

# Solvent Mediated Modulation of the Au-S Bond in Dithiol Molecular Junctions

Johnson Dalmieda<sup>1</sup>, Wanzhuo Shi<sup>1</sup>, Liang Li<sup>1</sup>, Latha Venkataraman<sup>1,2\*</sup>

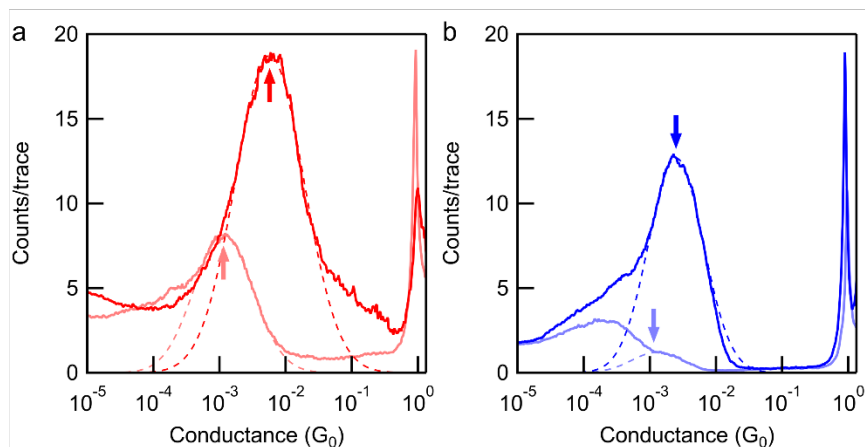
<sup>1</sup>Department of Chemistry, Columbia University, New York, NY 10027

<sup>2</sup>Department of Applied Physics, Columbia University, New York, NY 10027

## S1. Materials.

1-bromonaphthalene (97%; CAS 90-11-9) and benzene-1,4-dithiol (97%; CAS 624-39-5) were both purchased from Alfa Aesar. Biphenyl-4,4'-dithiol (95%; CAS 6954-27-4) was purchased from Millipore Sigma. 1-chloronaphthalene (tech. 85%, remainder 2-chloronaphthalene; CAS 90-13-1) and gold wire (0.25 mm dia, Premion® 99.998% metals basis; CAS 7440-57-5) were both purchased from Thermo Scientific. *p*-terphenyl-4,4''-dithiol was purchased from Sigma-Aldrich (95%; CAS 174706-21-9).

## S2. Concentration Dependence.

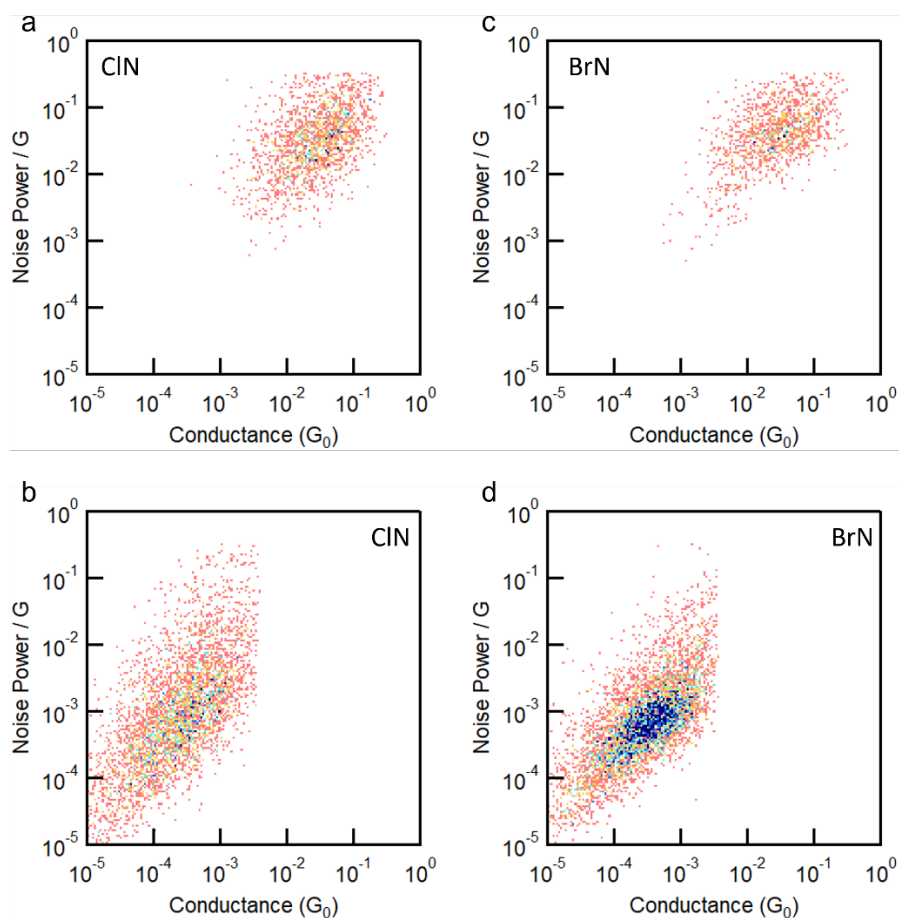


**SI Figure 1.** 1D histograms of TPDT in a) CIN and b) BrN in 100  $\mu\text{M}$  (dark) and 10  $\mu\text{M}$  (light) concentrations. Dashed lines are the Gaussian fit to the conductance peaks, and arrows highlight the fit maxima.

## S3. Flicker Noise Analysis.

Flicker noise measurements were conducted as described in detail before.<sup>1, 2</sup> We first formed junctions with BDT and TPDT at a bias of 500 mV, held the junction for 150 ms and measured the conductance with a 100 kHz sampling rate. At least 2,000 traces that sustain a molecular junction were selected for the analysis. We obtained the average molecular conductance

( $G$ ) and the normalized noise power (power spectral density (PSD)/ $G$ ) from the hold period. The PSD was calculated from the square of the integral of a discrete Fourier transform of the measured conductance between 100 Hz and 1,000 Hz. These frequency limits are constrained by the mechanical stability of STM-BJ setup (100 Hz) and the input noise of the current amplifier (1,000 Hz). Using the calculated parameters, we create 2D histograms of the normalized integrated noise power *versus* the average conductance. The relationship between noise power and molecular conductance is derived by determining the scaling exponent ( $n$ ) for which  $\text{PSD}/G^n$  and  $G$  are not correlated. For BDT in CIN (Figure S2a-b), the noise-conductance relation in the high conductance peak exhibits a dependence of  $G^{1.3}$ , indicating through-bond coupling, whereas the noise-conductance relation for the low conductance peak shows a dependence of  $G^{1.9}$ , indicating through-space coupling. This same noise-conductance relation is observed for BDT junctions formed in BrN (Figure S2c-d). This indicates that the high conductance peak is due to single molecule phenomena, whereas the low conductance peak is due to the formation of dimers in solution.



**SI Figure 2.** Two-dimensional histograms of flicker noise power against junction conductance for a) the high conductance peak for BDT in CIN, b) low conductance peak for BDT in CIN, c) high conductance peak for BDT in BrN, d) low conductance peak for BDT in BrN.

#### S4. Binding energies.

To obtain the values for binding energy ( $E_{\text{binding}}$ ), we take the total energy of the 1,4-benzenedithiol (BDT) molecule an Au tetrahedron through an Au-S bond with an H atom also bound to the Au. ( $E_{\text{BDT}+\text{H}+\text{Au}}$ ) and subtract from that value the total energy of a free BDT molecule with SH terminations ( $E_{\text{BDT}}$ ) and a free Au tetrahedron ( $E_{\text{Au}}$ ) (Eq. S1).

$$E_{\text{binding}} = E_{\text{BDT}+\text{H}+\text{Au}} - E_{\text{BDT}} - E_{\text{Au}} \quad (\text{S1})$$

This energy is for the simultaneous breaking of the S-H bond on BDT, and the formation of an Au-S bond and an Au-H bond on the Au tetrahedron. To obtain the bond strength of the Au-S bond, we subtract the energy of an Au tetrahedron bound to an H atom ( $E_{\text{Au-H}}$ ) and the energy of a BDT radical ( $E_{\text{BDT}^*}$ ) from the total energy of the fully bound system (Eq. S2).

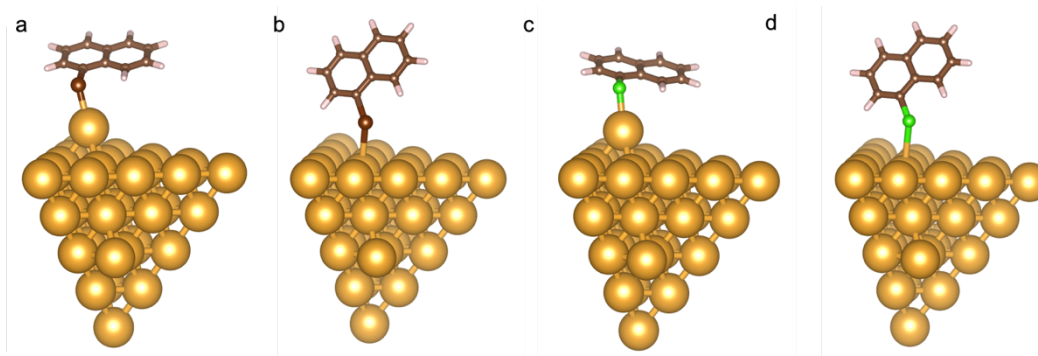
$$E_{\text{Au-S}} = E_{\text{BDT}+\text{H}+\text{Au}} - E_{\text{BDT}^*} - E_{\text{Au-H}} \quad (\text{S2})$$

#### S5. Solvent Binding Energies

We calculate the binding energies of the ClN and BrN as detailed in the main manuscript and report the values here. The geometry for each configuration is shown in SI Figure S1.

	Au-X bond distance (Å)	X-C bond distance (Å)	Au-X-C angle	Binding Energy (eV)
ClN-Adatom	2.53	1.78	110.8°	-0.389
ClN-Atop	3.47	1.76	130.6°	-0.059
BrN-Adatom	2.62	1.95	110.5°	-0.511
BrN-Atop	3.31	1.94	129.4°	-0.112

**SI Table 1.** Bond distances, bond angles, and binding energies of BrN and ClN in both geometries attached to a 4-layer Au tetrahedron. The Cl-C bond distance in free ClN is 1.76 Å and the Br-C bond distance in free BrN is 1.93 Å.



**SI Figure 3.** The optimized geometries of solvent molecule on Au cluster showing different binding motifs for a) BrN on adatom, b) BrN on an atop site c) ClN on adatom, d) ClN on an atop site

## References:

1. Adak, O.; Rosenthal, E.; Meisner, J.; Andrade, E. F.; Pasupathy, A. N.; Nuckolls, C.; Hybertsen, M. S.; Venkataraman, L., Flicker noise as a probe of electronic interaction at metal–single molecule interfaces. *Nano letters* **2015**, *15* (6), 4143-4149.
2. Magyarkuti, A.; Adak, O.; Halbritter, A.; Venkataraman, L., Electronic and mechanical characteristics of stacked dimer molecular junctions. *Nanoscale* **2018**, *10* (7), 3362-3368.