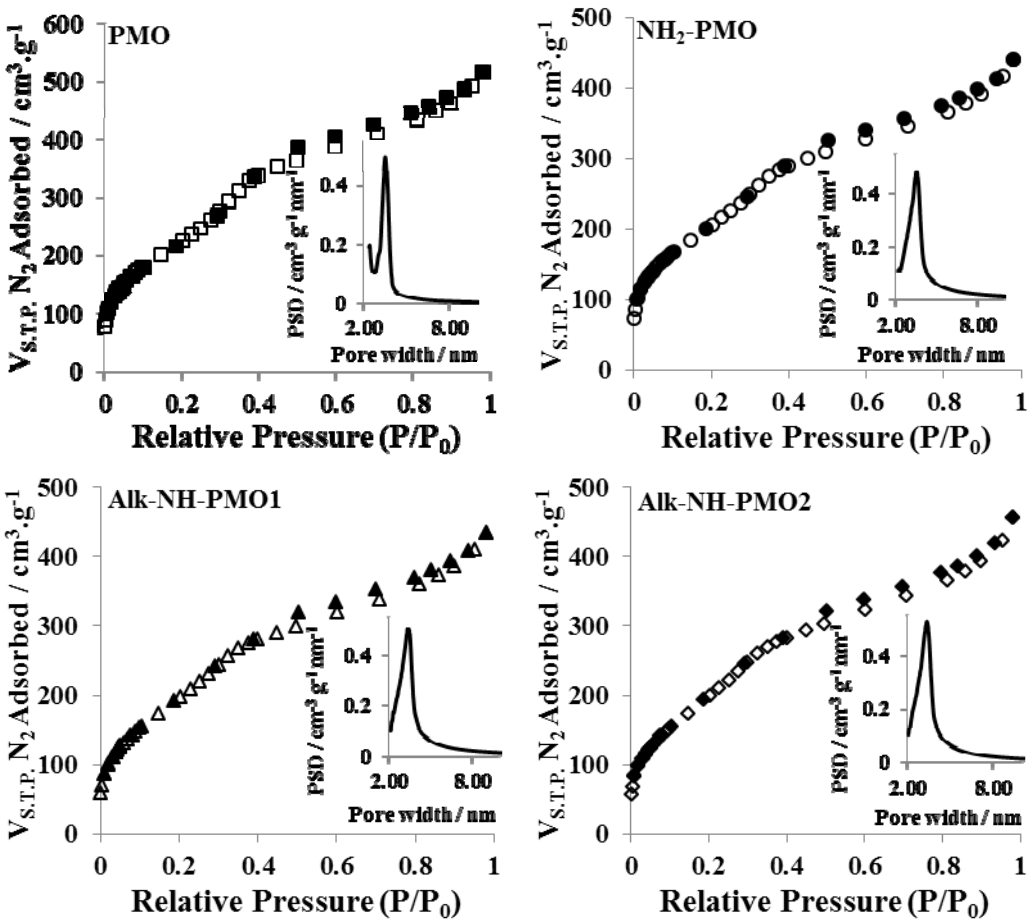

Figure S3. -196 ºC N_2 isotherms of PMO ((□) adsorption; (■) desorption)), NH_2-PMO ((○) adsorption; (●) desorption)), Alk-NH-PMO1 ((Δ) adsorption; (▲) desorption)) and Alk-NH-PMO2 ((◊) adsorption; desorption (♦)).

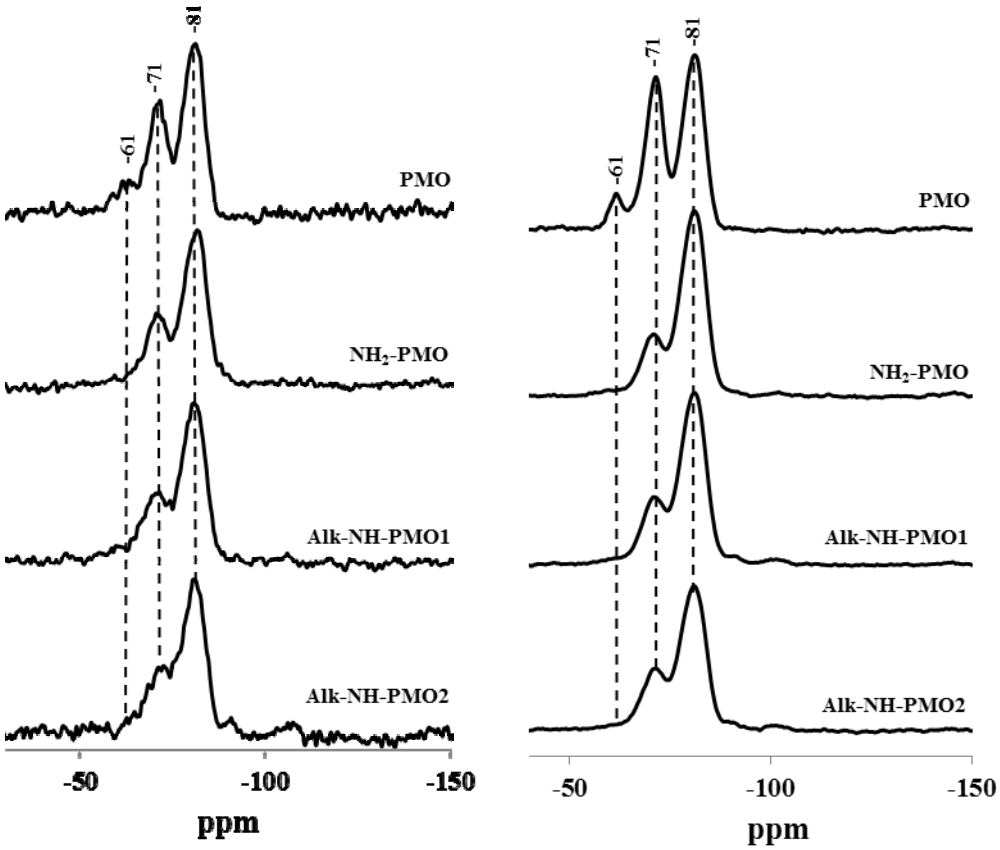

Figure S4. ^{29}Si MAS (left) and CP-MAS (right) NMR spectra of PMO, NH_2-PMO, Alk-NH-PMO1 and Alk-NH-PMO2.

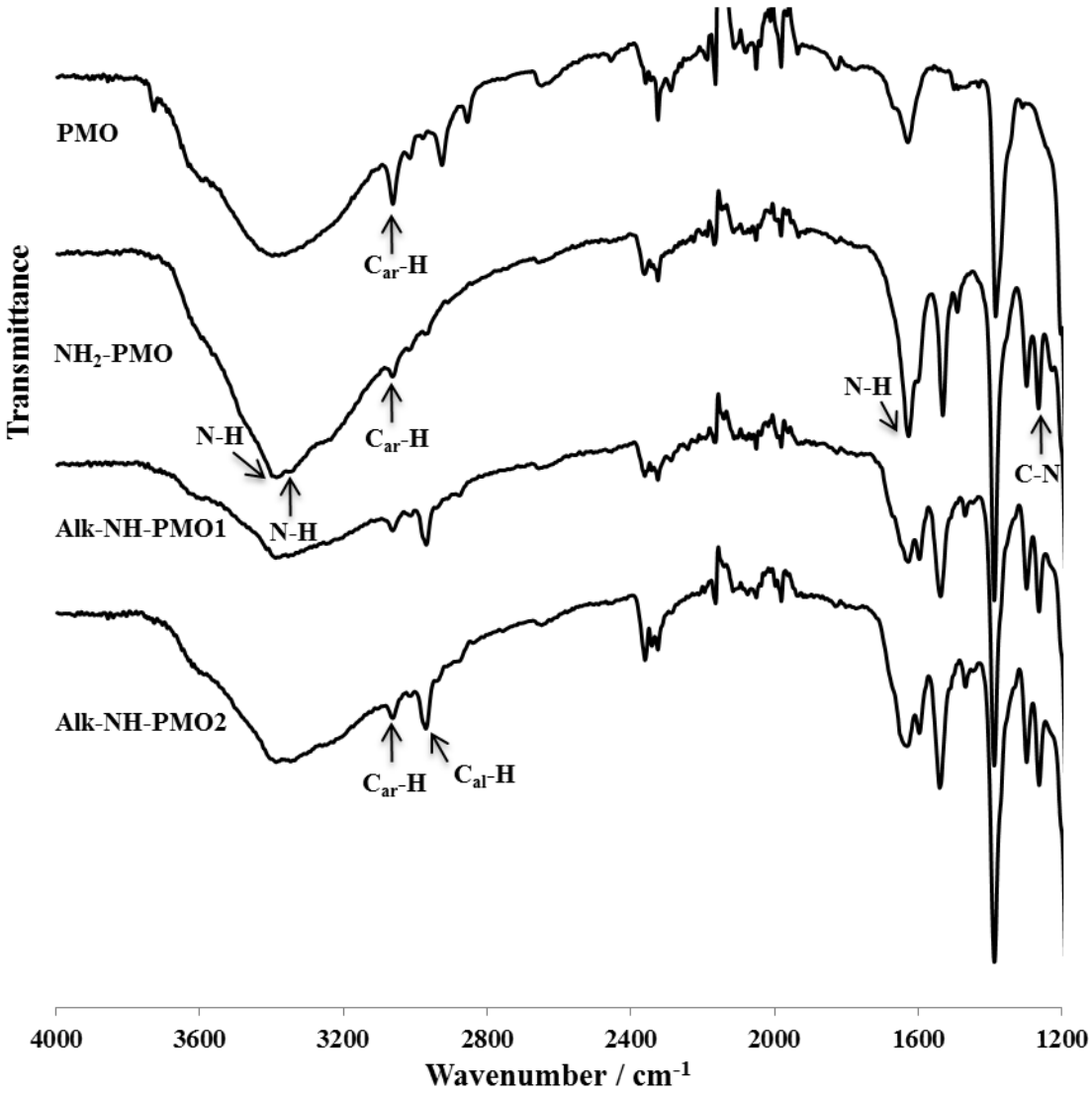

Figure S5. FTIR (ATR) spectra of PMO, NH_2-PMO, Alk-NH-PMO1 and Alk-NH-PMO2 in the range of 1200 - 4000 cm^{-1} (C_{ar} and C_{al} despite for aromatic and aliphatic carbons, respectively).

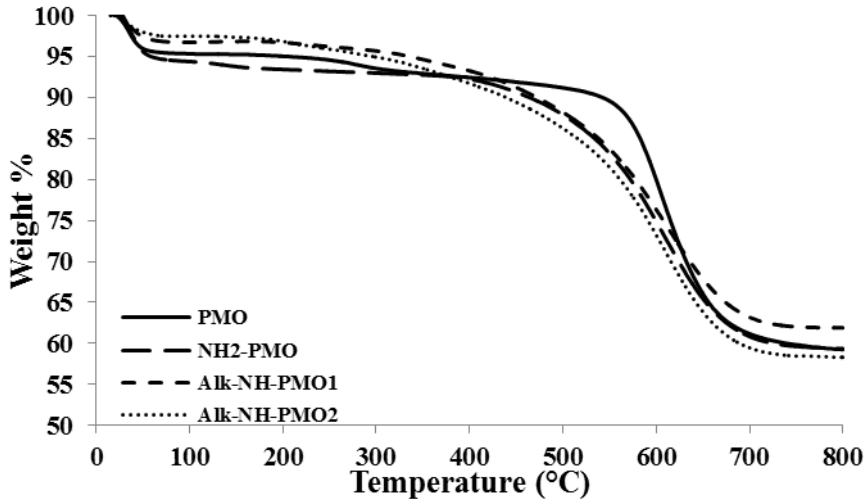

Figure S6. TGA of PMO, NH_2-PMO, Alk-NH-PMO1 and Alk-NH-PMO2.

Table S2. Elemental analyses of PMO, NH_2-PMO, Alk-NH-PMO1 and Alk-NH-PMO2.

Sample	% N	% C	% H
PMO	0.10	38.89	2.75
NH_2-PMO	3.03	35.81	2.92
Alk-NH-PMO1	2.96	37.50	3.37
Alk-NH-PMO2	3.00	38.05	3.44