

Errata sheet

This errata sheet lists errors and their corrections for the doctoral thesis of Hailiang Xu, titled “Study the Influence of Quantum Interference on the Electrical Conductance and Thermoelectric Properties of Molecular Junctions: Synthesis and Thermoelectricity”, Lund University, 2021. ISBN: 978-91-7422-820-5.

Location	Error	Correction
Page 2	“This thesis mainly describes our efforts towards the study of the quantum interference of <u>electronic</u> conductance and thermoelectric properties in molecular junctions.”	“This thesis mainly describes our efforts towards the study of the quantum interference of electrical conductance and thermoelectric properties in molecular junctions.”
Page 16	“Otherwise, it will show a <u>QI</u> in the MJs, such as <i>meta</i> -configuration (Scheme 1.1 <i>b</i>).”	“Otherwise, it will show QI patterns in MJs , such as <i>meta</i> -configuration (Scheme 1.1 <i>b</i>).”
Page 18	“For instance, <u>in the research of Wu’s et al.</u> , ²² conductances of molecules 1-4 are $(1.2 \pm 0.1) \times 10^{-4} G_0$...and $(5.9 \pm 2.4) \times 10^{-6} G_0$, respectively (Figure 1.5).”	“For instance in Wu’s research , ²² the conductance values of molecules 1-4 are $(1.2 \pm 0.1) \times 10^{-4} G_0$...and $(5.9 \pm 2.4) \times 10^{-6} G_0$, respectively (Figure 1.5).”
Page 21	“A lot <u>difference of</u> electrode materials have been employed in the SMEs for the study of charge transport, such as Ag, ²⁶⁻³⁰ Pt ³⁰⁻³³ and Au ³⁴⁻³⁶ in metals, and graphene ³⁷⁻³⁹ in nanostructures.”	“A lot of different electrode materials have been employed in the SMEs for the study of charge transport, such as Ag, ²⁶⁻³⁰ Pt ³⁰⁻³³ and Au ³⁴⁻³⁶ in metals, and graphene ³⁷⁻³⁹ in nanostructures.”
Page 22	“According to <u>the type of connection</u> , there are two kinds of <u>coupling</u> , dative interactions (covalent bond with coordination) through electron donors and covalent binding through reactions (Figure 2.2). ⁵ ”	“According to the types of connection with the electrodes , there are two kinds of couplings , dative interactions (covalent bond with coordination) through electron donors and covalent binding through reactions (Figure 2.2). ⁵ ”
Page 27	“But the transmission of molecular junctions based on <i>meta</i> -OPE3 derivatives has been proven to not be completely suppressed, ^{13, 74, 75} which provides the opportunities to tune <u>the efficiency of thermoelectric power</u> in <i>meta</i> -OPE3-based molecular junctions through manipulating the structure of molecules.”	“But the transmission of molecular junctions based on <i>meta</i> -OPE3 derivatives has been proven to not be completely suppressed, ^{13, 74, 75} which provides the opportunities to tune the conductance of meta -OPE3-based molecular junctions through manipulating the structure of molecules.”
Page 34	“ <u>$\beta(2,12)$</u> -substituted porphyrins.”	“ $\beta(7,17)$ -substituted porphyrins.”
Page 39	“They proposed specific single-molecule junctions based on the <u>$\beta(2,13)$</u> -linked Zn porphyrin terminated with thiol groups (Figure 2.19 <i>b</i> and <i>c</i>).”	“They proposed specific single-molecule junctions based on the $\beta(8,17)$ -linked Zn porphyrin terminated with thiol groups (Figure 2.19 <i>b</i> and <i>c</i>).”
Page 52 “Addition” Line 22 in second paragraph		“ Besides, the electron-withdrawing effect of -NO₂ group may lower the HOMO energy away from Fermi level to increase the ΔE and to result in a lower conductance of MJs. Thus, the strong EWG nitro group (-NO ₂) is a good choice of substituent to change the conduction properties of the basic OPE3 compounds in our project.”

Page 53 Table 3.1	“(a) benzene dibromide (1.0 equiv.)”	“(a) <i>m</i>-dibromobenzene (1.0 equiv.)”
Page 101 Table 4.1, entry 9	“TFA (0.5 equiv.), CH ₂ Cl ₂ , reflux , 4 h.”	“TFA (0.5 equiv.), CH ₂ Cl ₂ , reflux , 4 h.”
Page 106 Table 4.2, entry 3, 4, 6-8	“DCM, 0 °C to rt.”	“DCM, 0 °C to rt.”
Page 107 Scheme 4.34	“(1) TFAA, 2,6-lutide , TFA, -78 °C, 15 h.”	“(1) TFAA, 2,6-lutidine , TFA, -78 °C, 15 h.”
Page 112 Table 4.3, entry 3	“TFA (0.5 equiv.), CH ₂ Cl ₂ , reflux , 4 h.”	“TFA (0.5 equiv.), CH ₂ Cl ₂ , reflux , 4 h.”
Paper III Page 24 compound 45	“1.32 (d, <i>J</i> = 14.4 Hz, 18 H).”	“1.34 (s, 9H), 1.30 (s, 9H).”

Abstract

Single-molecule junctions provide the unique insight to study the charge transport and energy conversion in the thermoelectric devices. The transmission coefficient $T(E)$, which is strongly affected by quantum interference (QI , either destructive or constructive patterns), is the key point of electron transport in molecules. From the theoretical calculations and the simple resonance-analysis method, QI can be probably envisaged in the molecular systems, which further are designed and synthesized based on this prediction. The aim of this thesis is to describe the efforts of the design, synthesis and application of the molecules to study the QI on the charge transport in single-molecule junctions.

Chapter 1 introduces the concepts of the electron transport in single-molecule junctions, including the transmission coefficient $T(E)$, conductance (G) and Seebeck coefficient (S). The correlations between $T(E)$, G and S are emphasized, which strengthen to understand the principle of charge transport in single-molecule junctions. Additionally, the method for the prediction of QI in molecular junctions is briefly presented.

Chapter 2 presents the components of single-molecule junctions and the development of the molecules which are used for the charge transport in molecular junctions. Based on our previous study, which Au-*meta*-OPE3-Au exhibited the destructive QI effects, four *meta*-OPE3 derivatives substituted with $-\text{NO}_2$ and $-\text{NMe}_2$ at central phenylene ring were synthesized and employed to study the destructive QI in single-molecule junctions. The experiment results show that the destructive QI can be tuned through changing the positions of substituents and offer a better understanding how the substituents influence the electron transport. The investigation of β -linked porphyrin compounds terminated with two methylthio groups in single-molecule junctions suggests that the zinc porphyrin complex (**Zn-P1**) junctions yield a higher thermopower (with $\sim 13 \mu\text{V/K}$) compared with its free-base porphyrin **P1** junctions (with $\sim 8 \mu\text{V/K}$). This result shows that **Zn-P1** junctions display the destructive QI effects.

Chapter 3 details the design and the optimization for the synthesis of *meta*-OPE3 derivatives, which can provide a systematic study of the influence of QI on the charge transport in single-molecule junctions. Several synthetic strategies are used to optimize the synthesis of a variety of *meta*-OPE3 derivatives substituted with different functional groups at central and side benzene ring(s). Substituents at side benzene rings, which can generate the “push→pull” effect due to the different polarities, are first introduced into *meta*-OPE3 system. More than 20 *meta*-OPE3 derivatives have been successfully synthesized, and 4 compounds have been used for the study the conductivity and thermoelectricity in molecular junctions. The application of all these molecules in molecular junctions will provide deeper insights to study the correlations between molecular structures and transport properties.

Chapter 4 presents the development of the porphyrin synthesis and detail the whole synthesis of our targeted porphyrins. Four porphyrins have been successfully synthesized over more than 10 steps using the MacDonald [2+2] approach and [3+1] method, respectively. The synthesis of the key intermediates, tripyrrane and dipyrromethane, are investigated and optimized since the properties of the substrates in the condensation with pyrrole are totally different. The packing of porphyrin **P2** due to the strong π - π stack has been testified by the ^1H NMR spectrum and the absorption spectrum.

Popular science summary

Speaking of electricity generation, one might relate it to energy sources like fossil, solar, wind, water or nuclear. However, the non-renewable fossil fuels (petroleum, coal and natural gas) are still the largest energy sources for electricity generation to date. Increasing the utility of renewable materials in electricity generation is of importance, since development of these techniques might reduce the use of the limited fossil fuels, thus promoting the environmental sustainability. Thermoelectric devices, which directly convert heat into electricity *via* a thermocouple, offer great opportunities. Different from thermal power station, where combustion energy is first converted to mechanical energy and then to electrical energy, thermoelectric devices utilize the temperature difference on each side to directly create a voltage. This indicates that the collection of heat, such as the industrial waste heat, can also be used as a potential resource for the electricity generation.

Although thermoelectric devices have received more and more attention due to its innovative and promising use in the electricity generation, it still stays on the lab stage, since scouting molecules with great efficiency of charge transport and scaling up the devices are difficult. However, well-developed theoretical studies provide the instructions and insights for the design of molecules, and the continuous experimental results show a more and more clear trend of the thermoelectricity in single-molecule junctions. The generated conductivity (presented by conductance, G) and thermoelectricity (presented by Seebeck coefficient, S) in single-molecule junctions depend on the transmission function $T(E)$, which is a key quantity of charge transport and strongly affected by quantum interference (QI , either constructive or destructive) effects. G and $T(E)$ are positively correlated, whereas S and $T(E)$ are negatively correlated. The constructive QI is a quantum effect that enhances the transmission to result in a large G and a small S while the destructive QI leads to a small G and a large S in single-molecule junctions. These QI effects indicate that the molecules with less electron transmission (or show destructive QI effects) will generate a higher thermoelectricity in single-molecule junctions. This theory leads the direction of the design and synthesis of our target molecules.

In the current thesis, we designed and synthesized a variety of small molecules, specifically *meta*-OPE3 derivatives and porphyrins, to study the influence of QI on the conductivity and thermoelectric properties in single-molecule junctions. All of these molecules have the π -conjugated system, which is expected to have a large impact on the patterns of $T(E)$. Measurements of our *meta*-OPE3 derivatives showed that Au-*meta*-OPE3 (derivatives)-Au junctions exhibited a clear feature of destructive QI effects, which resulted in the generation of a lower conductance and a higher thermoelectricity compared with Au-*para*-OPE3-Au junctions. And the destructive QI effects could be tuned by substitution with different functional groups in *meta*-OPE3 derivatives. These results suggest that it is feasible to find more similar molecules as better candidates for the higher generation of thermoelectricity in *meta*-OPE3 based single-molecule junctions. More *meta*-OPE3 derivatives (> 20) are under systematical investigation, which will provide a better understanding of the charge transport in single-molecule junctions.

The investigation of β -linked porphyrin compounds in single-molecule junctions showed that zinc porphyrin complex exhibited a higher thermopower than its free-base porphyrin, which suggested that the pathway of electron transport in complexed porphyrin is different from that of free-base porphyrin. More porphyrin derivatives (complexed and free-base) are under synthesis and thermoelectric studies.

In summary, we investigated the influence of QI on the conductivity and thermoelectric properties in single-molecule junctions and testified the destructive QI effects could be controlled by the reasonable design and synthesis of the molecules. In the future, more relevant molecules employed in single-molecule junctions can be modified or investigated based on our studies.

The aim of the thesis

Thermoelectricity is defined as the formation of electricity directly from the conversion of temperature difference *via* a thermocouple. Hence, the thermoelectric devices offer a great possibility for the energy development, such as the novel electric generator directly utilizing the industrial waste heat. At meantime, the reduction of waste heat can also benefit the environment. One attractive topic in the studies of thermoelectricity is the influence of quantum interference on the conductivity and thermoelectricity in single-molecule junctions, which are presented by conductance (G) and Seebeck coefficient (S), respectively. These two parameters are controlled by the transmission function $T(E)$ in molecular junctions. G and $T(E)$ are positively correlated, whereas S and $T(E)$ are negatively correlated. For our project, a smaller G and a larger S generated in the single-molecule junctions are our targets.

In single-molecule junctions, $T(E)$ is determined by the energetic alignment (ΔE) and the broadening (Γ) of the conducting orbital. Usually, small molecules with a short π -conjugated system generate a larger Γ , due to the strong coupling of their orbitals with the metal, which results in a smaller $T(E)$. As a consequence, the corresponding single-molecule junctions display a smaller G and a larger S . Numerous studies have pointed out that ΔE and Γ are influenced by the anchor groups and backbone of the molecules. Thus, through the reasonably molecular design, G and S can be tuned and a systematic investigation can be performed.

In this thesis, we have designed and synthesized two series of molecules, specifically *meta*-OPE3 and β -linked porphyrin derivatives. These molecules are picked based on the pioneering theoretical study of Dr. K. Georg Lind Pedersen (*meta*-OPE3 derivatives) and Prof. Heiner Linke (porphyrins), and further theoretical studies were carried out through the collaboration with Prof. Fabian Pauly. As one of our targets, the *meta*-OPE3 compounds with fully short π -conjugated system lead to more efficient charge transport than the saturated molecules, due to the smaller HOMO-LUMO gap (~ 3 eV) than that in the saturated molecules (~ 7 eV). The Au-*meta*-OPE3-Au junctions exhibit the destructive QI effect, which suppress the electron transmission in π -channels to result in a smaller G and a larger S . The result indicates that the conductivity and thermoelectricity in *meta*-OPE3-based molecular junctions can be tuned through the manipulating the structures of *meta*-OPE3 derivatives, i.e. introduction of different functional groups. As the other major target, Porphyrin-based molecular junctions provide a great chance for the electron transport, due to their large 18π -conjugated system. The theoretical studies show that β -linked porphyrins (i.e. **P1** and **Zn-P1**) would generate a higher thermoelectricity than *meso*-linked porphyrins in single-molecule junctions. We have successfully designed and synthesized over 20 *meta*-OPE3 derivatives substituted with different functional groups and 4 β -linked porphyrin compounds. These molecules will be used by our collaborator, Prof. Pramod Reddy, in single-molecule junctions to verify these theories.

Chapter 2 focuses on the development of single-molecule junctions based on the *meta*-OPE3 and β -linked porphyrin compounds. Compared with the current theoretical and experimental studies, we show the further progress how to tune the charge transport through the manipulation of molecular structures in single-molecule junctions.

Chapter 3 presents the specific design and synthesis of *meta*-OPE3 derivatives. This chapter aims at the optimization of the whole synthesis, including the introduction of functional groups at central and side benzene rings, the Sonogashira coupling for the construction of the backbone in *meta*-OPE3 compounds, and the Ti-mediated functional group for the formation of anchor groups. Additionally, the *meta*-OPE3 derivatives with the “push→pull” effect are introduced for the first time, which may have a great potential to influence the electron transport in single-molecule junctions through the changed electron density of the backbone in the molecules.

Chapter 4 describes the development of the synthesis of porphyrins and present the whole synthesis of our targeted porphyrins. The reasonable retrosynthetic analysis provides the best synthetic routes, the MacDonald [2+2] approach and [3+1] method for the ring-closing step of porphyrins. In this chapter, the synthesis of two kinds of β -linked porphyrins is detailed using totally different methods, and the properties of intermediates are discussed.

The appendix is about the experimental procedures and the data of characterization for the unpublished compounds. The compounds in the manuscripts are not included in this part.