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> Role of Tailor-Made Additives in Controlling Vapour Growth Asymmetry Along Polar Axis of α-Resorcinol Crystal: A Molecular-scale Study

> > **Electronic Supplementary Information**

(12 pages)

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### **Electronic Supplementary Information (ESI)**

### **S1. Methodology Section**

With a view to understanding the mechanism of molecular conformation and tailor-made additives and their effect on asymmetric growth, we derived and expression for rate of growth which is controlled by kinetics and thermodynamic of the molecular growth processes. The growth of crystals faces,  $R_{red}^{(hkl)}$  is usually governed by spiral growth mechanism and given by,<sup>1</sup>

$$R_{red}^{(hkl)} = \mathbf{v}_{step(hkl)}^{kink} d_{hkl} / \lambda_0^{(hkl)} \qquad \qquad \mathbf{\mathsf{NERGEFORMAT}} (1)$$

where  $v_{step(hkl)}^{kink}$ ,  $\lambda_0^{(hkl)}$  and  $d_{hkl}$  are step velocity, step spacing and inter-planner distance of (hkl) face, respectively. The step velocity depends on the net flux of host molecules entering ( $N_{step(hkl)}^{impure}$ ) and leaving ( $N_{step(hkl)}^{impure(eq)}$ ) at the kink sites in the ledges and kink density as a function of driving force.<sup>2</sup> Considering the kinetics and thermodynamic aspect of adsorption of host molecule in the ledges and impurities/additives at surface, the rate of growth from vapour,  $R_{red(hkl)}^{impure}$  in presence of tailor-made auxiliaries can be expressed as<sup>3</sup>

$$R_{red(hkl)}^{impure} \propto \frac{2Td_{hkl} \ln(1+\sigma) \left\{ N_{step(hkl)}^{impure} - N_{step(hkl)}^{impure} \right\}}{\left| \phi_{step(hkl)}^{impure} - 0.5 \ln(1+\sigma) \right|^{\frac{1}{2}}} \right| \times \text{MERGEFORMAT (2)}$$

where, R, T and  $\sigma$  are gas constant, temperature and supersaturation, respectively. The adsorption of the additive molecule creates an additional growth barrier during the integration of the solute molecules and, thus, advancing steps energy increases with increasing concentration of additive. With lattice energy of  $E_{latt}$ , bulk enthalpy of fusion  $\Delta H^{fusion}$ , coordination number  $n_{hkl}$ , adsorption energy of host molecule  $E_{(hkl)}^{solute/surf}$ , adsorption energy of additive molecule  $E_{(hkl)}^{iadditive/surf}$  and surface coverage  $\theta_{hkl}$ , the average step energy,  $\phi_{step(hkl)}^{impure}$  can be expressed as,

$$\phi_{step(hkl)}^{impure} \approx \left\{ \frac{E_{latt} - cE_{(hkl)}^{solute/surf} + (1/c)E_{(hkl)}^{carrier-gas/surf} + \theta_{hkl}E_{(hkl)}^{additive/surf}}{E_{latt}} \right\} \frac{\Delta H^{fusion}}{n_{hkl}} \land \text{MERGEFORMAT}$$

The third term in the above expression arises due to growth hindrance from adsorption of additive molecules at the surface. With saturated mole fraction of solute concentration  $C_{eq}$ , supersaturation,  $\sigma$  can be approximated as,

$$\sigma = (c - c_{eq}) / c_{eq} \qquad \qquad \land * \text{ MERGEFORMAT (4)}$$

At the given temperature,  $C_{eq}$  is estimated from the vapour pressure data. In equilibrium, surface coverage is defined as<sup>4,5</sup>

$$\theta_{hkl} = \frac{K_{additive(hkl)}c_{additive}}{1 + K_{additive(hkl)}c_{additive}} \land * \text{MERGEFORMAT} (5)$$

where  $K_{additive(hkl)}$  and  $c_{additive}$  are Langmuir constant and mole fraction of additive concentration per solute molecule, respectively. The Langmuir constant is given by,<sup>2</sup>

$$K_{additive(hkl)} = \exp\left(\frac{\Delta H_{additive(hkl)}^{ad} - \Delta H_{additive}^{fision}}{RT}\right) \quad \text{`* MERGEFORMAT (6)}$$

where  $\Delta H_{additive(hkl)}^{ad}$  and  $\Delta H_{additive}^{fusion}$  are enthalpies of adsorption and fusion of additive, respectively. It is intriguing to note here that, in competitive adsorption model, presence of impurity can be seen as a competition between the crystallizing solute molecules and the impurity species for the preferential adsorption sites. Keeping in mind that the crystallization is a thermally activated process and, as such, usually represented by the Arrhenius equation, the effective flux of solute molecules in the presence of additive,  $N_{step(hkl)}^{impure}$  seen by the surface may be written in the form,

$$N_{step(hkl)}^{impure} = \frac{c_{eq}^{3} (1+\sigma)^{3}}{\left\{ c_{eq}^{3} (1+\sigma)^{2} + \exp\left(\frac{-\Delta E_{(hkl)}^{carrier-gas/surf}}{RT}\right) + cc_{eq}^{2} (1+\sigma)^{2} \frac{\theta_{hkl}}{(1-\theta_{hkl})} \exp\left(\frac{-\Delta E_{(hkl)}^{additive/surf}}{RT}\right) \right\}}$$
 \\*  
MERGEFORMAT (7)

where  $N_{step(hkl)}^{impure}$  reduces to  $N_{step(hkl)}^{impure(eq)}$  at  $\sigma = 0$  and  $\Delta E_{(hkl)}^{carrier-gas/surf}$  and  $\Delta E_{(hkl)}^{additive/surf}$  are given by,

$$\Delta E_{(hkl)}^{carrier-gas/surf} = E_{(hkl)}^{carrier-gas/surf} - E_{(hkl)}^{solute/surf} \quad \backslash * \text{MERGEFORMAT} (8)$$

and

$$\Delta E_{(hkl)}^{additive/surf} = E_{(hkl)}^{additive/surf} - E_{(hkl)}^{solute/surf} \qquad \land * \text{MERGEFORMAT (9)}$$

The third term in the denominator of eq \\* MERGEFORMAT (7) represents growth hindrance that occurred due to the adsorption of additive auxiliaries at the crystal surface. The details derivation of above growth rate expression has been described in detail elsewhere.<sup>3</sup> We have already applied the above-described methodology to investigate the effect of biuret on aqueous crystallization of the urea crystal. The details of the results are discussed in Ref. 3.

## S2. Supplementary data and figures

#### S2.1. Symbol and notation of different steps configurations

Following eight different steps configurations  $(C_1 - C_8)$  have been created at the surfaces of (011) and  $(0\overline{1}\overline{1})$  faces of  $\alpha$ -resorcinol to determine adsorption energy landscape of the host molecules in two different orientations of resorcinol molecules say  $M_1$  and  $M_2$ , which are related by the *a*-glide. Within each pair, molecules  $M_1$   $(M_1^i \text{ and } M_1^{ii})$  and  $M_2$   $(M_2^i \text{ and } M_2^{ii})$  are related by the *n*-glide.

 $C_{I}$ : adsorption of  $M_{2}^{i}$  molecule in presence of array of molecules  $M_{2}^{ii}M_{1}^{ii}M_{1}^{i}...$   $\left(\frac{M_{2}^{i}}{M_{2}^{ii}M_{1}^{ii}M_{1}^{i}}\right)$ 

 $C_2$ : adsorption of  $M_2^{ii}$  molecule in presence of array of molecules  $M_2^i M_1^{ii} M_1^i \dots \left( \frac{M_2^{ii}}{M_2^i M_1^{ii} M_1^i} \right)$ 

 $C_3$ : adsorption of  $M_2^i$  molecule in presence of array of molecules  $M_1^{ii}M_1^iM_2^{ii}...\left(\frac{M_2^i}{M_1^{ii}M_1^iM_2^{ii}}\right)$ 

 $C_4$ : adsorption of  $M_2^{ii}$  molecule in presence of array of molecules  $M_1^{ii}M_1^iM_2^{ii}...$   $\left(\frac{M_2^{ii}}{M_1^{ii}M_1^iM_2^{ii}}\right)$ 

 $C_5$ : adsorption of  $M_1^i$  molecule in presence of array of molecules  $M_1^{ii}M_2^{ii}M_2^i...$   $\left(\frac{M_1^i}{M_1^{ii}M_2^{ii}M_2^i}\right)$ 

 $C_6$ : adsorption of  $M_1^{ii}$  molecule in presence of array of molecules  $M_1^i M_2^{ii} M_2^i \dots \left(\frac{M_1^{ii}}{M_1^i M_2^{ii} M_2^i}\right)$ 

 $C_7$ : adsorption of  $M_1^i$  molecule in presence of array of molecules  $M_2^{ii}M_2^iM_1^{ii}...$   $\left(\frac{M_1^i}{M_2^{ii}M_2^iM_1^{ii}}\right)$ 

 $C_8$ : adsorption of  $M_1^{ii}$  molecule in presence of array of molecules  $M_2^{ii}M_2^iM_1^{ii}...\left(\frac{M_1^{ii}}{M_2^{ii}M_2^iM_1^{ii}}\right)$ 

# S2.2. Optimized structures of surface-additive interface



Figure 1. Optimized structures of surface-additive interface on which  $R_3(\gamma)$ -resorcinol has docked in two different orientation, namely (a)  $M_1$  (b)  $M_2$  at (011) face and (c)  $M_1$  (d)  $M_2$  at  $(0\overline{11})$  face.





Figure 3. Same as Figure 1 but for orcinol.



Figure 4. Same as Figure 1 but for phloroglucinol.



Figure 5. Same as Figure 1 but for pyrogallol.



Figure 6. Same as Figure 1 but for hydroquinone.

Table 1. The BSSE-uncorrected adsorption energies (kJ/mol) of the host molecule in different steps configurations at the surface of  $(0\overline{11})$  and (011) faces from the vapour phase. The BSSE-correction to the adsorption energies in the relaxed steps configurations are shown in the parenthesises.

Face	$E_{(hkl)}^{host / surf}$ (kJ/mol) in steps configuration								
1 400	$M_2^i$	$M_2^{ii}$	$M_2^i$	$M_2^{ii}$	$M_1^i$	$M_1^{ii}$	$M_1^i$	$M_1^{ii}$	
	$M_2^{ii}M_1^{ii}M_1^{i}$	$M_2^i M_1^{ii} M_1^i$	$M_1^{ii}M_1^{i}M_2^{ii}$	$M_1^{ii}M_1^{i}M_2^{ii}$	$M_1^{ii}M_2^{ii}M_2^{i}$	$M_1^i M_2^{ii} M_2^i$	$M_2^{ii}M_2^iM_1^{ii}$	$M_2^{ii}M_2^iM_1^{ii}$	
	${\mathcal C}_I$	${\mathcal Q}_2$	$\mathcal{C}_3$	$C_4$	$C_5$	$\mathcal{C}_6$	$\mathcal{Q}_7$	$\mathcal{C}_8$	
$(0\overline{1}\overline{1})$	-38.4	-40.8	-34.1	-36.5	-37.0	-39.2	-34.2	-36.3	
	(-10.1)	(-13.1)	(-10.4)	(-11.2)	(-12.2)	(-14.1)	(-10.9)	(-11.8)	
	(a-phase)	(a-phase)	(a-phase)	(a-phase)	(a-phase)	(a-phase)	(a-phase)	(a-phase)	
(011)	-36.1	-42.5	-32.3	-38.7	-40.1	-44.8	-35.4	-39.0	
	(-10.9)	(-13.2)	(-10.2)	(-12.2)	(-9.7)	(-12.2)	(-9.0)	(-11.4)	
	(a-phase)	(a-phase)	(a-phase)	(a-phase)	(β-phase)	(β-phase)	(β-phase)	(β-phase)	

Conformers/tailor- made auxiliaries	Enthalpy of fusion (kJ/mol)	Face (hkl)	$E_{(hkl)}^{additive / surf}$ (kJ mol <sup>-1</sup> ) in		
			orientation		
			$M_1$	$M_2$	
$R_2(\beta)$ conformer	20.9	$(0\overline{1}\overline{1})$	-24.0 (-9.2)	-23.7 (-9.3)	
		(011)	-21.4 (-5.9)	-26.1 (-8.7)	
$R_3(\gamma)$ conformer	18.9	$(0\overline{1}\overline{1})$	-24.1 (-8.4)	-24.3 (-8.8)	
		(011)	-24.2 (-7.6)	-29.2 (-10.0)	
2-methylresorcinol	19.5	$(0\overline{1}\overline{1})$	-29.1 (-10.4)	-26.7 (-9.2)	
		(011)	-25.6 (-8.8)	-23.5 (-8.4)	
Orcinol	19.5	$(0\overline{1}\overline{1})$	-26.3 (-9.3)	-28.1 (-10.2)	
		(011)	-24.5 (-6.9)	-22.9 (-8.8)	
Phloroglucinol	23.1	$(0\overline{1}\overline{1})$	-28.3 (-9.4)	-25.2 (-9.0)	
		(011)	-25.5 (-8.2)	-25.0 (-9.1)	
Pyrogallol	23.1	$(0\overline{1}\overline{1})$	-29.2 (-10.8)	-30.9 (-11.9)	
		(011)	-32.6 (-11.2)	-27.9 (-10.4)	
Hydroquinone	17.3	$(0\overline{1}\overline{1})$	-27.9 (-10.6)	-27.0 (-10.5)	
		(011)	-21.5 (-5.9)	-24.4 (-8.5)	

Table 2. The BSSE-uncorrected adsorption energy (kJ/mol) of different conformers of resorcinol and tailor-made auxiliaries at  $(0\overline{11})$  and (011) faces of  $\alpha$ -resorcinol crystal from vapour. The BSSE-correction to the adsorption energies in the relaxed steps configurations are shown in the parenthesises

Reference

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Figure 7. Effect of (a)  $\gamma$ -phase conformer of resorcinol, (b) orcinol, (c) phloroglucinol, (d) pyrogallol and (e) hydroquinone admixture on the growth rate of  $(0\overline{1}\overline{1})$  and (011) faces of  $\alpha$ -resorcinol crystal from vapour as function of additive concentration and supersaturation at saturation temperature 91 °C.

S2.4.



Figure 8 Ratio of impure and pure growth rate of (a)  $\gamma$ -phase conformer of resorcinol, (b) orcinol, (c) phloroglucinol, (d) pyrogallol and (e) hydroquinone admixture  $(0\overline{1}\overline{1})$  and (011) faces of  $\alpha$ -resorcinol containing as function of additive concentration and supersaturation at saturation temperature 91 °C.



Figure 9. Vapour growth anisotropy  $(R_{(0-1-1)}/R_{(011)})$  along polar axis of  $\alpha$ -resorcinol crystal containing (a)  $\gamma$ -phase conformer of resorcinol, (b) orcinol, (c) phloroglucinol, (d) pyrogallol and (e) hydroquinone admixture at saturation temperature 91 °C and 60 °C.