

## **Electronic Supplementary Information**

Herein are presented in details the experimental procedures and the characterization tools. Figures S1 to S5 are also shown.

## Experimental

All the preparations were carried out in a purified argon atmosphere passing through successive columns of BTS-catalyst and phosphorus pentoxide by means of standard Schlenk manipulations and vacuum/argon-line techniques. The samples were handled in an argon-filled glove box (MBraun MB200B) where the O<sub>2</sub> and H<sub>2</sub>O concentrations were kept at < 0.1 ppm.

The operating procedure to synthesize borazine from AB has been adapted from the literature.<sup>18c</sup> In a typical reaction, a 1 L vacuum solid-addition funnel and a reflux condenser were connected to a 2 L three-neck round-bottomed flask. One of the necks was connected to the argon-vacuum line and all the system was evacuated and then refilled with argon. 15.2 g (493.7 mol) of ammonia borane were introduced in the solid-addition funnel whereas 600 mL of tetraglyme were introduced in the flask. The exit of the reflux condenser was connected to a standard vacuum line equipped with three liquid nitrogen traps. Under vigorous stirring, the reaction mixture was carefully heated under controlled vacuum to 160 °C and the borazine was continuously removed as it is formed and recovered through a series of three traps which were put in liquid nitrogen at the exit of the reflux condenser. A hold time of 2h30 was maintained at 160 °C to achieve the reaction. Borazine was distilled under reduced pressure by trap-to-trap and the colorless liquid retained in the last trap was in final transferred under reduced pressure toward a Schlenk which was placed in liquid nitrogen. 8.35g of borazine (103.68 mol, 63 % rel. to B) was recovered without further purification. It should be mentioned that elemental analysis cannot be performed due to the poor thermal stability of borazine at RT.

IR (CsI windows/cm<sup>-1</sup>):  $\nu(\text{N-H}) = 3451 \text{ m}$ ;  $\nu(\text{B-H}) = 2509 \text{ m}$ ; ;  $\nu(\text{B-N}) = 1454 \text{ s}$ ;  $\delta(\text{B-N-B}) = 897 \text{ m}$ .  
<sup>1</sup>H NMR (300 MHz/CDCl<sub>3</sub>/ppm):  $\delta = 3.6\text{-}5.8$  (quadruplet, 3H, BH), 5.3-5.9 (triplet, 3H, NH). <sup>11</sup>B NMR (96.29 MHz/C<sub>6</sub>D<sub>6</sub>/ppm):  $\delta = 30.1$  (br).

The spray-pyrolysis process has been described in details in previous papers published by our groups.<sup>19</sup> The experimental set-up is composed of a nebulized spray generator (RBI, Meylan, France), in which the spray is generated by a piezoelectric device (barium titanate). Frequency (800 kHz) and power (100 W) alimentations are adjusted to obtain the aerosol. The aerosol temperature is first held at 15 °C by a regulated water circulation to avoid borazine evaporation and/or condensation. The piezoelectric device generates an ultrasound beam that is directed to the liquid-gas interface; a fountain forms at the surface followed by the generation of the spray resulting from vibrations at the liquid surface and cavitations at the gas-liquid interface. The borazine is directly introduced in the aerosol generating chamber under nitrogen, then aerosolized and carried to the pyrolysis furnace with a 0.5 mL min<sup>-1</sup> nitrogen flow rate. The thermal decomposition of borazine is performed in a hot alumina tube containing an isothermal zone of 0.1 m in length. The fast heating rate implies gaseous species generation leading to powder formation by a chemical vapour condensation route. The

particles are finally trapped into two collectors placed before the vacuum pump and containing filter-barriers made of microporous alumina (pore size of 1  $\mu\text{m}$ ). The yield was estimated to be 0.22 g  $\text{min}^{-1}$ . After their synthesis, the powders are stored inside an argon-filled glove-box. In a typical experiment, 27 mL (21.9 g) of borazine are used to produce 6.5 g of white color powders.

Anal. Found ( $\text{wt}\%$ ): H < 0.3; B, 44.4; N, 54.7; O, 0.8.

2 g of the BN nanopowders are placed into boron nitride boats, and then introduced in a graphite furnace (Gero 5 Model HTK 8). The furnace chamber is subsequently suctioned with a pump charged with nitrogen before heating. A cycle of ramping at 10  $^{\circ}\text{C min}^{-1}$  is used to heat the sample at 2000  $^{\circ}\text{C}$  with a holding time of 1 h, before cooling down to RT at 10 $^{\circ}\text{C min}^{-1}$ ; then, a flow (200 mL  $\text{min}^{-1}$ ) of nitrogen is passed through the furnace.

Anal. Found ( $\text{wt}\%$ ): B, 50.0; N, 49.4; O, 0.6.

The BN nanopolyhedrons are used in two different states: as it is (**1**) and after ball-milling (denoted as **2**). The milling process of **1** is performed under inert condition (argon) with a planetary ball-miller (Retsch PM100). The process described has been optimized (in terms of mass, ratio balls/BN, time, rotation) to our conditions. Typically, degassed **1** (at 150  $^{\circ}\text{C}$  under dynamic vacuum for 24 h) is introduced into a stainless steel reactor (25 mL). Balls in stainless steel are added (weight ratio balls:**1** of 20). The milling process is done at 600 rpm for 1 h. The as-obtained material **2** is finally sieved.

The infiltration of ammoniaborane is performed as follows. The host material **1** or **2** (100 mg) is degassed at 150  $^{\circ}\text{C}$  under dynamic vacuum for 24 h in a Schlenk tube, and then cooled to 0  $^{\circ}\text{C}$ . In an argon-filled glove box, a concentrated solution of ammoniaborane (100 mg; Sigma Aldrich, 97 %) is prepared using 0.5 mL of anhydrous THF (Sigma Aldrich). The ammoniaborane solution is injected into the Schlenk tube containing **1** or **2** kept under static vacuum and at 0  $^{\circ}\text{C}$ . By capillary action, the ammoniaborane solution fills rapidly the channels of the host, which is evidenced by vigorous effervescence. When the effervescence stops, the sample is put under ultrasonic treatment for 20 min at 0  $^{\circ}\text{C}$ . Finally, the as-obtained sample **1@AB** or **2@AB** (weight ratio **1**:AB or **2**:AB of 1) is dried under dynamic vacuum for 48 h at 0  $^{\circ}\text{C}$ . The composite samples obtained are denoted **1@AB** and **2@AB**. Both samples are transferred in an argon-filled vial and then stored in a fridge at 3-4  $^{\circ}\text{C}$ .

## Characterizations

The Transmission Electron Microscopy (TEM) studies (electron diffraction patterns and images) were carried out with a JEOL 2010F transmission electron microscope ( $C_s = 1 \text{ mm}$ ) operating at 200kV. The SAED patterns were recorded with a camera length of 800mm. For the TEM characterization, a small piece of sample was crushed in an agate mortar containing ethanol and a droplet was deposited on a copper grid covered with holey carbon film.

The characterization of the samples was performed by  $N_2$  adsorption/desorption (Sorptomatique 1990 Series), powder X-ray diffraction (Bruker D5005 powder diffractometer,  $CuK\alpha$  radiation,  $\lambda = 1.5406 \text{ \AA}$ , the sample was protected from air and moisture by using a Kapton® film), and diffuse reflectance Fourier transform infrared spectroscopy (FTIR Nicolet 380).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements (done at least thrice to ensure results reproducibility) were performed with TGA/SDTA 851e and DSC1 (Mettler Toledo) under the following conditions: sample mass 9-10 mg, aluminium crucible of 100  $\mu\text{l}$  with a pinhole, heating rate of  $5 \text{ }^\circ\text{C min}^{-1}$ , temperature range 25-200  $^\circ\text{C}$ , and atmosphere of  $N_2$  ( $60 \text{ ml min}^{-1}$ ). Both instruments were calibrated in the studied range of temperature. The melting points and melting enthalpies of three standards (gallium, naphthalene and indium) were used for the calibration of the DSC in terms of heat flow and temperature. Concerning the TGA, the melting points of four compounds (phenyl salicylate, naphthalene, benzoic acid and indium) obtained from the DTA signals were used for the sample temperature calibration. The purity of  $H_2$  was analysed by mass spectrometry (Anelva, MQA200TS) coupled to the TGA apparatus.

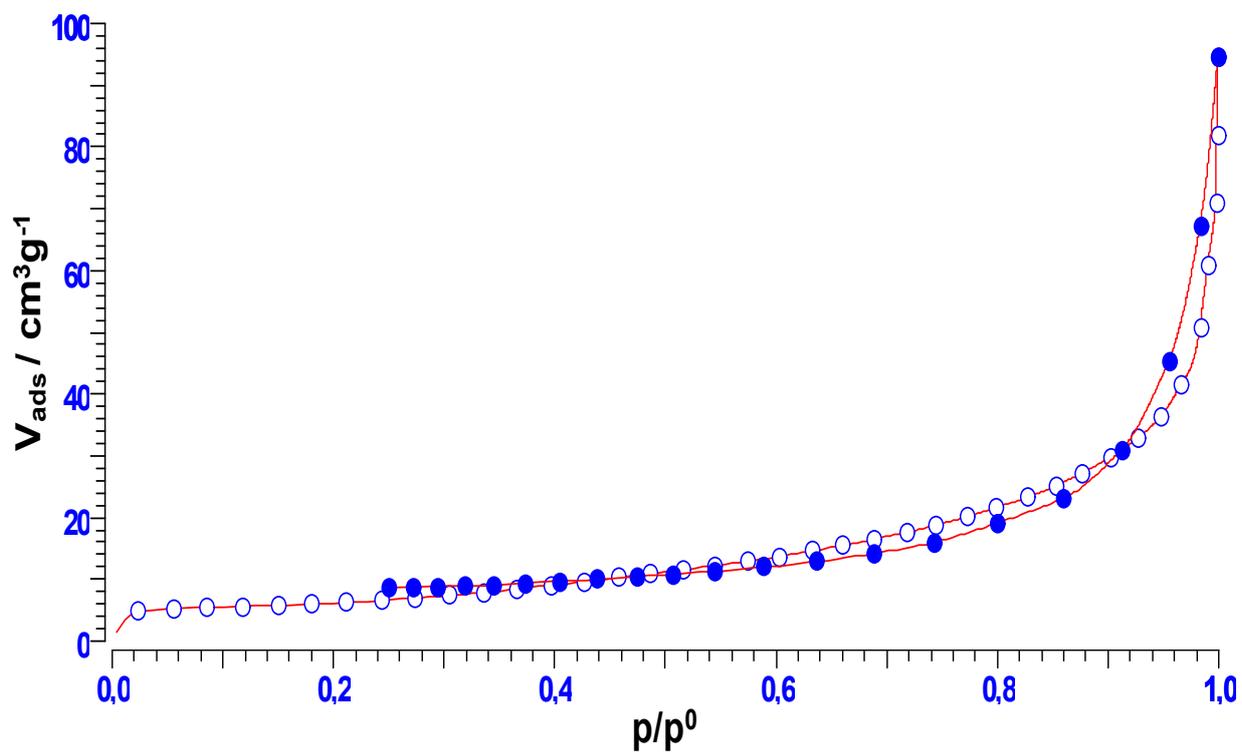
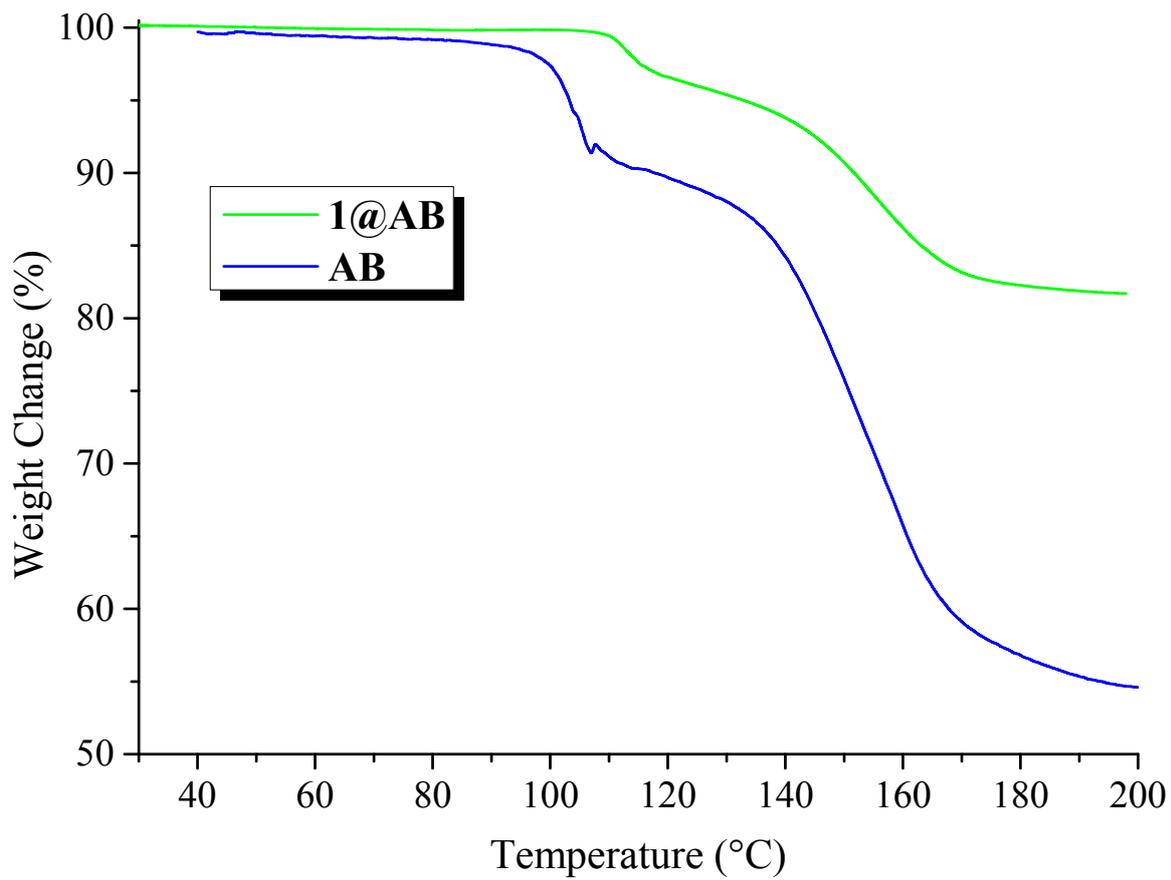


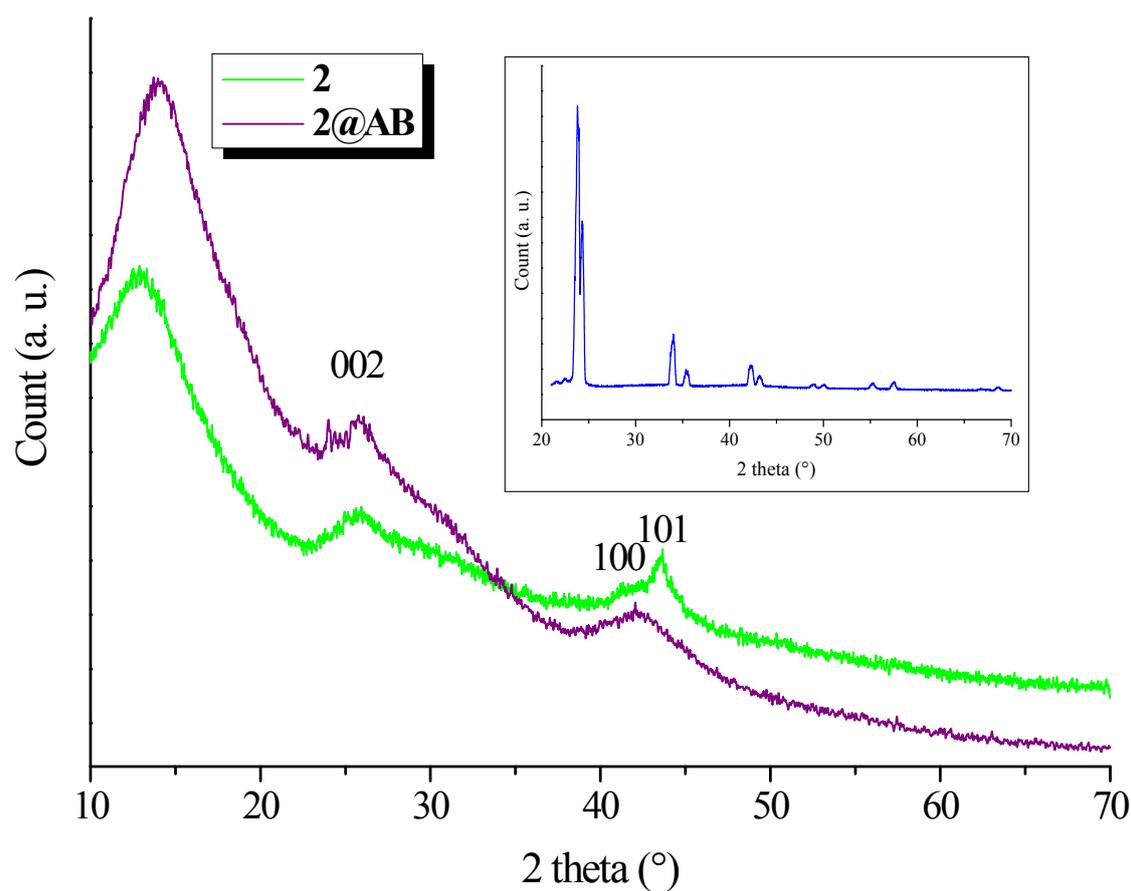
Fig. S1.  $\text{N}_2$  adsorption-desorption isotherm of **1** recorded at  $-196$  °C.



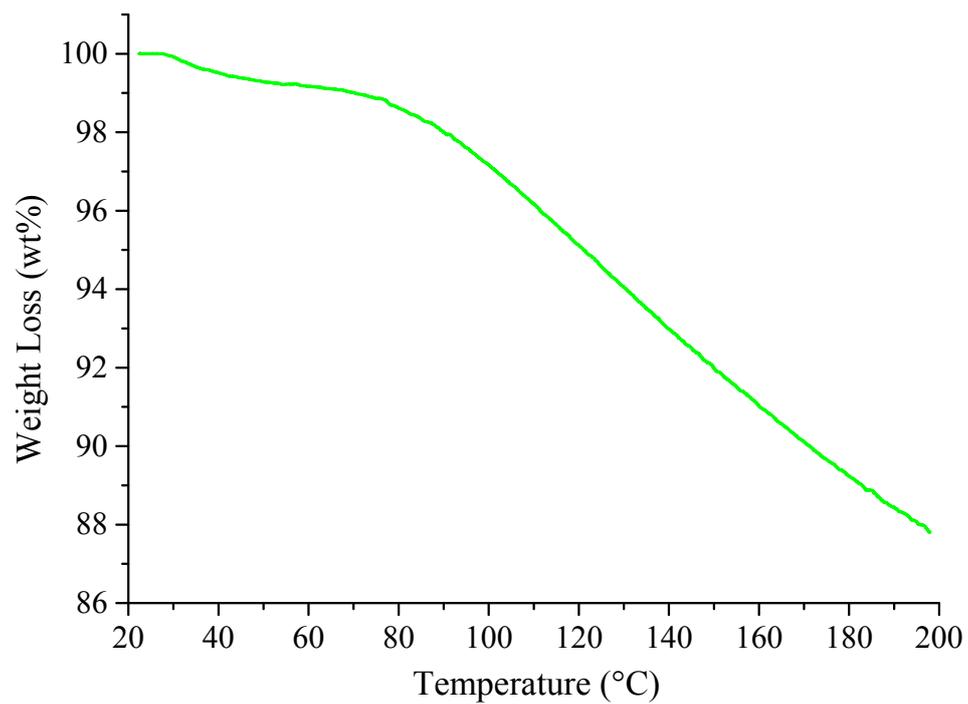
**Fig. S2.** TGA results for **1@AB** and **AB** ( $N_2$ , heating rate  $5\text{ }^\circ\text{C min}^{-1}$ ).



**Fig. S3.** Dispersion of 1 (a), 2 (b) and 5 (c) wt% of 2 in 2 mL of THF with after 168 h.



**Fig. S4.** Powder XRD patterns of 2 and 2@AB (and corresponding XRD of AB in insert) The peak positions and the relative intensities were characterized by comparison with JCPDS files of the standard material (JCPDS card No 34-0421).



**Fig. S5.** TGA results for **2@AB** after its regeneration ( $N_2$ , heating rate  $5\text{ }^\circ\text{C min}^{-1}$ ).