Electronic Supplementary Material (ESI) for Chemical Communications

Hierarchically Porous Nanostructures through Phosphonate-Metal Alkoxide Condensation and Growth Using Functionalized Dendrimeric Building Blocks

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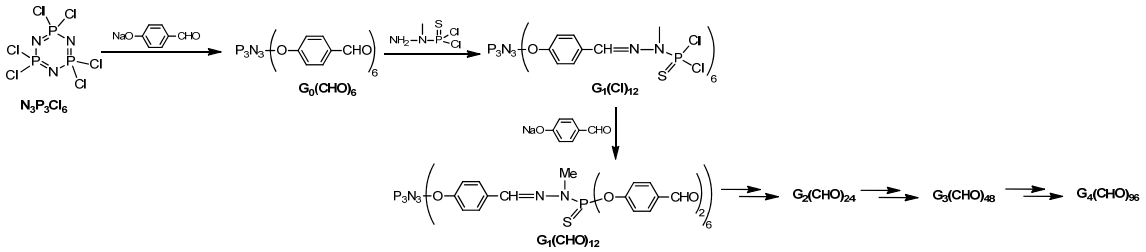
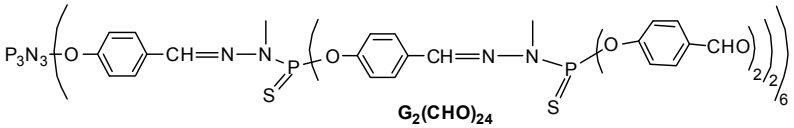
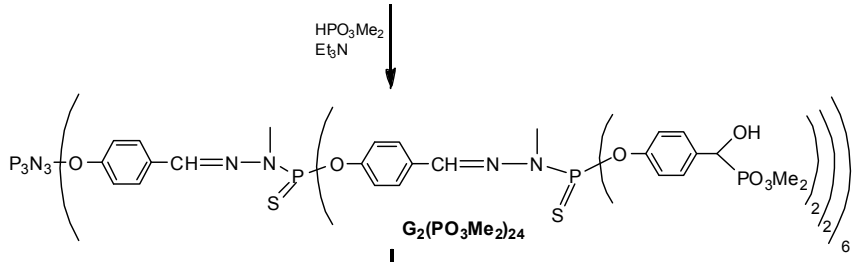
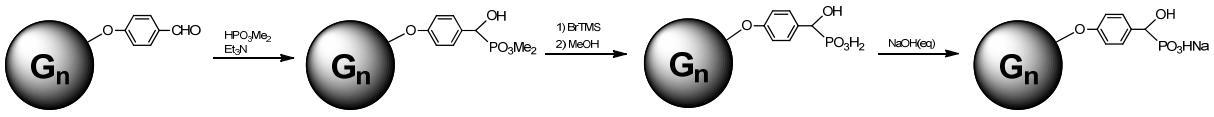
Electronic Supplementary Information

S1 : Synthesis and characterization of the starting dendrimers





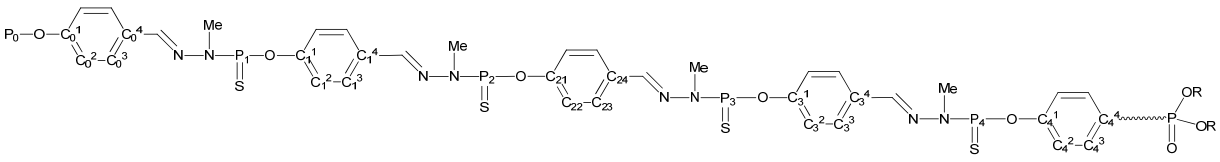


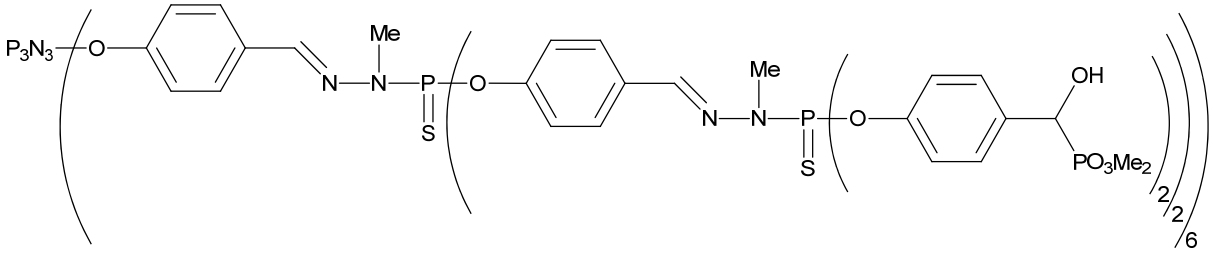


General

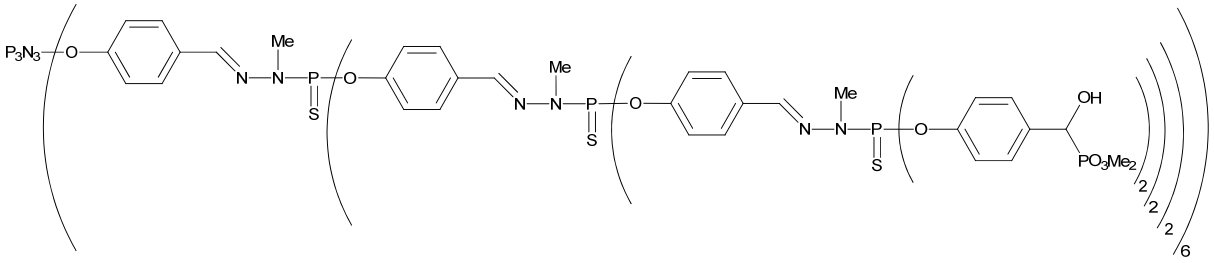
dendrimers Gn(CHO) were synthesized using published procedures [1]. All manipulations were carried out with standard high-vacuum and dry-argon techniques. Chemicals were purchased from Sigma-Aldrich or Strem and used without further purification; solvents were

dried and distilled by routine procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 25°C with Bruker AC 200, ARX 250, AV 300, DPX 300, AMX 400 or AV500 spectrometers. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P NMR and $SiMe_4$ for ^{1}H and ^{13}C NMR. Fourier transformed infrared (FTIR) spectra were obtained with a Perkin-Elmer Spectrum 100FT-IR spectrometer on neat samples (ATR FT-IR). The numbering used for NMR is shown on the following Figure.

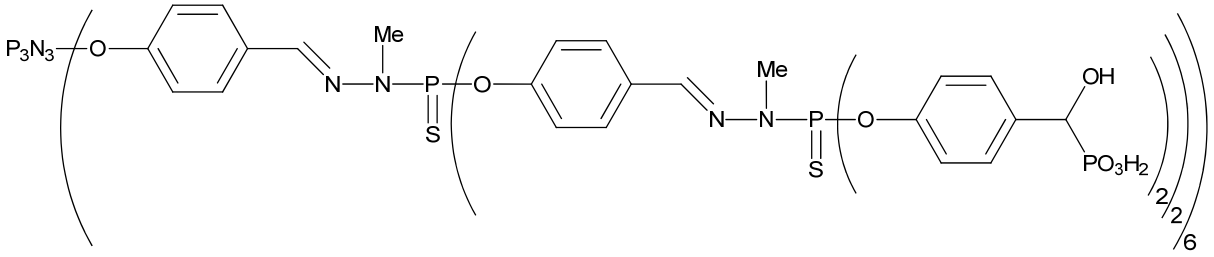




Dendrimer $G_2(CHO)_{24}$ (1.00 g, 0.146 mmol) was dissolved in THF (1 mL) then triethylamine (15 µL, 1.3 mmol) and dimethylphosphite (319 µL, 3.5 mmol) were added to the reaction mixture and left overnight under good stirring. The residue was washed by a mixture of THF/Et_2O (1/1) to afford the desired compound as a white powder in 80% yield. ^{31}P-{^{1}H} NMR (DMSO d6): δ = 11.7 (s, P_0), 27.10 (s, $P(O)(O\text{-}CH_3)_2$), 66.1 (s, $P_{1,2}$). ^{1}H NMR (DMSO d6): δ = 3.29 (d, $^{3}J_{HP}$ = 9.2 Hz, 54H, CH_3-N-P_1, CH_3-N-P_2), 3.49 (d, $^{2}J_{CP}$= 10.9 Hz, 72H, P(O)-O-CH_3), 3.55 (d, $^{2}J_{CP}$ = 10.6 Hz, 72H, P(O)-O-CH_3), 5.00 (dd, $^{3}J_{HH}$ = 5.4 Hz , $^{2}J_{HP}$ = 15.7 Hz, 24H, CH-P(O)), 6.30 (dd, $^{3}J_{HH}$ = 5.4 Hz, $^{2}J_{HP}$ = 15.7 Hz, 24H, OH), 7.0-8.0 (m, 186H, H_{arom}, CH=N). ^{13}C {^{1}H}NMR (DMSO d6): δ = 32.8 (d, $^{2}J_{CP}$ = 11.3 Hz, CH_3-N-$P_{1,2}$), 52.7 (d, $^{2}J_{CP}$ = 6.2 Hz, CH_3-O-P(O)), 53.2 (d, $^{2}J_{CP}$ = 6.3 Hz, CH_3-O-P(O)), 68.2 (d, $^{1}J_{CP}$ = 163.0 Hz, C-OH), 120.4 (s, C_2^2), 120.8 (br, C_0^2), 121.4 (s, C_1^2), 128.2 (s, C_0^3), 128.2 (s, C_1^3), 128.7 (d, $^{3}J_{CP}$ = 3.7 Hz, C_2^3), 132.1 (s, C_0^4), 132.1 (s, C_1^4), 135.4 (s, C_2^4), 140.2 (br, CH=N-N(Me)-$P_{1,2}$), 149.4 (d, $^{2}J_{CP}$ = 3.8 Hz, C_2^1), 150.4 (s, C_0^1), 150.7 (d, $^{2}J_{CP}$ = 6.4 Hz, C_1^1). IR: υ(OH) 3271 cm^{-1}.



Dendrimer $G_3(CHO)_{48}$ (0.20 g, 1.35 10^{-2} mmol) was dissolved in THF (0.2 mL). Then triethylamine (10 µL, 0.80 mmol) and dimethylphosphite (59 µL 0.648 mmol,) were added to the reaction mixture and left 12h under good stirring. The residue was washed by a mixture of THF/Et_2O (1/1) to afford the desired compound as a white powder in 85% yield. ^{31}P-{^1H} NMR (DMSO d6): δ = 11.7 (s, P_0), 28.6 (s, $P(O)(O\text{-}CH_3)_2$), 66.4 (s, $P_{1,2,3}$). ^1H NMR (DMSO d6): δ = 3.40 (d, $^3J_{HP}$ = 10.7 Hz, 126H, CH_3-N-P_1, CH_3-N-P_2, CH_3-N-P_3), 3.60 (d, $^2J_{CP}$ = 13.2 Hz, 144H, P(O)-O-CH_3), 3.65 (d, $^2J_{CP}$ = 13.2 Hz, 144H, P(O)-O-CH_3), 5.10 (dd, $^3J_{HH}$ = 4.3 Hz, $^2J_{HP}$ = 15.3 Hz, 48H, CH-P(O)), 6.4 (dd, $^3J_{HH}$ = 4.3 Hz, $^2J_{HP}$ = 15.3 Hz, 48H, OH), 7.0-8.1 (m, 402H, H_{arom}, CH=N). $^{13}C\{^1H\}$NMR (DMSO d6): δ = 32.8 (br, CH_3-N-$P_{1,2,3}$), 52.7 (d, $^2J_{CP}$ = 6.3 Hz, CH_3-O-P(O)), 53.2 (d, $^2J_{CP}$ = 7.4 Hz, CH_3-O-P(O)), 68.1 (d, $^1J_{CP}$ = 162.8 Hz, CH-OH), 119.5 (s, C_1^2), 120.4 (br, C_3^2, C_0^2), 121.4 (s, C_2^2), 128.3 (br, C_0^3, C_1^3, C_2^3), 128.6 (d, $^3J_{CP}$ = 4.2 Hz, C_3^3), 132.1 (s, C_0^4, C_1^4, C_2^4), 135.5 (s, C_3^4), 140.2 (br, CH=N-N(Me)-$P_{1,2,3}$), 149.4 (d, $^2J_{CP}$ = 8.3 Hz, C_3^1), 150.6 (br, C_0^1, C_1^1, C_2^1). IR: υ(OH) 3271 cm^{-1}.

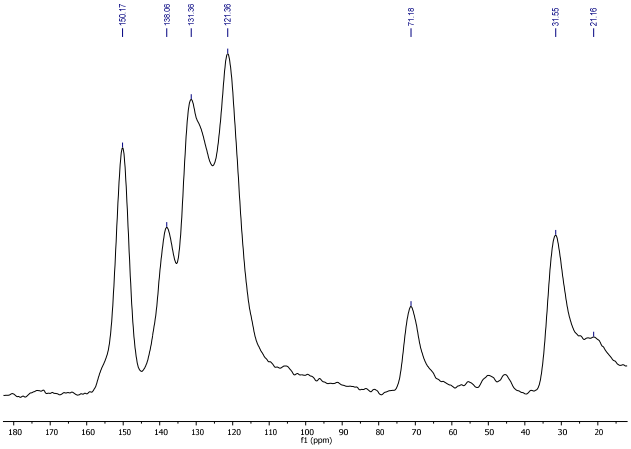


At 0°C (ice bath) the bromotrimethylsilane (304 µL, 2.3 mmol), was added slowly to a suspension of dendrimer $G_2(PO_3Me_2)_{24}$ (0.3 g, 3.16 10^{-2} mmol) in acetonitrile (1.5 mL) and triethylamine (304 µL, 2.3 mmol). The reaction mixture was left to react for 6 h at room temperature. Then the anhydrous methanol (1 mL) was added. After 2h, the reaction mixture was evaporated to dryness under reduced pressure. The residue was washed with water and ether and final compound was obtained as a white powder with a yield of 62%. ^{31}P-{^1H} NMR (DMSO d6): δ = 11.9 (s, P_0), 21.5 (m, $P(O)(OH)_2$), 66.00 (s, $P_{1,2}$). ^1H NMR (DMSO d6): δ = 3.06 (br, 54H, CH_3-N-$P_{1,2}$), 4.66 (d, $^3J_{HP}$ = 14.0 Hz, 24H, CH-OH), 3.7-5.2 (m, 72H, OH), 6.7-8.0 (m, 186H, H_{arom} CH=N). $^{13}C\{^1H\}$NMR (DMSO d6) : δ = 33.6 (s, CH_3-N-$P_{1,2}$),

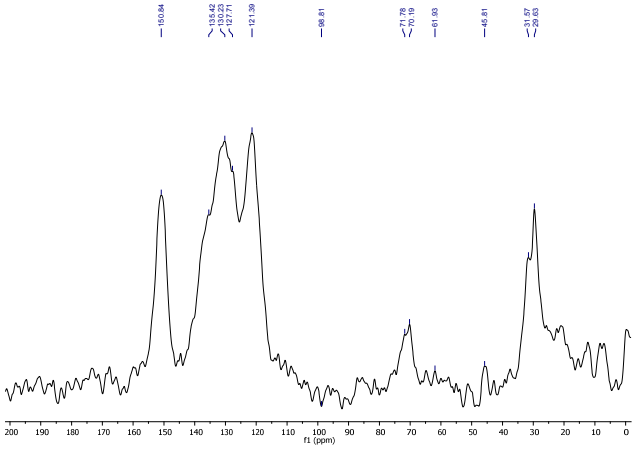
70.2 (d, $^{1}J_{CP}$ = 158.5 Hz, CH-OH), 121.0 (br, C_2^2, C_0^2), 122.0 (s, C_1^2), 129.5 (br, C_0^3, C_1^3, C_2^3), 132.8 (s, C_0^4, C_1^4), 137.4 (s, C_2^4), 141.0 (br, CH=N), 149.8 (br, C_2^1), 151.2 (br, C_0^1, C_1^1). IR: υ(OH) 3271 cm^{-1}.

[1] a) N. Launay, A. M. Caminade, R. Lahana, J. P. Majoral, *Angew. Chem. Int. Ed. Engl,.* 1994, **33**, 1589-1592.

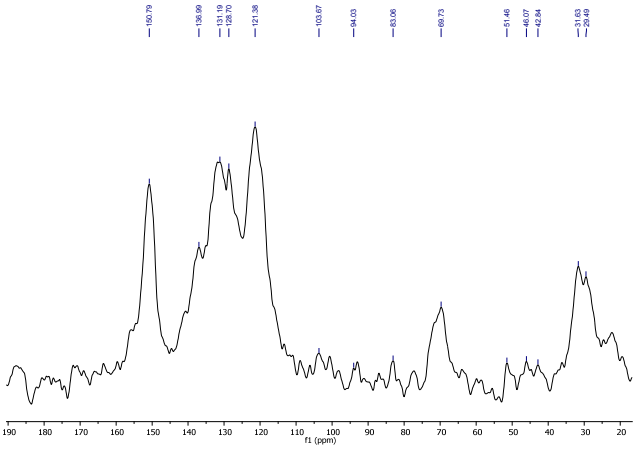
S2: ^{13}C MAS NMR of hybrid materials



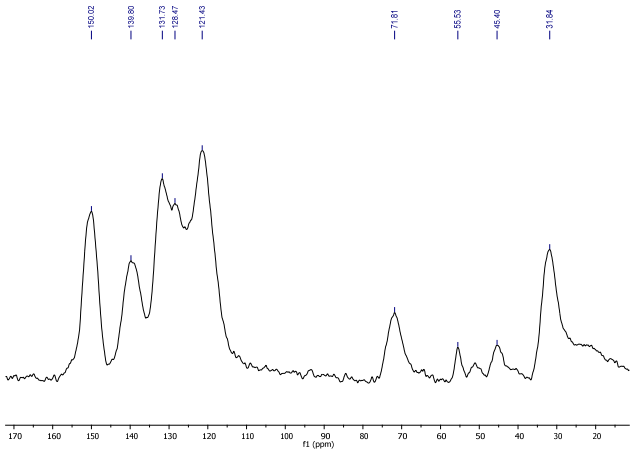
G2



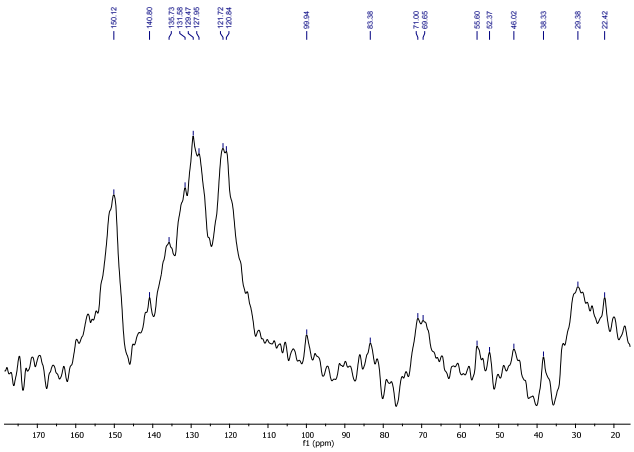
MG2-1/5



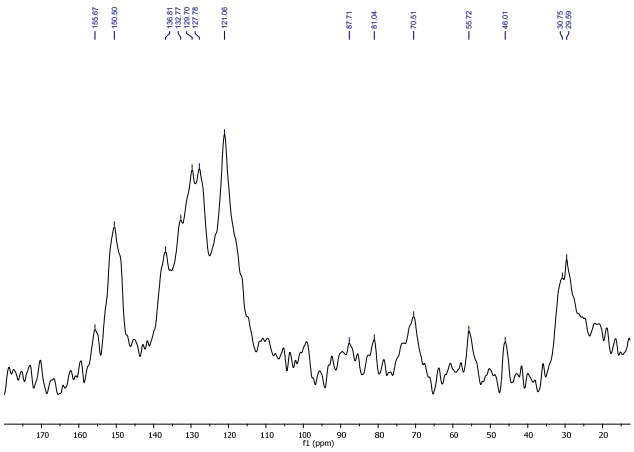
MG2-1/10



G4

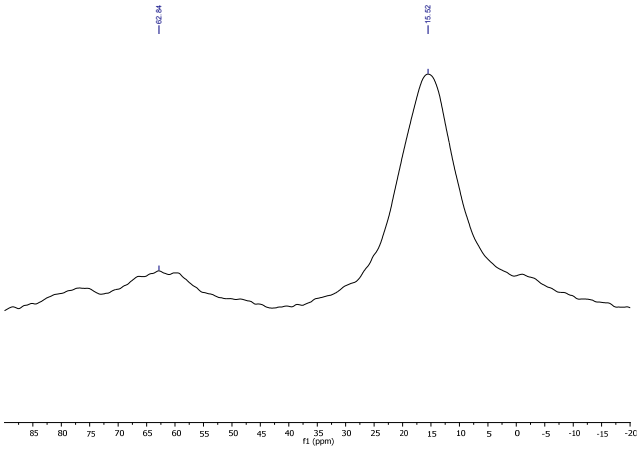


MG4-1/5

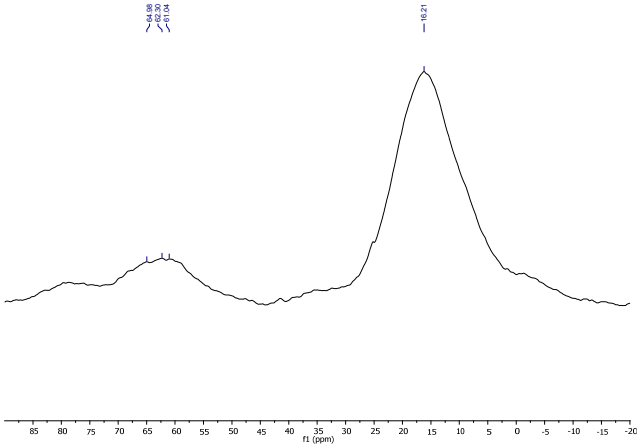


MG4-1/10

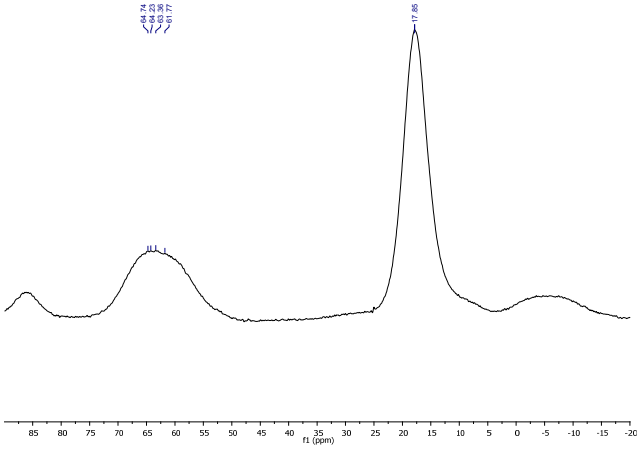
S3: ^{31}P MAS NMR of hybrid materials



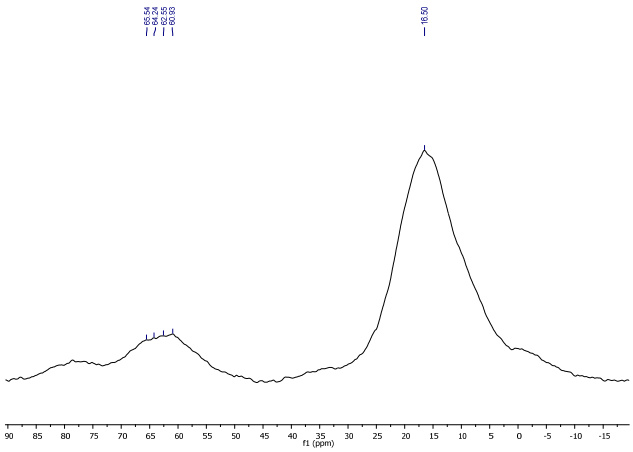
MG4-1/10



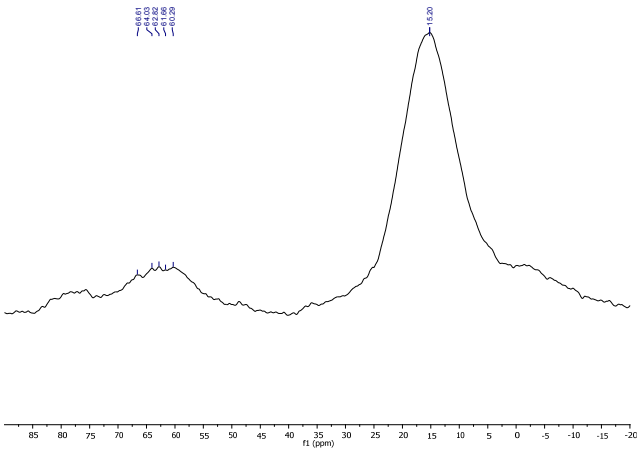
MG4-1/5



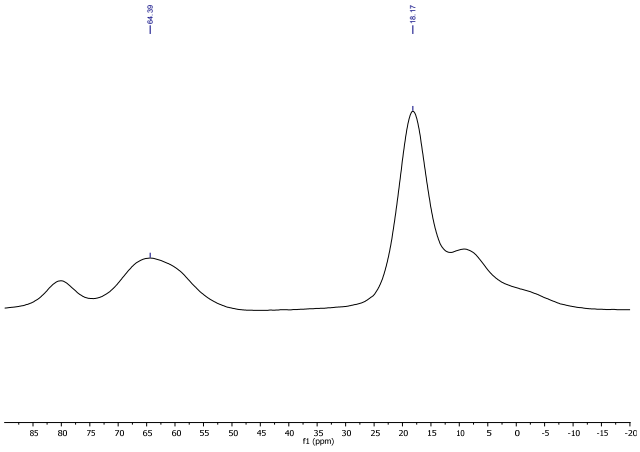
G4



MG2-1/10

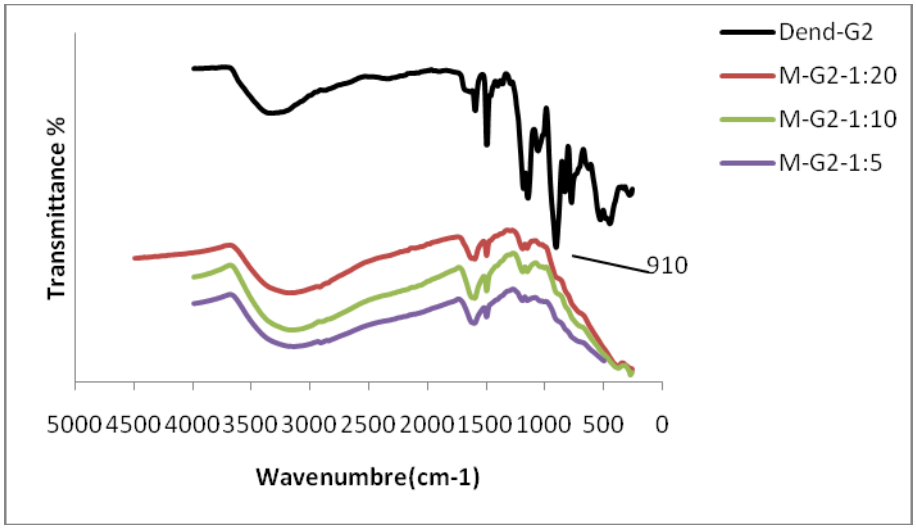


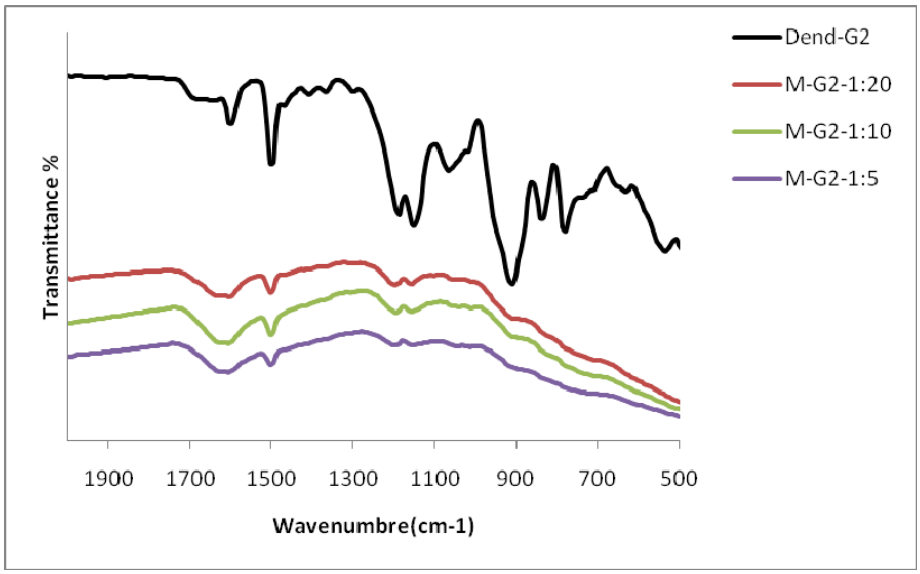
MG2-1/5

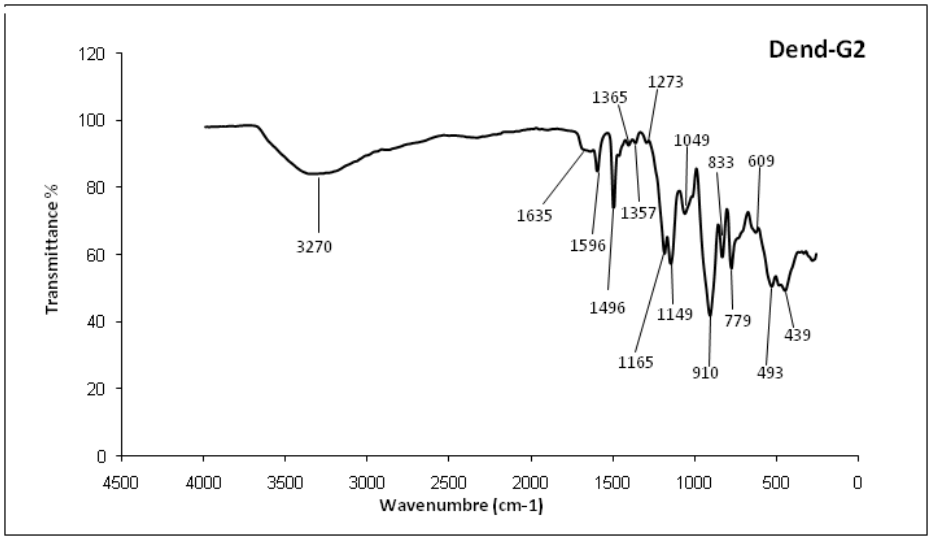


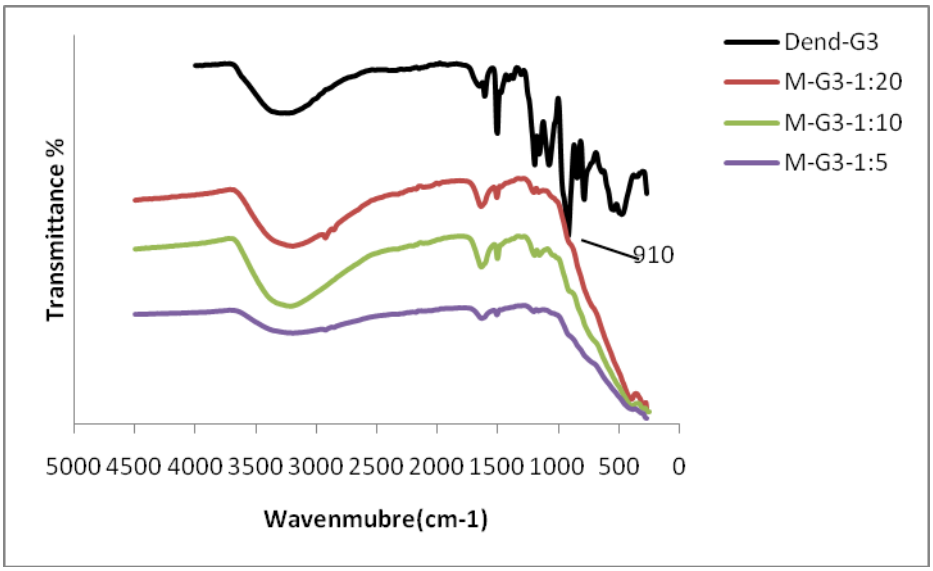
GC2

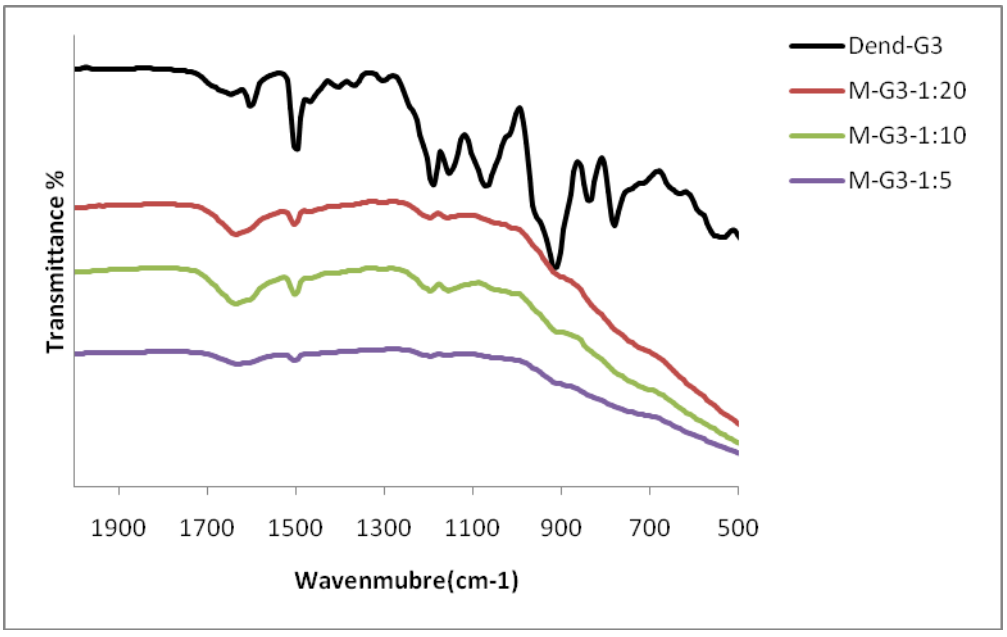
S4: FTIR of hybrid materials

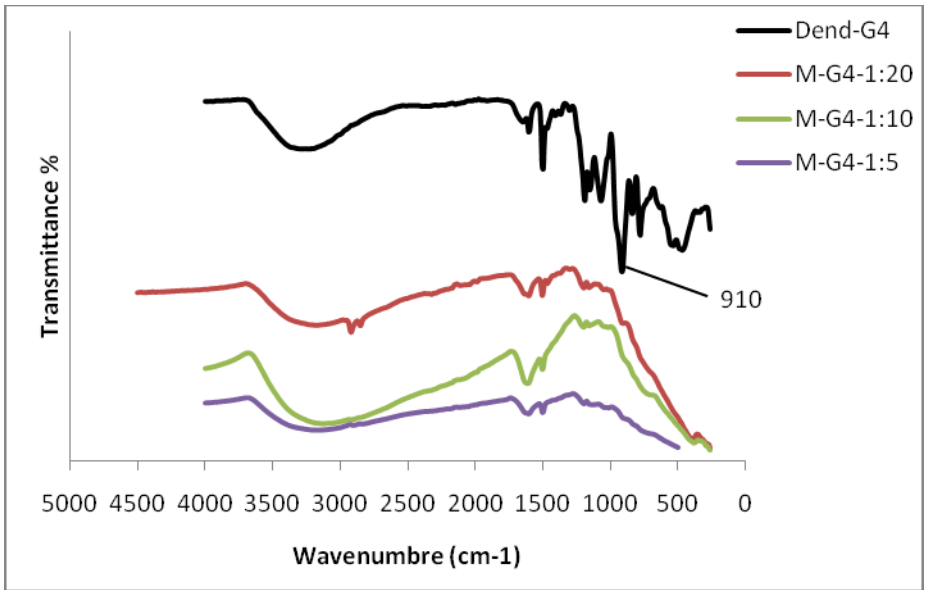


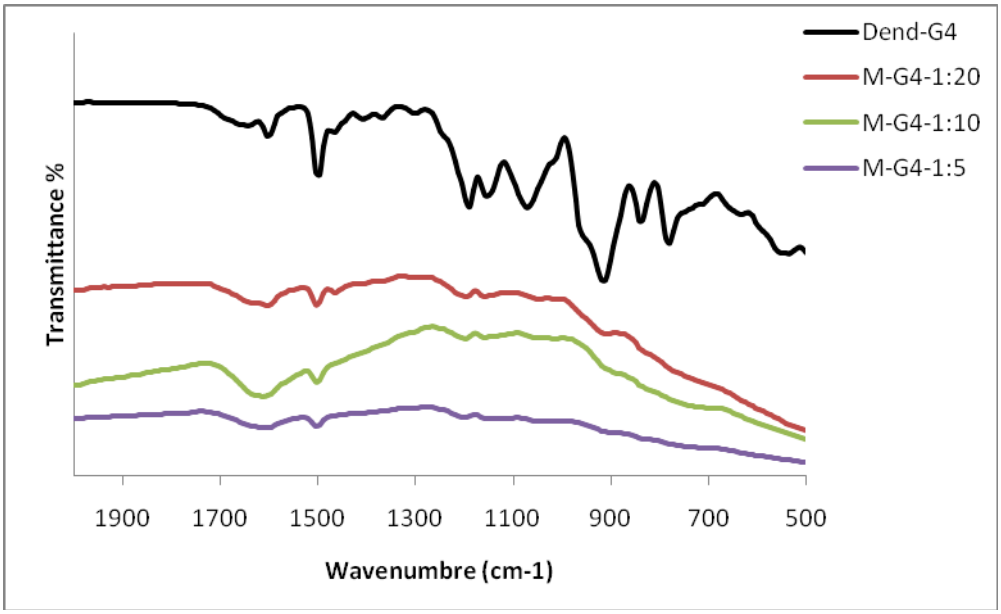




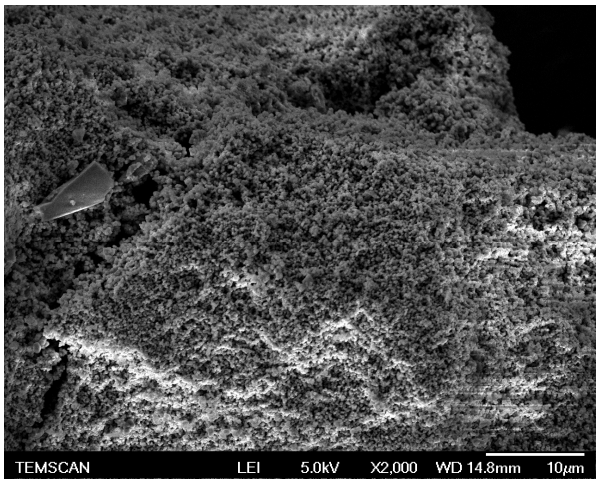




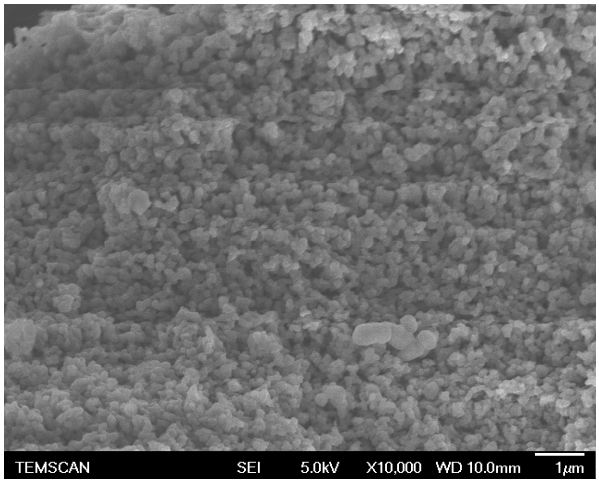




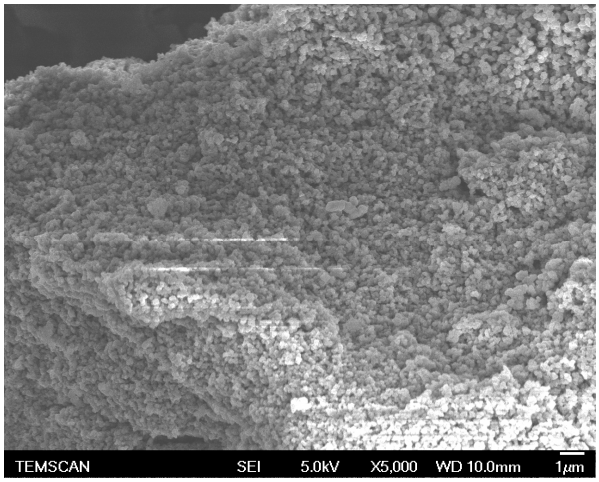
S5: SEM analysis of hybrid materials



M-G3-1/10

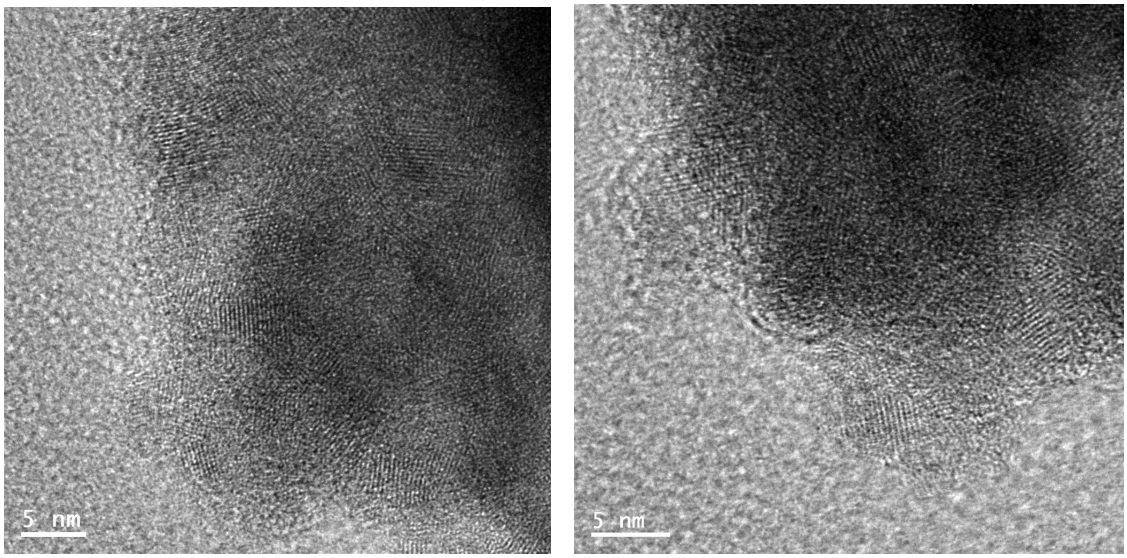


M-G2-1/5

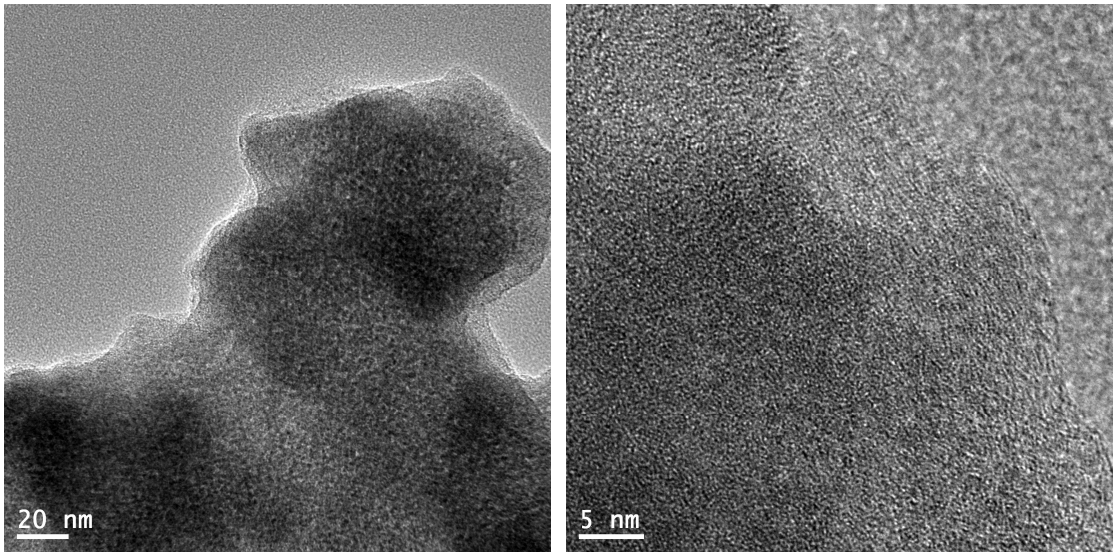


M-G4-1/5

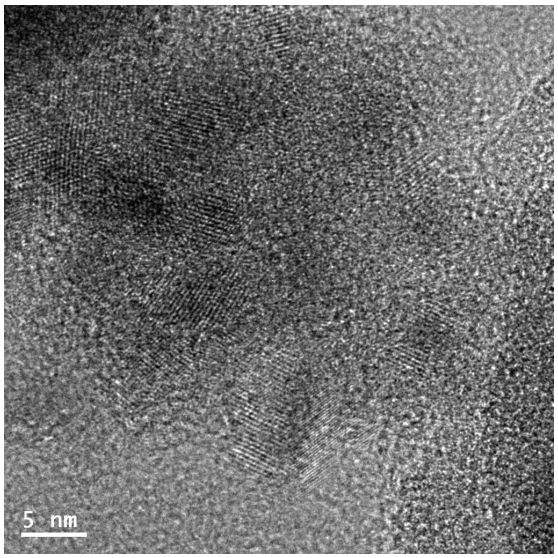
S6: TEM analysis of hybrid materials



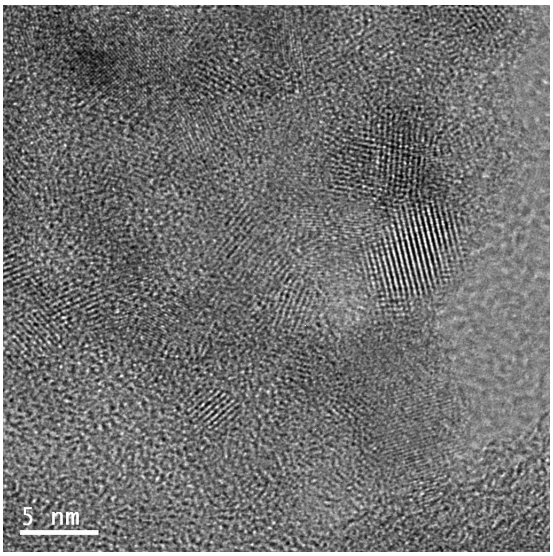
MG4-1/5



MG3-1/5



MG4-1/10



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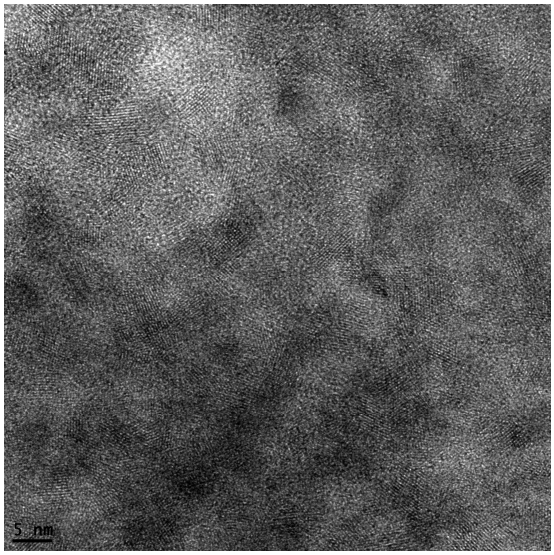
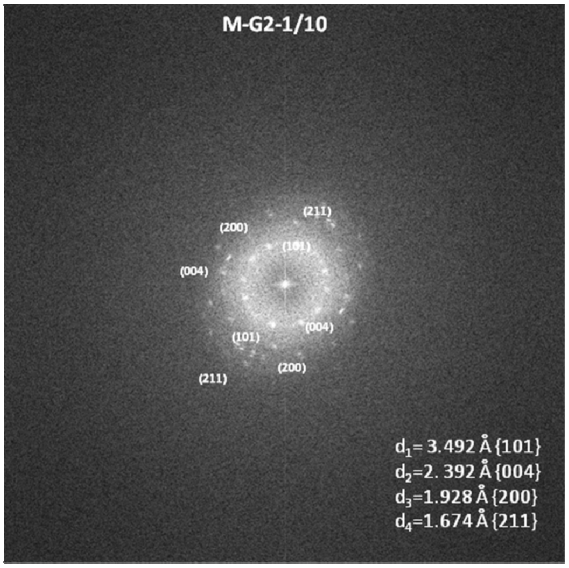
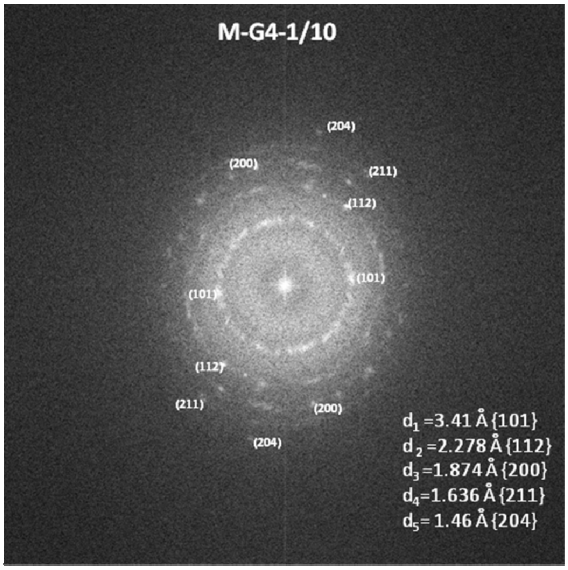
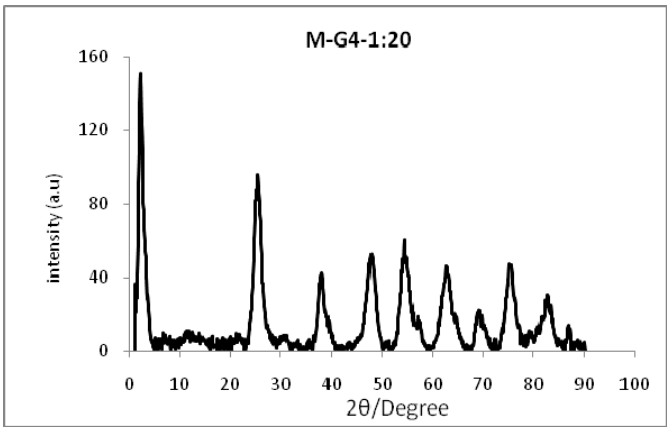


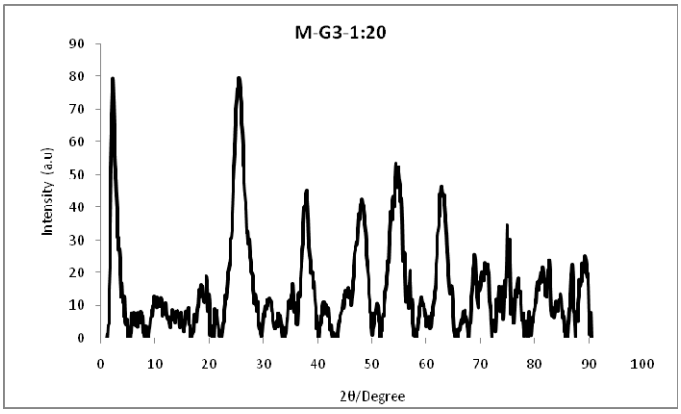
MG3-1/10

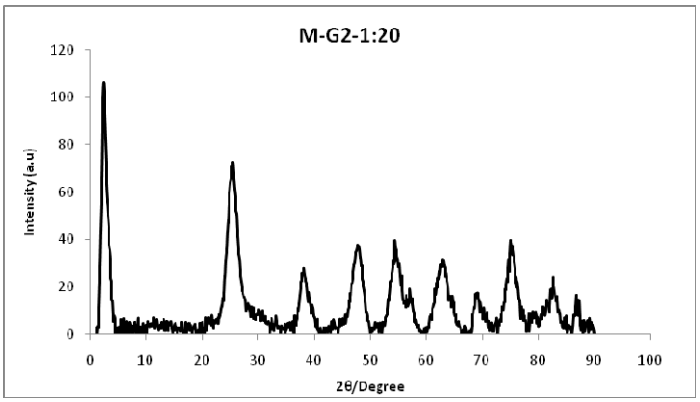




S7: X-ray diffraction analysis of hybrid materials

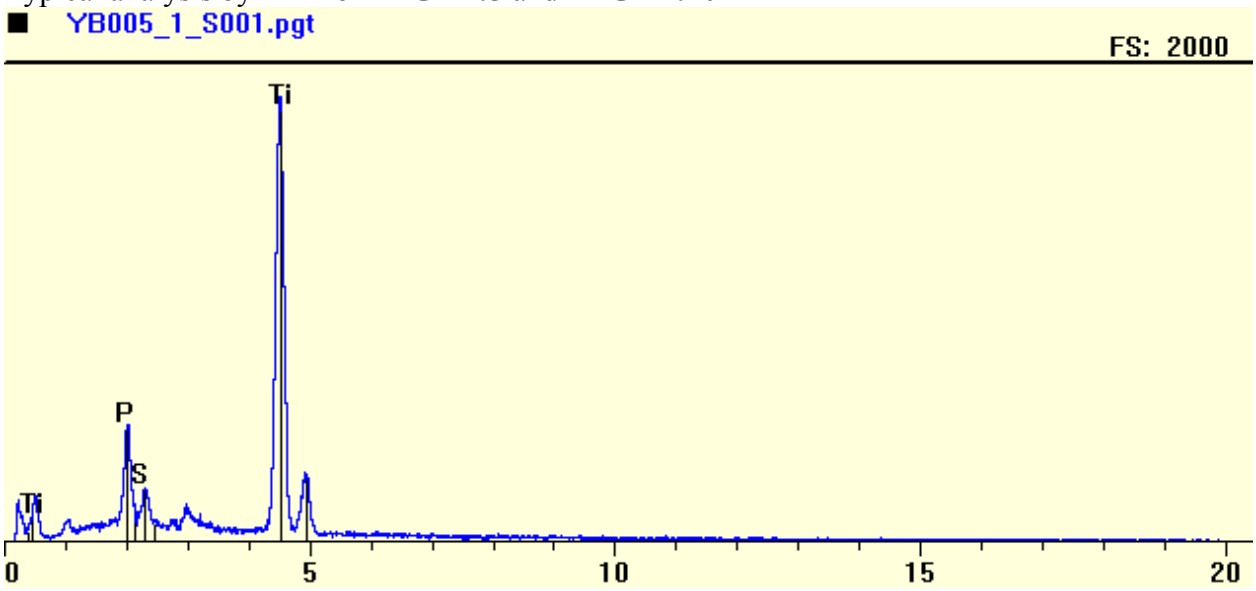




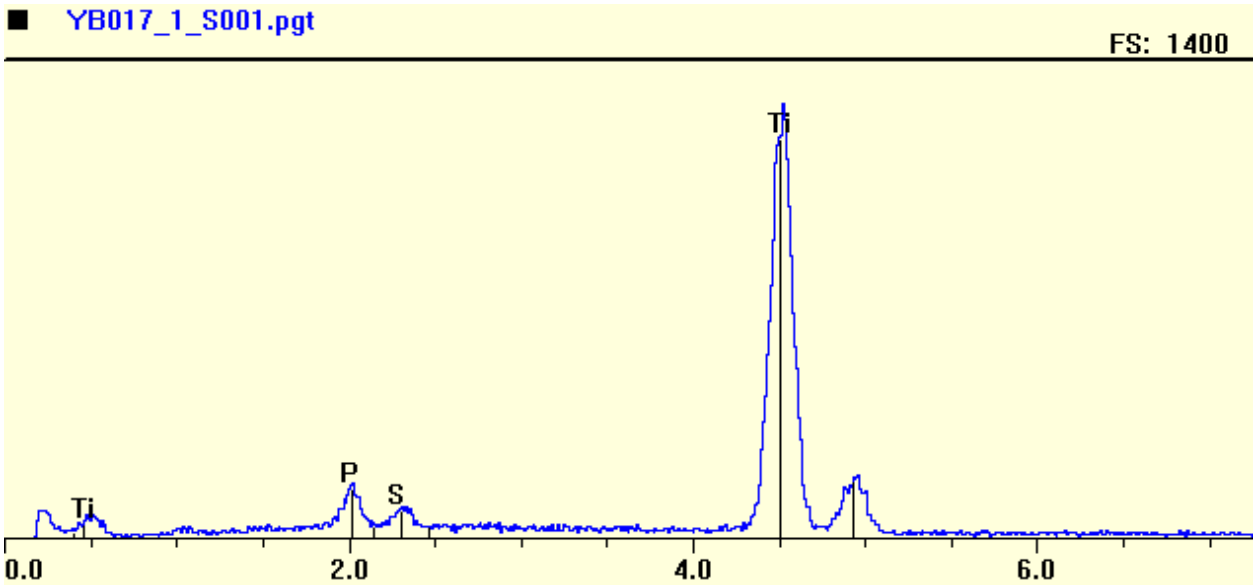


S8: EDX analysis of hybrid materials

Typical analysis by EDX of **M-G4-1:5** and **M-G2-1:10**



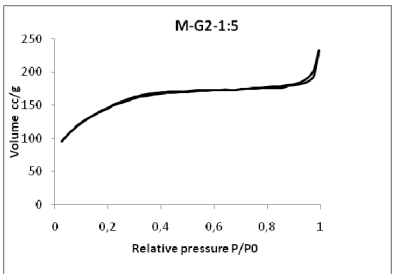
M-G4-1:5 (Experimental ratio dendrimer:Ti = 4.3 from At% of P and Ti)

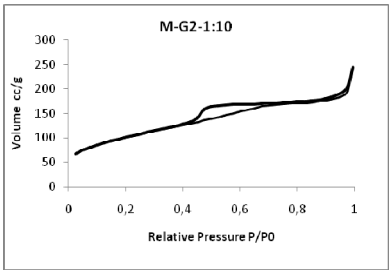


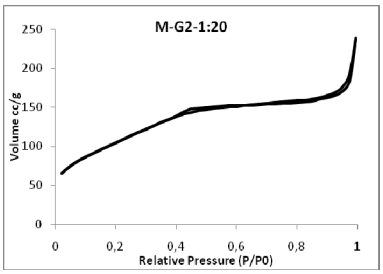
M-G2-1:10 (Experimental ratio dendrimer: Ti = 8.6 from At% of P and Ti)

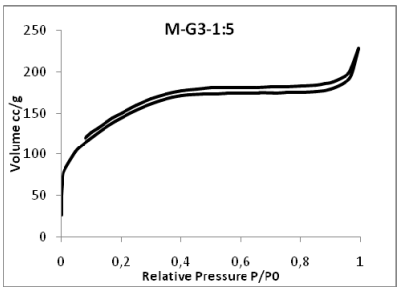
The homogeneity of hybrid materials and the absence of two separate phases have been ascertained after mapping different regions by EDX coupled SEM. The same ratio (P/Ti or (S /Ti) is obtained indicating similar dendrimer-titania composition in the whole of the material.

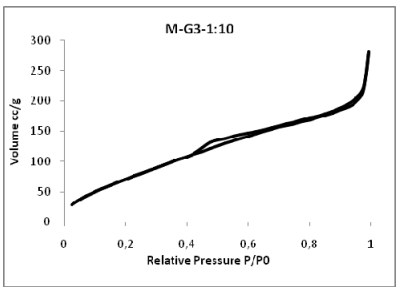
S9: Nitrogen sorption analysis of hybrid materials

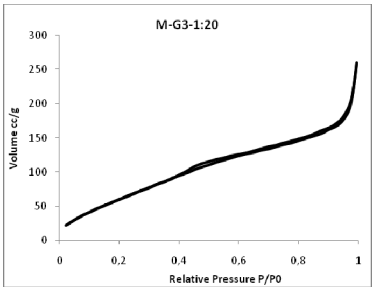


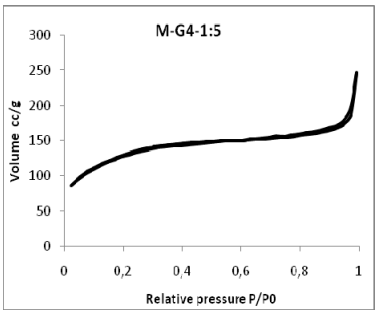


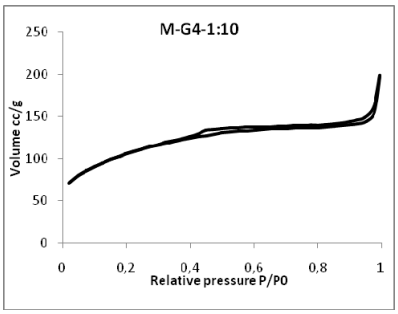


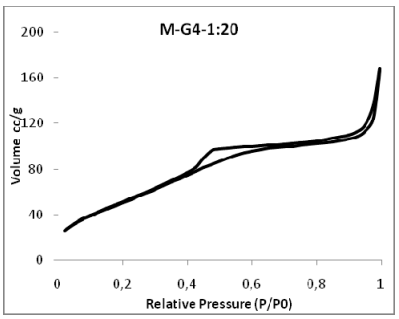




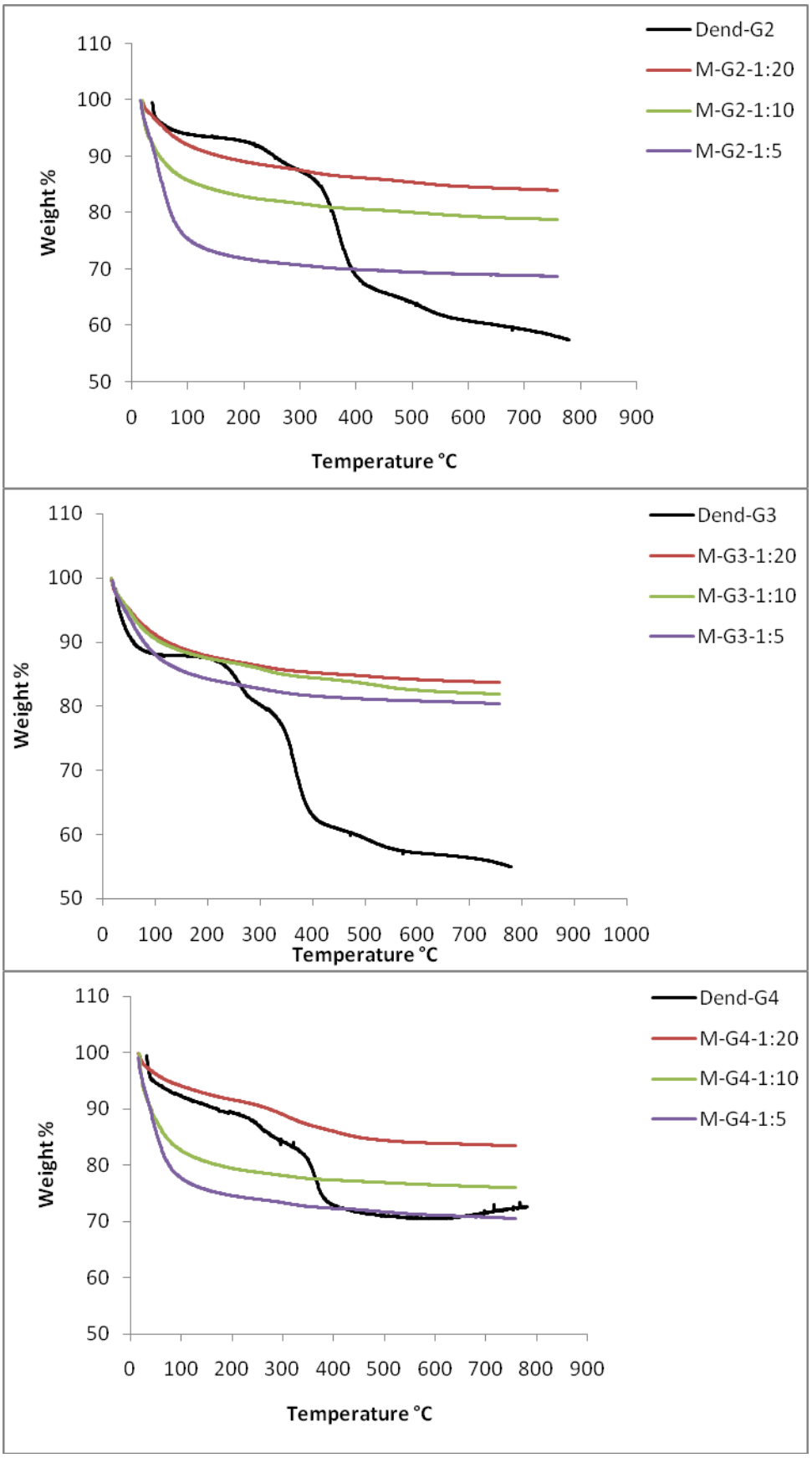




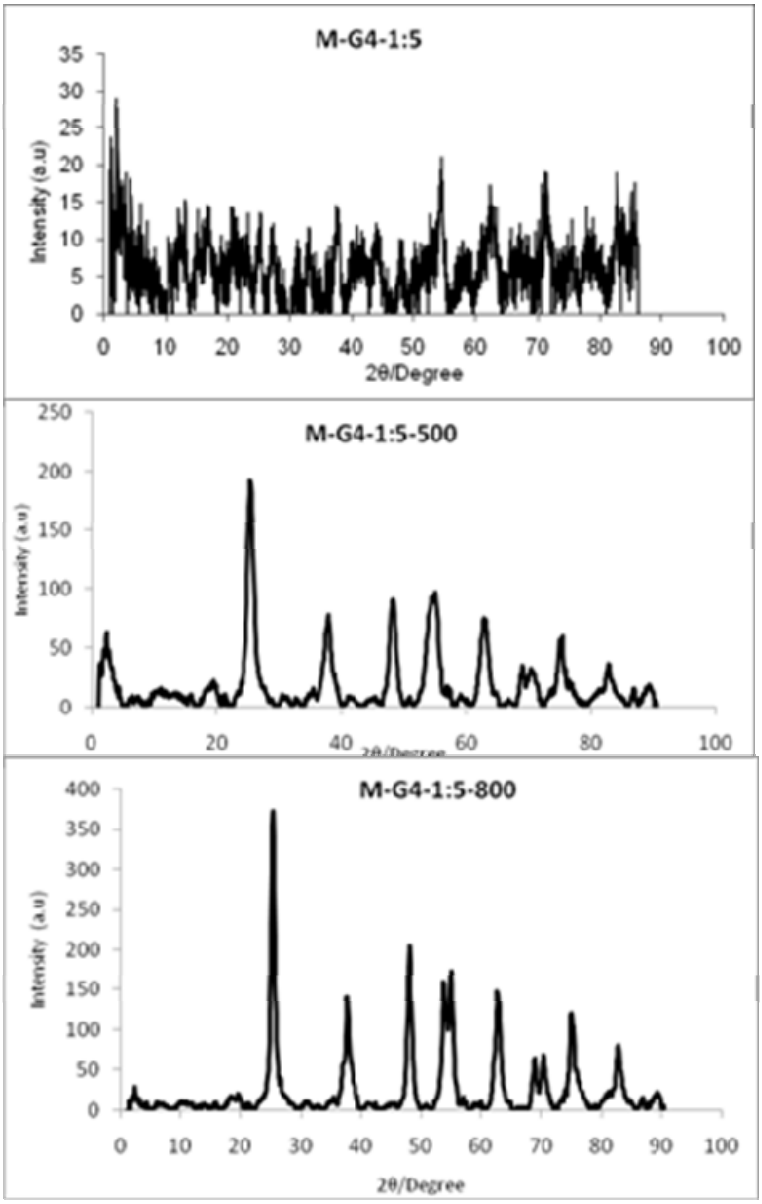




S10: TG analysis of hybrid materials



S11: X-ray diffraction analysis after calcinations.



Crystal size : 5 nm

Crystal size : 6.8 nm

Crystal size : 9.5 nm