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**The Research Grants Council of Hong Kong
NSFC/RGC Joint Research Scheme
Joint Completion Report**

*(Please attach a copy of the completion report submitted to the NSFC
by the Mainland researcher)*

Part A: The Project and Investigator(s)

1. Project Title

Detect Electroluminescence of Single Conjugated Polymers

2. Investigator(s) and Academic Department/Units Involved

	Hong Kong Team	Mainland Team
Name of Principal Investigator <i>(with title)</i>	Prof Lin Nian	Prof Liu Pei Nian
Post	Professor	Professor
Unit / Department / Institution	Physics/HKUST	Key Lab for Advanced Materials /East China University of Science and Technology
Contact Information	phnlin@ust.hk	liupn@ecust.edu.cn
Co-investigator(s) <i>(with title and institution)</i>		

3. Project Duration

	Original	Revised	Date of RGC/ Institution Approval <i>(must be quoted)</i>
Project Start date	1/1/2016		
Project Completion date	12/31/2019		
Duration <i>(in month)</i>	48		
Deadline for Submission of Completion Report	12/31/2020		

Part B: The Completion Report

5. Project Objectives

5.1 Objectives as per original application

1. To design and synthesize precursor monomers containing light-emitting functional groups
2. To perform on-surface polymerization of the precursor monomers
3. To detect the electroluminescence of single polymers using a low-temperature scanning tunneling microscope.

5.2 Revised Objectives

Date of approval from the RGC: _____

Reasons for the change: _____

6. Research Outcome

Major findings and research outcome

(maximum 1 page; please make reference to Part C where necessary)

1. Resonant Charge Transport in Conjugated Molecular Wires beyond 10 nm Range (*J. Am. Chem. Soc.*, **2016**, *138* (35), pp 11140–11143)

We used a scanning tunneling microscope to measure high-bias conductance of single polyporphyrin molecular wires with lengths from 1.3 to 13 nm. We observed several remarkable transport characteristics, including multiple sharp conductance peaks, conductances as high as 20 nS in wires with lengths of >10 nm, and nearly length-independent conductance (attenuation <0.001 Å⁻¹). Porphyrin-based molecular wires can mediate charge transport with attenuation factors below 0.1 Å⁻¹. Charge transport in these systems occurs via off-resonant tunneling in

short wires and hole polaron delocalization in long wires. In this work, we studied charge transport through biphenyl–porphyrin oligomer wires with lengths of 1.3 to 13 nm. The *bp-ppo* wires were synthesized using on-surface Ullmann reaction from precursor molecules of 5,15-bis(4-bromophenyl)-10,20-diphenylporphyrin (Br₂-TPP) on a Au(111) surface. We applied on-surface metalation to convert free-base *bp-ppo* wires to Fe-*bp-ppo* wires. We used the STM tip to lift the wires. We have demonstrated that the conductance of single porphyrin oligomer wires exhibits nearly decayless differential conductance ($\beta < 0.001 \text{ \AA}^{-1}$) at long range ($>6 \text{ nm}$). First-principles calculations revealed that the conductance is channeled by resonant transport through the delocalized LUMO. We anticipate that these findings will stimulate further efforts to use porphyrin oligomer wires to construct single-molecular electronics.

2. Negative Differential Conductance in Polyporphyrin Oligomers with Nonlinear Backbones (*J. Am. Chem. Soc.*, Article ASAP (2018).)

We study negative differential conductance (NDC) effects in polyporphyrin oligomers with nonlinear backbones. Using a low-temperature scanning tunneling microscope, we selectively controlled the charge transport path in single oligomer wires. We observed robust NDC when charge passed through a T-shape junction, bistable NDC when charge passed through a 90° kink and no NDC when charge passed through a 120° kink. Aided by density functional theory with nonequilibrium Green's functions simulations, we attributed this backbone-dependent NDC to bias-modulated hybridization of the electrode states with the resonant transport molecular orbital. We argue this mechanism is generic in molecular systems, which opens a new route of designing molecular NDC devices. In the past two decades, the NDC effect in molecular systems has been extensively studied driven by the fast development of molecular electronics. Most of the studies addressed short molecules with a linear backbone. Here we report our studies of single-molecule NDC effect in long molecular wires ($\sim 10 \text{ nm}$) with a nonlinear backbone. We find that nonlinear molecular backbones in polyporphyrin oligomer wires introduce NDC in resonant transport. The first-principles simulations reveal that hybridization of the electrodes' continuum states with the resonant transport molecular orbital is modulated by changing the external bias in a narrow bias window (-1.3 to -1.9 V). As a result, the transmission is strongly suppressed at higher bias, leading to NDC. Our findings exemplify how concerted action of electrode–molecule coupling, molecular orbital delocalization and external bias command charge transport in molecular junctions.

3. Collective Spin Manipulation in Antiferroelastic Spin-Crossover Metallo-Supramolecular Chains (*ACS Nano* 2020, 14, 9, 11283–11293)

Coupled spin-crossover complexes in supramolecular systems feature rich spin phases that can exhibit collective behaviors. Here, we report on a molecular-level exploration of the spin phase and collective spin-crossover dynamics in metallo-supramolecular chains. Using scanning tunneling microscopy, spectroscopy, and density functional theory calculations, we identify an antiferroelastic phase in the metal–organic chains, where the Ni atoms coordinated by deprotonated tetrahydroxybenzene linkers on Au(111) are at a low-spin ($S = 0$) or a high-spin ($S = 1$) state alternately along the chains. We demonstrate that the spin phase is stabilized by the combined effects of intrachain interactions and substrate commensurability. The stability of the antiferroelastic structure drives the collective spin-state switching of multiple Ni atoms in the same chain in response to electron/hole tunneling to a Ni atom *via* a domino-like magnetostructural relaxation process. These results provide insights into the magnetostructural dynamics of the supramolecular structures, offering a route toward their spintronic manipulations.

Potential for further development of the research and the proposed course of action
(*maximum half a page*)

Based on the results obtained in this project, we propose the following directions for future research:

1. The coherent charge transport discovered in this project shed lights on efficient luminescence in longer molecular wires. We anticipate such studies may yield fruitful results in efficient molecular luminescence. For example, to understand how light emission intensity is enhanced when coherent charge transport occurs.
2. The NDR effects observed in this project can be used to control the molecular luminescence, that is, to switch on/off luminescence. This is a promising concept for realizing single-molecule switches.
3. Combine magnetism with charge transport is very exciting in the field of spintronics. Our results of spin-state switching in organometallic wires may open a new route for studying spin-dependent charge transport in organometallic wires. Specifically, using the technique developed in this project, one can measure single-molecule conductance of the spin chains whose spin states are regulated by an external field.
4. Aggregate-enhanced emission (AIE) is an exciting phenomenon in molecular luminescence, which has been studied extensively. Using the technique developed in this project, it is highly interesting to study the luminescence of molecular systems containing AIE moieties. We are collaborating with Prof. Benzhong Tang, who is the pioneer of AIE research, to conduct a research project in this direction.

7. The Layman's Summary

(describe in layman's language the nature, significance and value of the research project, in no more than 200 words)

Organic light-emitting diodes (OLEDs) are widely used in television screens, computer monitors, mobile phones for displays as well as in solid-state light sources. Investigating the light emission at the single-molecule level is highly desirable since such studies may shed light on the single-molecule mechanism of OLEDs. In this project, we will employ on-surface polymerization to synthesize polymers containing light-emitting functional groups, and systematically investigate the electroluminescence occurring in the single polymers.

Part C: Research Output

8. Peer-reviewed journal publication(s) arising directly from this research project

(Please attach a copy of each publication and/or the letter of acceptance if not yet submitted in the previous progress report(s). All listed publications must acknowledge RGC's funding support by quoting the specific grant reference.)

The Latest Status of Publications				Author(s) <i>(bold the authors belonging to the project teams and denote the corresponding author with an asterisk*)</i>	Title and Journal/ Book <i>(with the volume, pages and other necessary publishing details specified)</i>	Submitted to RGC <i>(indicate the year ending of the relevant progress report)</i>	Attached to this report <i>(Yes or No)</i>	Acknowledged the support of this Joint Research Scheme <i>(Yes or No)</i>	Accessible from the institutional repository <i>(Yes or No)</i>
Year of publication	Year of Acceptance <i>(For paper accepted but not yet published)</i>	Under Review	Under Preparation <i>(optional)</i>						

2016 J1			G. Kuang, S.-Z. Chen, W. Wang, T. Lin, K.-Q. Chen, X. Shang, P. N. Liu*, N. Lin*	Resonant Charge Transport in Conjugated Molecular Wires beyond 10 nm Range, <i>J. Am. Chem. Soc.</i> , 2016 , <i>138</i> (35), 11140–11143	31 Dec. 2017	N	Y	Y
2018 J2			G. Kuang, S. -Z. Chen, L Yan, K. Q. Chen, X. Shang, P. N. Liu*, N. Lin*	Negative differential conductance in polyporphyrin oligomers with non-linear backbones, <i>J. Am. Chem. Soc.</i> , 2018 <i>140</i> (2), 570-573.	31 Dec. 2017	N	Y	Y
2018 J3			J. Liu, B. Xia, H. Xu, N. Lin*	Controlling the Reaction Steps of Bifunctional Molecules 1,5-Dibromo-2,6-dimethylphthalene on Different Substrates, <i>J. Phys. Chem. C</i>, 2018, 122, 24, 13001–13008	2020	Y	Y	Y
2019 J4			J. Liu, B. Xia, H. Xu, N. Lin*	Hydrogen Bond Induced Molecular Orbital Shift in One-Dimensional Molecular Self-Assemblies on Au(111), <i>SCIENTIA SINICA Chimica</i> , 2019 <i>9</i> , 564-572	2020	Y	Y	Y
2020 J5			J. Liu*, Y. Gao, T. Wang, Q. Xue, M. Hua, Y. Wang, L. Huang, N. Lin	Collective Spin Manipulation in Antiferroelastic Spin-Crossover Metallo-Supramolecular Chains, <i>ACS Nano</i> , 2020, <i>14</i> , 11283.	2020	Y	Y	Y

9. Recognized international conference(s) in which paper(s) related to this research project was/were delivered (Please attach a copy of each delivered paper. All listed papers must acknowledge RGC's funding support by quoting the specific grant reference.)

Month/Year/ Place	Title	Conference Name	Submitted to RGC (indicate the year ending of the relevant progress report)	Attached to this report (Yes or No)	Ackno wledge d the support of this Joint Resear ch Schem e (Yes or No)	Accessible from the institutional repository (Yes or No)
NOV/2017 SINGAPORE C1	CHARGE TRANSPORT THROUGH ON-SURFACE SYNTHESIZED OLIGOMERS	ELECTRONIC STRUCTURE AND PROCESSES AT MOLECULAR-BASED INTERFACES	31 Dec. 2017	N	Y	Y
December, 2019, Okazaki , Japan C2	Design, Synthesis and Characterization of Low-Dimensional Conjugated Metal-Organic Coordination Structures on surfaces	Forefront of Measurement Technologies for Surface Chemistry and Physics in Real-Space, k-Space, and Real-Time	2020	Y	Y	Y

10. Student(s) trained (Please attach a copy of the title page of the thesis.)

Name	Degree registered for	Date of registration	Date of thesis submission/ graduation
Guowen Kuang	Ph.D	Aug 15, 2013	Aug. 31, 2017

11. Other impact (e.g. award of patents or prizes, collaboration with other research institutions, technology transfer, etc.)

N.A.

12. Statistics on Research Outputs (Please ensure the summary statistics below are consistent with the information presented in other parts of this report.)

	Peer-reviewed journal publications	Conference papers	Scholarly books, monographs and chapters	Patents awarded	Other research outputs (Please specify)
No. of outputs arising directly from this research project [or conference]	5	2	0	0	