Oxygen Incorporation in Rubrene Single Crystals

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Supporting Information

XPS

XPS shows that the surfaces of these crystals display no elemental signature other than carbon and do not readily react with ambient gases (Fig. S1), provided exposure to visible light is minimized. Rubrene that has been stored in the dark for periods of up to a year shows only a single carbon peak around 285 eV, (~1 atomic % of oxygen is the detection limit). Despite thicknesses on the order of 100 – 1000 µm, XPS does not display electrical charging, consistent with a high-mobility material. However, a week long exposure of rubrene to the standard indoor fluorescent lighting in air results in a noticeable oxygen signal and a small rigid shift in apparent binding energy (of all photoemission peaks) common to insulators (Fig. S1, green curve). Some oxygen, corresponding to less than a monolayer of rubrene peroxide, is also detected by XPS in about 24 hours under these photo-oxidation conditions (Fig. S1, inset). This oxygen is most likely covalently bound to rubrene as the intensity of the oxygen peak remains unchanged for samples kept in UHV for several days. This is further corroborated by the high binding energy shoulder present in the carbon 1s spectrum (Fig. S1, right panel) which is indicative of oxidized carbon. We emphasize that multiple experiments indicate that the rate of photo-oxidation appears to vary significantly depending on the crystal quality. This may be related to the variations of the density
of surface defects, bulk structural defects or compositional impurities in the crystals grown at different conditions.

The unit cell of single crystal rubrene contains 4 molecules in a volume of approximately $2.8 \times 10^{-21}$ cm$^3$ ($2800$ Å$^3$). If a monolayer of rubrene were fully oxidized to the endoperoxide (C$_{42}$H$_{28}$O$_2$) state in the top monolayer, this would correspond to an oxygen-to-carbon ratio, O/C, of about 0.05 (5 atomic %), the level shown in the inset in Fig. S1 by the horizontal red line. Assuming for simplicity that rubrene peroxide has a similar unit cell volume as rubrene, we can estimate the atomic concentration of oxygen at the surface in the case of a full monolayer of peroxide covering the crystal surface, $\sim 2.8 \times 10^{21}$ atoms/cm$^3$. As shown in the main paper, oxygen penetrates into the bulk of the crystal; therefore the xps peak area includes the O signal per layer.

Figure S1: XPS spectra of rubrene single crystals. The duration of exposure to air in the dark ranges from one week to one year (black, red and blue curves), and one week under illumination with a visible indoor fluorescent light (green curve). In the absence of light, rubrene crystals remain inert to atmospheric gases independent of the duration of exposure. However, combined with an exposure to visible light yields an oxygen signal at $\sim 530$ eV (green curve). Inset: dependence of atomic ratio O/C on the exposure time of rubrene to indoor lighting in air. The horizontal red line corresponds to the O/C level of a monolayer of rubrene peroxide, C$_{42}$H$_{28}$O$_2$, covering the entire surface. The figure on the right shows the detailed scan of the region corresponding to carbon. The photo-oxidized sample clearly shows a shoulder on the higher binding energy portion of the main peak. This indicates the presence of oxidized carbon species.

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attenuated by the escape depth of the oxygen. The XPS data suggest that the amount of oxygen at the surface of pristine rubrene crystals is much smaller than a monolayer of endoperoxide, even for the samples exposed to air for as long as a year.

**SIMS and SRIM calculation and ion implantation profile**

Calibration of the oxygen SIMS data was achieved using an ion implanted standard (see Fig. S2 below). A rubrene standard was prepared through $^{18}$O-ion implantation with beam energy of 80 keV and a dose of $1 \times 10^{15}$ atoms/cm$^2$. Fig. S2 depicts a typical SIMS depth profile used in calibration. This profile is in good agreement with the stopping and range of ions in matter (SRIM, www.srim.org) simulations for hydrocarbons with densities similar to that of the ideal single crystal rubrene. The slight shift between the actual and calculated depth profiles is possibly due to sample sputtering that occurred during the ion implantation.

![Figure S2](image)

**Figure S2**: Comparison between the depth profile of $^{18}$O ion implanted rubrene standard and SRIM calculations.

**Grand Canonical Monte Carlo Simulations**
OPLS-AA forcefield was used for rubrene. Carbons and hydrogens were modelled as Lennard-Jones particles with the following parameters: $\varepsilon_C/k_B=35.35\,\text{K}$, $\sigma_C=0.355\,\text{nm}$, $\varepsilon_H/k_B=15.15\,\text{K}$, $\sigma_H=0.242\,\text{nm}$. Simulation cell contained 8 (2×2×2) rubrene lattice cells shown in Fig.3 (main text, right panel). All atoms of the solid matrix were immobile, and the atomic coordinates and crystalline lattice parameters were taken from XRD data at ambient conditions. First, we considered sorption of Argon modeled as a single Lennard-Jones particle with parameters $\varepsilon/k = 120\,\text{K}$, $\sigma = 0.34\,\text{nm}$ at normal boiling temperature of 87.3K. Lorentz-Berthold combining rules were applied to calculate solid-fluid Lennard-Jones parameters. Even at the equilibrium bulk pressure of 100atm, Ar sorption in rubrene crystal was found negligible. We proceeded by considering smaller sorbate molecules: oxygen ($\sigma = 0.297\,\text{nm}$) and then He ($\sigma = 0.258\,\text{nm}$). Even at high equilibrium bulk pressures, sorption was found to be close to zero. Thus, Monte Carlo modeling shows that rubrene crystal has no intrinsic porosity.

**Temperature Dependence of Rubrene Photo-oxidation**

For this experiment the photo-oxidation conditions were as described in the text with an illumination time of 24 h. Heating was achieved by wrapping the oxidation chamber with an electrical heating tape. The temperature was monitored by a thermocouple located inside the chamber near the sample. The heating commenced with illumination and equilibrium temperatures for all samples were reached within 2 h. Interestingly, the decrease in bulk $^{16}\text{O}$ (Fig. S4, right) observed in samples photo-oxidized at elevated temperatures was not observed in the crystal heated for 24 h. in the dark (e.g., not photo-oxidized).
**Figure S3:** AFM images of a rubrene crystal heated at 85 °C for 24 h in oxygen atmosphere under illumination (left) and in the dark (right).

**Figure S4:** Comparison of $^{16}$O levels in rubrene samples. These levels remain approximately the same for pristine crystals and crystals photo-oxidized near room temperature (left). However, a systematic decrease in this baseline level is demonstrated for crystals photo-oxidized in environments with increased temperatures (right).