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Efficient conducting channels formed by the π-π stacking in single [2,2]paracyclophane molecules

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The electronic transport properties of single [2,2]paracyclophane molecules directly connected to gold and platinum electrodes have been investigated both theoretically and experimentally by using first-principles quantum transport simulations and break-junction experiments. For comparison, investigations on [3,3]- and [4,4]-paracyclophanes have also been performed. Our calculations show that the strength of the π-π interaction in paracyclophanes is critically dependent on the inter-ring distance. In contrast to [4,4]paracyclophane in which the π-π interaction is very weak due to the large inter-ring distance, the π-π interaction in [2,2]- and [3,3]-paracyclophanes is rather strong and dominates the electronic transport properties. In particular, for the asymmetric Au-[2,2]paracyclophane-Au junction in which the [2,2]paracyclophane molecule is connected to each gold electrode through a Au adatom and the two Au adatoms are attached in η^1-fashion to two carbon atoms in the benzene backbones connecting with different ethylene groups, the transmission coefficient at the Fermi level is calculated to be 1.0×10^{-2}, in excellent agreement with experiments. When the gold electrodes are replaced by platinum, the calculated transmission coefficient at the Fermi level of the symmetric Pt-[2,2]paracyclophane-Pt junction with one Pt adatom used as the linker group is increased to 0.83, demonstrating that the π-π stacking in [2,2]paracyclophane is efficient for electron transport when the molecule-electrode interfaces are electronically transparent. This is confirmed by our preliminary experimental studies on the Pt-[2,2]paracyclophane-Pt junctions, for which the low-bias junction conductance has reached 0.40 ± 0.02 G_0 (G_0 is the conductance quantum). These findings are helpful for the design of molecular electronic devices incorporating π-π stacking molecular systems. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3692184]

I. INTRODUCTION

Understanding electron transport at the single molecule level is crucial for the design and the construction of molecular electronic devices,[1,2] which are believed to have the potential of supplementing or replacing conventional silicon-based microelectronic devices. Besides conjugate molecules such as benzene and saturated molecules such as alkane chains, devices incorporating π-π stacking molecular systems have recently received much attention.[3–11] In molecular junctions formed by spontaneous π-π stacking,[3,4] the stacking geometry is extremely difficult to control.[4,5] This fact may be responsible for the occurrence of multiple π-type conductance peaks in junctions composed of two oligophenyleneethynylenes connected to gold electrodes.[4] In contrast, the atomic structure of paracyclophane molecules, especially of [2,2]paracyclophane, is much more determined.[12] This is an advantageous circumstance as it may allow us to establish a relation between the device performance and its structure. Schneebeli *et al.* have measured the conductance of a series of molecular wires with up to four π-π stacked benzene rings connected directly to gold electrodes,[11] and found that the molecular conductance decreases exponentially with increasing the number of stacked phenyl rings. The smaller value of the decay constant of these π-π stacked paracyclophanes compared with that of alkyl chains also indicates that the electron transport is through the π-system rather than the ethylene linker groups. Although the measured conductance of the Au-[2,2]paracyclophane-Au junction is only 0.96×10^{-2} G_0 (here $G_0 = \frac{2e^2}{h}$ is the conductance quantum), it is quite interesting to ask ourselves whether electrons can be transported through the [2,2]paracyclophane molecule efficiently in other junctions. This is particularly interesting in view of the fact that the inter-ring distance (3.097 Å) is much shorter than the sum of van der Waals radii (1.70 Å) of carbon[13] and that the much lower junction conductance may be caused by the resistance at the interfaces between the [2,2]paracyclophane molecule and the two electrodes. Intriguingly the inter-ring distance in paracyclophanes can be tuned systematically by changing the number of methylene groups[12] and thus the dependence of the transport efficiency on the inter-ring distance can be studied.

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In order to address these questions, in this work we investigate theoretically the electronic transport properties of the [2,2]-, [3,3]- and [4,4]-paracyclophane molecules sandwiched between gold and platinum electrodes. This is realized by employing the non-equilibrium Green's function (NEGF) formalism combined with density functional theory (DFT), i.e., the NEGF+DFT approach.[14–22] Our calculations demonstrate that, unlike for [4,4]paracyclophane, the through-space π-π interaction is the dominant conducting mechanism for [2,2]- and [3,3]-paracyclophanes due to their small inter-ring distance. More specifically, the zero-bias conductance of an asymmetric Au-[2,2]paracyclophane-Au junction, in which the two Au adatoms connecting [2,2]paracyclophane to two Au electrodes are attached to two carbon atoms in the benzene rings bonding with different ethylene groups, is calculated to be 1.0×10^{-2} G_0. This is consistent with the published experimental value of 0.96×10^{-2} G_0.[11] The replacement of the gold electrodes with platinum ones increases the maximum of the calculated transmission coefficient at the Fermi level to 0.83, illustrating that the π-π stacking in [2,2]paracyclophane can form an intrinsic efficient conducting channel for electron transport and that the [2,2]paracyclophane-Pt interface is more electronically transparent than the [2,2]paracyclophane-Au one. Such theoretical findings are corroborated by our measured conductance values of individual [2,2]paracyclophane molecules connected to gold and platinum electrodes. Here, single-molecule junctions are formed by using a scanning tunneling microscope (STM)-based break junction method.[23,24] Although the low-bias conductance of the Au-[2,2]paracyclophane-Au junctions is measured to be $(0.75 \pm 0.03) \times 10^{-2}$ G_0, very close to that obtained by Schneebeli *et al.*,[11] the conductance of the Pt-[2,2]paracyclophane-Pt junctions is much increased and reaches up to a value of 0.40 ± 0.02 G_0.

II. THEORETICAL AND EXPERIMENTAL PROCEDURES

A. Theoretical method

In this work, we use the DFT code SIESTA (Ref. 25) to study the atomic and electronic structure of both the Au-paracyclophane-Au and Pt-paracyclophane-Pt molecular junctions and the quantum transport code SMEAGOL (Refs. 21 and 22) to study their electronic transport. SIESTA is an efficient numerical implementation of DFT, in which improved Troullier-Martins pseudopotentials are used to describe the atomic cores and the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) is used for the exchange and correlation functional.[26,27] The wave-functions of the valence electrons are expanded over a finite-range numerical basis. By means of extensive optimization, a user-defined double-zeta plus polarization basis set is constructed for C and H and a single-zeta plus polarization one is used for Au and Pt. Geometry optimization is performed by conjugate gradient until the forces are smaller than 0.03 eV $Å^{-1}$.

SMEAGOL is a practical implementation of the NEGF + DFT approach.[21,22] Since SMEAGOL uses SIESTA as the DFT platform, we employ the same pseudopotentials, basis set, and GGA functional for both geometry relaxation and transport. Periodic boundary conditions are applied in the transverse directions (orthogonal to the transport). The unit cell of the extended molecule comprises one paracyclophane molecule and ten Au(111) or Pt(111) atomic layers with a (4 × 4) supercell. Furthermore, we use an equivalent cutoff of 200.0 Ry for the real space grid, while the charge density is integrated over 100 energy points along the semi-circle, 40 energy points along the line in the complex plane and 20 poles are used for the Fermi distribution (the electronic temperature is 25 meV). The transmission coefficient $T(E)$ of the molecular junctions is evaluated as

$$T(E) = \frac{1}{\Omega_{2DBZ}} \int_{2DBZ} T(\vec{k}; E) d\vec{k}, \tag{1}$$

where Ω_{2DBZ} is the area of the two-dimensional Brillouin zone (2DBZ) in the transverse directions. Here, we calculate the transmission coefficient by sampling 4×4 k-points in the transverse 2DBZ. The k-dependent transmission coefficient $T(\vec{k}; E)$ is obtained as

$$T(\vec{k}; E) = Tr\left[\Gamma_L G_M^R \Gamma_R G_M^{R+}\right], \tag{2}$$

where G_M^R is the retarded Green's function matrix of the extended molecule and $\Gamma_{L(R)}$ is the broadening function matrix describing the interaction of the extended molecule with the left (right) electrode. More details on the method can be found in Refs. 21 and 22.

B. Experimental method

The conductance measurement was carried out on a Nanoscope E STM (Veeco, US). The Au(111) and Pt(111) substrate surfaces were treated prior to each experiment by H_2 flame annealing followed by cooling down under the protection of high-purity nitrogen stream.[23] The STM tips were freshly formed by cutting gold or platinum wires (99.99% purity) of 1–1.5 mm in length and 0.25 mm in diameter. The conductance measurement was performed in tetradecane solution containing 1.0 mM of [2,2]paracyclophane, both of the chemicals being purchased from J&K chemical without any further purification. During the measurement, the STM tip was first driven toward the substrate until a gold or platinum nanocontact was fabricated, then the metal-[2,2]paracyclophane-metal junctions were formed when the STM tip was withdrawn from the substrate at 20 nm/s. This procedure was repeatedly performed while the evolution of the junctions was monitored by means of the conductance, G = I/V, under a bias voltage of 25 mV between the STM tip and the metal substrate. The preamplifiers used for gold and platinum were 1 and 1000 nA V^{-1}, respectively.

III. RESULTS AND DISCUSSION

A. The atomic and electronic structure of [2,2]-, [3,3]- and [4,4]-paracyclophane molecules

The [2,2]paracyclophane is the smallest member of the paracyclophanes family and previous studies have shown that

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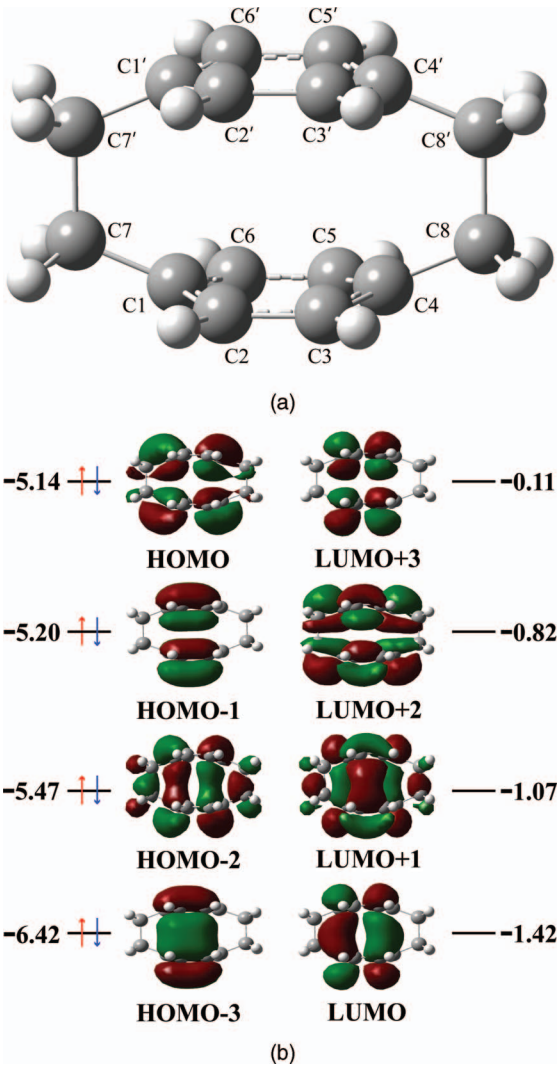

FIG. 1. The optimized atomic structure (a) and frontier molecular orbitals ranging from HOMO-3 to LUMO+3 (b) of [2,2] paracyclophane in the D_2 symmetry.

the PBE GGA functional works well for this molecule when large all-electron atomic orbital basis sets are employed.[13] In order to test the pseudopotentials and the basis functions of the hydrogen and carbon atoms built for this work, we first optimize the atomic structure of [2,2]paracyclophane (Fig. 1(a)). Some typical bond lengths and the dihedral angle characterizing the molecular symmetry are listed in Table I. As we can see from the table, the relaxed [2,2]paracyclophane molecule has a D_2 symmetry with the C(Ar)-C-C-C(Ar) dihedral angle (8.85°) being slightly underestimated when compared to the experimental value (12.6°). Considering the tiny D_2-D_{2h} barrier of about 0.2 Kcal mol^{-1},[13] [2,2]paracyclophane with the D_{2h} symmetry may be present at room temperature. The differences between the bond lengths calculated by using SIESTA and those obtained from the x-ray crystal structure are less than 0.02 Å, confirming the appropriateness of the pseudopotentials and basis functions of the C and H atoms. In particular, the inter-ring distance is calculated to be 3.106 Å, very close to the experimental value of 3.097 Å.

TABLE I. Typical geometrical parameters of [2,2]paracyclophane with the D_2 symmetry, the bond distances are in units of Angstrom.

	Siesta	Expt.[a]
C7-C7′	1.609	1.593
C1-C7	1.510	1.508
C1-C2	1.404	1.399
C2-C3	1.397	1.396
C1-C1′	2.793	2.782
C2-C2′	3.106	3.097
∠C1C7C7′C1′	8.85°	12.6°

[a]Reference 13.

Since the junction conductance is significantly affected by the coupling of molecular orbitals to the energy bands of the electrodes near the Fermi level, the frontier molecular orbitals ranging from the HOMO-3 to the LUMO+3 of [2,2]paracyclophane are presented in Fig. 1(b). Here, HOMO and LUMO stand for the highest occupied molecular orbital and the lowest unoccupied molecular orbital, respectively. Clearly, these eight molecular orbitals are mainly formed by the HOMO and LUMO of the two benzene backbones, though their degeneracy is lifted because of the much lower symmetry in [2,2]paracyclophane. For example, the HOMO of [2,2]paracyclophane, which has a nodal surface between the two rings, is dominated by the two benzene HOMO states with two allylic-like fragments. In contrast, the [2,2]paracyclophane LUMO is formed by the two benzene LUMO states with no density on the two carbon atoms connecting to the ethylene chains and considerable bonding characters are shown in the inter-ring region. The HOMO-LUMO gap of [2,2]paracyclophane is calculated to be 3.72 eV, which is about 1.4 eV smaller than the benzene HOMO-LUMO gap (5.15 eV) calculated with the same PBE functional. This indicates an extended effective π-conjugation due to the strong through-space π-π interaction. It should be noted that, due to the self-interaction error contained in the PBE GGA functional,[28] the HOMO level of [2,2]paracyclophane is calculated to be −5.14 eV, much higher than the negative of its ionization potential (8.1 eV).[29]

For both the [3,3]- and [4,4]-paracyclophanes, only the trans isomer is considered here.[12] The [3,3]paracyclophane inter-ring distance is optimized to be 3.312 Å, i.e., it is overestimated by about 0.01 Å when compared to the measured value of 3.30 Å.[30] Although the π-π interaction in [3,3]paracyclophane is slightly weaker than that in [2,2]paracyclophane due to the increased inter-ring distance, both the shape of the frontier molecular orbitals (Fig. S1 in the supplementary material)[31] and the HOMO-LUMO gap (3.59 eV) of [3,3]paracyclophane are very similar to those of [2,2]paracyclophane. However, the situation is markedly different for [4,4]paracyclophane. Its inter-ring distance is calculated to be 4.058 Å, about 0.07 Å larger than the measured value of 3.990 Å.[32] As this inter-ring distance is much larger than the sum of the van der Waals radii of two carbon atoms, the π-π interaction in [4,4]paracyclophane is the weakest among the members of the paracyclophane family investigated here. Thus, when compared to the [2,2]- and [3,3]-paracyclophanes, the frontier molecular orbitals of [4,4]paracyclophane show a much weaker bonding character in the

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inter-ring region (Fig. S2 in the supplementary material), and the HOMO-1 and HOMO-2 states also interchange their order. Furthermore, the HOMO-LUMO gap of [4,4]paracyclophane is calculated to be 4.53 eV, more than 0.8 eV larger than those of both [2,2]- and [3,3]-paracyclophanes.

B. Electronic transport properties of [2,2]-, [3,3]-, and [4,4]-paracyclophanes connected to gold electrodes

Next we investigate the electronic transport properties of paracyclophanes sandwiched between two gold electrodes. First, we consider a symmetric Au-[2,2]paracyclophane-Au junction (see Fig. 2(a)), in which the [2,2]paracyclophane molecule is connected to each gold electrode through a gold adatom and these are attached in the η^1-fashion to two carbon atoms of the benzene backbones connecting with the same ethylene group. The C-Au bond lengths are optimized to be 2.345 Å and the binding energy of [2,2]paracyclophane adsorbed on the Au(111) surface through one gold adatom is calculated to be 0.61 eV, in good agreement with that (0.74 eV) obtained from a cluster model.[11]

In Fig. 2(b), we present the transmission spectrum of the symmetric Au-[2,2]paracyclophane-Au junction, together with the transmission projected onto the frontier molecular orbitals of [2,2]paracyclophane obtained by using our previously developed scattering states projection method.[33,34] As we can see, all the relevant transmission peaks are far away from the Fermi level, E_F. Above E_F, the LUMO, LUMO+1, and LUMO+2 states contribute together to the broad transmission peak around at 2.0 eV (the energies are taken with respect to $E_F = 0$). Below E_F the sharp transmission peak centered at -1.6 eV is dominated by the HOMO-1, whereas the HOMO and HOMO-2 make contributions to the broad transmission peak below -1.8 eV. Around the Fermi level the transmission is mainly contributed by the tails of the HOMO and HOMO-2, thus that tunneling is the dominant conducting mechanism. Finally the transmission coefficient at the Fermi level is calculated to be 4.1×10^{-2}, i.e., it is about four times larger than the experimental value of 0.96×10^{-2}.[11]

The electronic coupling at the [2,2]paracyclophane-Au interfaces can be analyzed by looking at the changes in the local density of states (LDOS) of the Au adatom before and after it is contacted by the [2,2]paracyclophane molecule. As shown in Fig. 2(c), the LDOS of the Au adatom on the Au(111) surface in absence of the molecule has mainly s-character around the Fermi level, with the 5d orbitals forming a sharp peak at about -2.1 eV together with a small shoulder at a slightly higher energy. When the [2,2]paracyclophane molecule is attached to the adatom (see Fig. 2(d)) the 5d LDOS gets significantly broadened by the interaction but it remains distributed mainly below -1.0 eV. As such the transmission of the Au-[2,2]paracyclophane-Au junction is very small around the Fermi level.

Besides the symmetric Au-[2,2]paracyclophane-Au junction, an asymmetric model is also possible (see Fig. S3 in the supplementary material). The largest difference between these two junction models is that in the asymmetric one the two Au adatoms on the Au surfaces are attached to two carbon atoms of the benzene backbones connecting to two

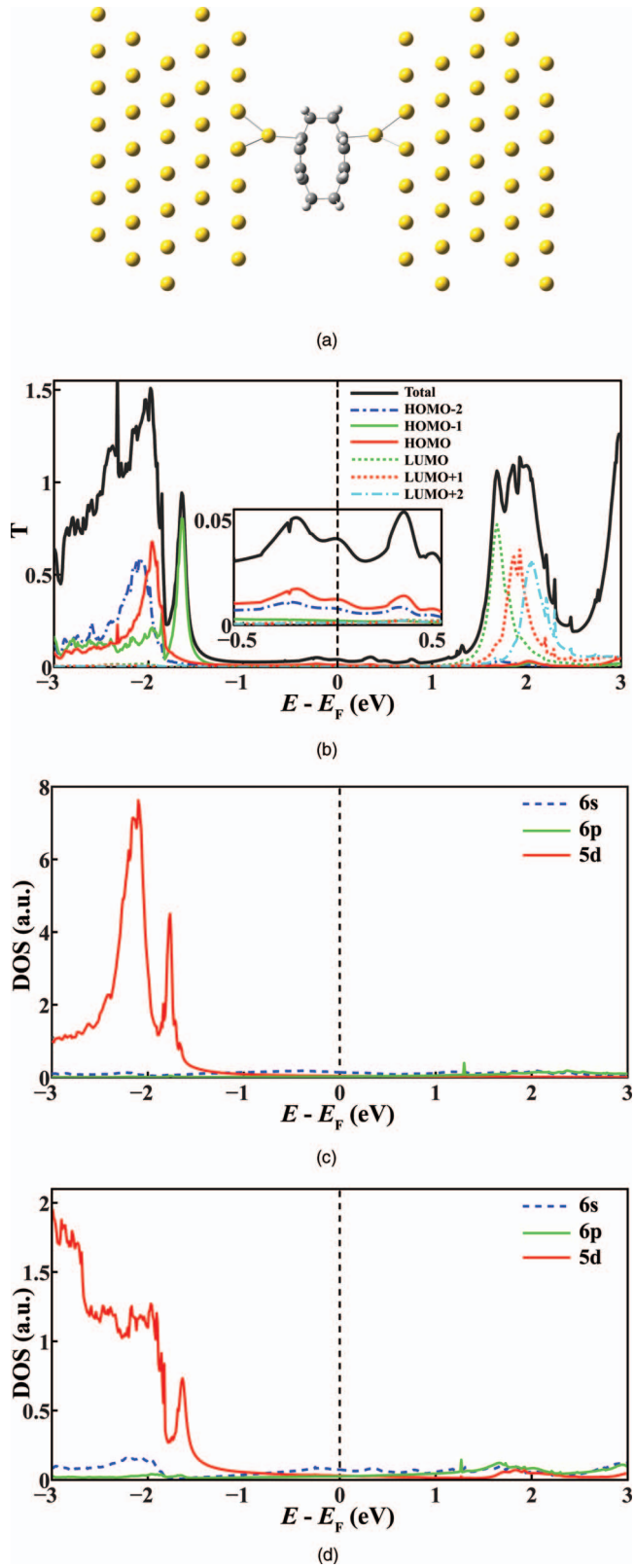

FIG. 2. (a) The optimized atomic structure of the symmetric Au-[2,2]paracyclophane-Au junction, (b) energy-dependent transmission function together with the projected transmission onto frontier molecular orbitals of [2,2]paracyclophane, the LDOS of the Au adatom on the Au(111) surface before (c) and after (d) the [2,2]paracyclophane molecule attached.

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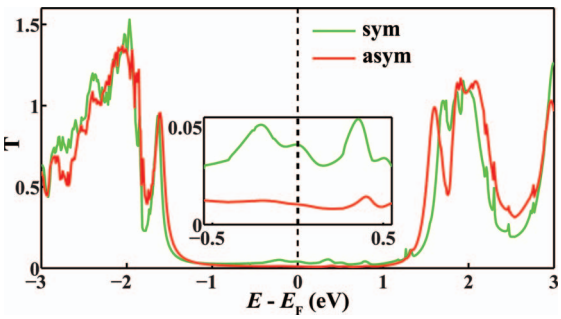

FIG. 3. The equilibrium transmission spectrum of the asymmetric Au-[2,2]paracyclophane-Au junction. The transmission spectrum of the symmetric Au-[2,2]paracyclophane-Au junction is also given for comparison.

different ethylene groups. As shown in Fig. 3, the overall shape of the transmission spectrum of the asymmetric model is almost identical to that of the symmetric one, especially in the energy range below the Fermi level. This suggests that the conducting mechanism of these two junction models is the same. However, the transmission coefficient at the Fermi level is now only 1.0×10^{-2}, which compares much better with experiments.[11]

Since the HOMO and HOMO-2 states of [2,2]paracyclophane both receive some contributions from molecular orbitals of the two ethylene groups (see Fig. 1(b)), the above molecular orbital analysis does not allow us to draw the conclusion that the conduction through the Au-[2,2]paracyclophane-Au junction is dominated by the π-π interaction between the two benzene rings. In order to clarify the role played by the through-bond and the through-space interactions in the conducting mechanism of the paracyclophanes, we further construct symmetric junction models for both the [3,3]- and [4,4]-paracyclophane molecules connected to two gold electrodes. Their transmission spectra are given in Fig. 4. Although the overall shape of the transmission curve of the Au-[3,3]paracyclophane-Au junction is similar to that of Au-[2,2]paracyclophane-Au, they are both totally different from that of Au-[4,4]paracyclophane-Au. In particular, the transmission coefficient at E_F for Au-[3,3]paracyclophane-Au is 3.5×10^{-2}, i.e., it is very close to that of the symmetric Au-[2,2]paracyclophane-Au junction. In contrast $T(E_F)$ for

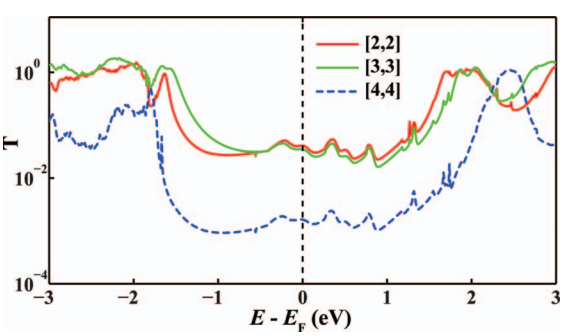

FIG. 4. The equilibrium transmission spectra of the symmetric Au-[3,3]paracyclophane-Au and Au-[4,4]paracyclophane-Au junctions. The transmission spectrum of the symmetric Au-[2,2]paracyclophane-Au junction is also given for comparison.

Au-[4,4]paracyclophane-Au is only 1.7×10^{-3}, namely it is about 20 times smaller than those of the other two junctions.

As we have seen, [2,2]-, [3,3]- and [4,4]-paracyclophane molecules are all composed of two benzene rings linked together by different methylene groups. Although experimental results on the dependence of the conductance of two π-stacked benzene rings on their inter-ring distance are still unavailable at present, investigations on the conductance of alkane chains are well documented.[24,35,36] It has been established that the conductance of alkane chains decreases exponentially with increasing the number of methylene groups, i.e., $G \propto e^{-\beta N}$, where β is the tunneling decay constant and N is the number of methylene groups. The measured values for β are reported to be about 1 per methylene group. If the conductance of [2,2]- and [3,3]-paracyclophanes connected to Au electrodes is dominated by the through-bond interaction, one can expect that the conductance of the Au-[3,3]paracyclophane-Au junction will decrease by a factor of e^{-1} compared to that of the Au-[2,2]paracyclophane-Au junction. Note that here we assume the same β as in alkane chains and we acknowledge the fact that the bonding structure of the [3,3]paracyclophane-Au interface is almost identical to that of the [2,2]paracyclophane-Au one. Clearly this argument appears inconsistent with the calculated values reported above. Thus, we can now conclude that the conductance of [2,2]- and [3,3]-paracyclophanes connected to gold electrodes is dominated by the through-space π-π interaction between the two benzene rings. As such their low-bias conductance is not very sensitive to small changes of the inter-ring distance. However, for [4,4]paracyclophane the conducting mechanism should be changed to the through-bond one, since the calculated conductance of the symmetric gold-[4,4]paracyclophane-gold junction is close to the experimental value of the conductance of the Au-1,4 diaminobutane-Au junction.[36]

C. Electronic transport properties of [2,2]- and [3,3]-paracyclophanes connected to platinum electrodes

Although π-π interaction dominates the conductance of the Au-[2,2]paracyclophane-Au junction, the calculated transmission coefficient at the Fermi level is only 4.1×10^{-2} (symmetric junction). It is then quite interesting to find out whether such a low conductance is determined by the [2,2]paracyclophane-Au interface or by the intrinsic nature of [2,2]paracyclophane.[37] Since both experimental and theoretical studies have demonstrated that the electronic coupling of molecules with platinum is usually stronger than that with gold,[38–41] we now explore the electronic transport of paracyclophanes connected to two Pt electrodes.

Just as for the case of gold electrodes, we construct a symmetric model for the Pt-[2,2]paracyclophane-Pt junction, in which [2,2]paracyclophane is connected to each platinum electrode through a Pt adatom and the Pt-C bond length is optimized to be 2.176 Å. Since the binding energy of [2,2]paracyclophane adsorbed on the Pt(111) surface through one Pt adatom is calculated to be 1.27 eV, the Pt-[2,2]paracyclophane-Pt junction appears rather stable.

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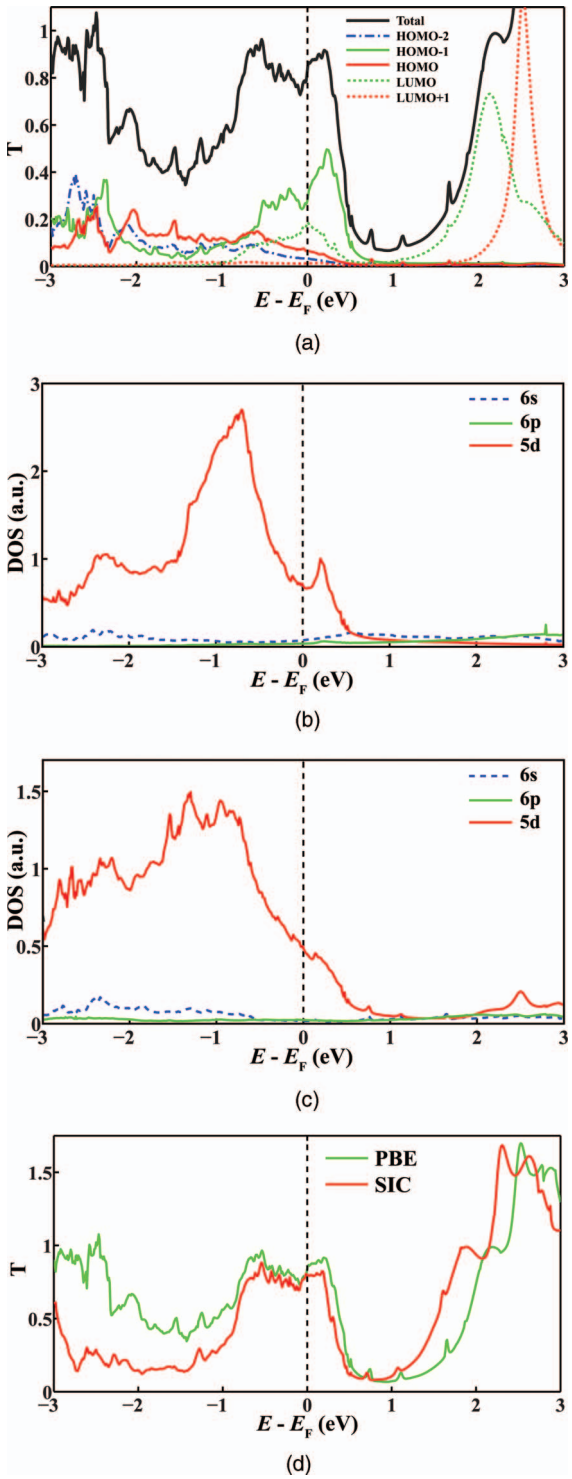

FIG. 5. (a) The equilibrium transmission spectrum of the symmetric Pt-[2,2]paracyclophane-Pt junction calculated with the PBE GGA functional, together with the projected transmission onto frontier molecular orbitals of [2,2]paracyclophane; the LDOS of the Pt adatom on the Pt(111) surface before (b) and after (c) the [2,2]paracyclophane molecule attached, (d) the equilibrium transmission spectrum of the same junction calculated with the ASIC scheme.

Figure 5(a) shows the zero-bias transmission curve of the symmetric Pt-[2,2]paracyclophane-Pt junction. In contrast to its gold counterpart, where a transmission trough appears around the Fermi level (see Fig. 2(b)), for Pt-[2,2]paracyclophane-Pt at E_F there is a high transmission plateau. In this case $T(E_F)$ is determined to be 0.83, i.e., it is only 17% lower than the experimental value of a benzene molecule connected directly to two platinum electrodes.[42] This indicates that not only the electronic coupling at the [2,2]paracyclophane-Pt interface is very strong but also that the π-π stacking in [2,2]paracyclophane provides a very efficient channel for electron transport.

The projection of the transmission of the Pt-[2,2]paracyclophane-Pt junction onto the frontier molecular orbitals of [2,2]paracyclophane shows that the conducting channel around E_F is mainly contributed by the HOMO-1, LUMO, HOMO, and HOMO-2 (Fig. 5(a)). In contrast to the unoccupied molecular orbitals such as the LUMO and the LUMO+1 that provide relatively sharp transmission peaks, the occupied molecular orbitals ranging from the HOMO to the HOMO-2 make contributions to the transmission in a very broad energy range, suggesting that such occupied molecular orbitals have a significant interaction with platinum and thus hybridize strongly with the electrodes. This is corroborated by the analysis of the LDOS of the Pt adatom. In contrast to the case of Au adatoms on the Au(111) surface, the LDOS of the uncontacted Pt adatom on the Pt(111) surface shows a very broad d-like peak spanning from far below the Fermi level to about 0.5 eV above it (Fig. 5(b)). When the [2,2]paracyclophane molecule is attached to the adatom, the overall shape of the LDOS changes significantly and a number of fine features appear (Fig. 5(c)), demonstrating the strong coupling between the molecule and the electrodes. Since the LDOS of the Pt adatom originating from the 5d atomic shell extends to above the Fermi level, the efficient coupling between the Pt 5d atomic orbitals and the π-type molecular orbitals of [2,2]paracyclophane makes the transmission of the Pt-[2,2]paracyclophane-Pt junction approaching unity at the Fermi level.

It is well known that molecular levels calculated by using local and semi-local exchange and correlation functionals (the local density approximation (LDA) or the generalized gradient approximation (GGA)) are too high in energy due to the self-interaction error.[28] This may result in an incorrect alignment of molecular levels with the Fermi energy of the electrodes and thus in an unphysical large transmission at around E_F. It is therefore interesting to explore whether or not the calculated large transmission plateau around the Fermi level for Pt-[2,2]paracyclophane-Pt (Fig. 5(a)) is genuine or it is simply an artifact of the self-interaction error contained in the PBE GGA. The atomic self-interaction correction (ASIC) scheme applied to the non-equilibrium quantum transport problem is used to carry out this analysis.[41,43–47] The ASIC corrections are only applied to the C and H atoms in [2,2]paracyclophane, but not to the platinum ones of the electrodes as the self-interaction error in metals is small. The semi-empirical scaling factor α, which is a measure of the deviation of the ASIC potential from the exact SIC one, is set to be 0.96, thus that the HOMO of [2,2]paracyclophane in the gas phase is shifted downward to -8.1 eV (i.e., it corresponds to the negative of the experimental ionization potential).

The transmission curve of the symmetric Pt-[2,2]paracyclophane-Pt junction calculated with the ASIC approach is shown in Fig. 5(d). As we can see, the overall

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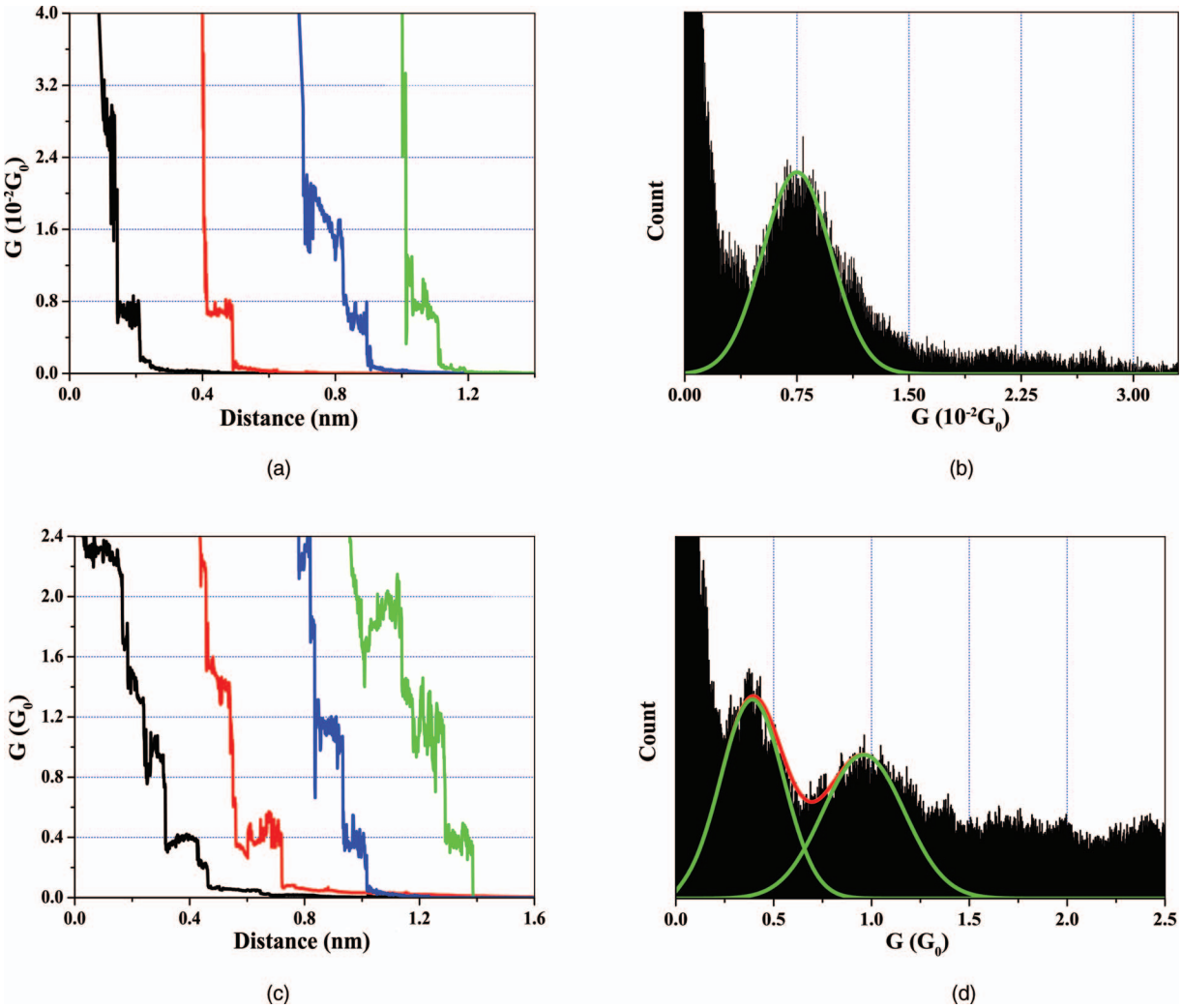

FIG. 6. Individual conductance traces for the [2,2]paracyclophane molecule with two electrodes, gold (a) and platinum (c); the corresponding conductance histograms with the gold (b) and platinum (d) electrodes, in which the peaks are fitted with a GAUSSIAN function.

shape of $T(E)$ in the energy range [−0.75 eV, 1.0 eV] follows closely that calculated with PBE. As a consequence $T(E_F)$ is still as high as 0.80, illustrating the robustness of the high transmission of the Pt-[2,2]paracyclophane-Pt junction. Since $T(E_F)$ receives contributions mainly from the extended π-type molecular orbitals of [2,2]paracyclophane, which couple strongly with the conducting states of the Pt electrodes, i.e., from rather extended orbitals, it is expected that the self-interaction corrections are small. This is the reason for the stability of the large transmission coefficient at E_F to the choice of DFT functionals.

Furthermore, we also calculate the transmission of the symmetric Pt-[3,3]paracyclophane-Pt junction (see Fig. S4 in the supplementary material). When compared to the Pt-[2,2]paracyclophane-Pt junction, the transmission peaks become sharper and $T(E_F)$ is reduced to 0.35. These changes should be ascribed to the relatively weak π-π interaction between the two benzene rings in [3,3]paracyclophane, because the optimized C-Pt bond length (2.209 Å) and the binding energy (1.26 eV) of [3,3]paracyclophane adsorbed on the Pt(111) surface through the Pt adatom are very close to those for [2,2]paracyclophane.

D. Experimental validation of the predicted high conductance of [2,2]paracyclophane connected to platinum electrodes

In order to validate the predicted high conductance of the Pt-[2,2]paracyclophane-Pt junctions, we have also carried out some preliminary experimental studies. Single-molecule junctions are created by repeatedly forming and breaking Au or Pt point contacts with a modified scanning tunnel microscope (STM) in a 1.0 mM tetradecane solution of [2,2]paracyclophane molecules. The conductance is measured as a function of the relative tip/sample displacement to yield conductance traces, and these are used to generate conductance histograms (Fig. 6). As one can see, clear conductance plateaus appear in each of the conductance curves and the conductance histogram constructed for the Au-[2,2]paracyclophane-Au junctions shows a prominent peak at around 0.75 $\times$ 10^{-2} G_0 (see Fig. 6(b)). This value is very close to that obtained by Schneebeli *et al.*,[11] demonstrating the reliability of our experimental technique. When the gold electrodes are replaced by platinum, the junction conductance of [2,2]paracyclophane is indeed much larger. The corresponding conductance histogram (Fig. 6(d)) has a broad peak around 1.0 G_0

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indicating the formation of Pt-Pt quantum point contacts, and a clear peak is also visible at 0.40 G_0. This is attributed to the conductance of the Pt-[2,2]paracyclophane-Pt junctions because such peak does not appear in the conductance histogram of Pt-Pt contacts in pure tetradecane (Fig. S5 in the supplementary material). Considering the unknown and complex atomic structures of the [2,2]paracyclophane-Pt interface, it is quite understandable that our measured junction conductance is a little smaller than the above calculated value, since our anchoring model might deliver the maximum value of the junction conductance. On the one hand, similar results have been reported for the Au-[4,4]bipyridine-Au junctions.[48] On the other hand, when the [2,2]paracyclophane molecule is connected to one Pt electrode through one Pt adatom and to the other Pt electrode through a Pt_4 cluster in the pyramid form (Fig. S6 in the supplementary material), the calculated junction conductance is indeed decreased and becomes 0.62 G_0. Keeping the Pt_4 cluster unchanged and adding one more Pt atom near the Pt adatom will further decrease the junction conductance to 0.38 G_0, in good agreement with our measured value. This analysis then indicates that, although the magnitude of the calculated conductance is similar to that of the experiments, its precise value depends rather sensibly on the details of the molecule/electrode geometry.

IV. CONCLUSION

In this work, we have investigated the electronic transport properties of [2,2]-, [3,3]- and [4,4]-paracyclophanes attached to gold and platinum electrodes. Due to the small inter-ring distance, the π-π interaction between the two benzene rings in [2,2]- and [3,3]-paracyclophanes is rather strong. This is illustrated by the apparent bonding characters appearing in the inter-ring region of some frontier molecular orbitals and in the decreased HOMO-LUMO gap. In contrast, the inter-ring distance in [4,4]paracyclophane is much larger and thus the π-π interaction becomes weak. Therefore, different from [4,4]paracyclophane, the π-π interaction dominates the electronic transport properties of [2,2]- and [3,3]-paracyclophanes sandwiched between two gold electrodes and the zero-bias junction conductance is not very sensitive to small changes of the inter-ring distance. In particular, for the gold-[2,2]paracyclophane-gold junction the zero-bias conductance of the asymmetric model, in which two carbon atoms at the binding sites are connected to two different ethylene groups of [2,2]paracyclophane, is calculated to be 1.0×10^{-2} G_0 in excellent agreement with experiments. When the gold electrodes are replaced by platinum, the transmission coefficient at the Fermi level of the symmetric Pt-[2,2]paracyclophane-Pt junction is increased to 0.83, demonstrating that the π-π stacking in [2,2]paracyclophane is very efficient for electron transport and that the electronic coupling at the [2,2]paracyclophane-Pt interface is significantly improved over that at the [2,2]paracyclophane-Au one. This has been confirmed by our preliminary experimental studies on the low-bias conductance of the Pt-[2,2]paracyclophane-Pt junctions. Our findings are helpful not only for the design of molecular electronic devices incorporating π-π stacking molecular systems, but also for the investigations of the contacts between carbon nanotubes and graphene nanoribbons which are also dominated by the π-π interactions.

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