EXPERIMENTAL

Structural characterization

The typical average thickness of the in vacuo grown picene films as monitored by a quartz crystal microbalance (QCM) was 30 nm. The actual film topography as measured by atomic force microscopy (AFM) shows that the film consists of picene islands with typical lateral dimensions of several 100 nm and heights of up to 80 nm (Fig. S1 (a)). Such 3D island growth mode is expected on an inert substrate (here: chemically cleaned and oxidized Si(100)). While the individual islands are crystalline, the overall film appears azimuthally disordered with well-developed texture along the c-axis, i.e., perpendicular to the surface, as inferred from the sharp Bragg peaks in the x-ray diffractogram (XRD) in Fig. S1 (b). The resulting c-axis parameter of 13.51 Å confirms that the molecules grow in a standing mode.

Doping concentration

The atomic K concentration \( x \) of the doped picene films (K\(_x\)picene) has been determined from the intensity ratio of the C 1s and K 2p photoemission core level spectra, taking into account the relative photoionization cross sections. The latter is essentially an atomic property and has experimentally been calibrated by independent photoemission measurements of K-intercalated fullerences (K\(_3\)C\(_{60}\)), which is an easily reproducible compound of well-defined stoichiometry. Note that the relative cross-section ratio \( \sigma_{C1s}/\sigma_{K2p} \) thus determined is about 30 % smaller than the value obtained from the theoretical cross-sections of Yeh and Lindau [1]. This implies that previous photoemission studies which use the calculated values overestimate the K concentration by the same amount.
FIG. S2: Photoemission spectra of Kₚicene in a range of ∼5 eV of the HOMO region for various K-doping concentrations. Spectra are shown for x = 0...3. (a) energies as measured, (b) energetically aligned on the spectral features of the x = 3 compound.

Non-equilibrium effects

Figure S2(a) shows a series of valence band spectra as measured for a full range of K concentrations from x = 0 to 3. The main effect at low doping (x < ∼1) is a shift of the overall spectrum away from the experimental Fermi energy µ_exp (which corresponds to the kinetic photoelectron energy where a metal in electrical contact with the sample would display its Fermi edge) and the appearance of a small peak (F₁) in the former band gap. Closer inspection reveals that most of its spectral weight is actually located well above the Fermi energy for x = 0 and only gradually moves below µ_exp with larger doping, until the peak finally converges to a constant binding energy for x > ∼1, resulting in a gapped spectrum. This anomalous behavior clearly signals a non-equilibrium situation where a homogeneous chemical potential cannot be defined in the film-substrate system in the early doping stages. A possible explanation by a surface photovoltage (SPV), often encountered in metal-semiconductor contacts, can be ruled out, because we do not observe the characteristic temperature and intensity dependence of the SPV [2–5].

A detailed analysis of identical behavior in another alkali metal-doped organic semiconductor (para-sexiphenyl) has demonstrated that it can be traced back to the inability of a purely van der Waals-coupled molecular system to establish an equilibrium chemical potential throughout the film [6]. In such a situation the energy alignment refers rather to the vacuum level and thus depends on work functions. Charge fluctuations induced by alkali-metal doping will restore thermodynamical equilibrium. Note however, that our potassium deposition method leads to a concentration gradient which decays from the surface into the film. Low K dosage then leads to a doped Kₚicene surface layer with little or even no K present deeper in the film, maintaining the non-equilibrium situation described above. For higher concentrations the film will become doped throughout, hence restoring a well-defined chemical potential. The observed effect should be less pronounced for thinner films, as is indeed the case for the photoemission results of Mahns et al. [7].
We thus take our $x = 3$ data as an intrinsic equilibrium spectrum and have energetically realigned all other spectra at its spectral features in Fig. S2(b), showing gapped behavior for all concentrations. The observation of spectral weight near the Fermi level reported by Okazaki et al. [8] for a nominal doping of $x = 1$ is attributed to the non-equilibrium behavior of peak $F_1$, which also explains why a clear Fermi edge could not be identified in that study.

**STRUCTURE PREDICTION**

The relaxation of $K_x$picene candidate structures was performed using Fast Inertial Relaxation Engine (FIRE) algorithm [9], employing Vienna Ab-initio Simulations Package (VASP) [10, 11] with the Projector Augmented Wave basis (PAW) [12, 13] in the Generalized Gradient Approximation (GGA) as a force and stress tensor calculator with plane-wave cutoff of 400 eV and Brillouin zone sampled by Monkhorst-Pack $k$-point mesh of $5 \times 5 \times 5$ $k$-points. Structures were relaxed until the maximal force acting on ions and maximal stress tensor component fell below 0.01 eV/Å and 0.01 GPa, respectively. Fig. S3 shows the structures we obtained. We have compared our structures to theoretically obtained lattice parameters published in Ref. 14. Obtained equilibrium volumes agree with our results within 2% in all cases, but there are some discrepancies in lattice parameters and angles. Without detailed knowledge of the structures in Ref. 14 it is not possible to say anything further on the degree of agreement.

**DETAILS OF DYNAMICAL MEAN FIELD THEORY CALCULATIONS**

We align Fermi levels of DFT spectra with active bands removed and DMFT spectral functions at $E = 0$. While the DFT Fermi level is known for $K_1$picene and $K_3$picene, as they are metallic, and for $K_2$picene with an error bar given by the tiny energy gap of 60 meV, the DMFT chemical potential follows from the demand that the filling is unchanged compared to the DFT calculation.