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厦门大学理学博士学位论文

2,5-二羧基噻咯与噻咯低聚物的合成、反应 及性能研究

Study on the Synthesis, Reaction and Property of
2,5-Dicarboxylsiloles and Silole Oligomers

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**Study on the Synthesis, Reaction and Property of
2,5-Dicarboxylsiloles and Silole Oligomers**

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2,5-二羧基噻咯与噻咯低聚物的合成、反应及性能研究

摘 要

本论文共分五章，包括官能化噻咯及含噻咯环聚合物的研究应用新进展；2,5-二羧基噻咯的合成及性能研究；1,1-二甲基-2,5-二羧基噻咯与过渡金属的配位聚合反应研究；噻咯低聚物的合成、性质及应用研究；研究工作的结论与展望。

第一章为绪论，评述了官能化噻咯及噻咯聚合物的研究进展与应用前景，本章共分五部分。第一部分简单介绍了噻咯环独特的电子结构；第二部分对噻咯的芳香性及其金属配合物的性质作了简单评述；第三部分重点介绍了官能化噻咯现有的合成方法，并对各种方法的优缺点分别进行了评述；第四部分介绍了含有噻咯环的聚合物的研究现状；第五部分对噻咯小分子与聚合物的应用作以分类总结。在此基础上，我们提出了本论文的研究设想。

第二章主要研究了2,5-二羧基噻咯的合成及发光性能。该章的研究成果拓宽了噻咯小分子的应用范围，对开发官能化噻咯在硅基蓝色发光材料、非线性光学材料等领域的应用具有积极意义。本章分为两节。

第一节以苯乙炔为原料，采用有机锂法，使苯乙炔与丁基锂反应得到中间产物苯乙炔锂，然后再与四种不同的氯硅烷反应，得到了一系列取代基种类和数目均不相同的苯乙炔基硅烷，对其结构进行了表征。该法所用原料可以直接获得，产率较高，副反应较少，产物具有较高纯度，为噻咯小分子及聚合物的合成打下了良好的基础。

第二节采用苯乙炔基硅烷的内向-内向型分子内还原关环法，首次在噻咯环的2,5-位引入了羧基，得到三个新的噻咯小分子化合物：1,1-二甲基-2,5-二羧基噻咯、1,1-二苯基-2,5-二羧基噻咯及1-甲基-1-苯乙炔基-2,5-二羧基噻咯。

采用室温溶剂挥发法,首次获得了 1,1-二甲基-2,5-二羧基噻咯的晶体结构。考察了这些噻咯小分子化合物的热力学性能及发光性能。发现此类噻咯小分子的发光性能和普通有机发光材料不同:通常有机发光化合物在溶液中表现出良好的发光性能,而固体粉末状态或制成薄膜时分子易发生团聚,生成与基态原子(或分子)相似的不发光或弱发光物质,致使发光效率减弱或完全丧失发光特性。但我们合成的 2,5-二羧基噻咯在溶液中不发光,而固体(包括薄膜)状态下能够发射出较强的蓝绿光。这种良好的发光性能使其有望在硅基发光二极管、蓝色激光二极管、有机电发光材料及非线性光学材料等领域得到广泛应用。同时,我们对 2,5-二羧基噻咯产生独特发光现象的原因进行了分析,推测导致其固态荧光效率增强的原因是其分子之间通过氢键相互缔合所形成的刚性结构。本节中,我们还首次尝试了四苯乙炔基硅烷发生分子内双还原关环反应合成带四个羧基的噻咯螺环化合物的可行性,发现反应后最终得到的都是四苯乙炔基硅烷的聚合物,而不是目标产物。

第三章首次用 1,1-二甲基-2,5-二羧基噻咯作为配体,室温下分别与镉、钴、镍等过渡金属离子进行溶液中的自组装,得到了三个结构新颖的配位聚合物晶体。通过对其单晶结构的分析,发现配位聚合反应后配体的环 Si-C 键均发生断裂, Si 原子以及与其相连的两个甲基被脱除,同时噻咯环 3,4-位上的两个苯环发生了顺反异构化。反应后 1,1-二甲基-2,5-二羧基噻咯(DCS)变成了(trans)-3,4-二苯基-2,4-二己烯-二酸(DHA)。即实际参与配位聚合的是 DHA 而不是 DCS。噻咯环 Si-C 键的化学稳定性较差是断键的主要原因。此外,由于配合物的生成过程极为复杂,金属离子的配位特性及所用的溶剂、反应温度等外界条件也可能成为噻咯环 Si-C 键的断裂的原因。尽管未得到目标产物,但该研究工作尤其是双核镉钴配合物的成功合成无疑为新型配合物的设计和组装以及新型几何和拓扑学的发展作出了一定的贡献。探索合适的反应原料,优化反应的溶剂、温度等条件,组装出含噻咯环的配位聚合物,仍是下一步研究工作的重点。

第四章首次采用一锅煮法，使苯乙炔基硅烷关环所得到的中间产物 2,5-二锂噻咯直接与含卤素的双官能团化合物 2,6-二溴吡啶、二氯苯基磷及 1,4-二苄氯反应，得到了三种共轭程度不同的噻咯低聚物。对低聚物的结构进行了表征，对其形貌、热学性能、发光性能、导电性及电化学性能进行了详细研究，并初步探讨了低聚物用于农用转光膜的可行性。研究发现，主链含有刚性苯环的噻咯-对苯二亚甲基共聚物呈现晶态，而另外两种低聚物噻咯-吡啶 (α) 共聚物和噻咯-苯基磷共聚物都是以典型的非晶态存在的。对低聚物热力学性能的研究表明，刚性较强的噻咯-对苯二亚甲基共聚物的热稳定性最好；对其导电性能的研究发现本征态的低聚物基本不具备导电性，经 HCl、HClO₄ 及 I₂ 掺杂后，其电导率数值虽然有了一定提高，但仍达不到预期的效果，这可能与低聚物自身的结构、性质及掺杂方法有关；通过循环伏安，初步研究了低聚物的电化学性能，结果表明高氯酸锂作支持电解质时，其氧化还原过程是不可逆的，具体历程除与其自身的结构和性质有关外，受溶剂影响显著。本章中，我们对低聚物的发光性能作了详细研究，发现此类低聚物无论在溶液中，还是固体（包括薄膜）状态，都具有良好的发光性能，有望在发光二极管、激光二极管以及紫外光探测器等方面得到应用。发光波长除与低聚物的存在状态及外界环境因素有关外，主要取决于本身的结构。因此，通过改变主链结构及存在状态，可以实现对发光颜色的调节。本章中，我们还进一步考察了低聚物用于农用转光膜的可行性，发现噻咯-苯基磷共聚物可以吸收太阳光中的紫外光，发射出易被植物吸收的蓝紫光，具有优良的“转光膜”特性，有望用于农作物的塑料大棚，以提高农作物产量。

第五章总结了本论文研究工作的创新性，并对该研究工作的进一步发展提出了设想。

关键词：噻咯，羧基，配位聚合物，低聚物，合成，发光性能，应用

Study on the Synthesis, Reaction and Property of 2,5-Dicarboxylsiloles and Silole Oligomers

Abstract

This dissertation consists of five chapters, including the research and progress in synthesis and application of functionalized siloles and silole polymers, synthesis and characterization of 2,5-dicarboxylsiloles, coordination polymerization of 1,1-dimethyl-2,5-dicarboxylsilole with transitional metals, synthesis, property and application of silole oligomers, the conclusion and prospect of the present research work.

In chapter one, the research progress and application prospect of functionalized siloles and silole polymers are reviewed. This chapter consists of five parts, which are the unique electronic structures of silole ring, the metal complex and aromatic property of siloles, synthetic methods of functionalized siloles; research and progress of silole polymers, and application of silole molecules and polymers, respectively. The research objective for this dissertation is also presented in this chapter.

In chapter two, the research work on the synthesis and luminescence of 2,5-dicarboxylsiloles is described. The results enlarge the application range of silole molecules and have positive effects on developing silane blue emission materials and non-linear optical materials. This chapter is divided into two sections.

In section one, a series of phenylethynylsilanes are synthesized following the method of “organolithium”, the procedure of which is as follows: Reaction of phenyl acetylene with n-butyllithium gives lithium phenylacetylide as a byproduct.

By trapping with four different chlorosilanes a series of phenylethynylsilanes with different substitutes are synthesized in good yields. The structure of the phenylethynylsilanes are characterized by infrared spectrum(IR), nuclear magnetic resonance(NMR), mass spectrum(Ms) and elemental analysis(EA). The method of “organolithium” has four merits, which are facile materials, high efficiency, little side reaction and high purity. Accordingly, it gives much benefit to the subsequent syntheses of silole small molecules and oligomers.

In section two, first synthesis of 2,5-dicarboxylsiloles is reported based on "endo-endo" mode intramolecular reductive cyclization of phenylethynylsilanes. Three new silole molecules are synthesized, *i.e.*, 1,1-dimethyl-2,5-dicarboxylsilole(**2-5**), 1,1-diphenyl-2,5-dicarboxylsilole(**2-6**), and 1-dimethyl-1-phenylethynyl-2,5-dicarboxylsilole(**2-7**). Crystal structure of **2-5** is obtained by room temperature volatilization of **2-5** in ethanol. Thermal and luminescent properties of 2,5-dicarboxylsiloles are studied. It is found that this kind of molecules has different photoluminescence from common organic luminescent material: Most luminescent organic and polymeric compounds are highly emissive in their dilute solutions but become weakly luminescent when fabricated into thin films. The loss of luminescence efficiency is thought to be caused by aggregation of single molecules in the films. However, exactly the opposite effect is found in 2,5-dicarboxylsiloles. They are hardly luminescent in solutions but emit strong blue-green light in solid state(including thin films). This unique luminescence was analyzed and discussed. It is speculated that the cause of this phenomenon is the rigid conjugating structure by hydrogen bonds between siloles molecules. This good luminescence presents them good alternatives in such domains as silane light emitting diodes(LEDs), blue laser diodes, organic electroluminescent diodes, non-linear optical materials, etc. In this section the double reductive cyclization of

the tetra-(phenylethynyl)-silane to give the spiro-compound is also attempted. The result is that all attempts to generate silole spiro-compound gives not the target molecule but polymeric products.

In chapter three, three novel coordination polymers are obtained by self-assembling of 1,1-dimethyl-2,5-dicarboxylsilole with such transitional metals as cadmium(II), cobalt(II) and nickel(II) at room temperature. Single crystal X-ray diffraction shows that Si-C bond of the silole ring is cleaved and the silicon atom together with the two methyl groups are off. Meanwhile, two phenyl groups on the 3,4-positions of the silole ring are isomerized. Consequently, 1,1-dimethyl-2,5-dicarboxylsilole(DCS) has changed into trans-3,4-diphenyl-2,4-dihexalene-diacid (DHA). It is speculated that the cleavage of the Si-C bond is mainly caused by its instability. Although the target coordination polymers are not achieved, this research especially the successful synthesis of the cobalt(II) coordination polymer contributes to the development of geometry and topology undoubtedly. Searching for more proper reaction materials and conditions, *i.e.*, solutions and temperatures to construct coordination polymers with complete silole ring is still on further study.

In chapter four, three silole oligomers, including silole-pyridine(α) copolymer(**4-1**), silole-phenylphosphine copolymer(**4-2**), and silole-*p*-phenyl-dimethylene copolymer(**4-3**), were synthesized by reaction of 2,5-dilithium silole with 2,6-dibromopyridine, dichlorophenylphosphine and α,α' -dichloro-*p*-xylene, respectively. The structure of each oligomer is characterized, the morphology, thermal performance, luminescent property, and electrochemical behavior of which are also discussed. Further study also disclosed the light-transferring property of each oligomer. It is found that **4-3**, which has rigid phenyl rings on the main chain, presents crystal state and best thermal stability, while the other two

oligomers show non-crystal state and relatively poor thermal stability. Study on the electric ability of the oligomers implies that all the oligomers are poor conductors even after adulterating with hydrochloric acid, perchlorate acid and iodine. Probably it is account for the structure of the oligomers and the mode of adulterating. Electrochemical behavior are studied by means of cyclic voltammetry measurements. It indicates that the redox process is irreversible and is affected by solvents when lithium perchlorate is chosen as supporting electrolyte. In this chapter, photoluminescence of the oligomers is studied in detail. All the copolymers emit strong light both in solutions and in solid state including thin films. This excellent luminescent property presents them good application prospect in OLEDs, laser diodes and ultraviolet detectors. The wavelength of maximum emitting depends not only on the factor of environments and existing states of the oligomers but the structure of the main chains. Therefore, the color of the light can be controlled by changing the structure of the oligomers. Feasibility of applying oligomers to agricultural light transferring thin films is also studied. The silole-phenylphosphine copolymer (**4-2**) can absorb the UV light of sunlight and emit violet-blue light which can be easily absorbed by plants. This property permits it possible application in plastic cote in order to improve the yields of crops.

In the final part of the dissertation, chapter five, the innovation of the dissertation is concluded and the prospect of this research is given.

Keywords: silole, carboxyl group, coordination polymer, oligomer, synthesis, photoluminescence, application.

目 录

中文摘要.....	I
英文摘要.....	IV
第一章 绪论.....	1
1.1 噻咯简介及噻咯环独特的电子结构.....	1
1.2 噻咯的芳香性及其金属配合物.....	4
1.3 官能化噻咯合成方法.....	7
1.3.1 炔的内向-内向 (<i>endo-endo</i>) 型分子内还原关环法.....	7
1.3.2 环内金属转换法.....	10
1.3.3 1,4-二锂丁二烯衍生物与氯硅烷交联反应法.....	12
1.3.4 噻咯环上的亲电取代反应法.....	14
1.3.5 炔基硅烷的 1,1-有机硼化反应法.....	17
1.3.6 路易斯酸催化炔分子内氢化硅烷化反应法.....	19
1.3.7 小结.....	20
1.4 含有噻咯环聚合物的研究现状.....	21
1.4.1 聚 2,5-噻咯.....	21
1.4.2 聚 1,1-噻咯.....	22
1.4.3 噻咯与其它 π 电子体系共聚物.....	22
1.5 噻咯小分子及聚合物的应用.....	24
1.5.1 有机发光材料.....	24
1.5.2 有机电子传输材料.....	26
1.5.3 空穴传输材料.....	28
1.5.4 小结.....	28

1.6 本论文的设想与目的.....	29
1.7 参考文献.....	30
第二章 2,5-二羧基噻咯的合成及性能研究.....	44
第一节 苯乙炔基硅烷的合成及表征.....	44
2.1.1 前言.....	44
2.1.2 实验部分.....	45
2.1.2.1 试剂与仪器.....	45
2.1.2.2 合成路线.....	46
2.1.2.3 合成实验.....	47
2.1.3 结构表征.....	48
2.1.3.1 IR 光谱.....	48
2.1.3.2 ¹ HNMR 谱图.....	49
2.1.3.3 ¹³ CNMR 谱图.....	51
2.1.3.4 Ms 谱图.....	53
2.1.3.5 元素分析(EA).....	55
2.1.4 小结.....	55
第二节 2,5-二羧基噻咯的合成及发光性能研究.....	56
2.2.1 前言.....	56
2.2.2 实验部分.....	57
2.2.2.1 试剂与仪器.....	57
2.2.2.2 分析测试方法.....	58
2.2.2.3 合成路线.....	59
2.2.2.4 合成实验.....	60
2.2.3 结构表征.....	61
2.2.3.1 晶体结构.....	61

2.2.3.2	IR 光谱	65
2.2.3.3	¹ H NMR 谱图	66
2.2.3.4	¹³ C NMR 谱图	68
2.2.3.5	Ms 谱图	70
2.2.3.6	元素分析 (EA)	71
2.2.4	结果与讨论	71
2.2.4.1	熔点	71
2.2.4.2	差热分析 (DSC)	72
2.2.4.3	热稳定性 (TG-DTA)	73
2.2.4.4	溶解性	74
2.2.4.5	紫外吸收	74
2.2.4.6	发光性能	75
2.2.5	本节小结	82
2.2.6	参考文献	83

第三章 1,1-二甲基-2,5-二羧基噻咯与过渡金属的配位聚合反应

	研究	87
3.1	前言	87
3.1.1	配位聚合物的组成和结构	87
3.1.2	配位聚合物的合成和研究方法	90
3.1.3	配位聚合物的应用	90
3.1.4	本章目标	91
3.2	实验部分	92
3.2.1	试剂和仪器	92
3.2.2	分析测试方法	93
3.2.3	合成实验	93

3.3 结果与讨论.....	95
3.3.1 配合物 3-1.....	95
3.3.2 配合物 3-2.....	99
3.3.3 配合物 3-3.....	105
3.3.4 DCS 与其它过渡金属离子的配合反应.....	109
3.4 本章小结.....	110
3.5 参考文献.....	110

第四章 噻咯低聚物的合成、性质及应用研究..... 114

4.1 前言.....	114
4.2 实验部分.....	115
4.2.1 试剂与仪器.....	115
4.2.2 测试方法.....	116
4.2.3 合成路线.....	118
4.2.4 合成实验.....	118
4.3 结构表征.....	120
4.3.1 分子量分布.....	120
4.3.2 IR 数据.....	121
4.3.3 ^1H NMR 谱.....	121
4.3.4 ^{13}C NMR 谱.....	123
4.4 结果与讨论.....	124
4.4.1 溶解性研究.....	124
4.4.2 低聚物的形貌.....	125
4.4.3 热力学性能.....	126
4.4.4 发光性能.....	128
4.4.5 电化学性能.....	135

4.4.6 导电性能.....	138
4.4.7 转光膜性能初步探讨.....	139
4.5 本章小结.....	141
4.6 参考文献.....	142
第五章 论文的创新性和研究工作的展望.....	145
5.1 论文的创新性.....	145
5.2 研究工作的展望.....	146
附录：博士期间发表和交流的论文.....	147
致谢.....	148

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