Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

1. LDOS of π – LUMO bonding state

The localized density of states (LDOS) at the Γ point was plotted for π – LUMO bonding state of trinaphthyelene molecule attached to the DB dimer by [4+2] addition on outer ring (Fig. S1). The LDOS shows that the π – LUMO bonding state has an important molecular contribution and is coupled to the surface through the DB dimer states.

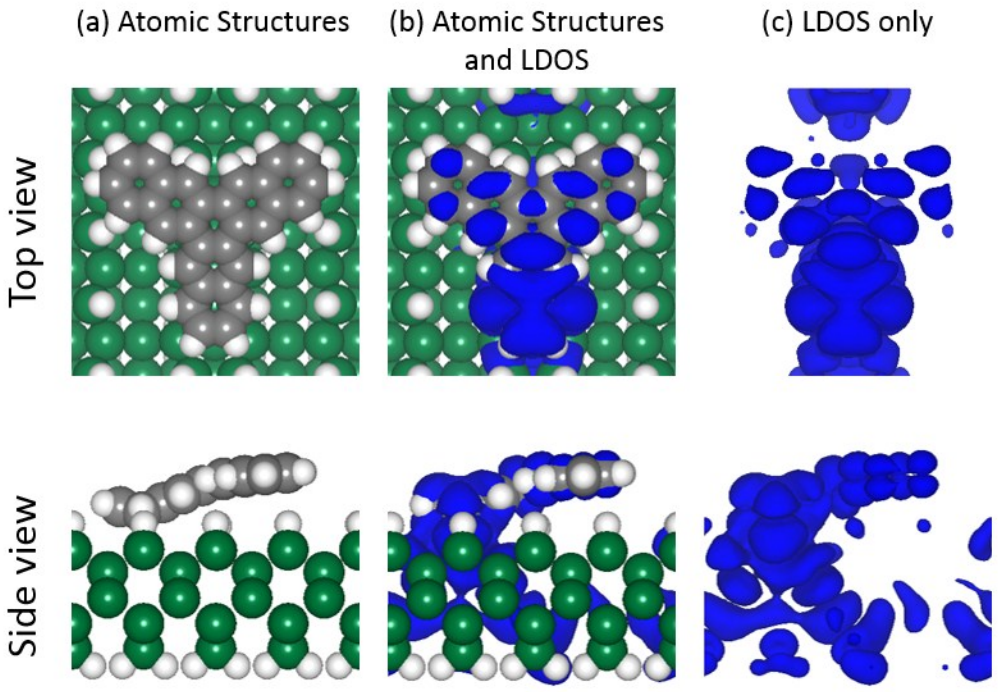

Figure S1. Top and side views of (a) atomic structures, (b) atomic structure and LDOS, and (c) LDOS only for π – LUMO bonding state of trinaphthylene molecule attached to the DB dimer by [4+2] addition on outer ring at the Γ point.

2. Band structures and PDOS of trinaphthylene molecule on a Ge(001):H DB dimer

The EHMO band structures and PDOS of trinaphthylene molecule on a Ge(001):H DB dimer at different heights were calculated to determine how the bonding and anti-bonding states evolve with the molecule-surface distance (Fig. S2). Note that the trinaphthylene molecule was kept at the deformed structure ([4+2] addition on outer ring), and only the distance between the molecule and surface was varied. As the molecule is positioned closer to the surface, π and π* states interact with LUMO and HOMO states, respectively, and are shifted in energy. Although the π – LUMO and π* – HOMO bonding states are observable on the PDOS plots, no significant peaks are observed in the conduction band (Fig. S2h) because the anti-bonding π – LUMO and π* – HOMO interaction have large dispersion in the band structure (Fig. S2b-d).

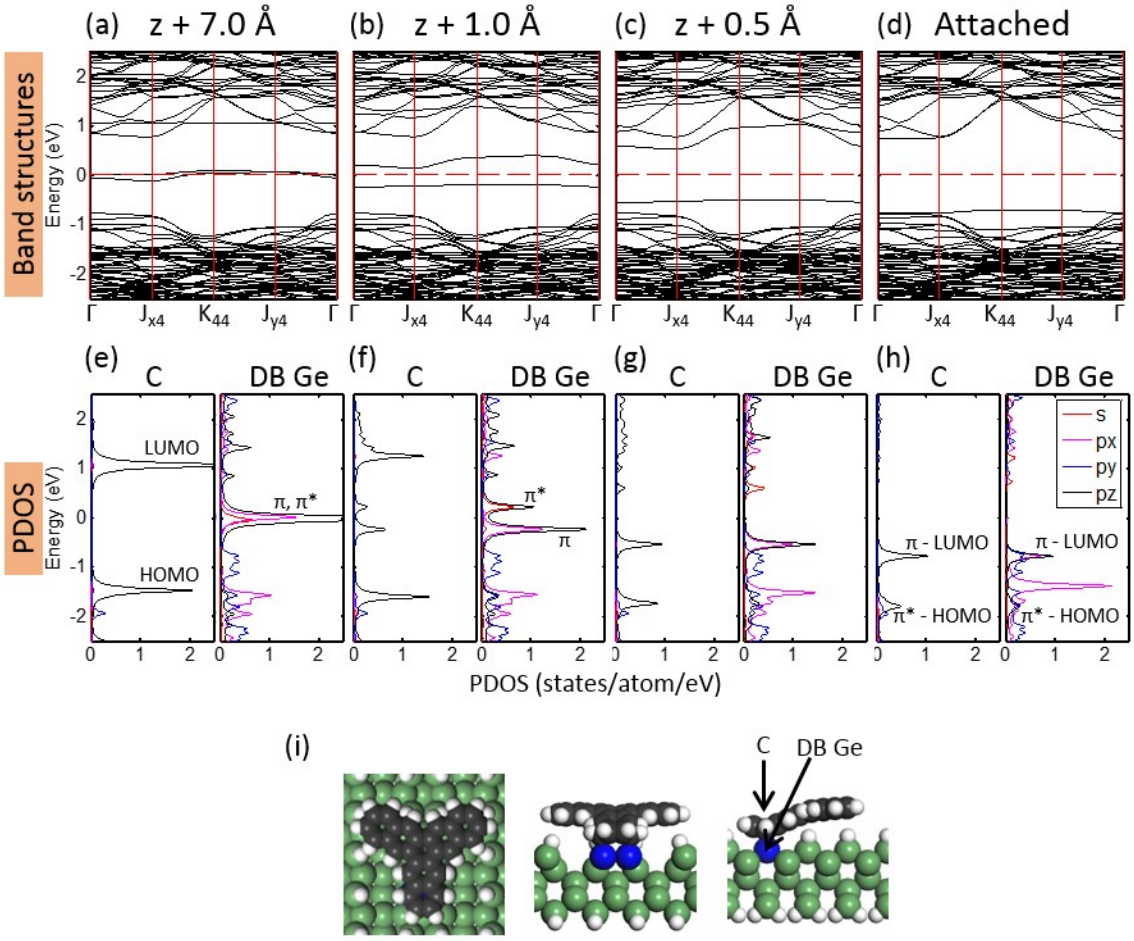

Figure S2. Band structures of trinaphthylene on a Ge(001):H DB dimer shifted higher in height compared to the attached geometry ([4+2] addition on outer ring) by (a) 7.0 Å, (b) 1.0 Å, (c) 0.5 Å, and (d) 0 Å (attached). (e)-(h) Corresponding PDOS (Γ point) projected on C atom above the DB and DB Ge atom. The geometry of trinaphthylene molecule was kept at deformed structure, and only the molecule-surface distance was varied. (i) Unit cell (4×4, 5-layer slab) used in the band structure and PDOS calculations. The atoms used for PDOS are labeled.