Precise Regulation of Ultralow Conductance Attenuation in Single-Molecule Hexabenzocoronene Oligomers

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ABSTRACT: Efficient long-range charge transport within molecular wires, which hinges upon ultralow length-dependent conductance attenuation, is essential for molecular electronics and optoelectronics applications. In this study, a series of hexabenzocoronene oligomers are synthesized, and their charge transport behaviors are investigated by using both dynamic and static single-molecule junction techniques. Remarkably, hexabenzocoronene oligomer-based dynamic single-molecule junctions with gold electrodes show an exceptionally low conductance attenuation coefficient of ~0.046 Å⁻¹, while static single-molecule junctions based on graphene electrodes exhibit a triple value of conductance attenuation. Via the introduction of ionic liquid gates, the molecular conductance is regulated



effectively, reducing the attenuation coefficient by more than 50%, due to precise control of the energy offset between the Fermi level of the electrodes and the molecular energy levels. These findings, particularly the efficient control of the molecular conductance attenuation at ultralow levels, indicate a novel approach to achieving long-range transport for practical molecular electronics.

ong conjugated molecules or molecular wires generally require efficient charge transport over long distances with minimal energy losses or decoherence. This is highly significant for the practical application of functional molecular devices and circuits. The length-dependent conductance is a fundamental property of a molecular wire that reflects the charge transport mechanism and performance.¹⁻³ In long-range molecular wires (typically >5 nm in length), electrons primarily transport through an incoherent hopping process that is usually thermally activated, resulting in pronounced temperature dependence and a linear relationship between the molecular length and the conductance. In contrast, in shorter molecular wires ($\leq 4-5$ nm), direct tunneling becomes the dominant charge transport mechanism under low bias voltages, and this mechanism is independent of temperature.³⁻⁷ The molecular conductance then demonstrates exponential attenuation with increasing molecular length L, which can be expressed as $G \propto \exp(-\beta L)$, with the attenuation coefficient β being determined by fitting.^{8–10} The magnitude of the attenuation coefficient reflects the efficiency of charge transport in molecules. A lower β value signifies higher transmission efficiency over longer distances, with

simultaneous reductions in energy losses and scattering during charge transport. This enhancement can significantly improve the performance and stability of molecular devices significantly. To achieve efficient and reliable long-range transport, it is therefore essential to fabricate conductive molecular wires with the lowest attainable β value.

Single-molecule junction (SMJ) techniques enable direct measurement and manipulation of individual molecules.^{2,11} The electrical conductance of molecular wires with various lengths can be quantified using SMJ techniques such as the scanning tunneling microscope-based break junction (STM-BJ),¹² the mechanically controllable break junction,¹³ the graphene–molecule–graphene (GMG) SMJ,¹⁴ and other approaches. These methods have been used to investigate β

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values across a variety of systems, including alkane oligomers, $^{15-17}$ thiophene oligomers, 18,19 and benzene oligomers, 8,20,21 where the values typically fall between 0.2 and 1 Å⁻¹. In highly conjugated molecules, efficient coupling between the $\pi - \pi$ orbitals enables connections between molecular modules. In addition, the extended delocalization of molecular orbitals over long distances allows efficient electron transmission, thereby reducing conductance attenuation. Recent studies using the STM-BJ technique have observed ultralow β values of 0.02 Å⁻¹ in porphyrin oligomers with molecular lengths ranging from 2 nm to 3.75 nm.²² Furthermore, porphyrins with metal complexes have also exhibited similarly low conductance attenuation.^{23,24} However, the primary factors and regulatory mechanisms of the attenuation coefficients remain undetermined. Some researchers have emphasized intrinsic molecular properties, e.g., conjugation and energy gap, as the main determinants of molecular conductance attenuation,⁹ whereas other research has highlighted anchoring groups between molecules and electrodes,^{25,26} electron-vibration interactions,²⁷ and environmental factors.^{28,29} To develop high-performance and functionalized molecular devices, an approach providing efficient control of molecular conductance and enabling ultralow attenuation has emerged as a critical and pressing requirement.

Hexabenzocoronene (HBC) is a highly conjugated polycyclic aromatic hydrocarbon molecule that consists of six benzene rings arranged around a central hexagonal core.^{30–32} This unique structure causes the delocalized π electrons in HBC derivatives to be distributed extensively along the armchair direction, similar to armchair graphene nanoribbons with extremely narrow widths. Here, we synthesize a series of HBC oligomers and explore their conductance properties using STM-BJ and GMG-SMJ techniques. Ultralow conductance attenuation coefficients are achieved, close to the lowest reported value to date,^{22,27,33,34} and these factors can also be effectively regulated using gate electric fields.

The conductance and conductance attenuation of molecular wires depend on the energy gap, conjugation degree, and the position of conductive orbitals relative to the Fermi level of the electrodes.^{23,35-37} We have synthesized a series of HBC oligomers, denoted by $(HBC)_n$, with *n* having values of 1, 2, and 3 for monomers, dimers, and trimers that result in molecular lengths of ~2.29, ~3.55, and ~4.85 nm, respectively (Schemes S1-S4, and Figures S1-S9). The predicted gaps between the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of these oligomers are ~3.32, ~3.17, and ~3.1 eV (Figure S10 and Figure 2d), respectively. In addition, the frontier molecular orbitals of HBC oligomers with various dihedral angles are calculated, revealing that the sensitivity of the HOMO-LUMO gap to the twisting angles is relatively low (Figure S11). Note that the HOMO-LUMO gap and its variation with molecular length for HBC oligomers are comparable to other typical molecular wires with low conductance attenuation coefficients (see details in Table S1).

To investigate the length-dependent conductance of these HBC oligomers systematically, single-molecule junctions were constructed from different $Au-(HBC)_n$ -Au configurations using the dynamic STM-BJ technique (Figure 1a), which enabled statistical conductance measurements. In this approach, a gold tip moves toward and away from a gold substrate, thus continuously forming and then breaking a



Figure 1. Charge transport of Au-(HBC)_n-Au single-molecule junctions. (a) Schematic illustration of an Au-(HBC)_n-Au singlemolecule junction. The anchoring group between the molecule and the electrode is an amino group. (b) 2D current versus bias voltage (I-V) histograms of Au-(HBC)_n-Au single-molecule junctions with Gaussian-fitted lines. (c) Logarithm of conductance (log G) versus the distance between the molecular anchoring nitrogen atoms $(d_{\rm NN})$ with error bars for $({\rm HBC})_n$ (n = 1, 2, 3) at a $V_{\rm D} = -0.1$ V. The inset shows the β values obtained under different bias voltages ranging from 0.1 to 1.0 V with steps of 0.1 V. (d) Plot of β values for the different molecular systems, with the abscissa representing the length of a single unit within the molecule $(d_{\rm unit})$. The molecules are categorized into eight types, including alkanes,^{15,16,25} alkenes,^{40,41} alkynes,^{42,43} benzene,⁴⁴ polycyclic compounds,^{4,20,45,46} heterocyclic compounds,^{18,19,22,27,38,47-52} imines,³ and endocyclic compounds.^{10,41} The specific molecular structures are presented in Table S2.

single-molecule junction. Currents were measured repeatedly as a function of bias voltage (i.e., I-V characteristics) at a fixed tip-to-substrate distance in a 1,2,4-trichlorobenzene (TCB) solution that contained 0.1 mM target molecules. Figure 1b illustrates the two-dimensional (2D) I-V histograms that were collected from thousands of individual plots, showing slight differences in average currents of the HBC oligomers under Gaussian fitting conditions (Figures S12–S14). In addition, we conducted a control experiment by protonating the amino groups and observed the disappearance of conductance states. This demonstrates that the measured conductance originates from the Au-amino contacts instead of Au- π contacts (Figure S15). For example, at a bias voltage of -0.1 V, the conductance values measured for the monomer, dimer, and trimer were ~0.854, ~0.382, and ~0.252 nS, respectively. Based on the formula $G = G_0 \exp(-\beta L)$ and by approximating L to be d_{NN} , this system demonstrates an extremely low attenuation coefficient of $\beta \approx 0.046 \pm 0.008 \text{ Å}^{-1}$ (Figure 1c). The inset illustration in Figure 1c shows that β is minimally influenced by bias voltages, excluding bias-induced errors in the measured results. When compared with previously studied molecular systems, including alkanes, alkenes, alkynes, and polycyclic/heterocyclic compounds, only porphyrin oligomers and our HBC oligomers exhibit ultralow conductance attenuation coefficients in the range from ${\sim}0.02~\text{\AA}^{-1}$ to



Figure 2. Charge transport characteristics of graphene– $(HBC)_n$ –graphene single-molecule junctions. (a) Schematic illustration of a graphene– $(HBC)_n$ –graphene single-molecule junction. The anchoring group between the molecule and the electrode is an amino group. (b) I_D vs V_D characteristics with error bars (replicated from five successfully connected junctions) for graphene– $(HBC)_n$ –graphene single-molecule junctions. The inset shows the I_D vs V_D characteristics for the trimer. (c) Log G vs d_{NN} characteristics with error bars for $(HBC)_n$ (n = 1, 2, 3) at $V_D = -0.5$ V. The inset shows the β values obtained under different bias voltages ranging from -0.5 V to 0.5 V in steps of 0.1 V. (d) Calculated HOMO and LUMO of the HBC oligomers. The related molecular orbital diagrams for the HBC oligomers are shown in Figure S10. (e) Transmission path for the *p*-HOMOs of the HBC (monomer) devices. (f) $E_{p-HOMO} - E_{Fermi}$ vs d_{NN} characteristics of the Au– $(HBC)_n$ –Au (red) and graphene– $(HBC)_n$ –graphene (black) junctions. $E_{p-HOMO} - E_{Fermi}$ represents the energy offset of *p*-HOMO, relative to the Fermi level of the electrodes under the zero bias voltage.

0.046 Å⁻¹ (Figure 1d and Table S2). Their ultralow β values may arise from their robust conjugations, enhancing the charge transport and minimal molecular gap variations over the molecular length. The excellent chemical stability and self-assembly capability of HBC,³⁸ along with its thermal stability consistent with porphyrin,³⁹ make it an excellent choice for devices requiring high stability and complex electronic functions, particularly in the fields of nanotechnology and molecular recognition.

Although numerous studies have examined the critical factors affecting molecular conductance, including molecular conjugation, molecular energy levels, and molecule-electrode coupling, a lack of consensus remains with regard to the determining mechanism of conductance attenuation. This has prevented the establishment of an effective strategy to regulate molecular conductance attenuation. Although the attenuation coefficients for molecular conductance obtained from STM-BJ measurements are generally accepted,⁵³ technical limitations of STM-BJ measurements of long molecular wires, such as short platform lengths, have long existed. To avoid these problems, various other techniques are proposed, such as conducting probe atomic force microscopy (C-AFM)³ and GMG-SMJ techniques. Here, we introduce graphene electrodes to investigate the effect of distinct HBC-electrode interactions on tuning the molecular conductance attenuation. The static GMG-SMJ technique is used to construct a graphene- $(HBC)_n$ -graphene single-molecule junction,⁵⁴ which show good stability attributed to the covalent graphene-HBC contacts (Figure 2a and Figures S16-S18). Graphene electrodes provide efficient charge transport through the HBC oligomers with substantially increased conductance (see five successfully connected SMJs in Figure S19). When the drain voltage $V_{\rm D} = -0.5$ V, the average currents measured

for the monomer, the dimer, and the trimer are approximately -182.67, -33.46, and -3.89 nA (Figure 2b), respectively. By fitting the log *G* values with $d_{\rm NN}$ linearly, a conductance attenuation coefficient β of 0.138 ± 0.007 Å⁻¹ is obtained (Figure 2c) that is approximately three times larger than the β value obtained for Au-based junctions. Moreover, β remains unaffected by the applied $V_{\rm D}$ (see the inset of Figure 2c), ruling out the possibility of numerical errors.

To unravel the mechanism underlying the significant impact of electrode materials on β , we computed the molecular orbitals and transmission spectra of the HBC oligomers. Figure 2d illustrates that the HOMO-LUMO gaps of HBCs decline as the oligomers' elongation increases. The HOMOs of HBCs align more closely to the Fermi levels (equivalent to negative work functions) of both Au and graphene electrodes than the LUMOs (Figure S20). Consequently, the charge transport is likely to be governed primarily by HOMO within narrow bias windows. Despite the fact that the energy gap of the HBC oligomers decreases with increasing HBC units (Figure 2d), both calculated and experimental conductance values of the HBC oligomers diminish dramatically with increasing units (Figure S20). The calculated transmission spectra provide a further affirmation of this HOMO-dominant transport behavior for the $(HBC)_n$ junctions when both Au and graphene are used as electrode materials, with higher conductance again being indicated in the graphene-based junctions. To clarify the reasons for this variance in conductance with respect to the different electrodes, transmission pathways at the projected-HOMO level (E_{p-HOMO}) are analyzed (Figure 2e), revealing stronger graphene-HBC coupling and enhanced electron distribution throughout the graphene $-(HBC)_n$ -graphene junctions compared with the Au electrode-based cases (Figure S21). These findings arise from



Figure 3. Regulation of conductance attenuation in the graphene– $(HBC)_n$ –graphene single-molecule field-effect devices. (a) Schematic illustration of the single-molecule field-effect device structure with ionic liquid gating. (b) Schematic energy diagrams of the alignment of the molecular orbitals relative to the graphene electrode's Fermi level under different applied gate voltages. (c–e) Two-dimensional visualizations of dI/dV plotted versus V_G and V_D for the HBC monomer, dimer, and trimer, respectively. The gray dashed lines represent the auxiliary markers of the conductance diamond edges. (f) Log G versus d_{NN} characteristics of $(HBC)_n$ (where n = 1, 2, 3) over the range from $-2 V \le V_G \le 0 V$ in steps of 0.5 V; $V_D = -0.5 V$. (g) β vs V_G characteristics with error bars. (h) β vs $E_{p-HOMO} - E_{Fermi}$ from the HBC characteristics with error bars, where $E_{p-HOMO} - E_{Fermi}$ represents the average $E_{p-HOMO} - E_{Fermi}$ value from the monomer, dimer, and trimer, bars indicate the standard error.

the π -electron nature of HBC oligomers, which resembles that of graphene. The energy offset of the *p*-HOMO relative to the Fermi level of electrodes at zero bias voltage (E_{p-HOMO} – E_{Fermi}) varies more significantly with the number of HBC units in the graphene-based junctions than in the gold-based junctions, with the former slope $((E_{p-HOMO} - E_{Fermi})/d_{NN})$ being \sim 2.6 times greater than that in the latter case (Figure 2f and Figure S20). This behavior correlates perfectly with the changes observed in β across the electrodes and is by no means a coincidence. In fact, previous theoretical studies have highlighted how the energy offsets of molecular orbitals relative to the electrode's Fermi level can influence the length dependence of the molecular conductance,^{20,55,56} although there is a lack of experimental support of these results to date. Our data confirm this strong correlation between the energy offsets $(E_{p-HOMO} - E_{Fermi})$ and β .

Because a strong correlation exists between the energy offsets ($E_{p-\text{HOMO}} - E_{\text{Fermi}}$) and β , we propose to control both the molecular conductance and β by manipulating the energy offsets using a gate electric field. To this end, a single-molecule field-effect device is constructed (Figure 3a and Figure S22) by introducing a structure with an ionic liquid gate. As an ionic liquid, *N*,*N*-diethyl-*N*-(2-methoxyethyl)-*N*-methylammonium bis(trifluoromethylsulfonyl)imide (DEME-TFSI) is selected, because of its similarly sized anions and cations, wide electrochemical redox window, and high stability, and it can

generate a strong gate electrostatic field of ~10 MV/cm.^{57,58} When a negative gate voltage $(V_{\rm G})$ is applied, the cations accumulate toward the gate, while the anions gather near the molecules and the graphene electrodes, leading to a downshift in the Fermi level and an upshift in the molecular orbitals (Figure 3b). The typical two-dimensional (2D) visualization spectra for dI/dV vs V_D and V_G for the graphene-(HBC)_ngraphene single-molecule field-effect devices (Figures 3c-e) indicate nonresonant transport in the green low-conductance region and resonant transport based on the molecular HOMOs in the orange high-conductance region. When $V_{\rm D}$ remains constant as $V_{\rm G}$ changes from 0 V to -2 V, the absolute value of $I_{\rm D}$ then increases gradually (Figures S23 and S24). These characteristics demonstrate effective gate regulation in singlemolecule devices. During this regulation process, the leakage current (Figure S25) remains negligible. Simultaneously, theoretical simulations also illustrate the effective control applied by the gate voltage to the molecular conductance (Figure S26). In addition, the on/off ratios of the (HBC), junctions increased with increasing n (Figure S27), indicating that the HBC trimer offers the best gate control efficiency.

To investigate the gate dependence of β , the variations in log G, with respect to $d_{\rm NN}$, for the HBC oligomers under different gate voltages at $V_{\rm D} = -0.5$ V are shown in Figure 3f. As $V_{\rm G}$ increases gradually from 0 V to -1.5 V, a continuous and significant reduction in β is observed (Figure 3g), where β

reaches a minimum of ~0.058, representing a reduction of ~50%, when compared with the β value at $V_{\rm G}$ = 0 V (~0.116). However, when $V_{\rm G}$ increases further to -2 V, β begins to increase to ~0.065. When molecular energy levels are adjusted very close to the Fermi level, these orbitals become partially or largely occupied, leading to near saturation of charge transport via the molecular levels and thus potentially increasing the attenuation coefficient. Concurrently, it is noted that the variation of β with $V_{\rm G}$ is highly consistent with the changes in the average $E_{p-HOMO} - E_{Fermi}$ value of the HBC oligomers with $V_{\rm G}$ (Figure 3h), which stems from the linear variation of the molecular $E_{p-HOMO} - E_{Fermi}$ characteristics with $V_{\rm G}$ (Figure S28). Our experiments demonstrate effective modulation of β for the first time by altering $E_{p-HOMO} - E_{Fermi}$ via the gate voltage, leading to ultralow conductance atttenuation characteristics.

In summary, we have successfully synthesized a series of HBC oligomers and investigated their conductance attenuation characteristics by using both dynamic and static singlemolecule junction techniques. Both methods consistently show ultralow attenuation coefficients that are comparable to those of porphyrin wires. We also confirm the strong correlation between the attenuation coefficients and the energy offsets of molecular orbital levels with respect to the electrode's Fermi level. Inspired by this correlation, we then demonstrate an effective strategy to regulate conductance attenuation by introducing an ionic liquid gate. This study not only shows the efficient and reliable long-range transport in highly conjugated molecular devices but also presents a novel approach to modulate the molecular conductance attenuation and realize ultralow attenuation levels, which is essential for practical applications of high-performance and functionalized molecular devices.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.4c01521.

Synthesis and characterization of hexabenzocoronene compound, theoretical calculations, STM-BJ and GMG-SMJ measurements, supporting figures, and supporting tables (PDF)

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Notes

The authors declare no competing financial interest.

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