Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplemental Material:

Interface properties and dopability of an organic semiconductor: TAPP-Br variable as molecule but inert in the condensed phase

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1 Modelling of the dielectric function of MoO_3 and Ca.

MoO_3 ($\varepsilon_\infty = 3.1$, determined by using IR ellipsometry[1]) is described by 4 Brendel-oscillators in the range from 650 cm^{-1} to 2700 cm^{-1} as shown in Fig. 2b in the paper. For modelling the mixed layers, additional oscillators were added in the range of the molybdenum absorption below 1000 cm^{-1} to minimize uncertainties of the changed TAPP-Br component. Ca in the IR was described by a Drude-model

$$\varepsilon(\omega) = 1 - \frac{\omega_\mathrm{p}^2}{\omega^2 + i\omega\omega_\tau}, \qquad \text{(S1)}$$

in which ω_p describes the plasma frequency and ω_τ the electronic damping. Simultaneously fitting the relative transmittance spectra for thicknesses above 20 nm yields the Drude parameters $\omega_\mathrm{p} = 36750$ cm^{-1} and $\omega_\tau = 859$ cm^{-1}. Selected Ca fits are shown in Fig. S2.

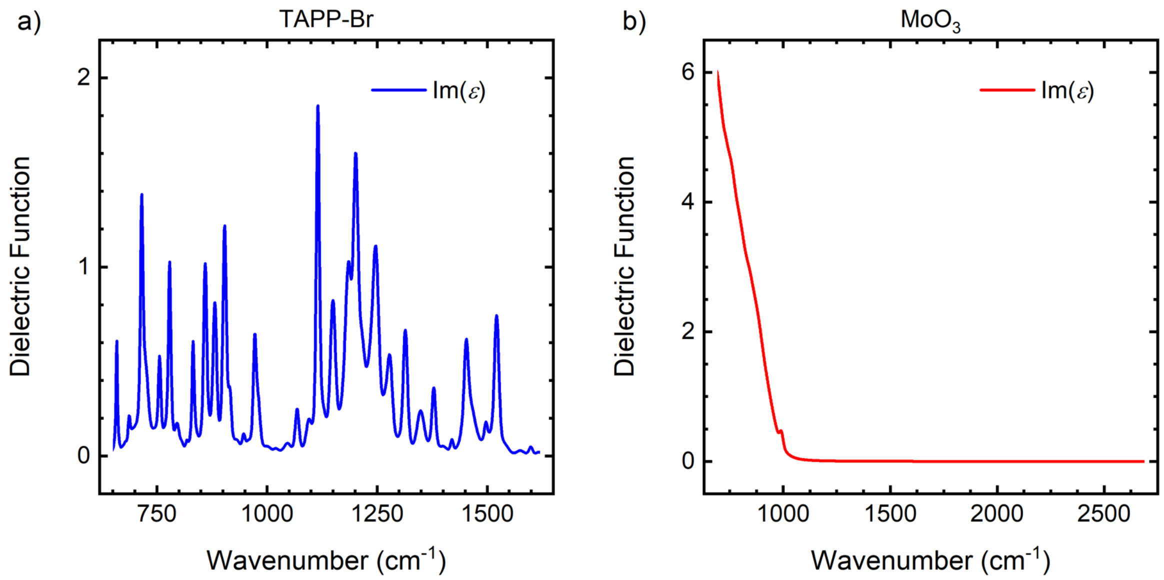

Fig. S1 Imaginary part of the dielectric functions which directly result from the model building shown in Fig. 2a,b in the paper.

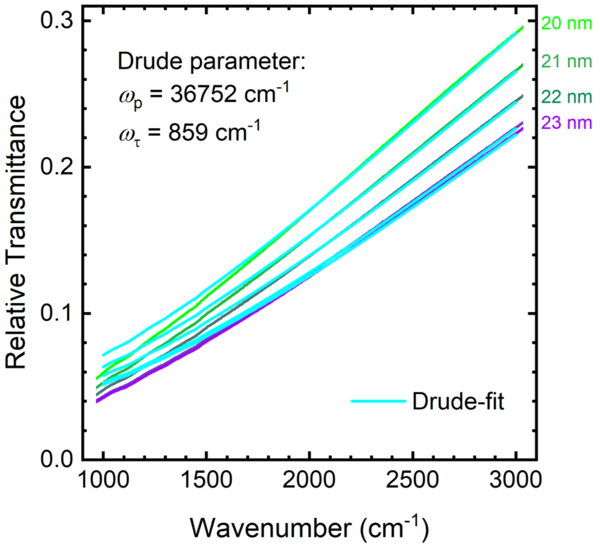

Fig. S2 Relative IR transmittance of Ca on silicon for particular thicknesses along with a Drude-fit (cyan lines). The data was adopted from Fig. 2c (see paper).

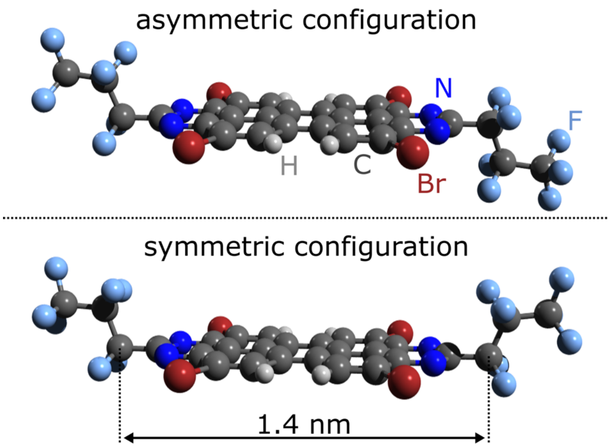

Fig. S3 Schematic representation of the TAPP-Br molecule. In the upper panel, the asymmetric configuration of the C_3F_7 side chains is shown. The lower panel shows the symmetric configuration of the side chains.

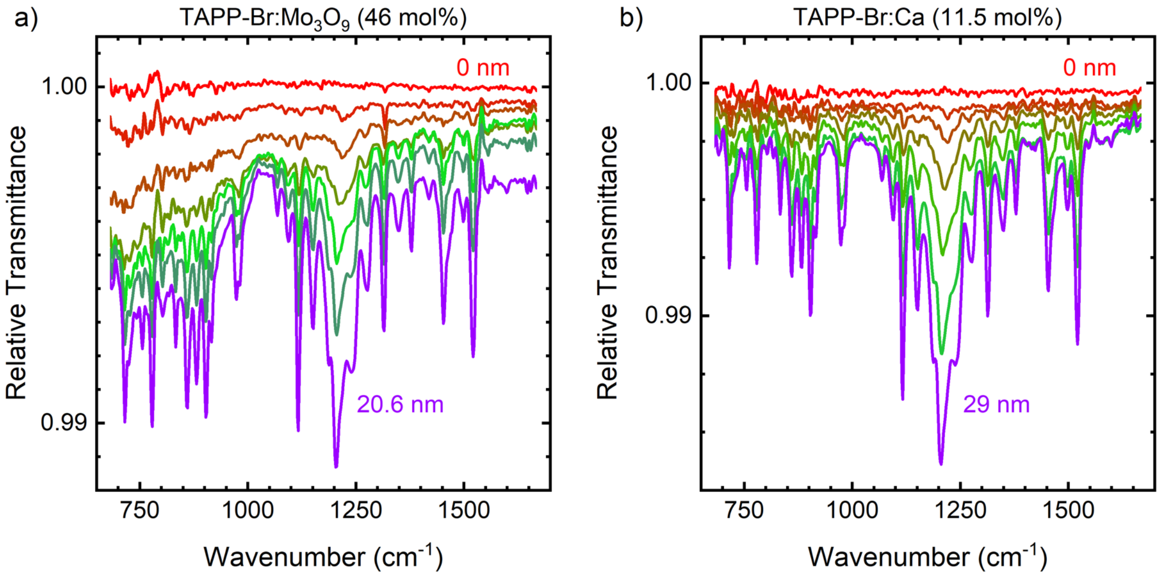

Fig. S4 Development of relative transmittance during co-evaporation of a) TAPP-Br and MoO_3 for a concentration of 46 mol% Mo_3O_9 and b) TAPP-Br and Ca for a concentration of 11.5 mol% Ca. The thickness of the total layer stack on SiO_x/Si is given.

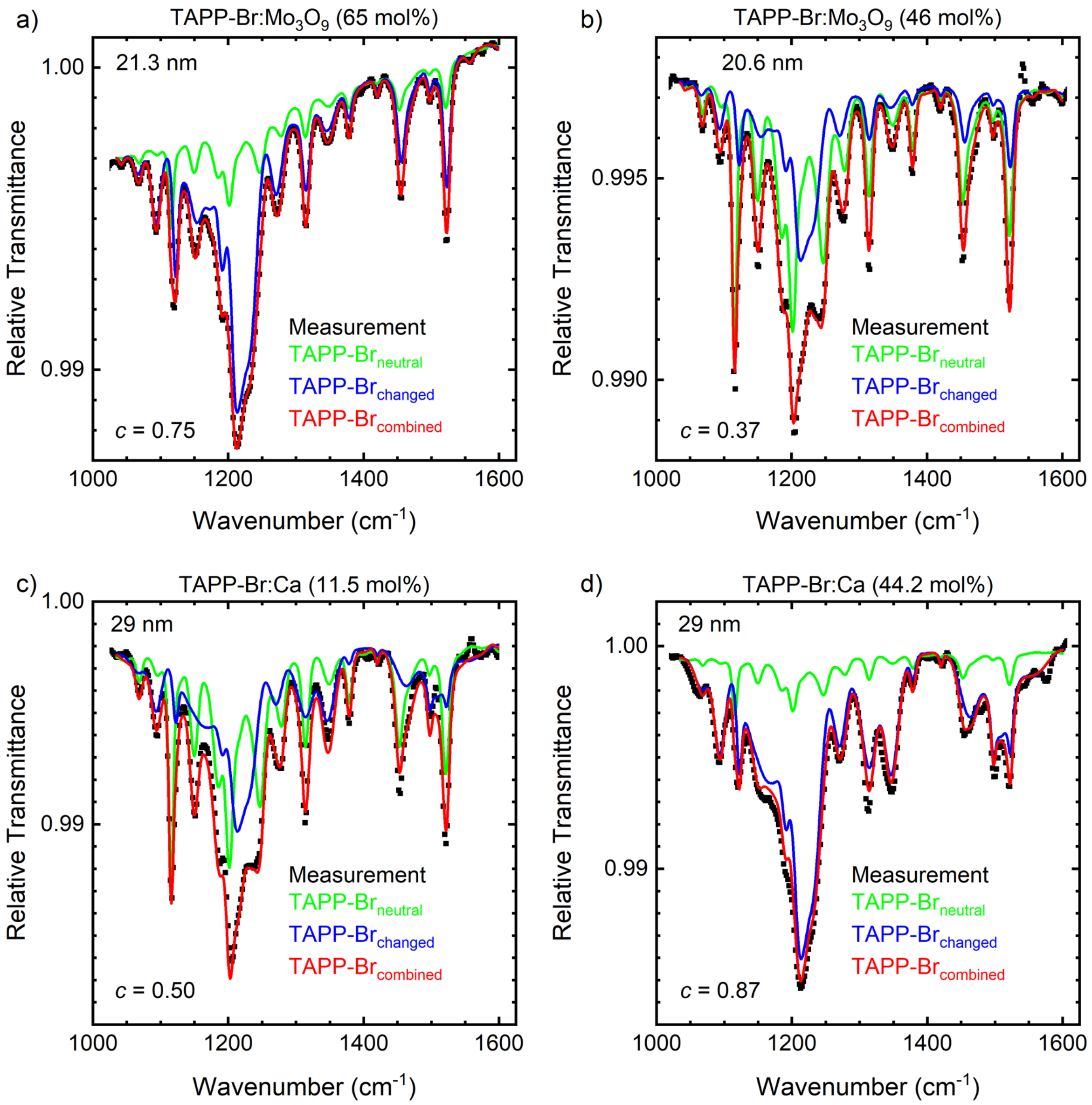

Fig. S5 Relative transmittance of the co-evaporated layers along with fit by the superposition model and the contributions of the neutral and the changed TAPP-Br component. Mixtures of TAPP-Br and MoO_3 are shown in a) and b), mixtures of TAPP-Br and Ca in c) and d), respectively. Consider the different ordinate scales.

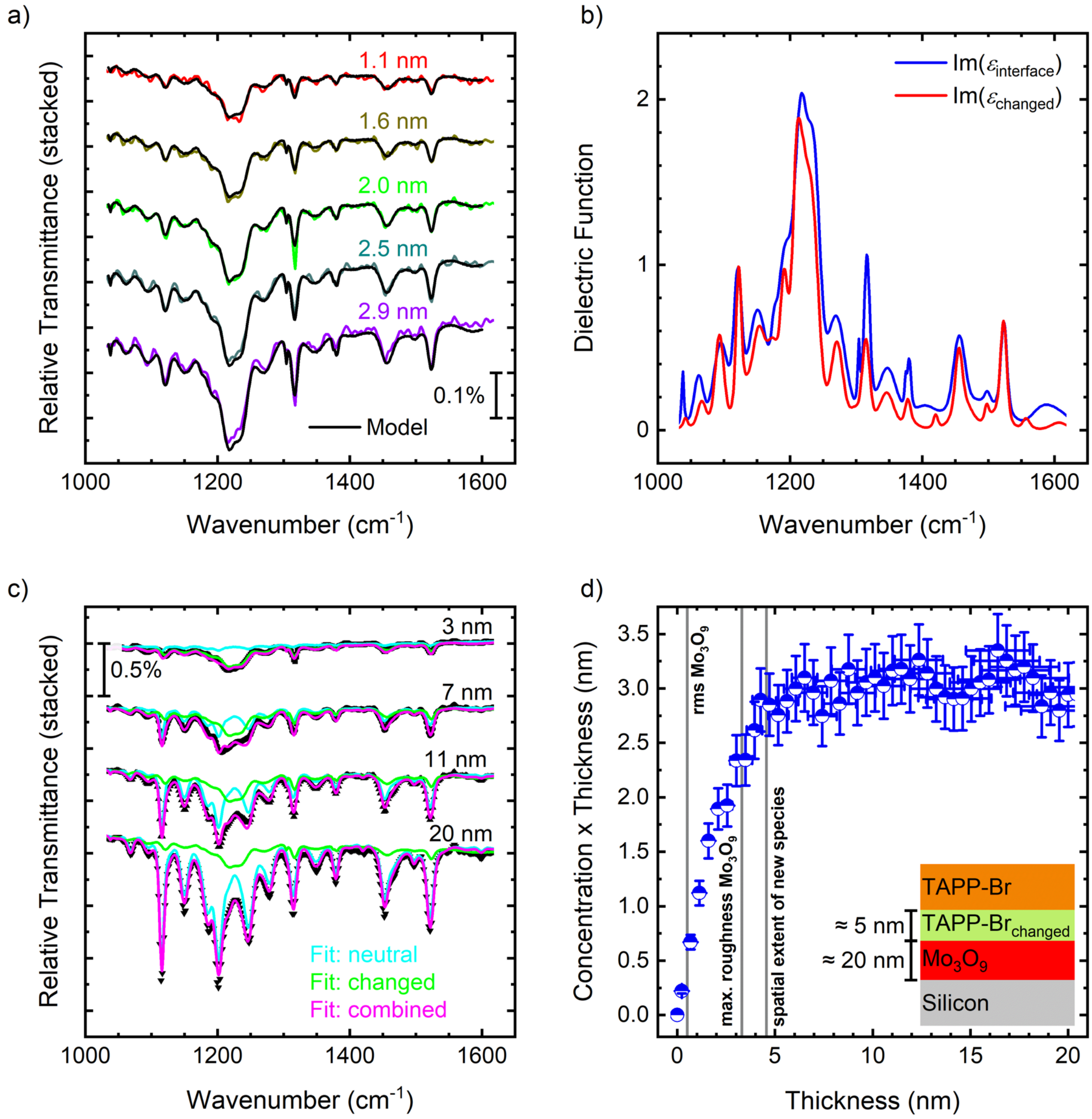

Fig. S6 a) Relative transmittance of TAPP-Br on ca. 20 nm MoO_3 along with a model for the interface species of TAPP-Br (black lines). No neutral TAPP-Br is present for small layer thicknesses ($d \leq 2.5$ nm). b) Imaginary part of the dielectric function of the interface species and the changed species (in mixtures with MoO_3) of TAPP-Br. c) Relative transmittance of TAPP-Br on ca. 20 nm MoO_3. The data was fitted with the superposition model (magenta lines) explained in the paper. The proportion of neutral (cyan lines) and interface (green lines) TAPP-Br is also shown. d) Amount (changed species multiplied by thickness) of the changed TAPP-Br species, evaluated from Fig. 6a, as a function of the layer thickness.

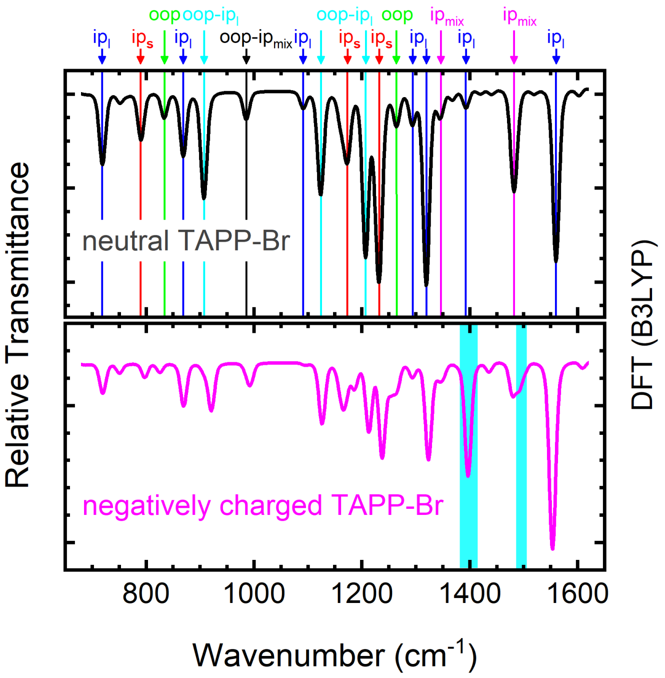

Fig. S7 Vibrational signature of a single TAPP-Br molecule in the gas phase, calculated by DFT (B3LYP/6-311G(d,p), Gaussian). The transmittance spectra were simulated according to ref 2 by using the commercial software Scout.^{3} A calculation of the neutral molecule (upper panel) as well as a calculation for the negatively charged molecule (lower panel) is shown.

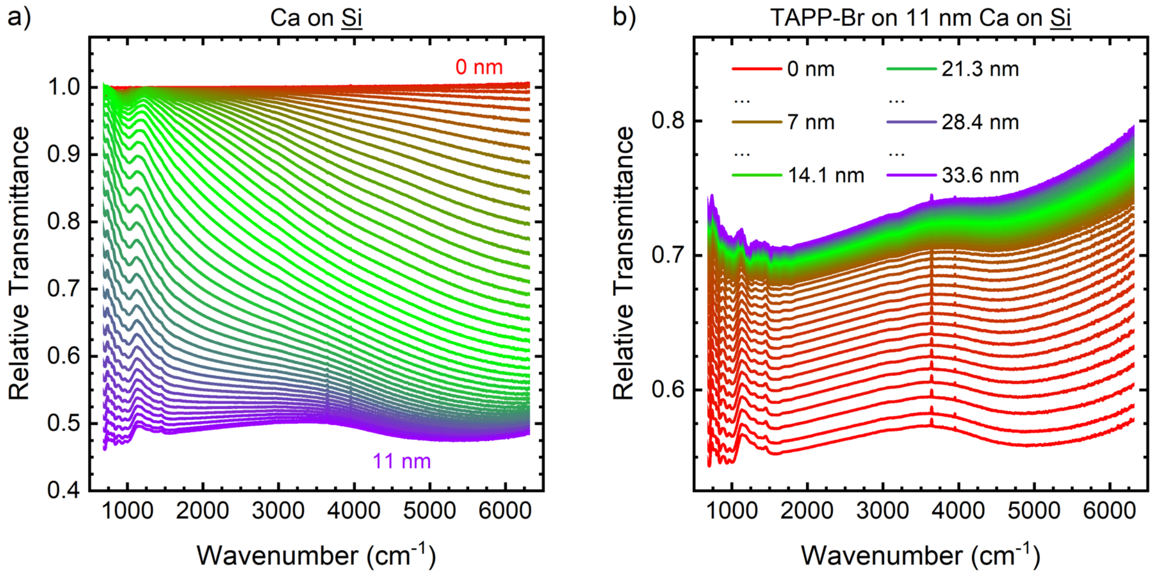

Fig. S8 Relative transmittance of a thin film on silicon, referenced to the silicon substrate. a) Growth of Ca on silicon. b) Growth of TAPP-Br on 11 nm Ca on silicon.

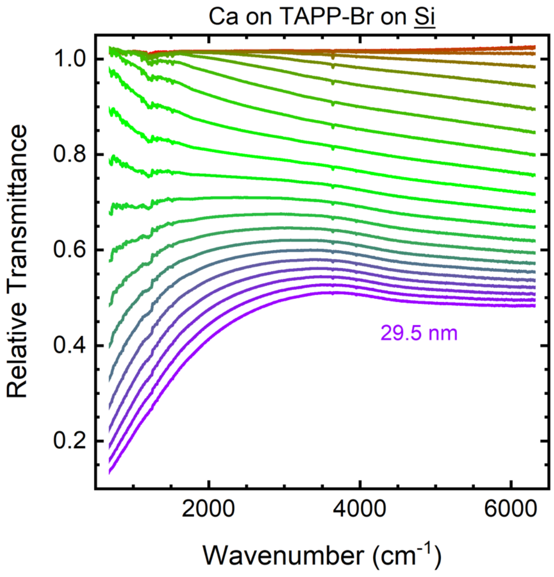

Fig. S9 Relative transmittance of Ca on 17.5 nm TAPP-Br, referenced to the Si substrate in the whole experimentally available range up to a Ca layer thickness of 29.5 nm. The fingerprint range with focus on low Ca coverages is shown in Fig. 10b in the paper.

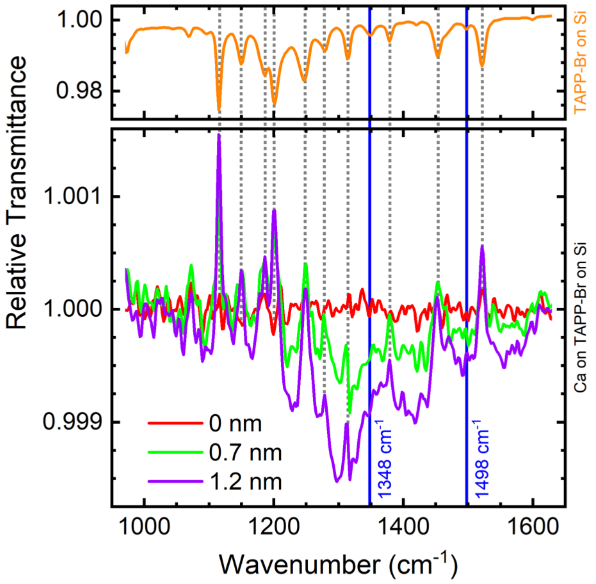

Fig. S10 Relative transmittance of Ca on 17.5 nm TAPP-Br, referenced to TAPP-Br on Si before starting the Ca deposition (lower panel). The spectral positions of the C-C vibrations of the aromatic rings are marked with blue lines, other typical vibrations of the undisturbed molecule with grey dotted lines. Obviously, at the C-C vibrations positions, no signal change above the noise level (see spectrum for 0 nm) is seen. The upper panel shows the vibrational signature of the TAPP-Br film on silicon as shown in Fig. 2a in the paper in order to verify that the features' spectral positions are in accordance with typical TAPP-Br vibrations. Due to the Ca absorption they point upwards.

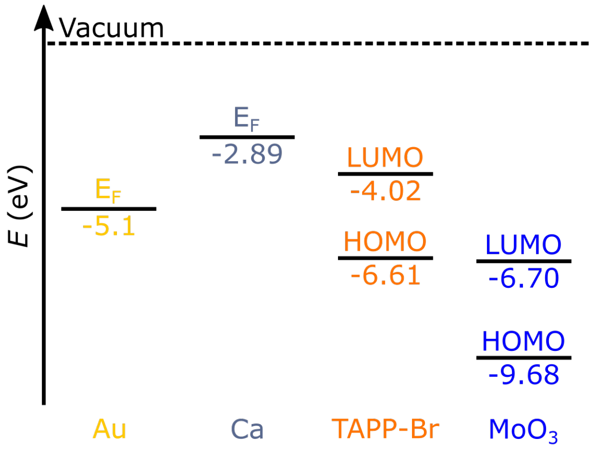

Fig. S11 Energy-level diagram of TAPP-Br, MoO_3, Ca, and Au. The values, relative to the vacuum level, were taken from literature.[4–7] As hole doping is not observed, the approach of vacuum level alignment (Schottky-Mott limit) and the combination of bulk and molecular data fails.

2 Reference experiment for the calibration of the evaporation rate

In order to determine the evaporation rate in terms of layer thickness for substances with unknown mass density, we evaporated a film with a thickness of ca. several ten nanometres on a silicon substrate. Subsequent, we gently scratched in the film and carried out large area (10 µm x 10 µm) AFM measurements in order to measure the height of the film. For the AFM measurements in the scratches we took care to inspect the silicon surface was not damaged by the scratching. Afterwards, the evaporation rate was adjusted to the AFM result.

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