

Single-molecule refrigerators: Substitution and gate effects

Yu-Shen Liu and Yu-Chang Chen

Citation: *Applied Physics Letters* **98**, 213103 (2011); doi: 10.1063/1.3593379

View online: <http://dx.doi.org/10.1063/1.3593379>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/98/21?ver=pdfcov>

Published by the *AIP Publishing*

Articles you may be interested in

[Carbon tips as electrodes for single-molecule junctions](#)

Appl. Phys. Lett. **99**, 123105 (2011); 10.1063/1.3643031

[Spin-filtering transport and switching effect of MnCu single-molecule magnet](#)

Appl. Phys. Lett. **96**, 192112 (2010); 10.1063/1.3430063

[A single molecule rectifier with strong push-pull coupling](#)

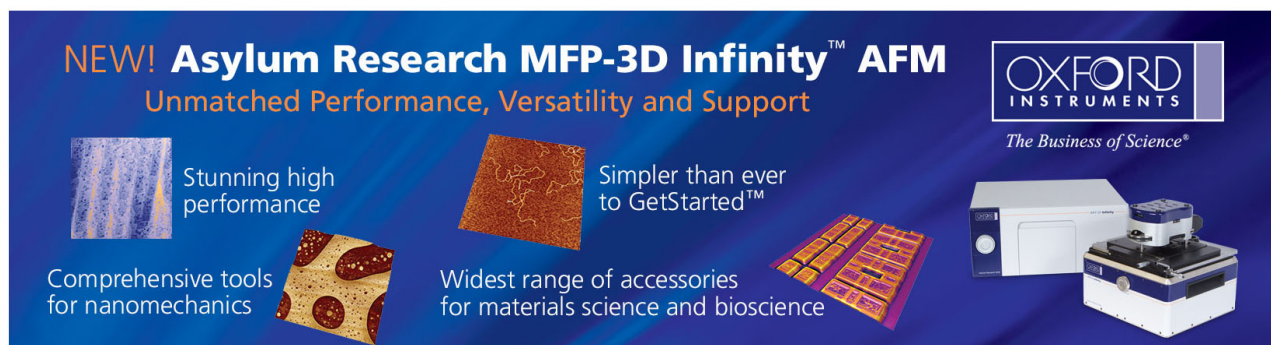
J. Chem. Phys. **129**, 204701 (2008); 10.1063/1.3020353

[First-principles calculation on the conductance of a single 1,4-diisocyanatobenzene molecule with single-walled carbon nanotubes as the electrodes](#)

J. Chem. Phys. **126**, 084705 (2007); 10.1063/1.2483760

[The symmetry of single-molecule conduction](#)

J. Chem. Phys. **125**, 184702 (2006); 10.1063/1.2363976



NEW! Asylum Research MFP-3D Infinity™ AFM
Unmatched Performance, Versatility and Support

OXFORD INSTRUMENTS
The Business of Science®

Stunning high performance

Simpler than ever to GetStarted™

Comprehensive tools for nanomechanics

Widest range of accessories for materials science and bioscience

Single-molecule refrigerators: Substitution and gate effects

Yu-Shen Liu^{1,a)} and Yu-Chang Chen^{2,b)}

¹*Jiangsu Laboratory of Advanced Functional Materials, College of Physics and Engineering, Changshu Institute of Technology, Suzhou 215500, People's Republic of China*

²*Department of Electrophysics, National Chiao Tung University, 1001 Ta Hush Road, Hsinchu 30010, Taiwan*

(Received 17 December 2010; accepted 28 April 2011; published online 24 May 2011)

Using a first-principles approach, we investigate the quantum cooling effects in single-molecule junctions. In comparison with the unsubstituted butanethiol single-molecule junction as a refrigerator, the amino-substituted butanethiol single-molecule junction shows significant enhancement in the coefficient of performance (COP). The enhancement is attributed to the appearance of new states in the neighborhood of chemical potentials due to amino substitution. The COP of butanethiol refrigerator can be improved further by the gate voltages. © 2011 American Institute of Physics. [doi:10.1063/1.3593379]

Since a single molecule to act as electronic circuit was proposed,¹ many researchers have paid considerable attention to the quantum transport properties of molecular-scale quantum devices.² More recently, the Seebeck coefficient S has been measured in molecular junctions.³ These experiments have inspired rapid theoretical developments in understanding the fundamental thermoelectric properties of various nanoscale junctions and designing the new-type thermoelectric devices at the nanoscale level.^{4–6}

Alkane molecular junctions have been extensively investigated due to their capability for self assembly.⁷ These junctions serve as testbeds for comparing experimental results with theoretical calculations. The main conductance mechanism involved in these self-assemble junctions is known as nonresonant tunneling, which arises from the larger gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. Consequently, alkane molecular junctions may not be good candidates for efficient device applications.

In this letter, we investigate the quantum cooling effects in the unsubstituted and amino-substituted alkanethiol molecular junctions. The coefficient of performance (COP) of the amino-substituted butanethiol refrigerator is larger than that of the unsubstituted alkanethiol junctions. The enhancement of COP is due to the new quantum states near the chemical potentials introduced by amino substitution. The COP of the unsubstituted and amino-substituted butanethiol junctions can be optimized further by the gate voltages.

Figures 1(a) and 1(b) show the schemes of the molecular junctions in three-terminal geometry, where the source-drain electrodes are modeled as electron jellium with $r_s=3$. The gate field is introduced as a capacitor consisting of two parallel circular charged disks separated at a certain distance from each other. The axis of the capacitor is perpendicular to the electron transport direction. One plate is placed close to the molecule while the other plate is placed far away from the molecule. The single-molecule refrigerator can be modeled by the Hamiltonian $H=H_0+V$, where H_0 is the Hamiltonian representing the bare metallic electrodes and V is the scattering potential of the single molecule. First, the wave

functions of the source-drain electrodes with applied bias V_B are calculated self-consistently using the Schrödinger and Poisson equations. Second, Green's function is calculated using the wave functions of the bare electrodes. When a molecule is included between the source drain electrodes, the nonequilibrium wave functions of the whole system are calculated by iteratively solving the Lippmann–Schwinger equation until self-consistency is obtained in the framework of the density functional theory in scattering approaches. Detailed theoretical descriptions can be found in Ref. 8. The wave functions are then applied to calculate the electronic thermal current flowing from the right (left) electrode,

$$J^{R(L)} = \frac{2}{h} \int dE (E - \mu_{R(L)}) \tau(E) [f_E^{R(L)} - f_E^{L(R)}], \quad (1)$$

where $f_E^{R(L)} = 1 / \{ \exp[(E - \mu_{R(L)}) / (k_B T_{R(L)})] + 1 \}$ is the Fermi–Dirac distribution of the right (left) electrode. Here, $\tau(E) = (\pi \hbar^2 / mi) \int d\mathbf{r}_\perp \int d\mathbf{K}_\parallel I_{EE, \mathbf{K}_\parallel}^{RR(LL)}(\mathbf{r})$ is the transmission function of the electron with energy E , in which $I_{EE', \mathbf{K}_\parallel}^{RR(LL)}(\mathbf{r}) = [\Psi_{E, \mathbf{K}_\parallel}^{R(L)}(\mathbf{r}) \times (\mathbf{r})]^* \nabla \Psi_{E', \mathbf{K}_\parallel}^{R(L)}(\mathbf{r}) - \nabla [\Psi_{E, \mathbf{K}_\parallel}^{R(L)}(\mathbf{r})]^* \Psi_{E', \mathbf{K}_\parallel}^{R(L)}(\mathbf{r})$, and $d\mathbf{r}_\perp$ represents an element of the metallic electrode surface.

We assume that the temperature of the left electrode is higher than that of the right electrode ($T_R \leq T_L$). On the basis of the second law of thermodynamics, the thermal energy can only flow from the hot electrode to the cold electrode in the absence of a bias $V_B=0$. Once a bias V_B is applied, the electric current can possibly carry a thermal current and thus take heat energy from the cold electrode to the hot electrode becomes possible. The molecular refrigerators set to work when $J^R > 0$, indicating that the thermal energy can be extracted from the cold (right) electrode to the hot (left) electrode. Using Sommerfeld expansion,⁹ Eq. (1) can be simplified as $J^R = -aV_B^2 + bV_B - c$, where $a = e^2 \tau(\mu) / h$, $b = 2e \pi^2 k_B^2 \tau'(\mu) T_R \Delta T / (3h)$, and $c = 2\pi^2 k_B^2 \tau(\mu) T_R \Delta T / (3h)$. We have assumed the relations $\tau(\mu_L) \approx \tau(\mu_R)$ and $\Delta T = T_L - T_R$. We further define the COP for the molecular refrigerators as $\eta = J^R / IV_B$, where J^R is the magnitude of the thermal energy extracted from the cold (right) electrode and IV_B is the power supplied by the battery, where I is the current traveling through the molecular refrigerators calculated by

^{a)}Electronic mail: ysliu@cslg.edu.cn.

^{b)}Electronic mail: yuchangchen@mail.nctu.edu.tw.

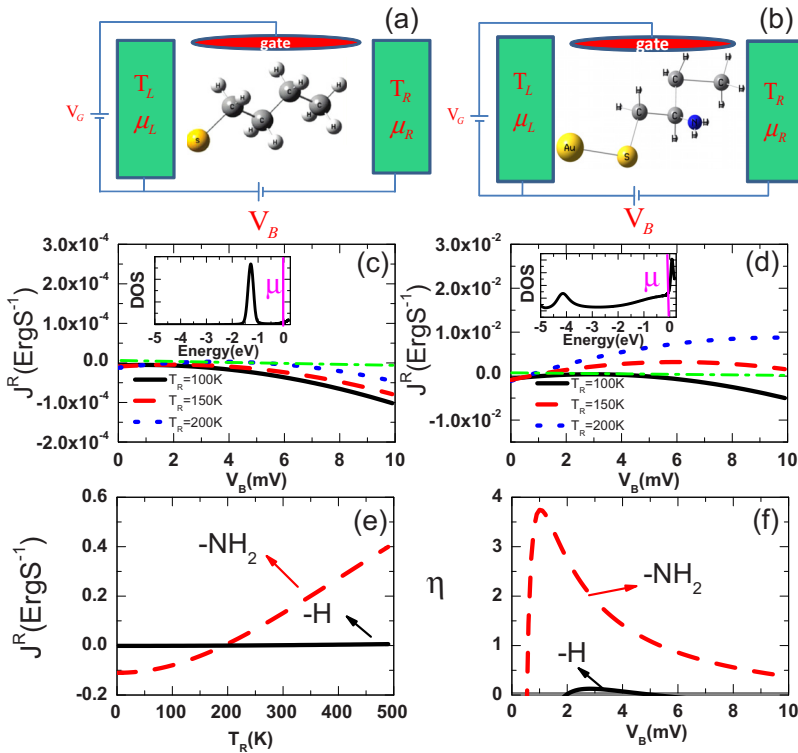


FIG. 1. (Color online) Schemes of (a) the unsubstituted and (b) amino-substituted butanethiol refrigerators. $T_{L(R)}$ and $\mu_{L(R)}$ are the temperature and chemical potential of the left (right) electrode. The applied bias is $V_B = (\mu_R - \mu_L)/e$ and the gate voltage is V_G . (c) and (d) show the J^R vs V_B for various values of T_R with $\Delta T = 1$ K in the unsubstituted and amino-substituted butanethiol refrigerators, respectively, where the insets show the corresponding DOS. (e) shows the J^R vs T_R for the unsubstituted (solid line) and amino-substituted (dashed line) junctions, where $\Delta T = 1$ K and $V_B = 6$ mV. (f) shows the η vs V_B for the unsubstituted (solid line) and amino-substituted (dashed line) junctions, where $T_R = 200$ K and $\Delta T = 1$ K.

$I = (2e/h) \int dE (f_E^R - f_E^L) \tau(E)$. It is noted that $IV_B = |J^R + J^L|$ due to energy conservation.

Figures 1(c) and 1(d) show the rates of thermal energy extracted from the right (cold) electrode (J^R) as a function of V_B for various values of T_R with $\Delta T = 1$ K in the unsubstituted and amino-substituted butanethiol refrigerators, respectively. In sharp contrast to the unsubstituted butanethiol refrigerator, the amino-substituted butanethiol refrigerator possesses a better cooling effects. The main reason is that electronic structures of the molecular junction can be changed when one of the hydrogen atoms attached to the second carbon atoms in the butanethiol molecule is substituted by using a side-coupled amino group [see Fig. 1(b)]. The nonresonant tunneling mechanism may be broken, and a sharp increase in the density of states (DOS) is obtained [see inset of Fig. 1(d)]. Consequently, some new quantum states can be introduced by using the amino substitution. The cooling effect is limited to a certain range of applied biases.⁶ When $\Delta T \ll T_R$, the minimum source-drain voltage (V_{th}) required to trigger the cooling effect is $V_{th} = (1/e) \times [\tau(\mu)/\tau'(\mu)](\Delta T/T_R)$. We note that V_{th} is proportional to ΔT and inversely proportional to T_R . This relationship is consistent with the numerical results shown in Figs. 1(c) and 1(d), where V_{th} decreases as T_R increases. Figure 1(e) compares J^R as a function of T_R for the unsubstituted and amino-substituted butanethiol refrigerators, where ΔT and V_B are fixed. The numerical results show that the J^R of the amino-substituted butanethiol refrigerator is sensitive to T_R . We denote the minimum temperature for possible cooling effect ($J_R > 0$) as T_{op} . When $T_R < T_{op}$, the molecular refrigerator does not function while the cooling effects may be possible when $T_R \geq T_{op}$. The operation temperature T_{op} approximates $T_{op} \approx 1/2[\alpha/V_B + \sqrt{(\alpha/V_B)^2 + \beta V_B}]$, where $\alpha = [\tau(\mu)\Delta T/e\tau'(\mu)]$ and $\beta = [6e\tau(\mu)/\pi^2 k_B^2 \tau'(\mu)]$. Figure 1(e) shows that $T_{op} \approx 200$ K for the amino-substituted junctions. Figure 1(f) shows η as a function of V_B for the unsubstituted

and amino-substituted butanethiol refrigerators, where $\Delta T = 1$ K. The graph shows that COP can be improved significantly when $-H$ is replaced by $-NH_2$. The maximum value of COP of the amino-substituted butanethiol molecular refrigerator is as large as 4 in this case. The maximum value of η can be expressed as $\eta_{max} = (\pi^2 k_B^2 / 12) \times [\tau'(\mu)/\tau(\mu)]^2 (T_R^3 / \Delta T) - (1/2)$. This expression predicts that COP can be enhanced further if T_R is increased. Figure 1(f) also shows that the unsubstituted butanethiol molecular refrigerator functions in a small range of biases between 2 and 5.2 mV when $T_R = 200$ K and $\Delta T = 1$ K, while the amino-substituted butanethiol junction can be operated in a wider range of biases, with the upper limit of bias exceeding 10 mV and the lower limit of bias approaching to 0.6 mV in this case.

Figures 2(a) and 2(b) show the operation temperatures (T_{op}) as functions of V_B and ΔT for the unsubstituted and amino-substituted butanethiol molecular refrigerators, respectively. The amino-substituted butanethiol molecular refrigerator can operate at a wider range of temperatures compared with the unsubstituted butanethiol molecular refrigerator. The minimum value of T_{op} can be approximately expressed as $(T_{op})_{min} = 1/2\sqrt{\beta V_B}$, when $\Delta T = 0$ K. Figures 2(c) and 2(d) show $(T_{op})_{min}$ as a function of V_B for the unsubstituted and amino-substituted butanethiol refrigerators, respectively, where $\Delta T = 0$ K. We observe that $(T_{op})_{min}$ in the amino-substituted butanethiol molecular refrigerator is suppressed compared with the unsubstituted junctions. The amino-substituted butanethiol refrigerator has a lower operation temperature compared with the vacuum diode, which has a operation temperature larger than 1000 K.¹⁰ When $V_B = 1$ mV, the operation temperatures of the proposed molecular refrigerators are around 75 K and 40 K for the unsubstituted and amino-substituted butanethiol junctions, respectively. The operation temperatures can be further suppressed as V_B decreases.

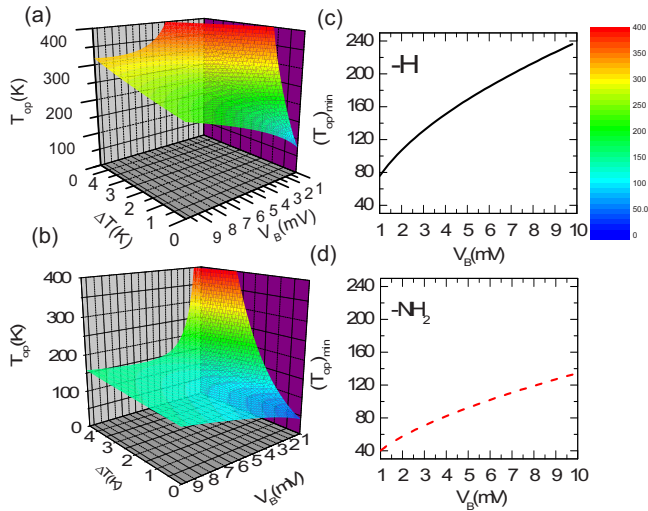


FIG. 2. (Color online) T_{op} vs ΔT and V_B in the (a) unsubstituted and (b) amino-substituted butanethiol refrigerators. $(T_{op})_{min}$ vs V_B in (c) the unsubstituted and (d) amino-substituted butanethiol refrigerators at $\Delta T=0$.

Recently, a longstanding challenge in creating the true molecular junctions with three-terminal geometry has been conquered experimentally in which the molecular orbitals were directly modulated by an external gate voltage.¹¹ In the first-principles calculations, we compare the gating effects on η and J^R for the butanethiol junctions before and after amino substitution in Fig. 3. Before the amino substitution, the rates of thermal energy extracted from the cold temperature (J^R) and the COP (η) increase as the gate voltages decrease. After the amino substitution, the rates of thermal energy extracted

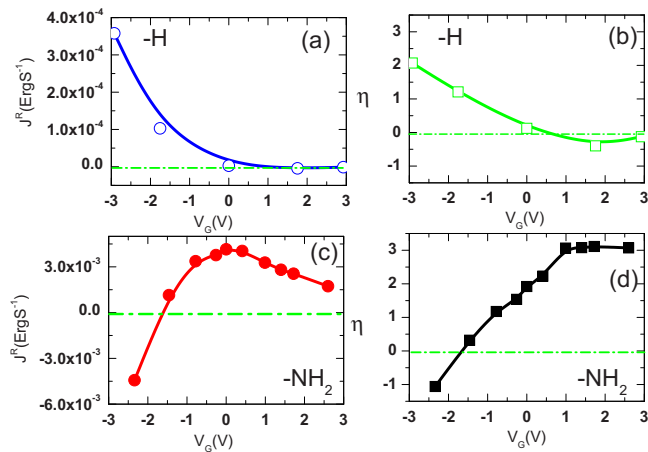


FIG. 3. (Color online) (a) J^R vs V_G and (b) η vs V_G for the unsubstituted butanethiol refrigerator. (c) J^R vs V_G and (d) η vs V_G for the amino-substituted butanethiol refrigerator, where $T_R=200$ K, $\Delta T=1$ K, and $V_B=3$ mV.

from the cold temperature (J^R) and the COP (η) increase as the gate voltages increase.

In conclusion, we propose molecular refrigerators based on the akanethiol molecular junctions. We compare the quantum cooling effects for the unsubstituted and amino-substituted butanethiol junctions using the first-principles approaches. The amino-substituted butanethiol junction has a better cooling effect because of some new states appearing near the chemical potentials introduced by amino substitution. The cooling effects of the unsubstituted and amino-substituted butanethiol junctions can be optimized further by the gate voltages.

Y.-S.L. acknowledges the supports from NFS China (Grant No. 10947130) and the Science Foundation of the Education Committee of Jiangsu Province (Grant No. 09KJB140001). Y.-C.C. is thankful for the supports from NSC (Taiwan) (Grant No. 97-2112-M-009-011-MY3) and the National Center for Theoretical Science (Taiwan) and the Ministry of Education (Taiwan) under MOE ATU plan.

¹A. Aviram and M. A. Ratner, *Chem. Phys. Lett.* **29**, 277 (1974).

²A. Aviram, *J. Am. Chem. Soc.* **110**, 5687 (1988); A. Harada, J. Li, and M. Kamachi, *Nature (London)* **364**, 516 (1993); M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and M. J. Tour, *Science* **278**, 252 (1997); W. D. Tian, S. Datta, S. Hong, R. Reifenberger, J. I. Henderson, and C. P. Kubiak, *J. Chem. Phys.* **109**, 2874 (1998).

³P. Reddy, S. Y. Jang, R. A. Segalman, and A. Majumdar, *Science* **315**, 1568 (2007); K. Baheti, J. A. Malen, P. Doak, P. Reddy, S. Y. Jang, T. D. Tilley, A. Majumdar, and R. A. Segalman, *Nano Lett.* **8**, 715 (2008); J. A. Malen, P. Doak, K. Baheti, T. D. Tilley, R. A. Segalman, and A. Majumdar, *ibid.* **9**, 1164 (2009).

⁴F. Pauly, J. K. Viljas, and J. C. Cuevas, *Phys. Rev. B* **78**, 035315 (2008); C. M. Finch, V. M. García-Suárez, and C. J. Lambert, *ibid.* **79**, 033405 (2009); Y. Dubi and M. Di Ventra, *Nano Lett.* **9**, 97 (2009); S. H. Ke, W. T. Yang, S. Curtarolo, and H. U. Baranger, *ibid.* **9**, 1011 (2009); Y. S. Liu and Y. C. Chen, *Phys. Rev. B* **79**, 193101 (2009); Y. S. Liu, Y. R. Chen, and Y. C. Chen, *ACS Nano* **3**, 3497 (2009); B. C. Hsu, Y. S. Liu, S. H. Lin, and Y. C. Chen, *Phys. Rev. B* **83**, 041404(R) (2011).

⁵Y. S. Liu and X. F. Yang, *J. Appl. Phys.* **108**, 023710 (2010); Y. S. Liu, F. Chi, X. F. Yang, and J. F. Feng *ibid.* **109**, 053712 (2011); Y. S. Liu, D. B. Zhang, X. F. Yang, and J. F. Feng, *Nanotechnology* **22**, 225201 (2011).

⁶Y. S. Liu, B. C. Hsu, and Y. C. Chen, *J. Phys. Chem. C* **115**, 6111 (2011).

⁷N. J. Tao, *Nat. Nanotechnol.* **1**, 173 (2006); D. J. Wold and C. D. Frisbie, *J. Am. Chem. Soc.* **122**, 2970 (2000); X. D. Cui, X. Zarate, J. Tomfohr, O. F. Sankey, A. Primak, A. L. Moore, T. A. Moore, D. Gust, G. Harris, and S. M. Lindsay, *Nanotechnology* **13**, 5 (2002); C. C. Kaun and H. Guo, *Nano Lett.* **3**, 1521 (2003); C. L. Ma, D. Nghiem, and Y. C. Chen, *Appl. Phys. Lett.* **93**, 222111 (2008).

⁸N. D. Lang, *Phys. Rev. B* **52**, 5335 (1995); M. Di Ventra, S. T. Pantelides, and N. D. Lang, *Appl. Phys. Lett.* **76**, 3448 (2000); Z. Yang, A. Tackett, and M. Di Ventra, *Phys. Rev. B* **66**, 041405(R) (2002).

⁹N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976).

¹⁰G. D. Mahan, *J. Appl. Phys.* **76**, 4362 (1994).

¹¹H. W. Song, Y. S. Kim, Y. H. Jang, H. J. Jeong, M. A. Reed, and T. H. Lee, *Nature (London)* **462**, 1039 (2009).