

### Supplementary Material

Cyclooctane. Monolayer and multilayer (absolute and difference) RAIR spectra of cyclooctane on Pt(111) are shown in supplementary Figure S1. The monolayer spectrum shown in the bottom half of the figure shows a broad region with bands appearing at 2881, 2898, 2913, 2932, and 2958  $\text{cm}^{-1}$ .<sup>1,2</sup> The broad feature seen between ~2600 and 2800  $\text{cm}^{-1}$  results from mode softening. The spectra of cyclooctane show bands more commonly expected for a polymethylene chain: major modes are seen at 2855 and 2925  $\text{cm}^{-1}$ , values consistent with assignments to  $\nu_s(\text{CH}_2)$  and  $\nu_a(\text{CH}_2)$  respectively.<sup>3</sup>

**Figure S1.** RAIR spectra of cyclooctane multilayer and monolayer on Pt(111). Lower panel shows absolute spectra for a monolayer and multilayer. Upper panel shows the multilayer difference spectra, showing only bands corresponding to multilayer species.

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(1) Hostetler, M. J.; Manner, W. L.; Nuzzo, R. G.; Girolami, G. S. *J. Chem. Phys.* **1995**, *99*, 15269-15278.

(2) Manner, W. L.; Dubois, L. H.; Girolami, G. S.; Nuzzo, R. G. *J. Phys. Chem. B* **1998**, *102*, 2391-2402.

(3) Snyder, R. G.; *J. Chem. Phys.* **1967**, *47*, 1316-1360.

Figure S1

