

## Supporting information

### Probing dynamic covalent chemistry in a 2D boroxine framework by *in-situ* near-ambient pressure X-ray photoelectron spectroscopy

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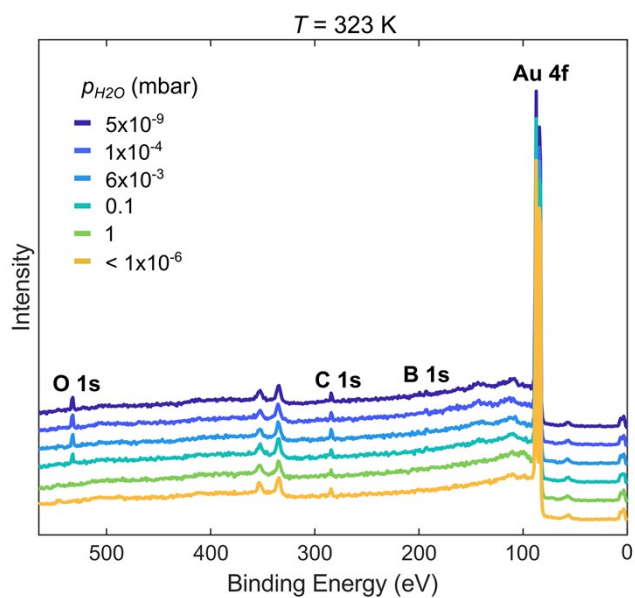
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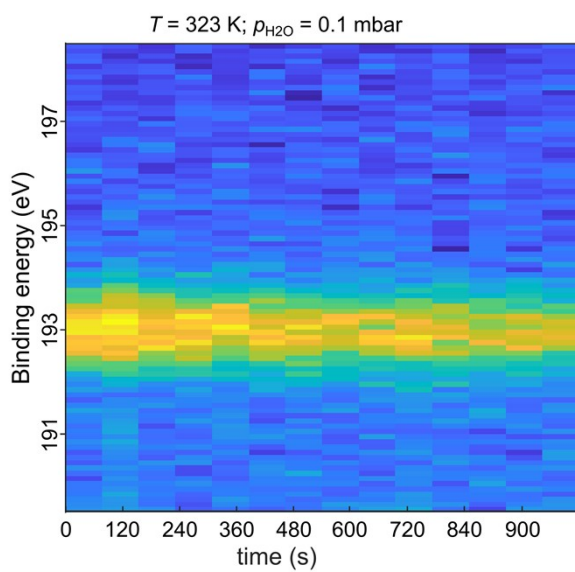
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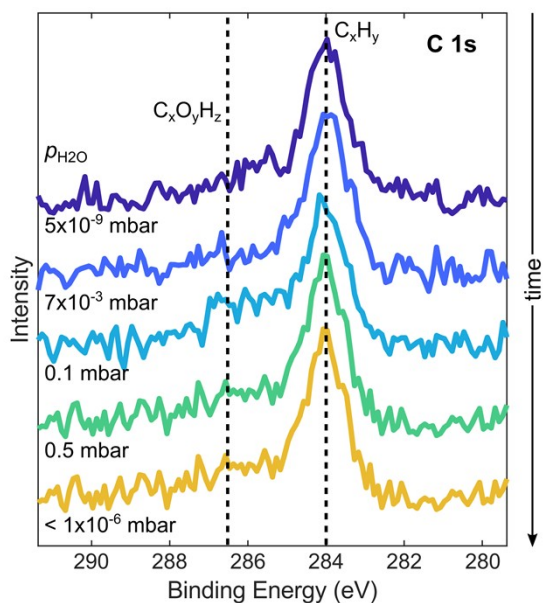
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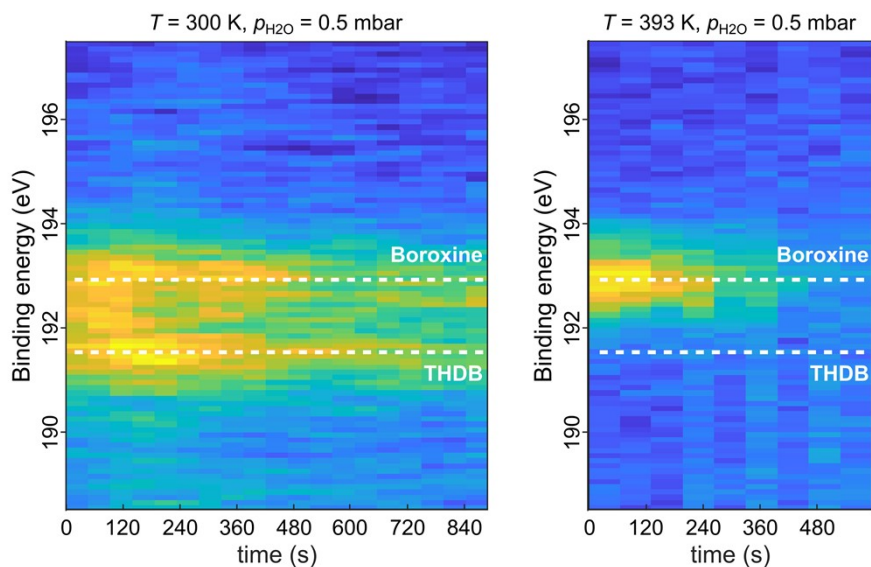
**Fig. S11.** Survey spectra acquired at  $T = 323 \text{ K}$  upon sequential increase of  $p_{\text{H}_2\text{O}}$  and after cell evacuation. Photon energy: 650 eV.



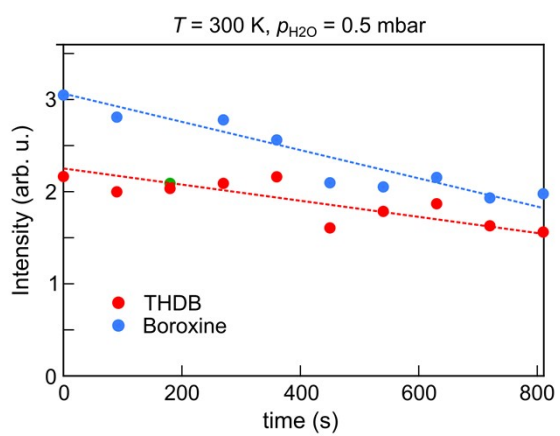
**Fig. S12.** Time-resolved B 1s spectra acquired at  $T = 323 \text{ K}$  and  $p_{\text{H}_2\text{O}} = 0.1 \text{ mbar}$ . Photon energy: 650 eV.



**Fig. S13.** Carbon-containing contaminations at NAP. C 1s spectra acquired at  $T = 300$  K upon sequential increase of  $p_{\text{H}_2\text{O}}$  and after cell evacuation. Photon energy: 650 eV. The intensity of hydrocarbon species ( $\text{C}_x\text{H}_y$ , 284.0 eV) is rather constant. Oxygen-containing carbon species ( $\text{C}_x\text{O}_y\text{H}_z$ ) are detected at 0.1 mbar at 286.5 eV, while their intensity diminish at 0.5 mbar.



**Fig. S14.** *In-situ* NAP-XPS characterization at  $p_{\text{H}_2\text{O}} = 0.5$  mbar. Time-resolved B 1s spectra acquired at  $T = 300$  K (left) and  $T = 393$  K (right). Photon energy: 650 eV. The binding energies corresponding to boroxine and THDB are indicated.



**Fig. S15.** *In-situ* NAP-XPS characterization at  $p_{\text{H}_2\text{O}} = 0.5 \text{ mbar}$ . Plot of the time-resolved B 1s spectra components: THDB (red) and boroxine (blue), with dashed lines as a guide to the eye.