

Simple Rules and the Emergence of Complexity in Surface Chirality

Matthew Forster^{1,2}, Rasmita Raval²

¹*Diamond Light Source, Diamond House, Harwell Science and Innovation Campus, Didcot, Oxfordshire. OX11 0DE*

²*Surface Science Research Centre, University of Liverpool, Liverpool, L69 3BX*

Chiral surfaces can be created by the adsorption of intrinsically chiral molecules, with the handedness defined by the molecule. Additionally, a second manifestation of chirality may arise due to the molecule-substrate interaction in the form of a chiral adsorption footprint. Thus, chiral surfaces may possess both handedness *and* 'footedness'. In recent work we have demonstrated that both the handedness and footedness within amino-acid monolayers on a Cu(110) surface may be determined at the single-molecule level using a combination of scanning tunnelling microscopy (STM), low energy electron diffraction (LEED), reflection absorption infrared spectroscopy (RAIRS) and density functional theory (DFT) calculations.¹⁻⁴ However, in general there is little understanding of how both these aspects of surface chirality unfold and express themselves in organized molecular layers. Here, we show that the ordering of handedness and footedness within the ($n \times 2$) assemblies of amino-acids on a Cu(110) surface may be understood on the basis of some simple generic rules. First, the 'carboxylate bonding rule' dictates how these surface-bonding groups staple the molecules into specific positions within an assembly, thus prescribing the organizational scaffolds allowed for a system. Second, the 'footedness rule' determines the chirality of the footprints that can be accommodated within this scaffold. Using these two rules we generate every possible footprint template that could be expressed by amino-acids packed into ($n \times 2$) adlayers on the Cu(110) surface, where $n = 3$ or 4 depending upon the molecule. Finally, we consider how these templates may be occupied by chiral molecules, and the different expressions of chirality that can emerge in both enantiopure and racemic systems, depending on whether the adsorbing molecule is single-footed or two-footed. From this, a surprising level of complexity in chiral ordering behavior emerges, with a manifold of possible outputs, ranging from enantiopure assemblies, segregated conglomerates, ordered racemic compounds to random solid solutions. The complexity in surface chirality is further compounded by the fact that different chiral organizations can emerge at both the handed and footed levels. The final adlayer that is adopted is governed by the third rule whereby interactions are optimized to create the most stable overlayer. Unlocking such generic rules enables the complexity of chiral organizations to be fathomed at a fundamental level and is key in knowledge-based design of surface chirality in fields as diverse as biomedical surfaces, enantioselective catalysis, chiral separations and non-linear optical devices.

References

1. M. Forster, M.S. Dyer, M. Persson, R. Raval, *J. Am. Chem. Soc.* **131**, 10173 (2009).
2. M. Forster, M.S. Dyer, M. Persson, R. Raval, *Angew. Chem. Int. Ed.*, **49**, 2344 (2010).
3. M. Forster, M.S. Dyer, M. Persson, R. Raval, *J. Am. Chem. Soc.* **133**, 15992 (2011).
4. M. Forster, M.S. Dyer, M. Persson, R. Raval, *J. Phys. Chem. C.* **115**, 1180 (2011).

Email corresponding author: matthew.forster@diamond.ac.uk ; r.raval@liverpool.ac.uk