Supporting Information for:

Exchange Reactions between Alkanethiolates and Alkaneselenols on Au{111}

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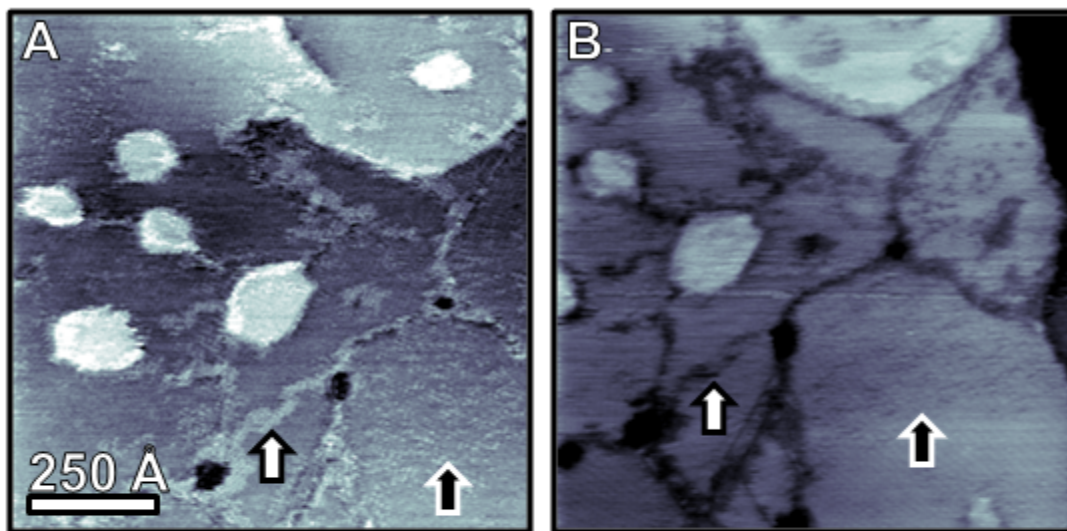
Supplemental Figure S1: Distribution of selenolate exchange and tip dependence of apparent height. A) Dodecaneselenolates inserted predominantly at decanethiolate SAM matrix defects appear protruding relative to the surrounding thiolates. In this example, insertion occurs at domain boundaries (white arrow), step edges, and within ordered domains, attributed to insertion at molecular vacancies (black arrow). B) A tip state change after continuous imaging resulted in inverted contrast for the two molecular species. Both insertion at domain boundaries and within the domain now appear less protruding than the surrounding decanethiolate matrix. Such tip state changes occur randomly, but are more common as SAM order declines and after repeated sample bias reversal experiments. It is important to attribute molecular identity carefully as such tip changes can give a false representation of molecular motion and SAM dynamics.
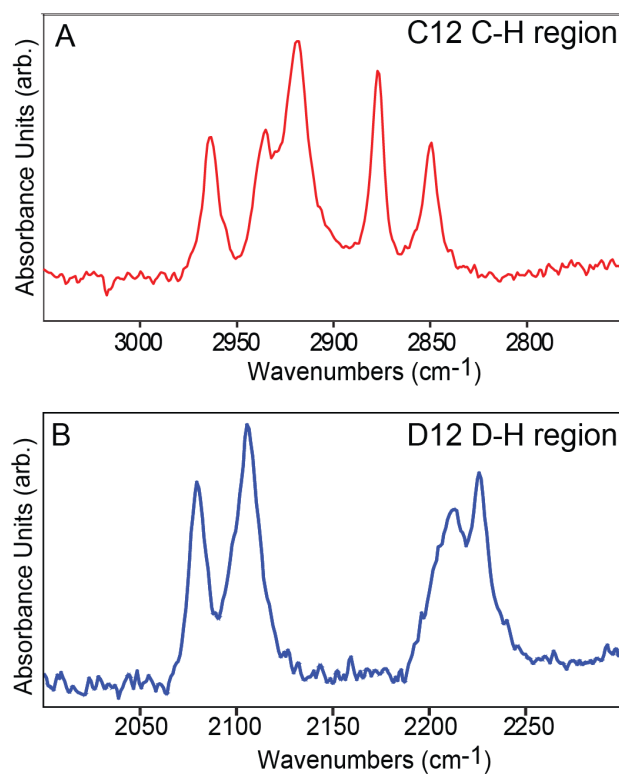
Figure S2: Carbon-hydrogen and carbon-deuterium stretches for 1-dodecanethiolate (C12, A) and perdeuterated 1-dodecanethiolate (D12, B) respectively.
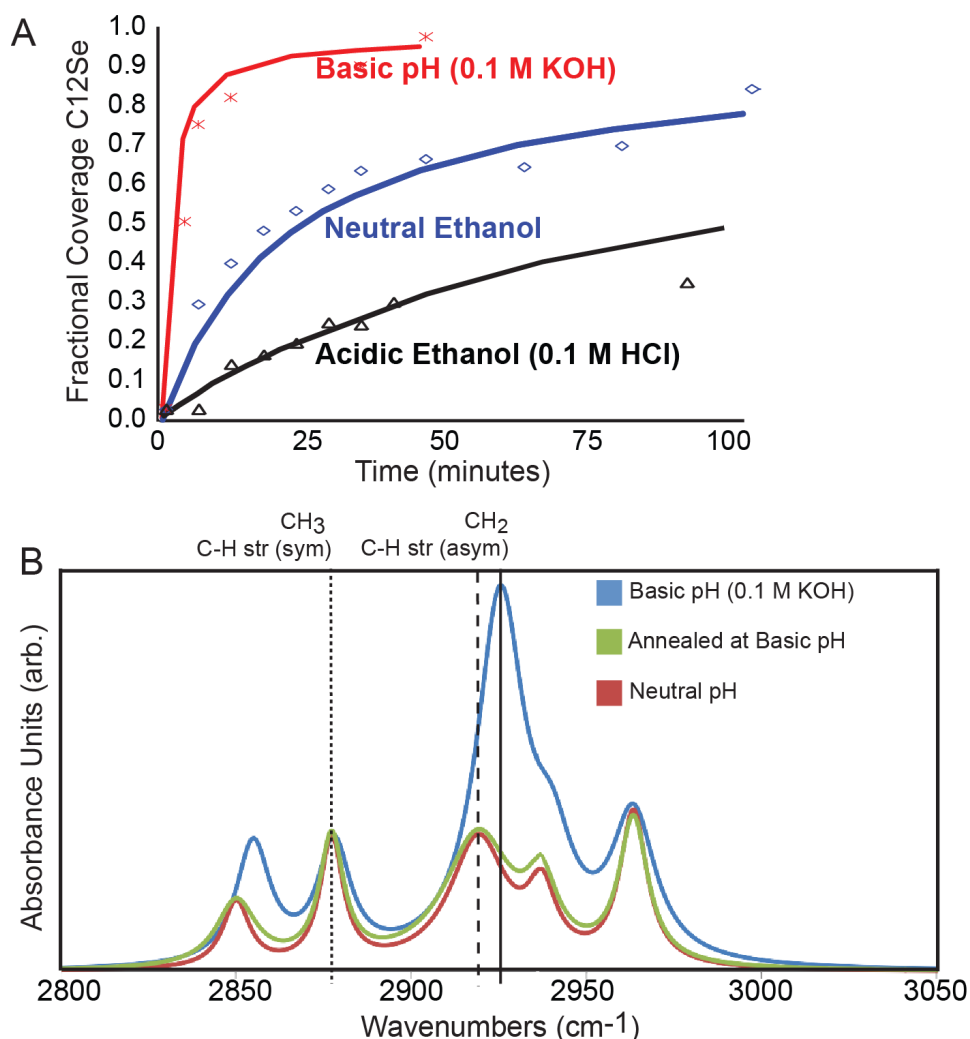
Figure S3: Effect of solution pH on perdeuterated 1-dodecanethiolate SAM exchange by 1-dodecaneselenol (C12Se) at 1 mM. A) Addition of aqueous KOH to 1 mM ethanolic C12Se markedly increases displacement rate, while similar addition of aqueous hydrochloric acid reduces the rate of exchange. B) Infrared reflectance spectra of the C-H region after 1 h base-catalyzed C12Se displacement (blue trace) compared to 24-h displacement at neutral pH. The methyl symmetric stretch at 2871 cm^{-1} have similar intensity, attributed to similar absolute coverage. Annealing in the basic solution for 24 h at elevated temperature results in a C12Se film largely indistinguishable from the neutral pH control sample. This is additional evidence that base-catalyzed exchange is disruptive to film structure but does not appreciably affect the underlying gold substrate.
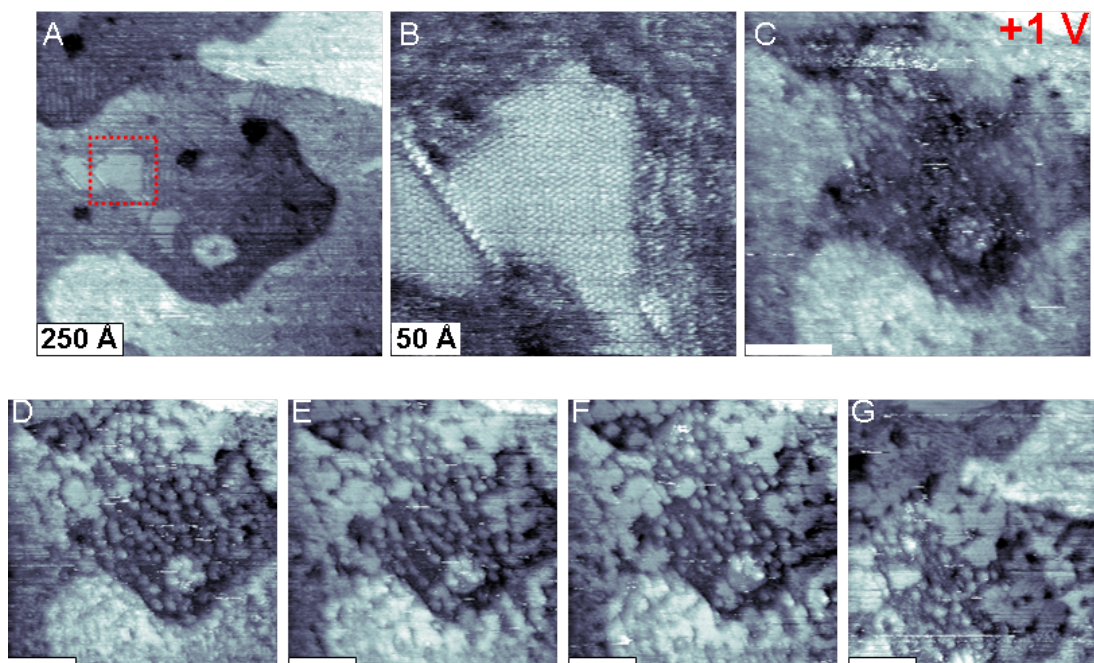
Figure S4: Imaging at positive bias at high relative 1-dodecaneselenol (C12Se) coverage (>25%) results in large-area reconfiguration of the monolayer structure. A) Islands of pristine 1-decanethiolate (C10) remaining after significant C12Se displacement, an example is enclosed in a red square. B) A high-resolution view of the C10 island in A. C) Imaging at +1 V sample bias results in a decrease in image resolution, consistent with molecular motion and place exchange between alkanethiolate and alkaneselenolate. D) Returning to -1 V sample bias reveals a scrambled interface. The discrete C10 islands and striped features have been replaced with a mottled structure. E-D) Continued imaging reveals motion and reconfiguration of the domains in the image. With the exception of C, images were collected at -1 V sample bias, and all images at 3 pA tunneling current. Images C-G shares the scale of image A.
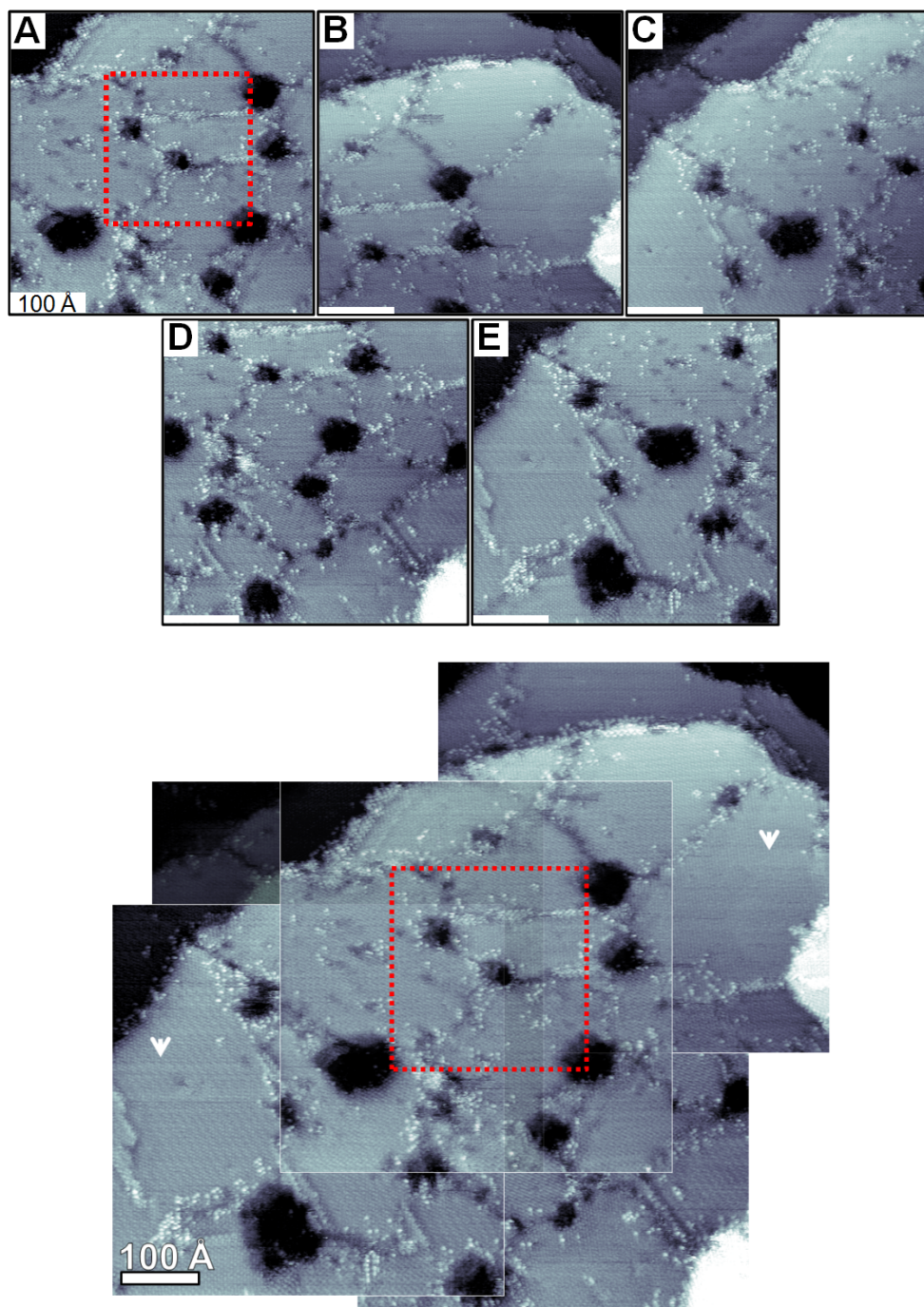
Figure S5: Images and aligned composite revealing the spatial distribution of molecules induced to move via tip-induced place-exchange reactions. A) The region highlighted by the red square at image center is the region scanned at +1 V sample bias for a full image acquisition time (~5 min). The protruding C12Se molecules are found in different positions after imaging at this potential. Domains in excess of 250 Å from the center of the imaged area are largely undisturbed by positive bias imaging, as indicated by the white arrows denoting pristine domains in the composite image (left and right).