# Dual-State Ambipolar Charge Transport In Antiaromatic [4]cyclodiben- 1 zopentalene Single-molecule Nanohoops. 2

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antiaromatic nanohoops.	14

**ABSTRACT:** Antiaromatic compounds are of great interest due to their narrow HOMO-LUMO gaps, high reactivity, and enhanced charge mobility, yet their role in single-molecule electronics is still not well understood. Using electrochemically controlled scanning tunneling microscopy break-junction (ECSTM-BJ) measurements, we compared the energy-alignment dependent conductance of the aromatic [10]cycloparaphenylene ([10]CPP) and the antiaromatic [4]cyclodibenzopentalene [4]CDBP). While [10]CPP showed a single conductance state via the HOMO, [4]CDBP exhibited two distinct states involving both the HOMO and LUMO. Our analysis and DFT calculations attribute this dual-state behavior to unique anchoring modes and energy-level realignment within a narrow HOMO-LUMO gap. This property enables electron- and hole-dominated pathways that depend on anchoring configuration and coexist at a fixed gate potential. This phenomenon, also observed in the [4]CDBP $\supset$ C<sub>60</sub> structure, highlights the potential of antiaromatic molecules for advanced molecular electronics.

## 24 INTRODUCTION

Antiaromatic compounds, defined by their cyclic and pla-25 26 nar structures with 4n delocalized  $\pi$ -electrons, have at-27 tracted significant research attention due to their distinct 28 physical and chemical properties.<sup>1-11</sup> Compared to their ar-29 omatic counterparts, antiaromatic compounds have elec-30 trons partially occupying anti-bonding molecular orbitals, 31 exhibiting enhanced reactivity,<sup>12, 13</sup> smaller HOMO-LUMO 32 energy gaps,<sup>14, 15</sup> increased charge mobility<sup>16, 17</sup> and mani-33 fest paratropic ring currents under magnetic field.<sup>6</sup> These 34 unique properties make antiaromatic compounds promis-35 ing candidates for constructing single-molecule electronic 36 devices. However, understanding how antiaromaticity in-37 fluences the electronic properties of single molecules re-38 mains a key challenge. Previous studies employing scanning 39 tunneling microscopy break-junction (STM-BJ)<sup>18</sup> tech-<sup>40</sup> niques have explored the conductance of both antiaromatic <sup>41</sup> and aromatic single molecules. For example, Shintaro et al.<sup>4</sup> 42 reported that antiaromatic molecules exhibit higher con-43 ductance than their aromatic counterparts due to their re-44 duced HOMO-LUMO energy gap. In contrast, other studies<sup>2,</sup> 45 <sup>3</sup> have observed comparable or even lower conductance in <sup>46</sup> antiaromatic systems, attributing these variations to factors 47 such as unfavorable energy-level alignment, destructive 48 quantum interference, or the electron-withdrawing nature

<sup>49</sup> of side groups. These inconsistencies highlight the complex-<sup>50</sup> ity of analyzing antiaromaticity's effects through conduct-<sup>51</sup> ance measurements at a fixed background potential.

In this work, we applied electrochemically controlled 52 53 STM-BJ (ECSTM-BJ) measurements<sup>19</sup> to actively tune mo-54 lecular energy levels and investigate the role of antiaroma-55 ticity in single-molecule charge transport. Our work focuses 56 on two hoop-shaped molecules: the aromatic [10]cyclopar-57 aphenylene ([10]CPP) and the antiaromatic [4]cvclodiben-58 zopentalene ([4]CDBP). The  $\pi$ -conjugated nanohoops pro-59 vide ideal platforms for probing and tuning electronic prop-60 erties, as their radial electron delocalization leads to nar-61 rower HOMO-LUMO energy gaps compared to linearly con-62 jugated systems.<sup>20</sup> Our measurements revealed that charge 63 transport through [10]CPP is governed primarily by the 64 highest occupied molecular orbital (HOMO), while [4]CDBP 65 exhibited two distinct conductance mechanisms, mediated 66 by both the HOMO and the lowest unoccupied molecular or-67 bital (LUMO). Notably, this dual-state ambipolar transport 68 persisted even when [4]CDBP encapsulates a C<sub>60</sub> guest mol-69 ecule. Through junction geometry analysis and density-70 functional theory (DFT) calculations, we attribute this be-71 havior to two key features of antiaromaticity: the reduced 72 HOMO-LUMO energy gap, which enhances sensitivity to en-73 ergy-level realignment, and the antiaromatic moiety's abil-74 ity to adopt distinct electrode-anchoring modes, facilitating 75 tuning of the energy-level alignment into the HOMO or LUMO dominated charge transport regime within the nar row HOMO-LUMO gap. These unique properties suggest a
 novel design for ambipolar devices, where switching is gov erned by anchoring modes rather than gate potentials. Our

<sup>5</sup> findings offer new insights into how antiaromaticity shapes
<sup>6</sup> the electronic properties of single-molecule junctions,
<sup>7</sup> opening pathways for design of innovative molecular and
<sup>8</sup> supramolecular devices.



<sup>10</sup> **Figure. 1**: Molecular structures, schematic view of molecular junction in STM break-junction measurement and single-molecule con-<sup>11</sup> ductance of [10]CPP and [4]CDBP in electrolyte solution. (a) Gate-controlled conductance measurement of a [4]CDBP molecule bind-<sup>12</sup> ing between two STM electrodes. The pink shades suggest regions with higher antiaromaticity. (b) Structures of [4]CDBP and <sup>13</sup> [10]CPP. (c)-(d) 2D conductance-distance histograms of (c) [10]CPP and (d) [4]CDBP. Inset: Representative conductance-distance <sup>14</sup> traces of (c) [10]CPP and (d) [4]CDBP. (e)-(f) 1D conductance histograms of (e) [10]CPP and (f) [4]CDBP. The solid curves are Gauss-<sup>15</sup> ian fitting of the conductance peaks. The numbers are  $5.50 \times 10^{-4}$  G<sub>0</sub> and  $2.04 \times 10^{-4}$  G<sub>0</sub> of peak positions.



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<sup>17</sup> **Figure. 2:** Electrochemically gated control of the single-molecule conductance of [4]CDBP and [10]CPP. (a)-(c) 1D conductance histograms collected at different gate voltages ( $V_g$  vs. Fc<sup>+</sup>/Fc) of (a) [10]CPP, (b) [4]CDBP (LC), (c) [4]CDBP (HC). The solid curves are the Gaussian fitting of the conductance peaks. (d)-(f) Plots of averaged conductance vs.  $V_g$  (vs. Fc<sup>+</sup>/Fc) for (d) [10]CPP, (e) [4]CDBP (LC), (f) [4]CDBP (HC). The value of hollow square dot in panel d comes from a conductance measurement with low junction fortantion yield (2%, Supplementary Fig. 21). The values of solid square dots are based on measurement with substantially higher yield 22 (>20%).

#### 23 RESULTS AND DISCUSSION

24 **Experimental design.** To study the electronic properties 25 of antiaromatic molecules at the single-molecule scale, we 26 performed electrochemically controlled STM-BJ measure27 ments (in solution under ambient conditions) of the con-28 ductance of [10]CPP and [4]CDBP at various electrochemi-29 cal potentials. The STM-BJ technique measures the conduct-30 ance of the metal-molecule-metal junctions formed during 31 repeated approaching and retraction of the STM tip relative

to the substrate (see Methods section for details). Simulta-2 neously, the tip displacement is recorded to provide infor-3 mation on the junction geometry. By controlling the tip-sub-4 strate bias voltage and the electrochemical gate voltage us-5 ing a bipotentiostat, we tune the energy-level alignment be-6 tween the electrode Fermi levels and the molecular orbital 7 levels (Methods, Figure. 1a). Conjugated nanohoops offer a 8 platform to study structure-property relationships and can 9 serve as hosts for supramolecular chemistry.<sup>21, 22</sup> Esser and 10 coworkers<sup>23</sup> compared [10]CPP and [4]CDBP with respect 11 to structural data (e.g. NMR, electrochemical and spectro-12 scopic properties), which showed antiaromaticity and a 13 small bandgap (~2.2 eV) for [4]CDBP, as well as revealing a 141:1 encapsulation of C<sub>60</sub> through a host-guest interaction. 15 Therefore we chose the two structurally similar hoop-16 shaped compounds, [4]CDBP and [10]CPP for our investiga-17 tion (Figure. 1b, see Supplementary texts 1-2 and Supple-18 mentary Figures. 1-13 for synthesis and characterization 19 details). Furthermore, we examined the antiaromaticity-in-20 duced properties in a [4]CDBP $\supset$ C<sub>60</sub> host-guest supramolec-21 ular complex (Figure. 5a).

Conductance measurements reveal two charge-22 23 transport pathways of [4]CDBP. We performed STM-BJ 24 conductance measurement for 2 µm solutions of [4]CDBP 25 and [10]CPP in chlorobenzene (CB) with 0.1 M tetrabu-26 tylammonium tetrafluoroborate (n-Bu<sub>4</sub>NBF<sub>4</sub>) as the sup-27 porting electrolyte. The insets of Figures. 1c and 1d depict 28 the individual conductance-distance traces of [10]CPP and 29 [4]CDBP, respectively. The plateaus observed on the traces 30 signal the formation and breakdown of Au-molecule-Au 31 junctions. Notably, while [10] CPP displayed conductance 32 plateaus around a single level, [4]CDBP exhibited plateaus 33 at two discrete conductance levels. The conductance plat-34 eaus of [10]CPP and the low-conductance (LC) state of 35 [4]CDBP were relatively flat and short compared with the 36 long and tilted plateaus of the high-conductance (HC) state 37 of [4]CDBP, which gradually decreased from  $G_0 = 2e^2/h$  $_{38}$  (77.4  $\mu$ S, h is Planck's constant and e is the electron charge) 39 without the feature of an Au-Au snapback.<sup>24, 25</sup> Two-dimen-40 sional (2D) conductance-distance histograms constructed 41 from thousands of traces (Figures. 1c and 1d) show only a 42 single high-count region for [10]CPP, whereas [4] CDBP dis-43 played both HC and LC high-count regions. Correspond-44 ingly, one-dimensional (1D) conductance histograms (Fig-45 ures. 1e and 1f) exhibited a single conductance peak at  $_{46}$  around 5.50 × 10<sup>-4</sup> G<sub>0</sub> for [10]CPP, while a wide peak at  $_{47}$  around 2.04×10<sup>-4</sup> G<sub>0</sub> (from the LC state and the tail of HC  $_{48}$  state) and a high-count region up to  $G_0$  (from the sloped 49 plateaus of the HC state) are observed for [4]CDBP. The con-50 ductance of [10]CPP slightly exceeded the reported con-51 ductance measured in 1,2,4-trichlorobenzene (TCB, 0.1 mM 52 concentration),<sup>20</sup> potentially due to the solvent effect. The 53 shapes of plateaus and the conductance distribution imply 54 the presence of two different junction types for [4]CDBP. 55 Separate histograms for the HC and LC state of [4]CDBP can 56 be found in Supplementary Figure. 15, where automatic 57 classification algorithms based on plateau length and snap-58 back events both effectively separate the two types of junc-59 tions.

Previous studies have shown that antiaromatic mole-60 61 cules can exhibit both comparable, increased<sup>4, 26</sup> and de-62 creased<sup>2, 3</sup> conductance. This variation was attributed to the 63 competition between the decrease in HOMO-LUMO energy 64 gap and energy-level alignment, destructive quantum inter-65 ference and electron-withdrawing effects of the side group. 66 In our study, we observed that [4]CDBP displayed one con-67 ductance state (HC) higher than [10]CPP and one conduct-68 ance state (LC) lower than [10]CPP. In addition to differ-69 ences in conductance, the HC and the LC states also differed 70 in plateau shape, the Au-Au snapback feature and flicker 71 noise power scale exponent (Supplementary Figure. 16), in-72 dicating the coexistence of two charge transport pathways 73 in [4]CDBP. The discrepancy between [10]CPP and [4]CDBP 74 cannot be solely explained by the decrease in HOMO-LUMO 75 energy gap due to antiaromaticity. Further exploration of 76 energy-level alignment details and electrode-molecule an-77 choring mode is required to elucidate the influencing mech-78 anism.

The two conductance states of [4]CDBP show ambi-79 80 polar charge-transport behavior. We carried out electro-81 chemically gate-controlled break-junction measurements 82 (Methods) to study the dominant molecular orbitals in-83 volved in charge transport through [10]CPP and [4]CDBP. 84 Precise tuning of the energy alignment between the elec-85 trode Fermi levels and the molecular orbital levels were 86 achieved using a bipotentiostat-controlled electrochemical 87 gate.<sup>27, 28</sup> This enabled us to look into the gate dependency <sup>88</sup> of the single-molecule conductance states. Figure, 2a and 89 Supplementary Table. 1 show that the conductance of  $_{90}$  [10]CPP increased moderately with the gate voltage (V<sub>g</sub>, 91 versus Fc<sup>+</sup>/Fc), indicating that the HOMO dominates the 92 charge-transport pathway, consistent with previous re-93 ports.<sup>20</sup> However, for [4]CDBP, the conductance of the LC 94 state decreased with Vg (Figure. 2b and Supplementary Ta-95 ble. 1), while that of the HC state increased with Vg (Figure. 96 2c and Supplementary Table. 1). The opposite gate depend-97 ency of the conductance suggests different charge transport 98 mechanisms for the two pathways of [4]CDBP, namely 99 HOMO transport for the HC state and LUMO transport for 100 the LC state. Furthermore, the conductance of [10]CPP (Fig-101 ure. 2d) and the LC state of [4]CDBP (Figure. 2e) showed  $_{\rm 102}$  relatively mild variations with  $V_{\rm g}$  , but the HC state of 103 [4]CDBP (Figure. 2f) exhibited sharp dependence on Vg. The 104 observation implies that the initial electrodes' Fermi level 105 is closer to the dominated charge transport level of 106 [4]CDBP-HC, i.e., the HOMO of [4]CDBP. The interpretation 107 is also supported by our current-voltage characterization, 108 where the fitted energy level offset is significantly smaller 109 for the HC state than the LC state.

Ambipolar charge-transport behavior has mainly been 111 investigated in the context of ambipolar field-effect transis-112 tors (FETs).<sup>19, 29, 30</sup> Typically, a narrow HOMO-LUMO energy 113 gap is a prerequisite for constructing ambipolar FETs. In 114 conventional ambipolar FETs, the main charge carrier 115 changes from electrons to holes, in response to a V<sub>g</sub> tuning 116 from the negative to the positive direction, resulting in en-117 hanced charge transport efficiency in both directions. How-118 ever, in those devices, electron-dominated transport and

hole-dominated transport do not coexist at a same gate po-2 tential. In contrast, we discovered that [4]CDBP exhibits 3 both a HOMO-mediated (hole-transport) pathway and a 4 LUMO-mediated (electron-transport) pathway at the same <sup>5</sup> gate potential. The ambipolar property is demonstrated by 6 the conductance increase of the LC state with increasingly  $_7\,negative~V_g$  and of the HC state with decreasingly negative <sup>8</sup> Vg. This unique property provides new strategies for build-9 ing molecular circuits with novel logic functions. The poten-10 tial applications of this discovery motivate us to elucidate 11 the origin of the peculiar electronic properties of [4]CDBP. 12 The two conductance states of [4]CDBP arise from 13 different molecule-electrode anchoring modes. To in-14 vestigate the origin of the dual-state ambipolar behavior of 15 [4]CDBP, we sought to analyze the geometry of the molecu-16 lar junction during the measurement. We calculated the tip 17 displacement from the electrodes' separation to junction 18 breakdown for each conductance decay curve (Methods) 19 and built histograms to analyze the average tip displace-20 ment. The tip displacement at junction breakdown was 0.30 21 nm for [10]CPP (Figure. 3a), 0.30 nm for the LC state of 22 [4]CDBP (Figure. 3b) and 0.84 nm for the HC state of 23 [4] CDBP (Figure. 3c). It is worth noting that the HC state ex-24 hibits a significantly longer plateau length than the LC state 25 for [4]CDBP. This observation is unusual for molecular junc-26 tions exhibiting multiple conductance states, as typically,

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27 the HC state is shorter than the LC state. We attribute this 28 phenomenon to the absence of a snapback event in HC junc-29 tions. In contrast, a sharp Au-Au breakdown was observed 30 for [10]CPP and the [4]CDBP LC state, necessitating the ad-31 dition of a 0.5 nm snapback distance to the tip displacement 32 when calculating the tip-substrate gap at junction break-33 down.<sup>24, 25</sup> Therefore, we estimated the junction length to be 34 0.80 nm for [10]CDBP, 0.80 nm for [4]CDBP LC and 0.84 nm 35 for [4]CDBP HC. The junction length was comparable for 36 [10] CDBP, [4] CDBP LC and HC states, but lower than the cal-37 culated outer diameter of the hoops (1.37 nm for [10]CPP 38 and 1.49 nm for [4]CDBP).(23) This suggests that the junc-39 tion geometry for the discussed conductance states tended 40 to be in a tilted conformation. Particularly, at the junction 41 breakdown, the LC and HC states of [4]CDBP should arise 42 from single-molecule junction conformations that only sub-43 tly differ from each other. However, at the formation of sin-44 gle-molecule junctions, the LC and HC state contrasted with 45 each other in that the LC state experienced Au-Au snapback, 46 while the HC state did not. The distinct behaviors are more 47 evident in the conductance correlation analysis<sup>31</sup> per-48 formed separately for the HC and LC states (Supplementary <sup>49</sup> Fig. 17). The sloped plateaus of the HC state indicate sliding 50 of the electrode along the hoop with low mechanical stabil-51 ity, which was also observed in the measurement of other 52 conjugated nanohoops.<sup>20</sup>



<sup>54</sup> **Figure. 3**: Analysis of the origin of the low- and high- conductance states of [4]CDBP. (a)-(c) Distribution of tip displacement <sup>55</sup> for (a) [10]CPP, (b) [4]CDBP (LC), (c) [4]CDBP (HC). The estimated tip-substrate-gap-size is marked in each panel. (d)-(e) <sup>56</sup> Proposed metal-molecule-metal configurations during the break-junction measurement of the (d) low- and (e) high-conduct-<sup>57</sup> ance states. (f)-(h) 1D conductance histograms of [4]CDBP modified at concentrations of ~0.5 µm, ~2 µm, ~4 µm.

Based on the provided information, we infer that the LC 1 <sup>2</sup> state of [4]CDBP can arise from the bridging of the molecule 3 between the two electrodes after Au-Au snapback, which is 4 commonly observed in break-junction measurements (Fig-5 ure. 3d). Conversely, the HC state of [4]CDBP likely resulted 6 from the sandwiching of the molecule between the elec-7 trodes during the tip approaching, preventing the tip from 8 forming an atom wire at the electrodes' separation. The ab-9 sence of a snapback feature has been previously reported in 10 single-molecule conductance measurements of a fullerene 11 moiety,<sup>32</sup> suggesting strong molecular adsorption and bind-12 ing to the electrode, supporting the HC model. Subse-13 quently, the tip slid from a proximal binding position to a 14 distal position on the [4]CDBP nanohoop, explaining the 15 lack of Au-Au snapback and the sloped plateau (Figure. 3e). 16 Additionally, this proposed explanation accounts for the 17 greater variation in tip displacement observed in the HC 18 state compared to the LC state of [4]CDBP (Figs. 3b and c), <sup>19</sup> in that greater uncertainty in electrode-molecule coupling 20 configurations and strength can be introduced by the rela-21 tively blunt tip, compared with the sharp tip freshly formed 22 from the breakdown of atomic gold filament. In principle, if 23 the above assumption holds true, increasing the local den-24 sity of molecules can elevate the probability of measuring 25 [4]CDBP in the HC state, as molecules would have a greater 26 chance of being sandwiched between the electrodes during 27 the tip approaching. Therefore, we investigated how the 28 probability of measuring HC and LC states is affected by the 29 molecular concentration. As shown in Figures, 3f-h, we con-30 ducted the single-molecule measurement in  $\sim 0.5 \mu m$ ,  $\sim 2$  $_{31}$  µm, and  $\sim$ 4 µm [4]CDBP solution. The HC state dominated 32 at the higher concentration and faded with decreasing con-33 centration. In contrast, the LC state gradually appeared and 34 was strengthened with decreasing concentration. This phe-35 nomenon confirms our assumption that the two conduct-36 ance states of [4]CDBP arise from different molecule-elec-37 trode anchoring modes. It should be noted that our findings 38 are specific to the current measurement conditions, and di-39 rect visualization of molecular orientation under vacuum 40 has not been conducted. Anchoring behavior can be influ-41 enced by environmental factors such as temperature, pres-42 sure, and the presence of solvent molecules.

<sup>43</sup> Previous studies have demonstrated a gating effect re-<sup>44</sup> sulting from variations in tip geometry in single-molecule <sup>45</sup> junctions.<sup>33</sup> While measuring [4]CDBP, different molecule-<sup>46</sup> electrode anchoring modes can lead to different tip geome-<sup>47</sup> tries (sharp tip for LC state and blunt tip for HC state). Con-<sup>48</sup> sequently, the electrode-molecule energy alignment can be <sup>49</sup> modulated by the tip geometry. Considering that the <sup>50</sup> HOMO-LUMO energy gap of [4]CDBP is reduced by its anti-<sup>51</sup> aromaticity, the impact of tip geometry resembles effective <sup>52</sup> gating, shifting charge transport from the HOMO to the <sup>53</sup> LUMO regime. Therefore, further investigation of the rela-<sup>54</sup> tion between the electronic properties and the contact ge-<sup>55</sup> ometry of [4]CDBP is crucial.

We performed theoretical calculations to gain deeper insights into the dual-state ambipolar conductance behavior so of [4]CDBP. The calculation includes optimization of the molecular structures and different gold-molecule-gold o junctions, followed by computation of the transmission <sup>61</sup> functions of [4]CDBP and [10]CPP, using density-functional <sup>62</sup> theory (DFT) combined with quantum-transport theory. <sup>63</sup> Specifically, the ground state Hamiltonian and overlap ma-<sup>64</sup> trix elements of each structure were self-consistently ob-<sup>65</sup> tained using the ab initio program SIESTA.<sup>34</sup> Along with our <sup>66</sup> home-made implementation of the non-equilibrium <sup>67</sup> Green's function method, GOLLUM,<sup>35</sup> the mean-field Hamil-<sup>68</sup> tonian from the converged DFT calculation was used to de-<sup>69</sup> termine the phase-coherent, elastic scattering properties of <sup>70</sup> each system, which consists of the scattering region, the left <sup>71</sup> and right gold leads (source and drain, respectively).

To gain a comprehensive understanding of electronic 72 73 properties, as a first step, the frontier molecular orbitals of 74 the studied molecules: HOMO, LUMO, HOMO-1, and 75 LUMO+1 were computed and shown in Supplementary Fig-76 ure. 22, which demonstrates that the HOMO-LUMO energy 77 gaps are 1.31 eV for [4]CDBP, 2.02 eV for [10]CPP and 0.94 78 eV for [4]CDBP⊃C<sub>60</sub> based on the exchange-correlation 79 functional and parameters chosen in the simulation (see 80 Supplementary Materials and Methods). Since the gold elec-81 trodes might probe different carbon sites of the target mol-82 ecules, due to the lack of generally used anchors such as -S 83 and -SMe, it is essential to determine the optimal binding 84 site and separation distance between these segments. A 85 variation in binding energies is found against different mol-86 ecule-electrode anchoring sites according to the energy 87 minima of these curves (Supplementary Figure. 23). More <sup>88</sup> specifically, it is found that the most stable interaction be-89 tween [4]CDBP and an Au-electrode occurs at the 2-carbon 90 bridge site (B5 or B6 on the pentalene in Supplementary 91 Figure. 24a), where the aromaticity is highest. The optimum  $_{92}$  distance is ~ 2.2 Å and the binding energy is approximately 93 -0.78 eV. In the case of [10]CPP, the stable interaction hap-94 pens at the 2-carbon bridge site containing one nodal car-95 bon with a distance of 2.2 Å from the gold tip and a binding 96 energy of approximately -0.54 eV (Supplementary Figure. 97 23d). The larger binding energy of [4]CDBP than [10]CPP 98 suggests stronger binding of [4]CDBP to the electrode, of-99 fering a possible explanation for the different anchoring 100 properties of [4]CDBP and [10]CDBP.

101 We further calculated the transmission function and 102 room-temperature conductance of [4]CDBP and [10]CPP. <sup>103</sup> When the Fermi energy lies in the HOMO-LUMO energy gap, 104 the conductance of [4]CDBP varies with binding site (Sup-105 plementary Figure. 24, the left electrode is fixed at the most 106 stable site B5/B6 and the right electrode displaces along the 107 molecule). In the case of [4]CDBP, with regard to the differ-108 ence in Au-Au snap-back feature, concentration depend-109 ency and gate dependency of the two conductance states, a 110 different electrode shape without one atop atom is proiii posed and constructed based on the assumption that no 112 fresh tip is produced during the pulling experiments meas-113 uring the HC states (Figure. 3e and Supplementary Figure. 114 26a). We calculated a series of transmission spectra at dif-115 ferent electrodes separations to mimic the pulling process 116 (Supplementary Figure. 26). The decrease in transmission 117 coefficient with distance is in agreement with the large 118 slope observed in the plateaus of the [4]CDBP HC state. For 119 comparison between 4[CDBP] and [10]CPP in terms of their

1 quantum-transport properties, we calculated the transmis2 sion function for [10]CPP (Figure. 4, green curve) and com3 pared it with that of the LC state of [4]CDBP (Figure. 4, black
4 curve, from the average of the transmission spectra of B5
5 and B6 shown in Supplementary Figure. 24) and that of the
6 HC state of [4]CDBP (Figure. 4, pink curve, from the trans7 mission spectra of J5 displayed in Supplementary Figure.
8 26). From Figure. 4, it is clear that [10]CPP and the HC state
9 of 4[CDBP] exhibit LUMO-dominated transport, while the
10 LC state of [4]CDBP is due to HOMO-dominated transport

<sup>11</sup> with lower conductance, especially in the highlighted re-<sup>12</sup> gion ( $-0.45 \sim -0.2$  eV). In addition, the smaller HOMO-<sup>13</sup> LUMO energy gap of ~1.3 eV for the antiaromatic molecule <sup>14</sup> [4]CDBP (~2.1 eV for [10]CPP) matches well with the <sup>15</sup> HOMO-LUMO energy gap in the isolated-molecule data. A <sup>16</sup> larger slope in transmission spectra around the highlighted <sup>17</sup> region for the HC state of [4]CDBP than that of [10]CPP and <sup>18</sup> the LC state of [4]CDBP supports the experimentally ob-<sup>19</sup> served phenomenon, where the HC state of [4]CDBP pos-<sup>20</sup> sesses sharper conductance gate dependency than that of <sup>21</sup> [10]CPP and the LC state of [4]CDBP. (Figures. 2d-f).



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<sup>23</sup> **Figure. 4:** DFT-based transmission functions for [10]CPP and [4]CDBP. (a) Schematic illustration for the 0.8 nm tip displace-<sup>24</sup> ment measured in the experiment based on the optimized configuration of the gold/molecule/gold sandwich junction <sup>25</sup> ([4]CDBP is chosen as the representative molecule). (b) Top views of those geometric structures for junctions [10]CPP, <sup>26</sup> [4]CDBP-LC and [4]CDBP-HC with detailed contact information. (c) DFT-based transmission spectra against the Fermi energy <sup>27</sup> ( $E_F$ ) in units of the quantum conductance  $G_0 = 77.4 \,\mu S$ . The green, black and pink curves represent [10]CPP, [4]CDBP-LC and <sup>28</sup> [4]CDBP-HC respectively.



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**Figure. 5:** STM-BJ measurement and electrochemically gated control of the single-molecule conductance and DFT-based transmission functions for the [4]CDBP $\supset$ C<sub>60</sub> complex. (a) Structures of [4]CDBP $\supset$ C<sub>60</sub>. (b)-(c) 2D (b) and 1D (c) conductance histograms of [4]CDBP $\supset$ C<sub>60</sub>. (d) Distribution of tip displacement for [4]CDBP $\supset$ C<sub>60</sub> (LC and HC). The estimated tip-substrate gap size is marked in each panel. (e)-(f) 1D conductance histograms collected at different gate voltages (V<sub>g</sub> vs. Fc<sup>+</sup>/Fc) of (e) [4]CDBP $\supset$ C<sub>60</sub> (LC), (f) [4]CDBP $\supset$ C<sub>60</sub> (HC). (g)-(h) Plots of averaged conductance vs. Fc<sup>+</sup>/Fc for (g) [4]CDBP $\supset$ C<sub>60</sub> (LC), (h)

1 [4]CDBP $\supset$ C<sub>60</sub> (HC). (i) Top views of those geometric structures for junctions [4]CDBP and [4]CDBP $\supset$ C<sub>60</sub> supramolecular sys-2 tem with detailed contact information based on the B5 site connection on the right electrode shown in Supplementary Figure. 3 22. (j) Transmission coefficients against the energy of electrons. The blue and black curves represent [4]CDBP and 4 [4]CDBP $\supset$ C<sub>60</sub>, respectively. The grey curve is the transmission function for the remaining [4]CDBP by removing the C<sub>60</sub> di-5 rectly based on the relaxed [4]CDBP $\supset$ C<sub>60</sub> (blue curve) and no further geometric optimization is performed.

The dual-state ambipolar behavior of [4]CDBP per-7 sists in supramolecular system. Given that [4]CDBP 8 serves as an attractive host for a C<sub>60</sub> guest,<sup>23</sup> it is appealing 9 to study the electronic properties of the [4]CDBP $\supset$ C<sub>60</sub> host-10 guest complex and to compare it with those of the empty 11 antiaromatic host. Tang et al. reported a conductance in-12 crease of a metallocycle structure upon encapsulation of a  ${\scriptstyle 13}$  C\_{60} guest and explained it with an additional through-guest <sup>14</sup> charge-transport pathway.<sup>36</sup> Similarly, we built a <sup>15</sup> [4]CDBP⊃C<sub>60</sub> host-guest complex and measured its single-16 molecule conductance. Figures. 5b-c summarize the con-17 ductance measurement of [4]CDBP⊃C<sub>60</sub>. Similar to 18 [4]CDBP, the [4]CDBP $\supset$ C<sub>60</sub> complex exhibited two conduct-19 ance states (Figure. 5b). In the 1D histogram, the HC state 20 contributes to a high-count region up to G<sub>0</sub> and the LC state 21 contributes to the apparent peak.

At  $V_g = 0$  V, the LC state of [4]CDBP $\supset$ C<sub>60</sub> (5.25×10<sup>-4</sup> G<sub>0</sub>) 22 23 exhibited higher conductance compared to [4]CDBP  $_{24}$  (2.29×10<sup>-4</sup> G<sub>0</sub>), although their HC states had roughly the 25 same conductance ([4]CDBP⊃C<sub>60</sub> at  $2.50 \times 10^{-3}$  G<sub>0</sub> and <sup>26</sup> [4]CDBP at  $2.51 \times 10^{-3}$  G<sub>0</sub>), suggesting enhanced charge 27 transport of the LC state upon binding the guest. The tip-28 substrate gap lengths of [4]CDBP $\supset$ C<sub>60</sub> (0.77 nm for LC and <sup>29</sup> 0.67 nm for HC. Figure, 5d) were slightly smaller than those 30 of [4]CDBP (0.80 nm for LC and 0.84 nm for HC). This de-31 crease in junction length can be explained by the decreased 32 flexibility of the host structure, when a C<sub>60</sub> guest is intro-33 duced.<sup>36</sup> The electrochemically gate-controlled conduct-34 ance measurement revealed a HOMO-dominated charge-35 transport mechanism for the HC state and a LUMO-36 dominated mechanism for the LC state (Figures. 5e-h and 37 Supplementary Table. 2), consistent with the empty 38 [4]CDBP. The robustness of the dual-state ambipolar charge <sup>39</sup> transport behavior in [4]CDBP⊃C<sub>60</sub> suggests that the elec-<sup>40</sup> tronic properties based on antiaromaticity can be extended 41 to supramolecular systems.

42 Furthermore, an in-depth analysis in terms of the quan-<sup>43</sup> tum transport properties for the [4]CDBP⊃C<sub>60</sub> host-guest 44 systems was carried out based on DFT. Figures. 5i and 5j il-<sup>45</sup> lustrates the transmission function of the [4]CDBP⊃C<sub>60</sub> 46 host-guest supramolecular system in the junction (B5 bind-47 ing site with tip-tip junction, Supplementary Figure. 25) in 48 comparison to that of the [4]CDBP host. Similarly, a LUMO-49 mediated electron tunneling mechanism is predicted when 50 [4]CDBP forms a host-guest complex with  $C_{60}$ . The ~1.0 eV 51 HOMO-LUMO energy gap for [4]CDBP⊃C<sub>60</sub> ([4]CDBP~1.3 52 eV) can be anticipated by the molecular orbitals (Supple-53 mentary Figure. 26). We presented the transmission spec-54 tra for the relaxed [4]CDBP (black curve) and the remaining 55 [4]CDBP residue after removing the C<sub>60</sub> guest (no further 56 geometrical relaxation: grey curve). This shows that elec-57 tron transport is enhanced by the C<sub>60</sub> guest through the 58 host-guest interaction in agreement with our experimental 59 observations. In addition, it is noted that transport is mainly

<sup>60</sup> LUMO-dominated, which agrees well with the molecular or-<sup>61</sup> bital calculation and charge transfer analysis that C<sub>60</sub> gains <sup>62</sup> 0.085 electron from the [4]CDBP host as an electron-defi-<sup>63</sup> cient moiety. This behavior is also predicted and observed <sup>64</sup> in the host-guest system studied in our previous work.(<sup>36</sup>) <sup>65</sup> The difference of energy-level alignment in transmission <sup>66</sup> 7function can be understood from the weaker charge trans-<sup>67</sup> fer in the [4]CDBP $\supset$ C<sub>60</sub> supramolecular system compared to <sup>68</sup> the more pronounced energy-level displacement for the <sup>69</sup> system studied in paper,<sup>36</sup> where 0.23 electron is trans-<sup>70</sup> ferred to C<sub>60</sub> from the host.

## 71 CONCLUSION

In this study, we investigated charge transport in the ar-73 omatic nanohoop [10]CPP and the antiaromatic [4]CDBP. 74 While [10]CPP exhibited a single conductance state, 75 [4]CDBP revealed a distinctive dual-state conductance gov-76 erned by ambipolar behavior. This was linked to different 77 molecule-electrode anchoring modes, effectively tuning the 78 energy-level alignment within the antiaromaticity-deter-79 mined narrow HOMO-LUMO gap. These unique properties 80 persisted in the [4]CDBP $\supset$ C<sub>60</sub> complex. Our findings pro-81 vide fundamental insights into antiaromaticity's role in sin-82 gle-molecule electronics and suggest new strategies for de-83 signing molecular devices.

#### 84 METHODS:

STM break-junction measurement: Single-molecule 85 <sup>86</sup> junction conductance was measured using an Agilent 5500 87 scanning tunneling microscope. The sample molecules 88 were dissolved in a chlorobenzene (CB, 99.9%, Aladdin) so-89 lution containing 0.1 M tetrabutylammonium tetrafluorob-90 orate (n-Bu<sub>4</sub>NBF<sub>4</sub>, 99%, Alfa Aesar). A gold film on mica, an-91 nealed in a butane flame for 30 seconds, served as the sub-92 strate electrode, while a freshly cut gold tip from a 0.25 mm 93 diameter wire (99.999%, Alfa Aesar), coated with polyeth-94 ylene, was employed as the STM tip electrode. A bias voltage 95 of 0.1 V was applied between the electrodes, and the tip was 96 repeatedly brought into and withdrawn from contact with 97 the substrate. This process enabled the formation of molec-98 ular junctions, and thousands of conductance-distance 99 traces were recorded to construct the conductance histo-100 grams.

**Electrochemically gate-controlled break-junction measurements:** Measurements were performed using an Agilent 5500 scanning tunneling microscope in combination with a built-in bipotentiostat. A platinum coil served as the quasi-reference electrode and another as the counter electrode. To minimize ionic leakage, the freshly cut tip was coated with polyethylene. A gate potential was applied between the tip and reference electrodes, while a constant bias potential of 0.1 V was maintained between the substrate and tip electrodes. The electrochemical window was the determined via cyclic voltammetry of the pure solvent and the solution of [4]CDBP (Supplementary Figure. 19), and the potential drift of the platinum quasi-reference electrode was characterized (Supplementary Figure. 20c). The gate voltage was calibrated against the Fc<sup>+</sup>/Fc couple by measuring the  $E_{1/2}$  potential of 1,1'-ferrocenedicarboxylic acid s using cyclic voltammetry (Supplementary Figure. 20b).

Junction length analysis: For each conductance-dis-7 tance trace, we calculated the tip displacement from the 8 breakdown of the gold-gold (Au-Au) junction (G<sub>0</sub>) to the 9 breakdown of the molecular junction. Aggregating thou-10 sands of such traces, we constructed one-dimensional (1D) 11 histograms of total tip displacement. To determine the junc-12 tion lengths, we incorporated a snapback distance of 0.5 nm <sup>13</sup> for [10]CPP and the LC states of [4]CDBP and [4]CDBP⊃C<sub>60</sub> 14 host-guest complexes. This snapback distance accounts for 15 the rapid retraction of the electrodes immediately after 16 breaking an atomic-scale gold filament, a phenomenon ob-17 served in scanning tunneling microscope break-junction 18 (STM-BJ) experiments. Notably, we did not apply this snap-19 back distance to the HC states of [4]CDBP and [4]CDBP $\supset$ C<sub>60</sub> 20 host-guest complexes, because gold filament did not form 21 during tip retraction in these cases. Average tip displace-22 ment values for [10]CPP, [4]CDBP (HC and LC), and <sup>23</sup> [4]CDBP $\supset$ C<sub>60</sub> (HC and LC) were obtained by performing 24 Gaussian fittings on the 1D conductance histograms for 25 each dataset.

### 26 ASSOCIATED CONTENT

27 Supporting Information

28 Additional experimental details, materials, and methods. (PDF)

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#### 41 Author Contributions

42 The manuscript was written through contributions of all au-

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44 the manuscript. / #These authors contributed equally.

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