

# Supporting Information

Perry et al. 10.1073/pnas.1207600109

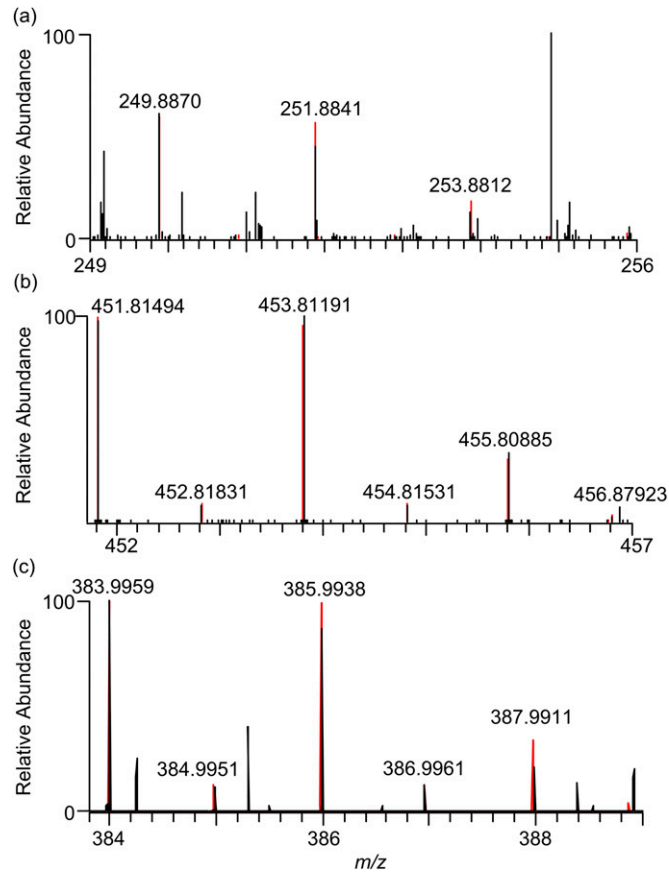


Fig. S1. Zoomed-in experimental (background is subtracted; black) and calculated (red) mass spectra showing (A)  $[2+Na]^+$ , (B)  $[4+Na]^+$ , and (C)  $[7+Na]^+$ .

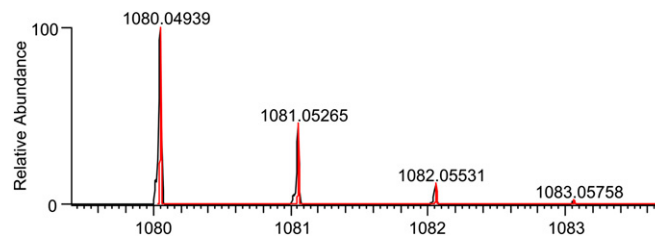
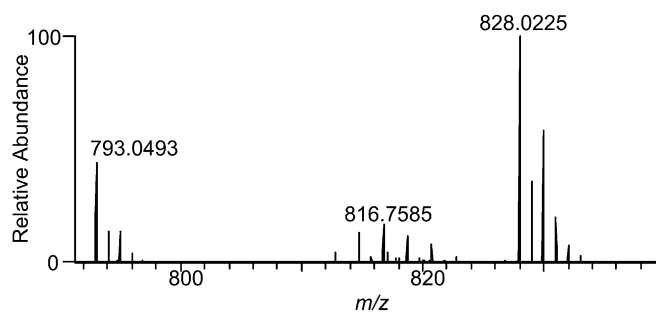


Fig. S2. Comparison of the experimental (black) and calculated (red) isotope distributions for  $[1\bullet 3]^+$ .

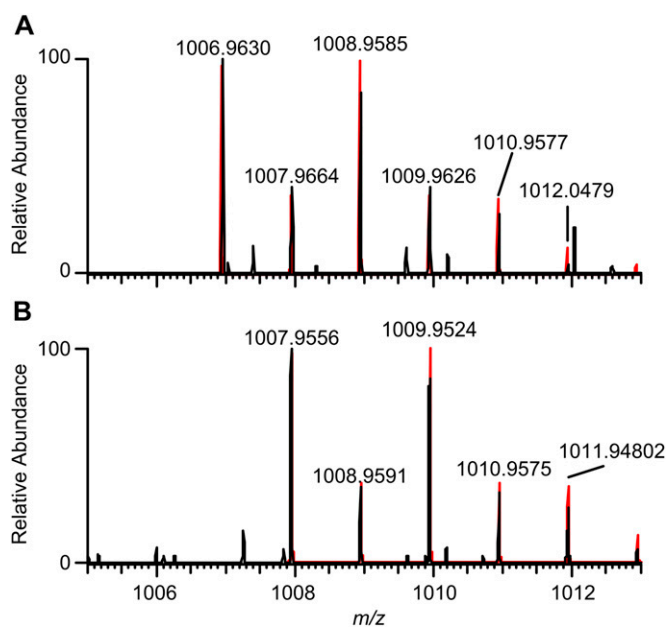








**Fig. S9.** Negative-mode DESI-MS spectra showing  $\text{Rh}^{2+}/\text{Rh}^{3+}$  species  $[\text{Rh}_2(\text{esp})_2\text{Cl}]^-$  at  $m/z$  793.0493 and  $[\text{Rh}_2(\text{esp})_2\text{Cl}_2]^-$  at  $m/z$  828.0225.



**Fig. S10.** Mass spectra of a bulk solution containing **1**, **2**, and **3** in  $\text{CH}_2\text{Cl}_2$  after several hours of reaction time. The spectra show experimental (black) and calculated (red) isotopic distributions for  $[\mathbf{8}+\text{Na}]^+$  using  $\text{Cl}_3\text{CCH}_2\text{OSO}_2^{14}\text{NH}_2$  (A) and  $\text{Cl}_3\text{CCH}_2\text{OSO}_2^{15}\text{NH}_2$  (B).