Supplementary Material (ESI) for CrystEngComm

First-Principle Prediction of Crystal Habits in Mixed Solvents: α-Glycine in Methanol/Water Mixtures

Sivashangari Gnanasambandam, Søren Enemark and Raj Rajagopalan*

Department of Chemical & Biomolecular Engineering and Singapore-MIT Alliance, National University of Singapore, 4 Engineering Drive 4, 117576 (Singapore)

Supporting Information

Table S1 Glycine/water/methanol mixtures for the crystal/bulk solution.

Plane		(010)	(011)
No. of crystalline glycine molecules		640	672
No. of solute glycine molecules		108	115
No. of methanol molecules		1174	1303
No. of water molecules		2827	2942
System dimensions (nm)	x	4.08	5.26
	y	13.59	13.21
	z	4.06	3.53

* To whom correspondence should be addressed. E-mail: raj@nus.edu.sg

Table S2 Orientations of the glycine molecules in a unit cell

Plane	Molecules[a]	θ_{CC}	ϕ_{CC}	θ_{CN}
(010)	1	81˚	290˚	64˚
	2	81˚	110˚	64˚
	3[b]	99˚	110˚	116˚
	4	99˚	290˚	116˚
(011)	1[c]	143˚	25˚	71˚
	2	24˚	228˚	88˚
	3	37˚	204˚	109˚
	4[c]	156˚	48˚	92˚

[a] Molecules numbers refer to Fig. S1. [b] Growth units for (010) surface. [c] Growth units for (011) surface.

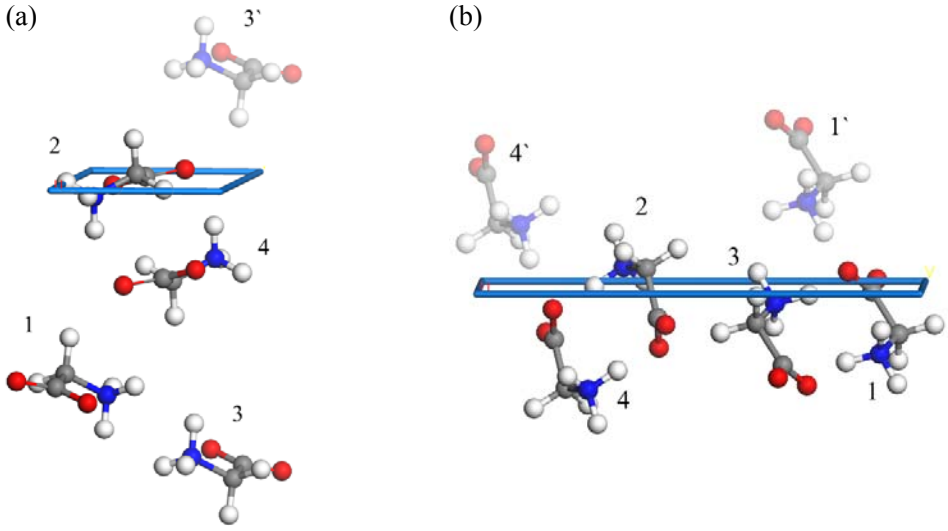

Fig. S1 Crystalline unit cell glycine molecules (numbered 1 to 4) shown together with the growth units (shaded molecules) for a) (010) and b) (011) surface. Crystal surface plane is indicated with blue rectangle.

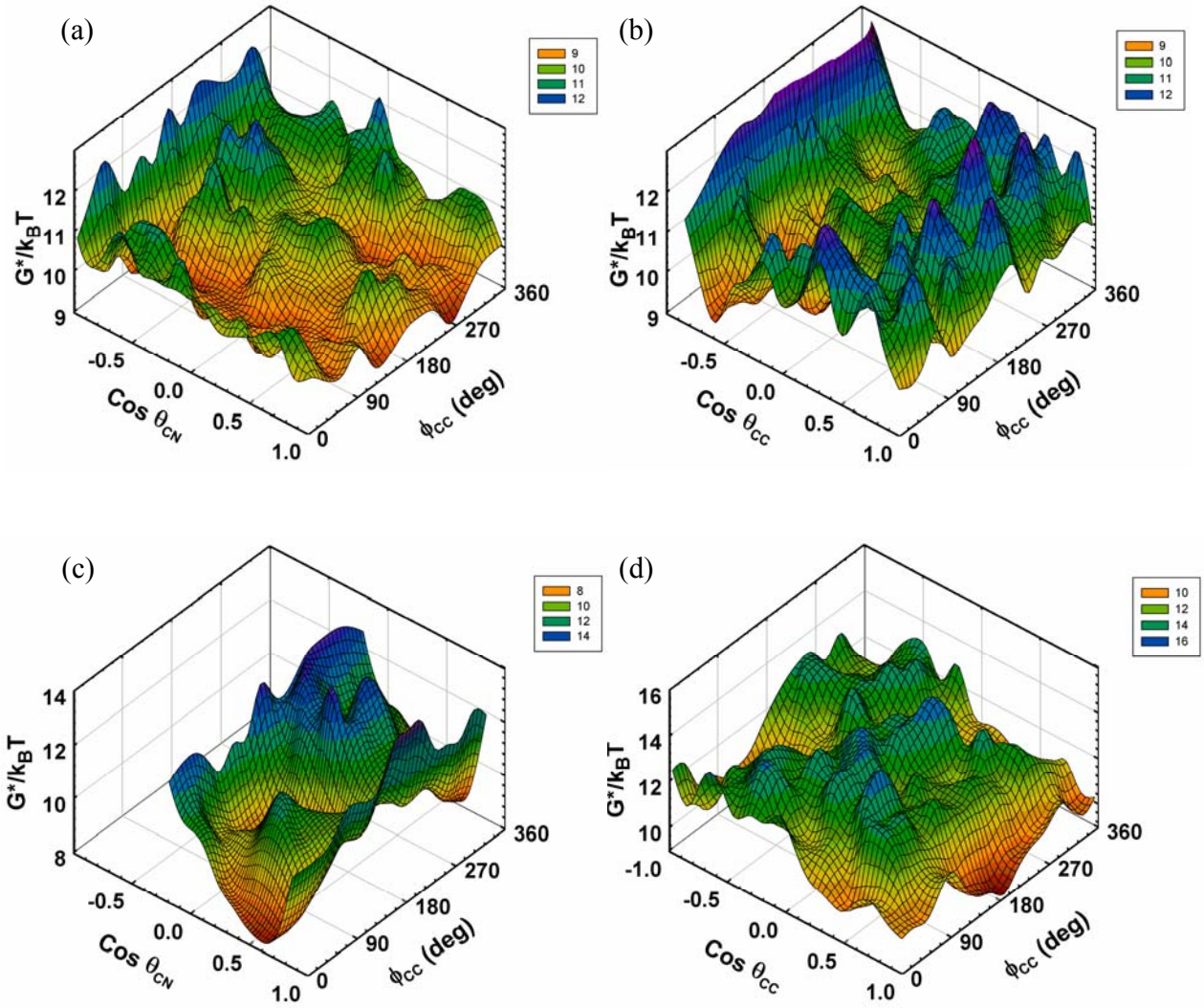

Fig. S2 Gibbs free energy surface plots shown for a) θ_{CC} = 99° and b) θ_{CN} = 116° for the (010) face, and for c) θ_{CC} = 156° and d) θ_{CN} = 92° for the (011) face. Energy is given in units of k_BT. Note that the actual Gibbs energy landscape is a function of the three angles, θ_{CC}, ϕ_{CC} and θ_{CN}, and hence is 4-dimensional. Here we show 3-dimensional surface plots where one angle is kept fixed. The surface plots correspond to the contour plots in Fig. 2, where the orientations of the growth units are also indicated.

Table S3 Molecular-level crystallographic properties and solvent-dependent properties and relative growth rate for the (010) and (011) planes of the glycine crystal.

Plane	(010)	(011)
Inter-planar distance, $d_{(hkl)}$ (nm)	1.1969	0.46741
Coordination number, $n_{(hkl)}$	4	4
Crystallographic orientation factor[a], $\xi_{hkl} = E_{hkl}^{slice} / E^{cr}$	0.9266	0.3671
Effective concentration of growth unit, $X_{A(hkl)}^{eff}$	0.0095	0.0100
Surface scaling factor[b], $C_{l(hkl)}^{*} \cong \ln X_{A(hkl)}^{eff} / \ln X_A$	1.2799	1.2671
Relative growth rate[c], R_{hkl}^{rel}	1	10

[a] E^{cr} refers to the lattice energy of the crystal and is equal to 306.018 kJ/mol. [b] X_A refers to the bulk concentration of glycine and is equal to 0.026. [c] The experimental value for the enthalpy of dissolution ($\Delta H^{diss}/k_BT$) is 12.47 in methanol/water systems (B. Palecz, Fluid Phase Equilib., 1996, **126**, 299-303.)