Supplementary Information

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

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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 $\tau_s$.
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.
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 $f_\infty$ 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 ~7 μl) on CYTOP surface in cyclohexane vapor: experimental data (dots) and model fitting (line). The time constant $\tau_l$ is 435 s ($\tau_s < 15$ 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 $\tau_l$ is 41.7 s ($\tau_s < 10$ s). 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 $\tau_s$ (2, 5, 10, 20s), indicating dewetting (i.e. increasing contact angle) and spreading (i.e. decreasing contact angle). The value of $\tau_l$ is fixed at 100 s.
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 μA). 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 \( n_\infty \) (the subscript \( \infty \) 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 \( p_s(t) = \frac{n(t)}{n} \) (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 \(^3\),

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

(S4)

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

\[
\gamma_{sv}(t) = \gamma_{sv0}e^{-t/\tau_s} + \gamma_{sv\infty}(1 - e^{-t/\tau_s})
\]

(S5)

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

\[
\gamma_{sv0} = \gamma_{lv0} \times \cos \theta_0 + \gamma_{sl0}
\]

(S6)
The values of $\gamma_{sl0}$, $\gamma_{sl\infty}$, $\gamma_{lv0}$, and $\gamma_{lv\infty}$ will be estimated in the next section. And the contact angle at the beginning $\theta_0$ and at the end $\theta_{\infty}$ 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 \[^3\],

$$\frac{dV(t)}{dt} = k_1[V_\infty - V(t)]$$  \hspace{1cm} (S8)

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

$$\frac{dV(t)}{dt} = k_2[V_\infty - V(t)]^2$$  \hspace{1cm} (S9)

or the Elovich’s equation \[^7-8\],

$$\frac{dV(t)}{dt} = \delta e^{-k_3 V(t)}$$  \hspace{1cm} (S10)

where $V(t)$ is the transient volume at time $t$, and $V_\infty$ 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 2nd 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.

Table S1. Fitting results of Fig. S1 using equations (8)~(10).

<table>
<thead>
<tr>
<th>Fitting equation</th>
<th>1st order</th>
<th>2nd order</th>
<th>Elovich’s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Correlation coefficient</td>
<td>0.987</td>
<td>0.998</td>
<td>0.977</td>
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<tr>
<td>Fitted $V_\infty$ (ml)</td>
<td>0.73</td>
<td>0.87</td>
<td>-</td>
</tr>
<tr>
<td>Fitted $k$</td>
<td>0.02547</td>
<td>0.04258</td>
<td>5.484</td>
</tr>
<tr>
<td>Fitted time constant (min)</td>
<td>39.3</td>
<td>23.5</td>
<td>-</td>
</tr>
<tr>
<td>Measured $V_\infty$ (ml)</td>
<td>0.76</td>
<td>0.76</td>
<td>0.76</td>
</tr>
</tbody>
</table>

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 $V_\infty$, then

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

(S11)

Let the proportion between $V(t)$ and $V_\infty$ 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
\[ p(t) = 1 - e^{-t/\tau_l} \]  

(S12)

where \( \tau_l \) 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,

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

(S15)

where \( \gamma_{sl0} \) and \( \gamma_{sl\infty} \) are the interface tension between the substrate at \( t=0 \) and at the thermal equilibrium, respectively. That is, \( \gamma_{sl0} \) 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 (\( \gamma_{HA} \)), and HMDS and cyclohexane (\( \gamma_{HCy} \)) the calculation.

\[
 \gamma_{sl0} \sim \gamma_{HA}
\]  

(S16)
\[ \gamma_{\text{sl}\infty} \sim \gamma_{HA}(1 - f_\infty) + \gamma_{HCy}f_\infty \]  

(S17)

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

\[ \gamma_{lv}(t) = \gamma_{lv0}[1 - p_l(t)] + \gamma_{lv\infty}p_l(t) \]  

(S18)

where \( \gamma_{lv0} \) and \( \gamma_{lv\infty} \) are the value of \( \gamma_{lv} \) 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 \( (\gamma_{AA}) \), and that of cyclohexane and air \( (\gamma_{CyA}) \) for the calculation.

\[ \gamma_{lv0} \sim \gamma_{AA} \]  

(S19)

\[ \gamma_{lv\infty} \sim \gamma_{AA}(1 - f_\infty) + \gamma_{CyA}f_\infty \]  

(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

\[ V_{\text{tot}}(t) = V_{a0} - r_e t + p_l(t)\frac{f_\infty}{1-f_\infty}V_{a\infty} \]  

(S22)

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

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

(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, \( \theta \), 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 \( \theta \) 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:

\[
R = r \cdot \sin \theta
\]  

(S25)
\[ h = r \cdot (1 - \cos \theta) \]  
\[ V = \frac{\pi h}{6}(3R^2 + h^2) \]  

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

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

Hence the radius \( R \) can be calculated from the volume:

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

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 \( \tau_s \) and \( \tau_l \). They can be affected by the initial volume of the droplet, the volume of the petri-dish 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

\[ R(e^{-t/\tau_l}) = \sum_{n=0}^{\infty} a_n (e^{-t/\tau_l} - b)^n \sim C_1 + C_2 e^{-t/\tau_l} = R_m \left( 1 - Ae^{-t/\tau_l} \right) \]
where $R_{\infty}$ and $A$ are independent on time $t$, $R_m$ is the radius at the end of stage I (the maximum), and $\tau'_l$ is estimated value for $\tau_l$ (e.g., $\tau'_l$ 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

$$\cos \theta(t) \sim \cos \theta_m (1 - Be^{-\frac{t}{\tau'_l}}) \quad (S31)$$

where $B$ is constant at time $t$ and $\theta_m$ is approximately the final contact angle in stage I (the minimum). Note that Eqs. (S30) and (S31) can only be used for rough estimating $\tau_l$. 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],

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

where $\gamma_l$ and $\gamma_s$ 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 $\tau_d$ (i.e. in the same order of magnitude), but only slightly changes the fitted $f_{\infty}$. This is because the critical part of the model, Eq. (S8), gives a dependence on time $e^{-t}$.

Table S2. Surface tensions of liquids and solid surfaces.

<table>
<thead>
<tr>
<th>liquid</th>
<th>Surface tension (20°C) (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>72.80</td>
</tr>
<tr>
<td>anisole</td>
<td>36.18 (15°C)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>--------</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>24.95</td>
</tr>
<tr>
<td>hexane</td>
<td>18.43</td>
</tr>
<tr>
<td>THF</td>
<td>26.40</td>
</tr>
<tr>
<td>chloroform</td>
<td>27.50</td>
</tr>
<tr>
<td>HMDS</td>
<td>32.0</td>
</tr>
<tr>
<td>SiO₂</td>
<td>60.0</td>
</tr>
<tr>
<td>CYTOP</td>
<td>19.0</td>
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References


