Final Technical Report

For DOE Award: DE-SC0021942

Project Title: Probing and Understanding the Spatial and Energy Distributions of Plasmonic Hot Carriers via Single-Molecule Quantum Transport

Under Principal Investigator: Kun Wang

Institution: Mississippi State University

Project Period: August 15, 2021 – August 15, 2023

Executive Summary

The generation of hot carriers in plasmonic nanostructures (PN) offers new transformative opportunities for a range of applications, including solar energy harvesting, photochemistry, and photodetection. To better understand such phenomena, this project aims to develop an experimental approach for studying and understanding hot carrier distributions in photoexcited plasmonic nanostructures. The proposed experimental approach, combining scanning probe-based single-molecule quantum transport measurements with plasmonic excitation methods, leverages the intrinsic quantum properties of nanoscopic single molecules as energy filters to selectively access hot carriers in a variety of plasmonic nanostructures. This report summarizes the key outcomes, impacts, and lessons learned in the first two years of the five-year project. The execution of this project is closed at Mississippi State University (MSU) due to the move of the principal investigator to University of Miami (UM). Over the project period from August 1, 2021 to August 15, 2023, important progress was made in achieving the project's goals, including the development of the scanning probe-based experimental platform, design and synthesis of the desired molecular candidates, and fabrication of plasmonic nanostructures. Insights from this research will offer unique opportunities for the development of technologies that will help transition the U.S. to a clean and sustainable society.

Accomplishments

The objective of this grant was to develop experimental method that leverages quantum transmission properties of single molecules toward detecting hot carriers generated in plasmonic nanostructures. In the first two years, significant progress has been made in Aims **1, 2, 3,** and **5** of the project. Key accomplishments are summarized below:

1. Aim 1&5: We completed the development and testing of scanning tunneling microscope break junction (STMBJ) setup for single-molecule quantum transport and thermoelectric

measurements and are integrating external optical excitation of plasmonic nanostructures into the STMBJ setup.

2. Aim 2: We have designed and synthesized various molecular materials, including open-shell donor-acceptor conjugated molecules and supramolecular materials, that demonstrate desired quantum transport properties for this project.
3. Aim 3: We have designed and fabricated large-area arrays of plasmonic nanoprisms on solid substrates as model plasmonic systems while simultaneously exploring the fabrication of other plasmonic systems.
4. Under the grant period, we have published 5 peer-reviewed journal articles in widely distributed scientific journals.
5. Our results have been presented in more than 5 conference or workshop talks and more than 8 departmental seminars, 3 outreach activities, and 2 special topic courses across Physics and Chemistry Departments at MSU.
6. Under the grant period, we have trained 3 graduate students (2 among underrepresented groups) and 2 undergraduate students at MSU.
7. We have initiated the development of nanofabrication and surface characterization capabilities at MSU.
8. Through this project, we have established more than 5 collaborations across the U.S., which will continue to have a positive long-term impact on this project.

Summary of Project Activities for the Grant Period

Development of Experimental Platform (Aim 1 & 5)

Aim 1 of the project focuses on developing an experimental platform for stable and repeatable single molecule transport measurements on the noble metal surface (eventually the PN surface). We developed and implemented a custom-built STM break junction (STMBJ) platform capable of stably trapping single molecules between STM tip and the metal substrate for charge transport measurements. We completed the instrumentation and performed testing and characterization of single-molecule transport, including electrical conductance and I-V measurements, on a variety of analyst molecular systems, including alkanethiol, open-shell donor-acceptor conjugated molecules, and supramolecules complexes, to verify the performance and functionality of the system. The developed STMBJ platform showed excellent stability and reliability for single-molecule quantum transport measurements. Specifically, for all molecules tested, we observed excellent junction stability (<1 angstrom drift for the period of 1s) and that the tip location can be mechanically controlled with angstrom-level precision, which is critical for subsequent measurements. The experimental setup and representative single-molecule conductance measurement results for different molecules are shown in Figure 1. Single-molecule junction stability was also tested with additional mechanical manipulation of the tip position (compression and elongation). The junction length agreed well with the molecular length, indicating a robust characterization of single-molecule transport. In addition, we have also integrated the thermoelectric transport capability to our STMBJ setup to enable the investigation of thermal effect associated with our junction system, a key feature required for Aim 5 of the project. The single-molecule thermoelectric measurements have also been tested on oligobenzene systems, which showed consistent and reproducible Seebeck coefficient consistent with previous reports. This platform has been extensively used to investigate several molecular systems designed for this project and the collected results have led to 2 manuscripts that are currently in preparation.

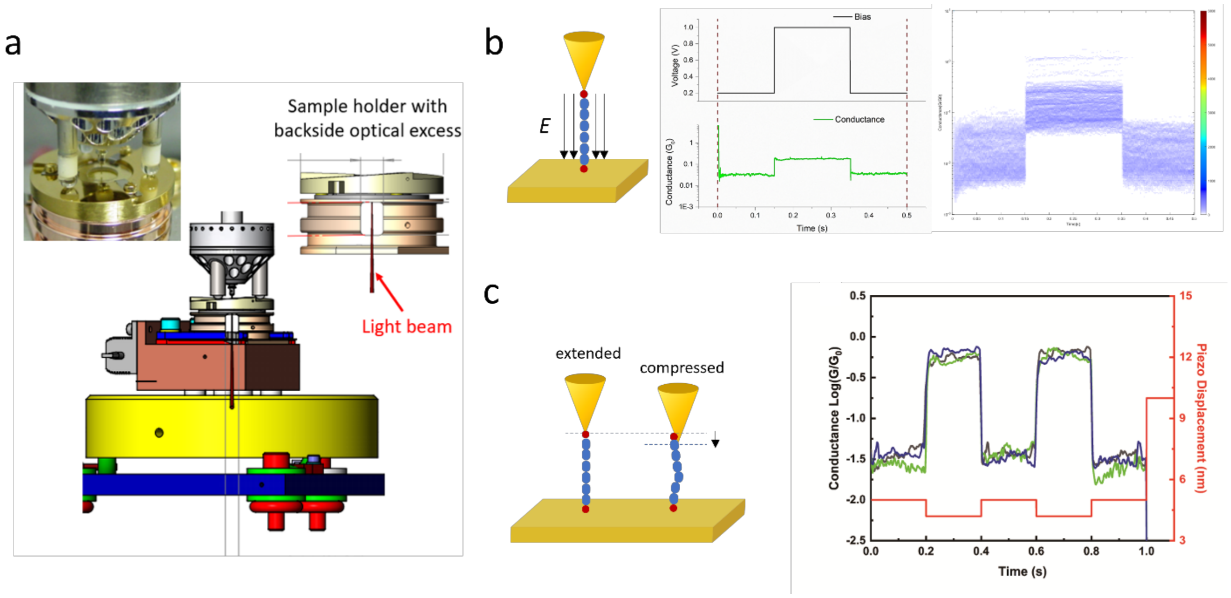

Figure 1. a) Schematic of the STMBJ setup. b) Schematic of bias modulation of single-molecule charge transport and representative experimental results showing excellent junction stability. c) Schematic of mechanical modulation of single-molecule charge transport and representative experimental data showing excellent junction stability under mechanical strain.

This home-built STMBJ platform is now ready for systematically studying single-molecule transport properties on plasmonic nanostructure surfaces and will serve as the main working horse for this project. We have also started the integration of optical illumination and imaging into the STMBJ for exciting the fabricated plasmonic nanostructures.

Design, Synthesis, and Characterization of Desired Molecular Materials (Aim 2)

The objective of the Aim 2 is to design, synthesize, and characterize molecular candidates with suitable transmission characteristics for accessing hot electrons and hot holes that are potentially distributed around the Fermi energy of noble metal PNs. To serve as an efficient energy filter for plasmonic hot carriers, molecules with a transmission resonance (i.e., molecular orbital) close to the Fermi level of the metal PNs are desired for this research. Ideally, at the single-molecule level, such molecular materials are expected to yield very efficient electron transmission or ultra-high conductance under low applied bias in a molecular junction. To minimize the impact of STM tip, relatively long molecules (with molecular length >5nm) that can facilitate efficient charge transport under low bias are the most sought-after for this project. Conventional high conductance molecular wires consist of π-conjugate building blocks. In these π-conjugated materials, charge transport at the single-molecule level is predominantly governed by coherent and off-resonance electron tunneling. However, despite the exploration of a vast chemical space, the intrinsic nature of off-resonance transport often limits the low-bias conductance of a single molecule to values that are a few orders of magnitude lower than the conductance quantum $1G_0$ even for very short molecules (e.g., 2nm long). Furthermore, in the tunneling regime, an increase of the molecular length results in an exponential conductance decay, making them insulating and not suitable for the proposed research. Therefore, the most desired molecular materials remain to be designed and developed.

To overcome this challenge, in collaboration with Prof. Jason Azoulay from GeorgiaTech, we successfully demonstrated the facile synthesis and characterization of robust, air-stable, and highly tunable molecular wires comprised of charge-neutral open-shell donor-acceptor molecules. Figure 2 displays the molecular structure of the open-shell macromolecular platform used in this study. Our molecular design includes the 4,4-dimethyl-4H-silolo[3,2-b:4,5-b']dithiophene donor which stabilizes the highest occupied molecular orbital (HOMO) and strong thiadiazoloquinoxaline acceptor whose lowest unoccupied molecular orbital (LUMO) promotes strong electronic correlations that enable a narrowing of the bandgap and quinoidal bonding patterns—features that form and stabilize unpaired spins within extended π-conjugated structures. The $-C_{16}H_{33}$ substituents on the donor control solubility and facilitate chain conformations with a high degree of electronic coherence enabling ultranarrow bandgaps and optimized bond-length alternation. This donor-acceptor combination results in a macromolecular structure with an orbital manifold in which valence a- and b-spins occupy singly occupied molecular orbitals (SOMOs) with a characteristic energy splitting between low and high-spin forms. We designed a synthetic approach to access end-functionalized variants compatible with STM-BJ measurements (Fig. 1a) to probe the evolution of electronic structure and conductance as a function of chain length (n). We utilized a microwave-mediated coupling methodology and copolymerization reaction to access designed molecules. Modification of the stoichiometry using a Carothers approach to control molecular weights (M_n) enabled rapid access to oligomers with M_n that span a wide range of molecular weight.

In this approach, the donor monomer in stoichiometric excess gives the degree of polymerization for a given fractional monomer conversion. This results in a macromolecular chain end-functionalized with the CPDT donor and reactive –$SnMe_3$ functionality. This was followed by *in-situ* end-group functionalization with (4-bromophenyl)(methyl)sulfane functionality known to bind to nano-structured gold STMBJ electrodes.

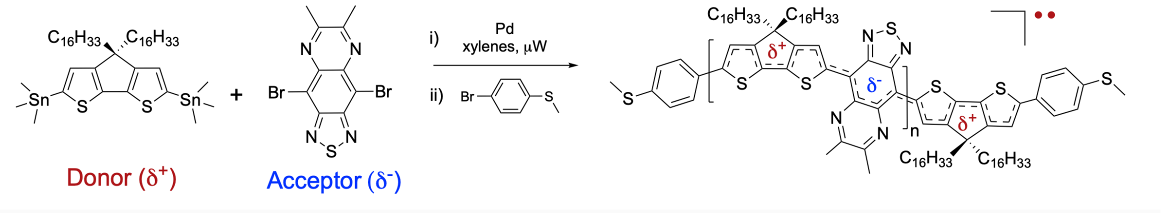

Figure 2. Synthetic strategy and chemical structure of open-shell donor acceptor molecules.

Through detailed single-molecule transport characterizations, we found that the designed open-shell donor-acceptor molecules exhibit remarkably high conductance of >$0.1G_0$ over distances longer than 20 nm (i.e., the entire macromolecular chain) and no discernable length-dependence. Key experimental results are shown in Figure 3. Noticeably, this molecular wire system is the most conductive single-molecule quantum wire at the tens of nanometer length scale, a length scale that has not been explored previously. The ultra-high conductance and extreme long-range transport exceed the best performing π-conjugated organic materials and contrast with conventional molecular systems where the intrinsic conductance decreases exponentially with molecular length. Based upon a homologous series of materials with increasing length, density functional calculations, and single-molecule transport measurements, the transport phenomena in this macromolecular platform are attributed to direct long-range resonant transport arising from the synergistic combination of extended π-conjugation, a correspondingly narrow HOMO-LUMO gap, and the open-shell electronic structure (i.e., diradicaloid character). These features synergistically enable good alignment of frontier molecular orbitals (FMOs) with the electrode Fermi energy (E_F) in the low-bias regime with a transmission resonance that does not shift or fade away with increasing molecular length, a long sought-after feature for molecular quantum wires. Such unique transport properties are ideal for probing plasmonic hot carriers as it allows one to decouple the potential plasmonic excitation on the STM tip by performing the transport measurements when the STM tip is placed relatively far (>5nm) from the PN surface. This helps to isolate the contribution of hot carriers generated on the PN substrate. Key to the proposed hot carrier studies is the understanding transmission function of the designed molecules. We performed systematic theoretical calculations and modeling based on density functional theory (DFT) and density functional tight binding (DFTB). As shown in Figure 4, our calculation revealed that the transmission resonances are located extremely close to the Fermi energy of metal substrate, which will afford direct access to hot carriers around the Fermi energy of PNs in subsequent studies.

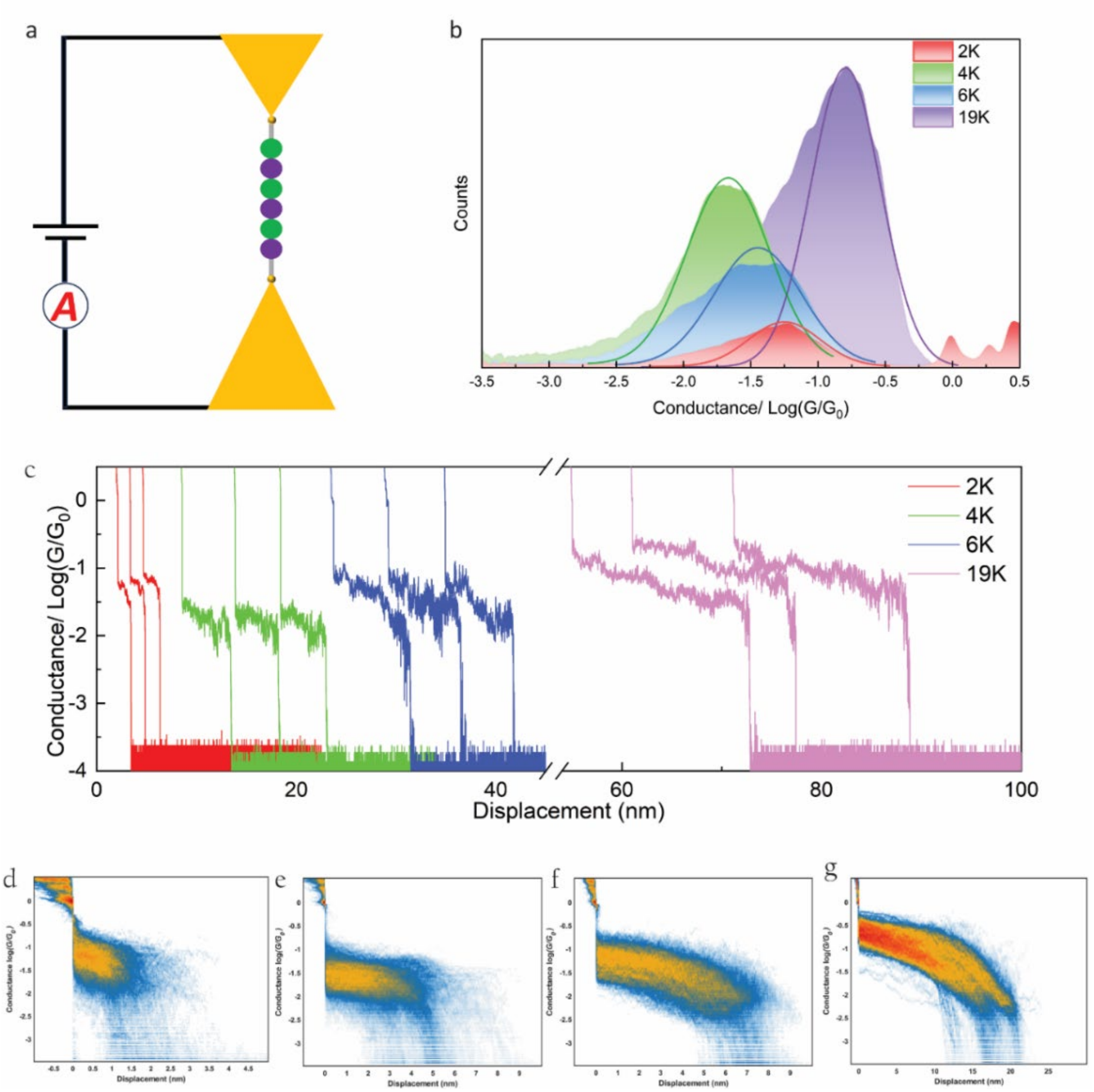

Figure 3. Conductance measurements of the single open-shell donor-acceptor molecular series. A) STM-BJ apparatus setup. b) One-dimensional conductance histograms of the single molecules with molecular weight of 2K 4K , 6K , and 19K in air. c) The representative conductance versus displacement traces of the single molecule series (2K, 4K, 6K, and 19K). All show molecular independent conductance features. d–g) Two-dimensional conductance histograms for the corresponding molecular series (2K, 4K, 6K, and 19K) with same data for 1D histograms shown in b.

The ability to further tune the transmission of the molecule is also critical. As shown in Figure 5, we further demonstrated that delicate mechanical perturbation (sub-nanometer compression) of the molecular conformation could enhance the molecular conductance by more than 50-fold. Specifically, the conductance can be further enhanced to $1\,G_0$ through external mechanical modulation, which represents the first observation of low-bias quasi-metallic transport in ultralong single-molecule wires. This is attributed to the fact that the diradical states at the two terminals of the molecular backbone are manipulated mechanically. Such ability to fine tune the transport properties under low junction bias will help us access hot carriers at different energy levels in the subsequent studies of this project. The manuscript of this work is currently in preparation and will lead to a publication soon.

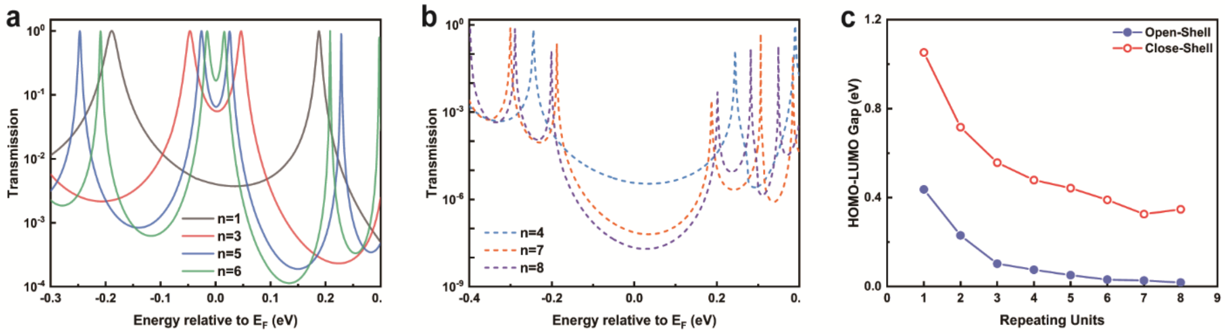

Figure 4. First-principal calculation results for the designed open-shell molecules with different number of repeating unit cells. Transmission function based on the DFTB calculations for (a) open-shell molecule with n = 1, 3, 5 and 6, and (b) closed-shell molecule with n = 4, 7 and 8. (c) Calculated HOMO-LUMO gap according to the DFTB calculations for both open-shell and closed-shell molecules with n = 1 to 8. Noticeably, our open-shell molecules yield transmission resonances very close to electrode Fermi energy and the HOMO-LUMO gap sharply narrows down with the increase of molecular length, in contrast to the behavior of the closed-shell control molecules.

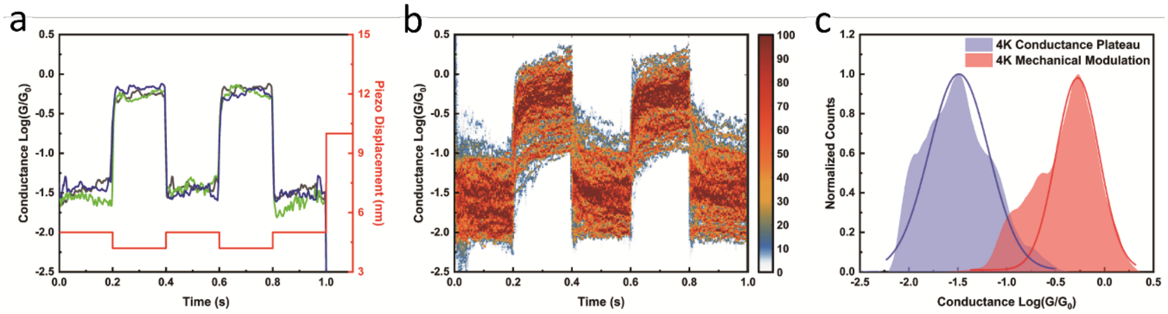

Figure 5. Mechanical modulation measurement on the single open-shell donor-acceptor molecules with a molecular weight of 4K (6 repeating units). a) Representative conductance vs time traces showing enhanced conductance at ~1G₀ upon mechanical compression. b) Two-dimensional conductance histogram of mechanically modulated single-molecule junctions. c) Conductance histogram for the compressed region (red) and stretched state (blue) of the conductance plateaus.

In parallel, we also explored other design and synthetic strategies for tuning the energy alignment of the molecular transmission resonance and noble metal, such as gold. Specifically, we explored the possibility of stably incorporate metal-center into aromatic molecules to enhance electron transmission and improve structural stability. Toward this direction, we designed and synthesized a series of carbolong complexes containing Os metal centers in the molecular backbone, possessing the unique Craig-Möbius aromaticity. These molecules have three metal-carbon bonds as a 7-carbon chain coordinated with an Os metal atom in the center, constructing tridentate chelation. Due to the unique dπ-pπ conjugation from the embedded metal atom, carbolong complexes exhibit outstanding chemical and physical features, such as chemical and structural stability and high electron transmission, which render them excellent candidates for this project. The molecular structure of the designed carbolong molecules are shown in Figure 6. Interestingly, inverse conductance decay – that is, conductance increase with the molecular length – was observed in the carbolong complexes, contradicting conventional organometallic systems (Figure 7a). The enhanced molecular conductance for longer molecules is of great benefit for this project. In collaboration with Prof. Hatef Sadeghi, we carried out the theoretical calculation of the transmission function of these carbolong complexes. As shown in Figure 7b, we found that the HOMO-LUMO gap rapidly deceases as the molecular length increases, which outperforms the decay of transmission probability at gold electrode Fermi energy, eventually leading to enhanced conductance for longer carbolong molecules. It is important to note that the designed carbolong complexes has a LUMO-dominated transmission peak that is around 0.5eV above the gold Fermi energy. Such transmission feature will allow us to access hot carriers distributed at higher energies, complementing the open-shell donor acceptor molecules mentioned above. The manuscript of this work is currently in preparation and will lead to publication soon.

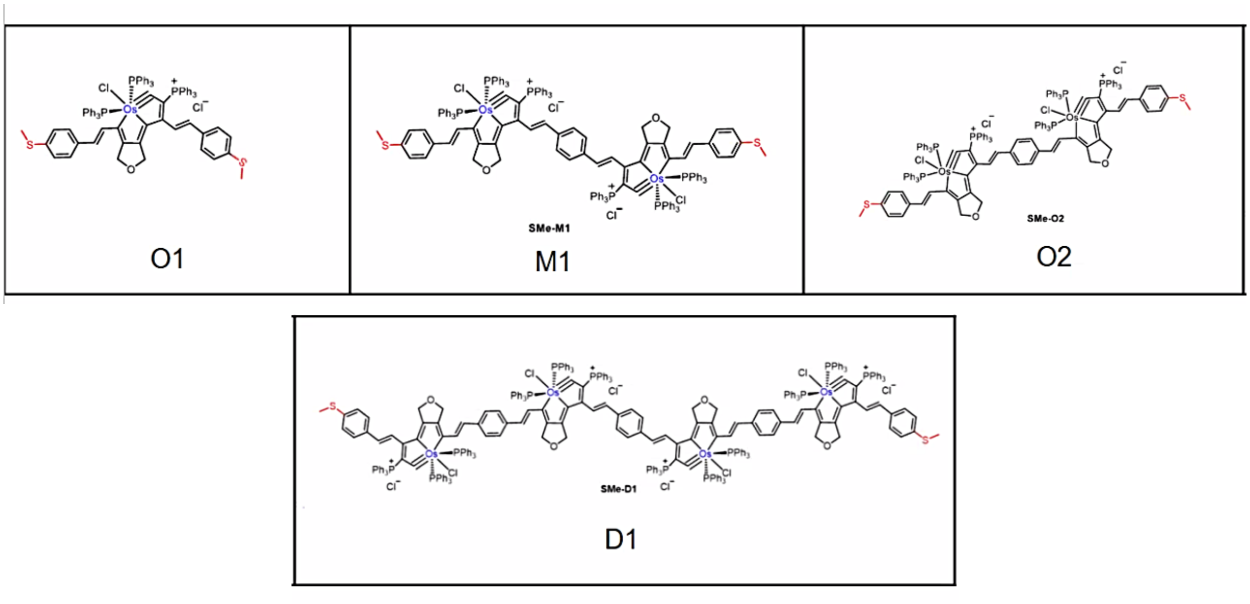

Figure 6. Investigated carbolong complex structures with different repeating units.

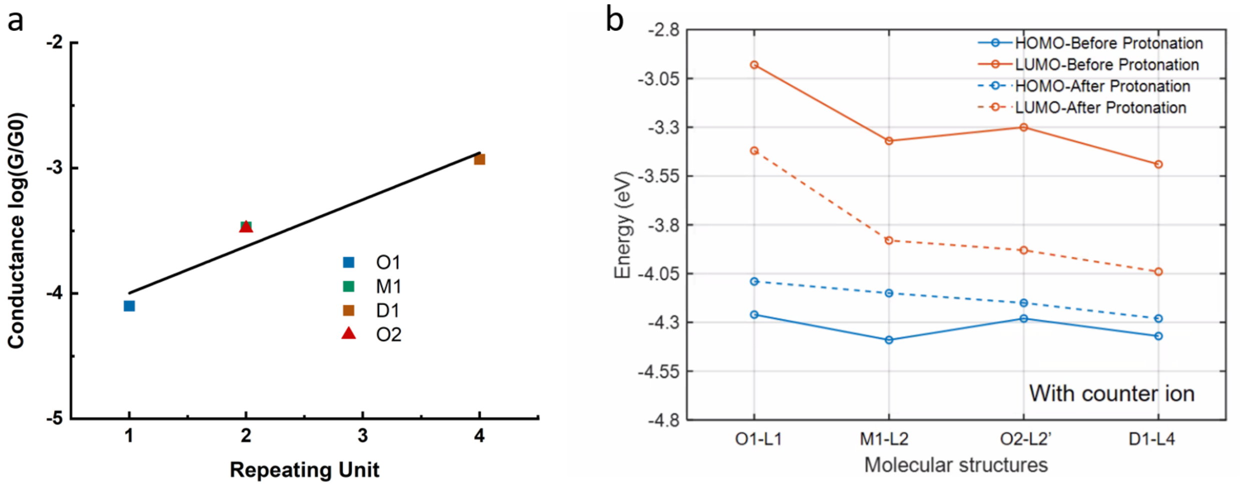

Figure 7. a) Measured single-molecule conductance for carbolong complexes with different repeating units. b) Theoretical calculation of the HOMO-LUMO gap of the carbolong complexes. Rapid shrinkage of the HOMO-LUMO gap is observed as the molecular length increases.

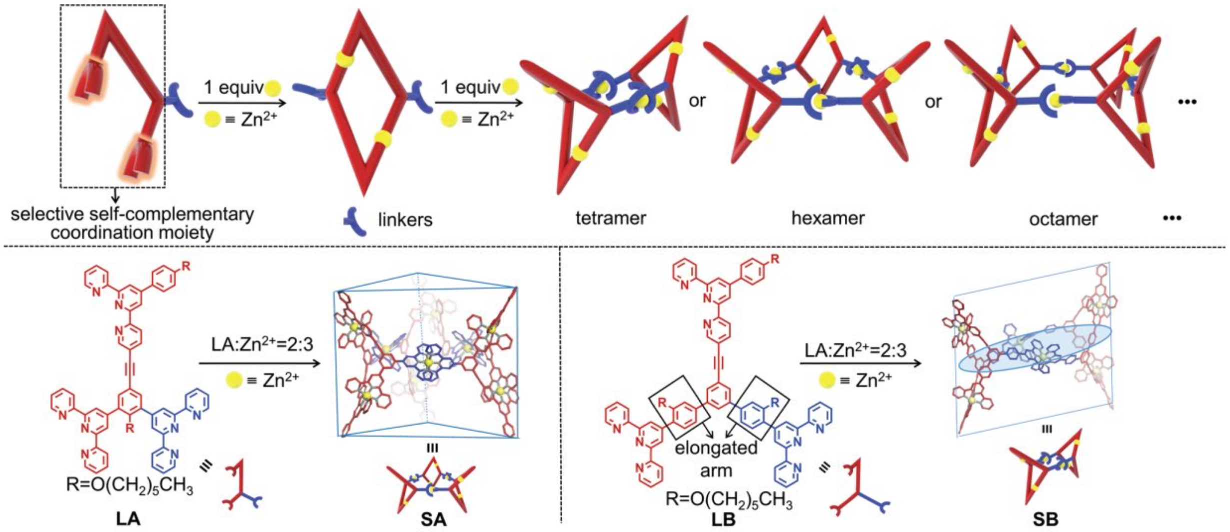

Figure 8. Synthetic strategy of SA and SB supramolecular nanostructures.

We also explored the possibility of harnessing supramolecular nanostructures for plasmonic hot carrier sensing as the unique non-covalent interactions in supramolecules hold promise for nanosensing (see ***MaterChemFront 2023*** paper in journal publication). Toward this end, we introduced the concept of self-coordination ligands to design and synthesize two meta-modified terpyridyl ligands with selective self-complementary coordination moiety (Figure 8). We then demonstrated their capability to assemble into two hourglass-shaped nanocages SA and SB is demonstrated. By changing the arm length of the ligands, hexamer (SA) and tetramer (SB) are successfully obtained, respectively. In-depth studies on the assembly mechanism of SA and SB indicate that the dimers could be formed first via self-complementary coordination and play important roles in controlling the resulting structures. Moreover, both SA and SB can undergo hierarchical self-assemblies to form large-scale nanostructures in solution as well as on solid–liquid interface, which are characterized by transmission electron microscope (TEM) and scanning tunneling microscopy (STM). It is further demonstrated that various higher-order assembly structures (e.g., nanowires) can be achieved by tuning the environmental conditions. This work is published in Small in 2023 (see more details in the ***Small 2023*** paper in journal publication section).

Fabrication of Plasmonic Nanostructures (Aim 3)

Aim 3 focuses on the fabrication of noble metal plasmonic nanostructures and integrating them into the STM setup for single molecule transport studies. Given the limited scanning area of a STM tip and the need for optical access, it is critical to fabricate samples with desired noble metal PNs covering a large area on a transparent conductive substrate. The transparent substrate will enable optical illumination to the PNs from the backside of the sample. In this regard, we extensively explored the fabrication of gold nanoprisms on ITO substrate using the nanosphere lithography method. Although numerous studies have reported fabrication of nanostructures using nanosphere lithography method on glass substrate, the protocol of reliably fabricating large-area uniform and high quality nanoprisms on ITO substrate remains to be explored. Through controlling various factors involved in the preparation, including nanosphere assembly, metal deposition, lift-off methods (mechanical lift-off vs chemical lift-off), and substrate clearning, we are able to develop a protocol to produce of gold nanoprism arrays covering large area (>20um x 20um) with controlled thickness on transparent ITO substrate. The fabrication schematic is shown in Figure 9. The fabrication processes were verified at each step with scanning electron microscope and atomic force microscope characterizations. Specifically, we found that for ITO substrate, the deposited gold film should be peeled off from the substrate using chemical peel off followed by mechanical peel off. Since the edges of the nano prisms majorly contribute to the plasmonic response of the nanoprism, this method is a effective way to tune the LSPR response of arrays of two-dimensional nanoprism. The progress made will serve as the basis for the planned studies of the single molecule quantum transport on various PN surfaces. In parallel, we are currently exploring the fabrication of other PN geometries on glass surface using electron-beam lithography.

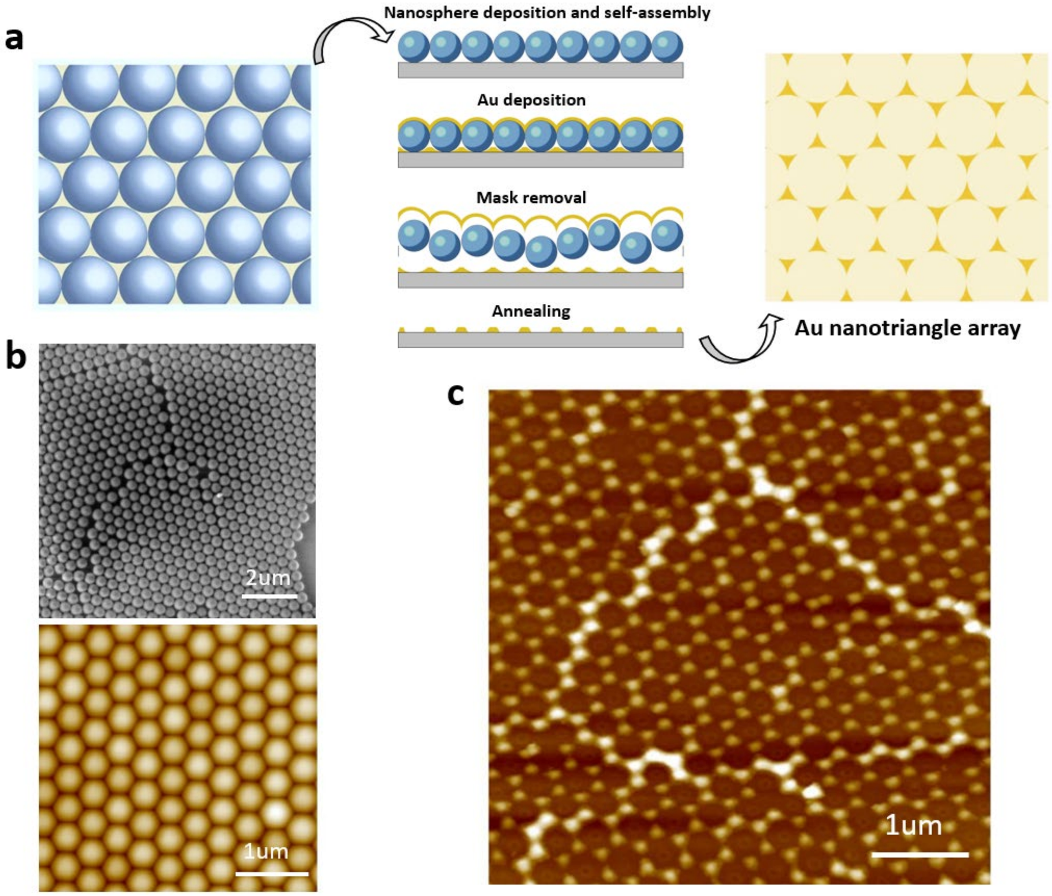

Figure 9. a) Schematic illustration of the nanosphere lithography method. b) Our preliminary results: SEM (top) and AFM (bottom) images of highly ordered assembly of single layer polystyrene nanospheres on ITO substrate. c) AFM image of large arrays of gold nanotriangle structures on ITO substrate after mask removal.

Broader Impacts

The research discoveries made in this project have broad impact on future molecular design for various applications, including nanoelectronics, molecular optoelectronics, and energy conversion as it paves a clear path toward creating molecular materials that can facilitate efficient long-range charge transport under low applied bias at ambient condition, a long-desired feature in related fields. It is worth noting the donor-acceptor diradical molecules developed in this project overcome the instability issues with existing radical systems, making air-robust highly conductive high-spin organic materials possible. In addition, the narrow bandgaps, open-shell structures, strong electron correlations, robust stability of the developed molecular systems are expected to offer new opportunities for molecular spintronics and quantum sensing. Furthermore, our work which introduced the concept of self-coordination ligands has greatly enriched the family of three-dimensional metallo-supramolecular architectures constructed with terpyridine-based ligands and will further shed light on the applications of metallo-supramolecules in nanoscale, molecular scale devices and fluorescent sensing.

Challenges and Lessons Learned

Throughout the duration of the project, we, as a newly established research lab, encountered several challenges that provided valuable learning experience. These challenges, along with the lessons learned, are outlined below:

> Technical challenges: The ambient non-liquid environment was a critical requirement for this project. However, the design and synthesis of chemically robust and air-stable radical organic molecules with narrow HOMO-LUMO gap have been a major challenge due to the intrinsic instability of radical materials. Through thorough discussion and communication with synthetic chemists, we established collaboration with Prof. Jason Azoulay from GeorgiaTech and employed a novel strategy for the successful synthesis of charge-neutral air-stable donor-acceptor open-shell diradical conjugated molecules. The design and synthesis strategies developed in this project will be extensively used in the future to tune the alignment of molecular transmission with different hot carrier energy windows.
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> COVID Impact: Our lab was founded in the middle of COVID19 pandemic, and this is also when this project started. The pandemic led to significant delay on instrument delivery and materials purchase, and personnel recruitment and training. To navigate through shortage of personnel at the beginning, we recruited talented undergraduate students to help setup the lab and get trained for simple lab operation and sample preparation. This has allowed us to smoothly transition to normal operation mode after instrument and graduate students arrived.
>
> Resource constraints: There is limited resource for nanofabrication and characterization at Mississippi State University. We navigated through this challenge by establishing connections and collaborations with other universities in Mississippi, including University of Southern Mississippi and University of Mississippi, and neighboring states, including University of Georgia, Georgia Tech, and University of Alabama, and national lab, OakRidge. By combining resources from multi-sources, we were able to make continuous progress on this project.
>
> Personal issues: As a newly established lab, all lab members were fresh graduate students when the project started. This also means significant time was devoted to get students trained on basic lab skills, instrument operation, and lab routines while all of them were taking required graduate-level courses. We navigate through this challenge by effective apply peer-training and highly efficient communication among team members. These

tough times at the beginning has prepared us to tackle future challenges in time management and communication.

Future Plan

Building upon the progress we have made in this project, we will continue to pursue the proposed activities after we move to University of Miami. We will complete the integration of external optical imaging and illumination into our STMBJ platform and carry out single-molecule transport measurements under controlled plasmonic excitation using the identified molecular candidates. Combining theoretical simulation and experimental characterization, we will continue to optimize and characterize new molecular systems suitable for the proposed study. We will continue to optimize the fabrication of large-area plasmonic nanostructures in different geometries on ITO substrate using different fabrication methods. This will allow us to initiate the investigation of the impact of PN geometries and materials. We will also continue the collaboration with theorists for the simulation, calculation, and optimization of our molecular systems and plasmonic nanoparticles and interpretation of our experimental results.

Products Developed Under this Grant

a. *Journal publications, accepted manuscripts, or other public releases of results.*

   Peer-Reviewed Journal publications:

   - "*Hourglass-Shaped Nanocages with Concaved Structures Based on Selective Self-Complementary Coordination Ligands and Tunable Hierarchical Self-Assembly*" Yaping Xu, Haixin Zhang, Haoyue Su, Jianjun Ma, Hao Yu, Kehuan Li, Junjuan Shi, Xin-Qi Hao, Kun Wang, Bo Song, Ming Wang, ***Small*** 19, 2300009 (2023)
   - "*The Pivotal Role of Non-Covalent Interactions in Single-Molecule Charge Transport*", Ridwan Ayinla, Mehrdad Shiri, Bo Song, Mahesh Gangishetty, Kun Wang, ***Materials Chemistry Frontiers*** 2023, 7, 3524-3542
   - *"Light-Driven Charge Transport and Optical Sensing in Molecular Junctions"* Chaolong Tang, Mehrdad Shiri, Haixin Zhang, Ridwan Tobi Ayinla, and Kun Wang*,* ***Nanomaterials*** 2022, 12(4), 698
   - *"Beyond Electrical Conductance: Progress and Prospects of Single-Molecule Junctions"* Chaolong Tang, Ridwan Tobi Ayinla, and Kun Wang, ***Journal of Materials Chemistry C*** 2022,10, 13717-13733

- *"Switching the Conductance of a Single Molecule: Lessons from Molecular Junctions"* Haixin Zhang, Mehrdad Shiri, Ridwan Tobi Ayinla, Zhe Qiang, and Kun Wang, ***MRS Communications*** 12, 495–509 (2022)

b. Presentations at academic conferences, workshops, and seminars

1. "Probing Quantum Transport and Energy Conversion at the Molecular Scale" Department of Physics and Astronomy, University of Alabama, Tuscaloosa, AL Mar 02, 2023
2. "Probing Quantum Transport and Energy Conversion at the Molecular Scale" Department of Physics and Astronomy, University of Maryland at Baltimore County Feb 15, 2023
3. "Navigating Materials Space at the Molecular Scale for Energy and Quantum Applications" Department of Physics and Astronomy, University of Missouri, Columbia, MO Feb 06, 2023
4. "Exploring Materials Space at the Molecular Scale for Optoelectronics, Energy, and Quantum Applications" Department of Physics, University of Miami, Coral Gables, FL Feb 01, 2023
5. "Probing Quantum Transport and Energy Conversion at the Molecular Scale" Department of Physics and Astronomy, Georgia State University, Atlanta, GA Jan 26, 2023
6. "Exploring Chemical Space at the Single-Molecule Level for Optoelectronics, Energy, and Quantum Applications" Department of Chemistry, University of Kentucky, Lexington, KY Jan 19, 2023
7. "Probing optoelectronics and energy conversion at the molecular scale" Southeast Division of APS Meeting, Oxford, MS Nov 03, 2023
8. "Scanning Probe Microscopy for the Characterization of Soft Matters and Nanomaterials" Southern Soft Matter Symposium, U. Southern Miss., Hattiesburg, MS July 11, 2022
9. "Probing Optoelectronics and Energy Conversion at the Molecular Scale" Jackson State University, Jackson, MS Feb 11, 2022
10. "Mapping Plasmonic Hot Carriers via Single Molecule Transport Measurements" ACS Pacifichem 2021, Hawaii, US Dec 16, 2021

Acknowledgements

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