

# Supporting Information

## Host – Guest Chemistry in Boron Nitride Nanotubes:

### Interactions with Polyoxometalates and Mechanism of Encapsulation

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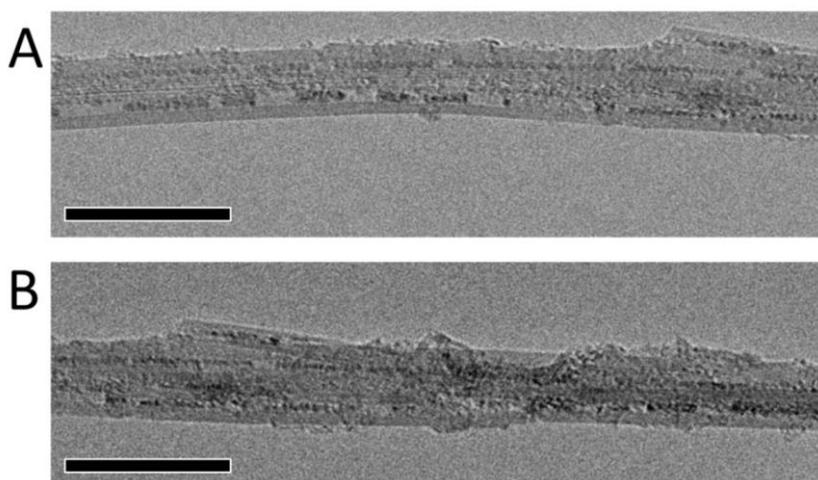
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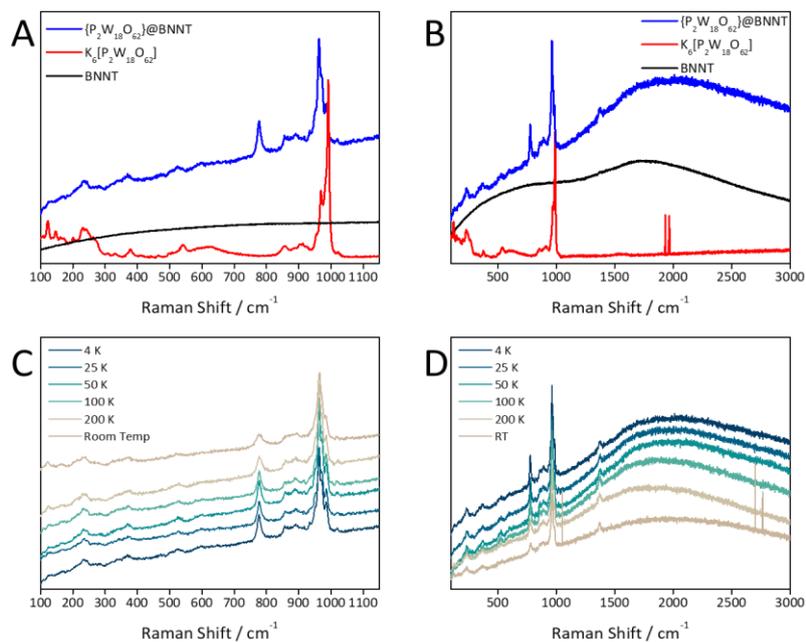
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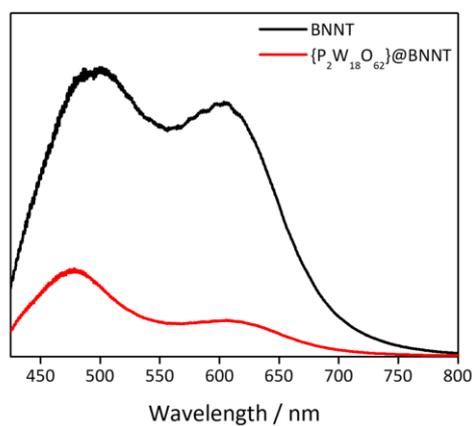
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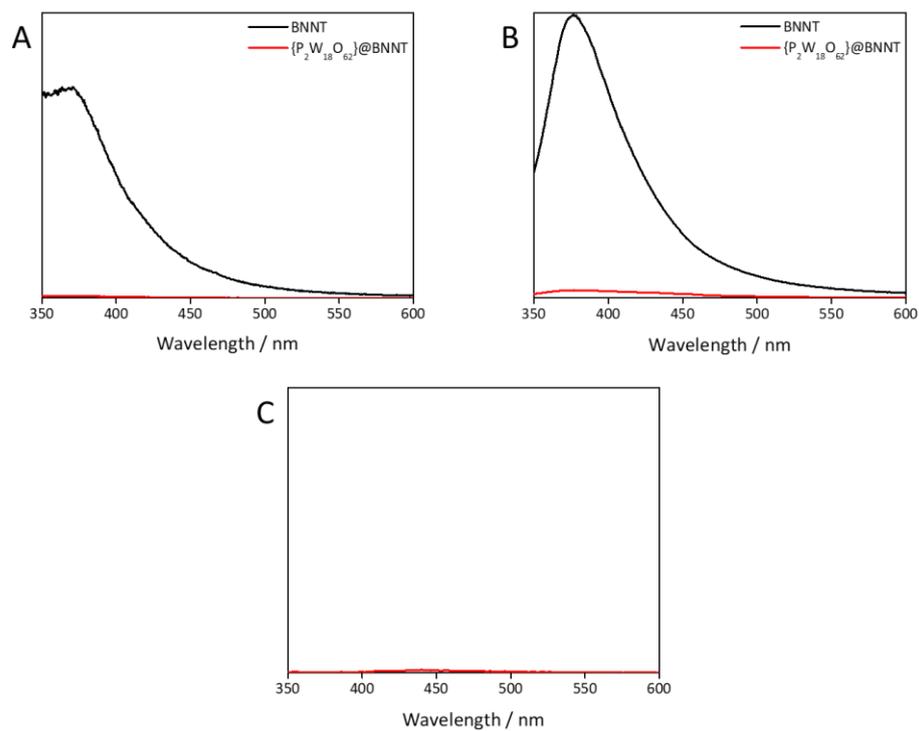
**Figure S1.** TEM images of POM@BNNT after (a) brief electron beam irradiation and (b) 30s electron beam irradiation. Images acquired at 80 kV. Scale bars are 20 nm.



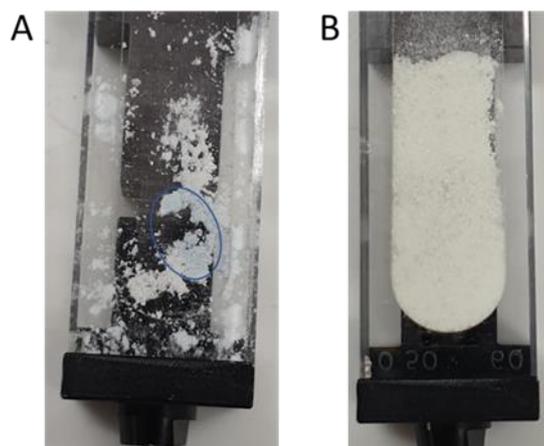
**Figure S2.** Raman spectra of BNNTs,  $K_6[P_2W_{18}O_{62}]$  and  $\{P_2W_{18}O_{62}\}@BNNT$  at 4 K (A & B). Variable temperature Raman spectra of  $\{P_2W_{18}O_{62}\}@BNNT$  (C & D). Acquired with an excitation wavelength of 532 nm. Spikes in the spectra are cosmic interference. Intensities across the spectra are not comparable.



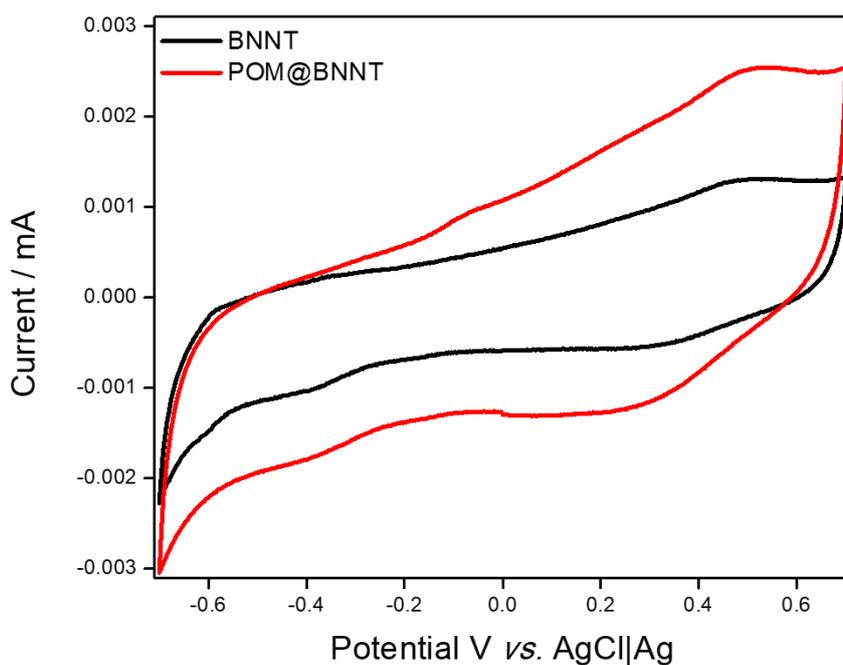
**Figure S3.** 405 nm PL spectra.



**Figure S4.** PL spectra of BNNTs and  $\{P_2W_{18}O_{62}\}@BNNT$  using excitation wavelengths of 250 nm (A) and 275 nm (B). (C) shows POM PL spectra using an excitation wavelength of 275 nm.



**Figure S5.**  $\{P_2W_{18}O_{62}\}@BNNT$  (A) and  $K_6[P_2W_{18}O_{62}]$  (B) materials after PL spectroscopy measurements. Blue colouration (corresponding to the illumination spot) is visible in the  $\{P_2W_{18}O_{62}\}@BNNT$  material (blue circle).



**Figure S6.** Cyclic voltammograms of thin films of BNNT (black trace) and POM@BNNT (red trace) recorded in 1M  $H_2SO_4$  at a scan rate of  $100 \text{ mV s}^{-1}$  with a glassy carbon working electrode (film deposited from 10 mg/mL DMF suspension) AgCl|Cl reference electrode and platinum counter electrode. No faradaic current from the encapsulated POMs was observed, likely due to the insulating nature of the BNNTs.