Tracking Noncovalent Interactions of π , π -Hole, and Ion in Molecular **Complexes at the Single-Molecule Level**

Hongyu Ju,[⊥] Boyu Wang,[⊥] Mengmeng Li,[⊥] Jie Hao, Wei Si, Shuxin Song, Kunrong Mei, Andrew C.-H. Sue,* Jinying Wang,* Chuancheng Jia,* and Xuefeng Guo*

Cite This: J. Am. Chem. Soc. 2024, 146, 25290-25298 Read Online ACCESS Metrics & More Article Recommendations s Supporting Information **ABSTRACT:** Noncovalent interactions involving aromatic rings, such as π stacking and π -ion interactions, play an essential role in molecular

recognition, assembly, catalysis, and electronics. However, the inherently weak and complex nature of these interactions has made it challenging to study them experimentally, especially with regard to elucidating their properties in solution. Herein, the noncovalent interactions between π and π hole, π and cation, and π -hole and anion in molecular complexes in nonpolar solution are investigated in situ through single-molecule electrical measurements in combination with theoretical calculations. Specifically, phenyl and pentafluorobenzyl groups serve as π and π -hole sites, respectively, while Li⁺ and Cl⁻ are employed as the cation and anion. Our findings reveal that, in comparison with homogeneous $\pi \cdots \pi$ interactions, heterogeneous $\pi \cdots \pi$ -hole and π --cation interactions exhibit greater binding energies, resulting in a



longer binding lifetime of the molecular junctions. Meanwhile, π ...Li⁺ and π -hole...Cl⁻ interactions present significantly distinct binding characteristics, with the former being stronger but more flexible than the latter. Furthermore, by changing the molecular components, similar conductivity can be achieved in both molecular dimers or sandwich complexes. These results provide new insights into π - and π -hole-involved noncovalent interactions, offering novel strategies for precise manipulation of molecular assembly, recognition, and molecular device.

INTRODUCTION

Noncovalent interactions involving aromatic rings are crucial in many chemical and biological processes due to their ubiquity, such as in molecular recognition,¹⁻³ supramolecular assembly,⁴⁻⁶ and catalysis.⁷⁻⁹ Another prominent characteristic of aromatic rings is the tunability of the electrostatic surface potential (ESP). Specifically, for the most prevalent benzene molecule, its conjugated π electrons and negative quadrupole moment have been extensively investigated to elucidate the noncovalent interactions, such as for $\pi \cdots \pi$ stacking and $\pi \cdots$ cation interactions.¹⁰⁻¹³ By replacement of the hydrogen atoms with electron-withdrawing substituents or the C-H units with heteroatoms, the ESP and quadrupole moment of the aromatic rings change from negative to positive. The positive electrostatic potential region in a molecular entity, perpendicular to the molecular framework, is named as π hole.^{14–16} In contrast to the π system, π -hole presents widespread attractive interactions with electrostatically negative sites, including anions, lone electron pairs, and π electrons.^{8,16,17} The nature of these π and π -hole-involved noncovalent interactions is mainly determined by the dispersion interactions and electrostatic interactions.¹⁸

Generally, the essential structural and thermodynamic insights into π or π -hole-involved interactions are mainly

obtained through X-ray diffraction analyses in the solid state and nuclear magnetic resonance (NMR) spectroscopy in solution, respectively.¹⁹⁻²³ In some cases, mass spectrometry and UV/vis spectroscopy have also been employed to analyze these interactions.²⁴ Despite significant efforts, it remains challenging to obtain real-time and in situ experimental proofs of noncovalent interactions in solution, the natural environment in which most noncovalent interactions come into play.²⁰ In comparison with these macroscopic studies, single-molecule measurements can be easily compatible with diverse microenvironments,²⁵⁻²⁷ thereby allowing for the revelation of the intrinsic molecular characteristics and subtle variations.^{28,29} By means of single-molecule techniques, the visualization and manipulation of elusive intra- and intermolecular noncovalent interactions, such as hydrogen bond, $^{30,31} \sigma \cdots \sigma$ stacking, $^{32} \pi \cdots \pi$ stacking,^{26,33} and guest...host interactions,^{34,35} have been achieved.^{36–38} Particularly, the scanning tunneling microscope

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Figure 1. Schematic diagrams of π - and π -hole-involved noncovalent interactions. (a) ESP of benzene with a nucleophilic π center (top) and hexafluorobenzene with an electrophilic π -hole center (bottom). ESP scale is ± 0.02 hartree/e. (b) Schematic diagrams of π ··· π stacking and π -hole··· π -hole stacking in homogeneous dimer (top), π - and π -hole-involved sandwich complexes with molecules and ions (bottom). R is the linker group for STM-BJ measurement.

break junction (STM–BJ) technique enables not only the efficient investigation of thermodynamically stable states but also the monitoring of the structural evolution under the mechanical force.³⁸ This technique has been utilized in the study of charge transport mechanisms, binding strengths, and dynamic behaviors of noncovalent interactions.^{39–41}

Benzene and hexafluorobenzene (HFB), with a nucleophilic π center and electrophilic π -hole center as illustrated in the ESP images respectively, are considered the most classical model molecules to investigate π and π -hole-involved interactions in both experimental and theoretical methods (Figure 1a).¹⁸ Herein, using monothiol-terminated benzyl mercaptan and pentafluorobenzyl mercaptan,³² along with benzene and HFB, lithium cation (Li⁺) and chloride anion (Cl⁻), $\pi \cdots \pi$ and π -hole $\cdots \pi$ -hole interactions in homogeneous dimers, as well as $\pi \cdots \pi$ -hole, $\pi \cdots$ cation, and π -hole \cdots anion interactions in sandwich complexes are investigated in solution at the single-molecule level via STM-BJ technique (Figure 1b). This design ensures a systematic determination of π and π -hole-involved interactions while avoiding potential confounding factors, such as coordination interactions and hydrogen bonds from heteroatoms and CH---anion interactions.^{20,42} Monatomic monovalent ions also provide an unambiguous model for molecular complexes due to their simplicity.²¹ Furthermore, the binding flexibility of π ···cation and π -hole---anion interactions is evaluated at the singlemolecular level through real-time measurements.

RESULTS AND DISCUSSION

Previous studies have explored diverse $\pi \cdots \pi$ stacking dimers resulting from the same component via STM–BJs in solution,^{32,33} indicating that the STM–BJ technique enables the exploration of other π -involved noncovalent interactions. Herein, we perform single-molecule electrical measurements in nonpolar dodecane solution containing the target molecules at a concentration of 0.1 mM at room temperature. Initially, only benzyl mercaptan is introduced in measurements to form a $\pi \cdots \pi$ dimer (D_H, Figure 2a), serving as a baseline to compare $\pi \cdots \pi$ interactions against other noncovalent interactions in subsequent measurements. Typical conductance-displacement individual traces obtained under 0.1 V bias are presented as black lines in Figures 2b and S2, showing a single conductance state arising from D_H. The two-dimensional (2D) conductance-displacement histograms consisting of thousands of traces are plotted in Figure 2b and confirm the conductance state of D_H by presenting a clear conductance cloud. The onedimensional (1D) histograms provide further statistical conductance analysis, revealing the most probable conductance value of $10^{-3.50}$ G_0 ($2e^2/h$, where e is the charge of an electron and h is Planck's constant) through Gaussian fitting (see the inset in Figure 2b). Although four intermolecular geometries of stacked benzene dimers have been theoretically proposed,⁹ the parallel displaced geometry should be responsible for our observed conductance state according to previous reports³² due to the higher stability and conductivity. Furthermore, the relatively lower conductance value also excludes the possibility of direct π ...Au contact for the observed results.³²

In contrast to benzene, HFB possesses an electrophilic π hole center with a positive quadrupole moment of 9.50 B.^{12,43} Due to the attractive interactions between benzene and HFB, the displaced sandwich complex and the chain structure with an alternating arrangement have been reported.44-46 Furthermore, both experimental studies and theoretical calculations (Figure S3) have proved that the phenyl ring center of benzyl mercaptan remains electrostatically negative.¹⁵ These facts indicate that we can explore $\pi \cdots \pi$ -hole interactions based on benzyl mercaptan and HFB by forming a π ···HFB··· π (T_{H-F}) sandwich complex (Figure 2d). When HFB (~0.1 M) is added into the benzyl mercaptan dodecane solution in conductance measurements, the typical individual traces (black lines in Figures 2e and S4) clearly show a new conductance plateau, which is different from that of D_H. The distinct conductance cloud in 2D conductance-displacement histograms (Figure 2e) and the conductance peak at $10^{-4.10}$ G₀ in



Figure 2. Electrical measurements of π -involved noncovalent interactions. (a, d, g) Schematic diagrams of D_H (a), T_{H-F} (d), and T_{H-Li}^+ (g) complexes. (b, e, h) 2D conductance-displacement histograms of D_H (b), T_{H-F} (e), and T_{H-Li}^+ (h) complexes. Typical single conductance-displacement traces are marked with black lines. Insets are the corresponding 1D logarithmic conductance histograms with Gaussian fittings. (c, f, i) 2D I-V histograms of D_H (c), T_{H-F} (f), and T_{H-Li}^+ (i) complexes. The yellow line represents the most representative current value from the Gaussian fitting. The colored bars represent the number of counts.

1D histograms (see the inset in Figure 2e) further indicate the formation of the new conductance state. Considering the introduction of HFB has a negligible effect on the properties of dodecane solution, such as viscosity and polarity, and HFB has a weaker binding ability to Au electrodes, T_{H-F} should be responsible for the new conductance state.^{47,48} This hypothesis is further supported by theoretical calculations below, which also explain the disappearance of the D_H state due to stronger $\pi \cdots \pi$ -hole interactions than $\pi \cdots \pi$ interactions.

Besides $\pi \cdots \pi$ and $\pi \cdots \pi$ -hole interactions between neutral molecules, $\pi \cdots$ cation interactions are of great importance in many systems.^{8,49} It has been reported that $\pi \cdots$ cation interactions can stabilize sandwich complexes and chain assemblies in an alternately stacking manner.^{50,51} Herein, the electrical and mechanical properties of $\pi \cdots$ cation interactions are investigated. Among various metal ions, alkali metal cations are considered because of the σ -type outer orbital to avoid the

interferences from $d\cdots\pi$ binding and binding directionality variation,⁵² and Li⁺ is finally chosen due to the small size and the high binding energy.⁵³ When Li⁺ (saturated lithium tetrafluoroborate solution) is introduced, a $\pi\cdots$ Li⁺ $\cdots\pi$ (T_{H-Li}⁺) sandwich complex is expected to be formed (Figure 2g), resulting in a new conductance state with the conductance peak at 10^{-3.80} G₀ (Figures 2h and S5). Furthermore, it is found that the introduction of HFB or Li⁺ has a negligible effect on the single-molecule conductance of 1,4-benzene dimethanethiol (Figure S6). Therefore, we can conclude that the distinct electrical characteristics result from $\pi\cdots\pi$ -hole or $\pi\cdots$ cation interaction-mediated sandwich complexes in the aforementioned measurements.

To gain further insight into the charge transport mechanism through π -involved noncovalent interactions, the current– voltage (I-V) characteristics and transition voltage spectrum (TVS) analyses are performed, where the transition voltage

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Figure 3. Theoretical calculations and lifetime measurements of π -involved noncovalent interactions. (a) Frontier molecular orbitals of D_{H} , $T_{H-F'}$ and T_{H-Li}^+ complexes (from left to right). (b) Transmission curves of D_{H} , $T_{H-F'}$ and T_{H-Li}^+ complexes. (c) Energy decomposition analyses of D_{H} , $T_{H-F'}$ and T_{H-Li}^+ complexes. (d-f) Lifetime measurements of D_{H} (d), $T_{H-F'}$ (e), and T_{H-Li}^+ (f) complexes under 0.2 V. Typical single conductance-junction lifetime traces are marked as gray lines. The color bar represents the number of counts.

 $(V_{\rm trans})$ is related to the energy difference between the closest molecular orbital and the Fermi level $(E_{\rm F})$ of the Au electrodes. The 2D I-V histograms of D_H, T_{H-F}, and T_{H-Li}⁺ are shown in Figures 2c,f,i and S7, and the I-V characteristics and the corresponding TVS of three noncovalent interactions present symmetrical features. An obvious $V_{\rm trans}$ at about ±0.6 V is observed for T_{H-Li}⁺. In contrast, no $V_{\rm trans}$ is observed within the voltage range of ±1.0 V for D_H and T_{H-F}. The difference in $V_{\rm trans}$ indicates that the effective barrier height for charge transport for T_{H-Li}⁺ is lower than that for D_H and T_{H-F}.

The charge transport pathways in molecular junctions, including through-bond or through-space, are closely related to the interface properties and have been regarded as the criterion for estimating noncovalent bindings in molecular junctions.⁵⁴ To further confirm the detection of desired noncovalent interactions in conductance and I-V measurements, the charge transport pathway is measured through flicker noise analysis, where the flicker noise power (PSD) is proportional to G^n . It is known that n = 1 indicates completely through-bond coupling, while n = 2 indicates completely through-space coupling.³⁶ As shown in Figure S8, the PSD scales as $G^{1.75}$, $G^{1.96}$, and $G^{1.85}$ for D_H, T_{H-F}, and T_{H-Li}⁺ junctions, respectively, indicating the charge transport is dominated by through-space coupling. These results support the hypotheses regarding the measurements of $\pi \cdots \pi$, $\pi \cdots \pi$ -hole, and $\pi \cdots$ cation interactions.

Theoretical calculations of D_H , T_{H-F} , and T_{H-Li}^+ have been performed to further understand the experimentally observed conductance states and noncovalent interactions. The frontier molecular orbitals of D_H , T_{H-F} , and T_{H-Li}^+ complexes support the through-space transport pathway (Figure 3a). The transmission spectra of the three junctions clearly show that the conductance magnitude near the Fermi level follows the order: $D_H > T_{H-Li}^+ > T_{H-F}$, aligning with the experimental results (Figure 3b). Furthermore, longer sandwich complexes composed of benzyl mercaptan and HFB are excluded based on theoretical analyses (Figure S9). The binding energies and energy decomposition of $D_{\text{H}},\,T_{\text{H}-\text{F}}$ and $T_{\text{H}-\text{Li}}{}^{+}$ complexes are also calculated, where the binding energy is defined as $E_{\rm b}$ = $E_{\text{complex}} \sum E_{\text{i}} = E_{\text{elec}} + E_{\text{ind}} + E_{\text{exch}} + E_{\text{disp}}$. As shown in Figure 3c, T_{H-Li}^{+} has the highest binding energy of -60.78 kcal mol⁻¹, which is mainly contributed by induction interactions. D_H has the smallest binding energy of -7.12 kcal mol⁻¹, primarily resulting from dispersion interactions. Meanwhile, the electrostatic interactions extracted from both T_{H-F} and $T_{H-Li}{}^{\!\!\!+}$ are larger than those from D_H under the action of quadrupolequadrupole and π -charge interactions. It is reported that π ... cation interactions are mainly attributed to the electrostatic and ion-induced polarization interactions, while the dispersion interactions generally play only a minor role.⁵³ Generally, the polarization contribution originates from the induced dipole in the π bond, while the reverse effect is negligible. Herein, the theoretical calculations are consistent with the previous reports.^{10,46,53,55}

Generally, noncovalent interactions tend to vary in different environments, and the binding stability is a significant factor for applications of noncovalent interactions. Precise manipulation of noncovalent interactions in subtle ways at the molecular level is a long pursuit. The STM–BJ technique offers various stimuli to affect the binding stability and lifetime of molecular junctions, such as local heating^{56,57} and strong electric fields.^{26,58} The bias responsiveness of binding lifetime for three π -involved noncovalent interactions in molecular junctions is investigated through conductance-time (G-t)



Figure 4. Characterizations of π -hole-involved noncovalent interactions. (a) Schematic diagrams of D_F , T_{F-H} , and T_{F-Cl}^- complexes (from left to right). (b) 1D logarithmic conductance histograms with Gaussian fittings of D_F , T_{F-H} , and T_{F-Cl}^- complexes. (c) I-V curves of D_F , T_{F-H} , and T_{F-Cl}^- complexes, which are from Gaussian fittings in 2D I-V histograms. (d) Frontier molecular orbitals of D_F , T_{F-H} , and T_{F-Cl}^- complexes (from left to right). The HOMO–LUMO gaps are marked. (e) Transmission curves of D_F , T_{F-H} , and T_{F-Cl}^- complexes. (f) Calculated total binding energy and energy decomposition analyses of D_F , T_{F-H} , and T_{F-Cl}^- bindings. (g) Schematic diagram of the binding flexibility in an ion-mediated sandwich complex. The complex conformation changes around its most stable conformation. (h) 1D logarithmic conductance histograms with Gaussian fittings of T_{H-Li}^+ and T_{F-Cl}^- in G-t measurements. (i) Scanning energy profile by relative separation of anchor groups.

measurements using the hovering mode (Figures S10-S12). A longer lifetime of conductance state reflects a stronger noncovalent binding. Because the lifetime for three π -involved junctions at 0.1 V bias is so long that it exceeds the measuring time of the experimental procedure, it indicates that all of the bindings are robust. However, three junctions present significantly different bias responsiveness with increasing bias. The lifetime of $D_{\rm H}$ and $T_{\rm H-F}$ is significantly reduced at 0.3 V bias, while the lifetime of T_{H-Li}^{+} only presents minor variation. We measure the lifetimes under 0.2 V bias to depict the differences between three interactions (Figure 3d-f). The conductance state of D_H possessing the weakest $\pi \cdots \pi$ interactions has the shortest lifetime, while $T_{\rm H-F}$ with moderate $\pi \cdots \pi$ -hole interactions shows a slightly increased lifetime for the corresponding conductance state, and the conductance state of T_{H-Li}^{+} has the longest lifetime due to the

strongest $\pi \cdots \pi$ -cation interactions. This conclusion is also consistent with the theoretical analyses of binding energy mentioned above. Through in situ G-t measurements, the binding energy levels of three types of π -involved noncovalent interactions are directly evaluated at the single-molecule level.

The above analyses focus on π -involved noncovalent interactions, including $\pi \cdots \pi$, $\pi \cdots \pi$ -hole, and $\pi \cdots \text{Li}^+$ interactions. For comparison, we further investigate π -hole-involved interactions. Herein, pentafluorobenzyl mercaptan (FBM), which has a positive π -hole region on the phenyl ring center (see the ESP in Figure S13), is selected as the π -hole site, while benzene serves as the interacting π site. Among halide ions, Cl⁻ is used to investigate π -hole…anion interactions, as it avoids possible nucleophilic attack on the carbon atoms like F⁻ and possesses higher binding energy compared with Br^{-.59,60} Similar to π -involved dimer and sandwich complexes, π - hole... π -hole, π -hole... π -hole, and π -hole... π -hole complexes are constructed and measured using the STM-BJ technique (Figure 4a). When only FBM is added in measurements, an obvious conductance plateau at $10^{-3.55}$ G₀ is obtained (Figure S14), which is attributed to the π -hole… π hole dimer (D_F) .⁴⁵ When ~0.1 M benzene is added to the measurements, a new conductance state attributed to the π hole... π ... π -hole (T_{F-H}) sandwich complex is observed at $10^{-4.10}$ G₀ (Figure S15). When Cl⁻ (saturated tetrabutylammonium chloride solution) is introduced into the FBM solution, another conductance state at $10^{-4.45}$ G₀ is obtained (Figure S16). The π -hole…Cl⁻… π -hole (T_{F-Cl}⁻) sandwich complex is expected to be responsible for the conductance state, according to previous studies.^{53,61} The 1D conductance histograms of D_F , T_{F-H} , and T_{F-Cl} complexes are presented to provide a clear conductance comparison through three noncovalent interactions (Figure 4b). The I-V curves are presented in Figure 4c, and the corresponding 2D I-Vhistograms and TVS are shown in Figure S17. Similarly, no V_{trans} is observed within the voltage range of ±1.0 V for D_F and T_{F-H} , while V_{trans} at about ±0.7 V is observed for T_{F-Cl} .

Interestingly, D_H and D_F present a very similar conductance value, although the fluorine substitution significantly changes the properties of the phenyl ring. Furthermore, T_{F-H} and T_{H-F} also unexpectedly present identical conductance values within the error of the measurements. The conductivity similarity for different dimers or sandwich complexes definitely shows that noncovalent interactions-bonded molecular complexes provide a general and convenient strategy to increase the structural diversity of molecular devices by changing molecular components.

Theoretical calculations of $D_{F\prime}$ $T_{F-H\prime}$ and T_{F-Cl}^{-} molecular complexes and junctions have been performed to provide a deeper understanding. Although the molecular energy gap of T_{F-CI} is much smaller than those of D_F and T_{F-H} (Figure 4d), the calculated conductance near the Fermi level for three molecular junctions follows the order: $T_{F-Cl}^{-} < T_{F-H} < D_{F}$ (Figure 4e), consistent with the experimental results. The energy decomposition analyses (Figure 4f) show that D_F has the smallest binding energy of -8.39 kcal mol⁻¹, and T_{F-Cl} has the highest binding energy of -34.32 kcal mol⁻¹. The important features of the six π - and π -hole-involved complexes are summarized in Table S1. Dispersion interactions are mainly responsible for D_{F} and $T_{\text{F}-\text{H}}$ while $T_{\text{F}-\text{Cl}}^{-}$ is mainly attributed to electrostatic interactions. Dispersion and induction interactions contribute almost equally to T_{F-Cl} . Similar to π -involved interactions, the electrostatic interactions in T_{F-H} and T_{F-Cl}^{-} are larger than those in D_F , reflecting the important role of positive quadrupole in complexes.^{53,62,63} It is reported that the polarization effect is more obvious in π ---cation interactions than that in π -hole---anion interactions,⁵³ which is consistent with the calculations of T_{H-Li}^{+} and T_{F-Cl}^{-} . The bias responsiveness of the binding lifetime for three π -hole-involved junctions is further investigated through G-t measurements (Figures S18-S20). All three bindings are robust with long lifetimes under 0.1 V bias, while the lifetimes for all of the bindings are significantly reduced to be indistinguishable under 0.3 V bias. Flicker noise analyses show that through-space coupling dominates charge transport in D_F and T_{F-H}, while through-bond coupling becomes more obvious in T_{F-Cl} (Figure S21).⁵⁴

One significant feature of noncovalent interactions is their dynamic behavior and flexibility to adapt to variations (Figure

4g), which endows them with abundant stimuli-responsiveness and unique advantages.⁶⁴ Herein, the dynamic behaviors of π ... cation and π -hole---anion interactions are analyzed through in situ G-t measurements (Figure 4h), where the full width at half-maximum (FWHM) obtained by Gaussian fitting for the conductance peak is used to evaluate the dynamic structural fluctuations. A smaller FWHM indicates a more rigid noncovalent binding. The FWHM of conductance peak for T_{H-Li}^{+} junction is 1.4 log(G/G₀), whereas a much smaller FWHM $(0.78 \log(G/G_0))$ is obtained for T_{F-Cl} junction (Figure 4h), indicating a more flexible binding feature of π ... cation interactions compared to π -hole---anion interactions. The variation of calculated binding energies of T_{H-Li}^{+} and $\mathrm{T_{F-Cl}}^-$ as a function of S–S distance also shows that $\mathrm{T_{H-Li}}^+$ has a shallower potential energy surface than $T_{F-\text{Cl}}^{-}$ (Figure 4i), which is consistent with the FWHM results. As indicated by binding energy calculations, T_{H-Li}^{+} has a larger binding energy than T_{F-Cl}-. Interestingly, the larger binding energy does not correspond to the smaller dynamic structural fluctuations in π ···cation and π -hole···anion interactions-bonded sandwich complexes. The different contributions of induction and electrostatic terms to π ---cation and π -hole---anion interactions may result in their different dynamic behaviors. Our results not only confirm the previously proposed construction of sandwich molecular complexes through $\pi \cdots \pi$ -hole and ion $\cdots \pi/\pi$ -hole interactions at the single-molecule level but also demonstrate the potentially high voltage tolerance of π …Li⁺ interactions. In addition, voltage-, force-, and time-dependent molecule---ion interactions underlie many biological and chemical processes, 65,66 and the distinct characteristics of π …Li⁺ and π hole…Cl⁻ interactions may provide valuable insights into these processes.

CONCLUSIONS

In conclusion, distinct noncovalent interactions based on aromatic rings, including $\pi \cdots \pi$ -hole, $\pi \cdots$ cation, and π -hole... anion, in molecular sandwich complexes in nonpolar solution are investigated using the STM-BJ technique. The bias responsiveness of the binding lifetimes of these noncovalent interactions is measured in situ, and consequently, the energy levels are directly evaluated at the single-molecule level. In comparison with $\pi \cdots \pi$ interactions, $\pi \cdots \pi$ -hole and $\pi \cdots$ cation interactions are much stronger, resulting in a longer binding lifetime under higher biases. Real-time in situ dynamic analyses show that the π ---cation complex has stronger noncovalent interactions, but the π -hole---anion complex presents smaller binding flexibility. Furthermore, $\pi \cdots \pi$ and π -hole $\cdots \pi$ -hole dimers present similar conductances, as do $\pi \cdots \pi$ -hole $\cdots \pi$ and π -hole $\cdots \pi \cdots \pi$ -hole sandwich complexes. Our findings provide novel insights into the characterization and regulation of noncovalent interactions involving π , π -hole, and ion and hold great promise for applications of noncovalent interactions in molecule and ion recognition, smart material design, and molecular devices because of the feasible molecular strategy.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c09504.

Molecular synthesis, experimental methods, theoretical calculations, supporting results and figures including dynamic break junction measurements, G-t measure

ments, I-V/G-V measurements, and flicker noise analyses (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Andrew C.-H. Sue College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, P. R. China; orcid.org/0000-0001-9557-2658; Email: andrewsue@xmu.edu.cn
- Jinying Wang Center of Single-Molecule Sciences, Institute of Modern Optics, Frontiers Science Center for New Organic Matter, Tianjin Key Laboratory of Microscale Optical Information Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350, P. R. China; Email: wangjynk@ nankai.edu.cn
- Chuancheng Jia Center of Single-Molecule Sciences, Institute of Modern Optics, Frontiers Science Center for New Organic Matter, Tianjin Key Laboratory of Microscale Optical Information Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350, P. R. China; Email: jiacc@nankai.edu.cn
- Xuefeng Guo Center of Single-Molecule Sciences, Institute of Modern Optics, Frontiers Science Center for New Organic Matter, Tianjin Key Laboratory of Microscale Optical Information Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350, P. R. China; Beijing National Laboratory for Molecular Sciences, National Biomedical Imaging Center, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China; o orcid.org/0000-0001-5723-8528; Email: guoxf@pku.edu.cn

Authors

- Hongyu Ju Center of Single-Molecule Sciences, Institute of Modern Optics, Frontiers Science Center for New Organic Matter, Tianjin Key Laboratory of Microscale Optical Information Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350, P. R. China; School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, P. R. China; orcid.org/0009-0001-5689-0597
- Boyu Wang Center of Single-Molecule Sciences, Institute of Modern Optics, Frontiers Science Center for New Organic Matter, Tianjin Key Laboratory of Microscale Optical Information Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350, P. R. China
- Mengmeng Li Center of Single-Molecule Sciences, Institute of Modern Optics, Frontiers Science Center for New Organic Matter, Tianjin Key Laboratory of Microscale Optical Information Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350, P. R. China
- Jie Hao Center of Single-Molecule Sciences, Institute of Modern Optics, Frontiers Science Center for New Organic Matter, Tianjin Key Laboratory of Microscale Optical Information Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350, P. R. China

Wei Si – Center of Single-Molecule Sciences, Institute of Modern Optics, Frontiers Science Center for New Organic Matter, Tianjin Key Laboratory of Microscale Optical Information Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350, P. R. China

Shuxin Song – Center of Single-Molecule Sciences, Institute of Modern Optics, Frontiers Science Center for New Organic Matter, Tianjin Key Laboratory of Microscale Optical Information Science and Technology, College of Electronic Information and Optical Engineering, Nankai University, Tianjin 300350, P. R. China

Kunrong Mei – School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.4c09504

Author Contributions

[⊥]H.J., B.W., and M.L. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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