

Figure S1: Optical micrographs of carbon tetrabromide crystals growing at each site shown in Figure 3. Here and in Figures S2–S4 the leftmost image shows an electron micrograph of each site, with the symbols inset into each designating the substrate as in Figure 3 to Figure 6. The three subsequent optical micrographs then show one experimental run featuring growth at that site: the leftmost image being before observed nucleation, the central one showing the first evidence of nucleation (indicated by a white arrow where it is not obvious) and the final image showing a developed crystal. Note that these optical micrographs are small parts of the full images obtained. Each has a scale of 330  $\mu$ m across its long side. The black rectangle in the bottom left of the leftmost optical image represents the scale of the adjacent electron micrograph for reference



Figure S2: Optical micrographs of camphor crystals growing at each site shown in Figure 4. See Figure S1 for details



Figure S3: Optical micrographs of norbornane crystals growing at each site shown in Figure 5. See Figure S1 for details. The black scale rectangle is reduced to two sides where it would otherwise obscure the view, and on one sample moved to the electron micrograph to represent the scale of the optical micrograph



Figure S4: Optical micrographs of hexachloroethane crystals growing at each site shown in Figure 6. See Figure S1 for details

## Quantitative comparison of substrate efficacy

Figures S5–S8 show the saturation of vapour within the cell, with respect to a crystal growing on the mica surface, at the time of each first observed nucleation for carbon tetrabromide, camphor, norbornane and hexachloroethane respectively. The different symbols designate particular substrates and agree with those used in Figure 3 to Figure 6. Vertical errors only are shown in the graphs as these include a contribution from the measurement error in the substrate temperature.

Carbon tetrabromide exhibited clear differences between the five substrates, with  $\diamond$  and  $\bigcirc$  nucleating at the lowest saturations, followed by  $\Box$ , then  $\blacklozenge$  and finally  $\blacksquare$  showing much greater nucleation saturations.

For camphor, there was very little quantitative difference between most of the eight substrates. However,  $\diamond$  and particularly  $\blacklozenge$  required lower saturations, and many of the results for  $\blacklozenge$  also seem to show a similar effect.

The saturation required to initiate norbornane crystallisation was highly dependent on the temperature of the mica substrate; presumably, if the substrate was not sufficiently cooler than the Teflon walls then crystals would nucleate on these, partially depleting the vapour phase. The mica needed to be cooled below room temperature, and some substrates needed to be cooled more than others to ensure nucleation. In particular  $\bullet$  needed a much cooler substrate for nucleation to be observed, suggesting that it was significantly less effective at promoting nucleation. Nucleation was observed on only six of the twelve runs on  $\bullet$ , and on three of the twelve runs on  $\blacktriangle$ . On all other substrates nucleation was observed every time. With the exception of  $\bullet$ , which required a larger saturation in order to induce nucleation, very little difference was seen between the substrates.

With hexachloroethane only small differences were seen between six of the eight substrates. However  $\Box$  and  $\blacktriangle$  required supersaturations around two and six times greater respectively than these substrates before nucleation was observed. It is thought that the results for  $\blacktriangle$  are likely to be anomalous, possibly resulting from an improperly sealed chamber.

For norbornane and hexachloroethane, little quantitative difference is observed in the ability of the two substrates common to all compounds ( $\diamond$  and  $\blacklozenge$ ) to promote nucleation, as can be seen in Figures S7 and S8. However, as can be seen from Figures S5 and S6, camphor nucleation occurs preferentially on  $\blacklozenge$  over  $\diamondsuit$ , whereas carbon tetrabromide shows the opposite effect.

There were several substrates on which no potential nucleation sites other than flat mica and step edges were available. These were: for carbon tetrabromide,  $\blacksquare$ ; for camphor,  $\triangle$ ; and for norbornane,  $\Box$ ,  $\bullet$  and  $\blacktriangle$ . There were none for hexachloroethane, however  $\Box$  would have been in this category but for what appears to be some foreign contaminant on the surface. It can be seen that several of these samples have higher saturation at nucleation than others with the same compound. Only one substrate containing more convoluted features was observed to nucleate a compound at a significantly higher saturation than one of these substrates: hexachloroethane substrate  $\blacktriangle$ .



Figure S5: Estimated vapour saturation at first observed nucleation of carbon tetrabromide on five mica substrates. Figure 3 shows electron micrographs of the dominant sites on these substrates



Figure S6: Estimated vapour saturation at first observed nucleation of camphor on eight mica substrates. Figure 4 shows electron micrographs of the dominant sites on these substrates



Figure S7: Estimated vapour saturation at first observed nucleation of norbornane on eight mica substrates. Figure 5 shows electron micrographs of the dominant sites on these substrates



Figure S8: Estimated vapour saturation at first observed nucleation of hexachloroethane on eight mica substrates. Figure 6 shows electron micrographs of the dominant sites on these substrates







Figure S10: Scanning electron micrographs of sites on substrate  $\blacklozenge$ , with site type designations