Supporting information

Solvent Effects and Its Role in Quantitative Manipulating the Crystal Growth: Benzoic Acid as Case Study

Yuan Wang,[a] *Zuozhong Liang*[b,*]

[a]School of Advanced Materials and Technology, Xidian University, Xi'an 710126, P.R. China

[b]School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710119, P.R. China

[*]Corresponding Author

E-mail: *liangzuozhong@snnu.edu.cn.*

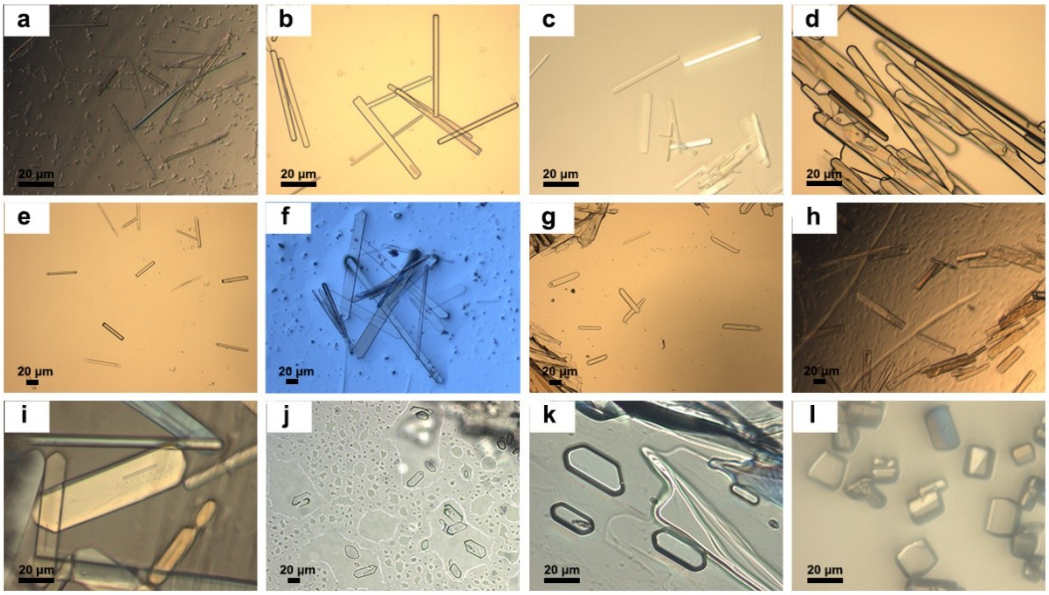

Figure S1. Observed benzoic acid crystals used for aspect ratio measurements. (a-*n*-heptane, b-carbon tetrachloride, c-toluene, d-dichloromethane, e-tetrahydrofuran, f-ethyl acetate, g-1,4-dioxane, h-ethanol, i-acetone, j-acetic acid, k-acetonitrile, and l-water.)

Table S1. The measured aspect ratio *AR* and the corresponding average value *R* in different solvents.

Solvents	*P*	*AR*	*R*
n-Heptane	0	21	20.25
		10.5	
		20	
		23.5	
		9	
		28	
		10.5	
		10	
		32	
		18.5	
		25	
		35	
Carbon tetrachloride	1.7	16.25	18.17

		16.25	
		11.67	
		17.71	
		24	
		18	
		23.33	
Toluene	2.3	15.14	13.65
		8.6	
		19.33	
		15.2	
		9.75	
		14	
		13.5	
Dichloromethane	3.4	15.8	13.66
		14.4	
		13	
		18	
		10.75	
		10	
Tetrahydrofuran	4.2	11	11
		15	
		10	
		10	
		12	
		10	
		9	
Ethyl acetate	4.3	13.4	9.98
		10	
		7.1	
		21.5	
		10.5	
		8.75	
		4.5	
		6.6	
		7.5	
1,4-dioxane	4.8	7	6.71
		6.5	
		7.5	
		4.5	
		9	
		6.5	
		6	
Ethanol	5.2	8	6.41

		6.67	
		6.5	
		7	
		4.33	
		4.33	
		4.67	
		7.67	
		5.33	
		6.67	
		9.33	
Acetone	5.4	3.72	4.74
		4.29	
		6.22	
Acetic acid	6.2	2	2.61
		2.67	
		3.33	
		2.67	
		2.5	
		2.5	
Acetonitrile	6.2	3	2.62
		2.5	
		2.17	
		2.8	
Water	9	2	1.53
		1.06	
		1.83	
		1.4	
		1.07	
		1.8	
		1.2	
		1.15	
		1.29	
		3	
		1	

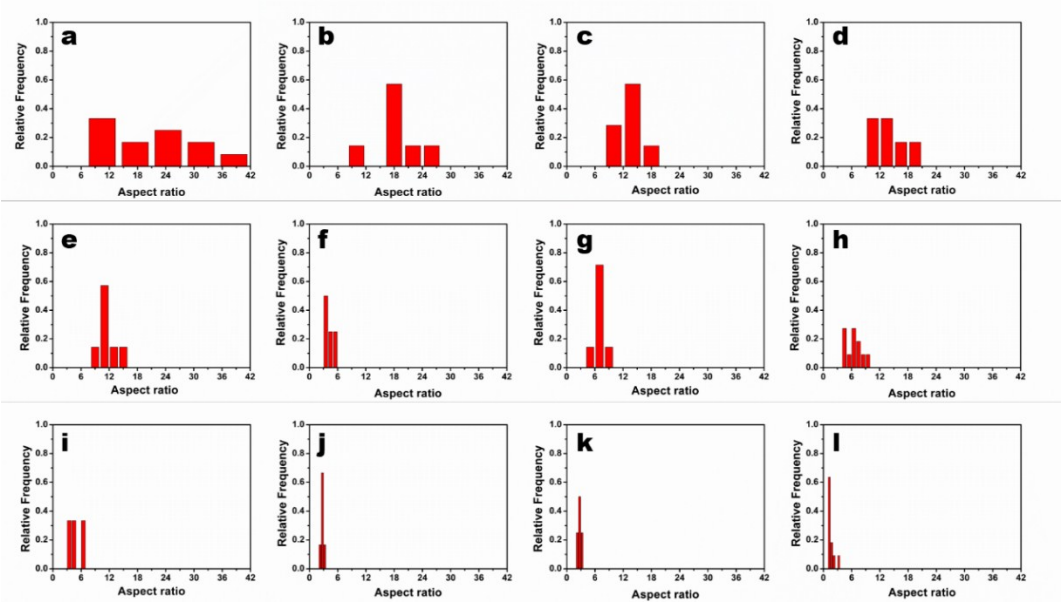

Figure S2. The aspect ratio distributions of observed benzoic acid crystals in different solvents (a-*n*-heptane, b-carbon tetrachloride, c-toluene, d-dichloromethane, e-tetrahydrofuran, f-ethyl acetate, g-1,4-dioxane, h-ethanol, i-acetone, j-acetic acid, k-acetonitrile, and l-water.).

Table S2. The solution/crystal interface interaction E_s, the correlation factor S, and the modified attachment energy E_{mod} (kcal/mol) of most exposed crystal faces ((002), (100), (10-2), (012), and (110)).

Solvents	*hkl*	E_s	S	E_{mod}
n-Butanol	(002)	−8.62	1.431	−1.94
	(100)	−12.67	1.596	−14.06
	(10-2)	−13.05	1.919	−7.53
	(012)	−13.51	1.388	−37.80
	(110)	−17.64	1.502	−35.74
n-Propanol	(002)	−8.42	1.431	−2.23
	(100)	−11.57	1.59	−15.83
	(10-2)	−11.94	1.91	−9.67
	(012)	−12.01	1.388	−39.88
	(110)	−15.69	1.50	-38.66
Isopropanol	(002)	−7.54	1.43	−3.74
	(100)	−13.01	1.60	−15.27

	(10-2)	−13.78	1.92	−8.67
	(012)	−14.00	1.39	−35.61
	(110)	−18.95	1.50	−34.09
Ethanol	(002)	−6.117	1.432	−5.522
	(100)	−9.659	1.596	−18.87
	(10-2)	−9.649	1.921	−14.03
	(012)	−9.631	1.388	−43.178
	(110)	−12.542	1.502	−43.386
Methanol	(002)	−4.13	1.432	−8.37
	(100)	−1.70	1.596	−31.58
	(10-2)	−1.97	1.921	−28.80
	(012)	−1.81	1.388	−54.04
	(110)	−2.48	1.502	−58.50

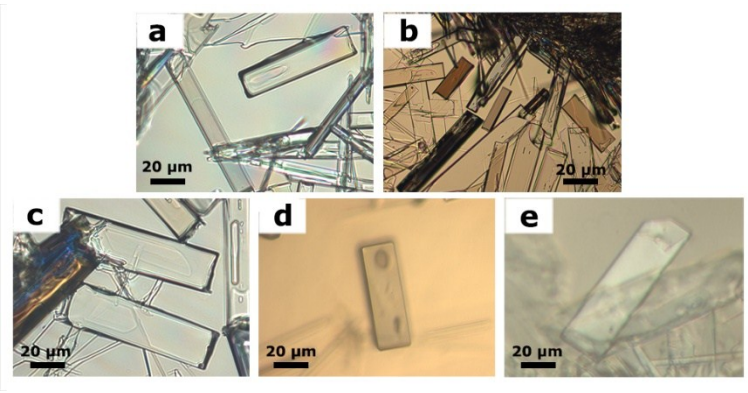

Figure S3. The observed crystals in different alcohol solvents (a-*n*-butanol, b-*n*-propanol, c−isopropanol, d−ethanol, and e−methanol).

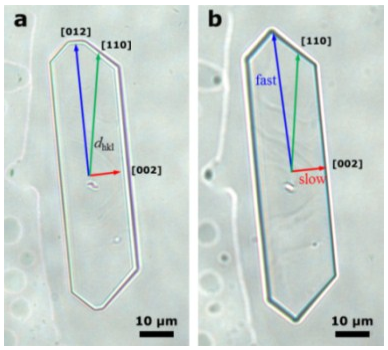

Figure S4. The observed BA crystals in acetic acid; the fastest growing face disappeared after a few seconds from the final crystal morphology.

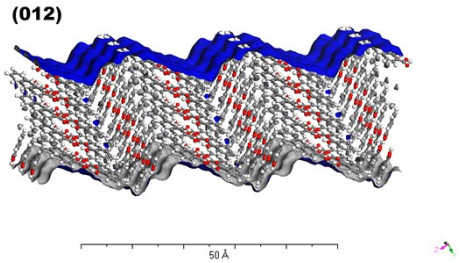

Figure S5. The molecular arrangement and surface roughness of the face (012). The roughness can be reflected from the value of correlation factor *S*.

Table S3. The adsorption energy (E_{ads}), rigid adsorption energy ($E_{rigid\ adsorption}$) and deformation energy ($E_{deformation}$) of five main faces ((012), (100), (002), (10-2), and (110)). The energy unit is kcal·mol^{-1}.

Solvents	Faces	$E_{adsorption}$	$E_{rigid\ adsorption}$	$E_{deformation}$
n-Butanol	(012)	−16.913	−17.147	0.234
	(100)	−17.278	−17.423	0.145
	(002)	−15.590	−16.259	0.669
	(10-2)	−20.294	−19.912	−0.381
	(110)	−15.094	−15.186	0.092
n-Propanol	(012)	−15.034	−15.166	0.132
	(100)	−16.660	−16.831	0.171
	(002)	−13.948	−14.118	0.171
	(10-2)	−18.965	−19.176	0.211
	(110)	−13.163	−13.302	0.139
Isopropanol	(012)	−14.674	−14.895	0.222
	(100)	−16.643	−16.391	−0.252
	(002)	−14.674	−14.371	−0.304
	(10-2)	−19.652	−19.454	−0.198
	(110)	−14.391	−14.495	0.103
Ethanol	(012)	−13.336	−13.475	0.139
	(100)	−15.483	−15.286	−0.197
	(002)	−13.436	−13.150	−0.286
	(10-2)	−17.161	−17.310	0.148
	(110)	−11.990	−12.186	0.197
Methanol	(012)	−11.809	−11.917	0.108
	(100)	−9.466	−9.544	0.077
	(002)	−11.992	−12.082	0.090
	(10-2)	−14.792	−14.908	0.116
	(110)	−12.246	−12.283	0.037

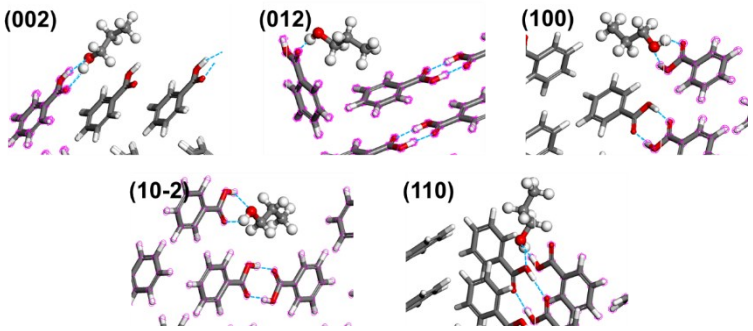

Figure S6. Adsorption configurations of the *n*-propanol molecule at main exposed surfaces ((002), (012), (100), (10-2), and (110)). The blue lines stand for the hydrogen bond interaction.

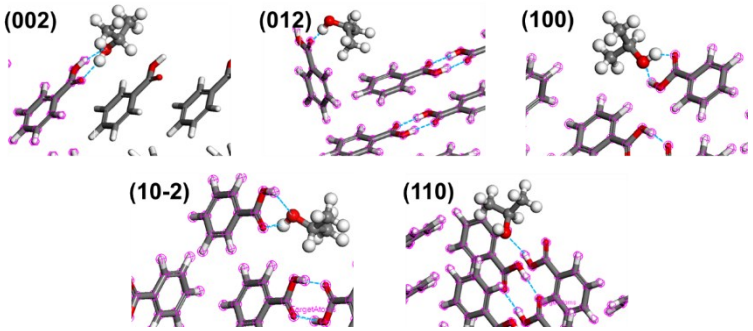

Figure S7. Adsorption configurations of the isopropanol molecule at main exposed surfaces ((002), (012), (100), (10-2), and (110)). The blue lines stand for the hydrogen bond interaction.

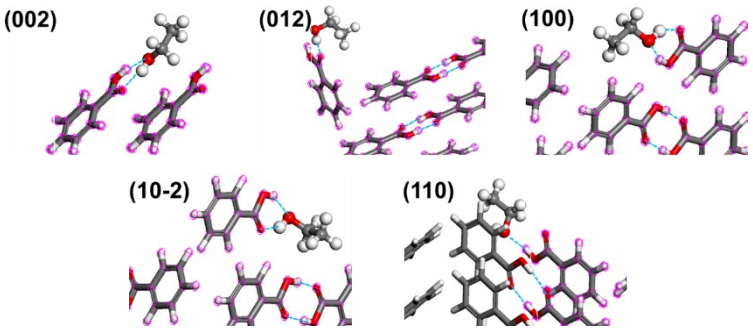

Figure S8. Adsorption configurations of the ethanol molecule at main exposed surfaces ((002), (012), (100), (10-2), and (110)). The blue lines stand for the hydrogen bond interaction.

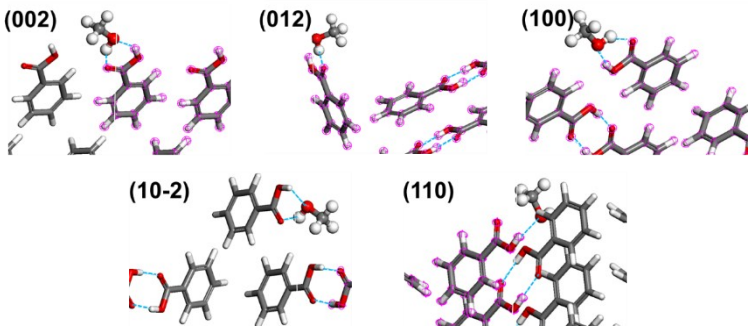

Figure S9. Adsorption configurations of the methanol molecule at main exposed surfaces ((002), (012), (100), (10-2), and (110)). The blue lines stand for the hydrogen bond interaction.