Supplementary Information for

How liquid-liquid phase separation induces active spreading

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Other supplementary materials for this manuscript include the following:
- Movies S1 to S5


**Supplementary Movies**

Movie S1. A 1µL droplet of DPnP-water mixture (φ = 0.1) heated on a completely wetting substrate. The heating starts from 25°C at a rate of ~1.8°C/s. The movie plays at real time.

Movie S2. Similar to Movie S1, but on a partially wetting substrate.

Movie S3. A 0.5µL droplet of PG-water mixture (φ = 0.5) on a completely wetting substrate. The heating starts from 25°C at a rate of ~1.8°C/s until the surface temperature reaches ~60°C. The movie plays at real time.

Movie S4. A high-resolution movie showing that the contact line advances first and microdroplets appear later. The movie starts at 0.2s before droplet spreading, and plays at 0.2× real time.

Movie S5. A 1.5µL droplet of DPnP-water mixture (φ = 0.8) heated on a completely wetting substrate. The heating is triggered from 25°C with a rate of ~1.8°C/s. The movie plays at real time.

**Supplementary Table**

| Name  | Mw     | ρ (g/cm³) | p_v (mmHg) | γ (mN/m) | Molecular structure |
|-------|--------|-----------|------------|----------|---------------------|
| DPnP  | 176.25 | 0.916     | 0.12       | 27.8     |                     |
| TPnP  | 234.33 | 0.935     | 0.0002     | 27.6     |                     |
| DPnB  | 190.28 | 0.913     | 0.068      | 28.4     |                     |

* Mw: molecular weight; ρ: density; p_v: vapor pressure; γ_LV: surface tension; µ: viscosity.
† For another component of binary droplets, H_2O, p_v = 23.8 mmHg and γ_LV ~ 72.4 mN/m at 25 °C.
‡ The LCST of DPnP-water mixture is 13.8°C at the DPnP mass fraction φ ~ 0.4 (2).

**Supplementary Figures**

![Fig. S1. Experimental phase diagrams, temperature T vs. mass fraction φ of mixture of water and three different glycol ethers: di(propylene glycol) propyl ether (DPnP; green circles), tri(propylene glycol) propyl ether (TPnP; red squares), and di(propylene glycol) butyl ether (DPnB, blue diamonds), (data from Ref. (2)).](image-url)

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Fig. S2. Droplet radius $R$ (symbols) and temperature $T$ (red lines) versus time $t$ for non-phase-separating PG-water binary droplets ($\phi = 0.5$). (a) Heating from 25 °C to ∼ 50 °C at a rate of ∼ 0.9 °C/s, with droplet size of around 1 µL. (b) Constant temperature of 25 °C, with droplet size of around 0.8 µL. Note the generally different time scales from the phase-separating cases.

Fig. S3. The apparent viscosities $\mu$ of water-rich ($\phi = 0.1$, a) and DPNP-rich ($\phi = 0.9$, b) binary mixture as a function of temperature $T$. The viscosity of water-rich mixture reaches a minimum at around $T \sim 40$ °C due to the phase-separated microdroplets. No apparent increase of viscosity of DPNP-rich mixture is seen, which is probably due to the minor effect of emulsion droplets compared to that of temperature.
Fig. S4. (a) Estimated capillary velocity \( U_{\text{cap}} = \frac{\gamma_{LV}}{\mu} \) of DPNP-water mixtures, water, toluene and PG-water mixture at the temperature of spreading. We assume that the effect of temperature on surface tension is insignificant, and adopt surface-tension values at room temperature \( T \sim 20 \^\circ C \). For the PG-water mixture, we use viscosity and surface tension of pure PG (4) to estimate the lower bound for the capillary velocity, corresponding to an upper bound of the capillary number (Fig. 2C in the main text). (b,c) Range of possible capillary numbers (gray shadows) for DPNP-water mixtures, based on capillary velocities obtained from water-rich (\( \phi = 0.1, 0.15 \), light & dark green circles, respectively) and DPNP-rich (\( \phi = 0.9 \), transparent light & dark green circles, respectively) mixtures at the temperature of spreading. In (b), the droplet spreads at \( T \sim 37 \^\circ C \); In (c), the droplet spreads at \( T \sim 25 \^\circ C \).

| \( \phi \)   | \( \mu^T \) (mPa.s) | \( \gamma_{LV} \) (mN/m) | \( U_{\text{cap}} \) (m/s) | Symbols |
|-------------|---------------------|--------------------------|--------------------------|---------|
| 0.10        | 0.87 \^\circ C      | 34.87                    | 40.08                    |         |
| 0.90        | 4.25 \^\circ C      | 27.71                    | 6.52                     |         |
| 0.15        | 1.72 \^\circ C      | 30.85                    | 17.94                    |         |
| 0.99        | 6.64 \^\circ C      | 27.71                    | 4.17                     |         |
| Water       | 1.06 \^\circ C      | 72.36                    | 68.26                    |         |
| Toluene     | 0.58 \^\circ C      | 28.52                    | 49.17                    |         |
| Pure PG     | 10.7 \^\circ C      | 38.57                    | 3.60                     |         |

Fig. S5. (a) The normalized maximal intensity contrast in the contact line region used to identify the visible nucleation event. The contrast signal grows rapidly at \( t_v \approx t_s + 0.44 \) s, where \( t_v \) and \( t_s \) represents the onset of visible microdroplet formation and of abrupt spreading, respectively. (b) The corresponding high-resolution images showing the motion of advancing contact line, followed by the visible microdroplet coarsening. The scale bar is 50 \( \mu \)m.
Fig. S6. Abrupt spreading of phase-separating binary droplets with different heating rates, mass concentrations, and glycol ethers. (a) Parameters of the measurements shown in (b,c). (b1 & b2) Droplet radius $R$ versus $t$, red vertical lines indicate the onset of spreading at $t = t_s$, with (b1) and without heating (b2). Note the different scales on the abscissae. (c) Normalized intensity signals to identify the onset of visible coarsening, as a function of $t - t_s$ to visualize the delay. In all experiments, the heating is triggered from 25 °C at $t = 0$, and the droplet size is around 1 µL.

Fig. S7. Schematic showing the on-site ellipsometric measurement of the precursor-film dynamics and simultaneous top-view monitoring of the main drop (not to scale). Here, $\alpha_i$ and $d$ refer to the angle of incidence and the distance between the center of laser spot and macroscopic contact line, respectively. The inset shows a typical experimental image captured from the top-view camera.
Fig. S8. (a) Dependence of ∆ and tanΨ on the angle of incidence αi before (red squares) and after (blue circles) droplet deposition on a fully wetting substrate. For αi around 57.5°, where ∆ is around 135°, ∆ is most sensitive to adsorption. (b,c) Change of ∆ when a droplet is suspended above (b) and deposited on (c) the substrate, where αi = 57.5°. Here, droplets are made up of DPhNP and water (φ = 0.1) with size of 5 µL, and the detection distance d to droplet edge is around 5 mm. A decrease of ∆ can be observed in both cases, followed by slight fluctuations, indicating that the development of precursor film is given by the evaporation-condensation mechanism (5, 6).

Fig. S9. The profile of ∆ (circles) and T (red line) as a function of t − ts for a high heating rate: 1.2 °C/min. No obvious increase of ∆ can be observed before droplet spreading.
Fig. S10. (a,b) Additional wettability test of DPnP-rich and water-rich droplets under/on plasma-treated (a) and ethanol-cleaned (b) cover glasses. All scale bars are 0.5 mm. (c) $\theta_{app}$ versus $t$ showing water-rich droplets spreading on the plasma-treated (red squares) and pinning on the ethanol-cleaned (blue diamonds) substrates. Note that the hydrophilic surfaces applied in Fig. 4 of the main text were all cleaned by piranha solutions.

References

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