Spectroscopic Properties of Rare Earth Complex Doped in Various Artificial Polymer Structure

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内 容 简 介

聚合物是通过化学键将小分子连接起来而形成的长链状大分子。由这种分子聚集形成的固体材料具有多层次的物质结构，这些结构会影响掺杂其中的各种功能基团的性质。本书将具有不同结构的稀土掺杂聚合物作为研究对象，从理论和实验的角度对这些聚合物进行了光谱分析、掺杂基质结构设计、发光性质与各层次结构的关系以及光量子调控等多方面的研究，包括各种新颖结构的设计和由其产生的各种特异性质。其中光量子调控是迅速发展的宽带通讯领域的关键技术，相应的基础和应用基础研究已形成一个由聚合物科学和光子学交叉而成的新兴学科——光子学聚合物科学。书中介绍的发光调控、三维光学存储和稀土掺杂聚合物光纤的光放大性质等均为光子学聚合物领域的最新进展。虽然本书是非常专业的学术专著，但是通过阅读，读者也能从中了解这一新兴交叉学科的概况。书中还列出了相关原始文献以满足感兴趣的读者进一步了解相关内容的需要。

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总　序

侯建国

（中国科学技术大学校长、中国科学院院士、第三世界科学院院士）

大学最重要的功能是向社会输送人才。大学对于一个国家、民族乃至世界的重要性和贡献度，很大程度上是通过毕业生在社会各领域所取得的成就来体现的。

中国科学技术大学建校只有短短的五十年，之所以迅速成为享有较高国际声誉的著名大学之一，主要就是因为她培养出了一大批德才兼备的优秀毕业生。他们志向高远、基础扎实、综合素质高、创新能力强，在国内外科技、经济、教育等领域做出了杰出的贡献，为中国科大赢得了“科技英才的摇篮”的美誉。

2008年9月，胡锦涛总书记为中国科大建校五十周年发来贺信，信中称赞说：半个世纪以来，中国科学技术大学依托中国科学院，按照全院办校、所系结合的方针，弘扬红专并进、理实交融的校风，努力推进教学和科研工作的改革创新，为党和国家培养了一大批科技人才，取得了一系列具有世界先进水平的原创性科技成果，为推动我国科教事业发展和社会主义现代化建设做出了重要贡献。

据统计，中国科大迄今已毕业的5万人中，已有42人当选中国科学院和中国工程院院士，是同期（自1963年以来）毕业生中当选院士数最多的高校之一。其中，本科毕业生中平均每1000人就产生1名院士和七百多名硕士、博士，比例位居全国高校之首。还有众多的中青年才俊成为我国科技、企业、教育等领域的领军人物和骨干。在历年评选的“中国青年五四奖章”获得者中，作为科技界、科技创新型企业界青年才俊代表，科大毕业生已连续多年榜上有名，获奖总人数位居全国高校前列。鲜为人知的是，有数千名优秀毕业生踏上国防战线，为科技强军做出了

重要贡献，涌现出二十多名科技将军和一大批国防科技中坚。

为反映中国科大五十年来人才培养成果，展示毕业生在科学研究中的最新进展，学校决定在建校五十周年之际，编辑出版《中国科学技术大学校友文库》，于2008年9月起陆续出书，校庆年内集中出版50种。该《文库》选题经过多轮严格的评审和论证，入选书稿学术水平高，已列为"十一五"国家重点图书出版规划。

入选作者中，有北京初创时期的毕业生，也有意气风发的少年班毕业生；有"两院"院士，也有IEEE Fellow；有海内外科研院所、大专院校的教授，也有金融、IT行业的英才；有默默奉献、矢志报国的科技将军，也有在国际前沿奋力拼搏的科研将才；有"文革"后留美学者中第一位担任美国大学系主任的青年教授，也有首批获得新中国博士学位的中年学者……在母校五十周年华诞之际，他们通过著书立说的独特方式，向母校献礼，其深情厚意，令人感佩！

近年来，学校组织了一系列关于中国科大办学成就、经验、理念和优良传统的总结与讨论。通过总结与讨论，我们更清醒地认识到，中国科大这所新中国亲手创办的新型理工科大学所肩负的历史使命和责任。我想，中国科大的创办与发展，首要的目标就是围绕国家战略需求，培养造就世界一流科学家和科技领军人才。五十年来，我们一直遵循这一目标定位，有效地探索了科教紧密结合、培养创新人才的成功之路，取得了令人瞩目的成就，也受到社会各界的广泛赞誉。

成绩属于过去，辉煌须待开创。在未来的发展中，我们依然要牢牢把握"育人是大学第一要务"的宗旨，在坚守优良传统的基础上，不断改革创新，提高教育教学质量，早日实现胡锦涛总书记对中国科大的期待：瞄准世界科技前沿，服务国家发展战略，创造性地做好教学和科研工作，努力办成世界一流的研究型大学，培养造就更多更好的创新人才，为夺取全面建设小康社会新胜利、开创中国特色社会主义事业新局面贡献更大力量。

是为序。

2008年9月

Preface

Rare earth ions have received great interest due to their intense emission peaks (half-maximum width <10 nm) in the visible and near-infrared region, and have been widely used in a variety of applications. Especially in the application of the optical signal amplification, much interest has been concentrated on rare earth doped inorganic materials because they are compatible with the present communication system.

Since the mid 90s of last century, photonics polymer has been well developed because polymer optical fiber (POF) was demonstrated in local area communications, and became a promising candidate for fiber to the desktop. Besides POF, many photonics polymers and their devices have been designed and exploited, which can be used in production, transmission, storage, display and modulation of photons, because photonics polymers are of characteristics of light weight, easy process and low price. The increasing awareness of the utility of photonics polymers also led to the work on rare earth complex doped polymers.

It has been known that luminescence of rare earth complexes is heavily affected by ligand absorption, ligand-to-ion energy transfer and material structure they doped in. In recent years, controlling luminescence of rare earth complex doped polymer by constructing polymer structure has received more and more interest to meet the need of novel photonics devices, because, there is much unknown that needs to be exploited in this developing field. For example, aggregates of rare earth complexes will be formed in polymer in this developing field, which are resulted from the difference in inherent energy between complexes and polymers. Efficiency of luminescence of rare earth complexes would be heavily quenching by such aggregates due to their quenching action. In order to get high efficiency, it

is necessary to investigate the existence and domain size of such aggregates in polymer samples, which depend on fabrication technique and process for the polymers. It has also been realized that micro-structure of polymer can control luminescence of rare earth complexes doped in the polymer. That is, by adjusting the micro-structure, the luminescence can be modulated, which has potential application in photonics devices.

Under this circumstance, in the past decade, research on rare earth complex doped polymers was carried out as one of photonics polymers in our group aiming at various photonics devices, such as amplifiers and lasers. Started with synthesis and characterization of rare earth complex doped polymers, research work in our group was mainly focused on spectroscopic properties of rare earth complex doped in polymers, and then gradually went deep into studies on relationship between luminescence and various polymer structures, including nanoparticles, micro-vesicles and fiber waveguides. During this period, it was gradually realized from the work that structural construction of rare earth containing polymer, from molecular level to wave-guide level, is necessary for application in photonics devices. This realization will guide our future work in developing new photonic devices based on rare earth containing polymers.

This book is composed of 9 chapters, and the content in each chapter is relatively independent with each other, although the main theme is still around of rare earth complex doped polymers. Chapter 1 provides a short description to the synthesis and characterization of rare earth complexes and their doped polymers. Chapter 2 deals with spectroscopic properties of rare earth complex doped polymer using Judd-Ofelt theory. During measurement of fluorescence, a red-shift in excitation was observed, and Chapter 3 presents a quantitative model to rectify this effect when fluorescence is measured. From Chapter 4 to Chapter 9, various unique polymer structures are introduced, with the main point on the modulation of luminescence from rare earth complexes in such unique structures. Most of the work has been published in academic journals, and part unpublished, which is concerned with some details and newly development in the research. These novel exploitations are expected to be published elsewhere, however, related phenomena are so close to the

theme of this book, it is reasonable to present them here.

Photonics polymer is a cross-discipline that encompasses photonics and polymer science. The challenge in polymer science is the application of photonics theory and its fundamental techniques. It is a demanding task, and requires the best approaches that photonics can provide. I gratefully here acknowledge the beneficial discussion and collaboration from Prof. Guangchan Guo (Photonics), Prof. Chi Wu (Polymer chemical physics), Prof. Hai Ming (Optical information), Prof. Ming Yin (Luminescence), Prof. Yingmei Li (Bio-photonics), Prof. Chen Gao (Condensed state physics), Prof. Keyi Wang (Near field optics), and Prof. Bin Zhu (Fiber optics). Without their help, it is impossible to fulfill the work in such a cross-discipline.

The research work concerned in this book was financially supported by National Natural Science foundation of China and Chinese Academy of Sciences, which is gratefully acknowledged here. There were many Ph. D candidates who dedicated their talent and endeavor to this creative study. Without their devotion, this work can not be accomplished. They are Hao Liang, Biao Chen, Jie Xu, Hongfang Jiu, Hui Zhao, Youyi Sun, Wei Su, Si Wu, Qing Yan, Yanhua Luo and Wenxuan Wu. Other students in my group also took part in discussion concerning this work. I sincerely express my gratitude here for the diligence and efforts made by all of them.

Finally, I would like to dedicate this book to my Alma Mater, University of Science and Technology of China, celebrating her 50 anniversary in 2008. In this campus, I have been studying, researching and living for nearly 30 years. This book will constitute a fitting memorial to these days.

Contents

Chapter 1 Synthesis and characterization of rare earth complex doped polymers

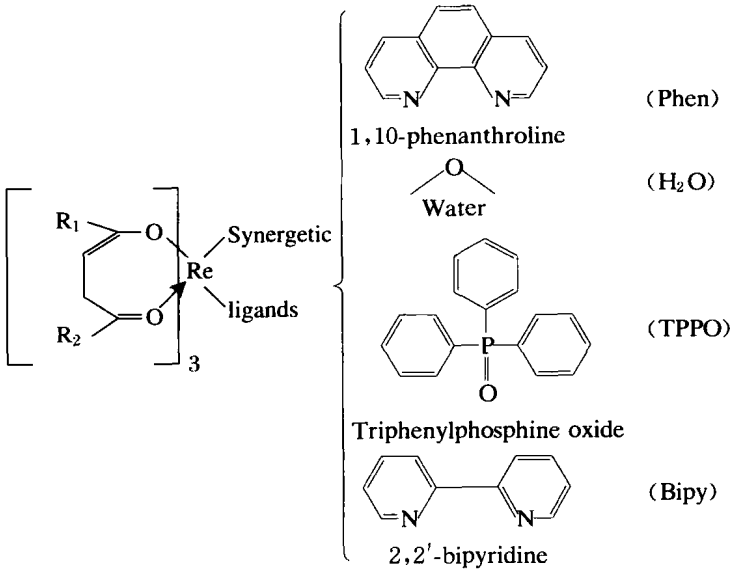
Rare earth ions have received great interest due to their intense emission peaks (half-maximum width $<$ 10 nm) in the visible and near-infrared region, and have been widely used in a variety of areas[1], such as fluoroimmunoassays[2], energy harvesting devices[3] and optical signal amplification[4], etc. Study on spectroscopic properties of rare earth complexes has been made a remarkable growth since intramolecular energy transfer within rare earth complexes was investigated in 1942[5]. At that time, polymer science and technology was just established as a new field of artificial materials. Since the earlier 70s last century, introducing rare earth complexes into polymer has been an active field interested by both polymer science and material science because this new kind of material combined distinguished luminescence of rare earth complexes with easy process, low price and light weight of polymers, especially in the application of photonics polymers[6~8]. Before detailed discussion about spectroscopic properties of the complexes, this chapter will present a short review about our work concerning synthesis and characterization of rare earth complex doped polymers.

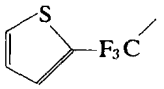
1.1 Synthesis of rare earth complex doped polymer

Comparing to other rare earth compounds, there are two advantages of rare earth complexes: one is that the complexes are of good

compatibility with polymers, and the other is that intramolecular energy transfer can enhance efficiency of luminescence of corresponding rare earth ions[5,9,10]. In order to ensure the second to be fulfilled, suitable ligands should be decided before synthesis of rare earth complexes.

In our research work, several ligands were selected to synthesize the complexes, which are shown in Figure 1.1. Detailed discussion about the relationship between their structure and properties will be carried out in corresponding chapters, and here a simple description for their synthesis is presented.



Biketone ligands	Symbol	R_1	R_2
Benzoylactonate	BA		
Dibenzoylmethanate	DBM		
Thenoyltrifluoroacetylactonate	TTA		

Re = Eu^{3+}, Tb^{3+}, Sm^{3+}, Pr^{3+}, Nd^{3+}, La^{3+}, Ce^{3+}, Y^{3+}, Er^{3+}, Gd^{3+}, Dy^{3+}

Figure 1.1 The structure of rare earth complexes studied in this book.

Synthesis for all of complexes are performed in a similar way that can

be found in the literature[11]. For example, the synthesis route for $Re(DBM)_3Phen$ can be seen in Scheme 1, from which it can be seen that the route can be divided into three steps:

(ⅰ) Synthesis of oxygen-containing ligands;

(ⅱ) Synthesis of complexes with water as synergetic ligands;

(ⅲ) Substitute water by organic ligand, such as 1,10-phenanthroline.

$$\begin{cases} Ph{-}CO{-}C \xrightarrow{NaC_2H_5O/C_2H_6O} Ph{-}CO{-}CH_2{-}CO{-}P \\ Re(NO_3)_3 + 6HNO_3 \longrightarrow 2Re(NO_3)_3 + 3H_2O \\ Re(NO_3)_3 + 3DBM \xrightarrow{NaOH/C_2H_6O} 3NaNO_3 + Re(DBM)_3 \cdot 2H_2O \\ Re(DBM)_3 \cdot 2H_2O + Phen \xrightarrow{C_2H_6O,\ backflow} Re(DBM)_3 \cdot Phen \end{cases}$$

Scheme 1.1 Synthesis route of complexes of $Re(DBM)_3Phen$ by chemical reaction.

It is worth to note here that there must be a little change in reaction conditions, such as solvents, temperature and pH, when different rare earth ion was adopted during preparation of the complexes. Details for controlling these can be traced in many relative published literatures[11]. All of the products obtained during our work have been characterized by infrared spectrum (IR), nuclear magnetic resonance (NMR) and elementary analysis. Results showed that expected complexes were obtained with spectrum pure.

Similar to organic dyes, rare earth complexes are relatively compatible with organic polymer comparing to inorganic rare earth ions. Generally speaking, there are three methods that have been used to introduce the complexes into polymer matrix. First, the complexes can be directly mixed with polymer[12]; Second, the rare earth containing monomer was firstly synthesized, and then polymerized or copolymerized with other monomers[13]; Third, by using organic salt of rare earth ions as dopant, compatible rare earth doped polymer can be obtained by adjusting organic groups[14], although such salts can be doped in polymers with low concentration. For rare earth complexes there is good compatibility between the complexes and polymers, and the concentration of the complexes can reach very high value.

During preparation of rare earth complex doped polymers, the complex was firstly dissolved into monomer (usually methyl

methacrylate, MMA, in our work), and then the mixture solution was solidification by bulk polymerization. The bulk polymers could be further used as performs for POF and re-dissolved into solution used in preparation of polymer film samples.

Because there is still a little difference in coherence energy between the complexes and polymers, homogeneous morphology can not obtained in such a way of preparation. Corresponding characterization should be done before explanation of any physical properties of the rare earth complex doped polymers.

1.2 Uniformity and thermal stability of rare earth complex doped polymer

There have been many models to account for wide ranges of experimentally observed phenomena for the ion doped polymer[15], different from which the rare earth complex doped polymer is expected to have little aggregates between ions because of organic ligands around ions. However, aggregates between complexes may be formed, which would cause heavy attenuation of photonics polymers if the aggregate is large enough to wavelength scale. Several methods have been developed to investigate such a morphology problem of rare earth complex doped polymer in our group, and some examples will be discussed in detail below.

1.2.1 X-ray diffraction of rare earth complex doped PMMA

Figure 1.2 shows the X-ray diffraction spectra of the samples (the concentration of $Eu(TTA)_3(TPPO)_2$ in PMMA is 3.0 wt%). All the sharp XRD peaks of pure $Eu(TTA)_3(TPPO)_2$ (b) has disappeared in the X-ray diffraction of $Eu(TTA)_3(TPPO)_2$ doped PMMA (a) made by the bulk polymerization described above.

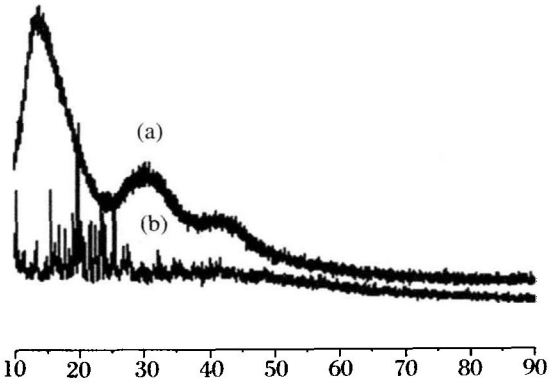


Figure 1.2 X-ray diffraction of (a) $Eu(TTA)_3(TPPO)_2$ doped PMMA and (b) pure $Eu(TTA)_3(TPPO)_2$. Adopted with permission from J. Guan *et al.*, *Journal of Non-Crystalline Solids*, 351, 849. Copyright @ 2005, Elsevier Science.

The three peaks of curve a are the characteristic diffuse scattering peaks of pure amorphous polymethyl methacrylate (PMMA). This indicates that the formation of a solid solution of $Eu(TTA)_3(TPPO)_2$ in PMMA and the doped PMMA is amorphous. Similar results also can be attained in other rare earth complex doped PMMA. It is worth to note that a care should be taken when explaining the result from X-ray measurement because low doping concentration can also result in no sensible diffraction peaks. Usually, other experimental methods should be adopted to obtain an authentic morphology characterization.

1.2.2 Near-field scanning analysis of rare earth complex doped PMMA

Near-field scanning optical microscopy (NSOM) has the ability to achieve a high spatial-resolution optical contrast and simultaneously measure the sample topography and transmission intensity. In this way, the effect produced by the wave of the surface can be eliminated. Due to this reason, it has been increasingly used for the investigation of nanodomain aggregates and even small-molecule systems[16]. By comparing the variation of transmission intensity with topography of the sample, the fractural cluster formation can be investigated[17]. A high doping concentration sample (the concentration of Eu-ion is 10000 ppm-