

Orthogonal Control of Transport Channels in Boron-Embedded Acenes

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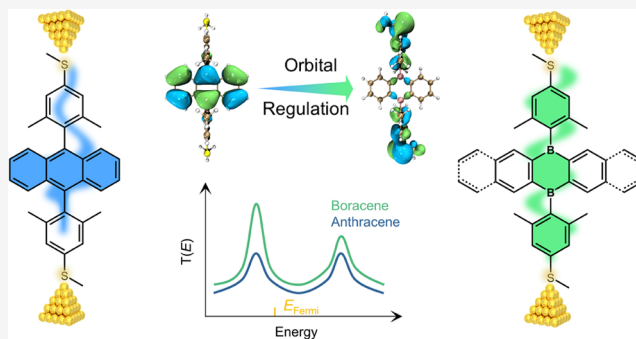


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ABSTRACT: Developing effective structural design strategies for regulating charge transport is a central focus in molecular electronics. The interplay between molecular symmetry and orbital distribution, facilitated by heteroatom substitution, presents opportunities for direct modulation in both resonant and off-resonance tunneling processes. In this study, scanning tunneling microscopy-break junction techniques and the first-principles calculations are employed to investigate the electronic properties of boron-embedded acenes. Compared to the parent acene, boron incorporation shifts the transport-dominating molecular orbital from a centrally localized distribution to a delocalized configuration across the orthogonal molecular backbone. This shift results in a 10-fold increase in conductance in the off-resonance region near zero bias and a 50-fold enhancement in conductance through near-resonant tunneling at high bias voltages. Notably, expanding the central acene fragment increases orbital asymmetry within molecular junctions, thereby compromising transport efficiency. However, applying a bias voltage gradually mitigates the symmetry-breaking effect, leading to through-backbone orbital distribution and a recovery in the near-resonant tunneling conductance. This orthogonal control of electronic transport channels provides a distinct strategy for the effective regulation of molecular conductance.



INTRODUCTION

The construction and regulation of charge transport in molecules is crucial for advancing molecular electronics.^{1,2} At the nanoscale, quantum effects, such as quantum confinement, quantum tunneling, and quantum interference, significantly influence electron transport, leading to distinctive behaviors in molecular electronic devices.^{3,4} For instance, destructive quantum interference can suppress off-resonance tunneling, enabling molecular transistors to achieve conductance-switching ratios exceeding 10^4 and subthreshold swings at the thermionic limit.^{5–7} Furthermore, antiresonance transmission dips arising from Fano resonance—resulting from the coupling between bound and continuum orbital states—can regulate molecular conductance through substituent control and electrochemical gating.^{8–10} However, these quantum control methods primarily impact off-resonance tunneling processes. The substantial and precise regulation of resonant tunneling remains a central research focus, but has been rarely studied, highlighting the need for more effective strategies to achieve precise control over both tunneling processes.

Chemical modification, especially heteroatom doping, can effectively alter conductive pathways, charge distribution, and orbital characteristics while preserving structural integrity, influencing both resonant and off-resonance tunneling processes.^{11–13} Previous research on heteroatom substitution

modifies molecular conductance by manipulating electronic properties, such as polarizability,¹⁴ electronegativity,¹⁵ geometrical conformation,¹⁶ and the degree of conjugation.¹⁷ Recently, boron incorporation within aromatic structures has garnered considerable attention, demonstrating enhanced conductivity,¹⁸ high optoelectronic performance potential,¹⁹ and enhanced catalytic reactivity.^{20,21} Particularly, the incorporation of boron into carbon lattices enables effective control over the frontier orbitals through the utilization of the unoccupied p_z orbital of boron atom, offering direct regulation of the resonant tunneling channels.^{22–24} In addition, the disruption of aromaticity caused by boron embedding creates a platform for orbital symmetry control, which is pivotal in charge transport.^{25–27} By investigating the synergistic effects of orbital manipulation and symmetry control through single-molecule electronic measurement techniques, we can refine electron pathways for resonant transport and elucidate novel quantum phenomena.

Received: December 11, 2024

Revised: February 11, 2025

Accepted: February 12, 2025

Published: February 21, 2025



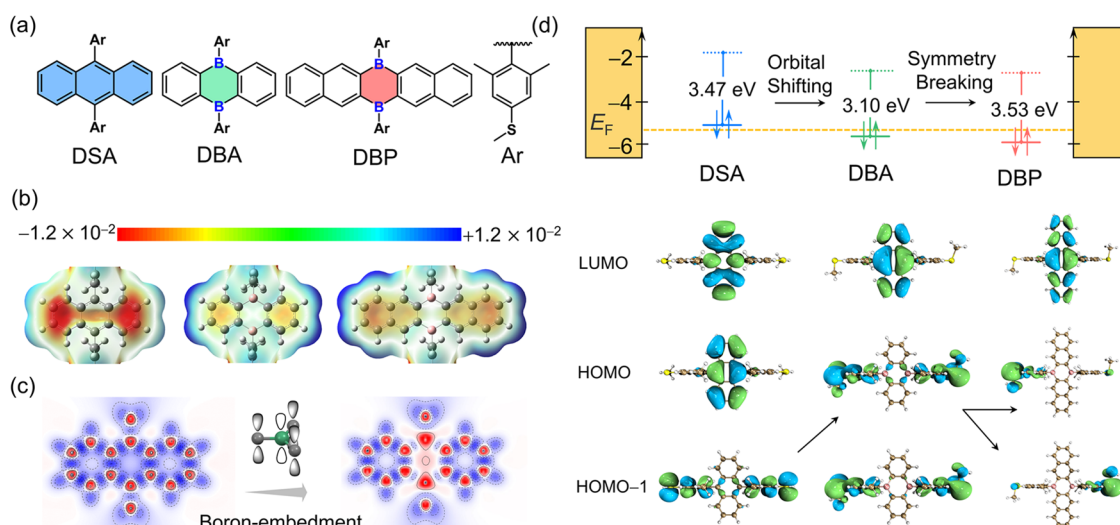


Figure 1. Design and electronic characteristics of DSA, DBA, and DBP molecules. (a) Chemical structures of DSA, DBA, and DBP. (b) Calculated electrostatic potential maps of DSA (left), DBA (middle), and DBP (right). The blue color represents the positive charge, while the red color represents the negative charge. ESP unit: Hartree/e. (c) Calculated 2D ICSS ($1)_{zz}$ maps of DSA (left) and DBA (right) at the plane of anthracene. The blue color represents strong aromaticity while red color represents the antiaromaticity. (d) Calculated frontier molecular orbital diagrams and energy levels for DSA (left), DBA (middle), and DBP (right).

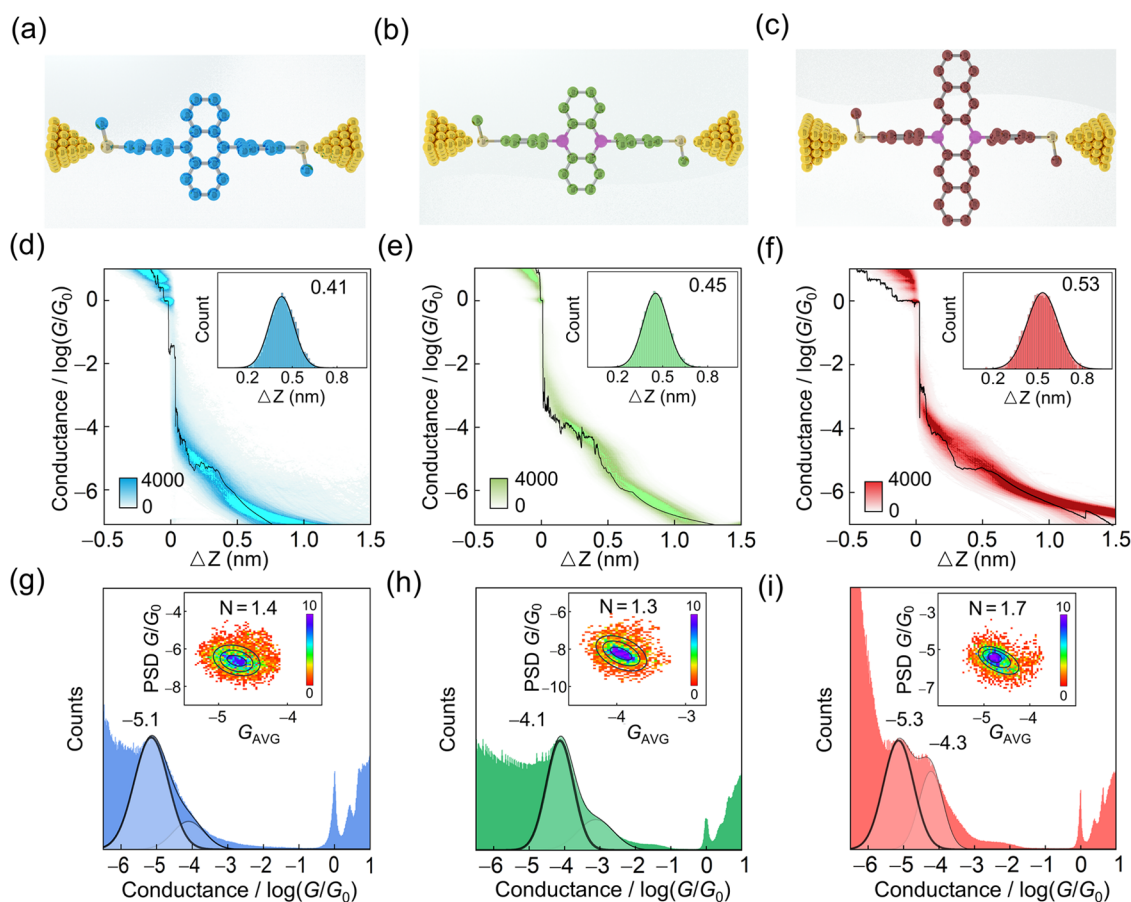


Figure 2. Single-molecule electrical measurements of DSA (left), DBA (middle), and DBP (right) molecules. (a–c) Schematic of anchor-to-anchor STM-BJ measurements of DSA (a), DBA (b), and DBP (c) single-molecule junctions. (d–f) 2D conductance-displacement histograms for DSA (d), DBA (e), and DBP (f) junctions. The color bar indicates the number of counts, while typical single traces are marked. The inset shows the plateau-length distribution. (g–i) 1D conductance histograms of DSA (g), DBA (h), and DBP (i) junctions. The inset shows 2D histogram of the normalized noise power versus average conductance for each junction, and only the low conductance state of DBP is considered.

In this study, we examine the orbital control of molecular charge transport using a combination of scanning tunneling

microscopy-break junction (STM-BJ) techniques and first-principles calculations. The electronic characteristics of boron-

embedded structures are systematically studied at the single-molecule level. Anthracene-based analogue with thiomethyl (SMe) phenyl groups serves as a model system due to their orthogonal configurations, which typically yield low conductance due to reduced conjugation and localized orbitals.²⁸ By embedding boron atoms into the anthracene scaffold, we achieve effective control over both off-resonance and near-resonant tunneling, providing new insights into the regulation of molecular conductance and functionalization of molecular devices.

■ RESULTS AND DISCUSSION

Molecular System Design. To investigate the impact of boron embedding on the orbital properties of acenes, diphenyl anthracene (DSA), 1,4-dihydrodiboranthracene (DBA), and 1,4-dihydrodiborapentacene (DBP) with SMe anchoring groups are synthesized (Figures 1a, S1–S6).^{22,29} With the methyl groups on 3,5-dimethylphenyl rings serving as protective and hindering units, all molecules exhibit two conjugated planes that are nearly orthogonal to each other, with dihedral angles close to 90°. Electrostatic potential (ESP) maps (Figure 1b) reveal that while DSA exhibits electron-rich characteristics in the anthracene area, DBA and DBP exhibit electron deficiency in C₄B₂ rings, comparatively. This distinct charge distribution feature indicates that the electron deficiency introduced by boron is corroborated by the antiaromatic character observed in the isotropic chemical shielding surface (ICSS) maps (Figures 1c and S7).^{23,45}

In terms of electronic orbital characteristics, molecular orbital energy diagrams (Figure 1d) illustrate that the lowest unoccupied molecular orbital (LUMO) of DBA closely resembles the highest occupied molecular orbital (HOMO) of DSA, while the orbital distribution of HOMO of DBA aligns closely with that of HOMO–1 of DSA, reflecting the direct and total molecular orbital reconstruction induced by boron embedment. This orbital reconstruction is also evident that the HOMO of DBA shifts from the localized central anthracene in DSA to a highly delocalized distribution across the molecular backbone. The HOMO energy levels for DSA, DBA, and DBP progressively decrease. Although DBP exhibits frontier orbitals with characteristics similar to those of DBA, its HOMO distribution is significantly more localized near the anchoring groups due to the symmetry difference that causes degeneracy breaking between HOMO and HOMO–1 in the corresponding pentacene derivative (Figure S8). The distinctive changes in orbital distribution within the orthogonal systems before and after boron substitution suggest unique conductive characteristics.

Exploring Charge Transport in Boron-Embedded Molecular Junctions. To investigate the electronic properties of highly reconstructed boron-embedded orthogonal systems, the charge transport characteristics of the three molecules are assessed using the STM-BJ technique. Single-molecule conductance (G) is measured in a solution of 1,2,4-trichlorobenzene (TCB) containing 0.5 mM of the respective target molecules by displacing the tip and substrate to form dynamic single-molecule junctions (Figure 2a–c). During the repeated formation of junctions, conductance plateaus are observed at G values exhibiting a negative exponent of G_0 (where $G_0 = 2e^2/h$) in individual traces. Representative individual traces of all molecules under 0.1 V are depicted in Figure S9. These conductance traces are then utilized to construct 2D conductance histograms. Compared to the

exponential decay characteristics observed in the 2D conductance-displacement histograms of pure TCB (Figure S10), the 2D histograms for the molecular solutions exhibit distinct single-molecule conductance platforms. Figure 2d presents the 2D conductance-displacement histograms of DSA, while Figure 2e presents those of DBA. A primary Gaussian-fitted conductance peak of DSA can be observed at $\approx 7.9 \times 10^{-6} G_0$ (≈ 0.64 nS), while that of DBA at $\approx 7.9 \times 10^{-5} G_0$ (≈ 6.4 nS), indicating a 10-fold conductance enhancement due to the boron embedment (Figure 2g,h). This is closely associated with the HOMO shifting from central localization to delocalization along the current direction, as shown in Figure 1d. The sloping profile observed in both 1D histograms is attributed to the interaction between the lateral benzene groups and the gold electrodes during the pulling process, possibly corresponding to unstable through-space transport states. As a result, although both DSA and DBA are primarily dominated by through-bond transport, their noise power scales with $G^{1.4}$ and $G^{1.3}$, respectively, in the 2D histogram of the noise power spectral density (PSD) (Figure 2g,h, inset).³¹

While boron embedment demonstrates conductance-shifting potential, the molecular conductance of DBP, which features a longer pentacene central unit, exhibits a more complex behavior. The single trace and 2D histograms of DBP (Figure 2f,i) reveal two plateau conductance signals: a shorter plateau length at $\approx 5.0 \times 10^{-5} G_0$ (≈ 4.03 nS) and a longer plateau at $\approx 5.0 \times 10^{-6} G_0$ (≈ 0.40 nS). The distinct plateau lengths of these states indicate different anchoring positions. The longer plateau length suggests the formation of a fully stretched anchor-to-anchor molecular junction, corresponding to the lower conductance state via through-bonding transport.³² This low conductance is likely due to the asymmetrically localized HOMO distribution across the orthogonal molecular backbone caused by the enlarged central region in DBP. During the stretching process of the gold tip, a more conductive through-space transport channel forms between the gold substrate and diborapentacene side when an anchor attaches to the gold tip (Figures S11 and S12). The effective through-space charge transport, indicative of the higher charge-carrier mobility of pentacene, is facilitated by the electron-withdrawing C₄B₂ center, forming an efficient donor–acceptor–donor junction.^{33,34} The plateau length statistics for DSA, DBA, and DBP are 0.41, 0.45, and 0.53 nm, respectively, without considering the Au–Au snap-back distance. The gradual increase in plateau lengths from DSA to DBA to DBP aligns well with the theoretically calculated results (Figure S13). The PSD of DBP scaling with $G^{1.7}$ and $G^{1.8}$ for low state and high state, respectively (inset of Figures 2i and S14), provides strong evidence supporting inseparable through-space transport behavior. Previous studies on the single-molecule conductance of similar pentacene-containing conjugate structures have reached the same conclusion through controlled experiments with single-ended anchors.³⁵ The intense interaction between DBP and gold leads to this inseparable anchor-acene transport,³⁶ combined with the symmetry-breaking HOMO distribution of DBP in the SMe group (Figure S15 and Table S1), showing a significantly higher through-space coupling of diborapentacene compared to the DSA and DBA systems.³⁷

Investigating the Transition of the Tunneling Processes under Bias Voltages. To further elucidate the transport characteristics of single-molecule junctions, current versus voltage (I – V) and conductance versus voltage (G – V)

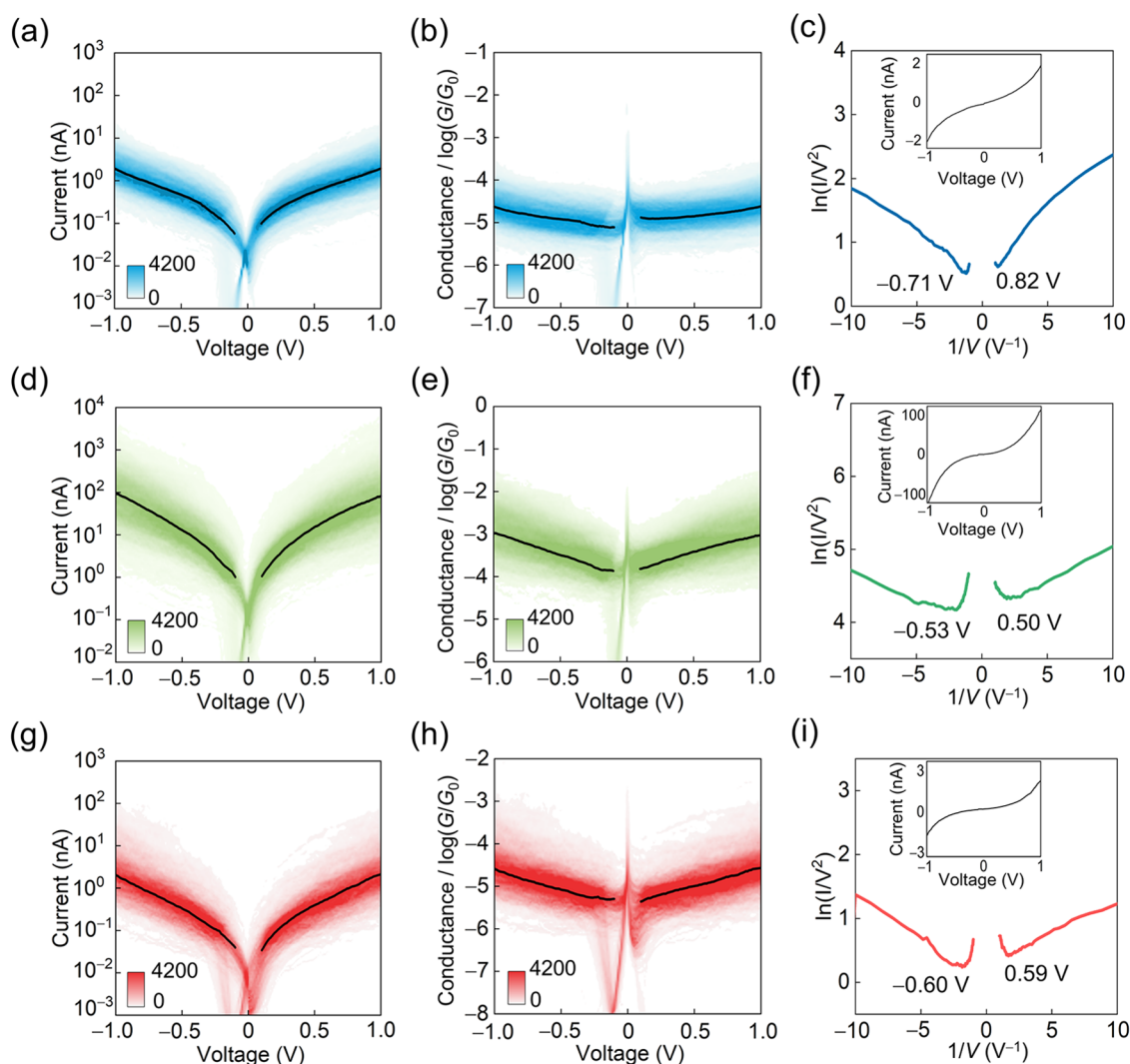


Figure 3. Charge transport characteristics for DSA (up), DBA (middle), and DBP (down). (a,d,g) 2D current versus voltage (I – V) histograms of DSA (a), DBA (d), and DBP (g) junctions. (b,e,h) 2D conductance versus voltage (G – V) histograms of DSA (b), DBA (e), and DBP (h) junctions. (c,f,i) Fowler-Nordheim plots constructed from the corresponding fitted I – V curves (black line) in (a), (d), and (g), respectively. The transition voltages for positive and negative polarities are marked out. The insets show the corresponding I – V curves on a linear scale.

characteristics are investigated. Figure 3a,d,g illustrate the 2D I – V histograms of DSA, DBA, and DBP junctions, while Figure 3b,e,h depict the 2D G – V histograms, respectively. At relatively low bias (less than ± 0.5 V), DBA exhibits the highest conductance, and DSA shows conductance higher than DBP. The transition voltage spectra (TVS), referring to the Fowler-Nordheim plot ($\ln(I/V^2)$ versus $1/V$), indicate that all junctions are operating in off-resonance tunneling processes (Figure 3c,f,i).^{38,39} The transition voltage (V_{trans}) in TVS for DSA, DBA, and DBP junctions are 0.82 (–0.71) V, 0.50 (–0.53) V, and 0.59 (–0.60) V, respectively, indicating that the charge transport changes from off-resonance tunneling to near-resonant tunneling process at a higher bias voltage.⁴⁰ As the bias voltage further increases, the boron-containing systems display a more significant conductance enhancement compared to all-carbon structures. For instance, DBA exhibits a conductance of $\approx 1.3 \times 10^{-3} G_0$ (≈ 105 nS) while DSA shows a conductance of $\approx 3.2 \times 10^{-5} G_0$ (≈ 2.6 nS) at 1 V, resulting in an enhancement of conductance difference to be near 50-fold. The conductance of the low-conductance state for DBP surpasses DSA at 1 V, also evident for distinctive

boron-embedded conductance raising. The I – V characteristics of all molecular junctions (Insets in Figure 3c,f,i) are in consistence with the theoretical nonzero bias transmission simulations (Figure S16). To be noted, the conductance state of DBP junctions displays two conductance bands consisting of both through-space transporting state (high-state) and through-anchor transporting state (low-state) (the higher state and bistate analysis is presented in Figure S17). While the TVS analysis exhibits lower V_{trans} for boron-embedded structures, the orbital energy characteristics of boron-embedded molecular junctions that are closer to the Fermi level require further study.

Theoretical Analysis of Charge Transport. To gain a comprehensive understanding of the effect of boron embedment on charge transport in acenes, we conduct the first-principles investigation that combines density functional theory (DFT) with nonequilibrium Green's functions (NEGF). Figure 4a illustrates the zero-bias transmission spectra of three single-molecule junctions, indicating that low-bias conductance is facilitated through an off-resonance tunneling process. This low-bias conductance is primarily

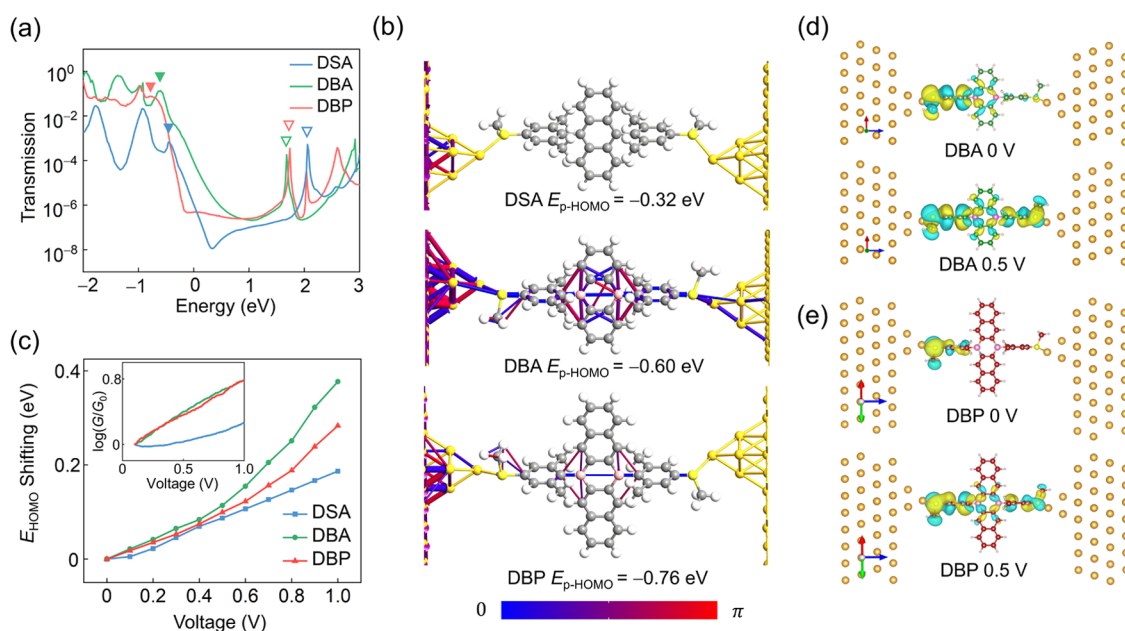


Figure 4. Theoretical simulations of the electronic transport characteristics and molecular property analysis. (a) Calculated transmission spectra of all three molecular junctions. The triangles mark out the positions of the transmission peaks corresponding to *p*-HOMOs (left) and *p*-LUMOs (right), respectively. (b) Transmission pathways of DSA, DBA, and DBP at respective *p*-HOMO energy levels. The demonstration threshold is set as 0.05, indicating the minuscule transport ability of DSA. (c) Calculated shifting of *p*-HOMOs under bias voltages through molecular energy spectrum analysis, zero-bias *p*-HOMO energy level of each junction is subtracted. Inset: experimental relative conductance $\log(G/G_0)$ under bias voltages. (d,e) Molecular projected self-consistent Hamiltonians of *p*-HOMO iso-surfaces of DBA and DBP with different electric fields. Under 0.5 V, the left electrode is applied +0.25 V while right electrode is applied −0.25 V.

determined by the transmission coefficient at the Fermi level, as articulated by the Landauer equation $G/G_0 = T(E_F)$.⁴¹ The predicted relative conductance of the acenes is consistent with experimental measurements, demonstrating the order DBA > DSA > DBP. Notably, the conductance under the off-resonance tunneling mechanism is predominantly influenced by the cumulative Lorentzian decay of the resonant conductance peaks associated with the *p*-HOMOs and *p*-LUMOs. Remarkably, the resonant conductance peaks of the *p*-HOMOs shift by up to 200-fold before and after boron embedment in acenes, while the *p*-LUMOs remain consistently low.

While *p*-HOMOs are considered as the dominant transport channels, the transmission pathways for all molecular junctions are calculated at their respective transmission peaks, as indicated by the solid arrows in Figure 4a.⁴² The transmission pathways of *p*-HOMOs are illustrated in Figure 4b, revealing a clear and effective conductive pathway along the molecular backbone for DBA, while DBP demonstrates a slightly weaker yet still discernible pathway. In contrast, DSA shows no discernible conductive pathway, which accounts for the lowest transport efficiency. Meanwhile, the *p*-LUMOs of all three junctions exhibit ineffective and asymmetric transmission features (Figure S18). The molecular projected self-consistent Hamiltonians (MPSHs), along with transmission eigenstates of the perturbed frontier orbitals (Figures S19 and S20), confirm the orbital distribution comparable to those of isolated molecules. These results confirm that boron embedment alters the centrally localized resonant transport channels of *p*-HOMO to a highly efficient delocalized feature along the transport backbone.⁴³ Although experimental low-bias results show limited enhancement due to orbital symmetry breaking and the off-resonance tunneling mechanism, boron embed-

ment exhibits significant potential for conductance modulation over several orders of magnitude under the resonant tunneling mechanism, theoretically.^{33,44}

The effective transport channels could be taken advantage of under high bias voltages, as boron-embedded structures exhibit drastic conductance enhancement (Figure 4c, inset). In addition to orbital distribution characteristics, the energy level shifting of *p*-HOMOs under different bias voltages is also simulated (Figure S21). As illustrated in Figure 4c, DBA and DBP exhibit a more pronounced tendency for HOMO shifting toward the Fermi level compared to DSA, indicating an enhanced orbital inclusion within the bias window under the influence of the electric field. This may result from a disruption of aromaticity after boron embedment, which could also account for the lowered TVS results observed in boron-embedded species (Figure S22).

The aromaticity breakage in the C_4B_2 center limits π -electron delocalization, and may be responsible for the symmetry-breaking of HOMO in DBP, which, combined with electrode coupling, leads to the symmetry breaking of *p*-HOMO in the DBA junction. However, when a potential field of 0.5 V is applied, the *p*-HOMOs of both DBA and DBP exhibit a significant field-dependent shift toward the right side of the electrode, while the *p*-HOMO of DSA shows minimal change (Figures 4d,e, S23–S27). At this bias voltage, both DBA and DBP display orbital distribution across the molecular backbone. The electric field-induced recovery of orbital symmetry, combined with the distinctive orbital energy shift, further enhances charge transport within boron-embedded orthogonal structures.

It is noteworthy that the stereoelectronic effect of the orthogonal system is also considered. When subjected to an external electric field, the biphenyl structures within the

orthogonal system tend to planarize and increase their conjugation, thereby enhancing molecular conductance.^{45,46} Theoretical simulations indicate that when an electric field is applied along the anchor direction, all molecules exhibit a tendency toward planarization. To simulate the field-induced stereoelectronic effect, extensive scanning of dihedral angles within the orthogonal system is performed. The potential energy surface reveals that DSA has a higher energy barrier toward planarization compared to boron-centered structures, indicating a more rigid structure (Figure S28). To account for the influence of the stereoelectronic effect, the MPSHs of preoptimized DSA and DBA under a 1 V, with dihedral angles of 70° and 64°, respectively (Figures S29 and S30) shows minimal difference with orthogonal structures. A control *I*–*V* experiment using a nonorthogonal all-carbon conjugated structure is further congruent with DSA, which demonstrates that the conductance influence of external electric field-induced planarization is negligible (Figures S31 and S32). Therefore, while field-induced planarization may benefit boron-embedded structures, the drastic conductance enhancement under bias voltages is primarily attributed to boron-induced orthogonal orbital modulation and field-regulated symmetry-breaking effect.⁴⁷

CONCLUSIONS

The electronic characteristics of boron-embedded acenes are systematically investigated at the single-molecule level. Boron embedding provides a direct orbital regulation strategy to control molecular conductance by redistributing molecular orbitals from a centrally localized configuration to a backbone-delocalized configuration. This change results in a 10-fold increase in the off-resonance process and a 50-fold enhancement in conductance through near-resonant tunneling. In addition, boron-embedded acenes tend to exhibit symmetry-breaking orbitals as the acene core enlarges. We find that the application of an electric field across the molecular backbone mitigates the symmetry-breaking effect, which may result from the loss of aromaticity, allowing orbitals to recover to a delocalized configuration that facilitates charge transport. The distinctive field-induced orbital energy shifting and stereoelectronic planarization analysis further demonstrate the charge transport efficiency in boron-embedded molecules. These findings reveal the intricate interplay between boron-based structural modification and electronic characteristics, offering significant potential for future applications in molecular electronics and functional organic material designs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c17477>.

Synthetic methods of target molecules; experimental methods, theoretical calculations including structural characteristics, isotropic chemical shielding surface maps, transmission analysis and state attribution, molecular projected self-consistent Hamiltonians and transmission eigenstates, transmission pathways, non-zero bias device eigenstate analysis; supporting STM-BJ test results of target molecules; field-induced planarization analysis, and atomic coordinates of all molecules (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We acknowledge primary financial supports from the National Key R&D Program of China (2024YFA1208100, 2021YFA1200102, 2021YFA1200101, 2022YFE0128700 and 2023YFF1205803), the National Natural Science Foundation of China (22173050, 22150013, 21727806, 22071120 and 21933001), Beijing National Laboratory for Molecular Sciences (BNLMS-CXXM-202407), and the Natural Science Foundation of Beijing (2222009).

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