Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

'Simple Rules and the Emergence of Complexity in surface Chirality'

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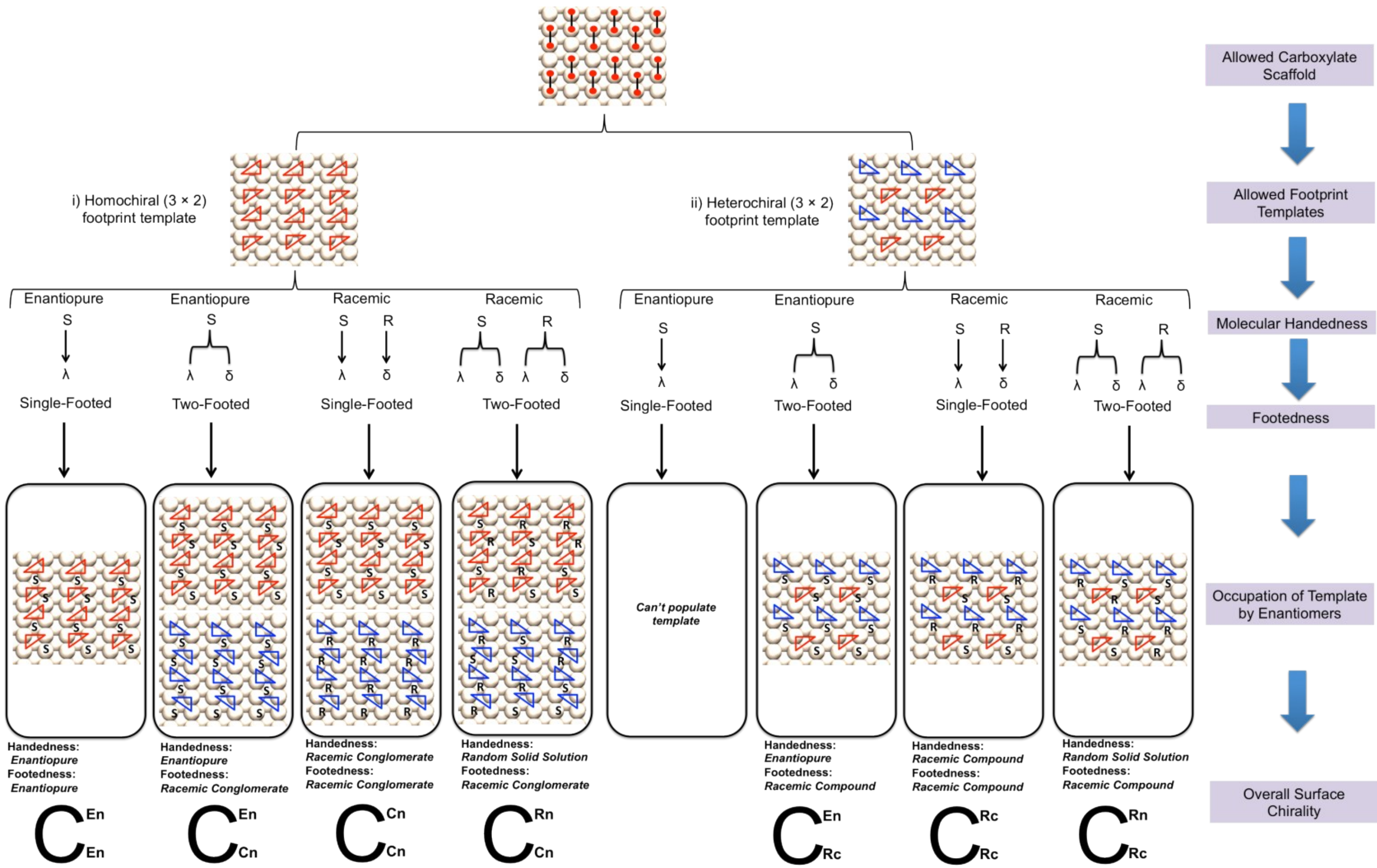
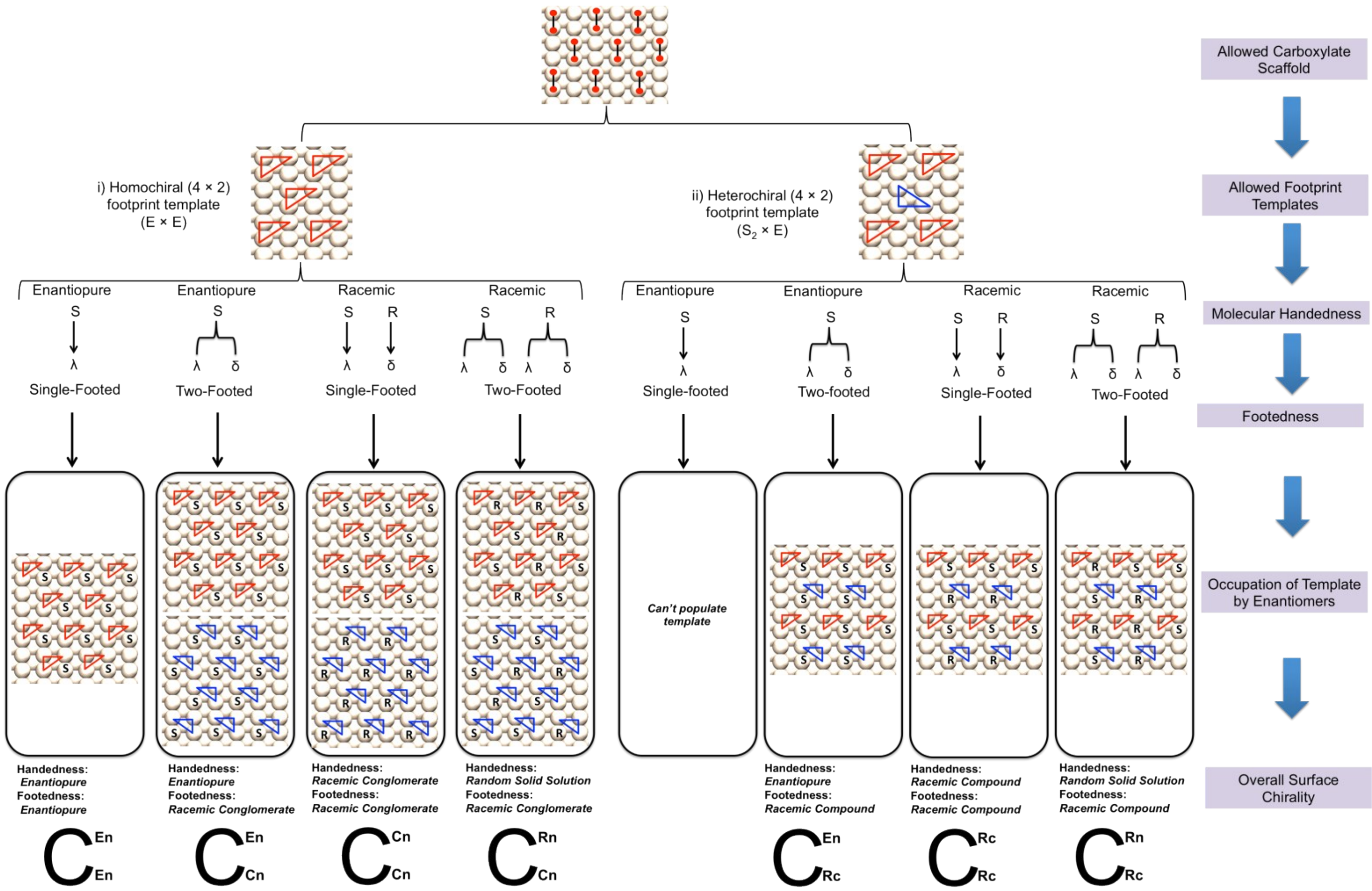

Allowed Carboxylate Scaffold
Allowed Footprint Templates
Molecular Handedness
Footedness
Occupation of Template by Enantiomers
Overall Surface Chirality
i) Homochiral (3 × 2) footprint template
ii) Heterochiral (3 × 2) footprint template
Enantiopure
Racemic
Single-Footed
Two-Footed
Can't populate template
Handedness: Enantiopure
Footedness: Enantiopure
Handedness: Enantiopure
Footedness: Racemic Conglomerate
Handedness: Racemic Conglomerate
Footedness: Racemic Conglomerate
Handedness: Random Solid Solution
Footedness: Racemic Conglomerate
Handedness: Enantiopure
Footedness: Racemic Compound
Handedness: Racemic Compound
Footedness: Racemic Compound
Handedness: Random Solid Solution
Footedness: Racemic Compound
C^{En}_{En}
C^{En}_{Cn}
C^{Cn}_{Cn}
C^{Rn}_{Cn}
C^{En}_{Rc}
C^{Rc}_{Rc}
C^{Rn}_{Rc}

Figure S1 Surface chirality generators for the (i) homochiral ($C_2 \times E$) and (ii) heterochiral ($S_2 \times E$) footprint templates within a (3 × 2) packing. The chiral outputs arising from the enantiopure and racemic adsorption of both single-footed and two-footed molecules are derived for each template and are labelled in terms of their overall surface chirality, C_F^H.



Allowed Carboxylate Scaffold
Allowed Footprint Templates
Molecular Handedness
Footedness
Occupation of Template by Enantiomers
Overall Surface Chirality
i) Homochiral (4 × 2) footprint template (E × E)
ii) Heterochiral (4 × 2) footprint template (S_2 × E)
Enantiopure
Enantiopure
Racemic
Racemic
Single-Footed
Two-Footed
Single-Footed
Two-Footed
Single-footed
Two-footed
Single-Footed
Two-Footed
Can't populate template
Handedness: Enantiopure Footedness: Enantiopure
Handedness: Enantiopure Footedness: Racemic Conglomerate
Handedness: Racemic Conglomerate Footedness: Racemic Conglomerate
Handedness: Random Solid Solution Footedness: Racemic Conglomerate
Handedness: Enantiopure Footedness: Racemic Compound
Handedness: Racemic Compound Footedness: Racemic Compound
Handedness: Random Solid Solution Footedness: Racemic Compound
C^{En}_{En}
C^{En}_{Cn}
C^{Cn}_{Cn}
C^{Rn}_{Cn}
C^{En}_{Rc}
C^{Rc}_{Rc}
C^{Rn}_{Rc}

Figure S2 Surface chirality generators for the (i) homochiral (E × E) and (ii) heterochiral (S_2 × E) footprint templates within a (4 × 2) packing. The chiral outputs arising from the enantiopure and racemic adsorption of both single-footed and two-footed molecules are derived for each template and are labelled in terms of their overall surface chirality, C^{H}_{F}.

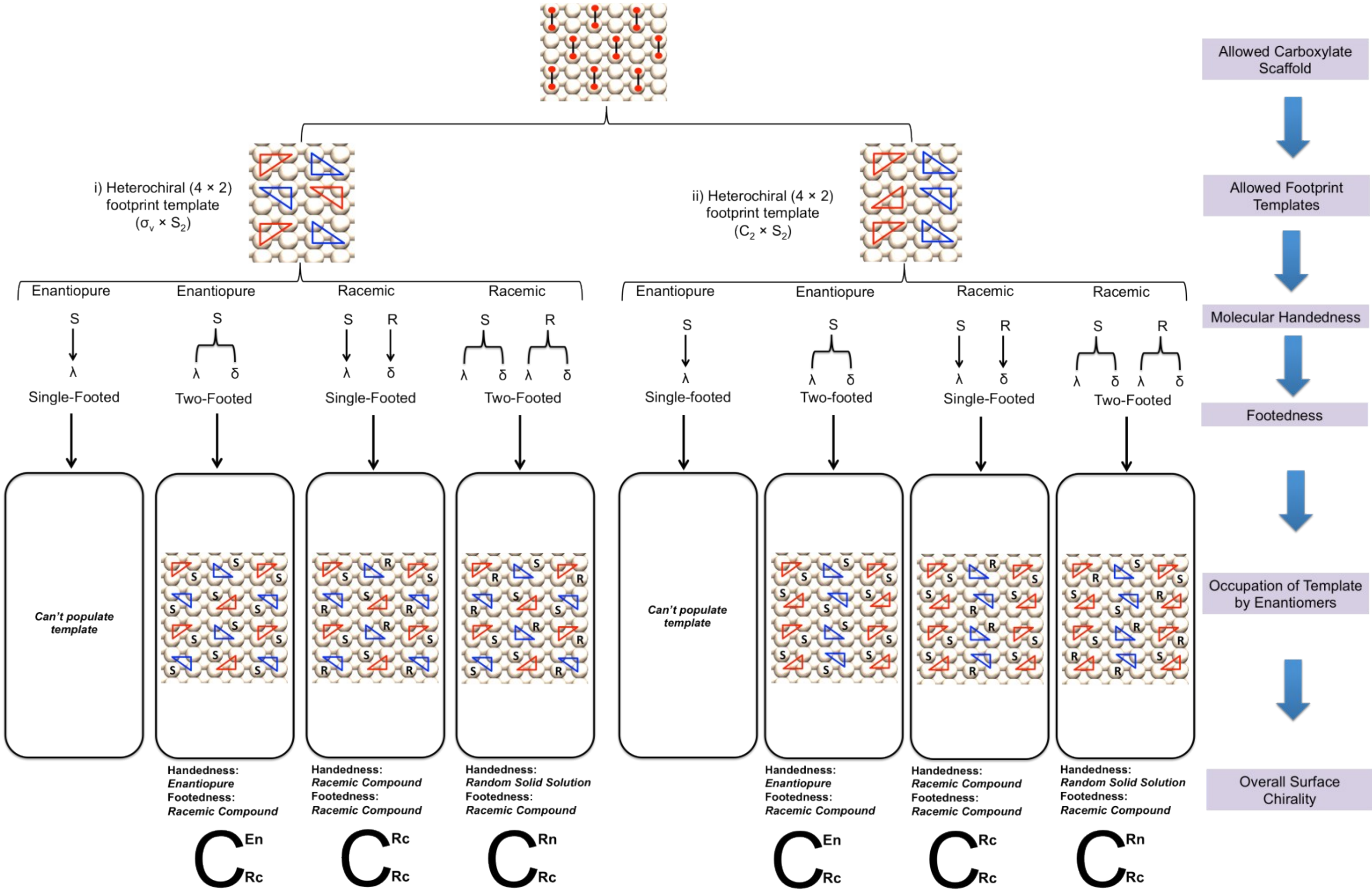
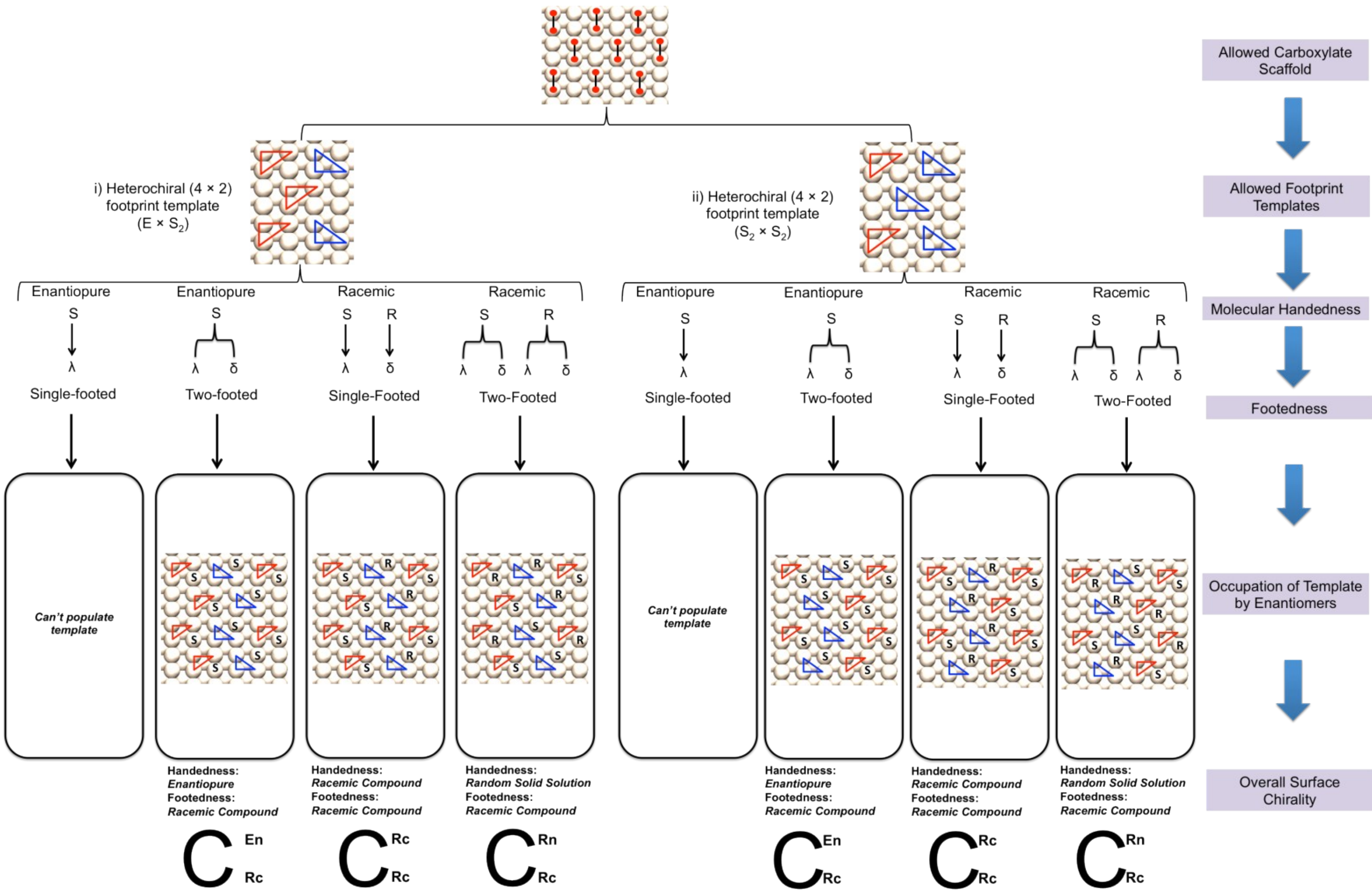


Figure S3 Surface chirality generators for the (i) heterochiral ($\sigma_v \times S_2$) and (ii) heterochiral ($C_2 \times S_2$) footprint templates within a (4×2) packing. The chiral outputs arising from the enantiopure and racemic adsorption of both single-footed and two-footed molecules are derived for each template and are labelled in terms of their overall surface chirality, C_F^H.



i) Heterochiral (4 × 2) footprint template (E × S2)
ii) Heterochiral (4 × 2) footprint template (S2 × S2)
Enantiopure
Enantiopure
Racemic
Racemic
S
λ
δ
R
Single-footed
Two-footed
Single-Footed
Two-Footed
Can't populate template
Handedness: Enantiopure Footedness: Racemic Compound
Handedness: Racemic Compound Footedness: Racemic Compound
Handedness: Random Solid Solution Footedness: Racemic Compound
C En Rc
C Rc Rc
C Rn Rc
Allowed Carboxylate Scaffold
Allowed Footprint Templates
Molecular Handedness
Footedness
Occupation of Template by Enantiomers
Overall Surface Chirality

Figure S4 Surface chirality generators for the (i) heterochiral (E × S_2) and (ii) heterochiral (S_2 × S_2) footprint templates within a (4 × 2) packing. The chiral outputs arising from the enantiopure and racemic adsorption of both single-footed and two-footed molecules are derived for each template and are labelled in terms of their overall surface chirality, C_F^H.

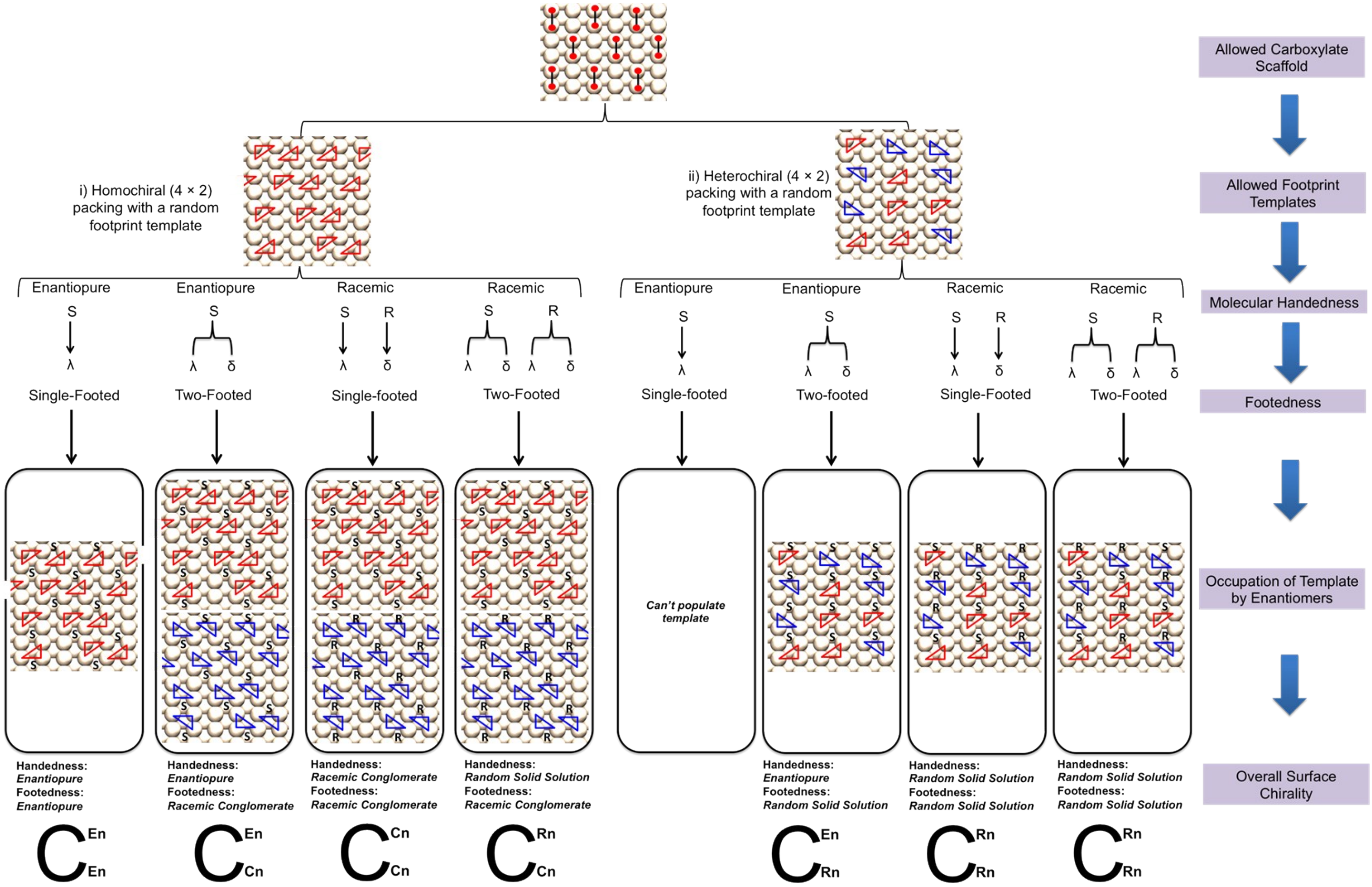


Figure S5 Surface chirality generators for (i) homochiral and (ii) heterochiral randomized footprint templates within a (4 × 2) packing. The chiral outputs arising from the enantiopure and racemic adsorption of both single-footed and two-footed molecules are derived for each template and are labelled in terms of their overall surface chirality, C_F^H.

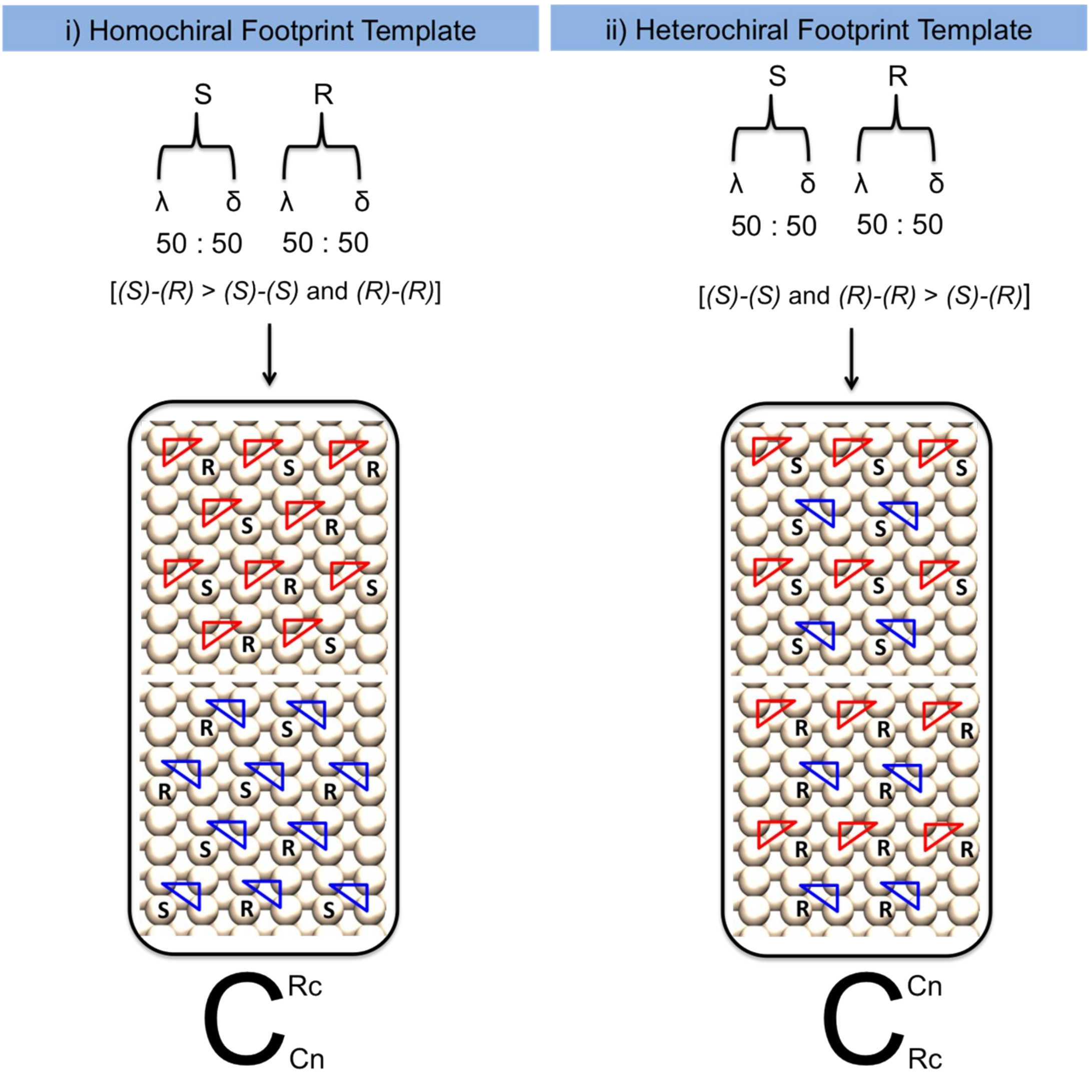


Figure S6. Examples of chiral surfaces that may arise from either a statistically rare event or tailored enantiospecific interactions within (i) a homochiral footprint template and (ii) a heterochiral footprint template. (i) For racemic adsorption of a two-footed molecule in a homochiral template, we would expect a random arrangement of enantiomers if *(S)* and *(R)* can occupy λ and δ footprints equally, leading to a surface described by, C^{Rn}_{Cn} (see surface chirality generators above). However, consider an event in which, by chance, enantiomers order as a racemic compound. The resulting surface would be a conglomerate in terms of the footprints but a racemic compound at the handedness level, C^{Rc}_{Cn} . This outcome is not disallowed by the rules but could only arise from a statistically rare event. Alternatively, enantiospecific interactions could be tailored such that heterochiral enantiomer interactions *(R)-(S)* are favoured over the homochiral interactions. In this instance, the chiral surface described by C^{Rc}_{Cn} could arise. (ii) Similarly, for racemic adsorption of a two-footed molecule in a heterochiral footprint template we would expect a random arrangement of enantiomers, C^{Rn}_{Rc} (see surface chirality generators above). However, a statistically rare event could also lead to a conglomerate at the handed level, C^{Cn}_{Rc}, should enantiomers organize in separate domains. Again, this is a statistically unlikely event, but it is not forbidden by the rules. Alternatively, a conglomerate within the heterochiral footprint template, C^{Cn}_{Rc} could arise if interactions between homochiral enantiomer pairs *(S)-(S)* and *(R)-(R)* are preferred over heterochiral ones *(R)-(S)*.