

Electronic Supplementary Information

Real-time monitoring of trap dynamics reveals the electronic states that limit charge transport in crystalline organic semiconductors

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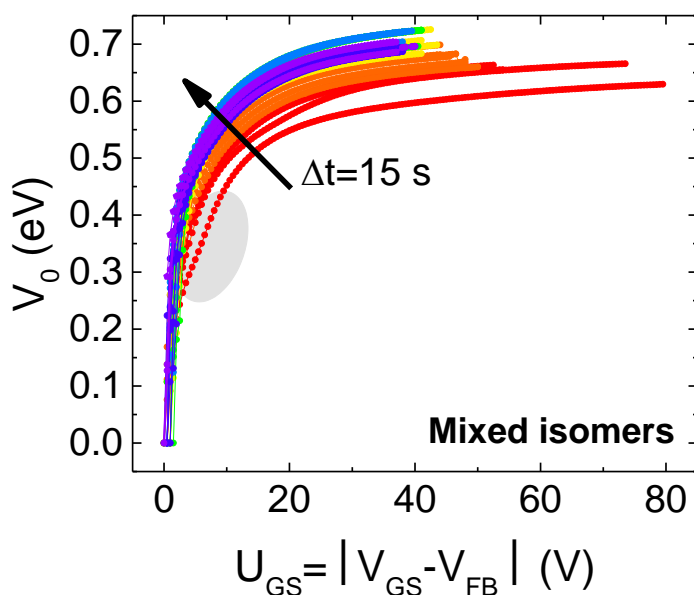


Fig. S1 Evolution of the interface potential function of a device consisting of crystallites of mixed isomers during exposure to ethanol vapor. The rainbow color scheme illustrates the time evolution of the spectrum from $t = 0$ s (red) to $t = 900$ s (violet). Gray shaded area highlights the changes in the curvature of the plots giving rise to the peak in the DOS spectrum.

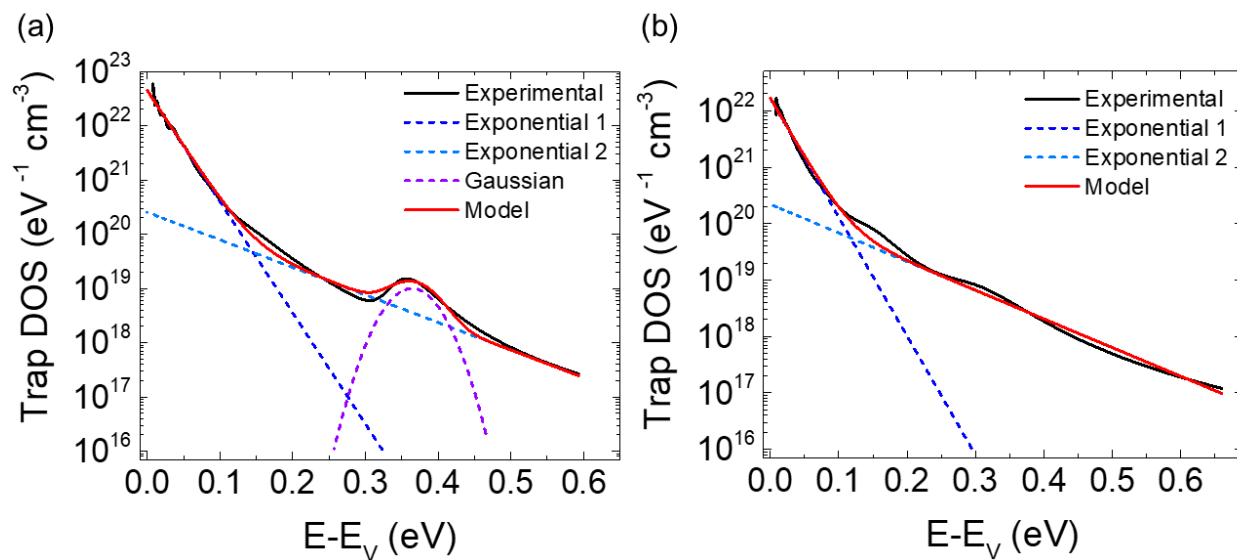


Fig. S2 Model fits (red solid lines) to experimental DOS spectrum (solid black lines) of a device with mixed isomers evaluated at different times: a) before exposure to ethanol vapor ($t = 0$ s) and b) after 900 s of exposure. Broken lines represent the individual distributions functions employed for the modelling.

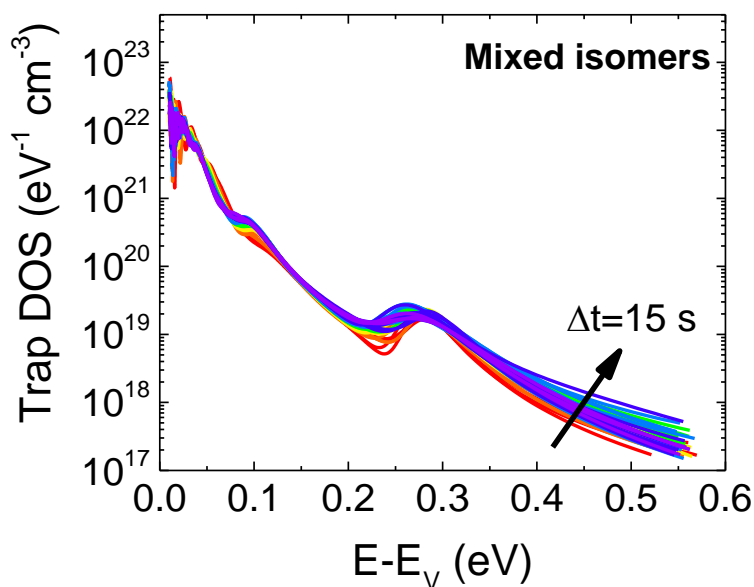


Fig. S3 Evolution of DOS spectrum of devices with mixed isomer grains during repetitive transistor measurements obtained every 15 s over a period of 15 min. The rainbow color scheme illustrates the time evolution of the spectrum from $t = 0$ s (red) to $t = 900$ s (violet). The peak persists over the entire duration of measurements.

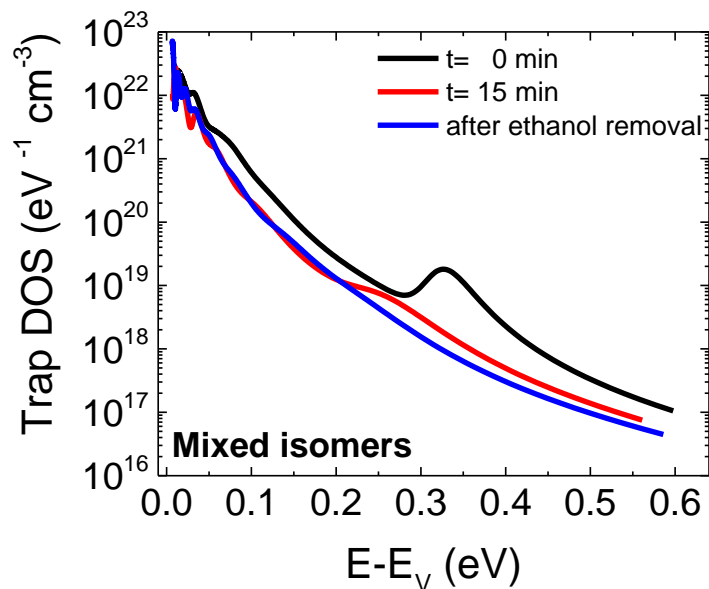


Fig. S4 Trap DOS spectra of a device with mixed isomer grains evaluated in the absence of bias stress. The black, red and blue curves represent the spectra evaluated before exposure to the solvent vapor, after 15 min of exposure and after removal of ethanol from the measurement chamber, respectively.

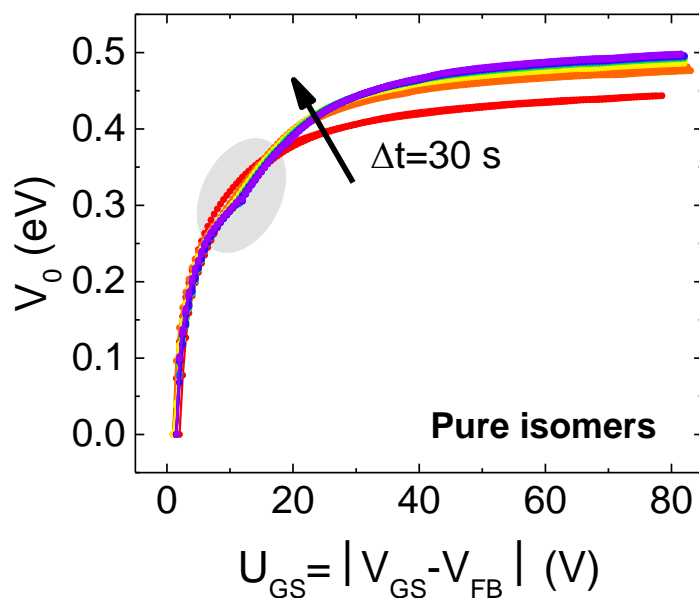


Fig. S5 Evolution of the interface potential function of a device consisting of pure isomer crystallites during exposure to ethanol vapor. The rainbow color scheme illustrates the time evolution of the spectrum from $t = 0$ s (red) to $t = 900$ s (violet). Gray shaded area highlights the changes in the curvature of the plots giving rise to the peak in the corresponding DOS spectrum.

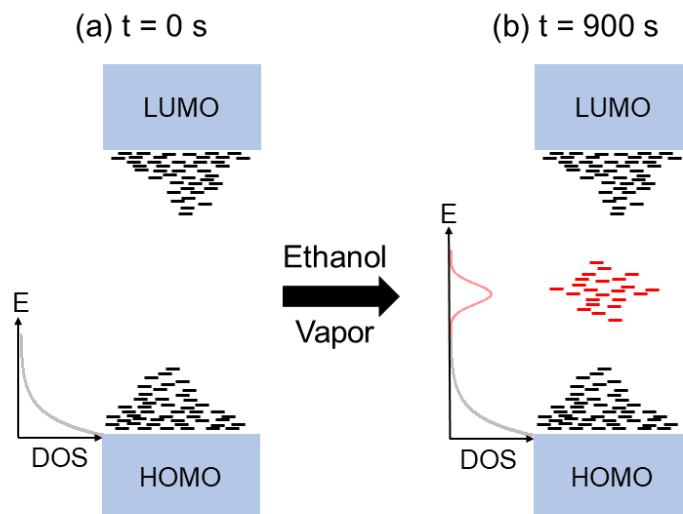


Fig. S6 Snapshots of the energetic distribution of localized band gap states at different times: a) before exposure and b) after 15 min of exposure to ethanol vapor. Deep and shallow states are marked in red and black respectively.

Table S1. Model parameters for the double exponential and Gaussian distributions employed to model the DOS spectra of a device consisting pure isomers. The spectrum at $t = 0$ s was modelled only using a double exponential distribution and therefore the Gaussian parameters are not applicable.

Model Parameter	$t = 0$ s	$t = 900$ s
N_1 ($\text{eV}^{-1} \text{cm}^{-3}$)	8.3×10^{22}	8.1×10^{22}
E_1 (meV)	14.4	16.1
N_2 ($\text{eV}^{-1} \text{cm}^{-3}$)	1.3×10^{21}	1.3×10^{21}
E_2 (meV)	53.4	65.8
A ($\text{eV}^{-1} \text{cm}^{-3}$)	N/A	1.4×10^{20}
E_{peak} (eV)	N/A	0.22
σ (meV)	N/A	12.0

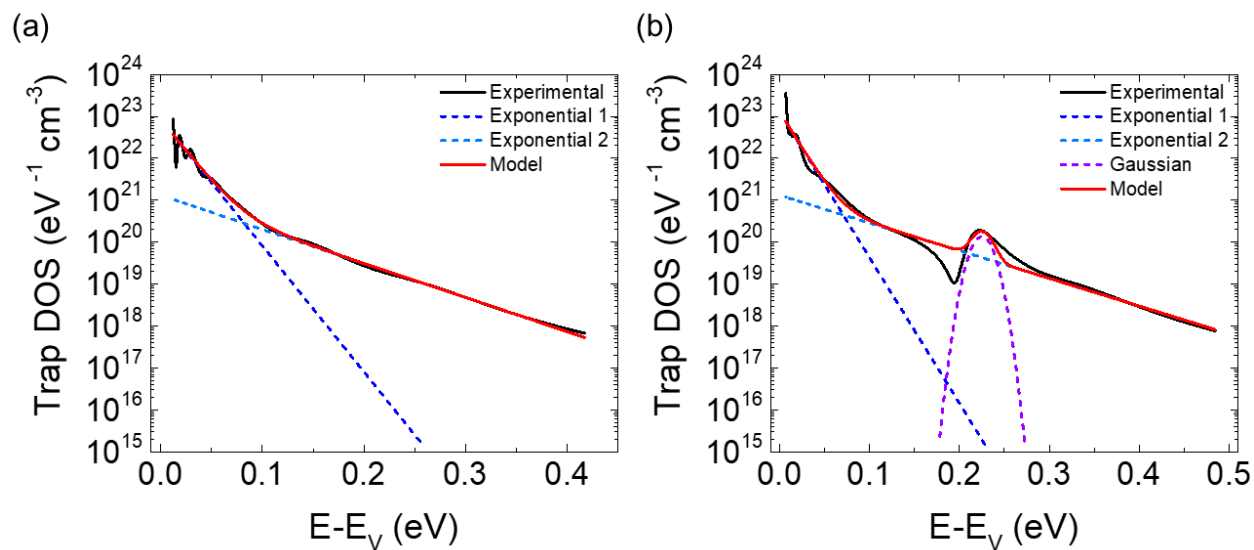


Fig. S7 Model fits (red solid lines) to experimental DOS spectrum (solid black lines) of a device with pure isomers evaluated at different times: a) before exposure to ethanol vapor ($t = 0$ s) and b) after 900 s of exposure. Broken lines represent the individual distributions functions employed for the modelling.

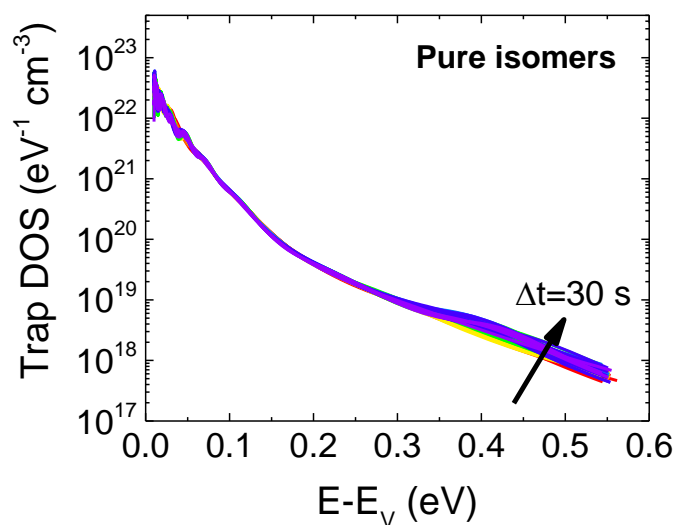


Fig. S8 Evolution of DOS spectrum of a device consisting of pure isomers during repetitive transistor measurements obtained every 30 s over a period of 15 min. The rainbow color scheme illustrates the time evolution of the spectrum from $t = 0$ s (red) to $t = 900$ s (violet). The spectra show no evidence for the generation of a peak.

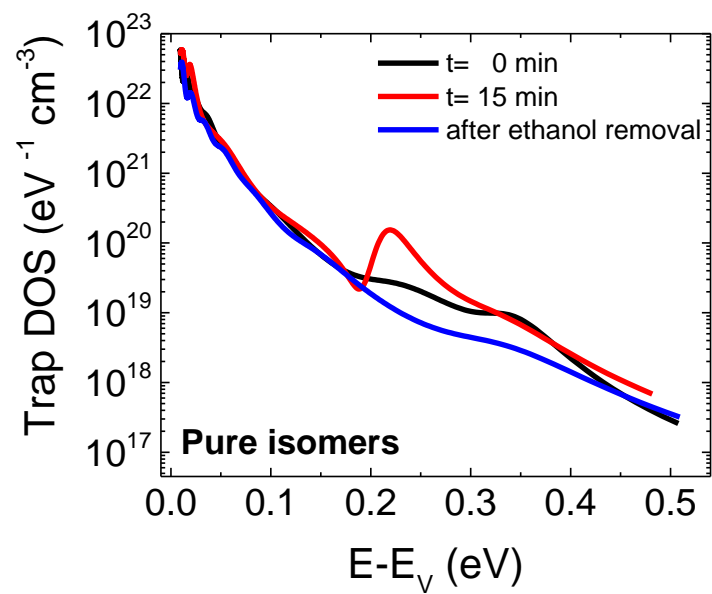


Fig. S9 Trap DOS spectra of a device with pure isomers evaluated in the absence of bias stress. The black, red and blue curves represent the spectra evaluated before exposure to the solvent vapor, after 15 min of exposure and after removal of ethanol from the measurement chamber, respectively.