(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 155 095 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
22.09.2004 Bulletin 2004/39

(21) Application number: **00901735.1**

(22) Date of filing: **31.01.2000**

(51) Int Cl.[7]: **C09K 11/06**

(86) International application number:
PCT/GB2000/000268

(87) International publication number:
WO 2000/044851 (03.08.2000 Gazette 2000/31)

(54) ELECTROLUMINESCENT MATERIALS

ELEKTROLUMINESZENZMATERIALEN

MATERIAUX ELECTROLUMINESCENTS

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

(30) Priority: **01.02.1999 GB 9901971**

(43) Date of publication of application:
21.11.2001 Bulletin 2001/47

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WO-A-98/55561 **WO-A-98/58037**

- **TEMPLETON, LIESELOTTE K. ET AL: "Anomalous scattering by praseodymium, samarium and gadolinium and structures of their ethylenediaminetetraacetate (edta) salts" ACTA CRYSTALLOGR., SECT. B (1982), B38(8), 2155-9 , XP002139485**
- **ARMAROLI N ET AL: "Luminescence properties of Eu, Tb, and Gdcomplexes of the hexadentate N-donor podand tris-3-(2-pyridyl)pyrazol-1ylhydroborate" CHEMICAL PHYSICS LETTERS,NL,AMSTERDAM, vol. 5-6, no. 276, 29 September 1997 (1997-09-29), pages 435-440, XP002074915**
- **"ULTRAVIOLET ELECTROLUMINESCENCE FROM AN ORGANIC LIGHT EMITTING DIODE" ADVANCED MATERIALS,DE,VCH VERLAGSGESELLSCHAFT, WEINHEIM, vol. 7, no. 11, 1 November 1995 (1995-11-01), pages 900-903, XP000537408 ISSN: 0935-9648**

EP 1 155 095 B1

Description

[0001] The present invention relates to electroluminescent materials which can emit light in the ultra-violet region of the spectrum and devices made using such materials.

[0002] Materials which emit light when an electric current is passed through them are well known and used in a wide range of display applications and organic polymers have been proposed as useful in electroluminescent devices, but using these polymers it is not possible to obtain pure colours, they are expensive to make and have a relatively low efficiency.

[0003] Another compound which has been proposed is aluminium quinolate, but this requires dopants to be used to obtain a range of colours and has a relatively low efficiency.

[0004] In an article in Chemistry letters pp 657-660, 1990 Kido et al disclosed that a terbium (III) acetyl acetonate complex was green electroluminescent and in an article in Applied Physics letters 65 (17) 24 October 1994 Kido et al disclosed that a europium (III) triphenylene diamine complexes was red electroluminescent but these were unstable in atmospheric conditions and difficult to produce as films.

[0005] The complexes disclosed in these articles had a relatively low photoluminescent efficiency and were only able to produce green or red light and other colours could not be produced.

[0006] An article by Templeton, Lieselottte et al in Acta Crystallogr. Sect. B (1982), B38(8) 2155-9 discloses the sodium salts of gadolinium EDTA but does not disclose that they are electroluminescent.

[0007] Patent Applications WO 98/58037 and WO 98/55561 disclose electroluminescent materials which emit light in the visible spectrum and disclose electroluminescent devices incorporating these materials and WO 98/55561 discloses gadolinium complexes that can emit electroluminescence light in the UV spectrum and discloses a gadolinium complex of a polyamine.

[0008] An article in Chemical Physics letters 276 (1997) 435-440 by Amaroli et al discloses a gadolinium complex of pyazolylborate polyamine which emits light in the 400nm to 500nm range as fluorescence but there is no diclosure of electroluminescence.

[0009] The wavelength of the emitted light from an organo metallic complex which is an electroluminescent material depends on the metal or metals and the ligands. In general the shorter the wavelength of the emitted light the harder it is to obtain effective electroluminescent materials and in particular electroluminescent materials which emit light in the ultra-violet region of the spectrum have hitherto not been possible to produce.

[0010] An electroluminescent material which can emit ultra-violet light would have a range of applications and would enable there to be a source of ultra-violet light without the need for high temperature or complex high energy or vacuum equipment and so could replace such sources of ultra-violet light.

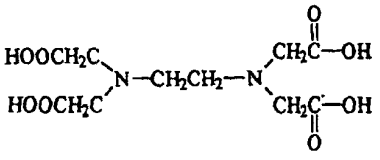
[0011] For example, there are devices and displays etc. where ultra-violet light is used to excite other materials to cause these other materials to fluoresce in the visible spectrum.

[0012] We have now devised electroluminescent devices in which there are organo-metallic complexes which can emit ultra-violet light.

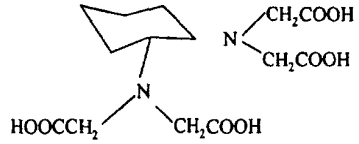
[0013] According to the invention there is provided an electroluminescent device which comprises sequentially an anode, a layer of an electroluminescent material and a cathode characterised in that the electroluminescent material is a gadolinium complex which emits ultra violet light which complex is selected from alkali metal salts of a complex of gadolinium and a polyamine ligand of formula A[Gd(polyamine)] where A is an alkali metal and complexes of formula $Gd[Ln(polyamine)]_3$ where Ln is lanthanide and (polyamine) is a polyamine ligand selected from EDTA, DCTA, DTPA and TTHA.

[0014] The gadolinium is in the III state.

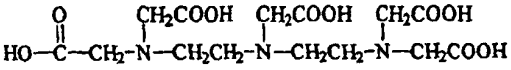
[0015] The structural formulae of EDTA, DCTA, DTPA and TTHA in the acetic acid form are shown below.



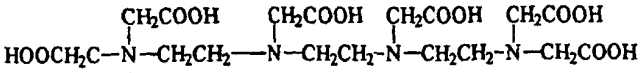
EDTA



DCTA



DTPA



TTHA

[0016] The organo metallic complexes can be made by the reaction of gadolinium chloride with an alkali metal salt of the amine e.g. the sodium salt, for EDTA the reaction is

$$GdCl_3 + Na_4\ (EDTA) \rightarrow Na^+\ [Gd(EDTA)]^-$$

[0017] For the other polyamine the corresponding alkali metal salt is used.

[0018] The lanthanide is selected from Gd, Sm, Eu, Tb, Dy.

[0019] Particularly preferred mixed complexes are the gadolinium complexes e.g. $Gd[Eu(EDTA)]_3$.

[0020] It has surprisingly been found that the lanthanide salts of the organo-metallic complexes exhibit a different electroluminescent spectrum than mixed organo-metallic complexes.

[0021] The mixed lanthanide salts can be made by reacting a lanthanide chloride with a lanthanide polyamine complex.

[0022] The materials of the present invention can be incorporated into electroluminescent devices which emit ultra-violet light and the invention includes such electroluminescent devices.

[0023] The ultra-violet light emitting devices of the invention comprise a transparent substrate which is a conductive glass or plastic material which acts as the anode, preferred substrates are conductive glasses such as indium tin oxide coated glass, but any glass which is conductive or has a conductive layer can be used. Conductive polymers and conductive polymer coated glass or plastics materials can also be used as the substrate. The electroluminescent material can be deposited on the substrate directly by evaporation from a solution of the material in an organic solvent. The solvent which is used will depend the material for example alcohols such as ethanol, ketones such as acetone and methyl acetylacetonate and chlorinated hydrocarbons such as dichloromethane are suitable in many cases.

[0024] Alternatively the material can be deposited by spin coating or by vacuum deposition from the solid state e.g. by sputtering or any other conventional method can be used.

[0025] In one embodiment there is a hole transporting layer deposited on the transparent substrate and the electroluminescent material is deposited on the hole transporting layer. The hole transporting layer serves to transport holes and to block the electrons, thus preventing electrons from moving into the electrode without recombining with holes. The recombination of carriers therefore mainly takes place in the emitter layer.

[0026] Hole transporting layers are used in polymer electroluminescent, devices and any of the known hole transporting materials in film form can be used.

[0027] The hole transporting layer can be made of a film of an aromatic amine complex such as poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl)-1,1'-biphenyl -4,4'-diamine (TPD), polyaniline etc.

[0028] Optionally dyes such as fluorescent laser dyes, luminescent laser dyes can be included so that these dyes fluoresce in the ultra-violet light to give emitted light of a particular colour spectrum.

[0029] Preferably the electroluminescent material is mixed with a polymeric material such as a polyolefin e.g. polyethylene, polypropylene etc. and preferably polystyrene.

[0030] Preferred amounts of active material in the mixture is from 95% to 5% by weight of active material and more preferably 25 to 20% by weight.

[0031] The hole transporting material can optionally be mixed with the electroluminescent material in a ratio of 5-95% of the electroluminescent material to 95 to 5% of the hole transporting compound. In another embodiment of the invention there is a layer of an electron injecting material between the cathode and the electroluminescent material layer, this electron injecting material is preferably a metal complex such as a metal quinolate e.g. an aluminium quinolate which will transport electrons when an electric current is passed through it. Alternatively the electron injecting material can be mixed with the electroluminescent material and co-deposited with it.

[0032] In a preferred structure there is a substrate formed of a transparent conductive material which is the anode on which is successively deposited a hole transportation layer, the electroluminescent material layer and an electron injection layer which is connected to the anode. The anode can be any low work function metal e.g. aluminium, calcium, lithium, silver/magnesium alloys etc.,

[0033] There can be a layer or layers containing a fluorescent material in the device so that the ultra-violet light emitted will cause the material to fluoresce and emit light of a particular colour spectrum.

[0034] The invention is described in the following examples.

Example 1

Gadolinium ethylenediaminetetraacetate sodium salt, Na[Gd(EDTA)]

[0035] Gadolinium chloride (10 mmol) was dissolved in water (5 ml). Ethylenediaminetetraacetic acid, tetrasodium salt hydrate (10 mmol) was dissolved in water (10 ml) and added portionwise to the gadolinium chloride solution. The solution became warm, and after ca. 15 minutes, a white precipitate was formed.

[0036] The mixture was left for a further 2 hours. The precipitate was filtered off to give a white solid which was washed with water (2 x 5 ml) and dried in air to yield Gadolinium ethylenediaminetetraacetate sodium salt, Na[Gd (EDTA)].

Example 2

Gadolinium europium ethylenediaminetetraacetate salts, $Gd[Eu(EDTA)]_3$

[0037] Europium ethylenediaminetetraacetate sodium salt Na[Eu(EDTA)] (4.5 mmol) was dissolved in methanol (30 m]). Gadolinium chloride (1.5 mmol) was dissolved in water (5 ml) and added portionwise to the europium ethylenediaminetetraacetate sodium salt solution. A white precipitate was immediately formed. The mixture was left for a further 1 hour. The precipitate was filtered off to give a white solid which was washed with methanol (2 x 10 ml) and dried in air to yield the product Gadolinium europium ethylenediaminetetraacetate salts, $Gd[Eu(EDTA)]_3$.

[0038] Photoluminescence was excited using 325mn line of Liconix 4207 NB, He/Cd laser. The laser power incident at the sample ($0.3mWcm^{-2}$) was measured by a Liconix 55PM laser power meter. The radiance calibration was carried out using Bentham radiance standard (Bentham SRS8, Lamp current 4,000A, calibrated by National Physical laboratories, England). The PL studies were carried out on samples or films. The Complexes of the examples were tested and the results shown in the Spectra attached as Figs. 1 and 2.

[0039] An electroluminescent device constructed with a film of the compounds of examples 1 and 2 with an indium coated glass as anode and an aluminium cathode emitted light in the ultra-violet spectrum when a low voltage was applied across the film. The light was emitted in the same spectrum ranges as in figs. 1 and 2

Claims

1. An electroluminescent device which comprises sequentially an anode, a layer of an electroluminescent material and a cathode **characterised in that** the electroluminescent material is a gadolinium complex which emits ultra violet light which complex is selected from alkali metal salts of a complex of gadolinium and a polyamine ligand of formula A[Gd(polyamine)] where A is an alkali metal and complexes of formula $Gd[Ln(polyamine)]_3$ where Ln is a lanthanide and (polyamine) is a polyamine ligand selected from EDTA, DCTA, DTPA or TTHA as herein defined.

2. An electroluminescent material as claimed in claim 1 **characterised in that** Ln is selected from Sm, Eu, Tb and Dy.

3. An electroluminescent material as claimed in claim 1 **characterised in that** the organic metal complex is Gd[Eu (EDTA)]$_3$.

4. An electroluminescent material as claimed in claim 1 **characterised in that** the organic metal complex is Na[Gd (EDTA)].

5. An electroluminescent device as claimed in any one of the preceding claims **characterised in that** the anode is a transparent glass or plastic material and there is a layer of a hole transmitting material deposited on the anode and the electroluminescent material is deposited on the hole transporting layer.

6. An electroluminescent device as claimed in claim 5 **characterised in that** the hole transporting material mixed with the electroluminescent material in a ratio of 5 to 95% of the electroluminescent material to 95 to 5% of the hole transporting material.

7. An electroluminescent device as claimed in claim 5 or 6 **characterised in that** the hole transporting layer is an aromatic amine complex.

8. An electroluminescent device as claimed in claim 7 in which the hole transporting layer is poly(vinylcarbazole), N, N'-diphenyl-N,N'-bis (3-methylphenyl) -1,1'-biphenyl -4,4'-diamine (TPD) or polyaniline.

9. An electroluminescent device as claimed in any one of the preceding claims **characterised in that** there is a layer of an electron injecting material between the cathode and the electroluminescent material layer

10. An electroluminescent device as claimed in any one claims 5 to 8 **characterised in that** there is an electron injecting material mixed with the electroluminescent material and co-deposited with it.

11. An electroluminescent device as claimed in claim 9 or 10 **characterised in that** the electron injecting material is a metal complex.

12. An electroluminescent device as claimed in claim 11 **characterised in that** the electron injecting material is an aluminium quinolate.

13. An electroluminescent device claimed in any one of the preceding claims in which the anode is selected from aluminium, calcium, lithium and silver/magnesium alloys.

Patentansprüche

1. Elektrolumineszenzvorrichtung, die nacheinander eine Anode, eine Schicht aus einem elektrolumineszierenden Material und eine Kathode umfaßt, **dadurch gekennzeichnet, daß** das elektrolumineszierende Material ein Gadoliniumkomplex ist, der UV-Licht emittiert, wobei der Komplex aus Alkalimetallsalzen eines Komplexes von Gadolinium und einem Polyamin-Liganden mit der Formel A[Gd(Polyamin)], wobei A ein Alkalimetall ist, und Komplexen der Formel Gd[Ln(Polyamin)]$_3$ ausgewählt ist, wobei Ln ein Lanthanoid ist und (Polyamin) ein Polyamin-Ligand ist, der aus EDTA, DCTA, DTPA oder TTHA ausgewählt ist, wie es hier definiert ist.

2. Elektrolumineszierendes Material nach Anspruch 1, **dadurch gekennzeichnet, daß** Ln aus Sm, Eu, Tb und Dy ausgewählt ist.

3. Elektrolumineszierendes Material nach Anspruch 1, **dadurch gekennzeichnet, daß** der organische Metallkomplex Gd[Eu(EDTA)]$_3$ ist.

4. Elektrolumineszierendes Material nach Anspruch 1, **dadurch gekennzeichnet, daß** der organische Metallkomplex Na[Gd(EDTA)] ist.

5. Elektrolumineszenzvorrichtung nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** die Anode ein transparentes Glas- oder Kunststoffmaterial ist und es eine Schicht eines Elektronenlücken übertragenden Materials gibt, die sich auf der Anode befindet, und das elektrolumineszierende Material auf der Elektronenlücken transportierenden Schicht angeordnet ist.

6. Elektrolumineszenzvorrichtung nach Anspruch 5, **dadurch gekennzeichnet, daß** das Elektronenlücken transportierende Material mit dem elektrolumineszierenden Material in einem Verhältnis von 5 bis 95 % elektrolumineszierendes Material zu 95 bis 5 % Elektronenlücken transportierendes Material gemischt ist.

7. Elektrolumineszenzvorrichtung nach Anspruch 5 oder 6, **dadurch gekennzeichnet, daß** die Elektronenlücken transportierende Schicht ein Komplex von einem aromatischen Amin ist.

8. Elektrolumineszenzvorrichtung nach Anspruch 7, wobei die Elektronenlücken transportierende Schicht Poly(vinylcarbazol), N,N'-Diphenyl-N,N'-bis-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamin (TPD) oder Polyanilin ist.

9. Elektrolumineszenzvorrichtung nach einem der vorstehenden Ansprüche, **dadurch gekennzeichnet, daß** zwischen der Kathode und der Schicht aus dem elektrolumineszierenden Material eine Schicht aus einem Elektronen injizierenden Material vorliegt.

10. Elektrolumineszenzvorrichtung nach einem der Ansprüche 5 bis 8, **dadurch gekennzeichnet, daß** ein Elektronen injizierendes Material vorliegt, das mit dem elektrolumineszierenden Material gemischt und gleichzeitig damit aufgetragen worden ist.

11. Elektrolumineszenzvorrichtung nach Anspruch 9 oder 10, **dadurch gekennzeichnet, daß** das Elektronen injizierende Material ein Metallkomplex ist.

12. Elektrolumineszenzvorrichtung nach Anspruch 11, **dadurch gekennzeichnet, daß** das Elektronen injizierende Material ein Aluminiumchinolat ist.

13. Elektrolumineszenzvorrichtung nach einem der vorstehenden Ansprüche, wobei die Anode aus Aluminium, Calcium, Lithium und Silber/Magnesium-Legierungen ausgewählt ist.

Revendications

1. Dispositif électroluminescent qui comprend séquentiellement une anode, une couche d'une matière électroluminescente et une cathode, **caractérisé en ce que** la matière électroluminescente est un complexe du gadolinium, qui émet une lumière ultraviolette, complexe qui est choisi parmi les sels de métal alcalin d'un complexe de gadolinium et un ligand polyamine de formule A[Gd(polyamine)] où A est un métal alcalin et des complexes de formule $Gd[Ln(polyamine)]_3$ où Ln est un lanthanide et (polyamine) est un ligand polyamine choisi parmi EDTA, DCTA, DTPA ou TTHA, tel que défini dans l'invention.

2. Matière électroluminescente selon la revendication 1, **caractérisée en ce que** Ln est choisi parmi Sm, Eu, Tb et Dy.

3. Matière électroluminescente selon la revendication 1, **caractérisée en ce que** le complexe de métal organique est $Gd[Eu(EDTA)]_3$.

4. Matière électroluminescente selon la revendication 1, **caractérisée en ce que** le complexe métallique organique est Na[Gd(EDTA)].

5. Dispositif électroluminescent selon l'une quelconque des revendications précédentes, **caractérisé en ce que** l'anode est un verre translucide ou une matière plastique et il existe une couche d'une matière émettrice de trous déposée sur l'anode et la matière électroluminescente est déposée sur la couche transportant des trous.

6. Dispositif électroluminescent selon la revendication 5, **caractérisé en ce que** la matière transportant des trous est mélangée avec la matière électroluminescente dans un rapport de 5 à 95% de la matière électroluminescente pour 95 à 5% de la matière transportant des trous.

7. Dispositif électroluminescent selon la revendication 5 ou 6, **caractérisé en ce que** la couche transportant des trous est un complexe d'amine aromatique.

8. Dispositif électroluminescent selon la revendication 7, dans lequel la couche transportant des trous est le poly (vinylcarbazole), la N,N'-diphényl-N,N'-bis(3-méthylphényl)-1,1'-biphényl-4,4'-diamine (TPD) ou la polyaniline.

9. Dispositif électroluminescent selon l'une quelconque des revendications précédentes, **caractérisé en ce qu'**il existe une couche d'une matière injectant des électrons entre la cathode et la couche de matière électroluminescente.

10. Dispositif électroluminescent selon l'une quelconque des revendications 5 à 8, **caractérisé en ce qu'**il existe une matière injectant des électrons mélangée avec la matière électroluminescente et co-déposée avec elle.

11. Dispositif électroluminescent selon la revendication 9 ou 10, **caractérisé en ce que** la matière injectant des électrons est un complexe métallique.

12. Dispositif électroluminescent selon la revendication 11, **caractérisé en ce que** la matière injectant des électrons est un quinoléate d'aluminium.

13. Dispositif électroluminescent selon l'une quelconque des revendications précédentes, dans lequel l'anode est choisie parmi l'aluminium, le calcium, le lithium et les alliages argent/magnésium.

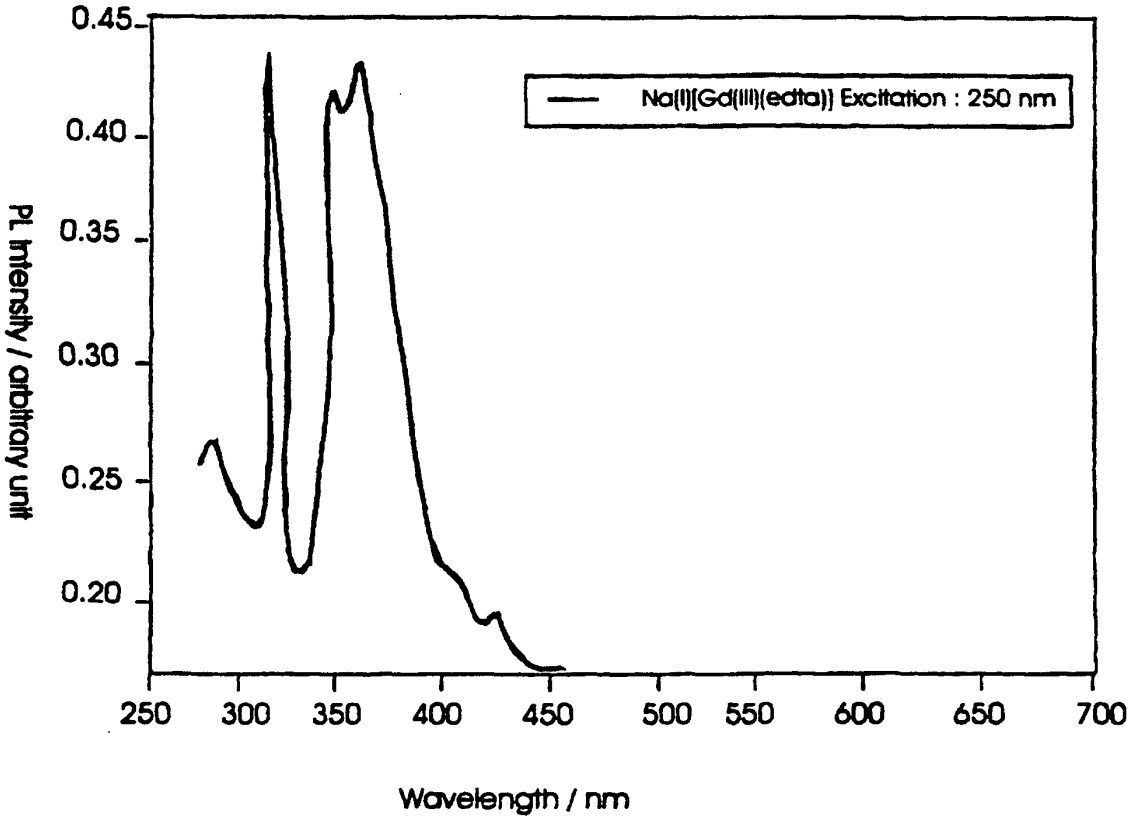

0.45
0.40
0.35
0.30
0.25
0.20
PL Intensity / arbitrary unit
Na(I)[Gd(III)(edta)] Excitation : 250 nm
250
300
350
400
450
500
550
600
650
700
Wavelength / nm

Fig. 1

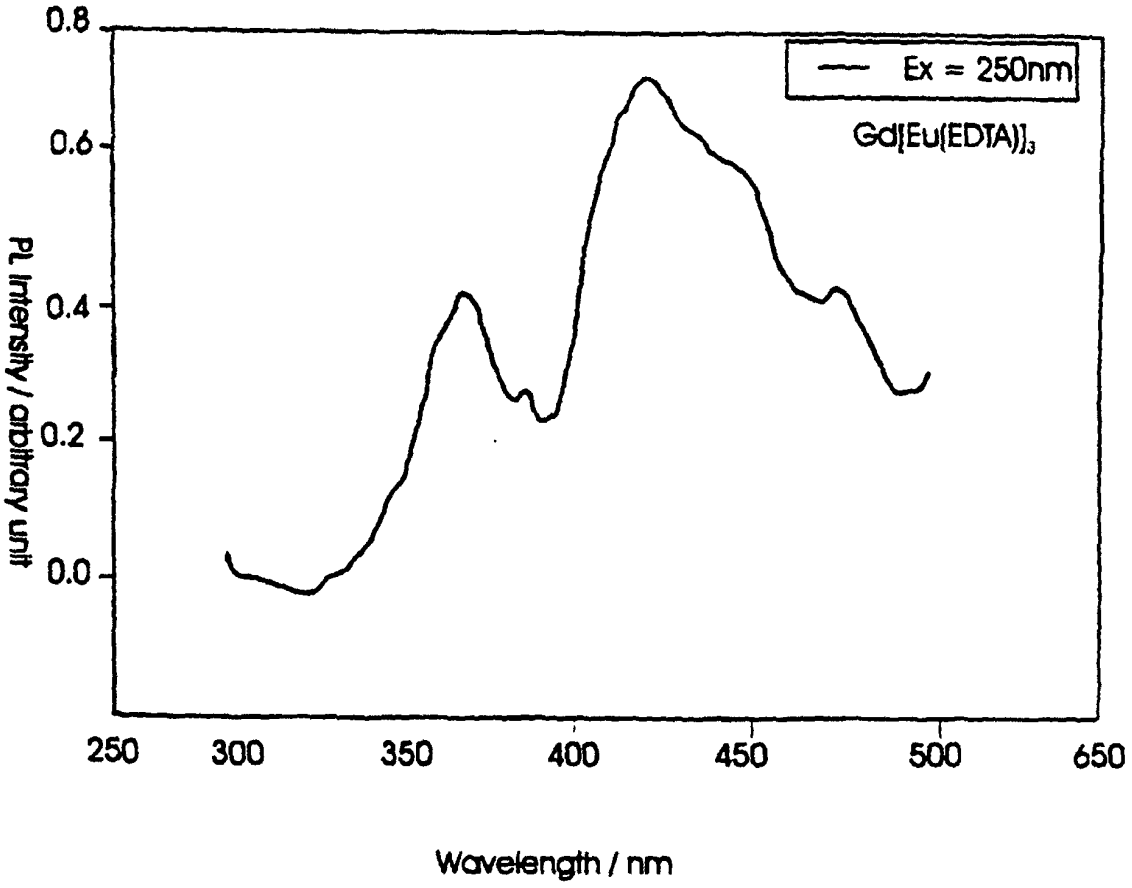
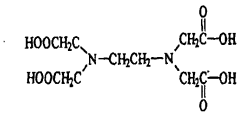

0.8
0.6
0.4
0.2
0.0
PL Intensity / arbitrary unit
Ex = 250nm
Gd[Eu(EDTA)]3
250
300
350
400
450
500
650
Wavelength / nm

Fig. 2

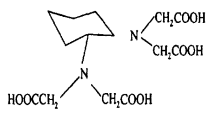
专利名称(译)	电致发光材料		
公开(公告)号	EP1155095B1	公开(公告)日	2004-09-22
申请号	EP2000901735	申请日	2000-01-31
申请(专利权)人(译)	南岸大学ENTERPRISES LIMITED		
当前申请(专利权)人(译)	南岸大学ENTERPRISES LTD.		
[标]发明人	KATHIRGAMANATHAN POOPATHY		
发明人	KATHIRGAMANATHAN, POOPATHY		
IPC分类号	H01L51/50 C09K11/06 H01L51/30		
CPC分类号	C09K11/06 H01L51/0089 H01L51/5012 Y10S428/917		
代理机构(译)	LUCAS，BRIAN RONALD		
优先权	1999001971 1999-02-01 GB		
其他公开文献	EP1155095A2		
外部链接	Espacenet		

摘要(译)

一种电致发光材料，其可形成在光谱的紫外区域发光的电致发光器件，其包含过渡金属，镧系元素或act系元素的有机金属络合物和多胺配体，特别是乙二胺四乙酸钠盐，Na [Gd（EDTA）]和钆乙基乙二胺四乙酸盐，Gd [Eu（EDTA）] 3？。



EDTA



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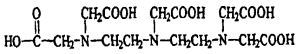

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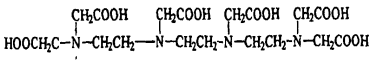

TTHA