Supplementary Information for
“Direct observation of anthracene clusters at ice surfaces”

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Mapping was performed using a Renishaw Invia Basis confocal Raman spectroscope equipped with a 20 mW ultra-violet (UV) nearly Gaussian laser (model: Cobolt ZoukTM series) of wavelength (354.8 ± 0.3) nm and a long working distance objective (Olympus, model LUCPLFLN40X) of numerical aperture 0.6. The instrument is calibrated with a 2400 line/mm diffraction grating and a 1040 × 256 pixel charge coupled device (CCD) detector. The objective focuses the laser to a sub-micron spot at its beam-waist and emission from the spot is acquired using the same objective for spectral analysis. The confocality settings for all measurements were: 65 µm slit-width at the confocal plane and 16 transverse pixels for binning the photoelectrons in the CCD. For the extended spectra shown in Figure 1 of the manuscript, 100% laser power and 30 s integration time were used. For mapping the distribution of anthracene on the frozen surfaces, an area of 300 × 300 µm at the focal plane was scanned at 3 µm step size and 0.5 s integration at each point. In a single, static acquisition, emission over a ~42 nm range can be collected if the centre of detection is at ~400 nm, covering the peaks at 380 nm to 420 nm. Maps were created by acquiring spectra in this static range at all coordinates in the scanned area. The extended spectra as shown in Figure 1(c) were not acquired during mapping owing to impractically long scan durations.

FIG. S1: Typical fluorescence spectra of anthracene on frozen surfaces showing the presence (red) and absence (blue) of monomer emission. The black dashed line is a 2nd order fitting of the profile in red in the range 378 – 390 nm to determine whether a fluorescence peak is observed. If the maximum of the fitted polynomial is observed between 378 nm and 382 nm, it is considered as fluorescence peak and is attributed to presence of monomer. For the spectrum in blue, no peak is observed at around 380 nm.
FIG. S2: Fluorescence intensity at 380 nm as a function of anthracene deposition time. The red circles indicate measured normalized intensities, and the black dashed line represents the exponential fit used to determine the deposition rate. We assume that the intensity plateaus when a monolayer is formed. Following the analysis by Mmereki et al., the data is fitted to an exponential rise to saturation, with the assumption that the asymptote in the intensity vs. time profile indicates formation of a complete monolayer. Our exponential fitting yields an observed rate constant of $k_{obs} = (0.06 \pm 0.02) \text{ s}^{-1}$ on a water surface, such that for a deposition duration $t$, the fraction of a monolayer formed is $(1 - e^{-k_{obs}t})$. Thus, total deposition times of 1, 5, 21, and 85 s correspond to $(6 \pm 2)\%$, $(25 \pm 8)\%$, $(67 \pm 14)\%$ and $(98 \pm 2)\%$ of a monolayer at the liquid water surface respectively.
Anthracene distribution on frozen surfaces

1-octanol (-20 °C)

DI water (-15 °C)

0.6 M NaCl (-15 °C)

Percent of formal monolayer deposited (%)

0 ± 2

67 ± 14

98 ± 2

FIG. S3: Distribution of anthracene across 300 × 300 µm areas of frozen surfaces after various periods of gas-phase anthracene deposition. For 1-octanol, intensity of the monomeric peak at around 380 nm is mapped and for ice and frozen NaCl solution, intensity at 420 nm is mapped. Due to the wide dynamic range of 10^5:1 of the detector and that of the fluorescence intensities among different samples and deposition times, the intensity maps are shown in log scale. The typical noise floor of the measurement is 10 counts at the experimental configurations, and hence \( \log_{10}(10) = 1 \) is subtracted from each intensity value. This ensures that counts lower than 10 are represented by 0 in the color-bar, while spectra with higher counts are shown on the maps with values on the colour bar ranging from 0 to 4 to represent counts between 10 and 10^5.
FIG. S4: Distribution of anthracene on the surface of frozen 0.2 μM aqueous solution at -15 °C. As with experiments in which anthracene was deposited to ice surfaces from the gas phase, anthracene distribution was in the form of clusters, and emission at 380 nm was not detected (FIG. 1(c) of the main manuscript). Due to the wide dynamic range of $10^5$ of the detector and that of the fluorescence intensities among different samples and deposition times, the intensity maps are shown in log scale. Intensities lower than ~0.5 on the log scale likely arise from anthracene molecules below the ice surface.
FIG. S5: Temporal evolution of anthracene emission intensity at 380 and 420 nm during and following gas-phase deposition to an ice surface at -15°C. The shaded regions represent the 95th percentile for three separate experiments. The green trace denotes the time period in which the ice sample was exposed to gas-phase anthracene. The sloped regions of this trace indicate periods in which gas phase anthracene concentrations within the microscopy chamber were increasing and decreasing. Within ~60 s of anthracene deposition, intensity at 380 nm increased until deposition was halted. At this point, fluorescence intensity plateaued and then decreased to levels below the noise floor. Intensity at 420 nm also increased during deposition, but with a lag compared to intensity at 380 nm. Intensity at 420 nm continued to increase after gas phase deposition ceased, and only began to decrease after intensity at 380 nm was negligible. This strongly suggests that anthracene adsorbs to the ice surface as monomers, then self-associates at the ice surface to form excimers and clusters.
References

1. Mmereki, B. T., and Donaldson, D. J., “Direct observation of the kinetics of an atmospherically important reaction at the air-aqueous interface”, *J. Phys. Chem. A*, 107, 11038-11042, 2003.

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