

A new alligator-clip compound for molecular electronics

Timo Jacob ^{*}, Mario Blanco, William A. Goddard III

*Materials and Process Simulation Center, Beckman Institute (139–74), California Institute of Technology,
1200 E. California Blvd., Pasadena, CA 91125, USA*

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Abstract

We used the B3LYP flavor of density functional calculations to study new alligator-clip compounds for molecular electronics with platinum electrodes. First, with commonly used S-based linkage molecule 3-methyl-1,2-dithiolane (MDTL) we find that after chemisorption on Pt(111) the most stable structure is ring-opened with a binding energy of 32.44 kcal/mol. Among several alternative alligator-clip compounds we find that P-based molecules lead to much higher binding energies. For the ring-closed structure of 3-methyl-1,2-diphospholane (MDPL) a binding energy of 47.72 kcal/mol was calculated and even 54.88 kcal/mol for the ring-opened molecule. Thus, MDPL provides a more stable link to the metal surface and might increase the conductance.

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1. Introduction

Molecular electronics (molecular switches and diodes) based on mechanically interlocked molecules such as catenanes and rotaxanes strung between metal electrodes through chemical manipulations have been demonstrated in the laboratory [1–10] and effort is now shifting toward improving the current–voltage characteristics [11–13] of these molecular devices. Recent theoretical work [14] indicates that changes in the HOMO and LUMO characteristics as a function of the interlocking configuration are responsible for the current–voltage characteristics. The first devices featured a thiol alligator-clip linker compound to attach one end of the molecular device to the metal surface but a noncovalent linkage at the other. More recently [15] experimental measurements on gold electrodes have shown that attaching 3-alkyl-1,2-dithiolanes (see Fig. 1) to both ends dramatically increases the on–off current ratio of these devices by two orders of magnitude, leading to a symmetric response as a function of source to drain voltage. Low temperature transport measurements using Pt break junctions provide information relating to such

molecular properties as electronic and vibrational states, and Coulomb, exchange, and spin-magnetic field interactions [15]. But it is not known whether these improvements are the result of surface binding energetics or due to changes in the molecular orbitals across the entire device.

Based on quantum mechanics (QM) studies, we conclude here that the performance of the current generation of S-based alligator-clips might be improved by increasing the binding to the metal surfaces, which would reduce the electrical resistance. Consequently, we examined alternative P-based alligator-clips, which we find lead to much stronger binding to the Pt surface than do the S-based systems. Since Ratner and coworkers [16–18] showed that the chemisorption process (thiol-complexes on gold electrodes) mainly affects the anchoring atom and the metal surface but not the rest of the molecule, we expect that these P-based alligator-clips will lead to improved device performance.

2. Theoretical method

To determine the binding strength of various alligator-clips to the surface, we used the B3LYP flavor of spin-unrestricted density functional theory (DFT), including the generalized gradient approximation plus exact ex-

^{*} Corresponding author. Fax: +62-65-850-918.

E-mail addresses: tj@wag.caltech.edu, wag@wag.caltech.edu

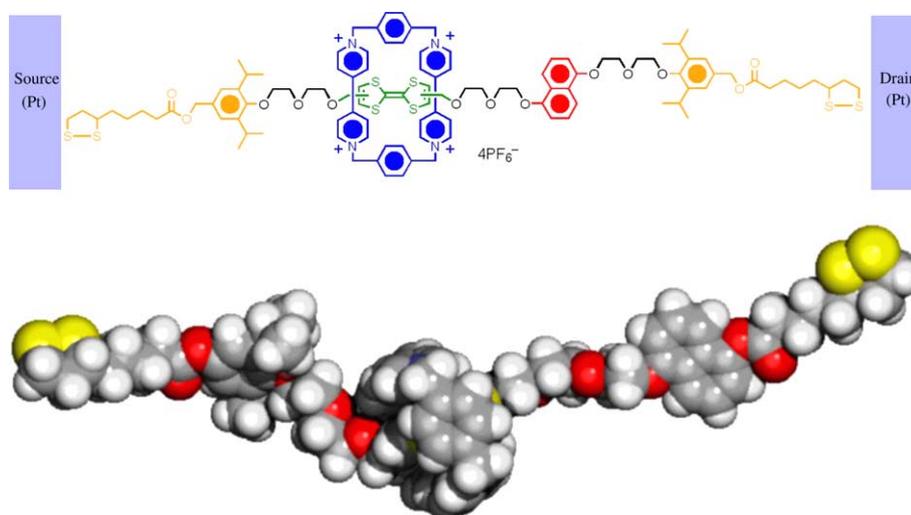


Fig. 1. Chemical structure of the molecular component ([2]rotaxane) in the Stoddart–Heath programmable molecular Switch. The ring molecule CBPQT (blue in the upper picture) is thought to shuttle between the TTF (green) and the naphthyl (red) sites upon application of a large voltage gradient. The state of the switch can be probed by application of a smaller field, where the TTF location leads to low current while the naphthyl location leads to current 15 times higher.

change [19,20]. For the platinum atoms the 60 core electrons (1s–4f) were treated by the Hay and Wadt core–valence relativistic effective-core potential (ECP), leaving 18 valence electrons [atomic ground state of Pt is $(5s)^2(5p)^6(5d)^9(6s)^1(6p)^0$] treated with the LACVP** basis set. All other elements are described with all electrons using the 6–31G** basis set. All ab initio cluster calculations were carried out with the JAGUAR program [21].

In [22] we showed that additional diffuse functions on the adsorbate atoms (even on the electronegative oxygen) have only a minor influence on adsorption energy and charge transfer. Since the ground states of the different systems have numerous unpaired spins, the total energy for all reasonable low-lying spin states were calculated self consistently. For each of these spin states different low-lying excitations between various occupied and unoccupied molecular orbitals were examined to ensure that we found the lowest energy spin state. Thus, after considering the lowest states for $S = 8–14$ we found the ground state to be $S = 11$ for both structures shown in Fig. 2.

The binding energies were calculated with respect to the total energies obtained from separate calculations of the bare cluster and the corresponding alligator-clip compound. In all binding energy calculations basis set superposition errors (BSSE) were taken into account.

The partial atomic charges shown in Fig. 3 were computed using the Mulliken population analysis.

3. Results and discussion

Previously [22] we showed that to represent the chemistry on the Pt(111) surface with a cluster requires a three-layer cluster with at least 28 atoms, and we have

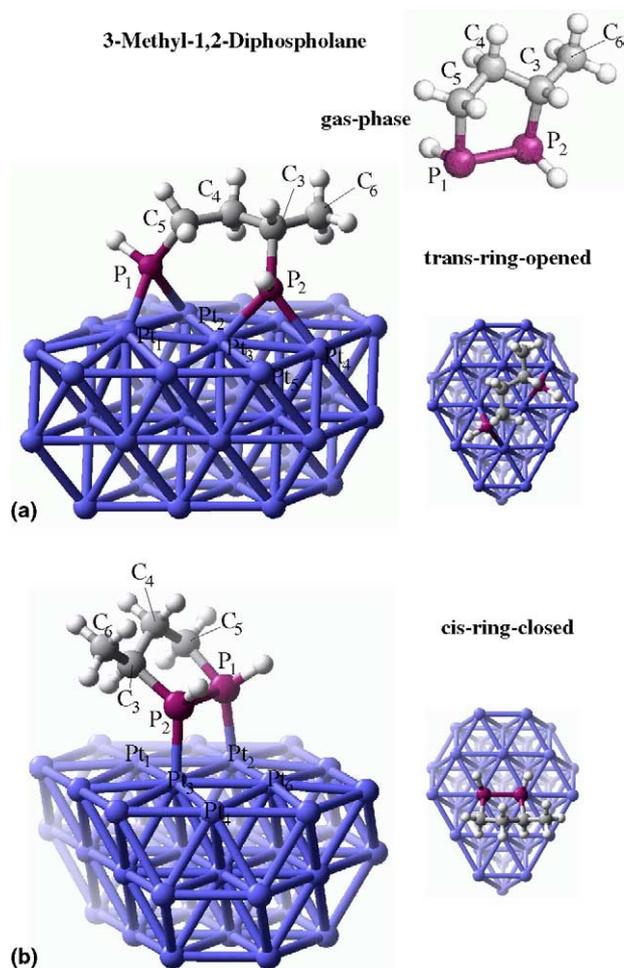


Fig. 2. Structures of the new alligator-clip molecule MDPL in gas-phase (upper right structure) and adsorbed on the Pt_{35} cluster with opened and closed five-member ring.

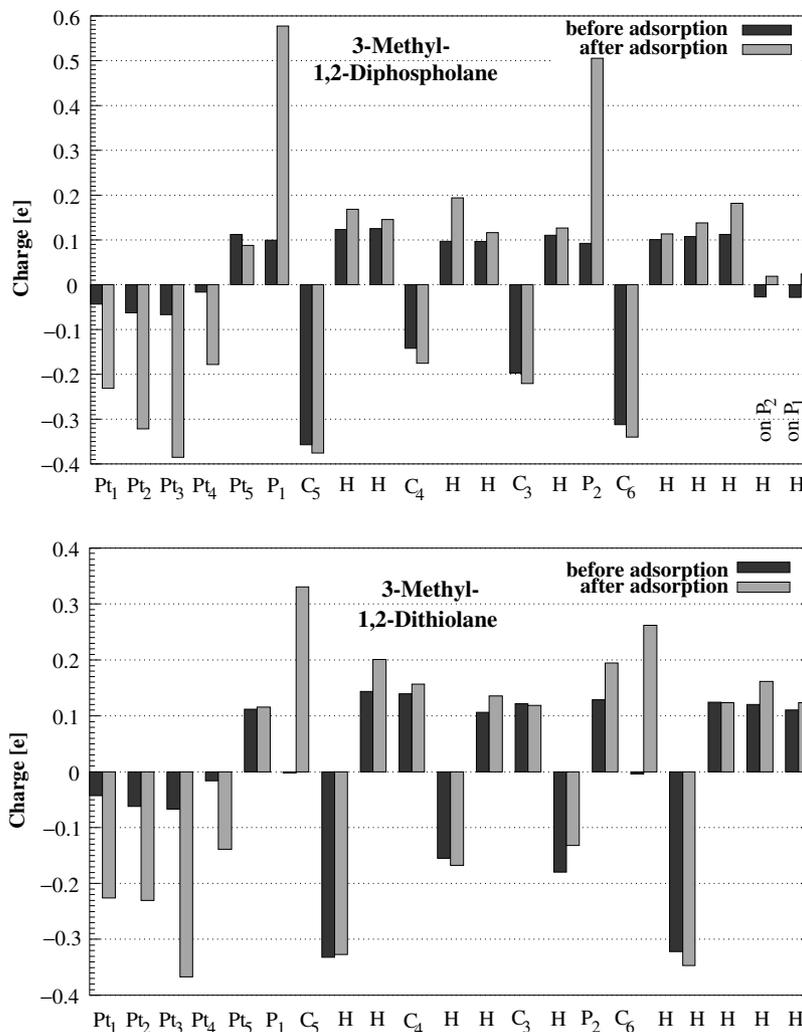


Fig. 3. Mulliken partial charges for ring-opened MDPL and MDTL before and after adsorption on the Pt cluster (labels see Fig. 2).

shown [23] that a 35 atom three-layer Pt cluster (hereafter Pt₃₅) is quite suitable for studies of adsorption. Pt₃₅ consists of 14 atoms in the first layer, 13 in the second layer, and eight atoms in the third layer (see Fig. 2). To find the correct ground state we first optimized the adsorbate molecule on the one-layer Pt₁₂ cluster [22], considering all plausible structures and spin states for each of the adsorbed molecules. Focusing on the significantly more stable structures on Pt₁₂, the final energetics were calculated by re-optimizing their geometries on the Pt₃₅ cluster. In order to prove this procedure we optimized ring-opened MDPL (see Fig. 2) on Pt₁₂ and Pt₃₅ independently, using the same initial geometry. For both systems we obtained the same surface binding sites of the P atoms with a difference in the bond length of only <0.06 Å. Comparing the carbon frameworks on Pt₁₂ and Pt₃₅ shows differences in the distances of <0.01 Å, and in the angles of <3°. Although this result indicates comparable structures, a larger Pt cluster is re-

quired to obtain correct energetics (see above). To include the dominant surface relaxation effects the four central Pt atoms in the top layer of Pt₃₅ were also allowed to freely relax.

First we calculated the adsorption on Pt(1 1 1) of the commonly used alligator-clip molecule 3-methyl-1,2-dithiolane (MDTL), a stable five-member ring structure in the gas phase (compare with Fig. 2). For the free gas-phase molecule we find two nearly degenerate conformations, with C₅–S₁–S₂–C₃ dihedral angles of 5.0° and 28.8° (the latter is only 0.22 kcal/mol less stable). Keeping the five-member ring intact leads to an adsorption energy on Pt(1 1 1) of 30.38 kcal/mol (with C₅–S₁–S₂–C₃ = 2.9°). However, opening the ring so that both S bind to the Pt(1 1 1) surface leads to a chemisorption bond of $E_{\text{bind}} = 32.44$ kcal/mol, relative to free ring MDTL. To interpret the latter result, consider that the calculated energy to break the S–S bond in the gas phase cyclic MDTL molecule is 50.48 kcal/mol, which

is 6.42 kcal/mol weaker than the calculated S–S bond energy of 56.90 kcal/mol for the molecule $C_2H_5-S-S-C_3H_7$. This 6.42 kcal/mol ring strain can be thought of a spring-loaded contribution to the chemisorption of MDTL to the Pt(111) surface. Including the ring opening energy, we can consider that each covalent bond of the S to Pt(111) is ≈ 41.5 kcal/mol.

Based on the studies on MDTL we considered binding several compounds to the Pt(111) surface. As mentioned above, structures were calculated with the Pt_{12} cluster and the final energetics were obtained with Pt_{35} . For each compound the binding energies to the Pt(111) surface are summarized at the end of Table 1. Replacing one sulfur atom with an oxygen (homologous to S) gives either 3-methyl-1,2-oxathiolane or 5-methyl-1,2-oxathiolane, which both form bonds to the surface weaker by 20 kcal/mol. Similarly, all N-based molecules (imidazole, 1,2,3-triazole, purine, 2,4-diazapentane) lead to bonds weaker by >6 kcal/mol (see Table 2).

However, replacing S with P in the bond to the surface leads to increased adsorption energies. We found that CH_3PH (methyl-phosphino), which forms one covalent bond on top of a Pt surface atom, has 12.24 kcal/mol higher adsorption energy than MDTL. Since in the most stable configuration (ring-opened) MDTL donates 0.833 e to the Pt cluster, the higher binding energy of methyl-phosphino is partly caused by the lower electronegativity of P compared to S, allowing even more

Table 1
Ground spin-states, binding energies, and adsorbate charges (from Mulliken population analysis) for several compounds after adsorption on Pt_{35}

System	Spin-state S	E_{bind} (kcal/mol)	Q (adsorb.) (e)
Pt_{35}	11	–	–
<i>MDPL (gas-phase)</i>			
ring-opened	1	–	–
<i>trans</i> -ring-closed	0	–	–
<i>Pt₃₅-MDPL</i>			
ring-opened (Fig. 2a)	11	54.88 4	+1.199
<i>cis</i> -ring-closed (Fig. 2b)	11	47.71 8	+1.214
<i>trans</i> -ring-closed	11	39.27 2	+0.936
<i>Pt₃₅-MDTL</i>			
ring-opened	11	32.44 4	+0.833
ring-closed	11	30.38 4	+1.101
Pt_{35} -5-methyl-1,2-oxathiolane	11	11.96 8	–
Pt_{35} -imidazole	11	26.50 3	–
Pt_{35} -1,2,3-triazole	11	17.75 9	–
Pt_{35} -purine	11	24.73 5	–
Pt_{35} -2,4-diazapentane	12	34.74 4	–
Pt_{35} -methanol	11	11.71 7	–
Pt_{35} -methyl-phosphino	21/2	44.68 6	–

In addition, the ground spin-states for the MDPL molecule are given.

Table 2
Structural information for free gas-phase MDPL and after adsorption on the Pt_{35} cluster (for structures and labels see Fig. 2)

System	Distances (Å)	Angles (°)
<i>MDPL (gas-phase)</i>		
ring-opened	$C_5-P_1 = 1.882$ $P_1-P_2 = 3.750$ $P_2-C_3 = 1.888$ $C_3-C_4 = 1.543$ $C_4-C_5 = 1.550$ $C_3-C_6 = 1.535$	$P_2-C_3-C_4 = 115.3$ $C_3-C_4-C_5 = 115.9$ $C_4-C_5-P_1 = 115.6$ $P_2-C_3-C_6 = 108.5$ $C_3-P_2-P_1-C_5 = 16.8$
<i>trans</i> -ring-closed	$C_5-P_1 = 1.891$ $P_1-P_2 = 2.249$ $P_2-C_3 = 1.912$ $C_3-C_4 = 1.536$ $C_4-C_5 = 1.532$ $C_3-C_6 = 1.532$	$C_5-P_1-P_2 = 93.6$ $P_1-P_2-C_3 = 94.2$ $P_2-C_3-C_4 = 107.1$ $C_3-C_4-C_5 = 110.2$ $C_4-C_5-P_1 = 110.6$ $P_2-C_3-C_6 = 111.9$
<i>Pt₃₅-MDPL</i>		
ring-opened (Fig. 2a)	$C_5-P_1 = 1.864$ $P_2-C_3 = 1.894$ $C_3-C_4 = 1.535$ $C_4-C_5 = 1.549$ $C_3-C_6 = 1.531$ $P_1-Pt_{1/2} = 2.261$ $P_2-Pt_{3/4} = 2.301$ $P_2-Pt_5 = 3.016$	$P_2-C_3-C_4 = 113.3$ $C_3-C_4-C_5 = 115.1$ $C_4-C_5-P_1 = 114.7$ $C_4-C_3-C_6 = 111.6$ $P_2-C_3-C_6 = 112.3$ $P_1-Pt_1-Pt_2-Pt_3 = 103.6$ $P_2-Pt_3-Pt_4-Pt_5 = 88.9$
<i>cis</i> -ring-closed (Fig. 2b)	$C_5-P_1 = 1.866$ $P_1-P_2 = 2.193$ $P_2-C_3 = 1.873$ $C_3-C_4 = 1.545$ $C_4-C_5 = 1.542$ $C_3-C_6 = 1.529$ $P_1-Pt_2 = 2.251$ $P_2-Pt_3 = 2.248$ $C_{3/4/5/6}-H = 1.094$ $P_{1/2}-H = 1.411$	$C_5-P_1-P_2 = 95.4$ $P_1-P_2-C_3 = 96.0$ $P_2-C_3-C_4 = 106.7$ $C_3-C_4-C_5 = 112.2$ $C_4-C_5-P_1 = 107.9$ $C_4-C_3-C_6 = 114.4$ $P_2-C_3-C_6 = 112.0$ $Pt_{2/3}-P_{1/2}-H = 120.5$ $C_3-P_2-P_1-C_5 = 1.0$ $S^{\parallel}-(C_3-P_2-P_1-C_5) = 36.2$

charge per atom to be transferred. In addition, since methyl-phosphino has only one P atom, which attaches to the surface, there are much lower steric interactions than with MDTL. Therefore, the three p-orbitals are less deformed (almost perpendicular to each other) than in MDTL, resulting in a higher binding energy.

The best system among the studied compounds is 3-methyl-1,2-diphospholane (MDPL, see Fig. 2), which has ring-opened and ring-closed structures on Pt(111) similar to MDTL (despite the additional H atom at each phosphorus). However, now the ring-closed structure can have *cis* or *trans* P–H bonds.

Gas-phase *trans*-MDPL also has two stable ring conformations with $C_3-P_1-P_2-C_5$ dihedral angles of 3.5° and 22.3° , but different from MDTL the twisted one is 2.1 kcal/mol less stable. We calculate that the energy to break the P–P bond of the ring structure is within 0.1 kcal/mol of the P–P bond of the molecule $C_2H_5-HP-PH-C_3H_7$. Thus, MDPL has no internal strain energy to provide the spring-loaded chemisorption found for MDTL.

After adsorbing on the surface two structures of MDPL are possible: ring-closed and ring-opened. Although the ring-closed structure can have *cis* or *trans* configuration, we will focus on the *cis*-closed-ring structure, which has a 8.45 kcal/mol higher binding energy. We also checked for a possible *cis*-ring-opened structure. However, after a geometry optimization we always obtained the *trans* configuration. Thus, our calculations led to binding energies of 47.72 kcal/mol for the *cis*-ring-closed (see Fig. 2b) and 54.88 kcal/mol for the *trans*-ring-opened structure (see Fig. 2a).

In the *trans*-ring-closed configuration both P are covalently bound to the surface ($P_{1/2}$ – $Pt_{2/3}$ = 2.248, 2.251 Å), leading to a bridge type binding. The carbon framework is tilted toward a μ_3 threefold position by 53.8° (angle between the surface normal S^\perp and the C_3 – P_2 – P_1 – C_5 plane) allowing further stabilization of the surface binding. Caused by the adsorption each P transfers a charge of ≈ 0.45 e to the adjacent Pt atom. This suggests that the P can be thought of as P^+ , making two covalent P–Pt bonds in addition to the P–C and P–H with the other electron transferred to the Pt cluster. Thus, the bonds on both P have tetrahedral orientations. All carbon and hydrogen atoms show nearly no change in charge due to adsorption, suggesting that the surface binding mainly influences the phosphorus atoms. Therefore, the comparison of the internal distances and angles of adsorbed *cis*-ring-closed MDPL with the free molecule also shows only little change.

In the more stable ring-open adsorbed MDPL (see Fig. 2a), which we focus on in the following discussion, each phosphorus forms covalent bonds to two Pt atoms (on bridge positions), with all four P–Pt distances from 2.26 to 2.30 Å and a P–P separation of 3.98 Å (2.25 Å in free ring-closed MDPL and 3.75 Å in free ring-opened MDPL). Including the energy required to open the ring in the free molecule ($DH(P-P)$ = 53.19 kcal/mol), we can consider that the binding energy of each phosphorus to Pt(111) is 54.0 kcal/mol (41.5 kcal/mol for MDTL), leading to a total adsorption energy of 108.0 kcal/mol. However, the presence and influence of the Pt surface certainly lowers the ring-opening energy. The net spin of the cluster+adsorbate is $S = 11$ (as for bare Pt_{35}), whereas forming two covalent bonds to the surface would have been expected to decrease it by $\Delta S = 1$ to $S = 10$. However, the Mulliken population analysis (see Fig. 3) shows that each phosphorus atom donates 0.4–0.5 e to the surface, with insignificant changes in the charge distribution of the rest of the MDPL. As for the *cis*-ring-closed case P can be thought of as P^+ , making two covalent P–Pt bonds in addition to the P–C and P–H with the other electron transferred to the Pt cluster. The C_3 – C_4 – C_5 and C_4 – C_5 – P_1 bond angles increase by only 4.1° to 4.9° upon breaking the P–P bond, indicating no strain energy. This can be compared to MDTL, which increases its C_3 – C_4 – C_5 and C_4 – C_5 – S_1 bond angles

by 9.2° and 10.5°, showing the effect of mainly relaxing ring strain. Indeed, all angles of the chemisorbed MDPL are close to the structure of the triplet state formed by breaking the P–P bond (e.g., C_3 – C_4 – C_5 and C_4 – C_5 – P_1 are $\approx 115^\circ$). Thus, the ring-open adsorbed molecule has a P_1 – P_2 distance compatible with bonding to the two surface bridge sites. This may explain in part the higher binding energy of the diphospholane versus the dithiolane compound. For both compounds the bridge binding may result from constraints in the carbon framework.

The charge analysis of the most stable structures using Mulliken populations (see Fig. 3) shows that for both ring-opened molecules (MDPL and MDTL) chemisorption to the surface leaves the charges of the carbon framework nearly unchanged, leading to a total charge transfer from the molecule to the Pt cluster of 1.199 e in case of ring-opened MDPL and 0.833 e for ring-opened MDTL. The localized (metal surface and anchoring atom of the alligator-clip compound) influence of partly changing the alligator-clip attachment is in agreement with Ratner's studies of thiol-complexes on gold clusters [16–18]. Since electron transfer from the heteroatom to the nearby Pt atoms seems to be important in binding these alligator-clip compounds, the stronger bond of MDPL is understood in terms of the lower electronegativity of P compared to S. Consequently, electron donor substituents to P_1 should further increase the binding to the Pt(111) surface. An additional possibility is for dissociative chemisorption of MDPL to the surface while displacing the H atoms to the surface.

4. Summary

In this Letter, we suggest a new alligator-clip compound, 3-methyl-1,2-diphospholane, for attaching rotaxanes and related molecules to metal surfaces. It should form stronger bonds to the Pt(111) surface than the MDTL alligator-clip compound. Since changing the atoms that are directly bonded to the surface from S to P leads to only minor effects on the charge and spin-density distribution of the remainder of the alligator-clip molecule, we expect the properties for the molecular switch to be nearly unaffected. However, MDPL may provide a more stable linkage between metal surface and molecular switches and diodes, reducing the risk of an open circuit. In addition, the less electronegative P might lead to bridging orbitals closer to the Fermi-surface of the metal, increasing the conductance. Comparing the properties for molecular switches using MDPL and MDTL linkages would provide insight into performance characteristics. The localized nature of the binding and the nearly identical structure and charge population characteristics beyond the heteroatoms sug-

gests that the differences between MDPL and MDTL will involve only the difference in bonding to the surface. Finally the role of the alligator-clip molecule as an electron donor points to further improvements by incorporating additional electron donor functional groups.

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