Supporting Information

Formation of Covalent Metal-Carbon Contacts Assisted by Ag^+ for Single Molecule Junctions

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1. Supplementary Methods

All alkyne-terminated chemical compounds for experiments were purchased from the commercial sources. P1, P1-MeO, P1-Meta and C7 were purchased from Tokyo Chemical Industry (TCI). TPE was customized from Hangzhou Order Science & Technology Co., Ltd.

All single molecule conductance measurements were performed using home-built scanning tunneling microscope break junction (STM-BJ) setup in ambient conditions. The standard conductance measurements were performed using Au STM tip and substrate in molecular solutions in propylene carbonate (PC) solvent with and without adding silver hexafluorophosphate ($AgPF_6$) salts. The Au STM tip was coated with apiezon wax to avoid ionic background current. All histograms are compiled from thousands of conductance traces without data selection.

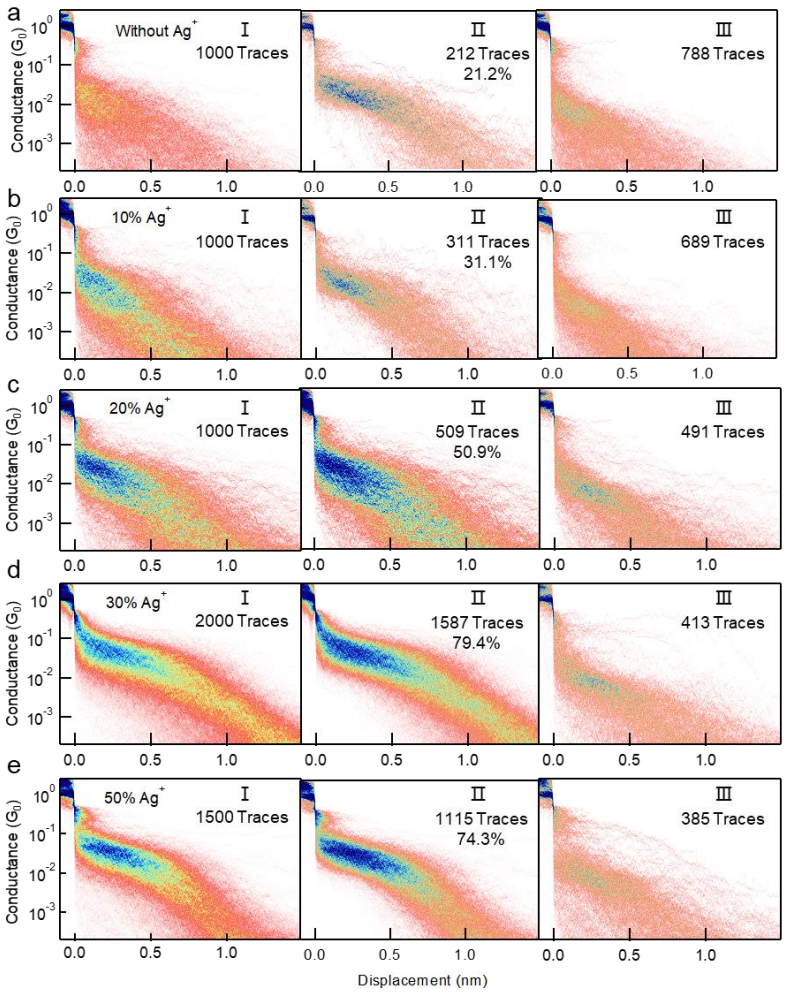
2. Supplementary Notes

Data clustering. In order to quantify the probability of junction formation after adding Ag^+ ions at various concentrations, we sorted the conductance traces measured at each concentration into two categories: junctions with a conductance of 10^{-1} G_0 ~ 10^{-2} G_0 (II), and all other traces (III) (see Supplementary Fig. 1). We observed that as the concentration of Ag^+ ions increased from 0 to 50%, the yield of junction formation, which is defined as the ratio of the number of traces showing a molecular conductance plateau to the total number of traces, increased from approximately 20% to 80%. Notably, the probability of junction formation reaches the maximum when the concentration of Ag^+ ions was approximately 30%.

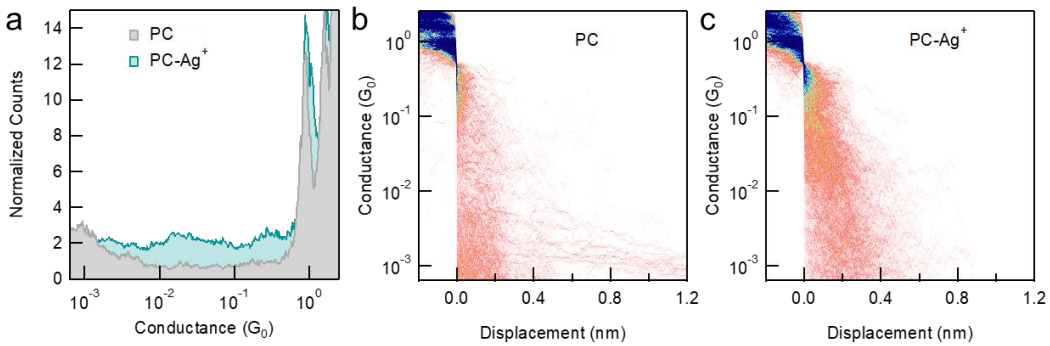
DFT calculations. We carried out DFT calculations using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional implemented by the Fritz Haber Institute ab initio molecular simulation (FHI-aims) packages.[1-3] Firstly, we optimized the geometries of alkyne-terminated molecules to find optimal molecular structures. To model the binding configurations of the molecular junctions, we covalently attached single Ag atoms to the two sides of the optimized molecules. After geometry optimization, the Au clusters containing 59 atoms were attached to the Ag atoms to form the junctions. The Landauer transmission across these junctions are finally

calculated using the nonequilibrium Green's function (NEGF) formalism.

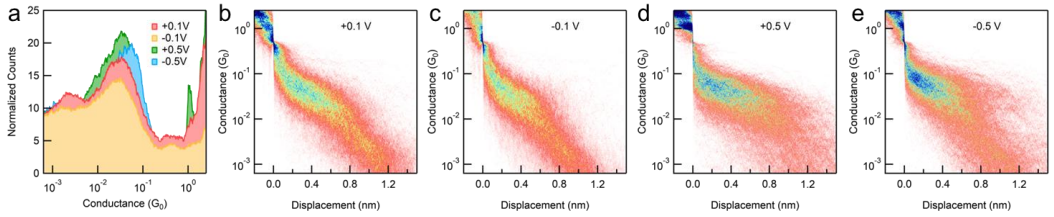
3. Supplementary Figures



Supplementary Fig. 1. (a-e) 2D conductance-displacement histograms compiled from traces for P1 measured with different concentrations of $AgPF_6$ additives. Panel I: 2D histograms compiled from the total traces. Panel II: 2D histograms compiled from the sorted traces with the conductance plateau corresponding to the molecular junctions. Panel III: 2D histograms compiled from the rest traces without typical molecular conductance features.



Supplementary Fig. 2. (a) Logarithm-binned 1D histograms of pure PC and PC with Ag^+ ions (~0.2 mM) measured at a bias of +0.1 V. (b) 2D conductance-displacement histograms of pure PC. (c) 2D conductance-displacement histograms of PC with Ag^+ ions (~0.2 mM). All histograms are compiled from 1000 traces without data selection.



Supplementary Fig. 3. (a) Logarithm-binned 1D histograms of P1 measured at different tip biases with ~40% $AgPF_6$ additives. Corresponding 2D conductance-displacement histograms measured at (b) +0.1 V, (c) -0.1 V, (d) +0.5 V and (e) -0.5 V. All histograms are compiled from 1000 traces without data selection.

4. Supplementary References

1. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
2. V. Havu, V. Blum, P. Havu and M. Scheffler, *J. Comput. Phys.*, 2009, **228**, 8367-8379.
3. V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, *Comput. Phys. Commun.*, 2009, **180**, 2175-2196.