

Supporting Information for

Substituent-Controlled Reversible Switching of Charge-Injection-Barrier Heights at Metal/Organic-Semiconductor Contacts Modified with Disordered Molecular Monolayers

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- The device with no modification layer on the electrodes

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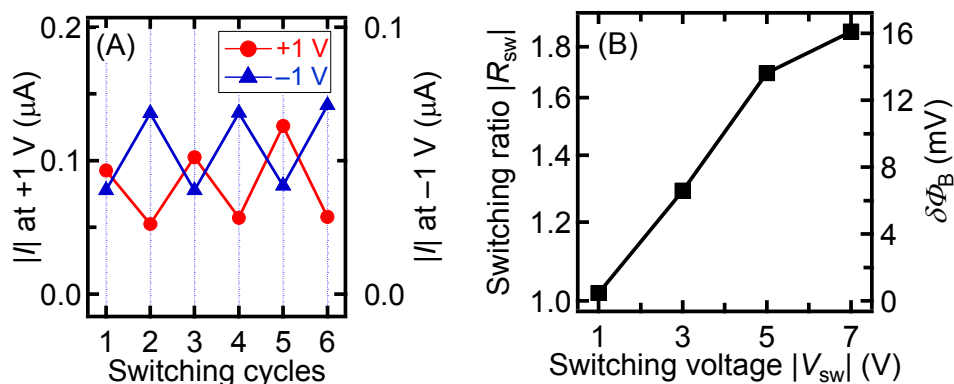


Figure S1. (A) Switching cycle of the absolute current $|I|$ with respect to the consecutive application of $V_{\text{sw}} = \pm 7$ V, and (B) the average R_{sw} as a function of $|V_{\text{sw}}|$ for the device with no modification layer. The change in the barrier height, $\delta\phi_{\text{B}}$, is also calculated by using Eq. (3) from the R_{sw} data.

Figure S1 shows the switching cycle and the $R_{\text{sw}}-V_{\text{sw}}$ characteristics of the device with no modification layer intentionally formed onto the Au electrodes. The R_{sw} values are lower than those of the B2T, BT and MBT devices (see Figure 3 in the main text), confirming that the higher R_{sw} values of these devices with modification layers originate from the presence of the modification layers. By contrast, the R_{sw} values are comparable to those of the NBT device. However, as explained in the next paragraph, this similarity is considered as coincidental.

For formation of the modification layers, the following steps were carried out: (1) cleaning of as-fabricated Au electrodes by oxygen plasma, (2) reduction of the slightly oxidized Au surface by immersion in ethanol, and (3) immersion in a 1 mM solution of each BT derivatives. The second and third steps were performed immediately following the corresponding preceding step. Thus, the molecular layer on the electrode surface should be exactly the BT derivative monolayer. Thus, the switching characteristics of the NBT device are considered to be the characteristics of the NBT layer. On the other hand, the third step was not performed for fabrication of devices with no modification layer. In this case, the surface of the reduced Au electrodes was contaminated by hydrocarbon molecules in the air during the lamination of rubrene crystals in ambient air. Thus, the observed weak switching of the device without intentionally formed monolayers is considered to originate from the unintentionally formed contamination layer.