

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
26 May 2006 (26.05.2006)

PCT

(10) International Publication Number
WO 2006/053834 A2

(51) International Patent Classification:

G11B 7/24 (2006.01) **C07F 15/04** (2006.01)
C07F 19/00 (2006.01)

(21) International Application Number:

PCT/EP2005/055742

(22) International Filing Date:

4 November 2005 (04.11.2005)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

04027630.5 22 November 2004 (22.11.2004) EP

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(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, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, 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), 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:

— without international search report and to be republished upon receipt of that report

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.

(54) Title: NEW MONOSUBSTITUTED SQUARIC ACID METAL COMPLEX DYES AND THEIR USE IN OPTICAL LAYERS FOR OPTICAL DATA RECORDING

(57) Abstract: The present invention relates to new monosubstituted squaric acid metal complex dyes and their use in optical layers for optical data recording, preferably for optical data recording using a laser with a wavelength up to 450 nm. The invention further relates to a write once read many (WORM) type optical recording medium capable of recording and reproducing information with radiation of blue laser, which employs a monosubstituted squaric acid metal complex dye in the optical layer.



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New monosubstituted squaric acid metal complex dyes and their use in optical layers for optical data recording

The present invention relates to new monosubstituted squaric acid metal complex dyes and their use in optical layers for optical data recording, preferably for optical data recording using a laser with a wavelength up to 450 nm.

The invention further relates to a write once read many (WORM) type optical recording medium capable of recording and reproducing information with radiation of blue laser, which employs a monosubstituted squaric acid metal complex dye in the optical layer.

10

Recently, organic dyes have attracted considerable attention in the field of diode-laser optical storage. Commercial recordable compact discs (CD-R) and recordable digital versatile discs (DVD-R) can contain, as recording layer, numerous dyes based on phthalocyanine, hemicyanine, cyanine and metallized azo structures. These dyes are suitable in their respective fields with the laser wavelength criteria. Other general requirements for dye media are strong absorption, high reflectance, high recording sensitivity, low thermal conductivity as well as light and thermal stabilities, durability for storage or non-toxicity.

For industrial application, these dyes have to be suitable for the spin coating process to prepare thin films, i.e. they have to be sufficiently soluble in the organic solvents generally applied in the spin coating process.

WORM (write once read many) type and erasable type optical recording media reproduce information by detecting variations in the reflectivity caused by physical deformation, by alterations of optical characteristics as well as by phase and magnetic properties of a recording layer before and after the recording.

Recordable compact discs (CD-R) are widely known as a WORM type optical recording medium. Recently, digital versatile discs (DVD) with increased information storage capabilities up to 4.7 GBytes have been commercialized.

The DVD-R technology adopts as a light source a red diode laser with a wavelength of 630-670 nm. Thereby the pit size and track interval can be reduced, increasing the information storage capacity by up to 6-8 times compared to CD-R's.

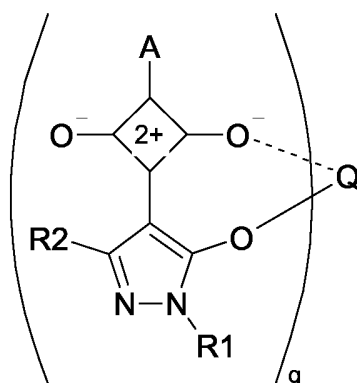
Blu-ray[®] discs (Blu-ray[®] disc is a standard developed by Hitachi Ltd., LG Electronics Inc., Matsushita Electric Industrial Co. Ltd., Pioneer Corporation, Royal Philips Electronics, Samsung Electronics Co. Ltd., Sharp Corporation, Sony Corporation, Thomson Multimedia) are going to be the next milestone in optical recording
5 technology. Its new specification increases the data storage up to 27 GBytes per recording layer for a 12 cm diameter disc. By adopting a blue diode laser with a wavelength of 405 nm (GaN or SHG laser diodes), the pit size and track interval can be further reduced, again increasing the storage capacity by an order of magnitude.

10 The construction of optical data recording media is known in the art. An optical data recording media generally comprises a substrate and a recording layer, the optical layer. Usually discs or wavers of organic polymeric materials are used as substrates. Preferred substrates are polycarbonate (PC) or polymethylmethacrylate (PMMA). The substrate has to provide an even and uniform surface of high optical quality. The optical layer is
15 deposited thereon in a thin and uniform film of high optical quality and defined thickness. Finally, a reflective layer, e.g. aluminium, gold or copper, is deposited upon the optical layer.

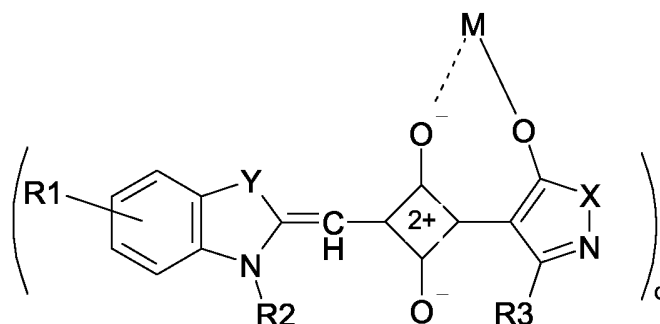
Advanced optical data recording media may comprise further layers, such as protective
20 layers, adhesive layers or additional optical layers.

To provide for a thin and uniform film of the optical layer, the material is usually deposited by spin coating, vacuum evaporation, jet coating, rolling coating or soaking. The preferred process in industry is spin coating to form an optical layer of about 70 nm
25 to 250 nm thickness. For the application in the spin coating process, the material of the optical layer has to be highly soluble in organic solvents.

EP 1334998 A1 (Kyowa Hakko Kogyo), **EP 1449890 A1** (Ricoh, Kyowa Hakko Kogyo), **EP 1335357 A1** (Kyowa Hakko Kogyo) and **EP 1267338 A2** (Kyowa Hakko
30 Kogyo) disclose squarylium metal chelate compounds represented by the following general formula, and a recording medium having a recording layer comprising such a squarylium metal chelate compound.



WO 2003085005 A1 (Kyowa Yuka KK) discloses a photopolymerizable composition comprising a metal complex of a squarylium compound of the following formula:



5

Matsui et al. (Dyes and Pigments 58, 2003, 219-226) disclose 3-Aryl-4-hydroxycyclobut-3-ene-1,2-dione, i.e. a monosubstituted squarylium compound, as sensitizers for TiO₂ solar cell.

10

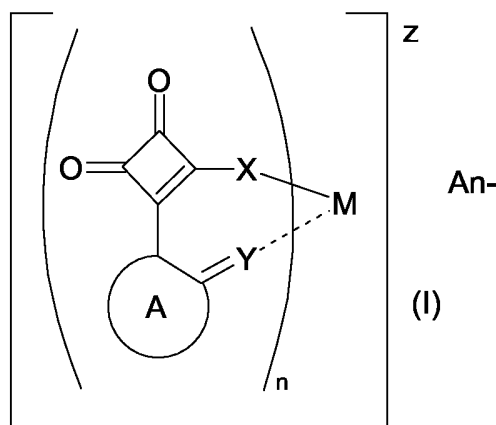
Surprisingly it now has been found, that metal complexes of monosubstituted squaric acid derivatives as described below are useful as dye compounds in optical layers for optical data recording media.

15 The present invention therefore relates to the new metal complexes of monosubstituted squaric acid compounds as described below and their use in an optical layer comprising metal complexes of monosubstituted squaric acid compounds and to the use of said optical layers for optical data recording media.

More particularly, the invention relates to a write once read many (WORM) type optical
20 data recording medium capable of recording and reproducing information with radiation

of blue laser of preferably 405 nm, which employs a monosubstituted squaric acid dye in the optical layer.

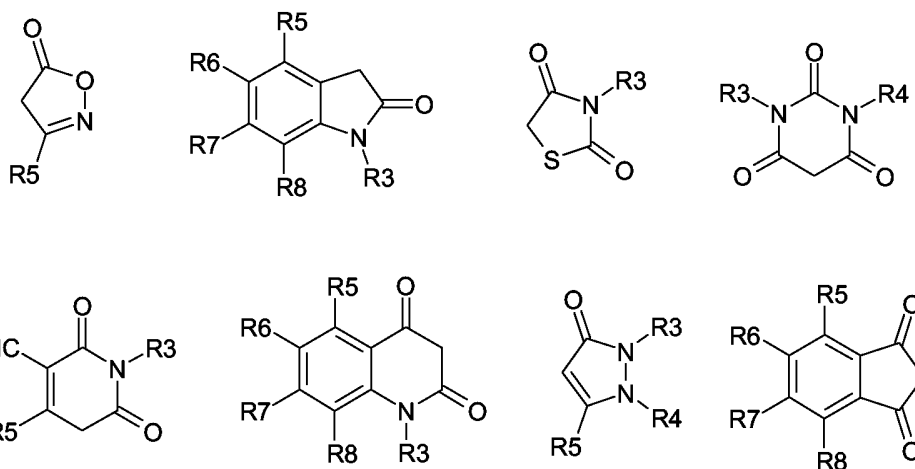
The present invention is directed to a dye compound of formula (I) or one of its
5 tautomeric forms.

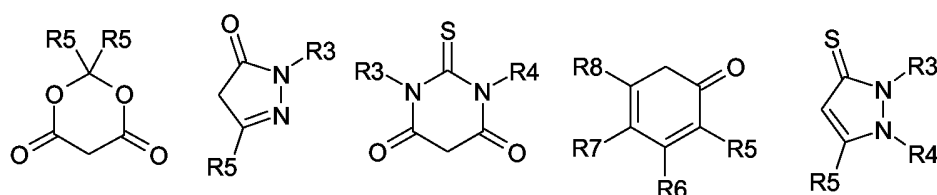


wherein

- X represents deprotonated hydroxy (-OH), thiol (-SH) or amine (NHR₁) wherein R₁ represents hydrogen, C₁₋₁₂ alkyl (being unsubstituted or substituted by hydroxy (-OH), C₆₋₁₂ aryl, halogen, -NR₉R₁₀', in which R₉ and R₁₀ are independently hydrogen, C₁₋₁₂ alkyl or C₆₋₁₂ aryl), benzyl or C₆₋₁₂ aryl;
10
- Y represents oxygen, sulfur, or imino-nitrogen N-R₂ wherein R₂ represents hydrogen, C₁₋₁₂ alkyl (being unsubstituted or substituted by hydroxy (-OH), C₆₋₁₂ aryl, halogen, -NR'R'', in which R' and R'' are independently hydrogen, C₁₋₁₂ alkyl or C₆₋₁₂ aryl), benzyl or C₆₋₁₂ aryl;
15
- z represents a charge from minus 2 to plus 2
- An⁻ represents an anion counter-part selected from inorganic anions such as iodine, fluorine, bromine, chlorine, perchlorate, hexafluoroantimonate, hexafluorophosphate, tetrafluoroborate, tetraphenylborate or organic anions such as dicyanoamide (N(CN)₂) or trifluoromethanesulfonimide (N(SO₂CF₃)₂); or
20
- An⁻ can also be an anionic azo metal complex
- M represents a metal ion;

- A is a five membered or six membered aromatic or heteroaromatic cycle which can be further substituted or annealed,
- n represents a whole number from 1 to 4.
- 5 In a preferred aspect, the present invention is directed to a dye compound of formula (I), wherein
- X represents deprotonated hydroxy (-OH) or thiol (-SH);
- Y represents oxygen or sulfur;
- z represents a charge from zero to plus one
- 10 An^- represents an anion counter-part selected from inorganic anions such as chlorine, perchlorate, hexafluoroantimonate, hexafluorophosphate, tetrafluoroborate, tetraphenylborate or organic anions such as dicyanoamide ($N(CN)_2$) or trifluoromethanesulfonimide ($N(SO_2CF_3)_2$); or
- An^- can also be an anionic azo metal complex
- 15 M represents a metal ion selected from the group consisting of Ca, Sr, Ba, Al, Ga, In, Sc, Y, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu;
- n represents a whole number from 1 to 4
- 20 A is selected to form one of the following groups or one of their tautomeric forms:





wherein

R₃ and R₄ represent independently of one another, represent hydrogen,

C₁₋₈ alkyl, wherein the alkyl can be unsubstituted or substituted by C₁₋₈ alkyl, hydroxy (-OH), by C₆₋₁₂ aryl or by -NR₉R₁₀ in which R₉ and R₁₀ are independently hydrogen, C₁₋₈ alkyl or C₆₋₁₂ aryl;

CX₃ where X can be chlorine, fluorine, bromine;

C₆₋₁₂ aryl, which is unsubstituted or substituted by C₁₋₈ alkyl, hydroxy (-OH), nitro (NO₂), cyano (-CN), halogen, by C₆₋₁₂ aryl, by -NR₉R₁₀ in which R₉ and R₁₀ are independently hydrogen, C₁₋₈ alkyl or C₆₋₁₂ aryl or by C₁₋₈ alkoxy (-OR);

R₅ to R₈ independently of one another, represent hydrogen, cyano (-CN), halogen, nitro (NO₂), hydroxy, linear or branched C₁₋₈ alkoxy (-OR) wherein the alkyl (R) can be unsubstituted or substituted by C₁₋₈ alkyl, hydroxy (-OH), by C₆₋₁₂ aryl or by -NR₉R₁₀ in which R₉ and R₁₀ are independently hydrogen, C₁₋₈ alkyl or C₆₋₁₂ aryl;

amino (NR₉R₁₀) in which R₉ and R₁₀ are independently hydrogen, C₁₋₈ alkyl or C₆₋₁₂ aryl or in which R₉ and R₁₀ can form a five- or six-membered ring which may contain further heteroatoms;

linear or branched C₁₋₈ alkyl, wherein the alkyl can be unsubstituted or substituted by C₁₋₈ alkyl, hydroxy (-OH), by C₆₋₁₂ aryl or by -NR₉R₁₀ in which R₉ and R₁₀ are independently hydrogen, C₁₋₈ alkyl or C₆₋₁₂ aryl;

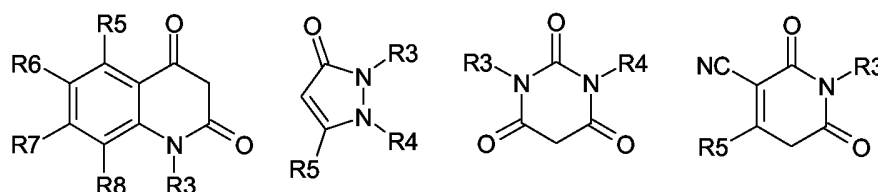
CX₃ where X can be chlorine, fluorine, bromine;

linear or branched C₁₋₈ alkylthio, wherein the alkyl can be unsubstituted or substituted by C₁₋₈ alkyl, hydroxy (-OH), by C₆₋₁₂ aryl or by -NR₉R₁₀ in which R₉ and R₁₀ are independently hydrogen, C₁₋₈ alkyl or C₆₋₁₂ aryl;

C₆₋₁₂ aryl, which is unsubstituted or substituted by C₁₋₈ alkyl, hydroxy (-OH), nitro (NO₂), cyano (-CN), halogen, by C₆₋₁₂ aryl, by -NR₉R₁₀ in which R₉ and R₁₀ are independently hydrogen, C₁₋₈ alkyl or C₆₋₁₂ aryl or by C₁₋₈ alkoxy (-OR).

In a more preferred aspect, the present invention is directed to a dye compound of formula (I), wherein

- X represents deprotonated hydroxy (-OH);
 Y represents oxygen;
 5 z represents a charge from zero to plus one
 An⁻ represents chloride
 M represents a metal ion selected from the group consisting of Al, Y, Zr, Cr, Fe, Co, Ni, Cu, Zn, Yb;
 n represents a whole number from 2 to 3
 10 A is selected to form one of the following groups or one of their tautomeric forms:



15 wherein

- R₃ and R₄ represent independently of one another, represent hydrogen, C₁₋₈ alkyl, wherein the alkyl can be unsubstituted or substituted by C₁₋₈ alkyl, hydroxy (-OH), by C₆₋₁₂ aryl or by -NR₉R₁₀ in which R₉ and R₁₀ are independently hydrogen, C₁₋₈ alkyl or C₆₋₁₂ aryl;
 20 C₆₋₁₂ aryl, which is unsubstituted or substituted by C₁₋₈ alkyl, hydroxy (-OH), nitro (NO₂), cyano (-CN), halogen, by C₆₋₁₂ aryl, by -NR₉R₁₀ in which R₉ and R₁₀ are independently hydrogen, C₁₋₈ alkyl or C₆₋₁₂ aryl or by C₁₋₈ alkoxy (-OR);
 R₅ to R₈ independently of one another, represent hydrogen, cyano (-CN), halogen,
 25 nitro (NO₂), hydroxy, linear or branched C₁₋₈ alkoxy (-OR) wherein the alkyl (R) can be unsubstituted or substituted by C₁₋₈ alkyl, hydroxy (-OH), by C₆₋₁₂ aryl or by -NR₉R₁₀ in which R₉ and R₁₀ are independently hydrogen, C₁₋₈ alkyl or C₆₋₁₂ aryl;

amino (NR_9R_{10}) in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl or in which R_9 and R_{10} can form a five- or six-membered ring which may contain further heteroatoms;

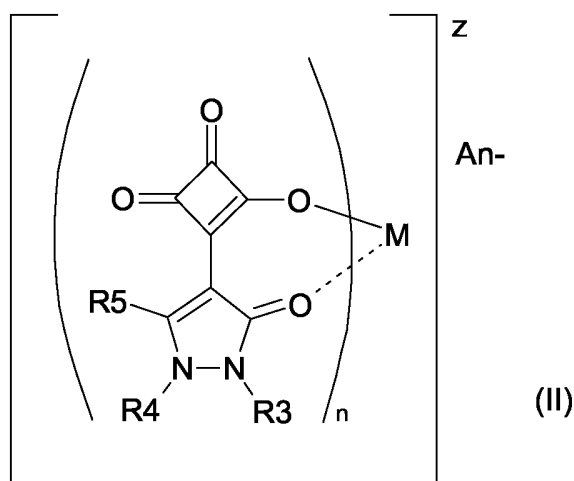
linear or branched C_{1-8} alkyl, wherein the alkyl can be unsubstituted or substituted by C_{1-8} alkyl, hydroxy ($-\text{OH}$), by C_{6-12} aryl or by $-\text{NR}_9\text{R}_{10}$ in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl;

CX_3 where X can be chlorine, fluorine, bromine;

linear or branched C_{1-8} alkylthio, wherein the alkyl can be unsubstituted or substituted by C_{1-8} alkyl, hydroxy ($-\text{OH}$), by C_{6-12} aryl or by $-\text{NR}_9\text{R}_{10}$ in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl;

$\text{C}_6\text{-C}_{12}$ aryl, which is unsubstituted or substituted by C_{1-8} alkyl, hydroxy ($-\text{OH}$), nitro (NO_2), cyano ($-\text{CN}$), halogen, by C_{6-12} aryl, by $-\text{NR}_9\text{R}_{10}$ in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl or by $\text{C}_1\text{-C}_8$ alkoxy ($-\text{OR}$).

In a most preferred embodiment, the present invention is directed to a dye compound of formula (II)



wherein

z represents a charge from zero to plus one;

An^- represents chloride;

M represents a metal ion selected from the group consisting of Al, Zr, Cr, Co, Ni, Cu, Zn;

- n represents a whole number from 2 to 3;
R₃ represents phenyl or p-tolyl,
R₄ represents methyl or benzyl,
R₅ represents methyl or phenyl.

5

The present invention further relates to an optical layer comprising a dye compound of formula (I) as described above and to the use of said optical layers for optical data recording media. An optical layer according to the invention may also comprise a mixture of two or more, preferably of two dye compounds of formula (I) as defined above.

10

The monosubstituted squaric acid metal complex dyes of formula (I) provide for particularly preferable properties when used in optical layers for optical data recording media according to the invention.

15

Preferred substrates are polycarbonate (PC) or polymethylmethacrylate (PMMA).

Organic solvents are selected from C₁₋₈ alcohol, halogen substituted C₁₋₈ alcohols, C₁₋₈ ketone, C₁₋₈ ether, halogen substituted C₁₋₄ alkane, or amides.

Preferred C₁₋₈ alcohols or halogen substituted C₁₋₈ alcohols are for example methanol, ethanol, isopropanol, diacetone alcohol (DAA), 2,2,3,3-tetrafluoropropanol, trichloroethanol, 2-chloroethanol, octafluoropentanol or hexafluorobutanol.

20

Preferred C₁₋₈ ketones are for example acetone, methylisobutylketone, methylethylketone, or 3-hydroxy-3-methyl-2-butanone.

Preferred halogen substituted C₁₋₄ alkanes are for example chloroform, dichloromethane or 1-chlorobutane.

25

Preferred amides are for example dimethylformamide or dimethylacetamide.

The optical layer (dye layer) obtained preferably has a thickness from 70 to 250 nm.

30

In a preferred aspect, the present invention provides for an optical layer suitable for high-density recording material, e.g. of the WORM disc format, in a laser wavelength range of from 350-450nm, preferably around 405 nm.

The dye compounds of formula (I) possess the required optical characteristics (such as high absorptivity, high recording sensitivity as example), an excellent solubility in organic solvents, an excellent light stability and a decomposition temperature of 250-300°C.

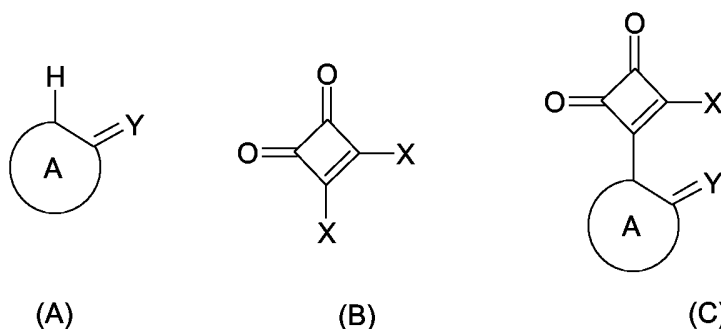
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Preparation of squaric acid metal complex dyes according to the invention

The monosubstituted squaric acid metal complex dyes of formula (I) are obtained by reacting a heterocyclic compound (A) with squaric acid derivative (B) in a polar solvent in a ratio of 1:1. The resulting monosquaric acid dye (C) is reacted with a metal salt which may be oxidized during the reaction procedure, in a polar solvent, with or without addition of an auxiliary base.

10

Anion exchange may be performed on compound (I) in an inert solvent under reflux condition with the corresponding counter-ion suitable for the exchange.



15

The process for the preparation of dyes of formula (I) can be described by the following steps:

- (a) a reaction between (A) and (B) to form the semisquaric acid (C).
- (b) reaction of the semisquaric acid (C) with a metal salt with or without using an auxiliary base
- (c) If compound (I) is charged positively, an anion exchange on compound (I) may be carried out using an inert solvent and a suitable counter-ion.

20

The preferred solvent of the condensation step (step (a)) of (A) and (B) is selected from the group consisting of ketones (acetone, methylethylketone), alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol), halogenated solvents (dichloromethane, trichloromethane) or aromatic solvents (benzene, toluene, o-,m-,p-xylenes, o-dichlorobenzene), or a mixture thereof.

25

The preferred solvent for the step (b) is selected from the group consisting of ketones (acetone, methylethylketone), alcohols (methanol, ethanol, 1-propanol, 2-propanol) or halogenated solvents (dichloromethane, trichloromethane), or a mixture thereof.

- 5 The preferred solvents for step (c) are methylethylketone, dichloromethane, acetonitrile or 2-propanol, or a mixture thereof.

Preparation of an optical layer

An optical layer according to the invention comprises a dye of formula (I) or a mixture
10 of dyes of formula (I).

A method for producing an optical layer according to the invention comprises the following steps

- (a) Providing a substrate,
15 (b) Dissolving a dye compound or a mixture of dye compounds of formula (I) in an organic solvent to form a solution,
(c) Coating the solution (b) on the substrate (a);
(d) Evaporating the solvent to form a dye layer.

20 Preparing of the high density optical recording medium

A method for producing an optical recording medium comprising an optical layer according to the invention comprises the following additional steps

- (e) sputtering a metal layer onto the dye layer
25 (f) applying a second polymer based layer to complete the disk.

A high-density data storage medium according to the invention therefore preferably is a recordable optical disc comprising: a first substrate, which is a transparent substrate with grooves, a recording layer (optical layer), which is formed on the first substrate surface using the dye of formula (I), a reflective layer formed on the recording layer, a
30 second substrate, which is a transparent substrate with grooves connected to the reflective layer with an attachment layer.

(a) Substrate

The substrate, which functions as support for the layers applied thereto, is advantageously semi-transparent ($T > 10\%$) or preferably transparent ($T > 90\%$). The support can have a thickness of from 0.01 to 10 mm, preferably from 0.1 to 5 mm.

5

Suitable substrates are, for example, glass, minerals, ceramics and thermosetting or thermoplastic plastics. Preferred supports are glass and homo- or co-polymeric plastics. Suitable plastics are, for example, thermoplastic polycarbonates, polyamides, polyesters, polyacrylates and polymethacrylates, polyurethanes, polyolefins, polyvinyl chloride, polyvinylidene fluoride, polyimides, thermosetting polyesters and epoxy resins.

The most preferred substrates are polycarbonate (PC) or polymethylmethacrylate (PMMA).

15 The substrate can be in pure form or may also comprise customary additives, for example UV absorbers or dyes, as proposed e.g. in JP 04/167239 as light-stabilizers for the recording layer. In the latter case it may be advantageous for the dye added to the support substrate to have an absorption maximum hypso-chromically shifted relative to the dye of the recording layer by at least 10 nm, preferably by at least 20 nm.

20 The substrate is advantageously transparent over at least a portion of the range from 350 to 500 nm, so that it is permeable to at least 90% of the incident light of the writing or readout wavelength.

(b) Organic solvents

25 Organic solvents are selected from C_{1-8} alcohol, halogen substituted C_{1-8} alcohols, C_{1-8} ketone, C_{1-8} ether, halogen substituted C_{1-4} alkane, or amides.

Preferred C_{1-8} alcohols or halogen substituted C_{1-8} alcohols are for example methanol, ethanol, isopropanol, diacetone alcohol (DAA), 2,2,3,3-tetrafluoropropanol, trichloroethanol, 2-chloroethanol, octafluoropentanol or hexafluorobutanol.

30 Preferred C_{1-8} ketones are for example acetone, methylisobutylketone, methylethylketone, or 3-hydroxy-3-methyl-2-butanone.

Preferred halogen substituted C₁₋₄ alkanes are for example chloroform, dichloromethane or 1-chlorobutane.

Preferred amides are for example dimethylformamide or dimethylacetamide.

5 **(c) Recording layer**

The recording layer (optical layer) is preferably arranged between the transparent substrate and the reflecting layer. The thickness of the recording layer is from 10 to 1000 nm, preferably from 30 to 300 nm, especially about 80 nm, for example from 60 to 120 nm.

10

The use of dyes of formula (I) results in advantageously homogeneous, amorphous and low-scattering recording layers having a high refractive index. The absorption edge is surprisingly steep even in the solid phase. Further advantages are high light stability in daylight and under laser radiation of low power density with, at the same time, high
15 sensitivity under laser radiation of high power density, uniform script width, high contrast, and also good thermal stability and storage stability.

20

The recording layer, instead of comprising a single compound of formula (I), may also comprise a mixture of such compounds according to the invention. By the use of mixtures, for example mixtures of isomers or homologues as well as mixtures of different structures, the solubility can often be increased and/or the amorphous content improved.

25

For a further increase in stability it is also possible, if desired, to add known stabilizers in customary amounts, for example a nickel dithiolate as light stabilizer, as described in JP 04/025493.

30

The recording layer comprises a compound of formula (I) or a mixture of such compounds preferably in an amount sufficient to have a substantial influence on the refractive index, for example at least 30% by weight, more preferably at least 60% by weight, most preferably at least 80% by weight.

Further customary components are, for example other chromophores (for example those disclosed in W0-01/75873, or others having an absorption maximum at from 300 to 1000 nm), stabilizers, $^1\text{O}_2$ -, triplet- or luminescence quenchers, melting-point reducers, decomposition accelerators or any other additives that have already been described in optical recording media. Preferably, stabilizers or fluorescence-quenchers are added if desired.

When the recording layer comprises further chromophores, they may in principle be any dye that can be decomposed or modified by the laser radiation during the recording, or they may be inert towards the laser radiation. When the further chromophores are decomposed or modified by the laser radiation, this can take place directly by absorption of the laser radiation or can be induced indirectly by the decomposition of the compounds of formula (I) according to the invention, for example thermally.

Naturally, further chromophores or colored stabilizers may influence the optical properties of the recording layer. It is therefore preferable to use further chromophores or colored stabilizers, the optical properties of which conform as far as possible to those of the compounds formula (I) or are as different as possible, or the amount of further chromophores is kept small.

When further chromophores having optical properties that conform as far as possible to those of compounds formula (I) are used, preferably this should be the case in the range of the longest-wavelength absorption flank. Preferably the wavelengths of the inversion points of the further chromophores and of the compounds of formula (I) are a maximum of 20 nm, especially a maximum of 10 nm, apart. In that case the further chromophores and the compounds of formula (I) should exhibit similar behavior in respect of the laser radiation, so that it is possible to use as further chromophores known recording agents the action of which is synergistically enhanced by the compounds of formula (I).

When further chromophores or colored stabilizers having optical properties that are as different as possible from those of compounds of formula (I) are used, they advantageously have an absorption maximum that is hypso-chromically or batho-

chromically shifted relative to the dye of formula (I). In that case the absorption maxima are preferably at least 50 nm, especially at least 100 nm, apart.

5 Examples thereof are UV absorbers that are hypso-chromic to the dye of formula (I) or colored stabilizers that are bathochromic to the dye of formula (I) and have absorption maxima lying, for example, in the NIR or IR range.

Other dyes can also be added for the purpose of color-coded identification, color-masking ("diamond dyes") or enhancing the aesthetic appearance of the recording layer.
10 In all those cases, the further chromophores or colored stabilizers should preferably exhibit behavior towards light and laser radiation that is as inert as possible.

When another dye is added in order to modify the optical properties of the compounds of formula (I), the amount thereof is dependent upon the optical properties to be achieved. The person skilled in the art will find little difficulty in varying the ratio of
15 additional dye to compound of formula (I) until he obtains his desired result.

When chromophores or colored stabilizers are used for other purposes, the amount thereof should preferably be small so that their contribution to the total absorption of the recording layer in the range of from 350 to 500 nm is a maximum of 20%, preferably
20 a maximum of 10%. In such a case, the amount of additional dye or stabilizer is advantageously a maximum of 50% by weight, preferably a maximum of 10% by weight, based on the recording layer.

Most preferably, however, no additional chromophore is added, unless it is a colored
25 stabilizer.

Stabilizers, $^1\text{O}_2$ -, triplet- or luminescence-quenchers are, for example, metal complexes of N- or S-containing enolates, phenolates, bisphenolates, thiolates or bithiolates or of azo, azomethine or formazan dyes, such as bis(4-dimethylaminodithiobenzil)nickel
30 [CAS N° 38465-55.3]. Hindered phenols and derivatives thereof such as o-hydroxyphenyl-triazoles or -triazines or other UV absorbers, such as hindered amines (TEMPO or HALS, as well as nitroxides or NOR-HALS), and also as cations diimmonium, ParaquatTM or Orthoquat salts, such as [®]Kayasorb IRG 022, [®]Kayasorb

IRG 040, optionally also as radical ions, such as N,N,N',N'-tetrakis(4-dibutylaminophenyl)-p-phenylene amine-ammonium hexafluorophosphate, hexafluoroantimonate or perchlorate. The latter are available from Organica (Wolfen/DE); [®]Kayasorb brands are available from Nippon Kayaku Co. Ltd.

5

The person skilled in the art will know from other optical information media, or will easily identify, which additives in which concentration are best suited to which purpose. Suitable concentrations of additives are, for example, from 0.001 to 1000% by weight, preferably from 1 to 50 (% by weight, based on the recording medium of formula (I)).

10

(e) Reflecting layer

Reflecting materials suitable for the reflective layer include especially metals, which provide good reflection of the laser radiation used for recording and playback, for example the metals of Main Groups III, IV and V and of the Sub-groups of the Periodic

15 Table of the Elements. Al, In, Sn, Pb, Sb, Bi, Cu, Ag, Au, Zn, Cd, Hg, Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu and alloys thereof are especially suitable. Special preference is given to a reflective layer of aluminum, silver, copper, gold or an alloy thereof, on account of their high reflectivity and ease of production.

20

(f) Cover layer / Protective layer

Materials suitable for the cover layer / protective layer include plastics, which are applied in a thin layer to the support or the uppermost layer either directly or with the aid of adhesive layers. It is advantageous to select mechanically and thermally stable

25 plastics having good surface properties, which may be modified further.

30

The plastics may be thermosetting plastics and thermoplastic plastics. Preference is given to radiation-cured (e.g. using UV radiation) protective layers, which are particularly simple and economical to produce. A wide variety of radiation-curable materials are known. Examples of radiation-curable monomers and oligomers are acrylates and methacrylates of diols, triols and tetrols, polyimides of aromatic tetracarboxylic acids and aromatic diamines having C₁-C₄ alkyl groups in at least two

ortho-positions of the amino groups, and oligomers with dialkylmaleinimidyl groups, e.g. dimethyl maleinimidyl groups.

The recording media according to the invention may also have additional layers, for example interference layers. It is also possible to construct recording media having a plurality of (for example two) recording layers. The structure and the use of such materials are known to the person skilled in the art. Preferred, if present, are interference layers that are arranged between the recording layer and the reflecting layer and/or between the recording layer and the substrate and consist of a dielectric material, for example as described in EP 0353393 of TiO₂, Si₃N₄, ZnS or silicone resins.

The recording media according to the invention can be produced by processes known in the art.

Coating methods

Suitable coating methods are, for example, immersion, pouring, brush-coating, blade-application and spin-coating, as well as vapor-deposition methods carried out under a high vacuum. When pouring methods are used, solutions in organic solvents are generally used. When solvents are employed, care should be taken that the supports used are insensitive to those solvents. Suitable coating methods and solvents are described, for example, in EP-A-401 791.

The recording layer is preferably applied by spin-coating with a dye solution, solvents that have proved satisfactory are preferably alcohols, e.g. 2-methoxyethanol, n-propanol, isopropanol, isobutanol, n-butanol, amyl alcohol or 3-methyl-1-butanol or preferably fluorinated alcohols, e.g. 2,2,2-trifluoroethanol or 2,2,3,3-tetrafluoro-1-propanol, octafluoropentanol and mixtures thereof. It will be understood that other solvents or solvent mixtures can also be used, for example those solvent mixtures described in EP-A-511 598 and EP-A-833 316. Ethers (dibutyl ether), ketones (2,6-dimethyl-4-heptanone, 5-methyl-2-hexanone) or saturated or unsaturated hydrocarbons (toluene, xylene) can also be used, for example in the form of mixtures (e.g. dibutyl ether / 2,6-dimethyl-4-heptanone) or mixed components.

The person skilled in the art of spin-coating will in general routinely try out all the solvents with which he is familiar, as well as binary and ternary mixtures thereof, in order to discover the solvents or solvent mixtures which result in a high-quality and, at the same time, cost-effective recording layer containing the solid components of his choice. Known methods of process engineering can also be employed in such optimization procedures, so that the number of experiments to be carried out can be kept to a minimum.

The invention therefore relates also to a method of producing an optical recording medium, wherein a solution of a compound of formula (I) in an organic solvent is applied to a substrate having pits. The application is preferably carried out by spin-coating.

The application of the metallic reflective layer is preferably effected by sputtering, vapor-deposition in vacuum or by chemical vapor deposition (CVD). The sputtering technique is especially preferred for the application of the metallic reflective layer on account of the high degree of adhesion to the support. Such techniques are known and are described in specialist literature (e.g. J.L. Vossen and W. Kern, "Thin Film Processes", Academic Press, 1978).

20

Readout methods

The structure of the recording medium according to the invention is governed primarily by the readout method; known function principles include the measurement of the change in the transmission or, preferably, in the reflection, but it is also known to measure, for example, the fluorescence instead of the transmission or reflection.

25

When the recording material is structured for a change in reflection, the following structures, can be used: transparent support / recording layer (optionally multilayered) / reflective layer and, if expedient, protective layer (not necessarily transparent); or support (not necessarily transparent) / reflective layer / recording layer and, if expedient, transparent protective layer. In the first case, the light is incident from the support side, whereas in the latter case the radiation is incident from the recording layer side or, where applicable, from the protective layer side. In both cases the light detector

30

is located on the same side as the light source. The first-mentioned structure of the recording material to be used according to the invention is generally preferred.

When the recording material is structured for a change in light transmission, the following different structure comes into consideration: transparent support/ recording layer (optionally multilayered) and, if expedient, transparent protective layer. The light for recording and for readout can be incident either from the support side or from the recording layer side or, where applicable, from the protective layer side, the light detector in this case always being located on the opposite side.

Suitable lasers are those having a wavelength of 350-500 nm, for example commercially available lasers having a wavelength of 405 to 414 nm, especially semi-conductor lasers. The recording is done, for example, point for point, by modulating the laser in accordance with the mark lengths and focusing its radiation onto the recording layer. It is known from the specialist literature that other methods are currently being developed which may also be suitable for use.

The process according to the invention allows the storage of information with great reliability and stability, distinguished by very good mechanical and thermal stability and by high light stability and by sharp boundary zones of the pits. Special advantages include the high contrast, the low jitter and the surprisingly high signal/noise ratio, so that excellent readout is achieved.

The readout of information is carried out according to methods known in the art by registering the change in absorption or reflection using laser radiation, for example as described in "CD-Player and R-DAT Recorder" (Claus Biaesch-Wiepke, Vogel Buchverlag, Würzburg 1992).

The optical recording medium according to the invention is preferably a recordable optical disc of the WORM type. It may be used, for example, as a playable HD-DVD (high density digital versatile disc) or Blu-ray[®] disc, as storage medium for a computer or as an identification and security card or for the production of diffractive optical elements, for example holograms.

The invention accordingly relates also to a method for the optical recording, storage and playback of information, wherein a recording medium according to the invention is used. The recording and the playback advantageously take place in a wavelength range of from 350 to 500 nm.

5

It has been found, that the new dyes of formula (I) according to the invention enhance the photosensitivity and the stability to light and heat compared to dyes already known in the art. The new dyes of formula (I) according to the invention have a decomposition temperature of 250-350°C. Additionally, these compounds show an extremely good
10 solubility in organic solvents, which is ideal for the spin-coating process to manufacture optical layers.

Thus, it is of great advantage to use these new compounds in the recording layer of high-density recordable optical discs.

15

EXAMPLES

The following examples illustrate the invention without limiting the scope thereof.

In the following examples "part" is always part by weight unless indicated otherwise.

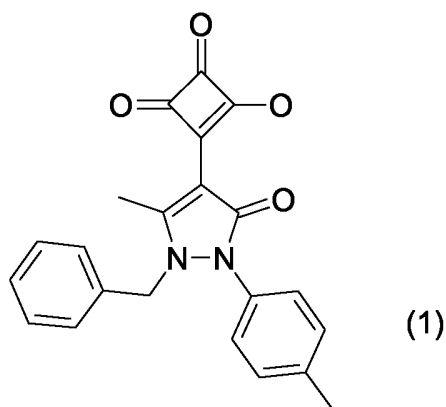
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Example 1

100 parts of 1-benzyl-5-methyl-2-p-tolyl-1,2-dihydro-pyrazol-3-one and 41 parts of 3,4-dihydroxy-3-cyclobutene-1,2-dione are refluxed for 7h in a mixture of 810 parts of 1-butanol and 390 parts of toluene. During refluxing, the reaction water is separated using
25 a water separator. After cooling, the precipitated product is filtered and washed with 1-butanol to yield 70 parts of 3-(1-Benzyl-5-methyl-3-oxo-2-p-tolyl-2,3-dihydro-1H-pyrazol-4-yl)-4-hydroxy-cyclobut-3-ene-1,2-dione.

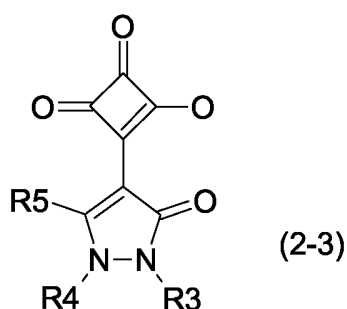
¹H-NMR (500MHz, D₆-DMSO): δ = 2.35 (s, 3H), 2.78 (s, 3H), 5.14 (s, 2H), 6.92 (m,
30 2H), 7.17 (m, 2H), 7.30 (m, 5H).

UV-Vis (MeOH) λ_{max}: 343 nm; ε (λ_{max}): 75 L·g⁻¹·cm⁻¹.

**Example 2-3**

The compounds are synthesized according to the procedures described for example 1.

5



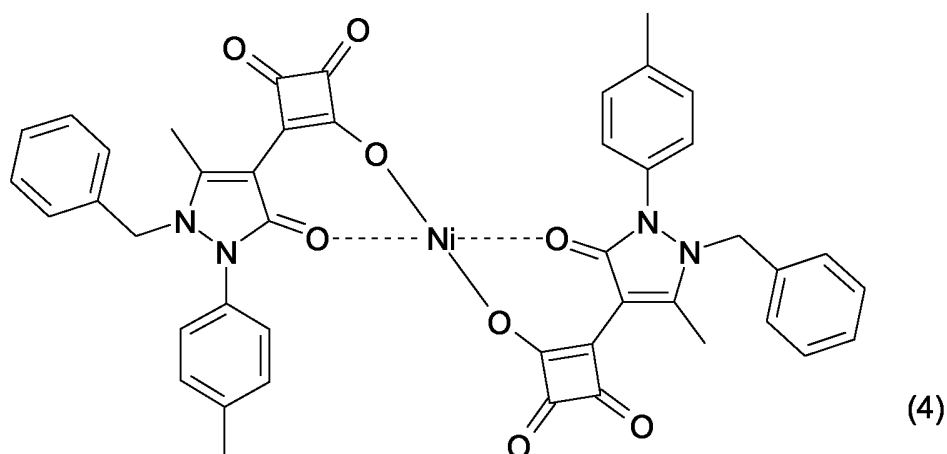
Example	R3	R4	R5	MS (MALDI negative mode)	UV $\lambda_{\max}/\epsilon$ ($\lambda_{\max}$) [nm; L/g·cm]
2	Ph	Me	Me	283[M-H] ⁻	343/87
3	Ph	Me	Ph	345[M-H] ⁻	350/40

10

Example 4

68 parts of the compound obtained in example 1 and 25 parts of nickel acetate tetrahydrate are refluxed in 1170 parts of ethanol for 30 minutes. After cooling, the precipitated product is filtered and washed with ethanol to yield 71 parts of bis[3-(1-benzyl-5-methyl-3-oxo-2-p-tolyl-2,3-dihydro-1H-pyrazol-4-yl)-4-hydroxy-cyclobut-3-ene-1,2-dione]nickel.

15



MS (MALDI negative mode): 713 [M-benzyl]⁻;

UV-Vis (MeOH) $\lambda_{\max}$: 338 nm; ϵ ($\lambda_{\max}$): 49 L·g⁻¹·cm⁻¹;

5 dec. point (TGA): 297°C;

solubility in 2,2,3,3-tetrafluoro-1-propanol: >30g/L.

Example 5-12

- 10 The compounds are synthesized according to the procedures described for example 4. Starting materials are the compounds obtained in examples 1-3, respectively.

Example	R3	R4	R5	n	M	charge (counterion)	UV $\lambda_{\max}/\epsilon$ ($\lambda_{\max}$) [nm; L/g·cm]
5	Ph	Me	Me	2	Ni	-	342/82
6	Ph	Me	Me	2	Cu	-	340/65
7	Ph	Me	Me	2	Co	-	340/50
8	Ph	Me	Me	3	Cr	-	331/46
9	Ph	Me	Me	2	Zn	-	340/63
10	Ph	Me	Me	2	Al	+1 (Cl ⁻)	337/64
11	Ph	Me	Me	3	Zr	+1 (Cl ⁻)	343/65
12	Ph	Me	Ph	2	Ni	-	350/20

Application Example

The optical and thermal properties of the new squaric acid metal complex dyes were studied. The dyes show high absorption at the desired wavelengths. In addition, the
5 shape of the absorption spectra, that still remains critical to the disc reflectivity and formation of clean mark edges, are composed of one major band, comprised in a range of from 330 to 500 nm.

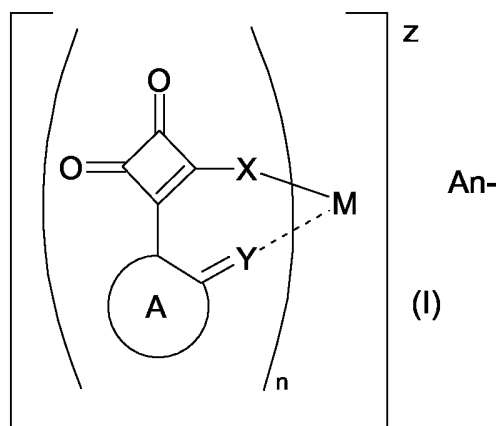
Light stabilities were found comparable to commercial dyes which usually are stabilised with quenchers for the use in optical data recording.

10 Sharp threshold of thermal decomposition within the required temperature range characterizes the new squaric acid metal complex dyes which are assumed to be desirable for the application in optical layers for optical data recording.

As a conclusion, the new squaric acid metal complex dyes are within the specifications
15 which are primarily required by the industry for the use of dyes in optical data recording, in particular in the next-generation optical data recording media in the blue laser range.

Claims

1. A dye compound of formula (I) or one of its tautomeric forms



5

wherein

- X represents deprotonated hydroxy (-OH), thiol (-SH) or amine (NHR₁) wherein R₁ represents hydrogen, C₁₋₁₂ alkyl (being unsubstituted or substituted by hydroxy (-OH), C₆₋₁₂ aryl, halogen, -NR₉R₁₀'), in which R₉ and R₁₀ are independently hydrogen, C₁₋₁₂ alkyl or C₆₋₁₂ aryl), benzyl or C₆₋₁₂ aryl;
- Y represents oxygen, sulfur, or imino-nitrogen N-R₂ wherein R₂ represents hydrogen, C₁₋₁₂ alkyl (being unsubstituted or substituted by hydroxy (-OH), C₆₋₁₂ aryl, halogen, -NR'R''), in which R' and R'' are independently hydrogen, C₁₋₁₂ alkyl or C₆₋₁₂ aryl), benzyl or C₆₋₁₂ aryl;
- z represents a charge from minus 2 to plus 2
- An⁻ represents an anion counter-part selected from inorganic anions such as iodine, fluorine, bromine, chlorine, perchlorate, hexafluoroantimonate, hexafluorophosphate, tetrafluoroborate, tetraphenylborate or organic anions such as dicyanoamide (N(CN)₂) or trifluoromethanesulfonimide (N(SO₂CF₃)₂); or An⁻ can also be an anionic azo metal complex
- M represents a metal ion;
- A is a five membered or six membered aromatic or heteroaromatic cycle which can be further substituted or annealed,
- n represents a whole number from 1 to 4.

2. A dye compound of formula (I) according to claim 1 wherein

X represents deprotonated hydroxy (-OH) or thiol (-SH);

Y represents oxygen or sulfur;

5 z represents a charge from zero to plus one

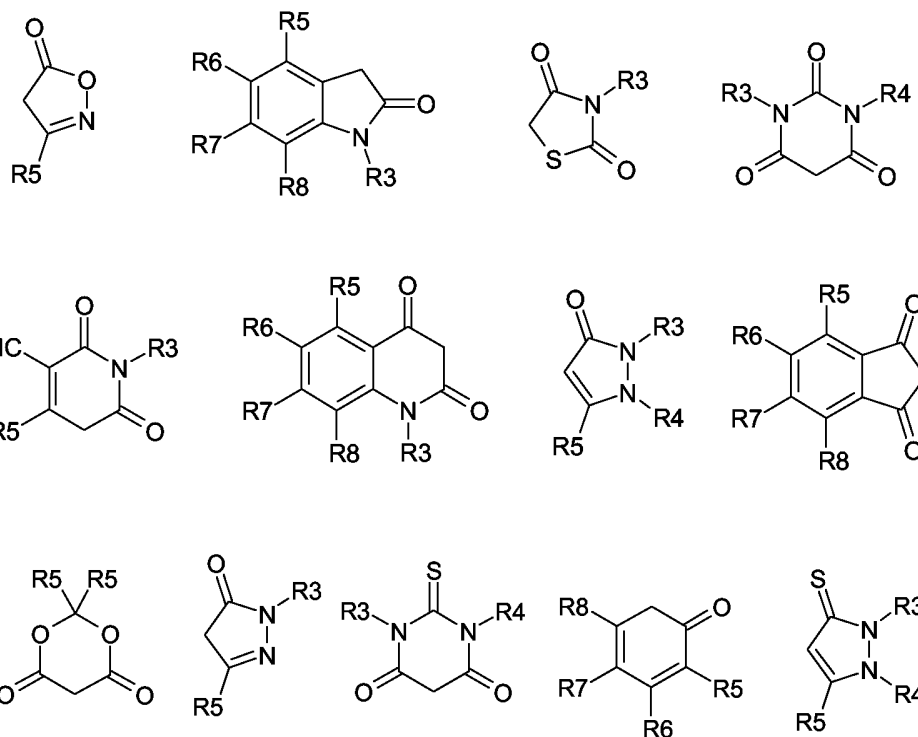
An⁻ represents an anion counter-part selected from inorganic anions such as chlorine, perchlorate, hexafluoroantimonate, hexafluorophosphate, tetrafluoroborate, tetraphenylborate or organic anions such as dicyanoamide (N(CN)₂) or trifluoromethanesulfonimide (N(SO₂CF₃)₂); or

10 An⁻ can also be an anionic azo metal complex

M represents a metal ion selected from the group consisting of Ca, Sr, Ba, Al, Ga, In, Sc, Y, Ti, Zr, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu;

15 n represents a whole number from 1 to 4

A is selected to form one of the following groups or one of their tautomeric forms:



wherein

R_3 and R_4 represent independently of one another, represent hydrogen, C_{1-8} alkyl, wherein the alkyl can be unsubstituted or substituted by C_{1-8} alkyl, hydroxy (-OH), by C_{6-12} aryl or by $-NR_9R_{10}$ in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl;

CX_3 where X can be chlorine, fluorine, bromine;

C_6-C_{12} aryl, which is unsubstituted or substituted by C_{1-8} alkyl, hydroxy (-OH), nitro (NO_2), cyano (-CN), halogen, by C_{6-12} aryl, by $-NR_9R_{10}$ in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl or by C_1-C_8 alkoxy (-OR);

R_5 to R_8 independently of one another, represent hydrogen, cyano (-CN), halogen, nitro (NO_2), hydroxy, linear or branched C_{1-8} alkoxy (-OR) wherein the alkyl (R) can be unsubstituted or substituted by C_{1-8} alkyl, hydroxy (-OH), by C_{6-12} aryl or by $-NR_9R_{10}$ in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl; amino (NR_9R_{10}) in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl or in which R_9 and R_{10} can form a five- or six-membered ring which may contain further heteroatoms;

linear or branched C_{1-8} alkyl, wherein the alkyl can be unsubstituted or substituted by C_{1-8} alkyl, hydroxy (-OH), by C_{6-12} aryl or by $-NR_9R_{10}$ in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl;

CX_3 where X can be chlorine, fluorine, bromine;

linear or branched C_{1-8} alkylthio, wherein the alkyl can be unsubstituted or substituted by C_{1-8} alkyl, hydroxy (-OH), by C_{6-12} aryl or by $-NR_9R_{10}$ in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl;

C_6-C_{12} aryl, which is unsubstituted or substituted by C_{1-8} alkyl, hydroxy (-OH), nitro (NO_2), cyano (-CN), halogen, by C_{6-12} aryl, by $-NR_9R_{10}$ in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl or by C_1-C_8 alkoxy (-OR).

3. A dye compound of formula (I) according to claim 1 wherein

X represents deprotonated hydroxy (-OH);

Y represents oxygen;

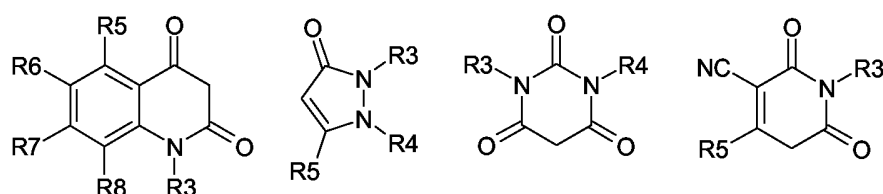
5 z represents a charge from zero to plus one

An⁻ represents chloride

M represents a metal ion selected from the group consisting of Al, Y, Zr, Cr, Fe, Co, Ni, Cu, Zn, Yb;

n represents a whole number from 2 to 3

10 A is selected to form one of the following groups or one of their tautomeric forms:



15 wherein

R₃ and R₄ represent independently of one another, represent hydrogen,

C₁₋₈ alkyl, wherein the alkyl can be unsubstituted or substituted by C₁₋₈ alkyl, hydroxy (-OH), by C₆₋₁₂ aryl or by -NR₉R₁₀ in which R₉ and R₁₀ are independently hydrogen, C₁₋₈ alkyl or C₆₋₁₂ aryl;

20 C₆₋₁₂ aryl, which is unsubstituted or substituted by C₁₋₈ alkyl, hydroxy (-OH), nitro (NO₂), cyano (-CN), halogen, by C₆₋₁₂ aryl, by -NR₉R₁₀ in which R₉ and R₁₀ are independently hydrogen, C₁₋₈ alkyl or C₆₋₁₂ aryl or by C₁₋₈ alkoxy (-OR);

25 R₅ to R₈ independently of one another, represent hydrogen, cyano (-CN), halogen, nitro (NO₂), hydroxy, linear or branched C₁₋₈ alkoxy (-OR) wherein the alkyl (R) can be unsubstituted or substituted by C₁₋₈ alkyl, hydroxy (-OH), by C₆₋₁₂ aryl or by -NR₉R₁₀ in which R₉ and R₁₀ are independently hydrogen, C₁₋₈ alkyl or C₆₋₁₂ aryl;

amino (NR_9R_{10}) in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl or in which R_9 and R_{10} can form a five- or six-membered ring which may contain further heteroatoms;

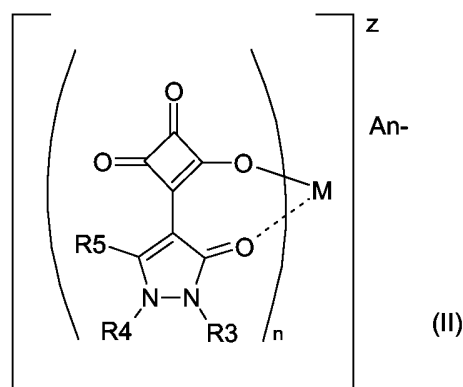
linear or branched C_{1-8} alkyl, wherein the alkyl can be unsubstituted or substituted by C_{1-8} alkyl, hydroxy ($-\text{OH}$), by C_{6-12} aryl or by $-\text{NR}_9\text{R}_{10}$ in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl;

CX_3 where X can be chlorine, fluorine, bromine;

linear or branched C_{1-8} alkylthio, wherein the alkyl can be unsubstituted or substituted by C_{1-8} alkyl, hydroxy ($-\text{OH}$), by C_{6-12} aryl or by $-\text{NR}_9\text{R}_{10}$ in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl;

$\text{C}_6\text{-C}_{12}$ aryl, which is unsubstituted or substituted by C_{1-8} alkyl, hydroxy ($-\text{OH}$), nitro (NO_2), cyano ($-\text{CN}$), halogen, by C_{6-12} aryl, by $-\text{NR}_9\text{R}_{10}$ in which R_9 and R_{10} are independently hydrogen, C_{1-8} alkyl or C_{6-12} aryl or by $\text{C}_1\text{-C}_8$ alkoxy ($-\text{OR}$).

4. A dye compound of formula (I) according to claim 1 wherein the dye compound is of formula (II)



wherein

z represents a charge from zero to plus one;

An^- represents chloride;

M represents a metal ion selected from the group consisting of Al, Zr, Cr, Co, Ni, Cu, Zn;

n represents a whole number from 2 to 3;

R_3 represents phenyl or p-tolyl,

R_4 represents methyl or benzyl,

R₅ represents methyl or phenyl.

5. An optical layer comprising at least one dye compound according to formula (I) as defined in claims 1 to 4 or a mixture of at least two dye compounds according to formula (I) as defined in claims 1 to 4.
6. A method for producing an optical layer according to claim 5, comprising the following steps
 - (a) providing a substrate
 - (b) dissolving a dye compound or a mixture of dye compounds of formula (I), as defined in claims 1 to 4 in an organic solvent to form a solution,
 - (c) coating the solution (b) on the substrate (a);
 - (d) evaporating the solvent to form a dye layer.
7. A method according to claim 6, wherein the substrate is polycarbonate (PC) or polymethylmethacrylate (PMMA).
8. A method according to claim 6, wherein the organic solvent is selected from C₁₋₈ alcohol, halogen substituted C₁₋₈ alcohols, C₁₋₈ ketone, C₁₋₈ ether, halogen substituted C₁₋₄ alkane, or amides.
9. A method according to claim 6, wherein the C₁₋₈ alcohols or halogen substituted C₁₋₈ alcohols are selected from methanol, ethanol, isopropanol, diacetone alcohol (DAA), 2,2,3,3-tetrafluoropropanol, trichloroethanol, 2-chloroethanol, octafluoropentanol or hexafluorobutanol;
the C₁₋₈ ketones are selected from acetone, methylisobutylketone, methylethylketone, or 3-hydroxy-3-methyl-2-butanone;
the halogen substituted C₁₋₄ alkanes are selected from chloroform, dichloromethane or 1-chlorobutane; and
the amides are selected from dimethylformamide or dimethylacetamide.
10. An optical recording medium comprising an optical layer according to claim 5.