Supplementary Information

Generating One-Dimensional Micro- or Nano-structures with In-Plane Alignment by Vapor-Driven Wetting Kinetics

Chuan Liu¹, Xuying Liu²,Yong Xu³, Huabin Sun³, Yun Li⁴, Yi Shi⁴, Michael V. Lee⁵, Toshikazu Yamada⁶, Tatsuo Hasegawa⁶, Takeo Minari²*, Yong-Young Noh³*

- 1. Absorption/desorption of cyclohexane into anisole.
- 2. Radius and contact angle of the anisole droplet in cyclohexane vapor on CYTOP.
- 3. Time evolution of the radius of a sessile anisole droplet.
- 4. Simulated radius and angle of a droplet with different values of τ_{s} .
- 5. Mixed solvent: Marangoni effect and *tears-of-wine*.
- 6. Crystallization of C8-BTBT manipulated by VDW on HMDS-surface.
- 7. Crystalline bundles formed by drop casting the cyclohexane solution of C8-BTBT.
- 8. Film formed by drop casting the anisole solution of C8-BTBT.
- 9. Molecular packing structure of C8-BTBT crystals.
- 10. Full model of vapor-driven wetting (VDW).



Figure S1. Set-up to measure the absorption of cyclohexane into anisole. A magnetic stir bar slowly rotated in the anisole (~1Hz). The weight of the inner petri-dish was measured at certain time intervals to track the weight of the adsorbed cyclohexane. The initial weight of anisole is 0.5462 g and the final weight of cyclohexane is 0.5867 g. Therefore the parameter f_{∞} is 0.58. Fitting is explained in the modeling part after all the figures.



Figure S2. Time evolution of the radius and contact angle of an anisole droplet (volume \sim 7 µl) on CYTOP surface in cyclohexane vapor: experimental data (dots) and model fitting (line). The time constant τ_l is 435 s (τ_s <15 s).



Figure S3. Time evolution of the radius of a sessile anisole droplet (volume ~0.5 µl) on HMDS surface: experimental data (dots) and model fitting (line). Time constants τ_l is 41.7 s (τ_s <10s). Note that in this case, the droplet size is much smaller than that presented in

Figures 1-3 in the main text, therefore the initial shrinking due to the adsorption of vapor on solid substrate can be observed as a slight decrease of the radius.



Figure S4. The simulated radius (open dots) and angle (dots) of a droplet with different values of τ_s (2, 5, 10, 20s), indicating dewetting (i.e. increasing contact angle) and spreading (i.e. decreasing contact angle). The value of τ_l is fixed at 100 s.

(a) Solvent mixing



Interval: 0.3s

(b) Mixed solvents drying



Figure S5. (a) Drop-casting a droplet of cyclohexane onto anisole resulted in sudden spreading followed by splitting into separate droplets. (b) When placing a droplet of anisole-cyclohexane mixture in open air, fingering instability appeared at the retracting edge that is similar to the "tears-of-wine" effect.



Figure S6. (a) The crystallization of C8-BTBT manipulated by VDW on HMDS-surface. (b) The crystallization of C8-BTBT of a droplet on HMDS-surface.



Figure S7. Left: Optical image of the crystals obtained from drying cyclohexane solution (1 mg/ml). Right: XRD signals of these crystals.



Figure S8. Left: Optical image of the crystals obtained from drying anisole solution (10 mg/ml). Right: XRD signals of these crystals.



Figure S9. Crystal structure (monoclinic) of C8-BTBT obtained from the mentioned solutions. Left: a view from the top. Right: a 3D view of the packing structure. Adapted from [¹].



Figure S10. Crystals formed using anisole droplet in chloroform vapor (a), THF tetrahydrofuran (b), and hexane vapor (c). The right images are the zoomed-in images of the left images.



Figure S11. Performance of transistors. (a) Differential mobility as a function of gate voltage (extracted from the data in Figure 5c). (b) Gate leakage current as a function of gate voltage (for a reference, the drain current at -40V is 40 μ A). The data include the data of forward and backward scanning.

Model for vapor driven wetting (VDW) of a liquid droplet

According to **Fig. 3**, three processes are involved: 1. Vapor molecules are adsorbed onto the substrate; 2. Vapor molecules diffuse into the droplet; 3. Anisole droplet evaporates. During the absorption process, diffused cyclohexane also evaporates into air but this process is negligible. We describe each process, calculate their effect on contact angle, and explain the evolution of radius and contact angle in stage 1, as shown in **Fig. 2** and **Fig. S2-4**.

1. The adsorption process

In this part we describe the adsorbed vapor on the substrate which causes a quick shrink of the liquid film.

Let the number of adsorbed vapor molecules at time t is n(t) and the adsorbed vapor molecules at infinite time (or the thermal equilibrium state) is n_{∞} (the subscript ∞ stands for values at the end of the stage I, a quasi-thermal equilibrium). Then the driving force for the adsorption at time t is proportional to the difference between the two,

$$\frac{dn(t)}{dt} = \beta [n_{\infty} - n(t)]$$
(S1)

We denote the proportion between them as $p_s(t) = n(t)/n$ (the subscript *s* stands for solid substrate) and then

$$\frac{dp_s(t)}{dt} = \beta [1 - p_s(t)]$$
(S2)

As $p_s(0)=0$ and $p_s(\infty)=1$, we derive the solution to (2):

$$p_{s}(t) = 1 - e^{-t/\tau_{s}}$$
(S3)

where $\tau_s = 1/\beta$ is a time constant measuring the adsorption on the substrate.

The interfacial surface tension between the substrate and vapor can be estimated by analogy to Starov's application of Antonov's rule [²],

$$\gamma_{sv}(t) = \gamma_{sv0} [1 - p_s(t)] + \gamma_{sv\infty} p_s(t)$$
(S4)

where γ_{sv0} and $\gamma_{sv\infty}$ are the value of γ_{sv} at the beginning (*t*=0) and the value at the infinite time (thermal equilibrium). Substitute (3) into (4), we get

$$\gamma_{sv}(t) = \gamma_{sv0} e^{-t/\tau_s} + \gamma_{sv\infty} \left(1 - e^{-t/\tau_s}\right)$$
(S5)

Here the energy could be calculated by Young's equation,

$$\gamma_{sv0} = \gamma_{lv0} \times \cos\theta_0 + \gamma_{sl0} \tag{S6}$$

$$\gamma_{lv\infty} = \gamma_{lv\infty} \times \cos\theta_{\infty} + \gamma_{sl\infty} \tag{S7}$$

The values of γ_{sl0} , $\gamma_{sl\infty}$, γ_{lv0} , and $\gamma_{lv\infty}$ will be estimated in the next section. And the contact angle at the beginning θ_0 and at the end θ_{∞} can be experimentally measured.

2. The absorption process

In this part we describe the absorbed vapor in the liquid droplet which causes a long spreading of the liquid film.

2.1 Model of the absorption process

In the sorption kinetics, the driving force is mainly described by the pseudo first-order rate equation [³],

$$\frac{dV(t)}{dt} = k_1 [V_{\infty} - V(t)]$$
(S8)

or the pseudo second-order rate equation [4-6],

$$\frac{dV(t)}{dt} = k_2 [V_{\infty} - V(t)]^2$$
(S9)

or the Elovich's equation [7-8],

$$\frac{dV(t)}{dt} = \delta e^{-k_3 V(t)}$$
(S10)

where V(t) is the transient volume at time t, and V_{∞} is the volume at the end of stage I (quasi-thermal equilibrium).

We performed a separate experiment to measure this process (**Fig. S1**) and put a magnet in anisole to stir very slowly (~0.5Hz). The change of the weight of the cyclohexane is shown in **Fig. S1**. Fittings results of equation (8)~(10) are shown below and are compared to experimentally measured data. Though the pseudo 2^{nd} order rate equation gives the highest correlation coefficient, the fitted volume of it deviates more severely from the experimentally measured value. Hence the pseudo first-order rate equation, i.e. equation (8), describes well enough the process and will be used below.

	1 st order	2 nd order	Elovich's
Fitting equation	$\ln(V_{\infty}-V(t))$ vs. k_1t	$t/V(t)$ vs. k_2t	$V(t)$ vs. $k_3 \ln(t)$
Correlation coefficient	0.987	0.998	0.977
Fitted V_{∞} (ml)	0.73	0.87	-
Fitted k	0.02547	0.04258	5.484
Fitted time constant (min)	39.3	23.5	-
Measured V_{∞} (ml)	0.76	0.76	0.76

Table S1. Fitting results of **Fig. S1** using equations $(8) \sim (10)$.

2.2. Absorption

Let the volume of the absorbed vapor molecules in the droplet at time *t* is V(t) and the volume at infinite time is V_{∞} , then

$$\frac{dV(t)}{dt} = \alpha [V_{\infty} - V(t)]$$
(S11)

Let the proportion between V(t) and V_{∞} is $p_{l}(t)$, then $p_{l}(t)=0$ at t=0, and $p_{l}(t)=1$ at thermal equilibrium, or infinite time in the ideal case (the subscript *l* stands for liquid droplet). Then

$$p_l(t) = 1 - e^{-t/\tau_l}$$
(S12)

where τ_l is a time constant measuring the absorption into the liquid droplet. In the fit, notice that a small amount of time should be deducted corresponding to the full establishment of the saturated cyclohexane vapor (~3 s).

Denote the volume of the anisole in the droplet at time *t* is $V_a(t)$. We introduce the volume fraction *f*:

$$f(t) = \frac{V(t)}{V(t) + V_a(t)}$$
(S13)

and so

$$f_{\infty} = \frac{V_{\infty}}{V_{\infty} + V_{a\infty}}$$
(S14)

2.3 Interfacial energies

The interfacial surface tension between the substrate and droplet is,

$$\gamma_{sl}(t) = \gamma_{sl0}[1 - p_l(t)] + \gamma_{sl\infty}p_l(t)$$
(S15)

where γ_{sl0} and $\gamma_{sl\infty}$ are the interface tension between the substrate at t=0 and at the thermal equilibrium, respectively. That is, γ_{sl0} is the interfacial energy between the substrate and pure anisole, and $\gamma_{sl\infty}$ is the interfacial tension between the substrate and the droplet of mixed anisole and cyclohexane.

For approximation, we use the interfacial energy between the HMDS and anisole (γ_{HA}), and HMDS and cyclohexane (γ_{HCy}) the calculation.

$$\gamma_{sl0} \sim \gamma_{HA}$$
 (S16)

$$\gamma_{sl\infty} \sim \gamma_{HA} (1 - f_{\infty}) + \gamma_{HCy} f_{\infty}$$
(S17)

Similarly, the interfacial surface tension between the droplet and vapor is,

$$\gamma_{l\nu}(t) = \gamma_{l\nu0} [1 - p_l(t)] + \gamma_{l\nu\infty} p_l(t)$$
(S18)

where γ_{lv0} and $\gamma_{lv\infty}$ are the value of γ_{lv} at the beginning and the value at the thermal equilibrium. In a similar approximation, we can use the interfacial energy between the anisole and air (γ_{AA}), and that of cyclohexane and air (γ_{CyA}) for the calculation.

$$\gamma_{lv0} \sim \gamma_{AA} \tag{S19}$$

$$\gamma_{l\nu\infty} \sim \gamma_{AA} (1 - f_{\infty}) + \gamma_{CyA} f_{\infty}$$
(S20)

3. Evaporation process

The volume of anisole in the droplet is $V_{a}(t)$ (the subscript "a" stands for anisole). Denote the average evaporation rate of anisole is denoted as r_{e} , and the volume is approximately

$$V_a(t) = V_{a0} - r_e t$$
 (S21)

where V_{a0} is the initial volume of anisole droplet. The total volume of the whole droplet is then

$$V_{tot}(t) = V_{a0} - r_e t + p_l(t) \frac{f_{\infty}}{1 - f_{\infty}} V_{a\infty}$$
(S22)

In the main text we assume $r_e=0$ for stage 1. Then $V_{a0}=V_a(t)=V_{a\infty}$ and

$$V_{tot}(t) = V_{a0} \left[1 + p_l(t) \frac{f_{\infty}}{1 - f_{\infty}} \right]$$
(S23)

4. Contact angle of the droplet

Because spreading is slow (>100s), we can use Young's equation to calculate the contact angle. At any time *t*, the contact angle of the droplet on the substrate is

$$\cos\theta(t) = \frac{\gamma_{sv}(t) - \gamma_{sl}(t)}{\gamma_{lv}(t)}$$
(S24)

Substituting Eq. (S5), (S15), and (S18) into (S24) and so we calculate the contact angle, θ , at any time, *t*.

5. Radius of the droplet

We assume the liquid keeps the spherical shape in stage I. This assumption is validated as the droplet used in **Fig. 2** in the main text was found to be spherical. The radius of the sphere cap *r* and the radius of the droplet at the contact circle is R(t). The relation between *r*, *R*, and θ are illustrated as below.



Figure S12. Sphere cap with radius *r* of the sphere and the radius *R* of the circle of the contact line.

The *V*(t) can be calculated by the following equations:

$$R = r \cdot \sin \theta \tag{S25}$$

$$h = r \cdot (1 - \cos \theta) \tag{S26}$$

$$V = \frac{\pi h}{6} (3R^2 + h^2)$$
(S27)

Substituting Eqs. S25 and S26 into Eq. 27 and using $\tan \frac{\theta}{2} = (1 - \cos \theta) / \sin \theta$, we have,

$$V = \frac{4\pi}{3}r^3 \cdot (\cos\theta + 2)\left(\sin\frac{\theta}{2}\right)^4 = \frac{\pi}{6}R^3 \cdot \tan\frac{\theta}{2}\left(3 + \tan^2\frac{\theta}{2}\right)$$
(S28)

Hence the radius *R* can be calculated from the volume:

$$R(t) = \left[\frac{6V_{tot}(t)}{\pi \tan \frac{\theta(t)}{2}(3 + \tan^2 \frac{\theta(t)}{2})}\right]^{1/3}$$
(S29)

Substituting Eq. (S23) and (S24) into Eq. (S29), then we can calculate the radius R(t). All the parameters can be experimentally measured or estimated except the two fitting parameters τ_s and τ_l . They can be affected by the initial volume of the droplet, the volume of the petridish and environmental temperatures.

6. A further simplified approximation

In the case that r_e is sufficiently small, in equation (19) all the terms relating to t in R(t) are in the form of $\exp(-t/\tau_s)$ or $\exp(-t/\tau_l)$. If $\tau_s \ll \tau_l$, R(t) can be approximately expressed as $F(\exp(-t/\tau_l))$. By using Taylor series, we get

$$R\left(e^{-t/\tau_{l}}\right) = \sum_{n=0}^{\infty} a_{n} \left(e^{-t/\tau_{l}} - b\right)^{n} \sim C_{1} + C_{2} e^{-t/\tau_{l}} = R_{m} \left(1 - A e^{-t/\tau_{l}}\right)$$
(S30)

where R_{∞} and A are independent on time t, $R_{\rm m}$ is the radius at the end of stage I (the maximum), and τ'_1 is estimated value for τ_l (e.g., τ'_l is 77.6 s for the data in **Fig. 3a** in the main text).

Similarly, from Eq. (S18) $\cos \theta$ can also be approximately described by

$$\cos\theta(t) \sim \cos\theta_m \left(1 - Be^{-t/\tau_l'}\right)$$
(S31)

where *B* is constant at time *t* and θ_m is approximately the final contact angle in stage I (the minimum). Note that Eqs. (S30) and (S31) can only be used for rough estimating τ_l . They do not contain certain physical meanings.

7. Parameters used in the model

The interfacial tensions between two substances were estimated using their own surface tension or surface energy in the empirical formula proposed by Li and Neumann [⁹],

$$\gamma_{ls} = \gamma_l + \gamma_s - 2\sqrt{\gamma_l \gamma_s} exp^{[m]} [-0.0001247(\gamma_l - \gamma_s)^2]$$
(S32)

where γ_1 and γ_s are the surface tension/energy of the liquid and solid respectively. We note that using this alternate estimation method Eq. (S32) does not significantly change the fitted time constant τ_d (i.e. in the same order of magnitude), but only slightly changes the fitted f_{∞} . This is because the critical part of the model, Eq. (S8), gives a dependence on time e^{-t}.

liquid	Surface tension (20 ^o C) (mN/m)
water	72.80
anisole	36.18 (15°C)

cyclohexane	24.95
hexane	18.43
THF	26.40
chloroform	27.50
HMDS	32.0
SiO ₂	60.0
СҮТОР	19.0

References

1. Izawa, T.; Miyazaki, E.; Takimiya, K. Molecular Ordering of High-Performance Soluble Molecular Semiconductors and Re-evaluation of Their Field-Effect Transistor Characteristics. *Adv. Mater.***2008**, *20*, 3388-3392.

2. Starov, V. M.; Kosvintsev, S. R.; Velarde, M. G. Spreading of Surfactant Solutions over Hydrophobic Substrates. *J. Colloid Interface Sci.* **2000**, *227*, 185-190.

3. Lagergren, S. About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar***1898**, *24*, 1-39.

4. Ho, Y.-S.; McKay, G. Sorption of dye from aqueous solution by peat. *Chem. Eng. J.***1998**, *70*, 115-124.

5. Ho, Y.-S.; McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.***1999**, *34*, 451-465.

6. Ho, Y.-S.; McKay, G. Kinetic models for the sorption of dye from aqueous solution by wood. *Process Saf. Environ*.**1998**, *76*, 183-191.

7. Low, M. J. D. Kinetics of Chemisorption of Gases on Solids. *Chem. Rev.***1960**, *60*, 267-312.

8. Ho, Y.-S. Review of second-order models for adsorption systems. *J. Hazard. Mater.***2006**, *136*, 681-689.

9. Li, D.; Neumann, A. Contact angles on hydrophobic solid surfaces and their interpretation. *J. Colloid Interface Sci.* **1992**, *148*, 190-200.