Supplementary Information for

Bias-Voltage Dependence of Tunneling Decay Coefficient and Barrier Height in Arylalkane Molecular Junctions with Graphene Contacts as a Protecting Interlayer

Table S1. Comparison of various non-evaporative top contact molecular junctions based on self-assembled monolayers.

top contact method	junction structure	yield	maximun junction area (μm^2)	decay coefficient (β) ($Å^{-1}$)	ref
transferred SLG[1)]	SLG/arylalkane/SLG	>80%	6.3×10^4	1.08 - 0.92	this study
liquid EGaIn	SLG/alkylamine/EGaIn	93%	1.9×10^3	0.82	S1
transferred rGO[2)]	Au/alkanethiol/rGO	not reported	~4	0.5	17
spin-coated PEDOT:PSS[3)]	Au/alkanedithiol/PEDOT:PSS	>95%	$\sim 1.0 \times 10^4$	0.57 - 0.66	11
Au NP[4)] solution	Au/alkanethiol/Au NP	>95%	4.9×10^3	0.81	S2
direct metal transfer	Au/alkanethiol/Au	~70%	~79	1.1	13
transferred MLG[5)]	Au/alkane(di)thiol/MLG	~90%	~16	0.85	15
transferred SLG	SLG/arylalkane/SLG	>80%	9.0×10^4	0.54[6)]	16

[1)] single layer graphene
[2)] reduced graphene oxide
[3)] poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
[4)] nanoparticle
[5)] multilayer graphene
[6)] this low β value may be due to rough substrate.

As summarized in table S1, the single layer graphene top contact effectively protects the molecular SAMs from penetration by the evaporated metal atoms, providing stable and high yield molecular junctions for investigating the intrinsic molecular charge transport. We also demonstrated the validation of the voltage-induced barrier lowering approximation to the graphene-based molecular junction as presented in this study.

The original Simmons model for molecular tunnel junctions is given by eq. (S1) [18,22]:

$$J = \frac{e}{4\pi^2\hbar d^2}\left\{\left(\Phi_B - \frac{eV}{2}\right)\exp\left(-\frac{2d\sqrt{2m}}{\hbar}\alpha\sqrt{\Phi_B - \frac{eV}{2}}\right) - \left(\Phi_B + \frac{eV}{2}\right)\exp\left(-\frac{2d\sqrt{2m}}{\hbar}\alpha\sqrt{\Phi_B + \frac{eV}{2}}\right)\right\} \quad \text{(S1)}$$

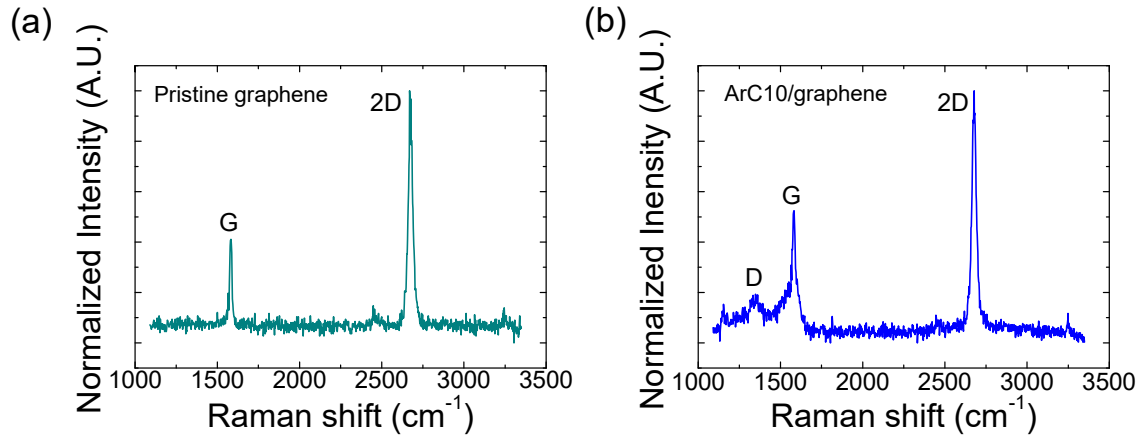

Figure S1. Raman spectrum for (a) a pristine and (b) ArC10-coverd graphene on Si/SiO_2 substrate.

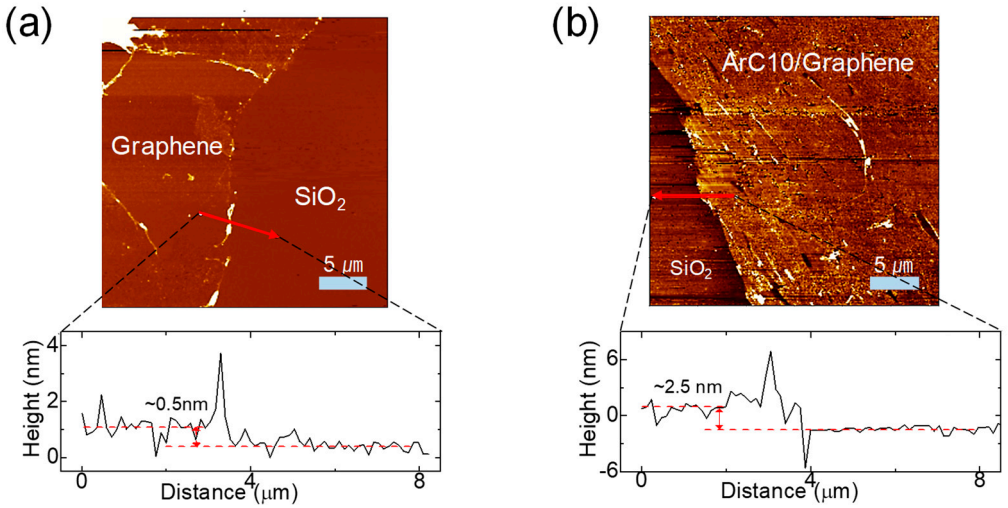

Figure S2. AFM topographical images and line profile analyses of (a) a pristine and (b) ArC10-coverd graphene on Si/SiO_2 substrate. The heights of a pristine and ArC10-coverd graphene are estimated to be 2.5 nm and 0.5 nm, respectively.

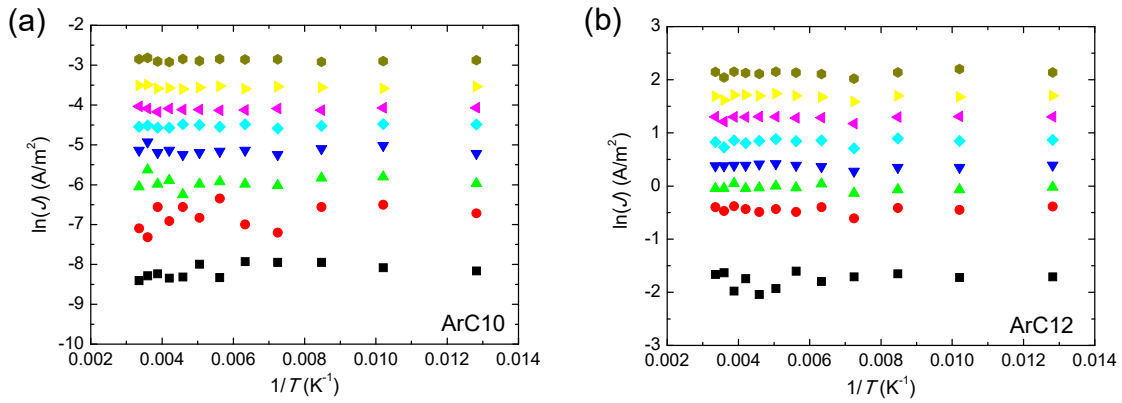

Figure S3. Arrhenius plots of (a) ArC10 and (b) ArC12 junctions. Temperature variation is from 298 to 78 K in 20 K steps at voltages from 0.1 (bottom points) to 1.5 V (top points) with 0.2 V steps.

References

S1. Song, P.; Sangeeth, C.S.S.; Thompson, D.; Du, W.; Loh, K.P.; Nijhuis, C.A. Noncovalent Self-Assembled Monolayers on Graphene as a Highly Stable Platform for Molecular Tunnel Junctions. Adv. Mater. 2016, 28, 631-639.

S2. Puebla-Hellmann, G.; Venkatesan, K.; Mayor, M.; Lörtscher, E. Metallic nanoparticle contacts for high-yield, ambient-stable molecular-monolayer devices. Nature 2018, 559, 232–235.