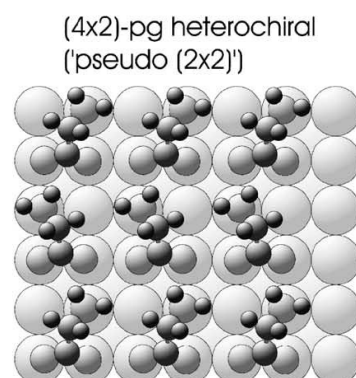
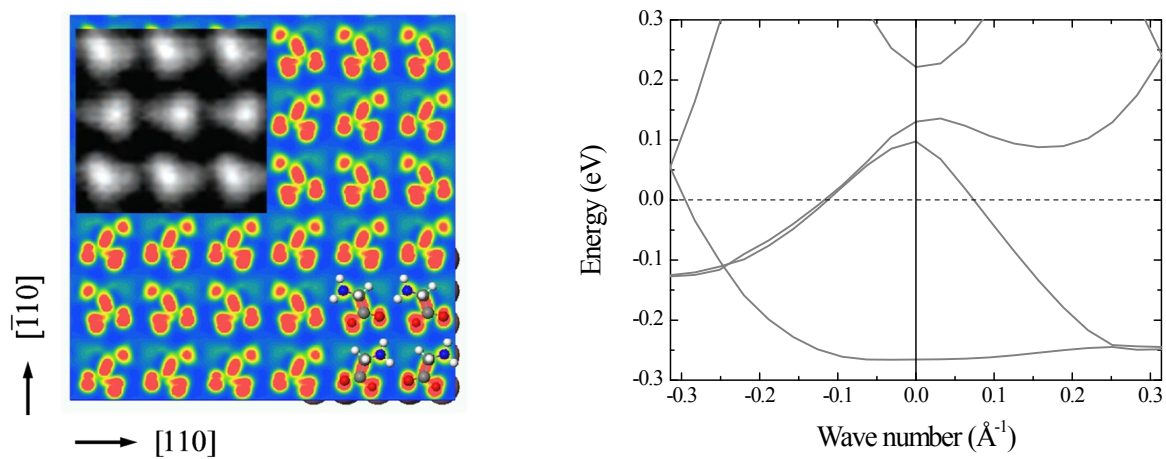


## SUPPLEMENTARY INFORMATION

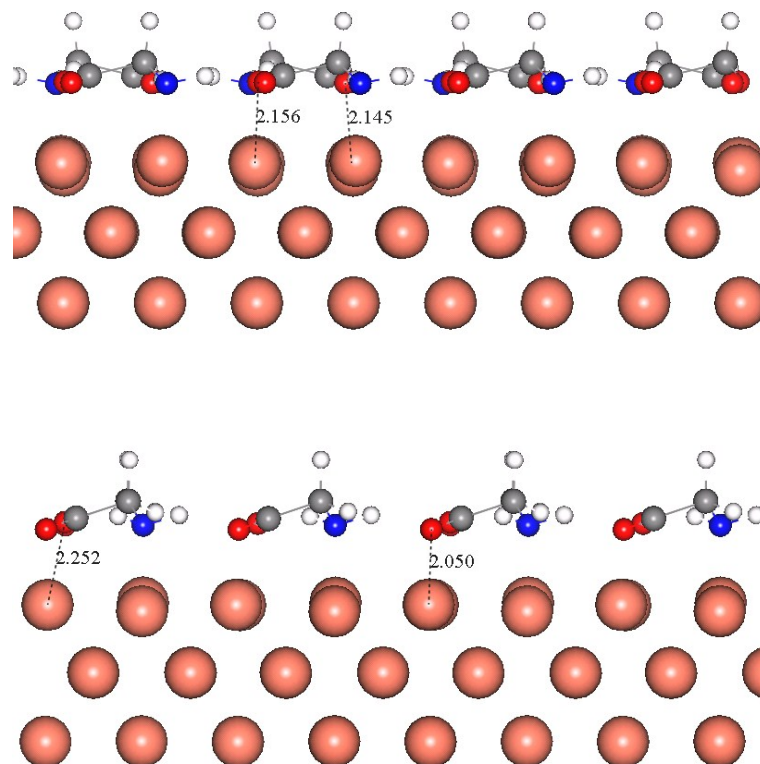
### “Self-Assembly of Glycine on Cu (001): the Tales of Temperature and Polarity”



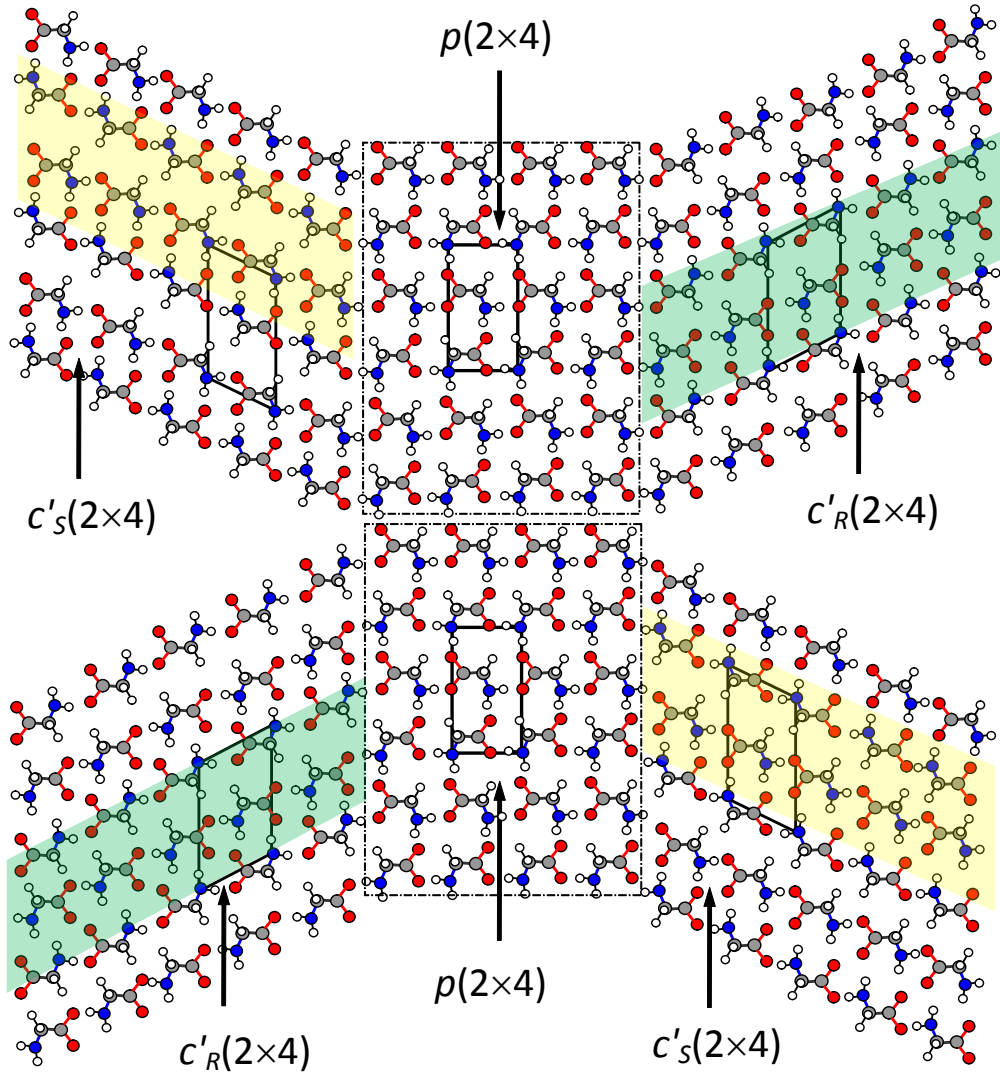
**Figure S1.** The head-to-tail  $p(2\times 4)$  structure adopted by Kanazawa *et al.* *J. Am. Chem. Soc.* **2007**, *129*, 740, proposed by Zhao *et al.* *Mater. Sci. Eng.* **2001**, *16*, 41, and Efstathiou *et al.* *Surf. Sci.* **2003**, *531*, 304. However, this model, only in the head-to-tail alignments, does not consider the influence of polarity to side neighbors, not mention to the HB network.



**Figure S2.** (Left) Simulated STM image for the structure adopted by Kanazawa *et al.* with experimental image shown in the inset, and (Right) corresponding electronic band structures, where no free-electron-like dispersions are found.



**Figure S3.** Comparison of the side view of our SA structures with the saturated glycinate molecules (upper panel) and the HT structures with unsaturated glycinate molecules (lower panel). As indicated in the main text, our free-standing SA structure has lower energy about 76 meV per molecule than the HT model. The glycinate molecule itself in our  $p(2\times 4)$  structure is *saturated* with H bonds. Thus, its free-standing structure is more stable than the HT *unsaturated* structure, but this will cause its adsorption on Cu substrate significantly weaker (This is why their total energy is lower at 0 K). It is clearly shown in the side view of the two structures that our saturated glycinate monolayer is quite flat on Cu surface, while the unsaturated monolayer is corrugated (an unsaturated oxygen atom strongly bonds to the Cu substrate with the short bond length of 2.05 Å).



**Figure S4.** Homochiral  $c'_S$  and  $c'_R$  phases constructed on the either side of the heterochiral  $p(2 \times 4)$  phase, where the  $c'_S$  phases locate on the upper-left and the lower-right corners (shifted by a Cu site upwards and downwards, respectively) and the  $c'_R$  phases on the lower-left and upper-right corners (shifted by a Cu site downwards and upwards, respectively). Both  $c'_S$  and  $c'_R$  phases are composed of hydrogen-bonded twin chains, marked in yellow and green, respective (similar to the structures shown in Figure 1 in Ref. [5]). Note that the four boundaries formed between the homochiral and heterochiral phases are completely different, but the connections obey our polarity compensation rule. The  $c'_S$  (or  $c'_R$ ) |  $p$  |  $c'_S$  (or  $c'_R$ ) mixed phases can be naturally formed, as well as the  $p$  |  $c'_S$  (or  $c'_R$ ) |  $p$  mixed phases. A special case with the  $p_1$  |  $c'_S$  |  $p_2$  mixed structures is experimental observed, as shown in

Figure 4.



**Figure S5.** The  $c(2\times 4)$  homochiral structure adopted by Kanazawa *et al.* *Phys. Rev. Lett.* **2007**, *99*, 216102, proposed by Zhao *et al.* *Mater. Sci. Eng.* **2001**, *16*, 41, and Efstathiou *et al.* *Surf. Sci.* **2003**, *531*, 304. In the  $c$  phase each glycinate row is shifted by one Cu site. However, similar to the  $p$  phase shown in Figure S1, only the head-to-tail interaction is considered in this model, and the influence of polarity to side neighbors is not included.