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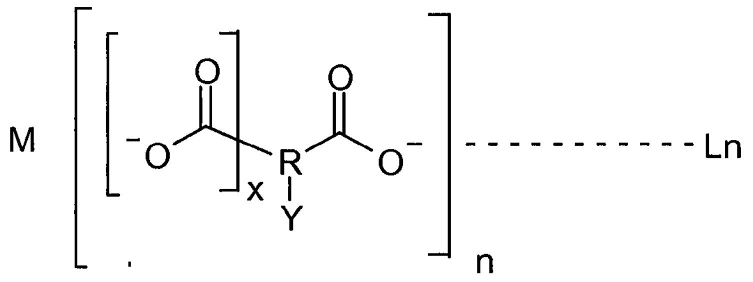


(57) Abstract: Luminescent lanthanide complex and inks containing the complex as well as its method of production and article including the complex, wherein the complex includes the formula: wherein M is chosen from the alkali cations Li^+, Na^+, K^+, $Rb^+$and Cs^+ and mixtures thereof and is present to neutralize charge of the complex; wherein Ln is chosen from the trivalent rare-earth cations of Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb and mixtures thereof; wherein R is a C_5 to C_6 heteroaryl:wherein Y is an optionally substituted C_3-C_8 heterocycloalkyl moiety linked to R by an N atom; wherein n is an integer of 3 or 5; and wherein x is an integer of 0 or 1.

WO 2014/048702 A1

LUMINESCENT LANTHANIDE COMPLEX, AND ARTICLES AND INKS CONTAINING THE LUMINESCENT COMPLEX

FIELD OF THE INVENTION:

[0001] The invention relates to the field of security documents, packaging or items of value and aims at improving the security level of such documents, packaging or items of value. The present invention preferably relates to paper based documents or substrates onto which can be applied or printed a composition comprising luminescent lanthanide complexes.

BACKGROUND OF THE INVENTION:

[0002] Secure documents such as currency, passports, or identity cards are increasingly counterfeited around the world. This situation is a very critical issue for governments and society in general. For example, criminal organizations may use fake passports or identity cards for trafficking of human beings. As reprographic technologies become more and more sophisticated, it becomes even more difficult to make a clear distinction between a fake document and the original. Document security has therefore a considerable impact on the economy of countries and also on victims of illicit traffic involving counterfeit documents.

[0003] Passports and identity cards are in general secure documents which contain a large number of protections, such as holograms, bar codes, encrypted data, specific papers or substrates, etc. Some protections are visible to the unaided eye ("overt" features), other protections are invisible ("covert" features) and their detection requires specific equipment.

[0004] Paper related documents which have valuable interest such as banknotes, fiduciary documents or even recently diplomas, such as diplomas from high schools and colleges and universities, are highly subject to counterfeit. In university or college or high school, for example, the level of security of diplomas made with paper is not enough to prevent illicit reproduction. Very often in such documents there is found as a control element the stamp of the college or university or high school, and eventually a hologram as a security feature. However, holograms are more susceptible to easy reproduction as printing techniques become more and more sophisticated. This permits counterfeiters to reproduce such documents of value, including the college or university or high school stamp.

[0005] In order to prevent such diversion there is a need to find alternative solutions to protect such documents, especially documents made with paper. Security inks comprising luminescent compounds are known to prevent such diversion and very often inkjet compositions are used to protect documents of value.

[0006] In US 2007/0225402 A1, which is incorporated by reference herein in its entirety, the use of an ultraviolet luminescent ink is disclosed, which is printed in form of indicia onto the document. The ultraviolet luminescent ink is invisible under natural light, such that the indicia can be only revealed under irradiation with UV light. This ultraviolet luminescent ink is useful for applying codes onto security documents such as passports or banknotes. In the cited document, printing processes, including silk screen, gravure, letterpress and offset printing are used to apply the invisible ultraviolet fluorescent inks.

[0007] Luminescent compounds in pigment form have been widely used in inks and other preparations (see U.S. Patent No. 6,565,770, WO 2008/033059 A2, WO 2008/092522 A1). Examples of luminescent pigments can be found in certain classes of inorganic compounds, such as the sulphides, oxysulphides, phosphates, vanadates, garnets, spinels, etc. of nonluminescent cations, doped with at least one luminescent cation chosen from the transition-metal or the rare-earth ions.

[0008] Another class of compound useful to produce luminescence in ink is formed by certain rare-earth metal complexes such as described in WO 2009/005733 A1 and its family member US 2009/0000509 A1 or in U.S. Patent No. 7,108,742, which are incorporated by reference herein in their entireties.

[0009] A particular process for imprinting secure documents with luminescent compounds, in particular luminescent rare-earth metal complexes, is inkjet printing, and more particularly thermal inkjet printing. Thermal inkjet printers use print cartridges having a series of tiny electrically heated chambers, constructed by photolithography. To produce an image, the printer sends a pulse of electric current through heating elements disposed in the back of each chamber, causing a steam explosion in the chamber, so as to form a bubble, which propels a droplet of ink through an orifice of the chamber onto the paper in front of it (hence the tradename Bubblejet®

for certain inkjet printers). The ink's surface tension, as well as the condensation and thus contraction of the vapor bubble, pulls a further charge of ink into the chamber through a narrow channel attached to an ink reservoir.

[0010] The ink used is aqueous (i.e., a water-based ink comprising pigments or dyes), and the print head is generally cheaper to produce than the equipment required for other inkjet technologies. However, its lifetime is short, and it is generally exchanged together with the empty ink cartridge.

[0011] A major problem encountered with inkjet printers is ink drying in the printhead's nozzles, causing the pigments and/or dyes to form a solid deposit that plugs the microscopic ink orifices. Most printers prevent this drying by automatically covering the printhead nozzles with a rubber cap when the printer is not in use. Abrupt power loss, or unplugging the printer before it has capping of the printhead can, however, cause the printhead to dry out. Further, even when capped - this seal being not perfect -, over a period of several weeks, the ink in the nozzles can dry out and plug them. Once ink begins to dry out in the nozzles, the drop volume is affected, the drop trajectory can change, or the nozzle can completely fail to jet any ink.

[0012] In the case of luminescent inkjet inks comprising rare earth metal complexes, the stability of the complex in water is critical to avoid nozzle obstruction. In order to prevent premature drying, adding water or solvent, to sufficiently dilute the ink, is an obvious solution. However, dilution with water or solvent reduces the intensity of luminescence (and thus the ease of detection) of the security document printed with such ink.

[0013] Another problem also very often encountered when using ink which comprises luminescent pigments when used, for example, in a water based ink composition with inkjet printer (very often used for printing security document or packaging of value made with paper), is their stability as well as degradation of the ink inside the nozzle of the printer by known mechanisms such as Kogation or precipitation.

[0014] Although rare earth metal complexes would represent a very useful way of imparting luminescence to inkjet inks, the problem of ink drying in the nozzles makes it often impossible to use the inkjet cartridges in their entirety, and causes thus increased ink cartridge consumption cost. This has not only an ecological and security impact, due to the "recycling" problem caused by such "used" cartridge, but also a non-negligible impact on the cost of printing.

[0015] US 2010/0307376 A1, which is incorporated by reference herein in its entirety, is directed to a lanthanide chelates and secure documents containing lanthanide chelates, and provides many advantages and overcomes many of the disadvantages of the prior art, especially disadvantages resulting from stability, premature drying and Kogation.

[0016] Despite the considerable interest of such luminescent inks, the paper which must be protected remains a problem, because not all luminescent inks will adhere to the surface of the paper. Additionally, more problematic is the fact that the ink used when printed onto paper type documents or items does not confer to the paper a high level of security. The security element present in such ink when printed to the paper is not fully revealed or its signal remains relatively weak which does not allow a full recognition of the genuine paper type document or items.

[0017] There is therefore still a need to have a specific and selected water based composition which allows to provide a high level of security when printed on a paper substrate, which allows allow an efficient level of recognition of the security element with a specific luminescent profile hard to reproduce comprised in water based ink composition and which also avoid the drawbacks of instability, kogation and precipitation inside the nozzle of the ink jet printer.

[0018] Thus, there is still a crucial need to solve the above mentioned problems in order to promote the efficient use of luminescent ink-jet inks based on rare earth metal complexes, and therefore to obtain correctly printed and protected security documents during the whole life of the ink cartridge.

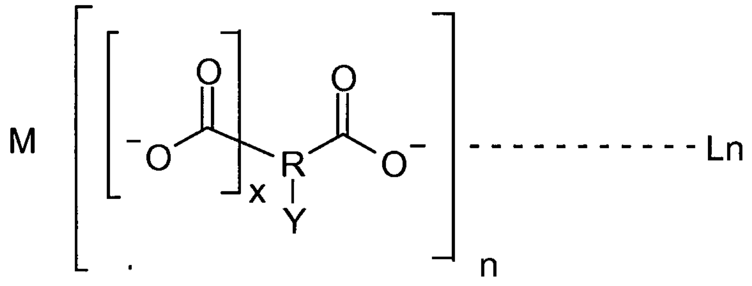
SUMMARY OF THE INVENTION:

[0019] The present invention overcomes the above described disadvantages by:

a) providing a stable and high level of luminescence with specific luminescent profile for efficient marking of paper documents of value during the whole life of the ink cartridge, which allows recognition easily and efficiently of the luminescence as well as its profile, and

b) avoiding nozzle obstruction responsible for the impossibility to use the ink cartridge in its entirety.

[0020] The foregoing is accomplished by providing an aqueous inkjet composition comprising at least one luminescent lanthanide complex of the formula:



wherein M is chosen from the alkali cations Li^+, Na^+, K^+, Rb^+ and Cs^+ and mixtures thereof and is present to neutralize charge of the complex;

wherein Ln is chosen from the trivalent rare-earth cations of Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb and mixtures thereof;

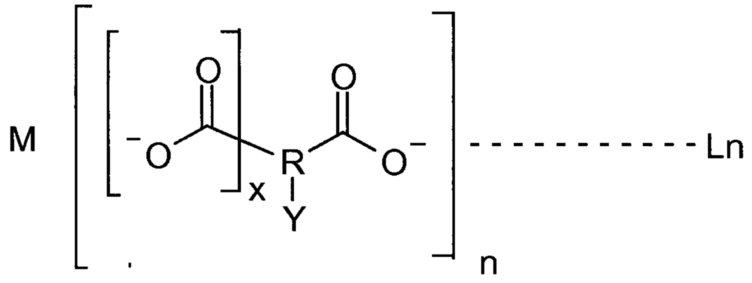
wherein R is a C_5 to C_6 heteroaryl;

wherein Y is an optionally substituted C_3-C_8 heterocycloalkyl moiety linked to R by an N atom;

wherein n is an integer of 3 or 5; and

wherein x is an integer of 0 or 1.

[0021] There is also provided a lanthanide complex according to the following formula:



wherein M is chosen from the alkali cations Li^+, Na^+, K^+, Rb^+ and Cs^+ and mixtures thereof and is present to neutralize charge of the complex;

wherein Ln is chosen from the trivalent rare-earth cations of Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb and mixtures thereof;

wherein R is a C_5 to C_6 heteroaryl:

wherein Y is an optionally substituted C_3-C_8 heterocycloalkyl moiety linked to R by an N atom, said C_3-C_8 heterocycloalkyl moiety carrying preferably at least a nitrogen atom in the cycle, said nitrogen atom being linked to R;

wherein n is an integer of 3 or 5; and

wherein x is an integer of 0 or 1.

[0022] The at least one luminescent lanthanide complex can be a recrystallized product having exact stoichiometry of 1:3.

[0023] The at least one luminescent lanthanide complex can be a recrystallized product having exact stoichiometry of 1:5.

[0024] Preferably, no excessive R component in free form is present in the ink.

[0025] An amount of Cl^- of the complex preferably does not exceed 0.1 wt% based of the total weight of the at least one luminescent lanthanide complex.

[0026] An amount of Cl^- of the complex can be between 0.1 wt% and 0.25 wt% based on the total weight of the complex.

[0027] The aqueous ink composition can include at least one hygroscopic substance, such as 5 to 45 wt% of the at least one hygroscopic substance, based on the total weight of the composition.

[0028] The at least one hygroscopic substance can be selected from primary, secondary or tertiary alcohol, lactams, polymeric glycol, glycol, and cyclic sulfone, and mixtures thereof.

[0029] The at least one hygroscopic substance can be selected from DL-hexane-1,2-diol, 2-pyrrolidone, sulfolane, tetramethylene sulfoxide, gamma-butyrolactone, 1,3-dimethyl-2-imidazolidinone, 2-propanediol, pentanediol, 1,2 hexanediol, trimethylolpropane, glycerol, ethyleneglycol, diethyleneglycol, polypropyleneglycol, polyethyleneglycol, ethanol, propanol, and butanol, and mixtures thereof.

[0030] The aqueous ink composition can include at least one visible dyestuff or pigment, such as 1 to 15 wt% of the at least one visible dyestuff or pigment, based on the total weight of the composition.

[0031] The at least one visible dyestuff or pigment can be selected from monoazo and/or disazo dyes, monoazo Cu-complexes dyes.

[0032] The aqueous ink composition can contain 1-15 wt% of the at least one luminescent lanthanide complex, based on the total weight of the composition.

[0033] R can be pyridine, imidazole, triazole, pyrazole, or pyrazine.

[0034] R taken together with the at least one carboxylic acid group attached thereto can be dipicolinic acid and/or 4-hydroxypyridine-2,6-dicarboxylic acid, and Ln can be chosen from the trivalent ions of Europium (Eu3+) and/or Terbium (Tb3+).

[0035] Y can be a moiety of aziridine, azetidine, imidazolidine, pyrrolidine, pyrrolidin-e-one, pyrrolidine-2-thione, thiomorpholine, morpholine, hexahydropyrimidine, piperazine, azepane, or azocane.

[0036] The C_3-C_8 heterocycloalkyl can be substituted with a C_1-C_6 alkyl or C_1-C_6 alkoxy.

[0037] There are also provided articles comprising the aqueous ink compositions.

[0038] There are also provided security documents comprising at least one layer made with the aqueous ink composition.

[0039] There are also provided processes for obtaining the at least one luminescent lanthanide complex comprising reacting one equivalent of precursor compound of a trivalent or pentavalent lanthanide ion Ln with 3 or 5 equivalents of the R component in the presence of the alkali cation M to neutralize the complex.

[0040] The precursor compound of the trivalent lanthanide ion Ln can be selected from the group consisting of oxides Ln_2O_3, chlorides $LnCl_3$, carbonates $Ln_2(CO_3)_3$ and acetates $Ln(CH_3COO)_3$.

[0041] The R component can be employed as a free acid H_2A together with a required amount of base, or as a monoalkali-salt HMA, or as a dialkali salt M_2A.

[0042] The components of the complex can be combined in aqueous solution, and the resulting complex can be recrystallized so as to separate it from byproducts of the reaction.

[0043] The article can be a banknote, passport, a security document, a value document, a diploma, a fiduciary document, a packaging, a ticket, a foil, a thread, a label or a commercial good.

[0044] The article can be a paper article.

[0045] The at least one luminescent lanthanide complex can be a recrystallized product.

[0046] Preferably, m can be 3 and/or x can be 1.

[0047] The optionally substituted C_3-C_8 heterocycloalkyl moiety can include at least one N atom in addition to the N atom through which Y is linked to R.

[0048] The optionally substituted C_3-C_8 heterocycloalkyl moiety can include at least one O atom.

[0049] The luminescent lanthanide complex can absorb in the ultraviolet and/or the blue region of the electromagnetic spectrum. The luminescent emission in these lanthanide complexes can be due to inner f-shell transitions such as: $^5D_0 \rightarrow {}^7F_1$ and $^5Do \rightarrow {}^7F_2$ for Eu (3+).

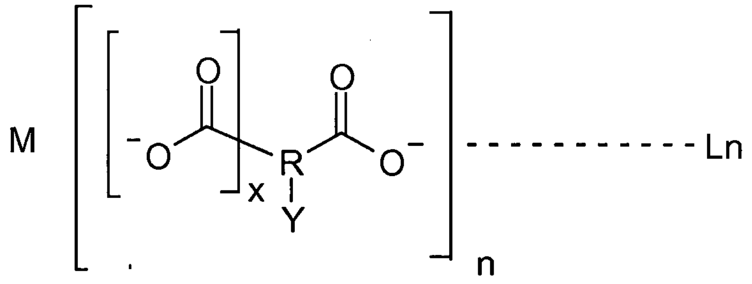
[0050] According to the present invention, a neat stoichiometric complex of the luminescent lanthanide complex is preferably used, rather than a solution of a rare-earth ion salt in a large excess of the R group. This is possible with R groups that form very stable anionic complexes with the rare-earth ion, such that no dissociation (hydrolysis or pyrolysis) occurs in aqueous solution upon heating. Hydrolysis would noteworthy lead to precipitates and corresponding nozzle obstruction.

[0051] Thus, according to the present invention, a neat luminescent lanthanide complex is preferably used. The use of such neat complex salt avoids any unnecessary excess of free R group in the ink, reducing thus its overall solid content, and therewith its tendency to obstruct (to clog) the inkjet nozzles through kogation or drying.

[0052] These and other features and advantages of the present invention will be more readily understood from a reading of the following detailed description by those of ordinary skill in the art. It is to be appreciated that certain features of the invention which are, for clarity, described above and below in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any subcombinaton. Further, reference to values stated in ranges include each and every value within that range.

DETAILED DESCRIPTION OF THE INVENTION:

[0053] According to the present invention, there is provided a lanthanide complex according to the following formula:



wherein M is chosen from the alkali cations Li^+, Na^+, K^+, Rb^+ and Cs^+ and mixtures thereof and is present to neutralize charge of the complex;

wherein Ln is chosen from the trivalent rare-earth cations of Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb and mixtures thereof;

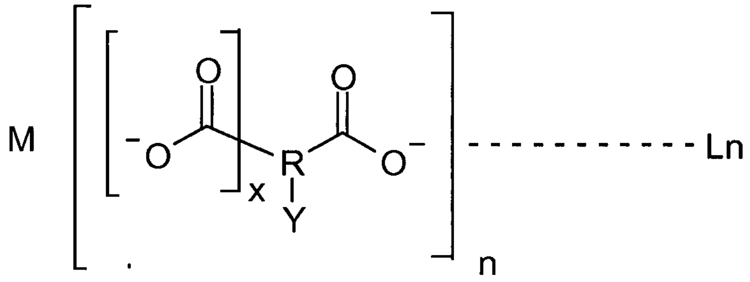
wherein R is a C_5 to C_6 heteroaryl:

wherein Y is an optionally substituted C_3-C_8 heterocycloalkyl moiety linked to R by an N atom;

wherein n is an integer of 3 or 5; and

wherein x is an integer of 0 or 1.

Moreover, there is provided an aqueous inkjet composition comprising at least one luminescent lanthanide complex of the formula:



wherein M is chosen from the alkali cations Li^+, Na^+, K^+, Rb^+ and Cs^+ and mixtures thereof and is present to neutralize charge of the complex;

wherein Ln is chosen from the trivalent rare-earth cations of Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb and mixtures thereof;

wherein R is a C_5 to C_6 heteroaryl;

wherein Y is an optionally substituted C_3-C_8 heterocycloalkyl moiety linked to R by an N atom;

wherein n is an integer of 3 or 5; and

wherein x is an integer of 0 or 1.

[0054] R is preferably pyridine, imidazole, triazole, pyrazole, or pyrazine. For example, R taken together with the at least one carboxylic acid group attached thereto can be, for example, dipicolinic acid, 4-hydroxypyridine-2,6-dicarboxylic acid, 4-amino-pyridine-2,6-dicarboxylic acid, 4-ethoxypyridine-2,6-dicarboxylic acid, 4-isopropoxypyridine-2,6-dicarboxylic acid and/or 4-methoxypyridine-2,6-dicarboxylic acid, preferably dipicolinic acid and/or 4-hydroxypyridine-2,6-dicarboxylic acid.

[0055] Y is preferably a moiety of aziridine, azetidine, imidazolidine, pyrrolidine, pyrrolidin-e-one, pyrrolidine-2-thione, thiomorpholine, morpholine, hexahydropyrimidine, piperazine, azepane, or azocane. Preferably, Y can be substituted with a C_1-C_6 alkyl, , such as a methyl, ethyl, isopropyl, etc., or C_1-C_6 alkoxy, such as a methoxy, ethoxy, isopropoxy, etc.

[0056] Preferably, the lanthanide ion is Europium (Eu3+) and/or Terbium (Tb3+}. Preferably, dipolinic acid or 4-hydroxypyridine-2,6-dicarboxylic acid are used in combination with Europium (Eu3+).

[0057] The at least one luminescent lanthanide complex is preferably a recrystallized product.

[0058] Preferably, m is 1 and/or x is 1.

[0059] The optionally substituted C_3-C_8 heterocycloalkyl moiety can include at least one N atom in addition to the N atom through which Y is linked to R. Moreover, the optionally substituted C_3-C_8 heterocycloalkyl moiety includes at least one O atom.

[0060] There is also provided processes for obtaining the at least one luminescent lanthanide complex. The process can include reacting one equivalent of precursor compound of a trivalent or pentavalent lanthanide ion Ln with 3 or 5 equivalents of the R component in the presence of the alkali cation M to neutralize the complex.

[0061] The precursor compound of the lanthanide ion Ln can be selected from the group consisting of oxides, chlorides, carbonates and acetates, such as Ln_2O_3, $LnCl_3$, $Ln_2(CO_3)_3$ and $Ln(CH_3COO)_3$

[0062] The R component can be employed as a free acid H_2A together with a required amount of base, or as a monoalkali-salt HMA, or as a dialkali salt M_2A.

[0063] The components of the complex can be combined in aqueous solution, and the resulting complex can be recrystallized so as to separate it from byproducts of the reaction.

[0064] For example, the components of the complex salt are combined in aqueous solution, e.g..

$$EuCl_3 + 3\ Na_2(dpa) \rightarrow Na_3\,[Eu\,(dpa)_3] + 3\ NaCl$$

and the resulting complex salt is preferably recrystallized, so as to separate it from byproducts of the reaction, such as NaCl, which are not desirable to achieve the goal of the invention, i.e., an ink with the lowest possible solid contents.

[0065] The lanthanide complex wherein Y is an optionally substituted C_3-C_8 heterocycloalkyl moiety linked to R by an N atom is particularly advantageous. Such lanthanide complex can have multiple emissions bands, such as, two emission bands, such as one emission band at a wavelength of around 230 nm to 275 nm, for example 254 nm, and another emission band at a wavelength of around 340 to 375 nm, for example, 366 nm. Lanthanide complexes being capable of having two emission bands, or two or more emission bands provide the ability for better anti-counterfeiting techniques by having more complicated emission measurements associated with the lanthanide complexes.

[0066] The advantage of the recrystallization process is to provide a luminescent lanthanide complex with a minimal by--product content. This has an impact on the solubility of the complex and on the drying or kogation phenomena. In a preferred embodiment the concentration of Cl^- present with the luminescent lanthanide complex is below 0.1% Cl^- of the total weight of the complex salt or 0.17% NaCl, respectively. To obtain high quality of print, the final chloride content of the luminescent lanthanide complex should not exceed 0.1 wt%. In case of an acceptable print quality, the chloride content of the complex salt can be between 0.1 wt% and 0.25 wt% of the luminescent lanthanide complex.

[0067] The at least one luminescent lanthanide complex can preferably be a recrystallized product having exact stoichiometry of 1:3 or having exact stoichiometry of 1:5.

[0068] The at least one luminescent lanthanide complex is preferably included in an aqueous ink composition. The aqueous ink composition preferably contains 1-15 wt% of the at least one luminescent lanthanide complex, based on the total weight of the composition, more preferably 1 to 8 wt%, and even more preferably 1 to 3 wt%.

[0069] Preferably, no excessive R component in free form is present in the ink.

[0070] In order to prevent the premature drying of the aqueous ink composition according to the present invention during the printing process, the aqueous inkjet ink of the invention further can comprise at least one hygroscopic substance. The at least one hygroscopic substance is preferably present at a concentration of 5 to 45 wt% of the at least one hygroscopic substance, based on the total weight of the composition, more preferably 10 to 45 wt% and even more preferably 20 to 45 wt%. The at least one hygroscopic substance can be selected from primary, secondary or tertiary alcohol, lactams, polymeric glycol, glycol, and cyclic sulfone, and mixtures thereof. For example, the at least one hygroscopic substance can preferably be selected from DL-hexane-1,2-diol, 2-pyrrolidone, sulfolane, tetramethylene sulfoxide, gamma-butyrolactone, 1,3-dimethyl-2-imidazolidinone, 2-propanediol, pentanediol, 1,2 hexanediol, trimethylolpropane, glycerol, ethyleneglycol, diethyleneglycol, polypropyleneglycol, polyethyleneglycol, ethanol, propanol, and butanol, and mixtures thereof.

[0071] The aqueous ink composition can also preferably include at least one visible dyestuff or pigment, such as 1 to 15 wt% of the at least one visible dyestuff or pigment, based on the total weight of the composition. The at least one visible dyestuff or pigment can be selected from monoazo and/or disazo dyes, monoazo Cu-complexes dyes. Examples of such dyestuff can be those produced by CIBA company under the name of IRGASPERSE Jet®.

[0072] Depending on the nature of the security documents to be imprinted, the printing ink according to the present invention can furthermore comprise customary additives, such as, for example, fungicides, biocides surfactants, sequestering agents, pH adjusters, co solvents or binders, such as, for example, acrylate binders, in the amounts customary for these additives.

[0073] There are also provided articles comprising the aqueous ink compositions either directly on the article or on a substrate, such as a label and/or a package associated with the article. For example, the aqueous ink according to the present invention can be used for authenticating an article, such as a banknote, a passport, a security document, a value document, a ticket, a foil, a thread, a label, a card, a diploma, a fiduciary document, a packaging, or a commercial good. For example, there can be provided a security document comprising at least one layer made with an ink according to the invention.

[0074] The ink according to the present invention is particularly useful for printing on paper, such as a paper article or paper label.

[0075] The aqueous ink according to the present invention is particularly suitable for thermal ink-jet printing which is an efficient inkjet printing technique for the coding and marking of products, packages or documents of value. Accordingly, the ink composition is preferably formulation for use thermal ink-jet printing.

[0076] The invention is further illustrated by the following non-limiting examples. Percentages are by weight. Those skilled in the art will recognize that many variations are possible within the spirit and scope of these examples, which are intended to be defined by the following claims and their equivalents in which all terms are meant in their broadest reasonable sense unless otherwise indicated.

[0077] The invention is further illustrated by the following non-limiting examples. Percentages are by weight unless otherwise indicated. Those skilled in the art will recognize that many variations are possible within the spirit and scope of these examples, which are intended to be defined by the following claims and their equivalents in which all terms are meant in their broadest reasonable sense unless otherwise indicated.

Examples:

Reference example 1

[0078] Synthesis of 4-chloropyridine-2,6-dicarboxylic acid (Cldpa)
To a solution of dichlorophenyl phosphine oxide (1.492 mol, 290.8 g) at 120°C slowly add under stirring chelidamic acid (0.373 mol, 75.0 g). Heat the reaction mixture at 120°C for 2hr under an inert atmosphere. Take care to avoid a too-fast formation of foam. After cooling at 80°C, the reaction mixture is poured into H_20 (1L). By gradually pouring, the reaction mixture can turn solid. The solid is filtered, washed twice with H20 and dried overnight at 70°C (97%).
1H NMR [(CD3)2SO]: δ 8.24 (s, 2H)

Example 2

[0079] Synthesis of 4-pyrrolidinopyridine-2,6-dicarboxylic acid (Pyrrodpa)
4-chloropyridine-2,6-dicarboxylic acid (0.238 mol, 48.0 g) is slowly added under stirring to a solution of pyrrolidine (0.952 mol, 67.8 g) at room temperature. Take care to avoid a too-fast addition leading to local temperature increase. Observe precipitation of a solid. The reaction mixture is heated at 120°C for 2hr. By gradually heating, the reaction mixture becomes solid. After cooling at 60°C, H_20 (80ml) is added and the mixture is stirred for 30min until the solid is completely dissolved. The solution is then acidified with HCl (2M) until pH=1. The formed precipitate is filtered, washed twice H_2O and dried overnight at 70°C (93%).
1H NMR [(CD3)2SO]: δ 7.25 (s, 2H), 3.44 (t, 4H), 2.01 (t, 4H)

Example 3

[0080] Synthesis of 4-Morpholino-pyridine-2,6-dicarboxylic acid (Morphodpa)

4-chloro-pyridine-2,6-dicarboxylic acid (0.025 mol, 5.0 g) is slowly added under stirring to a solution of morpholine (0.250 mol, 21.6 g) at room temperature. Care is taken to avoid a too-fast addition leading to local temperature increase. Precipitation of a solid is observed. The reaction mixture is heated at 120°C for 2hr. By gradually heating the reaction mixture becomes solid. After cooling at 60°C, H_20 (80ml) is added and the mixture is stirred for 30 min. until the solid is completely dissolved. The solution is then acidified with 2M HCl until pH=1. The formed precipitate is filtered, washed twice H_2O and dried overnight at 70°C (70%)

1H NMR [(CD3)2SO] δ : 7.59 (s, 2H), 3.72 (t, 4H), 3.44 (t, 4H)

Example 4

[0081] Synthesis of $Na_3[Eu(Pyrrodpa)_3]*nH_2O$

A solution of 2M NaOH is added to a suspension of 4-pyrrolidinopyridine-2,6-dicarboxylic acid (0.042 mol, 10.0 g) in 85 ml of distilled water to adjust the pH (pH~8) which results in complete dissolution of the reaction mixture. Then a solution of $EuCl_3.6H_2O$ (0.014 mol, 5.2 g) in 10 ml of H_2O is added and the reaction mixture is stirred at room temperature for 30 min. After stirring the mixture is first neutralized with 2M NaOH (pH~8) and then heated until 50°C. Once the temperature is reached, H_2O is added until a clear solution is obtained. Acetone (~2*VH_2O) is successively added to precipitate the complex and the mixture is cooled until room temperature. The precipitate is finally filtered, washed with acetone and dried overnight at 70°C.

Example 5

[0082] Synthesis of $Na_3[Tb(Pyrrodpa)_3]*nH_2O$

A solution of 2M NaOH is added to a suspension of 4-pyrrolidinopyridine-2,6-dicarboxylic acid (0.042 mol, 10.0 g) in 85 ml of distilled water to adjust the pH (pH~8) which results in complete dissolution of the reaction mixture. Then a solution of $TbCl_3.6H_2O$ (0.014 mol, 5.3 g) in 10 ml of H_2O is added and the reaction mixture is stirred at room temperature for 30min. After stirring the mixture is first neutralized with 2M NaOH (pH~8) and then heated until 50°C. Once the temperature is reached, H_2O is added until a clear solution is obtained. Acetone (~2*VH_2O) is successively added to precipitate the complex and the mixture is cooled until room temperature. The precipitate is finally filtered, washed with acetone and dried overnight at 70°C.

Example 6

[0083] Synthesis of $Na_3[Eu(Morphodpa)_3]*nH_2O$

A solution of 2M NaOH is added to a suspension of 4-morpholinopyridine-2,6-dicarboxylic acid (0.040 mol, 10.0 g) in 85 ml of distilled water to adjust the pH (pH~8) which results in complete dissolution of the reaction mixture. Then a solution of $EuCl_3.6H_2O$ (0.013 mol, 4.8 g) in 10 ml of H_2O is added and the reaction mixture is stirred at room temperature for 30 min. After stirring the mixture is first neutralized with 2M NaOH (pH~8) and then heated until 50°C. Once the temperature is reached, H_2O is added until a clear solution is obtained. Acetone (~2*VH_2O) is successively added to precipitate the complex and the mixture is cooled until room temperature. The precipitate is finally filtered, washed with acetone and dried overnight at 70°C.

Example 7

[0084] Synthesis of $Na_3[Tb(Morphodpa)_3]*nH_2O$

A solution of 2M NaOH is added to a suspension of 4-morpholinopyridine-2,6-dicarboxylic acid (0.040 mol, 10.0 g) in 85 ml of distilled water to adjust the pH (pH~8) which results in complete dissolution of the reaction mixture. Then a solution of $TbCl_3.6H_2O$ (0.013 mol, 4.9g) in 10 ml of H_2O is added and the reaction mixture is stirred at room temperature for 30 min. After stirring the mixture is first neutralized with 2M NaOH (pH~8) and then heated until 50°C. Once the temperature is reached, H_2O is added until a clear solution is obtained. Acetone (~2*VH_2O) is successively added to precipitate the complex and the mixture is cooled until room temperature. The precipitate is finally filtered, washed with acetone and dried overnight at 70°C.

Example 8

[0085] Example of formulation of an ink containing a complex according to the invention:

[0086] Black with fluorescent red (excitation at 254 and 366 nm):

To a solution of deionized water (40.5 g) are added 2-pyrrolidone 5 g) and 1,2-hexanediol (2.5 g). The solution is stirred at 500-600 rpm in order to obtain a homogenized solution. 2 g of $Na_3[Eu(Pyrrodpa)_3]*nH_2O$ are added to the solution, then heated at 40°C. until the complex is totally solubilized. The solution is cooled to ambient temperature, and then 18 g of Irgasperse® Jet Cyan RL, 13.65 g Irgasperse® Jet yellow RL and 4.35 g Irgasperse® Jet Magenta B are added, the mixture is stirred at 500-600 rpm around 20 minutes. After stirring, the solution is filtered to remove all insoluble compounds and unreacted products.

[0087] The black with fluorescent red ink obtained is packaged in a HP45 cartridge and is used with a Deskjet printer of the 960Cxi, 970Cxi, 980Cxi or 990Cxi series. Fluorescence is checked using a fisher Bioblock Scientific VL-4.LC lamp is well visible. In order to assess ink stability, two tests are performed:

Printing of 200 pages in a row followed by 2 to 4 days interruption and restart for another 400 pages.

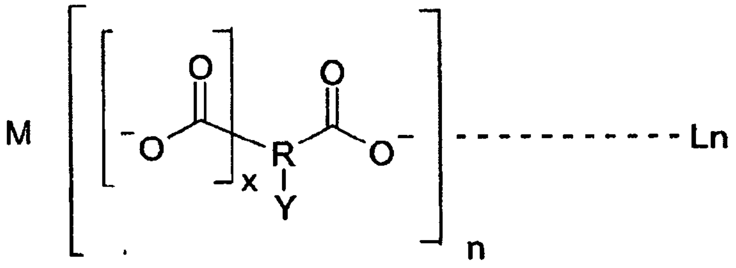
Short print tests are made after 1 week, 2 weeks, 3 weeks, 4 weeks and then every 4 weeks over a 6 month period.

[0088] No problems of printing and drying are expected with the ink according to the present invention during stability testing. In all cases fluorescence intensity for the inventive compounds would be expected to remain unchanged at very satisfactory level.

[0089] The foregoing examples are merely illustrative of some of the features of the invention. The appended claims are intended to claim the invention as broadly as it has been conceived and the examples herein presented are illustrative of selected embodiments from a manifold of all possible embodiments. Accordingly it is Applicants' intention that the appended claims are not to be limited by the choice of examples utilized to illustrate features of the present invention.

What is claimed is:

1. Aqueous inkjet ink composition comprising at least one luminescent lanthanide complex of the formula:



wherein M is chosen from the alkali cations Li^+, Na^+, K^+, Rb^+ and Cs^+ and mixtures thereof and is present to neutralize charge of the complex;

wherein Ln is chosen from the trivalent rare-earth cations of Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb and mixtures thereof;

wherein R is a C_5 to C_6 heteroaryl:

wherein Y is an optionally substituted C_3-C_8 heterocycloalkyl moiety linked to R by an N atom;

wherein n is an integer of 3 or 5; and

wherein x is an integer of 0 or 1.

2. The aqueous ink composition according to claim 1 wherein the at least one luminescent lanthanide complex is a recrystallized product having exact stoichiometry of 1:3.

3. The aqueous ink composition according to claim 1 wherein the at least one luminescent lanthanide complex is a recrystallized product having exact stoichiometry of 1:5.

4. The aqueous ink composition according to any of the preceding claims wherein no excessive ligand R component in free form is present in the ink.

5. The aqueous ink composition according to any of the preceding claims wherein an amount of Cl^- of the complex does not exceed 0.1 wt% based of the total weight of the complex

6. The aqueous ink composition according to any of the preceding claims wherein an amount of Cl^- of the complex is between 0.1 wt% and 0.25 wt% based on the total weight of the complex.

7. The aqueous ink composition according to any of the preceding claims further including at least one hygroscopic substance.

8. The aqueous ink composition according to any of the preceding claims further including at least one visible dyestuff or pigment.

9. The aqueous ink composition according to any of the preceding claims which contains 1-15 wt% of the at least one luminescent lanthanide complex, based on the total weight of the composition.

10. The aqueous ink composition according to claim 7 which contains 5 to 45 wt% of the at least one hygroscopic substance, based on the total weight of the composition.

11. The aqueous ink composition according to claim 8 which contains 1 to 15 wt% of the at least one visible dyestuff or pigment, based on the total weight of the composition.

12. The aqueous ink composition according to any one of claims 7 to 11 wherein the at least one hygroscopic substance is selected from primary, secondary or tertiary alcohol, lactams, polymeric glycol, glycol, and cyclic sulfone, and mixtures thereof.

13. The aqueous ink composition according to any one of claims 7 to 11 wherein the at least one hygroscopic substance is selected from DL-hexane-1,2-diol, 2-pyrrolidone, sulfolane, tetramethylene sulfoxide, gamma-butyrolactone, 1,3-dimethyl-2-imidazolidinone, 2-propanediol, pentanediol, 1,2 hexanediol, trimethylolpropane, glycerol, ethyleneglycol, diethyleneglycol, polypropyleneglycol, polyethyleneglycol, ethanol, propanol, and butanol, and mixtures thereof.

14. The aqueous ink composition according to claim 8 wherein the at least one visible dyestuff or pigment is selected from monoazo and/or disazo dyes, monoazo Cu-complexes dyes.

15. The aqueous ink composition according to any of the preceding claims, wherein R is pyridine, imidazole, triazole, pyrazole, or pyrazine.

16. The aqueous ink composition according to any of the preceding claims, wherein R taken together with the at least one carboxylic acid group attached thereto is dipicolinic acid and/or 4-hydroxypyridine-2,6-dicarboxylic acid, and wherein Ln is chosen from the trivalent ions of Europium (Eu3+) and/or Terbium (Tb3+).

17. The aqueous ink composition according to anyone of claims 1 to 16 wherein the group Y of the lanthanide complex is an optionally substituted C_3-C_8 heterocycloalkyl moiety carrying at least a nitrogen atom in the cycle, said nitrogen atom being linked to R.

18. The aqueous ink composition according to claim 17 wherein Y is a moiety of aziridine, azetidine, imidazolidine, pyrrolidine, pyrrolidin-e-one, pyrrolidine-2-thione, thiomorpholine, morpholine, hexahydropyrimidine, piperazine, azepane, or azocane.

19. The aqueous ink composition according to anyone of claims 1 to 18 wherein the C_3-C_8 heterocycloalkyl is substituted with a C_1-C_6 alkyl or C_1-C_6 alkoxy.

20. An article comprising the aqueous ink composition according to any of the preceding claims.

21. A security document comprising at least one layer made with the aqueous ink composition according to any one of claims 1 to 19.

22. Process to obtain the at least one luminescent lanthanide complex according to any of claims 1 to 19, comprising reacting one equivalent of precursor compound of a

trivalent or pentavalent lanthanide ion Ln with 3 or 5 equivalents of the R component in the presence of at least 3 or 5 equivalents of the alkali cation M.

23. Process according to claim 22, wherein the precursor compound of the trivalent lanthanide ion Ln is selected from the group consisting of oxides Ln_2O_3, chlorides $LnCl_3$, carbonates $Ln_2(CO_3)_3$ and acetates $Ln(CH_3COO)_3$.

24. Process according to one of claims 22 or 23, wherein the R component is employed as a free acid H_2A together with a required amount of base, or as a monoalkali-salt HMA, or as a dialkali salt M_2A.

25. Process according to one of claims 22 to 24, wherein the components of the complex are combined in aqueous solution, and the resulting complex is recrystallized so as to separate it from byproducts of the reaction.

26. The article according to claim 19, wherein the article is a banknote, passport, a security document, a value document, a diploma, a fiduciary document, a packaging, a ticket, a foil, a thread, a label or a commercial good.

27. The article according claim 20, wherein the article is a paper article.

28. The aqueous ink composition according to any of claims 1-19 wherein the at least one luminescent lanthanide complex is a recrystallized product.

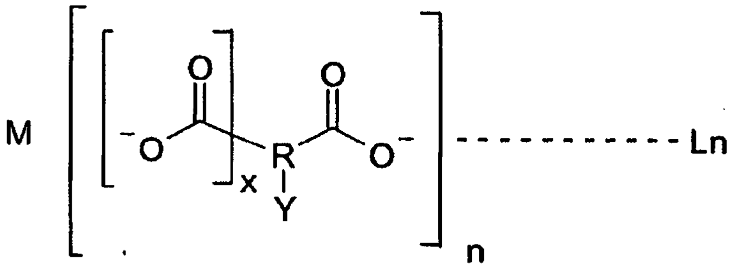
29. The aqueous ink composition according to any of claims 1-19 and 28 wherein m = 3.

30. The aqueous ink composition according to any of claims 1-19, 29 and 30 wherein x=1.

31. The aqueous ink composition according to any of claims 1-19 and 29-30 wherein the optionally substituted C_3-C_8 heterocycloalkyl moiety includes at least one N atom in addition to the N atom through which Y is linked to R.

32. The aqueous ink composition according to any of claims 1-19 and 29-31 wherein the optionally substituted C_3-C_8 heterocycloalkyl moiety includes at least one O atom.

33. A lanthanide complex according to the following formula:



wherein M is chosen from the alkali cations Li^+, Na^+, K^+, Rb^+ and Cs^+ and mixtures thereof and is present to neutralize charge of the complex;

wherein Ln is chosen from the trivalent rare-earth cations of Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb and mixtures thereof;

wherein R is a C_5 to C_6 heteroaryl:

wherein Y is an optionally substituted C_3-C_8 heterocycloalkyl moiety linked to R by an N atom;

wherein n is an integer of 3 or 5; and

wherein x is an integer of 0 or 1.

34. The lanthanide complex according to claim 33, wherein R is pyridine, imidazole, triazole, pyrazole, or pyrazine.

35. The lanthanide complex according to claims 33 or 34, wherein R taken together with the at least one carboxylic acid group attached thereto is dipicolinic acid and/or 4-hydroxypyridine-2,6-dicarboxylic acid and wherein Ln is chosen from the trivalent ions of Europium (Eu3+) and/or Terbium (Tb3+).

36. The lanthanide complex according to claims 33 to 35, wherein the group Y is an optionally substituted C_3-C_8 heterocycloalkyl moiety carrying at least a nitrogen atom in the cycle, said nitrogen atom being linked to R.36. The lanthanide complex according to any of claims 32-35 wherein Y is a moiety of aziridine, azetidine, imidazolidine, pyrrolidine, pyrrolidin-e-one, pyrrolidine-2-thione, thiomorpholine, morpholine, hexahydropyrimidine, piperazine, azepane, or azocane.

38. The lanthanide complex according to any of claims 33-37 wherein the C_3-C_8 heterocycloalkyl is substituted with a C_1-C_6 alkyl or C_1-C_6 alkoxy.

39. The lanthanide complex according of any of claims 33-38 wherein x=1.

40. The lanthanide complex according to any of claims 33-39 wherein the lanthanide complex is a recrystallized product.

41. The lanthanide complex according to any of claims 33-40 wherein m = 3.

42. The lanthanide complex according to any of claims 33-41 wherein the optionally substituted C_3-C_8 heterocycloalkyl moiety includes at least one N atom in addition to the N atom through which Y is linked to R.

43. The lanthanide complex according to any of claims 33-42 wherein the optionally substituted C_3-C_8 heterocycloalkyl moiety includes at least one O atom.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/068570

A. CLASSIFICATION OF SUBJECT MATTER
INV. B41M3/14 C09D11/00
ADD.

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)
B41M C09D

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 practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 402 986 B1 (JONES II GUILFORD [US] ET AL) 11 June 2002 (2002-06-11) column 6, lines 7-6; figures 1,5; examples -----	1-43
A	WO 2010/130681 A1 (SICPA HOLDING SA [CH]; ABOUTANOS VICKIE [CH]; TILLER THOMAS [CH]; REIN) 18 November 2010 (2010-11-18) claim 17; examples -----	1-43
A	EP 2 096 499 A1 (XEROX CORP [US]) 2 September 2009 (2009-09-02) paragraphs [0005], [0035] -----	1-43

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search 13 November 2013	Date of mailing of the international search report 02/12/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Sperry, Pascal

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/068570

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			CR	20110588	A	23-01-2012
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			KR	20090092251	A	31-08-2009
			US	2009214972	A1	27-08-2009

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B41M 3/14(2006.01)
C09D 11/38(2014.01)

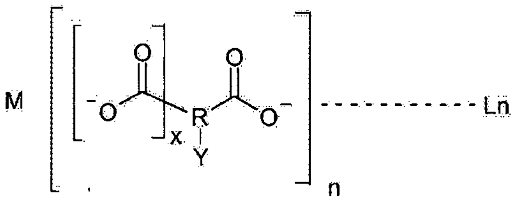
权利要求书3页 说明书10页

(54) 发明名称

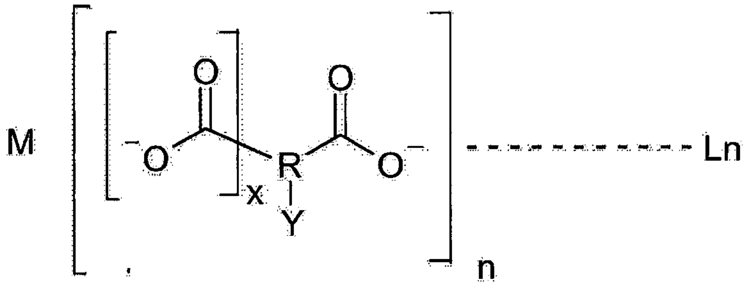
发光镧系元素配合物，以及包含该发光配合物的制品和油墨

(57) 摘要

发光镧系元素配合物和包含该配合物的油墨以及它的制备方法和包含该配合物的制品，其中配合物包括下式，其中M选自碱阳离子Li^+、Na^+、K^+、Rb^+和Cs^+及其混合物并存在以中和配合物的电荷；其中Ln选自如下各项的三价稀土阳离子：Ce、Pr、Nd、Sm、Eu、Gd、Tb、Dy、Ho、Er、Tm和Yb及其混合物；其中R为C_5-C_6杂芳基；其中Y为通过N原子连接在R上的任选取代的C_3-C_8杂环烷基结构部分；其中n为3或5的整数；且其中x为0或1的整数。



1. 水性喷墨油墨组合物，其包含至少一种下式的发光镧系元素配合物：



其中M选自碱阳离子Li^+、Na^+、K^+、Rb^+和Cs^+及其混合物并存在以中和配合物的电荷；

其中Ln选自如下各项的三价稀土阳离子：Ce、Pr、Nd、Sm、Eu、Gd、Tb、Dy、Ho、Er、Tm和Yb及其混合物；

其中R为C_5-C_6杂芳基；

其中Y为通过N原子连接在R上的任选取代的C_3-C_8杂环烷基结构部分；

其中n为3或5的整数；且

其中x为0或1的整数。

2. 根据权利要求1的水性油墨组合物，其中该至少一种发光镧系元素配合物为具有1:3的确切化学计量的再结晶产物。

3. 根据权利要求1的水性油墨组合物，其中该至少一种发光镧系元素配合物为具有1:5的确切化学计量的再结晶产物。

4. 根据前述权利要求中任一项的水性油墨组合物，其中油墨中不存在过量的游离形式的配体R组分。

5. 根据前述权利要求中任一项的水性油墨组合物，其中配合物的Cl^-量基于配合物的总重量为不超过0.1重量%。

6. 根据前述权利要求中任一项的水性油墨组合物，其中配合物的Cl^-量基于配合物的总重量在0.1重量%至0.25重量%之间。

7. 根据前述权利要求中任一项的水性油墨组合物，其进一步包含至少一种吸湿物质。

8. 根据前述权利要求中任一项的水性油墨组合物，其进一步包含至少一种可见染料或颜料。

9. 根据前述权利要求中任一项的水性油墨组合物，其包含基于组合物的总重量为1-15重量%的至少一种发光镧系元素配合物。

10. 根据权利要求7的水性油墨组合物，其包含基于组合物的总重量为5-45重量%的至少一种吸湿物质。

11. 根据权利要求8的水性油墨组合物，其包含基于组合物的总重量为1-15重量%的至少一种可见染料或颜料。

12. 根据权利要求7-11中任一项的水性油墨组合物，其中该至少一种吸湿物质选自伯、仲或叔醇、内酰胺、聚合二醇、二醇和环砜及其混合物。

13. 根据权利要求7-11中任一项的水性油墨组合物，其中该至少一种吸湿物质选自DL-己烷-1,2-二醇、2-吡咯烷酮、环丁砜、四亚甲基亚砜、γ-丁内酯、1,3-二甲基-2-咪唑啉酮、2-丙二醇、戊二醇、1,2己二醇、三羟甲基丙烷、甘油、乙二醇、二甘醇、聚丙二醇、聚

乙二醇、乙醇、丙醇和丁醇及其混合物。

14. 根据权利要求 8 的水性油墨组合物，其中该至少一种可见染料或颜料选自单偶氮和/或二偶氮染料、单偶氮 Cu- 配合物染料。

15. 根据前述权利要求中任一项的水性油墨组合物，其中 R 为吡啶、咪唑、三唑、吡唑或吡嗪。

16. 根据前述权利要求中任一项的水性油墨组合物，其中 R 与连接在其上的至少一个羧酸基团一起为吡啶二羧酸和/或 4- 羟基吡啶 -2,6- 二羧酸，且其中 Ln 选自三价离子铕 (Eu3+) 和/或铽 (Tb3+)。

17. 根据权利要求 1-16 中任一项的水性油墨组合物，其中镧系元素配合物的基团 Y 为环中带有至少一个氮原子的任选取代的 C_3-C_8 杂环烷基结构部分，所述氮原子连接在 R 上。

18. 根据权利要求 17 的水性油墨组合物，其中 Y 为氮丙啶、氮杂环丁烷、咪唑烷、吡咯烷、吡咯烷酮、吡咯烷 -2- 硫酮、硫代吗啉、吗啉、六氢嘧啶、哌嗪、氮杂环庚烷或氮杂环辛烷的结构部分。

19. 根据权利要求 1-18 中任一项的水性油墨组合物，其中 C_3-C_8 杂环烷基被 C_1-C_6 烷基或 C_1-C_6 烷氧基取代。

20. 一种制品，其包含根据前述权利要求中任一项的水性油墨组合物。

21. 安全文件，其包含至少一个用根据权利要求 1-19 中任一项的水性油墨组合物制备的层。

22. 得到根据权利要求 1-19 中任一项的至少一种发光镧系元素配合物的方法，其包括使 1 当量的三价或五价镧系元素离子 Ln 的前体化合物与 3 或 5 当量的 R 组分在至少 3 或 5 当量碱阳离子 M 的存在下反应。

23. 根据权利要求 22 的方法，其中三价镧系元素离子 Ln 的前体化合物选自氧化物 Ln_2O_3、氯化物 $LnCl_3$、碳酸盐 $Ln_2(CO_3)_3$ 和乙酸盐 $Ln(CH_3COO)_3$。

24. 根据权利要求 22 或 23 的方法，其中 R 组分作为游离酸 H_2A 与所需量的碱一起使用，或者作为单碱盐 HMA 或者作为二碱盐 M_2A 使用。

25. 根据权利要求 22-24 中一项的方法，其中将配合物的组分在水溶液中结合，并使所得配合物再结晶以从反应的副产物分离它。

26. 根据权利要求 19 的制品，其中制品为纸币、护照、安全文件、价值文件、证书、信托文件、包装、票、箔、丝线、标签或商品。

27. 根据权利要求 20 的制品，其中制品为纸制品。

28. 根据权利要求 1-19 中任一项的水性油墨组合物，其中该至少一种发光镧系元素配合物为再结晶产物。

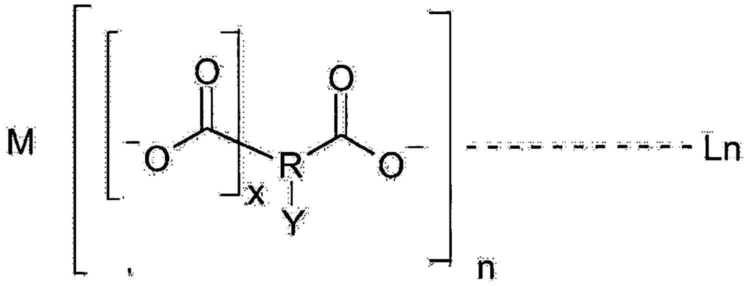
29. 根据权利要求 1-19 和 28 中任一项的水性油墨组合物，其中 $m = 3$.

30. 根据权利要求 1-19、29 和 30 中任一项的水性油墨组合物，其中 $x = 1$。

31. 根据权利要求 1-19 和 29-30 中任一项的水性油墨组合物，其中任选取代的 C_3-C_8 杂环烷基结构部分除将 Y 连接在 R 上的 N 原子外还包含至少一个 N 原子。

32. 根据权利要求 1-19 和 29-31 中任一项的水性油墨组合物，其中任选取代的 C_3-C_8 杂环烷基结构部分包含至少一个 O 原子。

33. 根据下式的镧系元素配合物：



其中 M 选自碱阳离子 Li^+、Na^+、K^+、Rb^+和 Cs^+及其混合物并存在以中和配合物的电荷；

其中 Ln 选自如下各项的三价稀土阳离子：Ce、Pr、Nd、Sm、Eu、Gd、Tb、Dy、Ho、Er、Tm 和 Yb 及其混合物；

其中 R 为 C_5-C_6杂芳基；

其中 Y 为通过 N 原子连接在 R 上的任选取代的 C_3-C_8杂环烷基结构部分；

其中 n 为 3 或 5 的整数；且

其中 x 为 0 或 1 的整数。

34. 根据权利要求 33 的镧系元素配合物，其中 R 为吡啶、咪唑、三唑、吡唑或吡嗪。

35. 根据权利要求 33 或 34 的镧系元素配合物，其中 R 与连接在其上的至少一个羧酸基团一起为吡啶二羧酸和/或 4-羟基吡啶-2,6-二羧酸且其中 Ln 选自三价离子铕 (Eu3+) 和/或铽 (Tb3+)。

36. 根据权利要求 33-35 的镧系元素配合物，其中基团 Y 为环中带有至少一个氮原子的任选取代的 C_3-C_8杂环烷基结构部分，所述氮原子连接在 R 上。

36. 根据权利要求 32-35 中任一项的镧系元素配合物，其中 Y 为氮丙啶、氮杂环丁烷、咪唑烷、吡咯烷、吡咯烷酮、吡咯烷-2-硫酮、硫代吗啉、吗啉、六氢嘧啶、哌嗪、氮杂环庚烷或氮杂环辛烷的结构部分。

38. 根据权利要求 33-37 中任一项的镧系元素配合物，其中 C_3-C_8杂环烷基被 C_1-C_6烷基或 C_1-C_6烷氧基取代。

39. 根据权利要求 33-38 中任一项的镧系元素配合物，其中 x = 1。

40. 根据权利要求 33-39 中任一项的镧系元素配合物，其中镧系元素配合物为再结晶产物。

41. 根据权利要求 33-40 中任一项的镧系元素配合物，其中 m = 3.

42. 根据权利要求 33-41 中任一项的镧系元素配合物，其中任选取代的 C_3-C_8杂环烷基结构部分除将 Y 连接在 R 上的 N 原子外还包含至少一个 N 原子。

43. 根据权利要求 33-42 中任一项的镧系元素配合物，其中任选取代的 C_3-C_8杂环烷基结构部分包含至少一个 O 原子。

发光镧系元素配合物，以及包含该发光配合物的制品和油墨

发明领域

[0001] 本发明涉及安全文件、包装或有价值物品的领域并旨在改进这类文件、包装或有价值物品的安全性水平。本发明优选涉及包含发光镧系元素配合物的组合物可应用或印刷在其上的纸基文件或基质。

[0002] 发明背景

[0003] 安全文件如货币、护照或身份证在世界范围内日益被伪造。该情形通常是对政府和社会而言非常危急的问题。例如，犯罪组织可使用假护照或身份证用于人类的非法勾当。由于复制技术变得越来越成熟，明显地区别假文件与原始文件变得甚至更困难。因此，文件安全性对国家的经济以及涉及伪造文件的违法交易的受害人具有相当的影响。

[0004] 护照和身份证通常为包含大量保护措施如全息图、条码、加密数据、特殊纸或基质等的安全文件。一些保护措施是肉眼可见的（“显性”特征），其它保护措施是不可见的（“隐性”特征），且它们的检测要求特殊设备。

[0005] 具有有价值利益的纸相关文件如纸币、信托文件或者甚至最近的证书，例如来自高中和学院和大学的证书非常容易被伪造。在大学或学院或高中中，例如用纸制成的证书的安全性水平不足以防止非法复制。在这类文件中，非常通常地发现学院或大学或高中的图章作为对照元件，以及最终全息图作为安全特征。然而，全息图更容易地复制，因为印刷技术变得越来越成熟。这容许伪造者复制这类价值文件，包括学院或大学或高中图章。

[0006] 为防止该转换，需要找到保护这类文件，尤其是用纸制成的文件的替代解决方法。已知包含发光化合物的安全油墨防止该转换，且非常通常地使用油墨组合物保护价值文件。

[0007] 在通过引用全部并入本文中的US 2007/0225402 A1中，公开了紫外线发光油墨的使用，所述油墨以标记的形式印刷在文件上。紫外线发光油墨在自然光下是不可见的，使得标记仅在用UV光照射下显示。该紫外线发光油墨用于将编码应用于安全文件如护照或纸币上。在所引用的文件中，使用印刷方法，包括丝网印刷、凹版印刷、活版印刷和胶版印刷应用不可见的紫外线荧光油墨。

[0008] 颜料形式的发光化合物广泛用于油墨和其它制剂中（参见美国专利No.6,565,770、WO 2008/033059 A2、WO 2008/092522 A1）。发光颜料的实例可在特定类别的无机化合物中找到，例如非发光阳离子的硫化物、氧硫化物、磷酸盐、钒酸盐、石榴石、尖晶石等，其掺杂有至少一种选自过渡金属或稀土离子的发光阳离子。

[0009] 用于在油墨中产生发光的另一类化合物由某些稀土金属配合物形成，例如描述于WO 2009/005733 A1及其家族成员US 2009/0000509 A1或美国专利No.7,108,742中，通过引用将其并入本文中。

[0010] 用发光化合物，特别是发光稀土金属配合物印刷安全文件的特定方法为喷墨印刷，更特别是热喷墨印刷。热喷墨印刷机使用具有一系列微型电加热室的印刷盒，其由光刻胶(photolithography)构成。为产生图像，印刷机将电流脉冲发送通过置于各个室后面的

加热元件，导致室中的蒸汽爆发，以形成气泡，其推动油墨滴通过室的孔到达它前面的纸上（此处对于某些喷墨印刷机，商品名**Bubblejet®**）。油墨的表面张力以及蒸气气泡的冷凝和因此的收缩将另一油墨进料通过连接在蓄墨池上的窄通道推入室中。

[0011] 所用油墨为水性的（即包含颜料或染料的水基油墨），且印刷头通常比其它喷墨技术所需的设备更便宜地生产。然而，它的寿命是短的，且它通常与空墨盒一起交换。

[0012] 喷墨印刷机遭遇的主要问题是印刷头喷嘴中的油墨干燥，导致颜料和／或染料形成固体沉积物，其阻塞微小油墨孔。大多数印刷机通过在不使用印刷机时自动地用橡胶帽覆盖印刷头喷嘴而防止该干燥。然而，在它具有印刷头盖帽以前的突然功率损失或者未堵塞印刷机，导致印刷头干透。另外，即使盖了帽一该密封不是完美的一经数星期的时间，喷嘴中的油墨可干透并堵塞它们。当油墨开始在喷嘴中干透时，影响液滴体积，液滴轨道可改变，或者喷嘴可能完全不能喷出任何油墨。

[0013] 在包含稀土金属配合物的发光喷墨油墨的情况下，配合物在水中的稳定性对避免喷嘴阻塞而言是关键的。为防止过早干燥，加入水或溶剂以充分稀释油墨是明显的解决方法。然而，用水或溶剂稀释降低用该油墨印刷的安全文件的发光强度（和因此降低检测的容易性）。

[0014] 当包含发光颜料的油墨例如用喷墨印刷机用于水基油墨组合物中（非常通常用于印刷用纸制成的安全文件或包装）时也非常通常遭遇的另一问题是它们的稳定性以及印刷机喷嘴内部的油墨通过已知的机制如沉积 (Kogation) 降解或沉淀而降解。

[0015] 尽管稀土金属配合物会代表使喷墨油墨发光的非常有用方法，喷嘴中油墨干燥的问题使得常常不可能完全使用喷墨盒，因此导致提高的墨盒消耗成本。这不仅由于该“废”墨盒导致的“再循环”问题而具有生态和安全性影响，而且对印刷成本具有不可忽略的影响。

[0016] 通过引用全部并入本文中的 US 2010/0307376 A1 涉及镧系元素螯合物和包含镧系元素螯合物的安全文件，并提供许多优点并克服现有技术的许多缺点，尤其是由稳定性、过早干燥和沉积 (Kogation) 产生的缺点。

[0017] 尽管这类发光油墨相当的重要，必须保护的纸仍是一个问题，因为不是所有发光油墨都会粘附在纸的表面上。另外，更有问题的是这一事实：印刷在纸类文件或物品上时使用的油墨不赋予纸高安全性水平。在印刷到纸上时存在于该油墨中的安全元件不完全显示或者它的信号保持较弱，这不容许完全识别真实纸类文件或物品。

[0018] 因此，需要具有特殊且选择的水基组合物，所述组合物容许在印刷在纸基质上时提供高安全性水平，这容许有效水平地识别具有包含在水基油墨组合物中的难以复制的特殊发光特征的安全文件且还避免喷墨印刷机的喷嘴内部的不稳定性、沉积 (kogation) 和沉淀的缺点。

[0019] 因此，关键的需要仍是解决上述问题以促进基于稀土金属配合物的发光喷墨油墨的有效使用，因此得到在墨盒的整个寿命期间正确印刷和保护的安全文件。

[0020] 发明概述

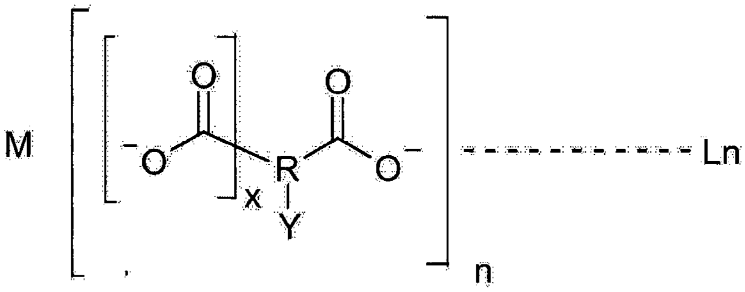
[0021] 本发明通过以下方式克服了上述缺点：

[0022] a) 在墨盒的整个寿命期间提供具有特殊发光特征以有效地标记有价值的纸文件的稳定且高水平的发光，这容许容易且有效地识别发光以及它的特征，和

[0023] b) 避免造成不可能完全使用墨盒的喷嘴阻塞。

[0024] 前述通过提供包含至少一种下式的发光镧系元素配合物的水性喷墨组合物而实现：

[0025]



[0026] 其中 M 选自碱阳离子 Li^+、Na^+、K^+、Rb^+和 Cs^+及其混合物并存在以中和配合物的电荷；

[0027] 其中 Ln 选自如下各项的三价稀土阳离子：Ce、Pr、Nd、Sm、Eu、Gd、Tb、Dy、Ho、Er、Tm 和 Yb 及其混合物；

[0028] 其中 R 为 C_5-C_6杂芳基；

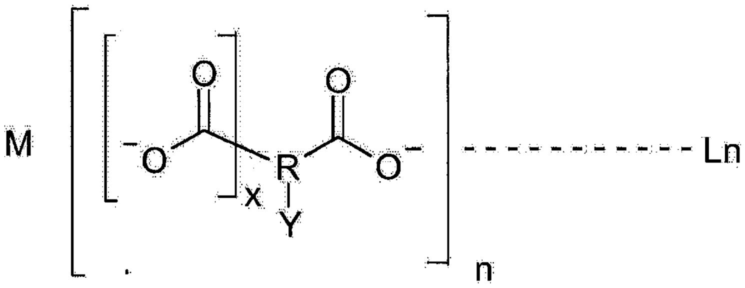
[0029] 其中 Y 为通过 N 原子连接在 R 上的任选取代的 C_3-C_8杂环烷基结构部分；

[0030] 其中 n 为 3 或 5 的整数；且

[0031] 其中 x 为 0 或 1 的整数。

[0032] 还提供根据下式的镧系元素配合物：

[0033]



[0034] 其中 M 选自碱阳离子 Li^+、Na^+、K^+、Rb^+和 Cs^+及其混合物并存在以中和配合物的电荷；

[0035] 其中 Ln 选自如下各项的三价稀土阳离子：Ce、Pr、Nd、Sm、Eu、Gd、Tb、Dy、Ho、Er、Tm 和 Yb 及其混合物；

[0036] 其中 R 为 C_5-C_6杂芳基；

[0037] 其中 Y 为通过 N 原子连接在 R 上的任选取代 C_3-C_8杂环烷基结构部分，所述 C_3-C_8杂环烷基结构部分优选在环中带有至少氮原子，所述氮原子连接在 R 上；

[0038] 其中 n 为 3 或 5 的整数；且

[0039] 其中 x 为 0 或 1 的整数。

[0040] 至少一种发光镧系元素配合物可以为具有 1:3 的确切化学计量的再结晶产物。

[0041] 至少一种发光镧系元素配合物可以为具有 1:5 的确切化学计量的再结晶产物。

[0042] 优选油墨中不存在过量的游离形式的 R 组分。

[0043] 配合物的 Cl^-量基于该至少一种发光镧系元素配合物的总重量优选不超过 0.1 重量%。

[0044] 配合物的 Cl^-量基于配合物的总重量可以为 0.1 重量%至 0.25 重量%。

[0045] 水性油墨组合物可包含至少一种吸湿物质，例如基于组合物的总重量为 5-45 重量%的至少一种吸湿物质。

[0046] 该至少一种吸湿物质可选自伯、仲或叔醇、内酰胺、聚合二醇、二醇和环砜及其混合物。

[0047] 该至少一种吸湿物质可选自 DL- 己烷 -1,2- 二醇、2- 吡咯烷酮、环丁砜、四亚甲基亚砜、γ - 丁内酯、1,3- 二甲基 -2- 咪唑啉酮、2- 丙二醇、戊二醇、1,2 己二醇、三羟甲基丙烷、甘油、乙二醇、二甘醇、聚丙二醇、聚乙二醇、乙醇、丙醇和丁醇及其混合物。

[0048] 水性油墨组合物可包含至少一种可见染料或颜料，例如基于组合物的总重量为 1-15 重量%的至少一种可见染料或颜料。

[0049] 该至少一种可见染料或颜料可选自单偶氮和 / 或二偶氮染料、单偶氮 Cu- 配合物染料。

[0050] 水性油墨组合物可包含基于组合物的总重量为 1-15 重量%的至少一种发光镧系元素配合物。

[0051] R 可以为吡啶、咪唑、三唑、吡唑或吡嗪。

[0052] R 与连接在其上的至少一个羧酸基团一起可以为吡啶二羧酸和 / 或 4- 羟基吡啶 -2,6- 二羧酸，且 Ln 可选自三价离子铕 (Eu3+) 和 / 或铽 (Tb3+)。

[0053] Y 可以为氮丙啶、氮杂环丁烷、咪唑烷、吡咯烷、吡咯烷酮、吡咯烷 -2- 硫酮、硫代吗啉、吗啉、六氢嘧啶、哌嗪、氮杂环庚烷 (azepane) 或氮杂环辛烷 (azocane) 的结构部分。

[0054] C_3-C_8杂环烷基可以被 C_1-C_6烷基或 C_1-C_6烷氧基取代。

[0055] 还提供包含该水性油墨组合物的制品。

[0056] 还提供包含至少一个用水性油墨组合物制成的层的安全文件。

[0057] 还提供得到该至少一种发光镧系元素配合物的方法，所述方法包括使 1 当量的三价或五价镧系元素离子 Ln 的前体化合物与 3 或 5 当量的 R 组分在碱阳离子 M 的存在下反应以将配合物中和。

[0058] 三价镧系元素离子 Ln 的前体化合物可选自氧化物 Ln_2O_3、氯化物 $LnCl_3$、碳酸盐 $Ln_2(CO_3)_3$和乙酸盐 $Ln(CH_3COO)_3$。

[0059] R 组分可作为游离酸 H_2A 与所需量的碱一起使用，或者作为单碱盐 HMA 或者作为二碱盐 M_2A 使用。

[0060] 配合物的组分可在水溶液中结合，并可使所得配合物再结晶以将它与反应副产物分离。

[0061] 制品可以为纸币、护照、安全文件、价值文件、证书、信托文件、包装、票、箔、丝线、标签或商品。

[0062] 制品可以为纸制品。

[0063] 该至少一种发光镧系元素配合物可以为再结晶产物。

[0064] 优选 m 可以为 3 和 / 或 x 可以为 1。

[0065] 任选取代的 C_3-C_8杂环烷基结构部分除将 Y 连接在 R 上的 N 原子外还可包含至少

一个 N 原子。

[0066] 任选取代的 C_3-C_8杂环烷基结构部分可包含至少一个 O 原子。

[0067] 发光镧系元素配合物可吸收电磁谱的紫外线和 / 或蓝光区。这些镧系元素配合物中的发光发射可能是由于内部 f- 壳跃迁，例如 ：对于 Eu(3+)，$^5D_0 \rightarrow {}^7F_1$和 $^5Do \rightarrow {}^7F_2$。

[0068] 根据本发明，优选使用发光镧系元素配合物的纯化学计量配合物，而不是稀土离子盐在大过量 R 基团中的溶液。用 R 基团，这可能形成具有稀土离子的非常稳定的阴离子配合物，使得在加热时水溶液中不发生离解（水解或热解）。水解会显著地导致沉淀物和相应的喷嘴阻塞。

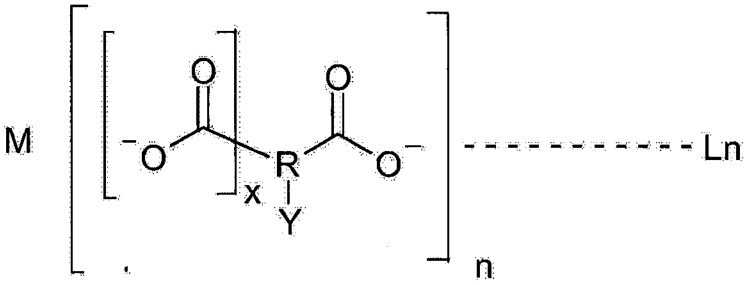
[0069] 因此，根据本发明，优选使用纯发光镧系元素配合物。这类纯配合物盐的使用避免了油墨中任何不必要的过量游离 R 基团，因此降低它的总固体含量，以及因此降低它通过沉积 (kogation) 或干燥而阻塞（堵塞）喷墨喷嘴的倾向。

[0070] 本发明的这些和其它特征和优点由本领域技术人员阅读以下详细描述而更容易地理解。应当理解为了清晰，在分开的实施方案上下文中上文和下文描述的本发明某些特征也可在单一实施方案中组合提供。相反，为了简便，单一实施方案上下文中描述的本发明各个特征也可分开地或者以任何子组合提供。另外，以范围描述的值的提及包括在该范围内的各个和每个值。

[0071] 发明详述

[0072] 根据本发明，提供根据下式的镧系元素配合物 ：

[0073]



[0074] 其中 M 选自碱阳离子 Li^+、Na^+、K^+、Rb^+和 Cs^+及其混合物并存在以中和配合物的电荷 ；

[0075] 其中 Ln 选自如下各项的三价稀土阳离子 ：Ce、Pr、Nd、Sm、Eu、Gd、Tb、Dy、Ho、Er、Tm 和 Yb 及其混合物 ；

[0076] 其中 R 为 C_5-C_6杂芳基 ；

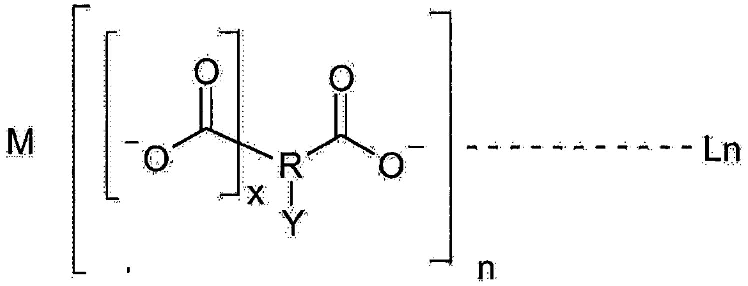
[0077] 其中 Y 为通过 N 原子连接在 R 上的任选取代的 C_3-C_8杂环烷基结构部分 ；

[0078] 其中 n 为 3 或 5 的整数 ；且

[0079] 其中 x 为 0 或 1 的整数。

[0080] 此外，提供包含至少一种下式的发光镧系元素配合物的水性喷墨组合物 ：

[0081]



[0082] 其中M选自碱阳离子Li^+、Na^+、K^+、Rb^+和Cs^+及其混合物并存在以中和配合物的电荷；

[0083] 其中Ln选自如下各项的三价稀土阳离子：Ce、Pr、Nd、Sm、Eu、Gd、Tb、Dy、Ho、Er、Tm和Yb及其混合物；

[0084] 其中R为C_5-C_6杂芳基；

[0085] 其中Y为通过N原子连接在R上的任选取代的C_3-C_8杂环烷基结构部分；

[0086] 其中n为3或5的整数；且

[0087] 其中x为0或1的整数。

[0088] R优选为吡啶、咪唑、三唑、吡唑或吡嗪。例如R与连接在其上的至少一个羧酸基团一起可以为例如吡啶二羧酸、4-羟基吡啶-2,6-二羧酸、4-氨基-吡啶-2,6-二羧酸、4-乙氧基吡啶-2,6-二羧酸、4-异丙氧基吡啶-2,6-二羧酸和/或4-甲氧基吡啶-2,6-二羧酸，优选吡啶二羧酸和/或4-羟基吡啶-2,6-二羧酸。

[0089] Y优选为氮丙啶、氮杂环丁烷、咪唑烷、吡咯烷、吡咯烷酮、吡咯烷-2-硫酮、硫代吗啉、吗啉、六氢嘧啶、哌嗪、氮杂环庚烷或氮杂环辛烷结构部分。优选Y可以被C_1-C_6烷基，例如甲基、乙基、异丙基等，或者C_1-C_6烷氧基，例如甲氧基、乙氧基、异丙氧基等取代。

[0090] 优选镧系元素离子为铕(Eu3+)和/或铽(Tb3+}。优选吡啶二羧酸或4-羟基吡啶-2,6-二羧酸与铕(Eu3+)组合使用。

[0091] 该至少一种发光镧系元素配合物优选为再结晶产物。

[0092] 优选m为1和/或x为1。

[0093] 任选取代的C_3-C_8杂环烷基结构部分除将Y连接在R上的N原子外还可包含至少一个N原子。此外，任选取代的C_3-C_8杂环烷基结构部分包含至少一个O原子。

[0094] 还提供得到至少一种发光镧系元素配合物的方法。该方法可包括使1当量的三价或五价镧系元素离子Ln的前体化合物与3或5当量的R组分在碱阳离子M的存在下反应以将配合物中和。

[0095] 镧系元素离子Ln的前体化合物可选自氧化物、氯化物、碳酸盐和乙酸盐，例如Ln_2O_3、$LnCl_3$、$Ln_2(CO_3)_3$和$Ln(CH_3COO)_3$。

[0096] R组分可作为游离酸H_2A与所需量的碱一起使用，或者作为单碱盐HMA或者作为二碱盐M_2A使用。

[0097] 可使配合物的组分在水溶液中结合，并可使所得配合物再结晶以将它与反应副产物分离。

[0098] 例如，将配合物盐的组分在水溶液中结合，例如：

[0099] $EuCl_3+3Na_2(dpa) \rightarrow Na_3[Eu(dpa)_3]+3NaCl$

[0100] 并优选将所得配合物盐再结晶，以将它与反应副产物如NaCl分离，所述副产物对

实现本发明目的，即具有尽可能低固体含量的油墨而言不是理想的。

[0101] 其中 Y 为通过 N 原子连接在 R 上的任选取代的 C_3-C_8杂环烷基结构部分的镧系元素配合物是特别有利的。这类镧系元素配合物可具有多个发射带，例如两个发射带，例如在约 230nm 至 275nm，例如 254nm 的波长下的一个发射带，和在约 340-375nm，例如 366nm 的波长下的另一发射带。能够具有两个发射带或者两个或更多个发射带的镧系元素配合物通过具有与镧系元素配合物有关的更复杂发射测量而能够提供更好的防伪技术。

[0102] 再结晶方法的优点是提供具有最小副产物含量的发光镧系元素配合物。这对配合物的溶解度和对干燥或沉积 (kogation) 现象具有影响。在一个优选实施方案中，发光镧系元素配合物存在的 Cl^-浓度分别在配合物盐总重量的 0.1% Cl^-或者 0.17% NaCl 以下。为得到高质量的印迹，发光镧系元素配合物的最终氯含量应不超过 0.1 重量%。在可接受的印刷质量的情况下，配合物盐的氯含量可以为发光镧系元素配合物的 0.1 重量%至 0.25 重量%。

[0103] 该至少一种发光镧系元素配合物可优选为具有 1:3 的确切化学计量或者具有 1:5 的确切化学计量的再结晶产物。

[0104] 该至少一种发光镧系元素配合物优选包含在水性油墨组合物中。水性油墨组合物优选包含基于组合物的总重量为 1-15 重量%，更优选 1-8 重量%，甚至更优选 1-3 重量%的至少一种发光镧系元素配合物。

[0105] 优选油墨中不存在过量的游离形式的 R 组分。

[0106] 为防止本发明水性油墨组合物在印刷方法期间的过早干燥，本发明水性喷墨油墨可进一步包含至少一种吸湿物质。该至少一种吸湿物质优选以基于组合物的总重量为 5-45 重量%，更优选 10-45 重量%，甚至更优选 20-45 重量%至少一种吸湿物质的浓度存在。该至少一种吸湿物质可选自伯、仲或叔醇、内酰胺、聚合二醇、二醇和环砜及其混合物。例如，该至少一种吸湿物质可优选选自 DL-己烷-1,2-二醇、2-吡咯烷酮、环丁砜、四亚甲基亚砜、γ-丁内酯、1,3-二甲基-2-咪唑啉酮、2-丙二醇、戊二醇、1,2 己二醇、三羟甲基丙烷、甘油、乙二醇、二甘醇、聚丙二醇、聚乙二醇、乙醇、丙醇和丁醇及其混合物。

[0107] 水性油墨组合物还可优选包含至少一种可见染料或颜料，例如基于组合物的总重量为 1-15 重量%的至少一种可见染料或颜料。该至少一种可见染料或颜料可选自单偶氮和/或二偶氮染料、单偶氮 Cu-配合物染料。这类染料的实例可以为以商品名 IRGASPERSE **Jet**® 由 CIBA 公司生产的那些。

[0108] 取决于待印刷的安全文件的性质，本发明印刷油墨还可包含对这些添加剂而言常用量的常规添加剂，例如杀真菌剂、杀生物剂、表面活性剂、螯合剂、pH 调节剂、助溶剂或粘合剂如丙烯酸酯粘合剂。

[0109] 还提供包含直接在制品或基质（如与制品有关的标签和/或包装）上的水性油墨组合物的制品。例如，本发明水性油墨可用于鉴定制品，例如纸币、护照、安全文件、价值文件、票、箔、丝线、标签、卡、证书、信托文件、包装或商品。例如可提供包含至少一个由本发明油墨制成的层的安全文件。

[0110] 本发明油墨特别用于印刷在纸，例如纸制品或纸标签上。

[0111] 本发明水性油墨特别适于热喷墨印刷，这是用于产品、包装或有价值文件的编码和标记的有效喷墨印刷技术。因此，油墨组合物优选为使用热喷墨印刷的配制剂。

[0112]　本发明通过以下非限定性实施例进一步阐述。百分数为重量计。本领域技术人员会认识到在这些实施例的精神和范围内的许多变化是可能的，其意欲受以下权利要求书及其等价物限制，其中除非另外说明，所有术语意指其最宽泛的合理意义。

[0113]　本发明通过以下非限定性实施例进一步阐述。除非另外说明，百分数为重量计。本领域技术人员会认识到在这些实施例的精神和范围内的许多变化是可能的，其意欲受以下权利要求书及其等价物限制，其中除非另外说明，所有术语意指其最宽泛的合理意义。

实施例：

[0114]　参考实施例 1

[0115]　4- 氯吡啶 -2,6- 二羧酸 (Cldpa) 的合成

[0116]　在 120℃下在搅拌下向二氯苯基氧化膦溶液 (1.492 摩尔，290.8g) 中缓慢地加入白屈氨酸 (0.373 摩尔，75.0g)。在 120℃下在惰性气氛下将反应混合物加热 2 小时。注意避免泡沫的太快形成。在 80℃下冷却以后，将反应混合物倒入 H_2O(1L) 中。通过逐步倾倒，反应混合物可变成固体。将固体过滤，用 H_2O 洗涤两次并在 70℃下干燥过夜 (97％)。

[0117]　1H NMR[(CD3)2SO]：δ 8.24(s,2H)

[0118]　实施例 2

[0119]　4- 吡咯烷并吡啶 -2,6- 二羧酸 (Pyrrodpa) 的合成

[0120]　在室温下在搅拌下将 4- 氯吡啶 -2,6- 二羧酸 (0.238 摩尔，48.0g) 缓慢地加入吡咯烷溶液 (0.952 摩尔，67.8g) 中。注意避免太快的添加，从而导致局部温度提高。观察固体的沉淀。将反应混合物在 120℃下加热 2 小时。通过逐步加热，反应混合物变成固体。在 60℃下冷却以后，加入 H_2O(80ml) 并将混合物搅拌 30 分钟直至固体完全溶解。然后将溶液用 HCl(2M) 酸化直至 pH ＝ 1。将形成的沉淀物过滤，用 H_2O 洗涤两次，并在 70℃下干燥过夜 (93％)。

[0121]　1H NMR[(CD3)2SO]：δ 7.25(s,2H),3.44(t,4H),2.01(t,4H)

[0122]　实施例 3

[0123]　4- 吗啉并 - 吡啶 -2,6- 二羧酸 (Morphodpa) 的合成

[0124]　在室温下在搅拌下将 4- 氯 - 吡啶 -2,6- 二羧酸 (0.025 摩尔，5.0g) 缓慢地加入吗啉溶液 (0.250 摩尔，21.6g) 中。注意避免太快的添加，从而导致局部温度提高。观察固体的沉淀。将反应混合物在 120℃下加热 2 小时。通过逐步加热，反应混合物变成固体。在 60℃下冷却以后，加入 H_2O(80ml) 并将混合物搅拌 30 分钟，直至固体完全溶解。然后将溶液用 2M HCl 酸化直至 pH ＝ 1。将形成的沉淀物过滤，用 H_2O 洗涤两次，并在 70℃下干燥过夜 (70％)。

[0125]　1H NMR[(CD3)2SO] δ ：7.59(s,2H),3.72(t,4H),3.44(t,4H)

[0126]　实施例 4

[0127]　$Na_3[Eu(Pyrrodpa)_3]*nH_2O$ 的合成

[0128]　将 2M NaOH 溶液加入 4- 吡咯烷并吡啶 -2,6- 二羧酸 (0.042 摩尔，10.0g) 在 85ml 蒸馏水中的悬浮液中以调整 pH(pH ～ 8)，这导致反应混合物完全溶解。然后加入 $EuCl_3.6H_2O$(0.014 摩尔，5.2g) 在 10ml H_2O 中的溶液，并将反应混合物在室温下搅拌 30 分钟。在搅拌以后，首先将混合物用 2MNaOH(pH ～ 8) 中和，然后加热直至 50℃。当达到该温

度时，加入 H_2O 直至得到清澈溶液。连续地加入丙酮（～ $2*VH_2O$）以使配合物沉淀并将混合物冷却直至室温。最后将沉淀物过滤，用丙酮洗涤并在 70℃下干燥过夜。

[0129] 实施例 5

[0130] $Na_3[Tb(Pyrrodpa)_3]*nH_2O$ 的合成

[0131] 将 2M NaOH 溶液加入 4- 吡咯烷并吡啶 -2,6- 二羧酸（0.042 摩尔，10.0g）在 85ml 蒸馏水中的悬浮液中以调整 pH（pH ～ 8），这导致反应混合物完全溶解。然后加入 $TbCl_3.6H_2O$（0.014 摩尔，5.3g）在 10ml H_2O 中的溶液并将反应混合物在室温下搅拌 30 分钟。在搅拌以后，首先将混合物用 2MNaOH（pH ～ 8）中和，然后加热直至 50℃。当达到该温度时，加入 H_2O 直至得到清澈溶液。连续地加入丙酮（～ $2*VH_2O$）以使配合物沉淀并将混合物冷却直至室温。最后将沉淀物过滤，用丙酮洗涤并在 70℃下干燥过夜。

[0132] 实施例 6

[0133] $Na_3[Eu(Morphodpa)_3]*nH_2O$ 的合成

[0134] 将 2M NaOH 溶液加入 4- 吗啉并吡啶 -2,6- 二羧酸（0.040 摩尔，10.0g）在 85ml 蒸馏水中的悬浮液中以调整 pH（pH ～ 8），这导致反应混合物完全溶解。然后加入 $EuCl_3.6H_2O$（0.013 摩尔，4.8g）在 10ml H_2O 中的溶液并将反应混合物在室温下搅拌 30 分钟。在搅拌以后首先将混合物用 2M NaOH 中和（pH ～ 8），然后加热直至 50℃。当达到该温度时，加入 H_2O 直至得到清澈溶液。连续地加入丙酮（～ $2*VH_2O$）以使配合物沉淀并将混合物冷却直至室温。最后将沉淀物过滤，用丙酮洗涤并在 70℃下干燥过夜。

[0135] 实施例 7

[0136] $Na_3[Tb(Morphodpa)_3]*nH_2O$ 的合成

[0137] 将 2M NaOH 溶液加入 4- 吗啉并吡啶 -2,6- 二羧酸（0.040 摩尔，10.0g）在 85ml 蒸馏水中的悬浮液中以调整 pH（pH ～ 8），这导致反应混合物完全溶解。加入 $TbCl_3.6H_2O$（0.013 摩尔，4.9g）在 10ml H_2O 中的溶液并将反应混合物在室温下搅拌 30 分钟。在搅拌以后首先将混合物用 2M NaOH 中和（pH ～ 8），然后加热直至 50℃。当达到该温度时，加入 H_2O 直至得到清澈溶液。连续地加入丙酮（～ $2*VH_2O$）以使配合物沉淀并将混合物冷却直至室温。最后将沉淀物过滤，用丙酮洗涤并在 70℃下干燥过夜。

[0138] 实施例 8

[0139] 包含本发明配合物的油墨配制实施例：

[0140] 黑色具有荧光红（在 254 和 366nm 下激发）：

[0141] 向去离子水溶液（40.5g）中加入 2- 吡咯烷酮（5g）和 1,2- 己二醇（2.5g）。将溶液以 500-600rpm 搅拌以得到均化溶液。将 2g $Na_3[Eu(Pyrrodpa)_3]*nH_2O$ 加入溶液中，然后在 40℃下加热直至配合物完全溶解。将溶液冷却至环境温度，然后加入 18g **Irgasperse®** Jet Cyan RL、13.65g **Irgasperse®** Jet yellowRL 和 4.35g **Irgasperse®** Jet Magenta B，将混合物以 500-600rpm 搅拌约 20 分钟。在搅拌以后，将溶液过滤以除去所有不溶性化合物和未反应产物。

[0142] 将所得黑色具有荧光红油墨包装在 HP45 墨盒中并用 960Cxi、970Cxi、980Cxi 或 990Cxi 系列的 Deskjet 印刷机使用。使用 fisher Bioblock Scientific VL-4.LC 灯检查荧光是非常可见的。为评估油墨稳定性，进行两个试验：

[0143] 按排印刷200页，其后中断2-4天，并再起动用于另外400页。

[0144] 在1星期、2星期、3星期、4星期以后以及然后经在6个月时间每4星期进行短印刷试验。

[0145] 在稳定性试验期间用本发明油墨没有预期印刷和干燥问题。在所有情况下，预期本发明化合物的荧光强度在非常满意的水平下保持不变。

[0146] 前述实施例仅为对本发明一些特征的说明。所附权利要求书意欲以它设想的一样宽地要求保护本发明，且本文提出的实施例为对从多种所有可能实施方案中选择的实施方案的说明。因此，申请人意欲所附权利要求书不受用于阐述本发明特征的实施例的选择限制。

Abstract

Luminescent lanthanide complex and inks containing the complex as well as its method of production and article including the complex, wherein the complex includes the formula: wherein M is chosen from the alkali cations Li^+, Na^+, K^+, $Rb^+$and Cs^+ and mixtures thereof and is present to neutralize charge of the complex; wherein Ln is chosen from the trivalent rare-earth cations of Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb and mixtures thereof; wherein R is a C_5 to C_6 heteroaryl:wherein Y is an optionally substituted C_3-C_8 heterocycloalkyl moiety linked to R by an N atom; wherein n is an integer of 3 or 5; and wherein x is an integer of 0 or 1.