Adsorption of benzoxaboroles on hydroxyapatite phases

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SUPPORTING INFORMATION

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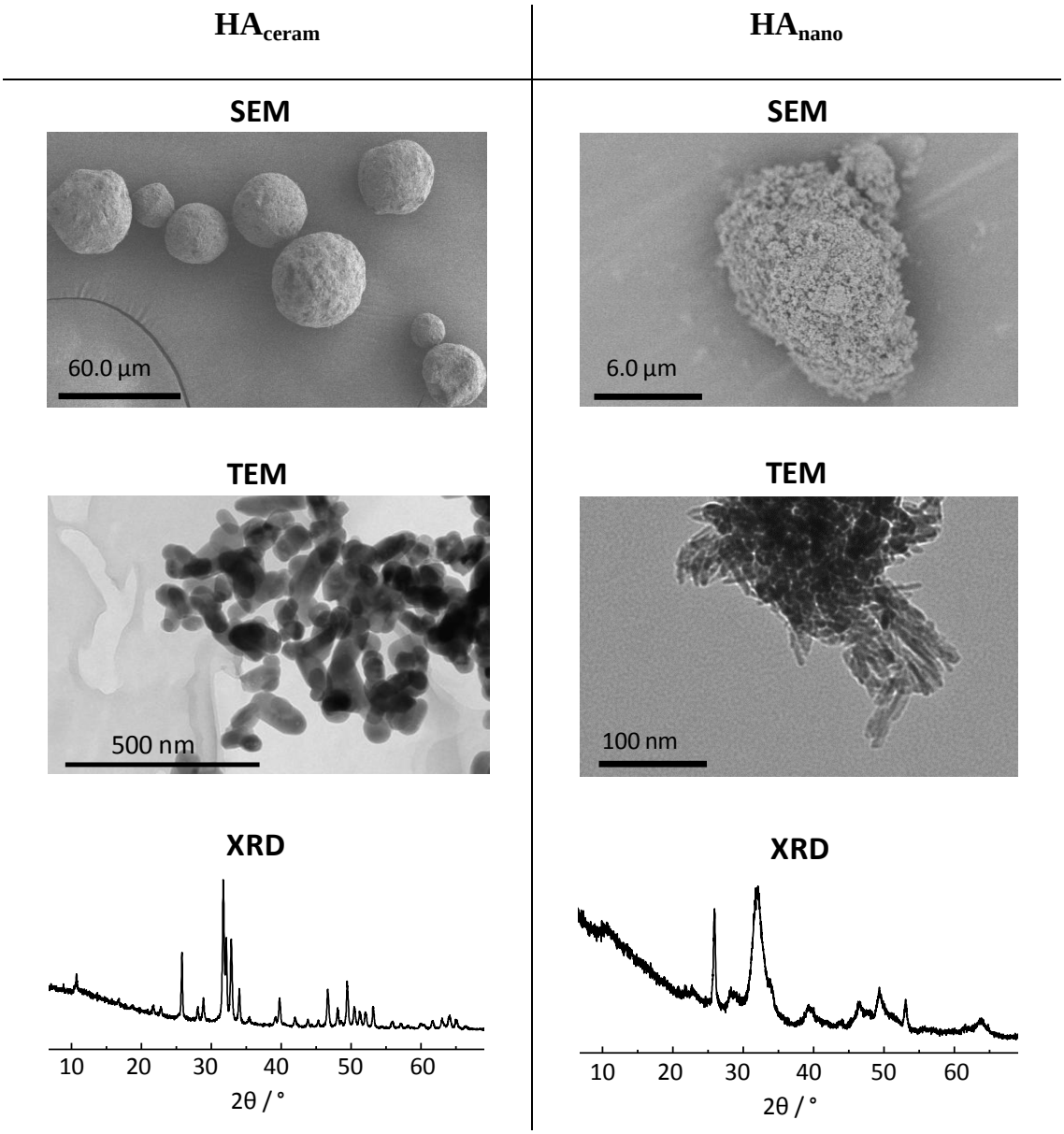
Figure S1. SEM, TEM and powder-X-ray diffraction characterizations of the HA_{ceram} and HA_{nano}.



Synthesis of $Ca(C_7H_6BO(OH)_2)_2.2H_2O$ (CaBBzx.2H_2O)

Microbeads of NaOH (100.2 mg, 2.5 mmol) of NaOH were dissolved in 7 mL of ultrapure H_2O, followed by 322.0 mg of BBzx (2.4 mmol). The benzoxaborolate anions were then precipitated by progressive addition of 1.5 mL of an aqueous solution of $CaCl_2$ (0.8 mol.L^{-1} solution, 1.2 mmol, 0.5 eq). The mixture was stirred for 1 hour at room temperature, during which the progressive formation of a white precipitate was observed. The suspension was filtered and then washed twice with 3 mL H_2O and twice with 3 mL Et_2O. The white powder was then dried for 48 h at 60°C (m = 99 mg, η = 22%). Elemental analysis calculated (%) for $Ca(C_7H_6BO(OH)_2)_2.2H_2O$: C 44.5, H 5.3, Ca 10.6, B 5.7; found: C 45.0, H 5.2, Ca 10.5, B 5.6.

CaBBzx.2H_2O could also be synthesized using a 1/1 H_2O/EtOH mixture instead of H_2O only. In this case, in a typical synthesis, 96.2 mg (2.4 mmol) of NaOH microbeads were dissolved in 7 mL of an H_2O/EtOH 1/1 mixture, before adding 321.5 mg of BBzx (2.4 mmol). Once the benzoxaborole dissolved, 1.5 mL of an aqueous solution of $CaCl_2$ (0.8 mol.L^{-1} solution, 1.2 mmol) were added drop by drop, leading to the immediate formation of a white precipitate. The suspension was stirred for 30 minutes at room temperature, and then filtered under vacuum on a fritted glass filter glass-frit. The precipitate was washed twice with 5 mL of the EtOH/H_2O mixture and twice with 5 mL of Et_2O. The white powder was then dried at 40 °C for 28 h (m = 298 mg, η = 66%). Elemental analysis calculated (%) for $Ca(C_7H_6BO(OH)_2)_2.2H_2O$: C 44.5, H 5.3, Ca 10.6, B 5.7; found: C 43.2, H 4.9, Ca 11.4, B 5.6.

Figure S2. SEM, XRD, IR and ^{11}B solid state NMR characterizations of CaBBzx.2H_2O.

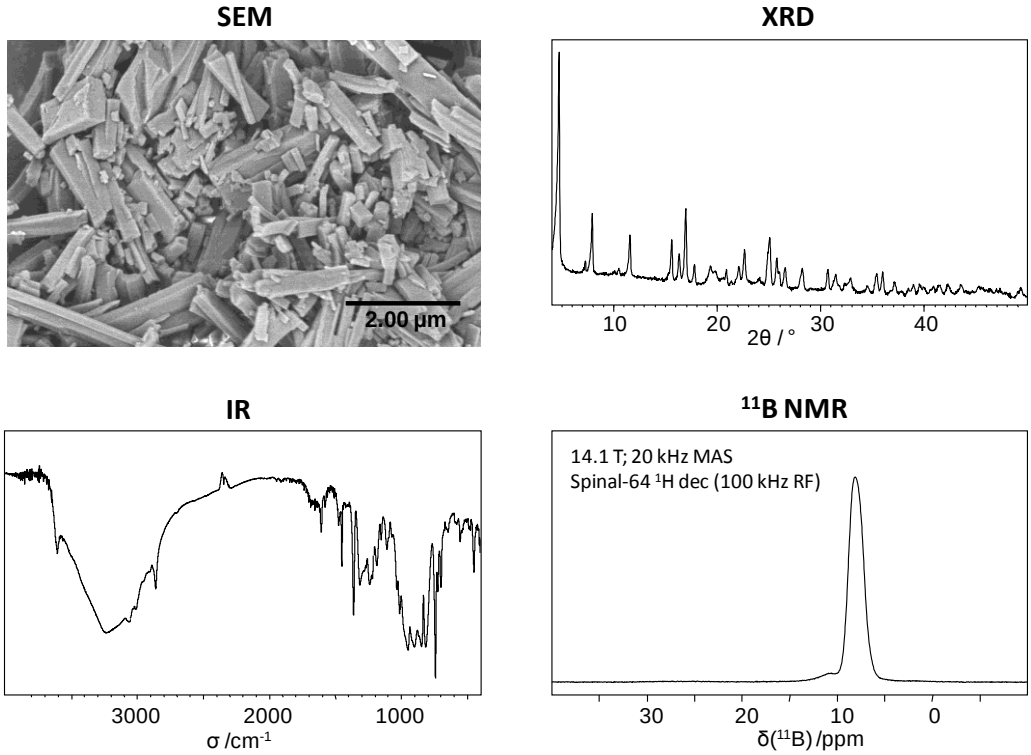
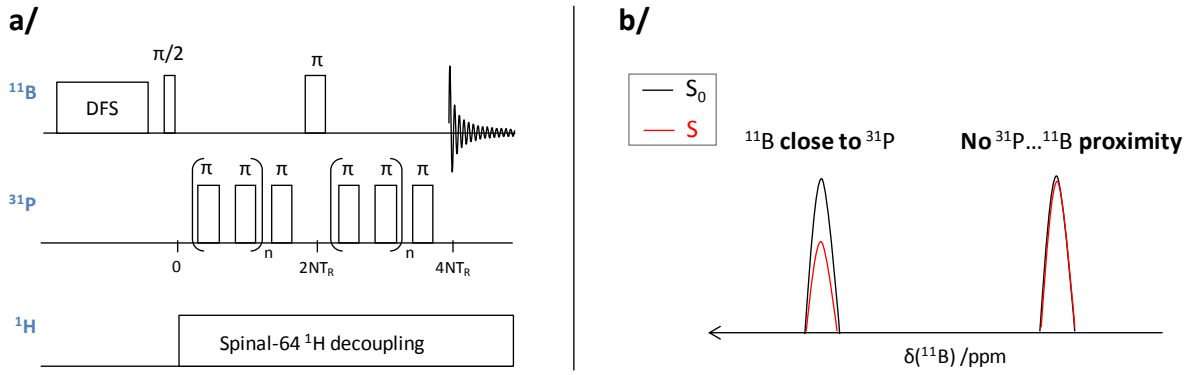


Figure S3. Schematic representation of the $^{11}B\{^{31}P\}$ DFS-REDOR NMR sequence used (a), and how the comparison of spectra acquired with (S) and without (S_0) the ^{31}P π pulses allows probing ^{11}B-^{31}P proximities (b).



The $^{11}B\{^{31}P\}$ REDOR NMR pulse sequence allows the study of ^{11}B-^{31}P through space proximities. With $^{11}B\{^{31}P\}$ REDOR, two ^{11}B NMR spectra are acquired and compared: one corresponds to a normal "spin echo" ^{11}B NMR spectrum (S_0), while the other has additional ^{31}P recoupling π pulses (S). The series of rotor-synchronized π pulses on ^{31}P allows reintroducing dipolar coupling to nearby boron atoms, causing them to "dephase" and their signal to decrease in intensity. By comparison of spectra acquired with and without the ^{31}P recoupling pulses, identification of ^{11}B-^{31}P proximities is possible.

Figure S4. Grafting of BBzx onto HA_{ceram}: kinetics (a) and isotherm (T = 22°C) (b).

For the grafting kinetics, the study was performed using a concentration of ~17 mmol.L^{-1} of BBzx in solution. For the isotherm, the grafting time was set to 6 h for each point. Error bars correspond to standard deviations over 2 to 5 independent repetitions of each experiment.

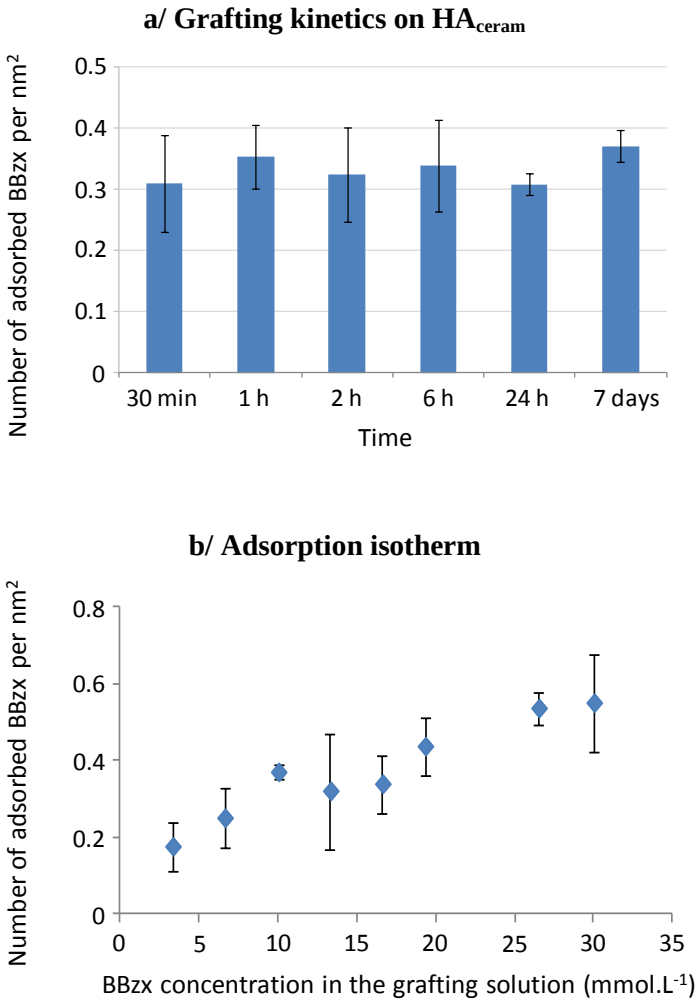
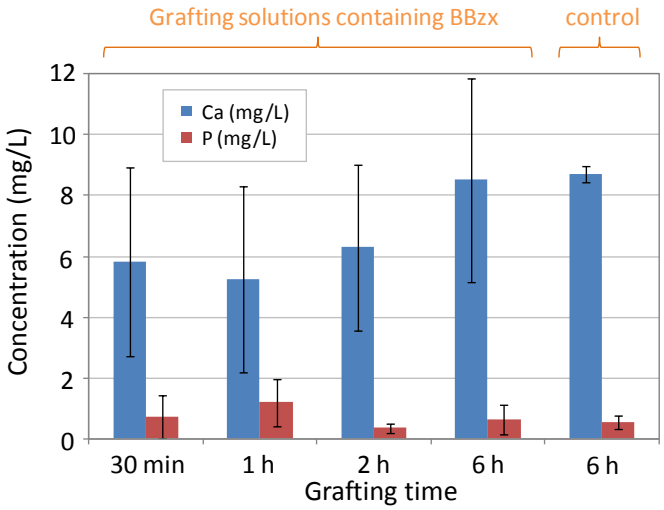


Figure S5. Variations in Ca and P supernatant concentrations as a function of grafting time (a) and BBzx concentration in solution (b).

The grafting was performed using a concentration of ~17 mmol.L^{-1} of BBzx in solution, and a reaction time of 6 hours. Error bars correspond to standard deviations over 2 to 5 independent repetitions of each experiment.

a/



b/

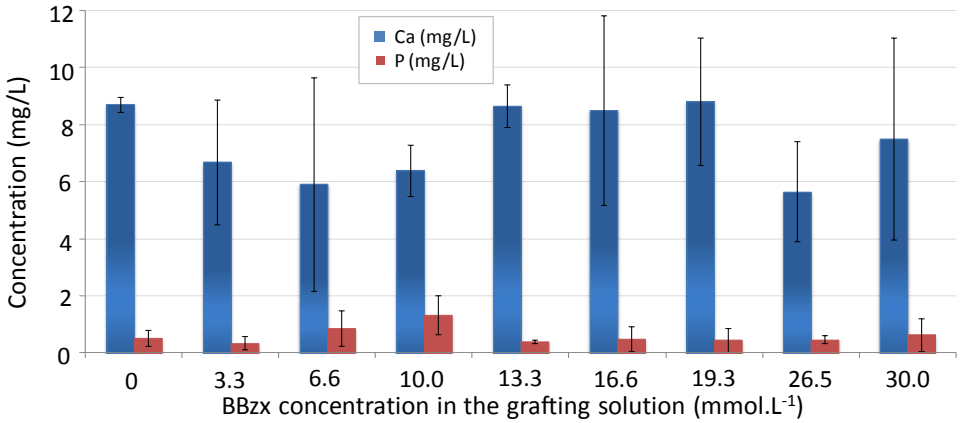


Figure S6. Kinetics of grafting of benzoate (PhC) and phenylphosphate (PhP) onto HA_{ceram}. Grafting densities were determined here by integration of ^{1}H solid state NMR spectra.

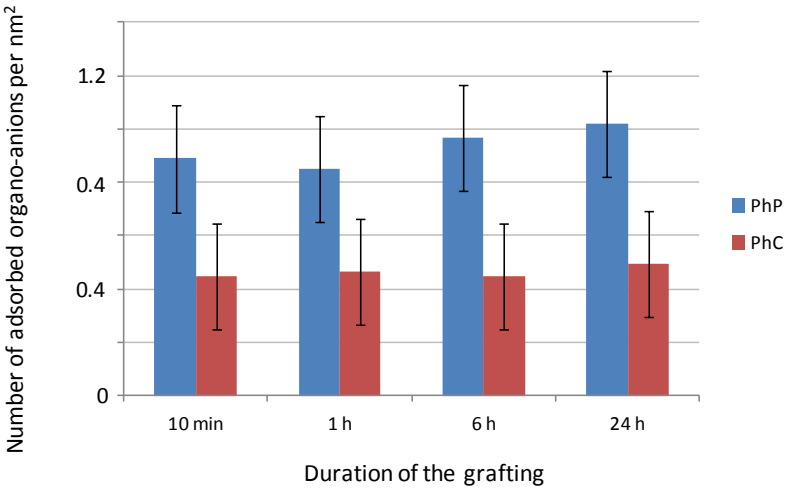


Figure S7. XRD powder patterns of bis-pipe-BBzx grafted HA_{ceram} (a) and of an HA phase grafted "*in situ*" (during precipitation) by bis-pipe-BBzx (b).

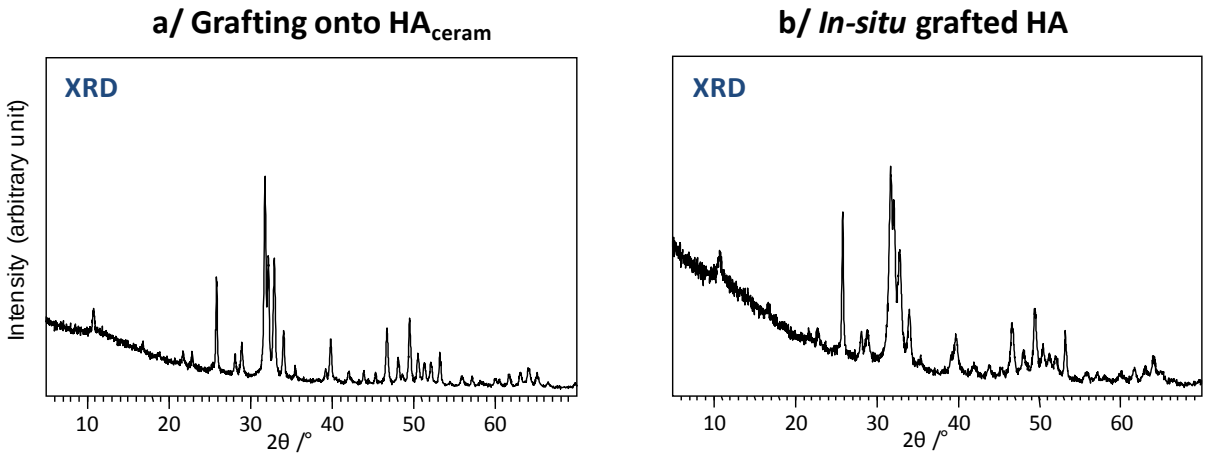


Figure S8. ^{11}B MAS NMR of a material obtained by "*in-situ*" grafting of BBzx on HA, in comparison to a borate-grafted HA phase prepared under similar conditions.

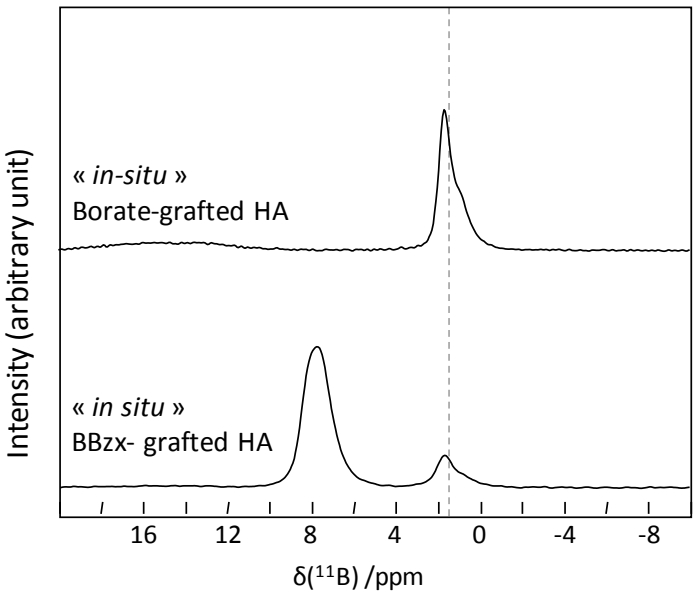


Figure S9. ^{11}B MAS NMR of a BBzx-grafted HA_{ceram} phase, after 36 months of storage at room temperature. A new resonance starts to appear at low frequencies, which could correspond to borates.