

综述

稀土发光材料在荧光成像中的应用

吴伯岳, 严秀平

南开大学化学学院分析科学研究中心, 天津 300071

摘要:

稀土发光材料由于具有荧光寿命长、发射峰半峰宽窄和Stokes位移大等发光性质, 在生命科学研究的各个领域, 包括荧光免疫分析、离子识别、蛋白质活性测定、核酸检测等, 有着广泛而重要的应用前景。本文以稀土配合物、稀土掺杂上转换材料和长余辉材料为代表, 就当前稀土发光材料的发光性质及其在生物成像标记方面的研究做一综述, 并对稀土发光材料, 特别是长余辉材料, 在荧光成像应用过程中存在的主要问题进行了讨论。

关键词: 稀土发光材料 荧光成像 稀土配合物 上转换材料 长余辉材料

Lanthanide Luminescence for Bioimaging

WU Boyue, YAN Xiuping

Research Center for Analytical Sciences, College of Chemistry, Nankai University, Tianjin 300071, China

Abstract:

Rare earth luminescent materials have long-life fluorescent emission, small full-width half-maximum (FWHM), and large Stokes shift, thereby have been receiving great attention in diverse applications, including fluorescence immunoassay, anion recognition, protein activity determination, nucleic acid detection. In this paper, the applications of rare earth complexes, lanthanide-doped upconversion nanoparticles, and persistent luminescence nanoparticles in bioimaging are reviewed, the main problems of the rare earth luminescent materials, particularly long persistent phosphors in fluorescent imaging are also discussed.

Keywords: Lanthanide luminescence Fluorescent imaging Lanthanide complex Upconversion luminescence Persistent luminescence nanoaprticles

收稿日期 2011-01-30 修回日期 2011-03-14 网络版发布日期

DOI: 10.3724/SP.J.1260.2011.00289

基金项目:

“973”计划项目(2011CB707703)

通讯作者: 严秀平, 电话: (022)23506075, E-mail: xiupingyan@gmail.com

作者简介:

作者Email: xiupingyan@gmail.com

参考文献:

1. Klostranec JM, Chan WCW. Quantum dots in biological and biomedical research: Recent progress and present challenges. *Adv Mater*, 2006, 18(15): 1953-1964
2. Smith AM, Gao X. Multicolor quantum dots for molecular diagnostic of cancer. *Expert Rev Mol Diagn*, 2006, 6(2): 231-244
3. Medintz IL, Uyeda HT, Goldman ER, Mattoussi H. Quantum dot bioconjugates for imaging, labelling and sensing. *Nat Mater*, 2005, 4(6): 435-446
4. Tang B, Huang H. Highly sensitive and selective near-infrared probe for zinc and its application to macrophage cells. *Chem Comm*, 2006, 34: 3609-3611
5. Kim S, Lim YT. Near-infrared fluorescent type II quantum dots for sentinel lymph node mapping. *Nat*

扩展功能

本文信息

- ▶ Supporting info
- ▶ [PDF\(1196KB\)](#)
- ▶ [\[HTML全文\]](#)
- ▶ [参考文献\[PDF\]](#)
- ▶ [参考文献](#)

服务与反馈

- ▶ [把本文推荐给朋友](#)
- ▶ [加入我的书架](#)
- ▶ [加入引用管理器](#)
- ▶ [引用本文](#)
- ▶ [Email Alert](#)
- ▶ [文章反馈](#)
- ▶ [浏览反馈信息](#)

本文关键词相关文章

- ▶ [稀土发光材料](#)
- ▶ [荧光成像](#)
- ▶ [稀土配合物](#)
- ▶ [上转换材料](#)
- ▶ [长余辉材料](#)

本文作者相关文章

- ▶ [吴伯岳](#)
- ▶ [严秀平](#)

PubMed

- ▶ [Article by Wu, B. Y.](#)
- ▶ [Article by Yan, X. P.](#)

Biotechnol, 2004, 22(1): 93~97

6. Chan WH, Shao NH, Lu PZ. CdSe quantum dots induce apoptosis in human neuroblastoma cells via mitochondrial- dependent pathways and inhibition of survival signals. *Toxic Lett*, 2006, 167(3): 191~200
7. Kirchner C, Liedl T, Kudera S, Pellegrino T, Munoz JA, Gaub HE. Cytotoxicity of colloidal CdSe and CdSe/ZnS nanoparticles. *Nano Lett*, 2005, 5(2): 331~338
8. Escribano P, Julián-López B, Planelles-Aragó J, Cordoncillo E, Viana B, Sanchez C. Photonic and nanobiophotonic properties of luminescent lanthanide-doped hybrid organic- inorganic materials. *J Mater Chem*, 2008, 18(1): 23~40
9. Bünzli J-CG, Comby S, Chauvin AS, Vandevyver CDB. New opportunities for lanthanide luminescence. *Biomaterials*, 2007, 25(3): 714~729
10. Hemmilä I, Mikkola VM. Time-resolution in fluorometry technologies, labels, and applications in bioanalytical assays. *Crit Rev Clin Lab Sci*, 2001, 38(6): 441~519
11. Butcher H, Kennette W, Collins O, Demoor J, Koropatnick JA. Sensitive time-resolved fluorescent immunoassay for metallothionein protein. *J Immunol Methods*, 2003, 272(1-2): 247~256
12. Charbonnière LJ, Hildebrandt N, Ziessel RF, Löhmansröben HG. Lanthanides to quantum dots resonance energy transfer in time-resolved fluoro-immunoassays and luminescence microscopy. *J Am Chem Soc*, 2006, 128(39): 12800~12809
13. Kimura H, Mukaida M, Watanabe M, Hashino K, Nishioka T, Tomino Y, Yoshida KI, Matsumoto K. Quantitative evaluation of time-resolved fluorescence microscopy using a new europium label: Application to immunofluorescence imaging of nitrotyrosine in kidneys. *Anal Biochem*, 2008, 372(1): 119~121
14. Montalti M, Prodi L, Zaccaroni N, Charbonnière LJ, Douce L, Ziessel RA. Luminescent anion sensor based on a europium hybrid complex. *J Am Chem Soc*, 2001, 123(50): 12694~12695
15. Yamada T, Shinoda S, Tsukube H. Anion sensing with luminescent lanthanide complexes of tris(2-pyridylmethyl)amines: Pronounced effects of lanthanide center and ligand chirality on anion selectivity and sensitivity. *Chem Commun*, 2002, 11: 1218~1219
16. Gunnlaugsson T, Leonard JP. H⁺, Na⁺ and K⁺ modulated lanthanide luminescent switching of Tb(III) based cyclen aromatic diaza-crown ether conjugates in water. *Chem Commun*, 2003, 19: 2424~2425
17. Li C, Law GL, Wong WT. Luminescent Tb³⁺ complex with pendant crown ether showing dual-component recognition of H⁺ and K⁺ at multiple pH windows. *Org Lett*, 2004, 6(26): 4841~4844
18. Ziessel R, Charbonnière LJ. Lanthanide probes for luminescence microscopy and anion sensing. *J Alloy Compd*, 2004, 374(1-2): 283~288
19. Thibon A, Pierre VA. Highly selective luminescent sensor for the time-gated detection of potassium. *J Am Chem Soc*, 2009, 131(2): 434~435
20. Wu M, Lin ZH, Schäferling M, Dürkop A, Wolfbeis OS. Fluorescence imaging of the activity of glucose oxidase using a hydrogen-peroxide-sensitive europium probe. *Anal Biochem*, 2005, 340(1): 66~73
21. Terai T, Kikuchi K, Iwasawa SY, Kawabe T, Hirata Y, Urano Y, Nagano T. Modulation of luminescence intensity of lanthanide complexes by photoinduced electron transfer and its application to a long-lived protease probe. *J Am Chem Soc*, 2006, 128(21): 6938~6946
22. Schäferling M, Wolfbeis OS. Europium tetracycline as a luminescent probe for nucleoside phosphates and its application to the determination of kinase activity. *Chem Eur J*, 2007, 13(15): 4342~4349
23. Schrenkhammer P, Rosnizeck IC, Duerkop A, Wolfbeis OS, Schäferling M. Time-resolved fluorescence-based assay for the determination of alkaline phosphatase activity and application to the screening of its inhibitors. *J Biomol Screen*, 2008, 13(1): 9~16
24. Duerkop A, Aleksandrova D, Scripinets Y, Yegorova A, Vityukova E. Sensitive terbium probes for luminescent determination of both alkaline phosphatase and codeine phosphate. *Ann N Y Acad Sci*, 2008, 1130: 172~178
25. Bobba G, Frias JC, Parker D. Highly emissive, nine-coordinate enantiopure lanthanide complexes incorporating tetraazatriphenylenes as probes for DNA. *Chem Commun*, 2002, 8: 890~891
26. Johansson MK, Cook RM, Xu J, Raymond KN. Time gating improves sensitivity in energy transfer assays with terbium chelate/dark quencher oligonucleotide probes. *J Am Chem Soc*, 2004, 126(50): 16451~16455
27. Yegorova A, Karasyov A, Duerkop A, Ukrainets I, Antonovich V. New luminescent terbium complex for the determination of DNA. *Spectrochimica Acta Part A: Molecul Biomolecul Spectro*, 2005, 61(1-2): 109~116
28. Nishioka T, Yuan JL, Yamamoto YJ, Sumitomo K, Wang Z, Hashino K, Hosoya C, Ikawa K, Wang GL, Matsumoto K. New luminescent europium (III) chelates for DNA labeling. *Inorg Chem*, 2006, 45(10): 4088~4096
29. Hashino K, Ikawa K, Ito M, Hosoya C, Nishioka T, Makiuchi M, Matsumoto K. Application of a fluorescent lanthanide chelate label on a solid support device for detecting DNA variation with ligation-based assay. *Anal Biochem*, 2007, 364(1): 89~91
30. Laitala V, Ylikoski A, Raussi HM, Ollikka P, Hemmilä I. Time-resolved detection probe for

- homogeneous nucleic acid analyses in one-step format. *Anal Biochem*, 2007, 361(1): 126~131
31. Bünzli JCG. Lanthanide luminescence for biomedical analyses and imaging. *Chem Rev*, 2010, 110(5): 2729~2755
 32. Soini E, Lövgren T, Reimer CB. Time-resolved fluorescence of lanthanide probes and applications in biotechnology. *Critic Rev Anal Chem*, 1987, 18(2): 1547~6510
 33. Hemmilä I, Laitala V. Progress in lanthanides as luminescent probes. *J Fluoresc*, 2005, 15(4): 529~542
 34. Scurlock RD, Wang B, Ogilby PR, Sheats JR, Clough RL. Singlet oxygen as a reactive intermediate in the photodegradation of an electroluminescent polymer. *J Am Chem Soc*, 1995, 117(41): 10194~10202
 35. Song B, Wang GL, Tan MQ, Yuan JL. A europium(III) complex as an efficient singlet oxygen luminescence probe. *J Am Chem Soc*, 2006, 128(41): 13442~13450
 36. Song B, Wang GL, Yuan JL. A new europium chelate-based phosphorescence probe specific for singlet oxygen. *Chem Commun*, 2005, 28: 3553~3555
 37. Tan MQ, Song B, Wang GL, Yuan JL. A new terbium(III) chelate as an efficient singlet oxygen fluorescence probe. *Free Radical Bio Med*, 2006, 40(9): 1644~1653
 38. Song CH, Ye ZQ, Wang GL, Yuan JL, Guan YF. A lanthanide complex-based ratiometric luminescent probe specific for peroxyxynitrite. *Chem Eur J*, 2010, 16(22): 6464~6472
 39. Ye ZQ, Wang GL, Chen JX, Fu XY, Zhang WZ, Yuan JL. Development of a novel terbium chelate-based luminescent chemosensor for time-resolved luminescence detection of intracellular Zn^{2+} ions. *Biosens Bioelectron*, 2010, 26(3): 1043~1048
 40. Hanaoka K, Kikuchi K, Kojima H, Urano Y, Nagano T. Development of a zinc ion-selective luminescent lanthanide chemosensor for biological applications. *J Am Chem Soc*, 2004, 126(39): 12470~12476
 41. Hanaoka K, Kikuchi K, Kobayashi S, Nagano T. Time-resolved long-lived luminescence imaging method employing luminescent lanthanide probes with a new microscopy system. *J Am Chem Soc*, 2007, 129(44): 13502~13509
 42. Vaisanen V, Harma H, Lilja H, Bjartell A. Time-resolved fluorescence imaging for quantitative histochemistry using lanthanide chelates in nanoparticles and conjugated to monoclonal antibodies. *Luminescence*, 2000, 15(6): 389~397
 43. Connally R, Veal D, Piper J. Time-resolved fluorescence microscopy using an improved europium chelate BHHST for the in situ detection of *Cryptosporidium* and *Giardia*. *Microsc Res Tech*, 2004, 64(4): 312~322
 44. Wu J, Ye ZQ, Wang GL, Jin DY, Yuan JL, Guan YF, Pipe J. Visible-light-sensitized highly luminescent europium nanoparticles: Preparation and application for time-gated luminescence bioimaging. *J Mater Chem*, 2009, 19(9): 1258~1264
 45. Jiang LN, Wu J, Wang GL, Ye ZQ, Zhang WZ, Jin DY, Yuan JL, Piper J. Development of a visible-light-sensitized europium complex for time-resolved fluorometric application. *Anal Chem*, 2010, 82(6): 2529~2535
 46. Yu JH, Parker D, Pal R, Poole RA, Cann MJ. A europium complex that selectively stains nucleoli of cells. *J Am Chem Soc*, 2006, 128(7): 2294~2299
 47. Pal R, Parker D. A single component ratiometric pH probe with long wavelength excitation of europium emission. *Chem Commun*, 2007, 5: 474~476
 48. Bünzli JCG, Chauvin AS, Vandevyver CDB, Song B, Comby S. Lanthanide bimetallic helicates for in vitro imaging and sensing. *Ann N Y Acad Sci*, 2008, 1130: 97~105
 49. 黄池宝, 樊江莉, 彭孝军, 孙世国. 双光子荧光探针研究及其应用. *化学进展*, 2007, 19(11): 1806~1812
Huang CB, Fan JL, Peng XJ, Sun SG. Progress and application of two-photon fluorescent probes. *Prog Chem*, 2007, 19(11): 1806~1812
 50. Picot A, D'Aléo A, Baldeck PL, Grichine A, Duperray A, Andraud C, Maury O. Long-lived two-photon excited luminescence of water-soluble europium complex: Applications in biological imaging using two-photon scanning microscopy. *J Am Chem Soc*, 2008, 130(5): 1532~1533
 51. Law GL, Wong KL, Man CWY, Wong WT, Tsao SW, Lam MHW, Lam PKS. Emissive terbium probe for multiphoton in vitro cell imaging. *J Am Chem Soc*, 2008, 130(12): 3714~3715
 52. Auzel F. Upconversion and anti-stokes processes with f and d ions in solids. *Chem Rev*, 2004, 104(1): 139~173
 53. Chen GY, Zhang YG, Somesfalean G, Zhang ZG, Sun Q, Wang FP. Two-color upconversion in rare-earth-ion-doped ZrO_2 nanocrystals. *Appl Phys Lett*, 2006, 89:163105~163107
 54. Sivakumar S, Diamente PR, van Veggel FCJM. Silica-coated Ln^{3+} -doped LaF_3 nanoparticles as robust down- and upconverting biolabels. *Chem Eur J*, 2006, 12(22): 5878~5884
 55. Heer S, Kümpe K, Güdel HU, Haase M. Highly efficient multicolour upconversion emission in transparent colloids of lanthanide-doped $NaYF_4$ nanocrystals. *Adv Mater*, 2004, 16(23-24): 2102~2105
 56. Chen GY, Somesfalean G, Zhang ZG, Sun Q, Wang FP. Ultraviolet upconversion fluorescence in rare-earth-ion-doped Y_2O_3 induced by infrared diode laser excitation. *Opt Lett*, 2007, 32(1): 87~89
 57. Altino?lu EI, Russin TJ, Kaiser JM, Barth BM, Eklund PC, Kester M, Adair JH. Near-infrared emitting

fluorophore-doped calcium phosphate nanoparticles for in vivo imaging of human breast cancer. ACS Nano, 2008, 2(10): 2075~2084

58. Vetrone F, Boyer JC, Capobianco JA, Speghini A, Bettinelli M. Concentration-dependent near-infrared to visible up-conversion in nanocrystalline and bulk $Y_2O_3:Er^{3+}$. Chem Mater, 2003, 15(14): 2737~2743

59. Pires AM, Serraa OA, Heer S, Güdel HU. Low-temperature upconversion spectroscopy of nanosized $Y_2O_3:Er,Yb$ Phosphor. J Appl Phys, 2005, 98(6): 063529

60. Pires AM, Serraa OA, Davolos MR. Morphological and luminescent studies on nanosized Er, Yb-yttrium oxide up-converter prepared from different precursors. J Lumin, 2005, 113(3-4): 174~182

61. Zijlmans HJMAA, Bonnet J, Burton J, Kardos K, Vail T, Niedbala RS, Tanke HJ. Detection of cell and tissue surface antigens using up-converting phosphors: A new reporter technology. Anal Biochem, 1999, 267(1): 30~36

62. Wang M, Wang M, Mi CC, Wang WX, Liu CH, Wu YF, Xu ZR, Mao CB, Xu SK. Immunolabeling and NIR-excited fluorescent imaging of HeLa cells by using $NaYF_4:Yb,Er$ upconversion nanoparticles. ACS Nano, 2009, 3(6): 1580~1586

63. Lim SF, Riehn R, Ryu WS, Khanarian N, Tung CK, Tank D, Austin RH. In vivo and scanning electron microscopy imaging of upconverting nanophosphors in Caenorhabditis elegans. Nano Lett, 2006, 6(2): 169~174

64. Chatterjee DK, Jalil RA, Zhang Y. Upconversion fluorescence imaging of cells and small animals using lanthanide doped nanocrystals. Biomaterials, 2008, 29(7): 937~943

65. Jalil RA, Zhang Y. Biocompatibility of silica coated $NaYF_4$ upconversion fluorescent nanocrystals. Biomaterials, 2008, 29(30): 4122~4128

66. Kumar R, Nyk M, Ohulchanskyy TY, Flask CA, Prasad PN. Combined optical and MR bioimaging using rare Earth ion doped $NaYF_4$ nanocrystals. Adv Funct Mater, 2009, 19(6): 853~859

67. Chermont QM, Chanéac C, Seguin J, Pellél F, Maîtrejean S, Jolivet J-P, Gourier D, Bessodes M, Scherman D. Nanoprobes with near-infrared persistent luminescence for in vivo imaging. Proc Natl Acad Sci USA, 2007, 104(22): 9266~9271.

68. Wu BY, Wang HF, Chen JT, Yan XP. Fluorescence resonance energy transfer inhibition for α -fetoprotein excreted during cancer cell growth using functionalized persistent luminescence nanoparticles. J Am Chem Soc, 2011, 133(4): 686~688

本刊中的类似文章

1. 乐加昌, 庞素珍, 孙文芳, 董世明, 王夺元. 类卟啉稀土配合物对于小鼠腹水肝癌细胞光敏损伤的研究[J]. 生物物理学报, 1994, 10(4): 634-640
2. 杨杰, 张智红, 骆清铭. 荧光蛋白研究进展[J]. 生物物理学报, 2010, 26(11): 1025-1035
3. 马喜波, 田捷, 杨鑫, 秦承虎, 朱守平, 薛贞文. 多模态分子影像对肝癌进展和血管生成的研究[J]. 生物物理学报, 2011, 27(4): 355-364

文章评论

反馈人	<input type="text"/>	邮箱地址	<input type="text"/>
反馈标题	<input type="text"/>	验证码	<input type="text"/> 5203