

Supplementary Information

Microwave-assisted functionalization of the Aurivillius phase $\text{Bi}_2\text{SrTa}_2\text{O}_9$: diol grafting and amine insertion vs. alcohol grafting

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Materials and methods

Microwave syntheses were performed with a microwave synthesis reactor Monowave 300 (Anton Paar) in non-acidic conditions and with a microwave synthesis reactor MultiwaveGO (Anton Paar) when aqueous acidic conditions are required. Elemental analyses for C, H and N were carried out by the Service d'Analyse of the Université de Strasbourg. The powder XRD patterns were collected with a Bruker D8 diffractometer ($\text{CuK}\alpha 1 = 0.1540598 \text{ nm}$) equipped with a LynxEye detector discriminating in energy. The SEM images were obtained with a JEOL 6700F microscope equipped with a field emission gun, operating at 3 kV in the SEI mode. FT-IR spectra were collected in ATR mode on a SpectrumII spectrometer (Perkin-Elmer). TGA-TDA experiments were performed using a TA instrument SDT Q600 (heating rates of $5^\circ\text{C}\cdot\text{min}^{-1}$ under air stream, using alumina crucibles). Solid state NMR ^{13}C ($I = 1/2$) experiments were performed with a 300 Bruker spectrometer at 75.47 MHz, using magic angle spinning (MAS) condition at 10 kHz and a 4 mm diameter size zirconia rotor. ^{13}C spectra obtained by proton enhanced cross-polarization method (CP) were referenced to the carbonyl of the glycine calibrated at 176.03 ppm. Recycling and Hartman-Hahn contact times were 5 s and 1250 μs , respectively. Spinal 64 ^1H phase-decoupling was applied during ^{13}C channel acquisition.

Caution: even though no problem was encountered in the course of this research, special care must be taken while working with sealed glass containers. Containers must be carefully checked for any defect, and replaced if necessary to avoid possible explosion. Concentrated chlorhydric acid is corrosive and irritating.

Synthetic procedures

$\text{Bi}_2\text{SrTa}_2\text{O}_9$ (BST) was synthesized according to published procedures.¹⁻⁴

$\text{H}_2\text{Bi}_{0.1}\text{Sr}_{0.85}\text{Ta}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$ (HST), $(\text{C}_2\text{NH})_{0.8}\text{H}_{1.2}\text{Bi}_{0.1}\text{Sr}_{0.85}\text{Ta}_2\text{O}_7 \cdot 3 \text{H}_2\text{O}$ ($\text{C}_2\text{N-HST}$) and $(\text{C}_4\text{NH})_{0.9}\text{H}_{1.1}\text{Bi}_{0.1}\text{Sr}_{0.85}\text{Ta}_2\text{O}_7 \cdot 3.8 \text{H}_2\text{O}$ ($\text{C}_4\text{N-HST}$) were synthesized according to published procedures.⁴

$(\text{NH}_4)_{0.7}\text{H}_{1.3}\text{Bi}_{0.1}\text{Sr}_{0.85}\text{Ta}_2\text{O}_7 \cdot 0.5 \text{H}_2\text{O}$ ($\text{NH}_3\text{-HST}$): 100 mg of HST was stirred in 20 mL of ammonia solution (26 %) at RT for one day. The obtained white powder was collected after three centrifugations (9000 g (26000 rpm with a radius of centrifugation of 11.5 mm), 5 min each) (the supernatant was replaced after each centrifugation by distilled water (twice) and acetone (last) in order to wash the product) and air-dried. Anal. Calcd. for $(\text{NH}_4)_{0.7}\text{H}_{1.3}\text{Bi}_{0.1}\text{Sr}_{0.85}\text{Ta}_2\text{O}_7 \cdot 0.5 \text{H}_2\text{O}$ ($M = 591.5 \text{ g/mol}$): H, 0.75; C, 0.0; N, 1.66. Found: H, 0.8; C, 0.0; N, 1.6. TGA weight loss at 570°C calcd : 5.1%. Exp : 6.3%.

Grafting of *n*-alcohols: 0.1 g (0.15 mmol) of C₄N-HST and a mixture of water (0.1 mL, 5.56 mmol) and *n*-alcohols (8 mL, 30-200 mmol) were sealed in a vial (volume 30 mL) (note: for some *n*-alcohols, for example *n*-dodecanol, heating at 70 °C is needed to obtain liquid state). Then the vial was heated in microwave oven (heating: from room temperature to 130°C in 2 min; holding time: 2 h; stirring speed: 800 rpm; maximum power: 70 W). In these conditions, the mean incident power was about 10 W and the autogenous pressure was in the range 0-6 bars, depending on the alcohol. After reactions, the samples were washed with acetone for three times by centrifugation (9000 g, 5 min) and air-dried. The results of elemental analysis and TGA and the proposed formulae are given in Table S1.

Table S1. Mass losses ascribed to the removal of water and of organic phase, elemental micro-analyses (C, H, N) and consistent proposed formulae for the insertion of aliphatic alcohols.

Products	Formula	Mass losses (water+ organic) Found (calcd) (%)	Mass losses (organic) Found (calcd) (%)	Mass losses (water) Found (calcd) (%)	C content Found (calcd) (%)	H content Found (calcd) (%)
C ₁ OH-HST	(CH ₃ O) _{1.5} H _{0.5} Bi _{0.1} Sr _{0.85} Ta ₂ O _{5.5} •0.4H ₂ O	4.7 (4.6)	3.7 (3.5)	1.0 (1.1)	3.05 (2.78)	1.05 (0.9)
C ₂ OH-HST	(C ₂ H ₅ O) _{1.1} H _{0.9} Bi _{0.1} Sr _{0.85} Ta ₂ O _{5.9} •0.3H ₂ O	5.8 (5.8)	4.8 (5.0)	1.0 (0.8)	4.45 (4.11)	1.15 (1.1)
C ₃ OH-HST	(C ₃ H ₇ O) _{1.1} H _{0.9} Bi _{0.1} Sr _{0.85} Ta ₂ O _{5.9} •0.3H ₂ O	7.5 (8.0)	6.6 (7.2)	0.9 (0.8)	6.40 (6.0)	1.47 (1.4)
C ₄ OH-HST	(C ₄ H ₉ O) _{1.0} H _{1.0} Bi _{0.1} Sr _{0.85} Ta ₂ O _{6.0} •0.3H ₂ O	9.0 (9.4)	8.0 (8.6)	1.0 (0.8)	7.40 (7.2)	1.58 (1.6)
C ₇ OH-HST	(C ₇ H ₁₅ O) _{0.9} H _{1.1} Bi _{0.1} Sr _{0.85} Ta ₂ O _{6.1} •0.3H ₂ O	14.5 (13.6)	13.8 (12.8)	0.7 (0.8)	13.48 (10.9)	2.52 (2.2)
C ₁₂ OH-HST	(C ₁₂ H ₂₅ O) _{0.9} H _{1.1} Bi _{0.1} Sr _{0.85} Ta ₂ O _{6.1} •0.2H ₂ O	19.3 (20.8)	18.9 (20.1)	0.4 (0.7)	17.79 (17.1)	3.20 (3.2)

Grafting of propan-2-ol and of benzyl-alcohol: the same procedure as above was used. The results of elemental analysis and TGA and the proposed formulae are given in Table S2.

Table S2. Mass losses ascribed to the removal of water and of organic phase, elemental micro-analyses (C, H, N) and consistent proposed formulae for insertion of bulky alcohols

Products	Formula	Mass losses (water+ organic) Found (calcd) (%)	Mass losses (organic) Found (calcd) (%)	Mass losses (water) Found (calcd) (%)	C content Found (calcd) (%)	H content Found (calcd) (%)	N content Found (calcd) (%)
propan-2-ol-HST	(C ₃ H ₇ O) _{0.6} H _{1.4} Bi _{0.1} Sr _{0.85} Ta ₂ O _{6.4} •0.7H ₂ O	6.5 (6.1)	4.5 (4.1)	2.0 (2.0)	4.18 (3.4)	1.33 (1.1)	0.0 (0)
tert-butanol-HST					3.46	1.37	0.82
benzyl alcohol-HST	(C ₇ H ₇ O) _{0.7} H _{1.3} Bi _{0.1} Sr _{0.85} Ta ₂ O _{6.3} •0.3H ₂ O	10.2 (10.4)	9.4 (9.6)	0.8 (0.8)	10.90 (8.9)	1.39 (1.0)	0.0 (0)

Grafting of α , ω -alkyldiols: the same procedure as above was used, with 1 mL of water (55 mmol) and 8 g of α , ω -alkyldiols (40-130 mmol). In these conditions, the mean incident power was about 5 W and the autogenous pressure was too low to be measured. The results of elemental analysis and TGA and the proposed formulae are given in Table S3.

Table S3. Mass losses ascribed to the removal of water and of organic phase, elemental micro-analyses (C, H, N) and consistent proposed formulae for insertion of diols.

Products	Formula	Mass losses (water+ organic) Found (calcd) (%)	Mass losses (organic) Found (calcd) (%)	Mass losses (water) Found (calcd) (%)	C content Found (calcd) (%)	H content Found (calcd) (%)
C ₂ (OH) ₂ -HST	(HOC ₂ H ₄ O) _{0.8} H _{1.2} Bi _{0.1} Sr _{0.85} Ta ₂ O _{6.2} ·0.9H ₂ O	7.6 (6.1)	4.9 (3.6)	2.7 (2.5)	3.75 (3.0)	1.11 (1.1)
C ₃ (OH) ₂ -HST	(HOC ₃ H ₆ O) _{0.6} H _{1.4} Bi _{0.1} Sr _{0.85} Ta ₂ O _{6.4} ·0.3H ₂ O	3.87 (4.9)	3.33 (4.1)	0.54 (0.9)	3.39 (3.4)	1.24 (1.0)
C ₄ (OH) ₂ -HST	(OC ₄ H ₈ O) _{0.5} H _{1.0} Bi _{0.1} Sr _{0.85} Ta ₂ O ₆ ·0.1H ₂ O	5.3 (5.0)	5.0 (4.7)	0.3 (0.3)	4.04 (4.0)	1.13 (0.9)
C ₇ (OH) ₂ -HST	(OC ₇ H ₁₄ O) _{0.3} H _{1.4} Bi _{0.1} Sr _{0.85} Ta ₂ O _{6.4} ·0.7H ₂ O	6.0 (6.9)	4.0 (4.8)	2.0 (2.1)	4.81 (4.1)	1.30 (1.2)
C ₈ (OH) ₂ -HST	(OC ₈ H ₁₆ O) _{0.3} H _{1.4} Bi _{0.1} Sr _{0.85} Ta ₂ O _{6.4} ·0.8H ₂ O	7.3 (7.8)	5.2 (5.4)	2.1 (2.3)	5.00 (4.7)	1.42 (1.3)
C ₉ (OH) ₂ -HST	(OC ₉ H ₁₈ O) _{0.3} H _{1.4} Bi _{0.1} Sr _{0.85} Ta ₂ O _{6.4} ·0.5H ₂ O	6.1 (7.6)	4.6 (6.1)	1.5 (1.5)	5.08 (5.3)	1.28 (1.3)
C ₁₂ (OH) ₂ -HST	(OC ₁₂ H ₂₄ O) _{0.3} H _{1.4} Bi _{0.1} Sr _{0.85} Ta ₂ O _{6.4} ·0.8H ₂ O	8.4 (10.2)	6.1 (7.9)	2.3 (2.3)	6.99 (6.8)	1.73 (1.6)

Grafting of 5-amino-1-pentanol: 50 mg of C₂N-HST were dispersed in a solution of 1 mL of 5-amino-1-pentanol in a mixture of 1 mL of THF and water (0.01, 0.02, 0.03, 0.04, 0.1 and 1.0 mL respectively). The mixture was placed in a 10 mL vial and heated by microwave irradiation at 130°C during 1 h (maximum incident power: 70 W). In these conditions, the mean incident power was about 10 W, and the autogenous pressure was about 5 bars. The obtained white powder was collected after three centrifugations (9000 rpm, 2 min each) (the supernatant was replaced after each centrifugation by acetone in order to wash the product) and air-dried. The results of elemental analysis and TGA and the proposed formulae are given in Table S4.

Table S4. Mass losses ascribed to the removal of water and of organic phase, elemental micro-analyses (C, H, N) and consistent proposed formulae.

water/THF (v:v)	Formula	Mass losses (water + organic) Found (calcd) (%)	Mass losses (organic) Found (calcd) (%)	Mass losses (water) Found (calcd) (%)	C content Found (calcd) (%)	H content Found (calcd) (%)	N content Found (calcd) (%)
1%	(H ₃ NC ₅ H ₁₀ O) _{0.5} H _{1.0} Bi _{0.1} Sr _{0.85} Ta ₂ O _{6.5} ·0.6H ₂ O	8.3 (8.8)	6.6 (7.1)	1.7 (1.8)	6.08 (4.9)	1.49 (1.2)	1.38 (1.1)
2%	(H ₃ NC ₅ H ₁₀ O) _{0.6} H _{0.8} Bi _{0.1} Sr _{0.85} Ta ₂ O _{6.4} ·0.9H ₂ O	11.4 (10.9)	8.2 (8.3)	3.2 (2.6)	6.11 (5.7)	1.72 (1.4)	1.52 (1.3)
4%	(H ₃ NC ₅ H ₁₀ OH) _{0.6} H _{1.4} Bi _{0.1} Sr _{0.85} Ta ₂ O ₇ ·1.3H ₂ O	12.9 (11.7)	7.5 (8.1)	5.4 (3.6)	5.99 (5.6)	1.77 (1.7)	1.49 (1.3)
10%	(H ₃ NC ₅ H ₁₀ OH) _{0.5} H _{1.5} Bi _{0.1} Sr _{0.85} Ta ₂ O ₇ ·1.4H ₂ O	12.6 (10.7)	7.1 (6.8)	5.5 (3.9)	6.31 (4.7)	2.03 (1.4)	1.47 (1.1)
100%	(H ₃ NC ₅ H ₁₀ OH) _{0.5} H _{1.5} Bi _{0.1} Sr _{0.85} Ta ₂ O ₇ ·1.3H ₂ O	12.1 (10.5)	7.1 (6.8)	5.0 (3.7)	6.08 (4.7)	1.89 (1.4)	1.52 (1.1)

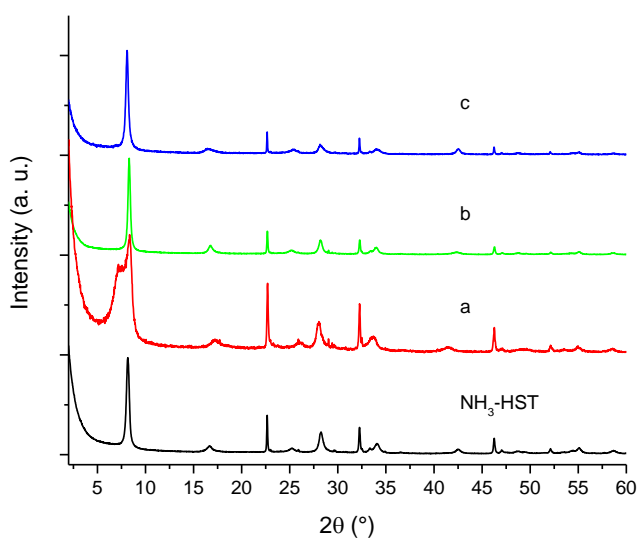


Figure S1. PXRD patterns of **NH₃-HST** and its reaction products with *n*-alcohols: (a): methanol; (b): ethanol; (c): propanol.

In addition to XRD patterns, IR spectra of reaction products between **NH₃-HST** and methanol, ethanol and propanol confirm the failure of the grafting reactions of propanol and ethanol and the incompleteness of the grafting reaction of methanol (Figure S2). For compound (a) (reaction with methanol) new signals indeed appear: the CH₃ group of methanol is visible at ν_{as} 2919 cm⁻¹ (ν_{as}) and 2817 cm⁻¹ (ν_s).^{5,6} Moreover, the C-O elongation band is blue shifted by about 140 cm⁻¹ with respect to MeOH ($\nu_{(CO)}$ band at 1034 cm⁻¹),⁵ indicating the deprotonation of the alcohol and the formation of the C-O-Ta motif (1171 cm⁻¹).⁷ However, the existence of signal at 1429 cm⁻¹, coming from the starting material, confirms the incompleteness of the grafting reaction.

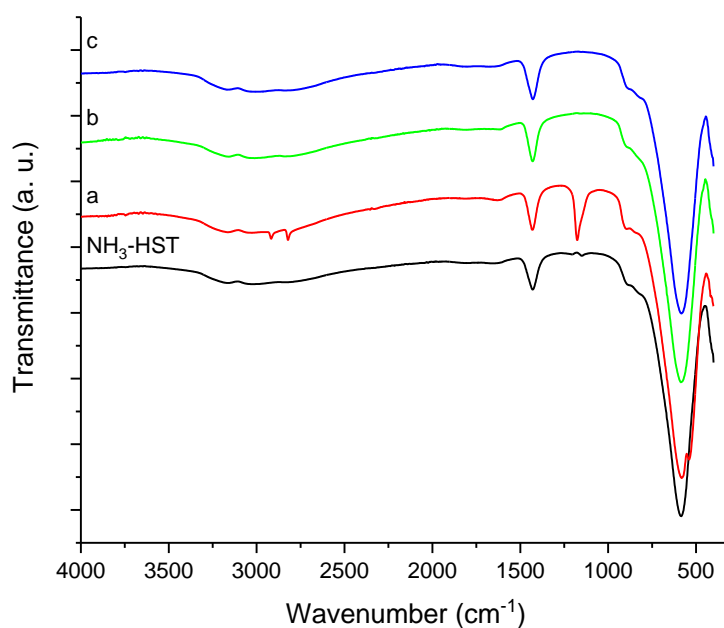


Figure S2. IR spectra of **NH₃-HST** and its reaction products with *n*-alcohols: (a): methanol; (b): ethanol; (c): propanol.

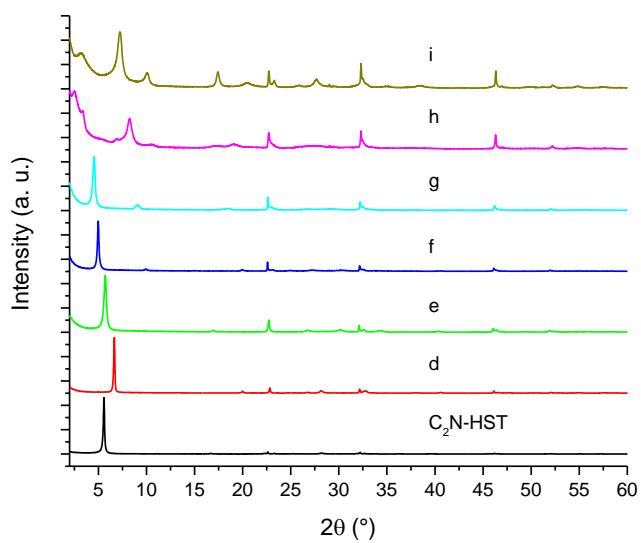


Figure S3. PXRD patterns of **C₂N-HST** and its reaction products ((d), (e), (f), (g), (h), (i)) with *n*-alcohols (C_nOH , $n = 1, 2, 3, 4, 7, 12$), respectively.

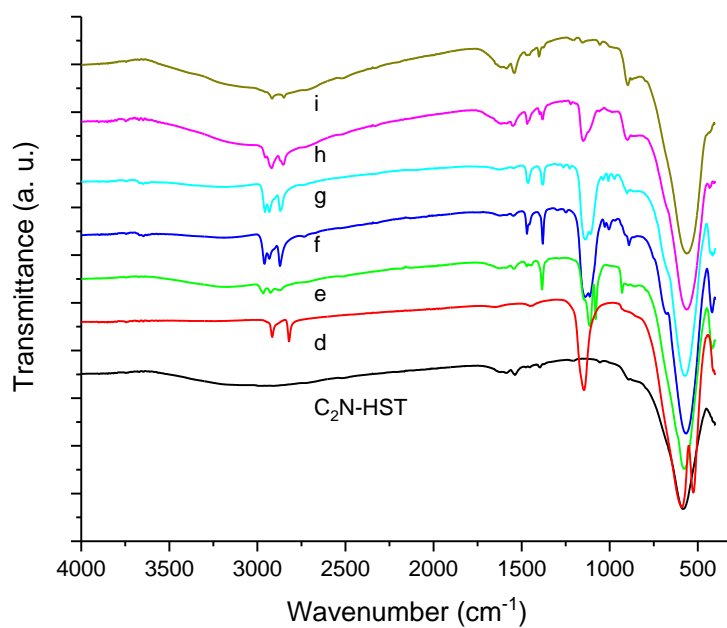


Figure S4. IR spectra of **C₂N-HST** and its reaction products ((d), (e), (f), (g), (h), (i)) with *n*-alcohols (C_nOH , $n = 1, 2, 3, 4, 7, 12$), respectively.

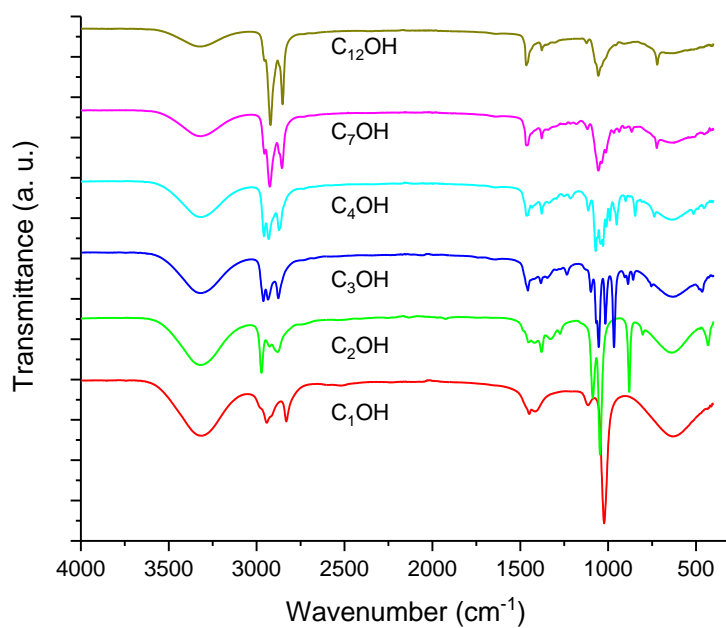


Figure S5. IR spectra of *n*-alcohols (C_nOH , $n = 1, 2, 3, 4, 7, 12$).

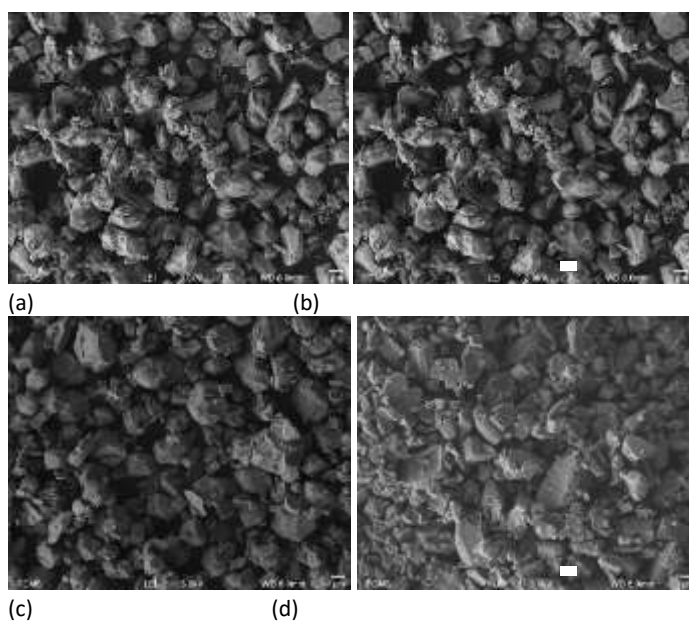


Figure S6. SEM images of (a) HST, (b) C₂OH-HST, (c) C₄OH-HST and (d) C₁₂OH-HST (The scale bars correspond to 1 μm).

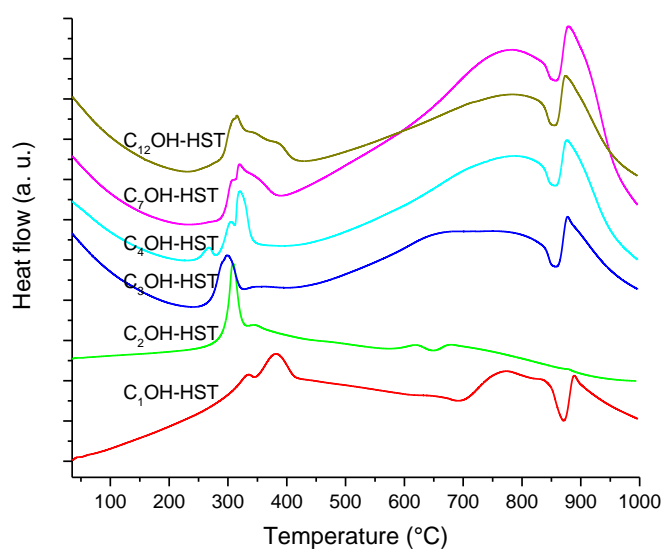
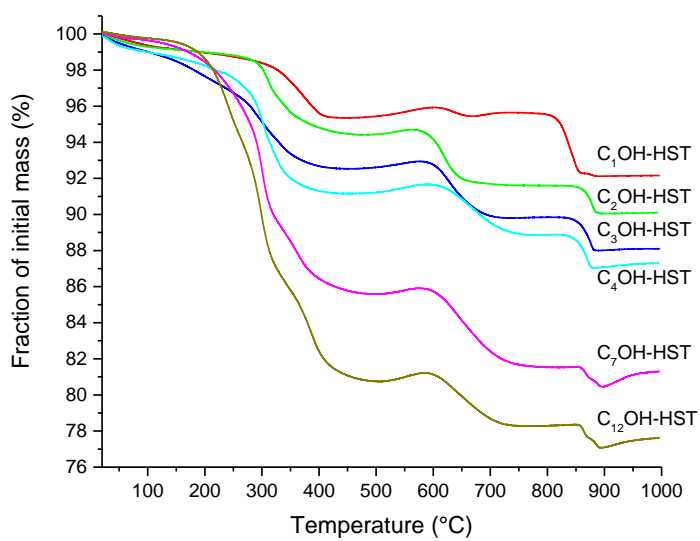


Figure S7. TGA (top) and TDA (bottom) curves of C₁OH-HST, C₂OH-HST, C₃OH-HST, C₄OH-HST, C₇OH-HST and C₁₂OH-HST.

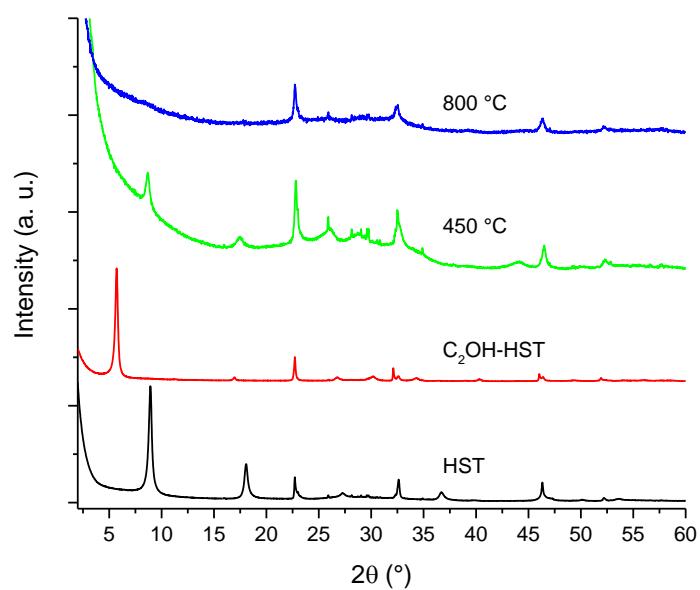


Figure S8. PXRD patterns of **HST**, **C₂OH-HST** and of the compounds obtained after thermal treatment products at 450 °C and 800 °C.

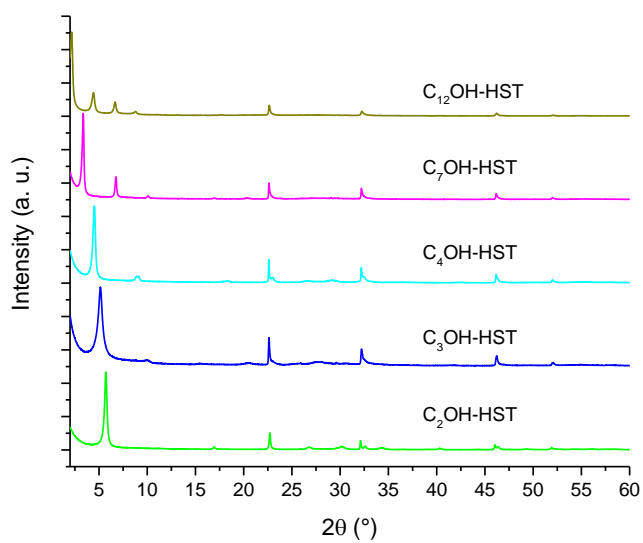


Figure S9. PXRD patterns of **C₂OH-HST** and its reaction products with *n*-alcohols (C_{*n*}OH, *n* = 3, 4, 7, 12).

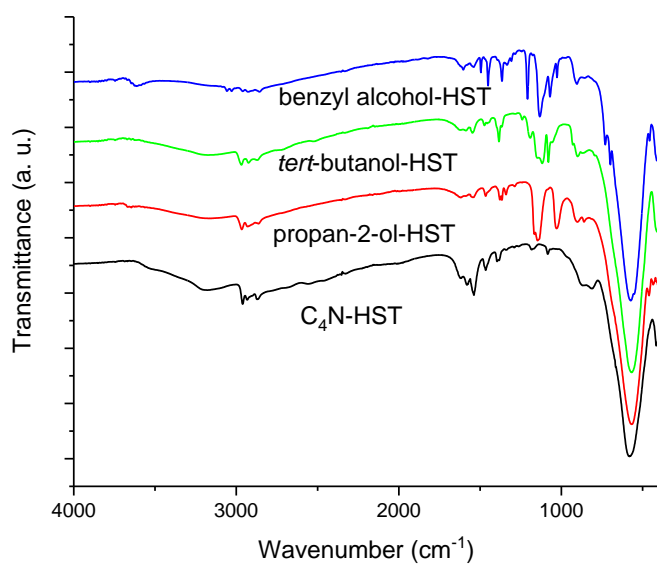


Figure S10. IR spectra of **C₄N-HST** and its reaction products with propan-2-ol, tert-butanol and benzyl alcohol.

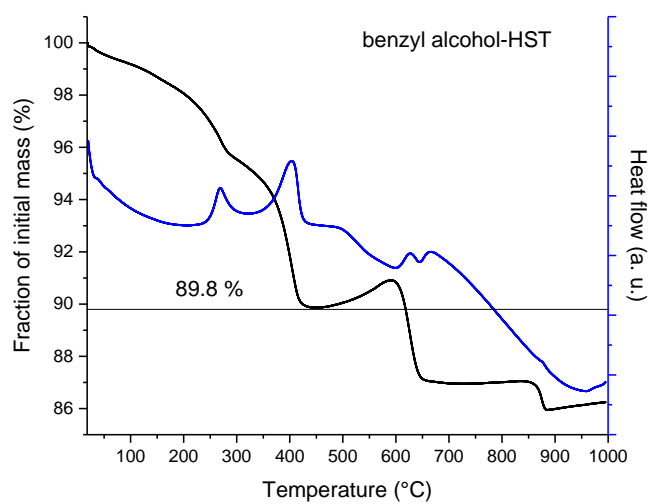
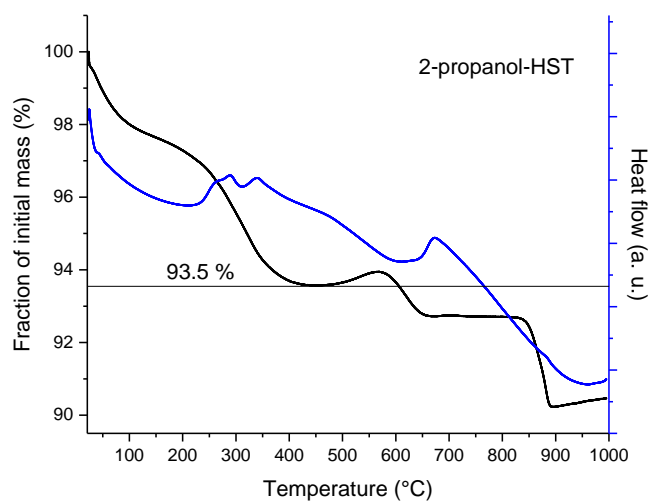


Figure S11. TGA and TDA curves for propan-2-ol-HST and benzyl alcohol-HST.

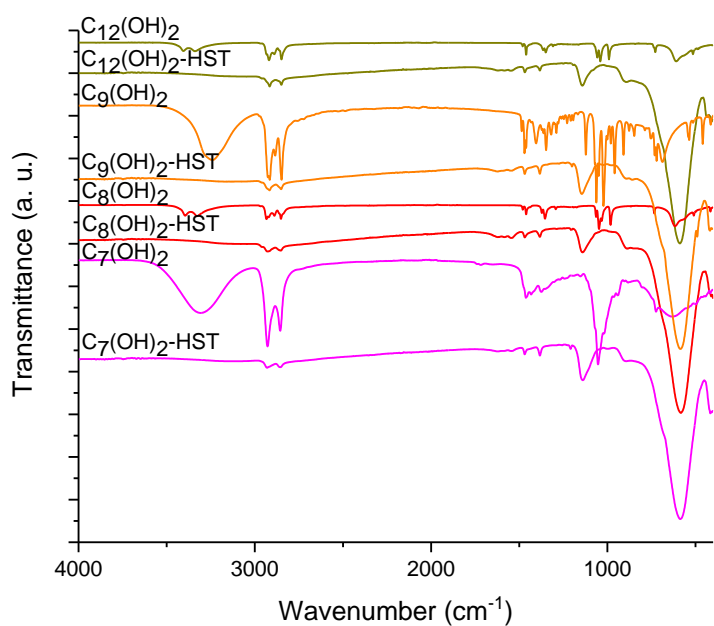


Figure S12. IR spectra of heptanediol, octanediol, nonanediol, dodecanediol, C₇(OH)₂-HST, C₈(OH)₂-HST, C₉(OH)₂-HST and C₁₂(OH)₂-HST.

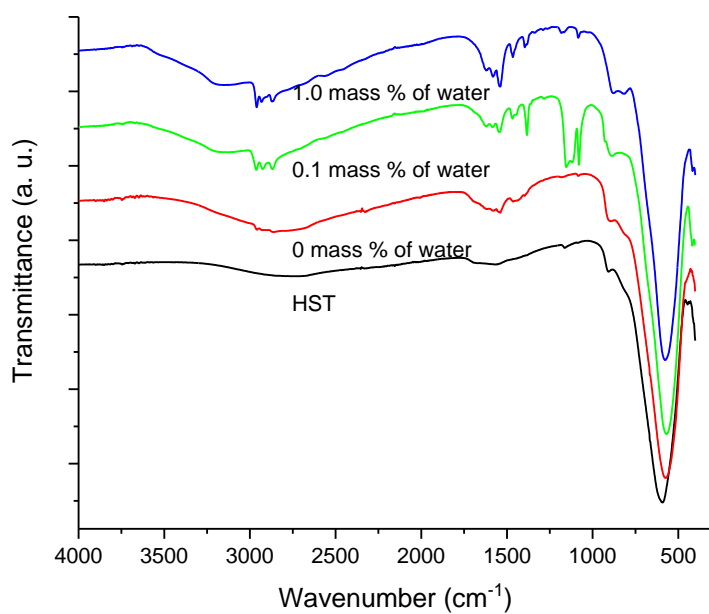


Figure S13. IR spectra of HST and its reaction products with an equimolar mixture of butylamine and ethanol and 0 mass %, 0.1 mass % and 1 mass % of distilled water.

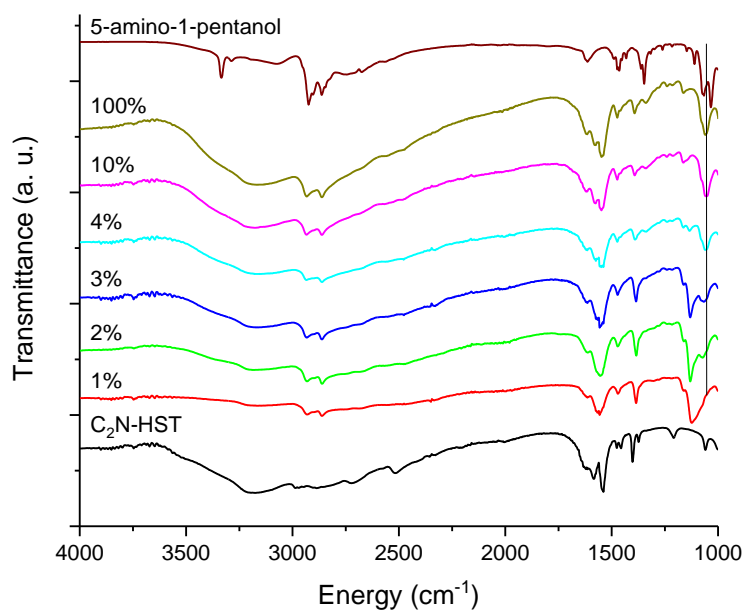


Figure S14. IR spectra of C₂N-HST and its reaction products with 5-amino-1-pentanol by using different quantities of water.

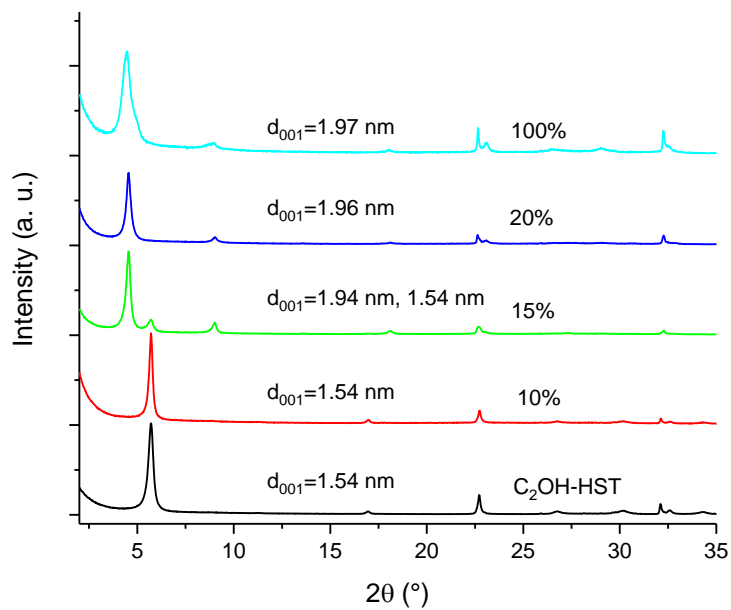


Figure S15. XRD patterns of C₂OH-HST and its reaction products with 5-amino-1-pentanol using different amounts of water.

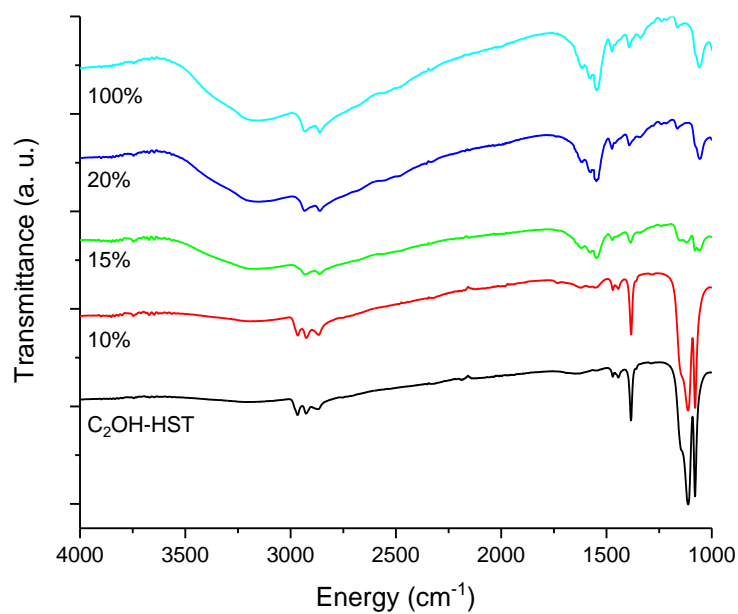


Figure S16. IR spectra of C_2OH -HST and its reaction products with 5-amino-pentan-1-ol using different amounts of water.

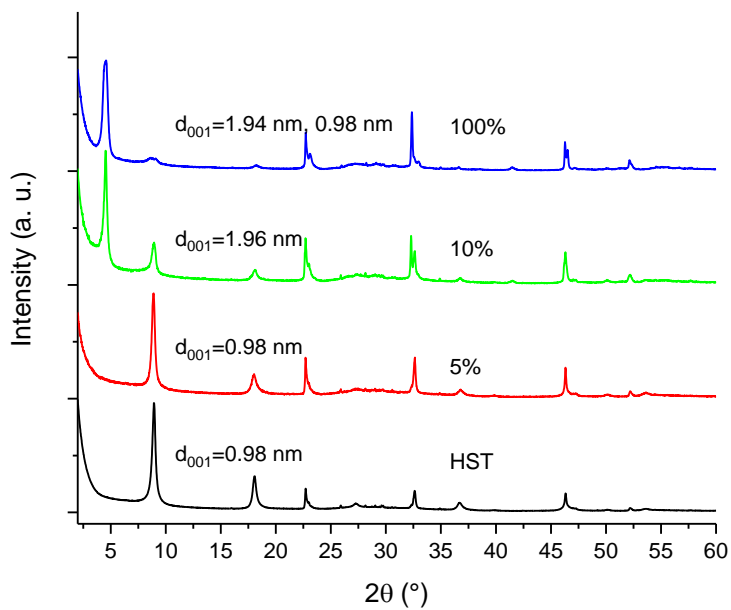


Figure S17. XRD patterns of HST and its reaction products with 5-amino-1-pentanol using different amounts of water.

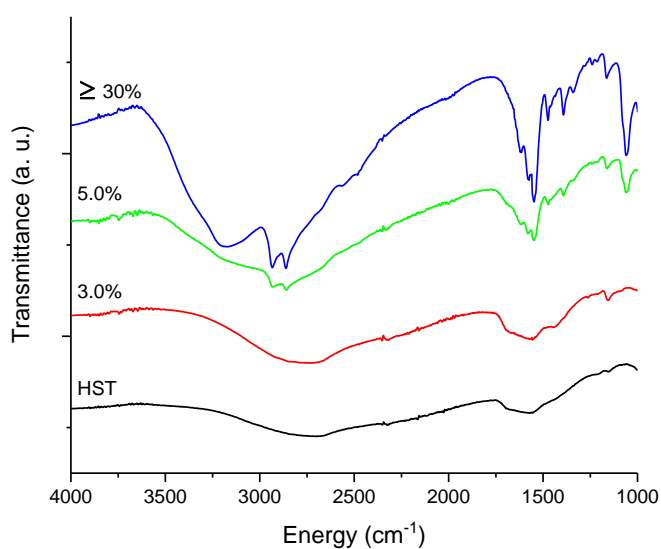


Figure S18. IR spectra of HST and its reaction products with 5-amino-pentan-1-ol using different amounts of water.

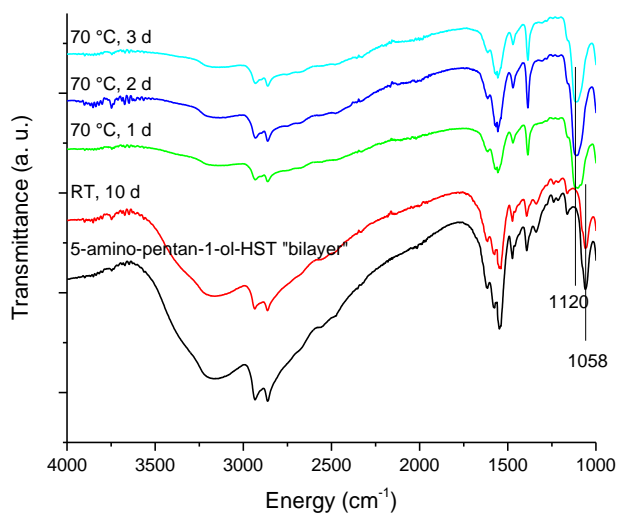


Figure S19. IR spectra of 5-amino-pentan-1-ol-HST "bilayer" and the products obtained after heating.

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