Supporting Information:

S1. Fit parameters of the N 1s spectrum shown in Figure 9

Components	402.20 eV	400.53 eV	399.85 eV	398.60
attribution	Dative bond	Pendent head	Pendent head	Dissociated head
Spectral weight	84%	5%	5%	6%

Table S1: Fit parameters obtained from the curve presented in Figure 9. The Gaussian width of all the components is 0.98 eV.

S2. STM imaging under 4×10^{-9} mbar

Figure S1 shows the adsorption sequence of TMEDA under a pressure of 4×10^{-9} mbar. Some TMEDA molecules were already deposited on the silicon sample before dosing started (Figure S1(a)). After an exposure of 4 min only a few molecules are adsorbed on the Si surface (Figure S1(b)). We see molecules both in CT and EB geometries. After an exposure of 9 min (Figure 12(c)), we can note the presence of numerous nucleation centers formed by the "EB" molecules, usually three molecules, sitting parallel to one another on adjacent Si rows. The STM image shows one brighter and fuzzy blob, that is ascribed to TMEDA in a single-head adsorption geometry. After 13 min of dosing (Figure S1(d)) the molecule tend to aligns along the Si rows. After 18 min (Figure S1(e)) the surface coverage of TMEDA becomes significantly higher, with most molecules aligned along the Si rows. A significant change in the configuration of the

adsorbed TMEDA molecules is seen after 22 minutes of dosing (Figure S1(f)), as already described in the main paper (Section 3.2.1), i.e. all the molecules previously orientated along the rows now becomes longer and thinner. The transition point occurs at a surface coverage similar to that in Figure 6(e-f) of the main paper. In the last stage of exposure there are very few changes (Figure S1(g)), the surface saturation is reached after 32 min exposure (Figure S1(h)) exhibiting an increased number of fuzzy molecules (single-head anchored molecules).

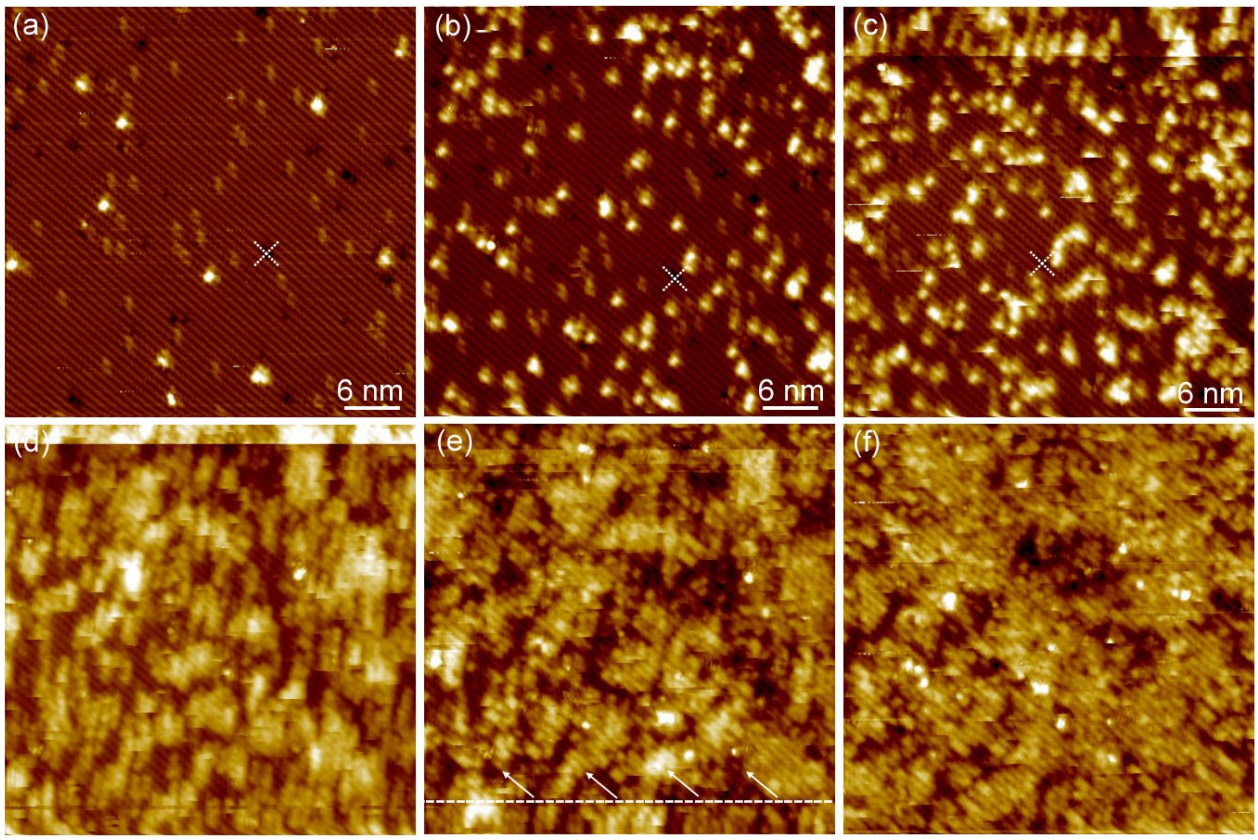

Figure S1. Consecutive STM images of Si(001) surface exposed to TMEDA at pressure $4\times s10^{-9}$ mbar for 32 min (7.2 L) . The time runs (not linearly) from the upper left to the lower right; the tip scanned from the bottom to the top of the image. (a) t = 0 min, (b) t = 4 min 30 sec, (c) t = 9 min 30 sec, (d) = 13 min 30 s, (e) t = 18min 37 s, (f) t = 22 min 55 sec, (g) t = 27 min 30 s and (h) t = 32 min 05 s. Images measured at 300 K, with V_b = -2.0 V and I = 0.1 nA, dimension

50nm × 50 nm. The dashed line in (g) indicates the brutal transition (Tp) from the original adsorption mode of TMEDA molecules towards the arrangement into molecular rows in the [110].