



Supplementary Figure 1

Impact of buffer layer thickness and dielectric constant. (a) Electron potential energy $-eV(z)$ within a 10 nm film of pentacene and an insulating buffer layer with a thickness from 5 to 20 nm with the dielectric constant $\epsilon_r = 14$ of MoO_3 and an effective work function of 6.5 eV. Also included is the limiting case of no buffer layer (top trace). (b) Electron potential energy $-eV(z)$ within a 10 nm film of pentacene on an insulating buffer layer (thickness 10 nm) with an effective work function of 6.5 eV and varying dielectric constants. The limiting case of no buffer layer, i.e., pentacene in direct contact with a metal ($\epsilon_r = \infty$), is shown as the topmost trace. (c) Summary of (a) and (b), visualizing that the total amount of band bending within the organic decreases with decreasing capacitance.

Supplementary Discussion

Impact of passivating buffer layers. In allowing for a different DOS, a different dielectric constant, and a different thickness for each discretization interval, our model is flexible enough to treat any buffer layer material on the same footing as the organic semiconductor. With a comprehensive treatment on the impact of buffer layers available in Ref. [1], however, we prefer to limit complexity here and restrict ourselves to perfect insulators by setting $D_H(E) = D_L(E) \equiv 0$ in Eq. (1) for a first layer of specified thickness and dielectric constant. Accordingly, we show in Supplementary Figure 1a the electron potential profile $-eV(z)$ within a 10 nm pentacene film on an insulator with $\epsilon = 14$ and $\Phi_{\text{eff}} = 6.5$ eV ($> IE = 4.8$ eV), thereby mimicking the Fermi level pinned case of a MoO_3 -covered gold electrode.^{2,3} As conjectured by Ley and coworkers,¹ $V(d)$ and, thus, the observed hole-injection barrier $\Delta_h = IE - [\Phi_{\text{eff}} - eV(d)] \approx 4.8 - [6.5 \text{ eV} - 2.1 \text{ eV}] = 0.4$ eV does not noticeably depend on the oxide thickness for the considered pentacene coverage, thereby justifying our neglecting it previously. What does change, however, is the partitioning of $V(d)$ between voltage drop across the dielectric and band bending in the organic film. The thinner the dielectric, the more band bending in the organic semiconductor occurs, because more charges accumulate in the pentacene film (not shown). This inverse dependence of charge density on oxide thickness is, of course, a well-known relationship in (O)FET theory. More specifically, the decisive quantity is the capacitance of the dielectric, which is inversely proportional to its thickness and directly proportional to its (relative) permittivity. The impact of the latter is shown in Supplementary Figure 1b for a 10 nm insulator. As less and less potential drops across the dielectric, the amount of charge and band bending in the

organic increases dramatically with increasing permittivity but, again, the observed Δ_h is hardly affected. Summarizing the results in Supplementary Figures 1a and 1b, Supplementary Figure 1c shows the compound effect of the buffer layer capacitance, which is largely independent of bulk disorder (cf. Figure 4c).

Supplementary References

1. Ley, L., Smets, Y., Pakes, C. I. & Ristein, J. Calculating the Universal Energy-Level Alignment of Organic Molecules on Metal Oxides. *Adv. Funct. Mater.* **23**, 794-805 (2013).
2. Sayer, M. & Mansingh, A. Transport Properties of Semiconducting Phosphate Glasses. *Phys. Rev. B.* **6**, 4629-4643 (1972).
3. Greiner, M. T. & Lu, Z. H. Thin-film metal oxides in organic semiconductor devices: their electronic structures, work functions and interfaces. *NPG Asia Mater.* **5**, e55 (2013).