Supporting information:

Insertion of methylene groups to functional molecule for high thermal stability and superior functionality of single-molecule transistors: first-principles study

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Contents:

S1. Experimental results and discussion on similar molecules

As is described in the main text, the results of the DFT study and our experimental results of similar molecules are in agreement. This section explains the results and discussion in detail.

We compare a π-conjugated highly fused oligosilole derivative with terphenyl (Tph) and phenyl (ph) groups (Tph–ph) and its derivative with two methylene groups inserted between thiol and phenyl groups (Tph–ph–CH$_2$). Figures S1a and b show their molecular structural formulas. The backbone structures and molecular lengths of Tph–ph and Tph–ph–CH$_2$ are almost the same as those of Bph and Bph–CH$_2$, respectively. We measure the drain bias (V) and drain current (I) characteristics of the Au(111) electrodes between which Tph–ph and Tph–ph–CH$_2$ are attached.

Experimental conditions are as follows. The heteroepitaxial spherical (HS)-Au/Pt nanogap electrodes on Si/SiO$_2$ (50 nm) substrates are used to fabricate single-molecule transistors, as reported in our previous paper[1]. Briefly, we first fabricate initial Pt-based nanogap electrodes with an ultrafine linewidth of 10 nm[2]. Then electroless gold plating (ELGP)[3] is employed to initial Pt-based nanogap electrodes by immersing the sample in a solution consisting of an Au-dissolved iodine tincture and L(+)-ascorbic acid. The nanogaps between a pair of heteroepitaxial spherical Au on initial Pt nanogap can be obtained after ELGP for the introduction of molecules. The molecular solution is prepared by dissolving Tph–ph and Tph–ph–CH$_2$ in dichloromethane solvent with concentration of 0.01 mM. The fabricated HS-Au/Pt nanogap electrodes is then directly immersed in the molecular solution for 2 days under ambient condition. During this process, the molecules can be chemisorbed between the Au electrodes by thiol anchors. The sample is then rinsed twice with dichloromethane and ethanol to remove residual molecules and blow up with nitrogen flow.

The I-V characteristics of single-molecule transistors are measured using a mechanical refrigerator-type prober (GRAIL10-LOGOS01S, Nagase, Japan) and a semiconductor device analyzer (B1500, Keysight, USA). The measurement temperature is controlled at 9 K, and the pressure in the measurement chamber evacuated by a 50 L/s turbo molecular pump is approximately 10^{-6} Pa.

Figure S2 shows the bias (V)–conductance (dI/dV) spectra of Tph–ph and Tph–ph–CH$_2$. These spectra do not show conductance in the V range of −0.6 – 0.6 V, and show some peaks in the outer range. According to the peak heights, molecules chemisorb on one side of the electrode and physisorb on the other side. These experimental results are consistent with the results of the DFT calculation indicated in the main text, in the sense that peak positions are in the similar scale.

As the no-conductance bias voltage range in the conductance spectra of Tph–ph is nearly consistent with the band gap (shown in Table 1), a one-side chemisorbed structure on the ph side is suggested because the pinning effect originating from the chemisorbed ph side[4] tends to make MOs follow almost rigidly with the electrode Fermi level[5].

The measurements of cross-linked structures require further study because of its low yield at this stage, which is expected to improve for more robust statistical analysis. From this viewpoint,

the confirmation of the consistency between DFT calculation and the experimental results is of great significance.
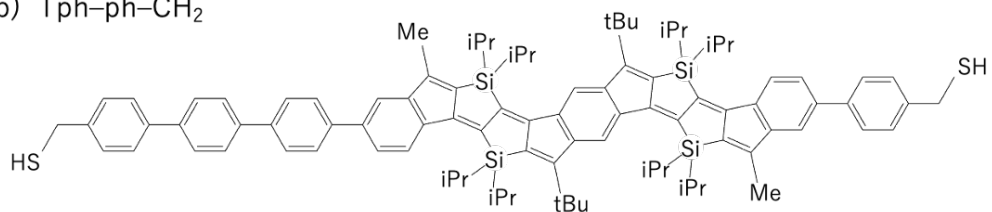
(a) Tph–ph
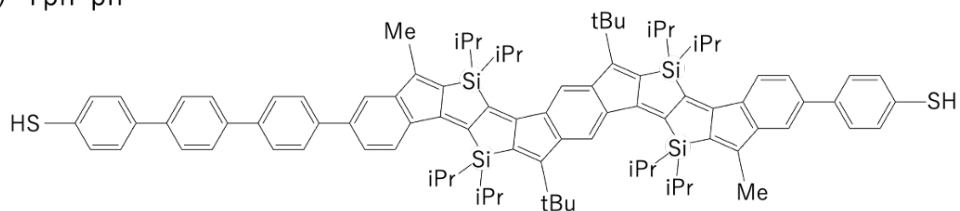
(b) Tph–ph–CH₂

Figure S1. Chemical structural formulas of π-conjugated highly fused oligosilole derivatives. (a) Molecule named Tph–ph.   (b) Molecule named Tph–ph–CH$_2$.
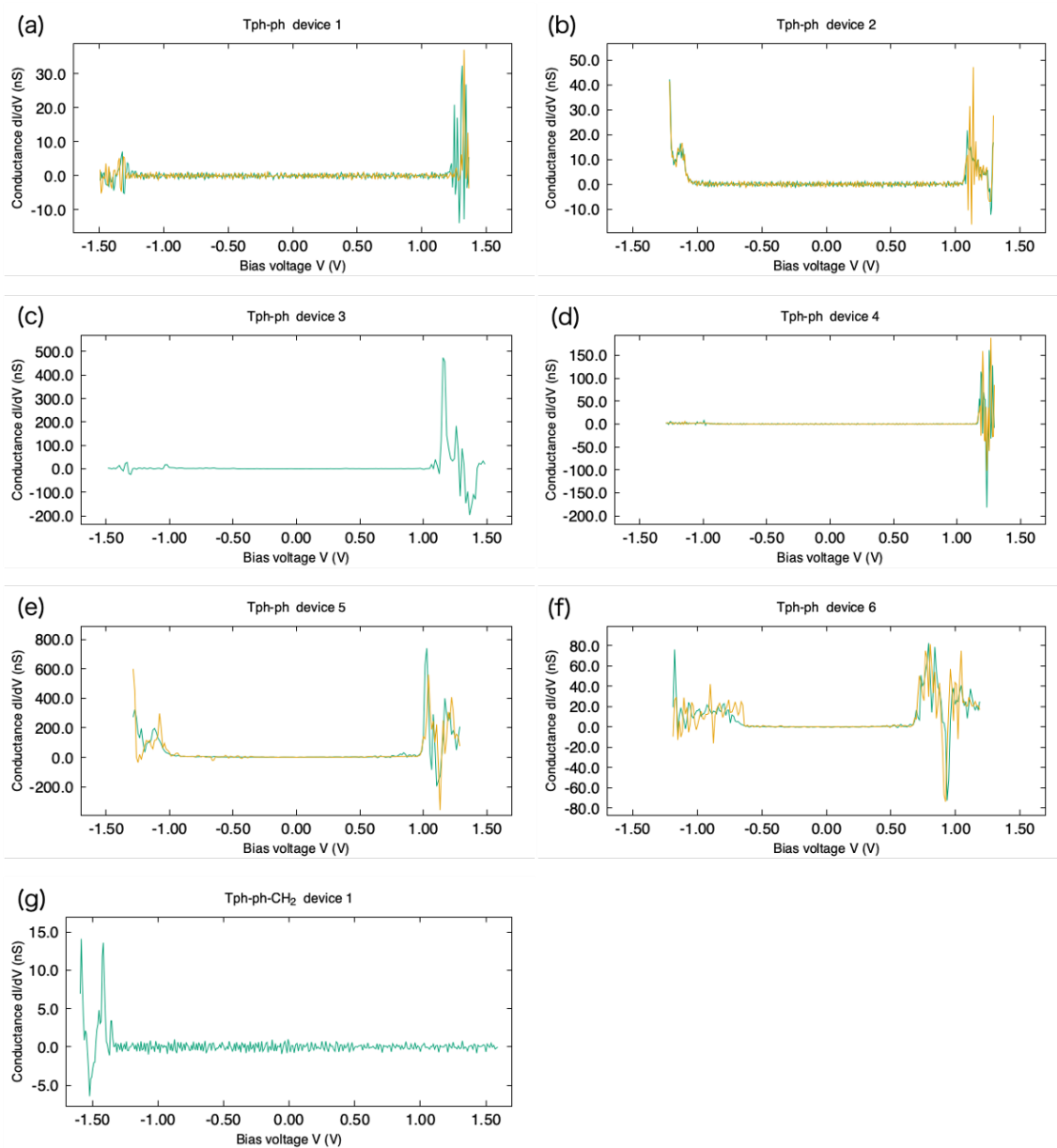
Figure S2. Experimental bias-conductance spectra. (a–f) Spectra of Tph–ph molecules of devices 1–6, respectively. (g) Spectrum of Tph–ph–CH$_2$. Green and yellow lines indicate charasteristics of forward and backward voltage sweeps, respectively.

S2. Computational details of the moieties of Bph and Bph–CH$_2$

In the main text, effects of orbital energies of the moieties of biphenylthiol and biphenylmethanethiol molecules on the transport properties of Bph and Bph–CH$_2$ are discussed. The computation process is described here.

From the obtained structures of Bph and Bph–CH$_2$ in Fig. 2 in the main text, the coordinates of the moieties of S atoms, inserted methylene groups, and biphenyl groups at the right-side edge are extracted. We add two new H atoms next to the C atom at the edge of biphenyl groups and the S atom for moieties to satisfy the octet rule. The ionic relaxation calculations are performed for new H atoms with the other ions fixed by the Vienna *ab initio* simulation package. The supercell size, applied pseudopotential, the functional, the cutoff energy of the plane wave basis set, and the threshold of relaxation convergency are all the same to the structure calculation of the Bph and Bph–CH$_2$ molecules between the Au electrodes. Integration over the Brillouin zone is carried out using the Γ point. The resulting structures are shown in Fig. S3.

The Fermi level and the orbital energies are calculated in the framework of DFT and real-space finite-difference method using the RSPACE code. No periodic boundary conditions are imposed. The pseudopotential, the treat of exchange-correlation interaction, the k-sampling, the supercell size and the grid spacing are all the same to the electronic structure calculation of Bph and Bph–CH$_2$ between the Au electrodes.
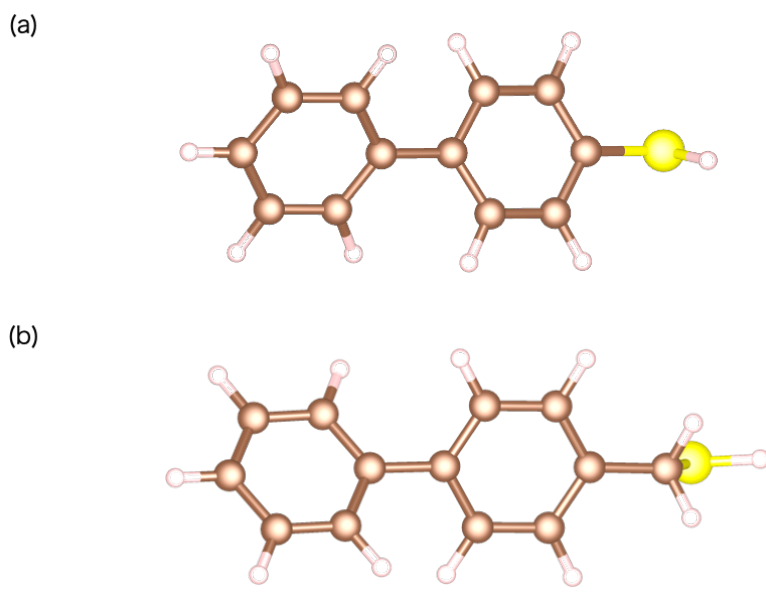
(a)

(b)

Figure S3. Structures of the moieties of Bph and Bph–CH$_2$. (a) Biphenylthiol molecule, the moiety of Bph. (b) Biphenylmethanethiol molecule, the moiety of Bph–CH$_2$.

References

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