

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
9 March 2006 (09.03.2006)

PCT

(10) International Publication Number
WO 2006/024997 A1(51) International Patent Classification⁷: **H01L 51/30**(21) International Application Number:
PCT/IB2005/052786

(22) International Filing Date: 25 August 2005 (25.08.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
04104233.4 2 September 2004 (02.09.2004) EP(71) Applicant (for all designated States except US): **KONINKLIJKE PHILIPS ELECTRONICS N.V.** [NL/NL];
Groenewoudseweg 1, NL-5621 BA Eindhoven (NL).

(72) Inventors; and

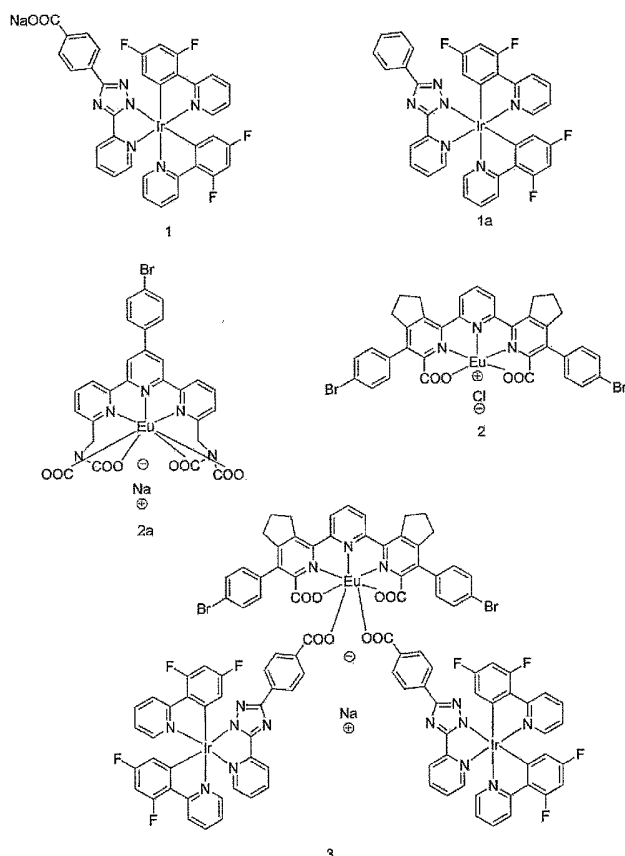
(75) Inventors/Applicants (for US only): **HOFSTRAAT, Johannes, W.** [NL/NL]; c/o Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL). **BRUNNER, Klemens** [AT/NL]; c/o Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL). **WEGH, Rene, T.** [NL/NL]; c/o Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL). **DE COLA, Luisa** [IT/NL]; c/o Prof.Holstlaan 6, NL-5656 AA Eindhoven (NL). **PLUMMER, Edward, A.** [GB/NL]; c/o Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL). **COPPO, Paolo** [IT/GB]; c/o Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL).(74) Agents: **TOL, Arie, J., W.** et al.; Prof. Holstlaan 6, NL-5656 AA Eindhoven (NL).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

[Continued on next page]

(54) Title: WHITE LIGHT-EMITTING DEVICE



(57) Abstract: The invention pertains to a light-emitting device comprising a light-emitting layer comprising a metal-organic donor-acceptor complex, characterized in that the metalorganic donor-acceptor complex has formula (1): (D-X)_n-A' wherein D stands for donor and is independently chosen from an Ir(III), Zn(II), Cu(II), and Os(II)-ligand complex, the ligands being such that a blue/green emission spectrum is obtained; A' stands for acceptor and is a Ru(II), Ir(III), Os(II), Pd(II), Pt(II), Re(I), Cu(I) or lanthanide(III)-ligand complex, the structure and composition being chosen such that an orange/red emission is obtained; X is independently selected from a bond and an organic linker moiety, and n is 1 or 2, satisfied the above requirements, and n is 1 or 2.



European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

White light-emitting device

The invention relates to a light-emitting (LE) device comprising a light-emitting layer comprising a metal-organic donor-acceptor complex. In particular the invention relates to an LE device which is capable of emitting white light. the invention further relates to novel LE compounds and to a method for obtaining white light.

5 The invention relates to an LE device that emits light when a suitable voltage is impressed on electrodes contained in the device or when the device is irradiated with electromagnetic radiation. LE devices can be used in applications like displays, lighting, and signage. Organic luminescent devices include organic material to facilitate light emission. Organic luminescent devices are particularly suitable for applications which require a large
10 light-emissive surface. A well-known variety of an organic LE device is the organic light emitting diode (oLED).

It is known that processes exist for the generation of red light and the switching between red and green light. An efficient charge transfer from a charge transporting material to such a co-ordinative dye in an organic layer of a light emitting device
15 such as a light-emitting diode (LED) or a light-emitting cell (LEC) has been described. LE devices emitting white light are only described recently, for instance in US 2002/0134984 and EP 1,398,363. The method disclosed therein comprises the use of two separate layers, one of which containing a red emitting metal complex and the second layer having a blue emitting metal complex. This method requiring two layers is very complicated and therefore
20 too expensive for commercial manufacturing.

It is an objective of the present invention to obtain an LE device comprising a single layer that is capable to emit white light. Contrary to the prior art it is thus necessary to obtain a luminescent compound that is covalently attached to or held by a non-covalent bond, e.g. through a coordinative bond, a hydrogen bond or a hydrophobic interaction in the close
25 vicinity of a metal-complex, or which is directly coupled to the metal-complex, such that the excited state energy of the blue/green emitting metal complex is partially transferred to the second, red/orange emitting compound, thus leading to a white emission spectrum of the bichromophoric compound. Such luminescent compound should have a very high quantum yield and the efficiency of energy transfer should be tunable so that various color

temperatures can be achieved, The favorable spin statistics of the metal donor complex will dominate the excitation properties of the bichromophoric system.

To this end it was found that a light-emitting device comprising a light-emitting layer comprising a metal-organic donor-acceptor complex, characterized in that the metal-organic donor-acceptor complex has formula (1):



wherein D stands for donor and is independently chosen from an Ir(III), Zn(II), Cu(II), and Os(II)-ligand complex, the ligands being such that a blue/green emission spectrum is obtained;

A' stands for acceptor and is a Ru(II), Ir(III), Os(II), Pd(II), Pt(II), Re(I), Cu(I), or lanthanide(III)-ligand complex, or, alternatively, a luminescent organic compound, such as a laser dye, the structure and composition being chosen such that an orange/red emission is obtained; X is independently selected from a bond and an organic linker moiety, and n is 1 or 2, satisfied the above requirements.

One specific class of luminophores, which may be particularly suitable as accepting luminophore is that of the lanthanides. These compounds give very pure and spectrally well-defined luminescence. The application of metal complexes as sensitizers in combination with lanthanides is especially interesting, since the excited state of the metal complex has a triplet character, which can directly transfer its energy to the excited state of the lanthanide ion. Sensitization of the lanthanide via another metal complex is very appealing since direct excitation of the lanthanide ions is not possible, because of their negligible absorption in any region of the spectrum (forbidden transitions) and the population of their excited state via energy transfer is the only accessible. The sensitized excitation of the lanthanide ion, which is enabled by the triplet character of the excited state of the donor metal complex, has significant advantage over the conventional excitation of the lanthanide ion, which generally proceeds in a two-step approach: first population of a highly energetic singlet state of the sensitizer, subsequently intersystem crossing to the lower-energy excited triplet state of the sensitizer, and finally transfer of energy to the excited state of the lanthanide ion. The main disadvantage of said prior art two-step approach is that it is almost impossible to use lanthanide ions in electroluminescent devices, because of the high energy of the singlet state of the sensitizer, which needs to be populated to start with. The present concept is devoid of such disadvantage.

In the context of the present invention, an electroluminescent compound is a compound which is capable of emitting light when a layer comprising such compound is

sandwiched between suitable electrodes and is subjected to a suitable voltage. For the purpose of this invention it may also be a combination of a charge transporting compound and a luminescent compound which is adapted to receive charges from the charge transporting compound to effect light emission. In general, in order to be electroluminescent, such compound is capable of accepting and/or transporting holes and/or electrons and emit light having a certain emission spectrum which is characteristic for the compound. In a more narrow sense, an electroluminescent compound accepts electrons and holes which may recombine to cause emission of a photon. Even more specific, the electroluminescent compound may be capable of exhibiting electroluminescence without assistance of charge transporting and light emission compounds in which case the electroluminescent compound accepts and transports holes and electrons which may recombine to cause light emission.

In another embodiment of the invention the device comprises a luminescent compound, which is an organic conjugated compound of low molecular weight, which is able to accept the energy of the metal donor complex, and which emits orange/red light.

Typically, organic conjugated compounds may be used having the formula (1):

$$(D-X)_n-A' \quad (1)$$

wherein D is $M(Y)_3$ wherein M is independently chosen from an Ir(III), Zn(II), Cu(II), and Os(II);

Y has independently the formula (2) or (3):

$NAr-Ar \quad (2);$

$NAr-NAr \quad (3);$

in which NAr is independently selected from pyridine, imidazole, triazole, oxazole, oxadiazole, diazole, diketone, thiazole, and thiadiazole, catechol, cyanide, thiocyanide, tetrazoles and carbonyl, which may be unsubstituted or substituted with at least one phenyl, halo, halomethyl, $(CH_2)_mCOOR'$ group, and/or polymer, and at least one of the ring nitrogen atoms is positioned an α -position with regard to the atom forming a bond with the NAr or Ar moiety;

Ar is phenyl, which may be unsubstituted or substituted with at least one phenyl, halo, halomethyl, $(CH_2)_mCOOR'$ group, and/or polymer; R' being independently selected from H, Na, K, Li, Ca, and Mg, and m is 0-3; and

one or more of the groups Ar and NAr may be replaced by catechol, cyanide, thiocyanide, tetrazole or CO, provided that at least one of groups Y contains at least one Ar or NAr moiety;

A' is M'Z, wherein M' is selected from Ir(III), Ru(II), Os(II), Pd(II), Pt(II), Re(I), Cu(I), and lanthanide(III);

Z stands for an aliphatic or aromatic group containing at least three nitrogen atoms, and which may be substituted by at least one of phenyl, halo, halomethyl,

5 (CH₂)_mCOOR', and a polymer, or Z stands for a luminescent organic compound of low molecular weight; and

X is selected from a bond, CR₂, NR, CO-NR, O, S, phenylene, thiophene, fluorene, dibenzofurane, dibenzothiophene, cyclopentylene, cyclohexylidene, cyclohexylene, and cyclohexane, in which R is independently H or C1-C12 alkyl and wherein each of the
10 phenylene, thiophene, fluorene, dibenzofurane, dibenzothiophene, cyclopentylene, cyclohexylidene, cyclohexylene, and cyclohexane moieties may be unsubstituted or substituted with one or more of C1-C12 alkyl, C1-C12 alkoxy, phenyl, phenoxy, biphenyl, (CH₂)_mCOOR', and halogen; wherein m and R' have the previously given meanings; and n is
1 or 2.

15 More specifically, the bond of group X may be a covalent, non-covalent, coordinative, hydrogen, electrostatic, or hydrophobic bond. If Z stands for a luminescent organic compound of low molecular weight, such compound is preferably a laser dye.

In a preferred embodiment the light-emitting compound is a compound of the above formula wherein D is Ir(Y)₃ and A' is M'Z, wherein Y independently has the formula
20 (2) or (3):



NAr is selected from pyridine, imidazole, triazole, oxazole, oxadiazole, thiazole, and thiadiazole, which may be unsubstituted or substituted with at least one phenyl,
25 halo, halomethyl, and/or (CH₂)_mCOOR' group, and at least one of the ring nitrogen atom is positioned an α -position with regard to the atom forming a bond with the NAr or Ar moiety;

Ar is phenyl, which may be unsubstituted or substituted with at least one phenyl, halo, halomethyl, and/or (CH₂)_mCOOR' group; and

one or more of the groups Ar and NAr may be replaced by catecholate,
30 cyanide, thiocyanide, tetrazole or CO, provided that at least one of groups Y contains at least one Ar or NAr moiety;

Z stands for an aliphatic or aromatic group containing at least three nitrogen atoms, and which may be substituted by at least one phenyl, halo, halomethyl, (CH₂)_mCOOR' group, polymer, or a nitrogen-containing laser dye; and

M' stands for Ir(III), Ru(II), Os(II), Pd(II), Pt(II), Re(I), Cu(I), Eu (III), Tb(III), Dy(III), Sm(III), or Tm(III); and R' and m have the previously given meanings.

If group Z and/or D is substituted by a polymer a conjugated polymer may be used. The conjugated polymer may be a cross-linked polymer, star polymer, dendrimer, or a linear chain polymer. In the context of the invention the term polymer includes oligomer and copolymers, terpolymers, and higher-order mers. The linear chain polymer may be a side-chain polymer having the electroluminescent moieties as pendant side-groups or a conjugated polymer having the LE structural units in the main chain. Examples of suitable electroluminescent polymers include those comprising a phenylenevinylene, a phenylene, a thiophene, a thienylvinylene, a fluorene or 9,9'-spirobifluorene unit. Polymers like polyphenylethylene, polyquinoxaline, polyvinylcarbazole, or copolymers thereof can also be used. Optionally such polymers are copolymerized with hole- or electron-transporting monomers such as triarylamine and oxadiazoles.

Alternatively, group Z may be a laser dye that is selected from phthalocyanine, naphthocyanine, cyanine, fluoresceine, rhodamine, squaraine, crocoaine, resorufine, oxazine, anthraquinone, substituted or unsubstituted polynuclear aromatic hydrocarbon, and substituted or unsubstituted heterocyclic polynuclear aromatic hydrocarbon dye.

The term "halo" as used herein stands for F, Cl, Br, or I. Particularly useful are F substituted moieties. The haloalkyl substituent is preferably trifluoromethyl.

The electroluminescent layer may contain further substances such as hole-transporting, electron-transporting, hole-blocking, electron-blocking or exciton-blocking compounds. Compounds which enhance or block charge injection from layers adjacent to the LE layer may also be used. Compounds known in the art as such for this purpose may be used.

The LE layer of the device is typically 10 to 300 nm thick. The LE material is conveniently deposited from solution by admixing with the polymer or directly, by spin-coating or ink-jet printing, screen printing, or another coating or printing or transfer method.

Unlike conventional organic LEDs which require a low-work function and thus chemically highly reactive electrode material to obtain efficient electron injection, the first and second electrode of the LE devices of the present invention may be both formed of high-work function material to observe the white light-emitting effect if the metal complex has charged ligands. Suitable electrode materials are conducting inorganic oxides (particularly preferred because they are optically transparent) such as indium tin oxide (ITO), zinc indium oxide, gallium indium oxide, gallium indium oxide, or conducting polymers like

polyethylenedioxythiophene and polyaniline, and metals such as Au, Al or Ag, Ba, Ca, or any other conductive thin metal film. The electrodes may be covered with a thin barrier layer of the type LiF/Al, LiF/Ba/Al, or LiF/Ca/Al. Preferred combinations of electrodes are ITO and gold, and ITO and BaAl.

5 The luminescent device may comprise further layers, electroluminescent devices comprising such further layers being known in the art as such. Known examples include hole-transporting, hole-injecting, electron-injecting, electron-transport, hole-blocking, electron-blocking and exciton-blocking layers.

 Having the capability of showing white light the (electro)luminescent device is
10 particularly suitable for lighting applications, such as decorative lighting and signage and advertising, and display applications, such as segmented and matrix display devices, both passive and matrix. Since the LE devices in accordance with the invention can be manufactured readily in any size, the luminescent devices in accordance with the invention may be used practically for any display size including television, when the white emissive
15 layer is used in combination with suitable color filters.

 By using the second luminophore, which is suitable on the basis of its electronic structure as acceptor of the energy, , the second luminophore acts as the species, which emits light in combination with the light of the first luminophore so that a mixture of the color of the emission of the first luminophore and the color of the second luminophore is
20 generated. The second luminophore can be chosen in such a way that the energy transfer conditions are fulfilled and furthermore can be tuned (i.e., constraints are put to the absorption spectrum of the second luminophore with respect to the emission spectrum of the metal complex), and connected to the first luminophore such that the distance between the metal complex and the luminophore is of the same order of magnitude as the Förster radius.
25 Such distance can be expressed as the distance between the metal, e.g. Ir ion of the donor and the emitting part e.g., the lanthanide ion of the acceptor. Suitable distances are 3-50 Å, more preferably 6 to 12 Å, most preferably 6 to 8 Å.

 The complexes of the invention satisfy a suitable combination of dyes for emitting white light, e.g. a blue Ir-complex to which an intense red/orange emitting dye with
30 high intrinsic stability is coupled to which part of the energy is transferred. The dye partially deactivates the excited state of the metal complex,. If the dye chosen has a very high quantum yield of luminescence, the emissive process will be very efficient, much more efficient than that of the Ir-complex as such. If, in addition, the dye is chosen to be a highly stable compound, e.g. a laser dye, also the stability of the device will improve.

In an alternative embodiment, which may have the additional advantage that the abundantly generated excited triplet states can be effectively harvested, the blue Ir complex is combined with an efficiently luminescent red/orange triplet emitter, such as a lanthanide complex. Lanthanide complexes are very stable emitters. Depending on the energy of the excited (triplet) state generated in the first Ir complex, luminescence can be generated from a range of lanthanides, the most suitable lanthanide ions in view of the color requirement are Eu(III), Sm(III) and Dy(III).

Careful choice of the composition of the bichromophoric complexes, in particular of the distance between the donor and the acceptor, and of the spacers connecting the donor and the acceptor pairs, allows for control of the relative emission of the two moieties. The electronic coupling between the two metal complexes will be tuned with appropriate σ or π conductive bridging ligands. In this way pure white emission of the acceptor can be obtained, but also a mix or combination of emissive colors can be realized, which is of great interest for lighting applications (in which broad-banded "white" emission is desired to give optimal color rendering). In a preferred embodiment the Ln(III)-ligand complex is an europium complex. Such complexes can be prepared similar to previously published procedures for similar complexes, purified via chromatography, and obtained as an amorphous powder.

These and other aspects of the invention will be apparent from and elucidated with reference to the drawings and the experiments described hereinbelow.

Fig. 1 shows a scheme of complexes according to the invention.

Fig. 2 shows a specific complex obtained by non-covalent bonding between an iridium complex (blue emitter) and an europium compound (red emitter), according to the invention.

Fig. 3 shows a schematic procedure for the preparation of covalent complex 6 and its formula according to the invention.

Fig. 4 shows the emission spectrum of complex 6 in CD₃OD solution upon excitation at 410 nm.

Fig. 5 shows the emission spectrum of complex 3 in CD₃OD solution upon excitation at 400 nm.

Fig. 6 shows an electroluminescent device.

Complexes A-C and B-C, herein below (Fig. 1) are examples of complexes of the invention, wherein A-C and B-C can be covalently bonded to each other or can be brought into each vicinity by coordination bonding. Moieties A and B correspond to complex A' of formula (1), whereas moiety C is an example of a complex D of formula (1). Complex C can be covalently attached to complex A or complex B. Complex C can also be attached to complex A or to complex B via coordination bonds to the metal center, or in any combination using covalent and non-covalent bonds. The system is designed to perform energy transfer from metal complex C to metal complex A or B, in such a way that part of the excitation is transferred, and mixed emission of both complexes is achieved. The energy transfer can be optimized by tuning the distance between the metal centers in a range of 3-50 Å, more preferably 6 to 12 Å, most preferably 6 to 8 Å.

Example 1

Specific complexes are exemplified in Fig. 2. Complexes 1 and 1a are examples of complex D of formula (1) and complexes 2 and 2a are examples of complex A' of formula (1). Complex (3) is an example of the white-emitting complex of the invention:

Complex 1 (see Fig. 2) was prepared according to previously published procedures for similar complexes, purified via chromatography, and obtained as an amorphous yellow powder. The UV-visible absorption spectrum was consistent with the unsubstituted analogue 1a, showing the MLCT (Metal to Ligand Charge Transfer) transition in the visible region and the π - π^* transitions, associated with the ligands, in the UV. It showed blue emission in dichloromethane, methanol or acetonitrile, with maxima centered at 460 nm and 491 nm (see Table 1), similarly to the unfunctionalized analogue 1a. The quantum yield of emission in a deaerated methanol solution was 17%, significantly lower than the unfunctionalized analogue 1a ($\Phi = 27\%$). The lifetime of the emitting species, measured by means of a streak camera interfaced to a pulsed laser tuned at 435 nm, was 1.4 μ s.

Complex 2 (see fig. 2) was prepared and purified according to previously published procedures and obtained as white powder, showing absorption in the UV region and the characteristic, well structured emission of Eu(III) complexes, mainly rising from a $^5D_0 \rightarrow ^7F_2$ transition, centered at 615 nm as expected, since this transition is particularly enhanced when Eu(III) ion is shielded. The quantum yield of emission was 33% in an air equilibrated, deuterated methanol solution. This value represent one of the highest quantum

yields of photoluminescence for an Eu(III) complex. As can be seen by the schematic formula, and confirmed by spectroscopic investigation in water, the europium complex has a low coordination number (5 or 7) and therefore 2 water or solvent molecules are coordinated to fill the coordination sphere. Such situation is ideal to assembly via carboxylate or chelating units a second metal complex. Therefore when complex 1 and 2 were stirred in methanol at room temperature, the formation of a bimetallic assembly occurred. Its structure could not be confirmed by NMR characterization due to the paramagnetic properties of Eu(III) but the mass spectra clearly indicated the formation of the complex. Furthermore, the photophysical behavior of the resulting product suggested 3 to be the only product in solution. Irradiation of the resulting assembly (diluted in deuterated methanol) with monochromatic light at 400 nm, where only the iridium moiety shows absorption bands, resulted in the emission of almost white light (chromaticity coordinates: X: 0.28 Y: 0.30), due to the residual emission of the blue-green iridium complex and the sensitized red emission of the europium component. Emission quantum yields and time resolved spectroscopy shows that the emission and lifetime of the iridium (III) emitting species, is reduced more than 7 times ($\tau = 220$ ns) with respect to complex 1 alone in a deareated deuterated methanol solution. The sensitization of the Eu(III) moiety, which emits with its own unchanged lifetime ($\tau = 1.4$ ms) suggests an energy transfer from the excited iridium moiety to the low lying excited state (5D_0) of the Eu component. If the emission is detected with a long delay, millisecond scale, by means of a streak camera, only the characteristic emission of the Eu moiety is observed. In order to establish the stoichiometry of the adduct in solution via the carboxylate belonging to the iridium complex 1, a titration of complex 1 against complex 2 was performed. It was immediately clear that the emission properties of the Eu moiety, upon excitation at 400 nm, improved, with respect to the emission of complex 1, up to a value of 2 units of iridium per Eu unit in solution. With number of Ir(III) centers in solution exceeding two, the emission is dominated by the blue-green region. It is clear that complex 1 could coordinate one or two iridium centers and the luminescence titration support the formation of a 2:1 (Ir:Eu) stoichiometry allowing a saturation of the coordination number and a good shield of the Eu complex from the solution. In the assembly therefore the europium emission is sensitized and the resulting emission (blue from the iridium and red from the europium) is white light. Quantum yield is approximately 7%.

In order to confirm that such stable assembly can occur only with complexes with a low coordination number, complex 2a (see Fig. 2) was reacted with complex 1 under analogous conditions. The resulting solution showed only iridium based emission, upon

excitation at 400 nm, suggesting no energy transfer to the europium moiety. This shows that binding of the metal complexes is indeed crucial and simply mixing them leads to a blue emission from the excited iridium since no energy transfer can occur. The different behavior was consistent with the hypothesis that the carboxylate coordinates the Eu moiety, and for complex 2a, in which the Eu ion is already fully coordinated by the cage-type ligand, no assembly can be formed. Further evidence came by reacting unsubstituted iridium complex 1a with complex 2. Also in this case, no Eu based emission was detected upon irradiation of the resulting solution at 400 nm.

Table 1

Complex	λ_{max} Em./nm	Φ	$\tau/\mu\text{s}$
1a	460, 491	0.17	1.4
1ab	461, 490	0.27	1.4
2c	615	0.33	1900
2ad	615	0.12	1900
3d	460, 491, 615	0.07	0.22 (Ir); 1400 (Eu)

Emission maxima, quantum yields of emission and lifetime of the emitting species. Quantum yields of complexes 1 and 1a were measured using quinine sulfate in H_2SO_4 0.5 M as a reference; 2, 2a, and 3 were measured using ruthenium tris-dipyridine chloride in distilled water as reference.

a: measurements performed in methanol; b: measurements performed in dichloromethane; c: measurements performed in D_2O ; d: measurements performed in CD_3OD .

Example 2

Complexes were prepared comprising (i) a blue emitting Ir-complex and (ii) a blue emitting Ir-complex as energy donor and an Eu-complex as acceptor (Fig. 3 and Fig. 4).

The blue-emitting Ir-complexes were subsequently introduced into electroluminescent devices (see Scheme 1 in Fig. 6). The devices have been constructed using a thickness of the active layer of 80 nm and the molar amount of the fluorinated iridium complexes present in 8% (weight) concentration. The solvent used was dichloromethane or chlorobenzene, depending on the solubility of the complex. The devices show blue emission when 6-7 V are applied across the device, with an external quantum efficiency of about 0.2%.

The blue emitting Ir-complexes were coupled to red-emitting Eu-complexes, that were applied as energy acceptors. The Ir(III) blue emitting complex was linked to the red-emitting Eu(III)-complex in solution. To a solution of 10^{-5} M of the bis iridium precursor was added a more concentrated (10 times in excess) solution of the Eu(DOTA) compound (see Fig. 3). The solution reacted at room temperature and upon excitation at 400 nm, where the europium compound does not absorb, the emission spectrum shown in Fig. 4 clearly shows the energy transfer from the blue emitting Ir-complex to the red-emitting Eu-complex, demonstrating energy transfer from the Ir-complex to the Eu-DOTA moiety (in circle).

Careful choice of the composition of the complex, in particular of the distance between the Ir donor and the lanthanide acceptor, allows for control of the relative emission of the two moieties. In this way pure red emission could be obtained, but also a mix or combination of emissive colors could be realized, which is of great interest for lighting applications (in which broad-banded "white" emission is desired to give optimal color rendering).

Example 3

The complexes of Fig. 2 were prepared as follows.

Complex 1 (Fig. 2)

Complex 1 was prepared according to a previously published procedure (Coppo, P.; Plummer, E. A.; De Cola, L., *Chem. Commun.*, 2004, 1774) and purified by chromatography over silica gel, using $\text{CH}_3\text{CN}-\text{H}_2\text{O}-\text{CH}_3\text{OH}$ mixtures to elute.

Complex 1a (Fig. 2)

Complex 1a was prepared and purified according to the previously published procedure of (Coppo, P.; Plummer, E. A.; De Cola, L., *Chem. Commun.*, 2004, 1774).

Complex 2 (Fig. 2)

Complex 2 was prepared and purified according to the previously published procedure of Kozhevnikov, V. N.; Kozhevnikov, D. N.; Rusinov, V. L.; Chupakhin, O. N.; König, B., *Synthesis*, 2003, 15, 2400.

Complex 2a (Fig. 2)

Complex 2a was prepared according to the procedure published by Mikkala, V.-M.; Helenius, M.; Hemmilä, I.; Kankare, J.; Takalo, H., *Helv. Chem. Acta*, 1993, 76, 1361. The reaction step involving the use of cyanide ions was performed under a gentle stream of nitrogen in a -20° C bath. The exhaust gas was allowed to bubble into a basic solution of NaClO, to oxidize the HCN developed in the reaction vessel. Spectroscopic data of complex 2a were consistent with those reported by Mikkala et al.

Complex 3 (Fig. 2)

Complex 1 (60 mg, 7×10^{-5} mol) was solubilized in 10 ml of methanol. Complex 2 (30 mg, 3.5×10^{-5} mol) was added portion wise. Na₂CO₃ (10 mg) was added in a portion and the mixture was stirred at reflux for 4 hours. The light yellow solution was cooled to room temperature and the solvent was evaporated under reduced pressure. The yellow powder was washed with abundant water to remove the excess of sodium carbonate, dried under vacuum, to give complex 3 as off-white amorphous powder (90 mg, 75%).

Example 4

Complex 6 of cage-type ligand 1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid} Eu(III) (Fig. 3) was prepared as follows.

10-[(2-pyridyl-3(1,2,4-triazol-5-yl)methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid tris(1,1-dimethylethyl) ester complex.

A suspension of 3-methyl-1,2,4-triazolylpyridine (0.100 g, 0.6 mmole), DO₃A tetrabutyl ester (0.250 g, 0.5 mmole), and sodium carbonate (0.105 g, 1 mmole) in 40 ml of acetonitrile was refluxed for 24 h under magnetic stirring. The mixture was cooled to room temperature and filtered on a fritted glass, and the filtrate was evaporated to afford a residue. This product was dissolved in 50 ml of CH₂Cl₂ and washed with water (2*30 ml) and then with 30% aq. NaClO₄ (3*50 ml). The solvent was removed under reduced pressure and the product purified by column chromatography (silica gel, CH₂Cl₂/MeOH 96/4) to afford 0.300 g (70%) of the ester complex as white solid.

10-[(2-pyridyl-3(1,2,4-triazol-5-yl)methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid.

A solution of 10-[(2-pyridyl-3(1,2,4-triazol-5-yl)methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid tris(1,1-dimethylethyl) ester complex (0.30 g, 0.42 mmole) in 10 ml of trifluoroacetic acid was stirred at room temperature for 4 h. The solvent

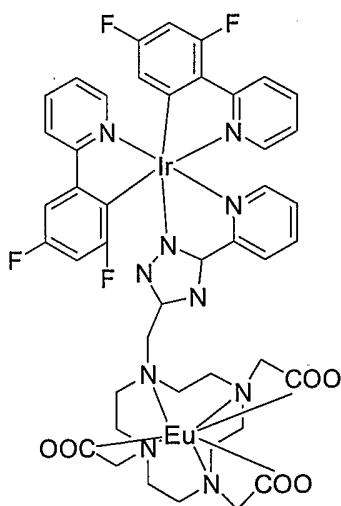
was evaporated, and the crude was triturated with diethyl ether to yield a white solid. The solvent was separated, and the residue was used without any further purification.

10-[2-pyridyl-3(1,2,4-triazol-5-yl)methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid europium salt

- 5 One equivalent of EuCl_3 was added to a solution of 10-[2-pyridyl-3(1,2,4-triazol-5-yl)methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid in 20 ml of methanol and refluxed for 2 h. After letting the reaction cooling to room temperature, few drops of triethylamine were added and the solution filtered. The solvent was removed under reduced pressure to afford an off-white powder. The solid was re-crystallized from methanol. The
10 final yield was 70%.

Complex 6.

- One equivalent of $[\text{Ir}_2(2,4\text{-diFphpy})_4\text{Cl}_2]$ (prepared and purified according to the previously published procedure of Coppo, P.; Plummer, E. A.; De Cola, L., Chem.
15 Commun., 2004, 1774) was dissolved in 10 ml of dichloromethane and added to a solution of [2-pyridyl-3(1,2,4-triazol-5-yl)methyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid europium salt in 20 ml of ethanol. The obtained solvent mixture was refluxed for 1 h. The solution was sub sequentially concentrated to a final volume of 10 ml and 20 ml of dichloromethane were added yielding a bright yellow precipitate. The solid was filtrate,
20 dissolved in methanol and re-precipitated adding diethyl ether. Yield 70%.



Complex 6

Spectroscopic characterization of the complexes.

The photophysical properties of the complex 6 were investigated in aerated solution of either deuterated methanol or in N,N-dimethyl formamide giving similar results. Complex 6 showed a typical iridium phenyl pyridine emission with a not well defined maximum at around 21800 cm^{-1} (460 nm), the lifetime decays of the Ir excited states can be fitted with mono exponential functions.

The iridium DO₃A complex 6 shows a lifetime of the excited state of 92 ns in DMF and 60 ns in MeOD. In presence of the Europium cation, complex 5, the lifetime of the excited state decreases to 37 and 24 ns respectively, the quantum yields quenching are proportional to the reduction of the life times. The quantum yield of the complex 4 is approximately of 0.007 (the reference used was Ru(bpy)₃²⁺). It was impossible determine the Eu(III) quantum yield because its luminescence is too weak compared to the iridium one. The lifetime of the europium emission results in the order of the millisecond region (0.7 ± 0.2 ms).

CLAIMS:

1. A light-emitting device comprising a light-emitting layer comprising a metal-organic donor-acceptor complex, characterized in that the metal-organic donor-acceptor complex has formula (1):



5 wherein

D is $M(Y)_3$ wherein M is independently chosen from an Ir(III), Zn(II), Cu(II), and Os(II);

Y has independently the formula (2) or (3):



in which NAr is independently selected from pyridine, imidazole, triazole, oxazole, oxadiazole, diazole diketone, thiazole, and thiadiazole, which may be unsubstituted or substituted with at least one phenyl, halo, halomethyl, $(CH_2)_mCOOR'$ group, and/or polymer, and at least one of the ring nitrogen atom is positioned at the α -position with regard to the atom forming a bond with the NAr or Ar moiety;

Ar is phenyl, which may be unsubstituted or substituted with at least one phenyl, halo, halomethyl, $(CH_2)_mCOOR'$ group, and/or polymer; R' being independently selected from H, Na, K, Li, Ca, and Mg, m is 0-3; and

one or more of the groups Ar and NAr may be replaced by catecholate, cyanide, thiocyanide, tetrazole or CO, provided that at least one of groups Y contains at least one Ar or NAr moiety;

A' is $M'Z$, wherein M' is selected from Ir(III), Ru(II), Os(II), Pd (II), Pt (II), Re(I), Cu(I), and lanthanide(III);

Z stands for an aliphatic or aromatic group containing at least three nitrogen atoms, and which may be substituted by at least one of phenyl, halo, halomethyl, $(CH_2)_mCOOR'$, and a polymer, or Z stands for a luminescent organic compound of low molecular weight; and

X is selected from a bond, CR_2 , NR, CO-NR, O, S, phenylene, thiophene, fluorene, dibenzofurane, dibenzothiophene, cyclopentylene, cyclohexylidene, cyclohexylene,

and cyclohexane, in which R is independently H or C1-C12 alkyl and wherein each of the phenylene, thiophene, fluorene, dibenzofurane, dibenzothiophene, cyclopentylene, cyclohexylidene, cyclohexylene, and cyclohexane moieties may be unsubstituted or substituted with one or more of C1-C12 alkyl, C1-C12 alkoxy, phenyl, phenoxy, biphenyl, (CH₂)_mCOOR', and halogen; wherein m and R' have the previously given meanings; and n is 1 or 2.

2. The light-emitting device of claim 1 wherein M is Ir(III).

10 3. The light-emitting device of claim 1 or 2 wherein M' is Eu(III).

4. The light-emitting device of claim 1 or 2 wherein D is Ir(Y)₃ and A' is M'Z, wherein Y independently has the formula (2) or (3):

NAr-Ar (2);

15 NAr-Nar (3);

NAr is selected from pyridine, imidazole, triazole, oxazole, oxadiazole, thiazole, and thiadiazole, which may be unsubstituted or substituted with at least one phenyl, halo, halomethyl, and/or (CH₂)_mCOOR' group, and at least one of the ring nitrogen atom is positioned at the α-position with regard to the atom forming a bond with the NAr or Ar moiety;

Ar is phenyl, which may be unsubstituted or substituted with at least one phenyl, halo, halomethyl, and/or (CH₂)_mCOOR' group; and

one or more of the groups Ar and NAr may be replaced by catecholate, cyanide, thiocyanide, tetrazole or CO, provided that at least one of groups Y contains at least one Ar or NAr moiety;

Z stands for an aliphatic or aromatic group containing at least three nitrogen atoms, and which may be substituted by at least one of phenyl, halo, halomethyl, (CH₂)_mCOOR' group, and polymer, or a laser dye; and

M' stands for Ir(III), Ru(II), Os(II), Pd(II), Pt(II), Re(I), Cu(I), Eu(III), Tb(III), Dy(III), Sm(III), or Tm(III); and R' and m have the previously given meanings.

5. The light-emitting device of any one of claims 1-3 wherein D is Ir(Y)₃ and A' is MZ, wherein, Y has independently the formula (2) or (3):

NAr-Ar (2);

NAr-Nar (3);

R' is independently selected from H, Na, K, Li, Ca, and Mg;

NAr is selected from pyridine, imidazole, triazole, oxazole, oxadiazole, thiazole, and thiadiazole, which may be unsubstituted or substituted with at least one phenyl, halo, halomethyl, and/or COOR' group, and when Y is formula (2) or (3) at least one of the ring nitrogen atoms is positioned at the α -position with regard to the atom forming a bond with the NAr or Ar moiety; Ar is phenyl, which may be unsubstituted or substituted with at least one phenyl, halo, halomethyl, and/or $(\text{CH}_2)_m\text{COOR}'$ group; and

one or more of the groups Ar and NAr may be replaced by catecholate, cyanide, thiocyanide, tetrazole or CO, provided that at least one of groups Y contains at least one Ar or NAr moiety;

Z stands for an aliphatic or aromatic group containing at least three nitrogen atoms, and which may be substituted by at least one phenyl, halo, halomethyl, or $(\text{CH}_2)_m\text{COOR}'$ group or polymer; or Z stands for a nitrogen-containing laser dye; and

M stands for Ir(III), Ru(II), or Ln(III), wherein Ln is selected from Ce, Eu, Tb, Eu, Dy, Sm, Nd, Yb, Er, and Tm.

6. The light-emitting device of any one of the preceding claims wherein halo is fluoro and halomethyl is trifluoromethyl.

20

7. The light-emitting device of any one of the preceding claim wherein the polymer is a polymer of phenylenevinylene, phenylene, thiophene, thienylvinylene, a fluorene or 9,9'-spirobifluorene structural unit or polymers like a polyphenylethylene, a polyquinoxaline, a polyvinylcarbazole, or copolymers thereof with hole- or electron-transporting monomers such as triarylaminines and oxadiazoles.

25

8. The light-emitting device of any one of the preceding claims wherein the laser dye is selected from phthalocyanine, naphthocyanine, cyanine, fluoresceine, rhodamine, squaraine, crocoaine, resorufine, oxazine, anthraquinone, substituted or unsubstituted polynuclear aromatic hydrocarbon, and substituted or unsubstituted heterocyclic polynuclear aromatic hydrocarbon dye.

30

9. The light-emitting device of any one of the preceding claims wherein the through space distance between Ir of moiety A and Ir, Ru or La of moiety A' is between 2 and 50 Å, preferably 6-12 Å, most preferably 6-8 Å.

5 10. The light-emitting device of any one of the preceding claims further comprising a pair of electrodes for affecting electroluminescence.

11. A light-emitting compound having the formula (1):

$$(D-X)_n-A' \quad (1)$$

10 wherein

D is $M(Y)_3$ wherein M is independently chosen from an Ir(III), Zn(II), Cu(II), and Os(II);

Y has independently the formula (2) or (3):

NAr-Ar (2);

15 NAr-NAr (3);

in which NAr is independently selected from pyridine, imidazole, triazole, oxazole, oxadiazole, diazole diketone, thiazole, and thiadiazole, catecholate, cyanide, thiocyanide, tetrazoles and carbonyl, which may be unsubstituted or substituted with at least one phenyl, halo, halomethyl, $(CH_2)_mCOOR'$ group, and/or polymer, and at least one of the
 20 ring nitrogen atom is positioned at the α -position with regard to the atom forming a bond with the NAr or Ar moiety;

Ar is phenyl, which may be unsubstituted or substituted with at least one phenyl, halo, halomethyl, $(CH_2)_mCOOR'$ group, and/or polymer; R' being independently selected from H, Na, K, Li, Ca, and Mg, m is 0-3; and

25 one or more of the groups Ar and NAr may be replaced by catecholate, cyanide, thiocyanide, tetrazole or CO, provided that at least one of groups Y contains at least one Ar or NAr moiety;

A' is $M'Z$, wherein M' is selected from Ir(III), Ru(II), Os(II), Pd(II), Pt(II), Re(I), Cu(I), and lanthanide(III);

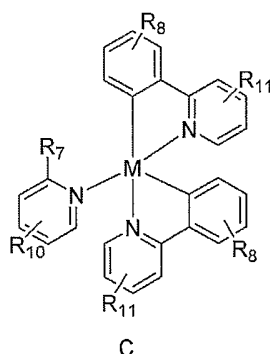
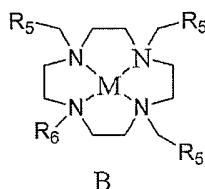
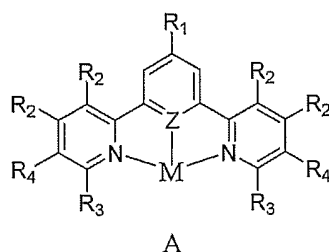
30 Z stands for an aliphatic or aromatic group containing at least three nitrogen atoms, and which may be substituted by at least one of phenyl, halo, halomethyl, $(CH_2)_mCOOR'$, and a polymer, or Z stands for a luminescent organic compound of low molecular weight; and

X is selected from a bond, CR_2 , NR, CO-NR, O, S, phenylene, thiophene,

fluorene, dibenzofurane, dibenzothiophene, cyclopentylene, cyclohexylidene, cyclohexylene, and cyclohexane, in which R is independently H or C1-C12 alkyl and wherein each of the phenylene, thiophene, fluorene, dibenzofurane, dibenzothiophene, cyclopentylene, cyclohexylidene, cyclohexylene, and cyclohexane moieties may be unsubstituted or
5 substituted with one or more of C1-C12 alkyl, C1-C12 alkoxy, phenyl, phenoxy, biphenyl, $(CH_2)_mCOOR'$, and halogen; wherein m and R' have the previously given meanings; and n is 1 or 2.

12. Method for obtaining white light emission by excitation of the light-emitting
10 device of any one of claims 1-8 at a wave length between 300 and 500 nm, or by applying a voltage over the electrodes of the light-emitting device of claim 9.

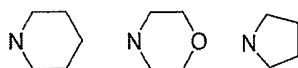
1/6



R_9 = Complex A or complex B, CH_3 , Phenyl, CF_3

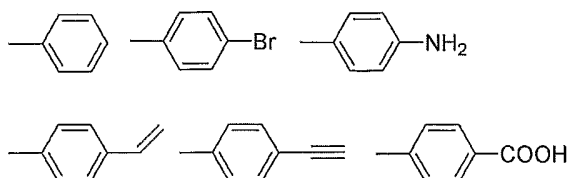
R_{10} = CF_3 , F

R_{11} = CH_3 , CF_3 , OCH_3 , OAlkyl, OH, NH_2 , $\text{N}(\text{CH}_3)_2$,



$Z = \text{C}; \text{N}$

R_1 = -Complex C, Phenyl-complex C, -H, $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, -nPropyl, -isopropyl, -terbutyl, -nhexyl, 2ethyl-hexyl



R_2 = -H, $-\text{CH}_3$, cyclo($-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), cyclo($-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$)

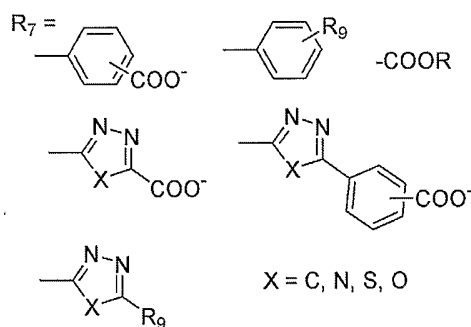
R_3 = COO^- , $\text{CH}_2\text{N}(\text{CH}_2\text{COO}^-)_2$

R_4 = -H, CH_3 , -terzbutyl, -phenyl, -p-bromophenyl, -p-iodophenyl

M = Ir(III), Re(II), Ru(II), Os(II), Pt(II), Zn(II), Eu(III), Sm(III), Tb(III),

R_5 = $-\text{COO}^-$, $-\text{SO}_3^-$

R_6 = Complex C, -H, $-\text{CH}_3$, $-\text{CH}_2\text{COO}^-$, $-\text{CH}_2\text{SO}_3^-$



R_8 = -H, -terzbutyl, nHexyl, 2-ethylhexyl, -2,4diF, -3,5diF, -2,4diCF₃, -3,5diCF₃, $-\text{SO}_3\text{H}$, $-\text{SO}_3\text{Me}$, SO_3Phenyl , $-\text{COOH}$, $-\text{SO}_2\text{CH}_3$, $-\text{SO}_2\text{Phenyl}$, -2,3,4,5tetraF

FIG.1

2/6

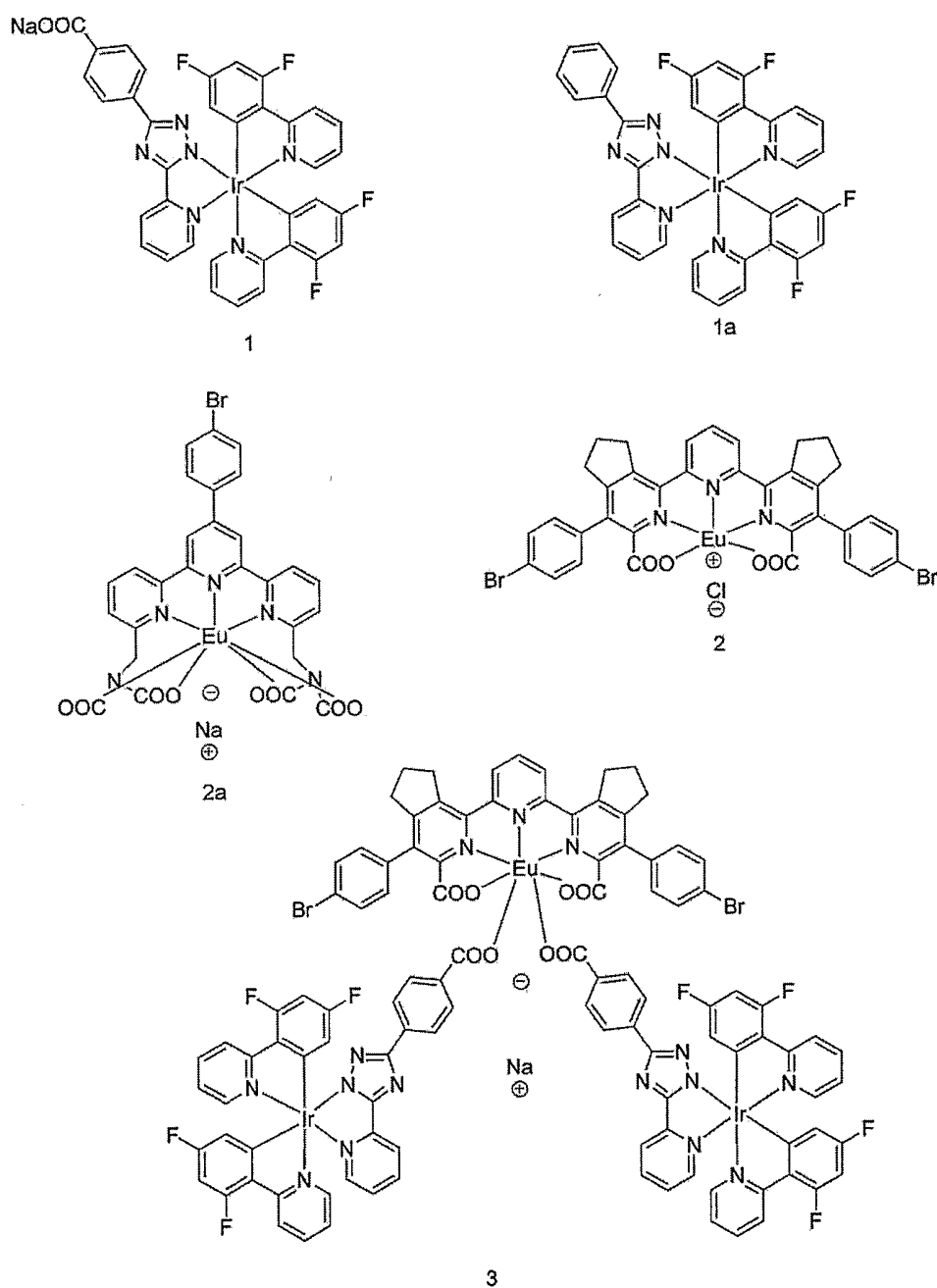


FIG.2

3/6

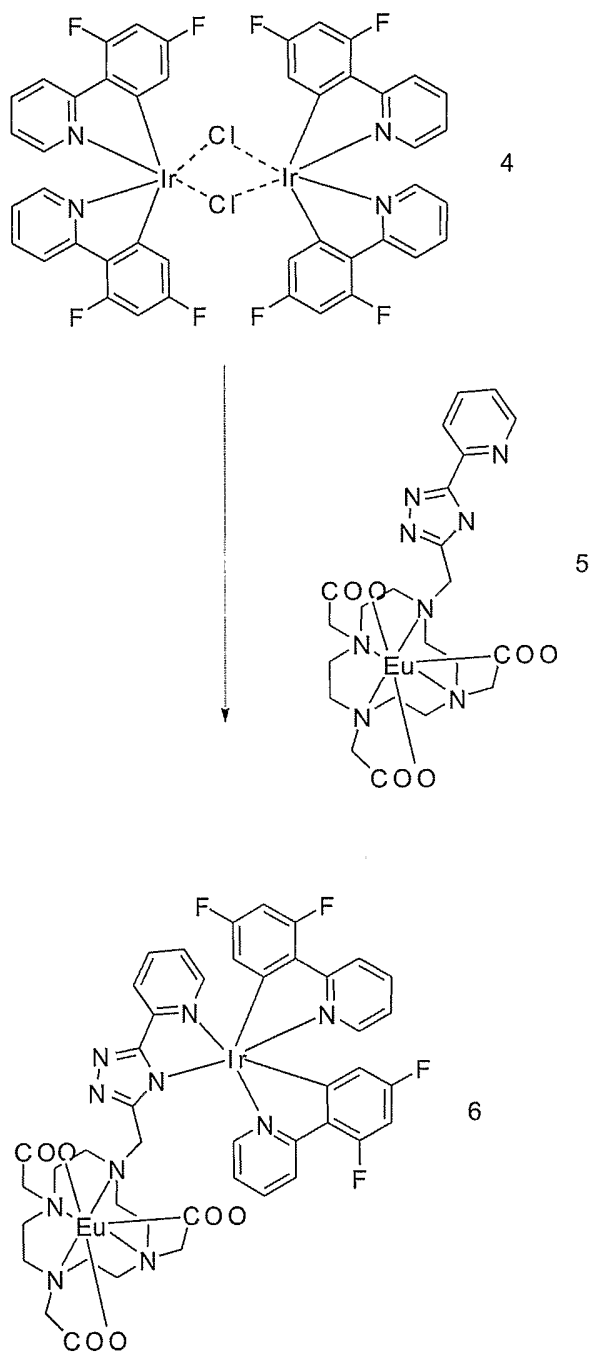


FIG.3

4/6

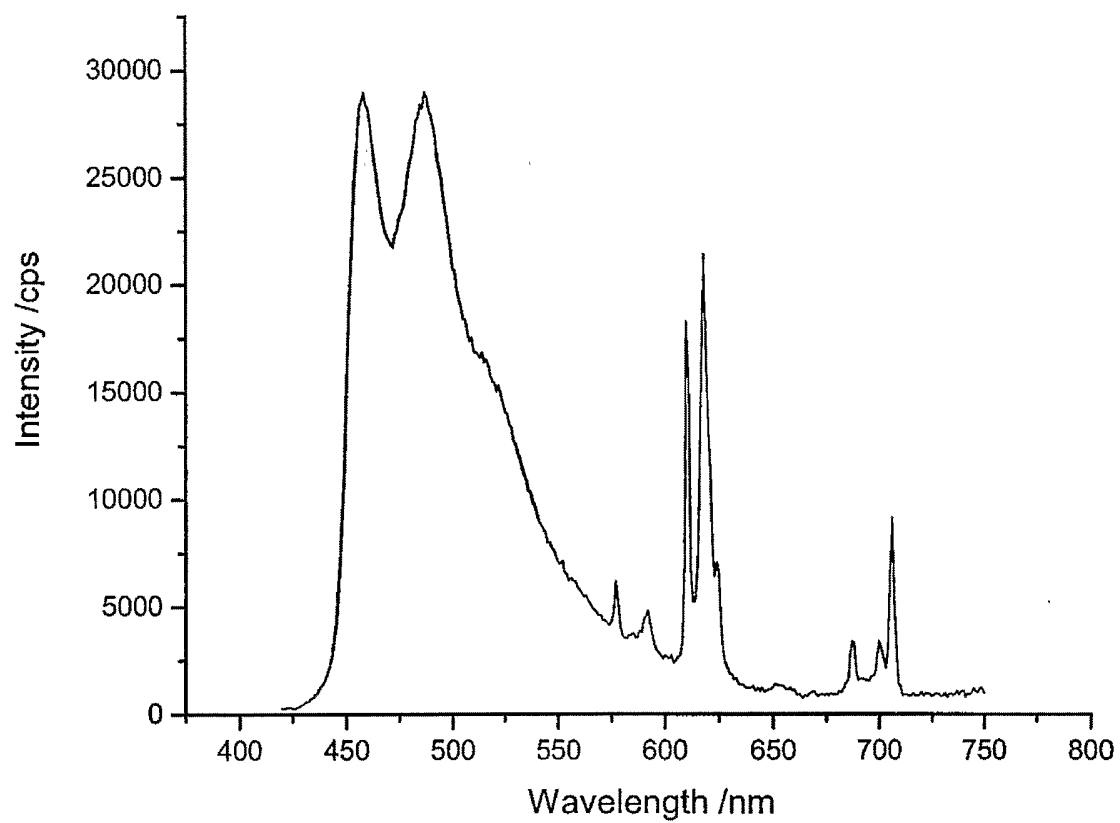


FIG.4

5/6

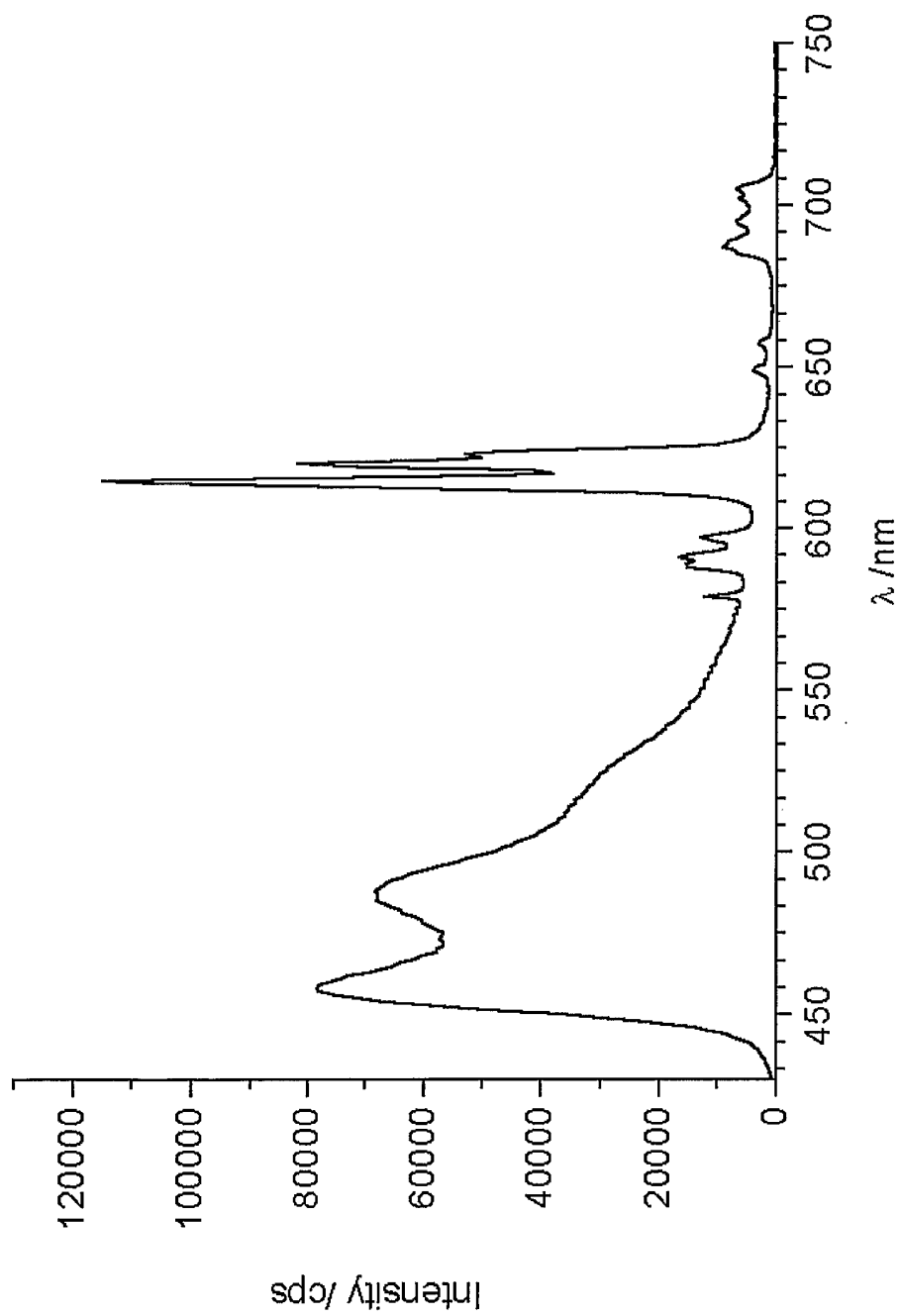
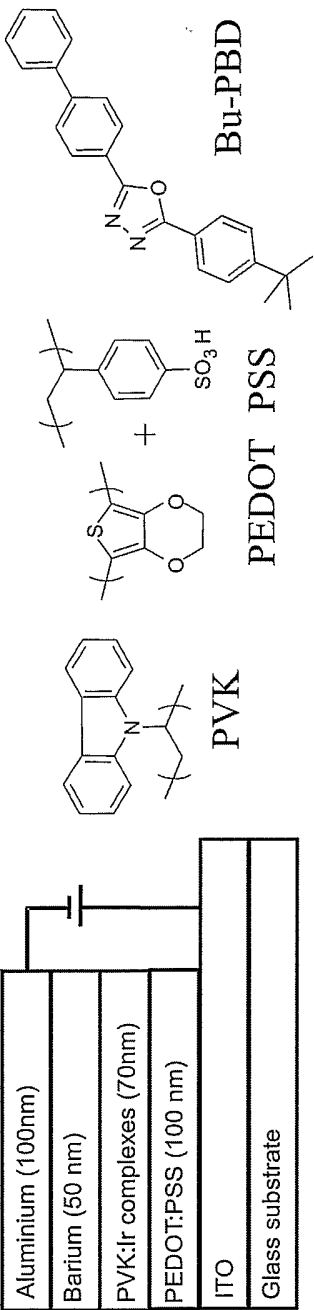


FIG.5



INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB2005/052786

A. CLASSIFICATION OF SUBJECT MATTER H01L51/30		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) H01L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, INSPEC, COMPENDEX		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/074629 A (ELAM-T LIMITED; KATHIRGAMANATHAN, POOPATHY) 12 September 2003 (2003-09-12) page 1 - page 5 page 13, line 7	1-12
X	WO 2004/058783 A (ELAM-T LIMITED; KATHIRGAMANATHAN, POOPATHY; PRICE, RICHARD; GANESHAMUR) 15 July 2004 (2004-07-15) page 9	1-12
----- -/--		
☒ Further documents are listed in the continuation of box C. ☒ Patent family members are listed in annex.		
* Special categories of cited documents : *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. * & * document member of the same patent family		
Date of the actual completion of the international search 22 December 2005		Date of mailing of the international search report 10/01/2006
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Wolfbauer, G

INTERNATIONAL SEARCH REPORT

Inter nal Application No

PCI/1B2005/052786

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	COPPO PAOLO ET AL: "White-light emission from an assembly comprising luminescent iridium and europium complexes" ANGEWANDTE CHEMIE - INTERNATIONAL EDITION, vol. 44, no. 12, 13 December 2004 (2004-12-13), pages 1806-1810, XP002356454 the whole document	1-12
A	EP 1 215 945 A (SANYO ELECTRIC CO., LTD) 19 June 2002 (2002-06-19) paragraph '0059!	1-12
A	COPPO P. ET AL.: "Tuning iridium(III) phenylpyridine complexes in the "almost blue" region" CHEM. COMMUN., no. 15, 30 June 2004 (2004-06-30), pages 1774-1775, XP002356455 cited in the application the whole document	1-12
A	KOZHEVNIKOV V. N. ET AL.: "Synthesis of Functionalized Fluorescent Europium(III) Terpyridyl Chelates" SYNTHESIS, no. 15, 25 September 2003 (2003-09-25), pages 2400-2404, XP002356456 cited in the application the whole document	1-12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB2005/052786

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 03074629	A	12-09-2003	AU	2003216994 A1		16-09-2003
			EP	1537188 A1		08-06-2005
			JP	2005519430 T		30-06-2005
WO 2004058783	A	15-07-2004	AU	2003290340 A1		22-07-2004
			EP	1578756 A1		28-09-2005
EP 1215945	A	19-06-2002	JP	2002184581 A		28-06-2002
			US	2002071963 A1		13-06-2002