

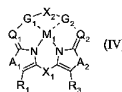
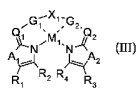
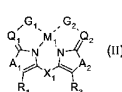
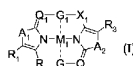
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(54) Title: OPTICAL RECORDING MATERIALS HAVING HIGH STORAGE DENSITY



(57) Abstract: The invention relates to new compounds of formula (I), (II), (III) or (IV) and their use in the recording layer of an optical recording medium comprising a substrate, a recording layer and optionally one or more reflecting layers. The instant compounds are of formula (I), (II), (III) or (IV) or tautomers thereof, wherein G1 and G2 are each independently of the other formula (V), (VI), (VII), (VIII), (IX), (X), (XI), X1 and X2 are each independently from the other a direct bond or a chain consisting of from 1 to 8 members each selected independently from the group consisting of CR₁₂=CR₁₃, C=CR₁₂R₁₃, CR₁₂R₁₃, C=O, C=S, C=N(R₁₄), N(R₁₄), O or S, preferably a direct bond or a chain consisting of 1, 2, 3 or 4 members, most preferred a direct bond or a chain CR₁₂R₁₃, C=O, C=S, C=N(R₁₄), N(R₁₄), O or S; A₁, A₂ and A₃ are CR₁₅R₁₆, formula (a), N(R₁₄), O, S, Se, N=C(R₁₈) or CR₁₉=CR₂₀, and A₄ is O, S or Se; M₁ is a transition metal of groups 9 to 12, preferably Co, Cu, Ni, Pd or Zn, especially Co, Cu or Ni, or is SiR₂₁R₂₂, GeR₂₁R₂₂, PR₂₁R₂₂ or AlR₂₁; and Q₁ and Q₂ are each independently of the other C(R₂₃), N or P. For the detailed definitions of the further substituents, see the description. Recording and playback are effected especially at a wavelength of from 350 to 500 nm, for example using a blue laser. The recording and playback quality is excellent and allows a high storage density.



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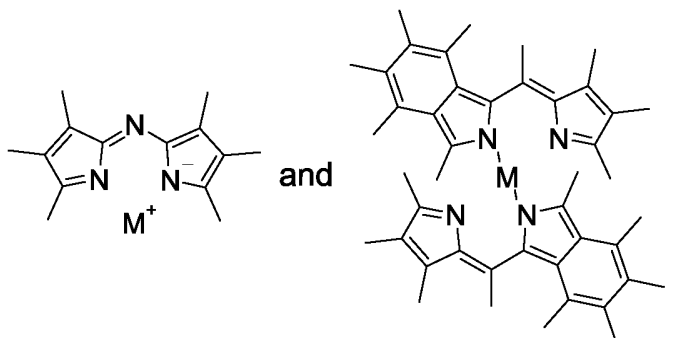
Optical recording materials having high storage density

The invention relates to new optical recording materials that have excellent recording and playback quality especially at a wavelength of 350-500 nm.

Recording and playback can be effected very advantageously with high sensitivity at the same wavelength, and the storage density that is achievable is significantly higher than in the case of known materials. In addition, the materials according to the invention have very good storage properties before and after recording, even under especially harsh conditions, such as exposure to sunlight or fluorescent lighting, heat and/or high humidity. In addition, their manufacture is simple and readily reproducible using customary coating processes, such as spin-coating.

JP-A-11/34500, JP-A-11/92479 and EP-A-0 903 733 disclose metal and boron

complexes of colorants of formulae



which can be used at from 520 to 690 nm for optical recording materials such as CD-R or DVD-R. Here too, however, the optical properties, especially the spectral properties in or near the UV range that are necessary for the highest possible storage densities, and the information density per unit surface area are not able to satisfy the highest demands as desired. The information density per unit surface area is far lower than is desirable.

WO 02/082 438 discloses the use of ionic salts, including those with metal complex anions, for optical recording materials. Those colorants are always substituted by alkyl, alkenyl, aryl or heteroaryl at the nitrogen atom. Their optical properties do not, however, fully satisfy increased demands. In particular, the refractive index as well as the absorption and the steepness of the absorption band on its long wavelength flank in the solid still leave something to be desired.

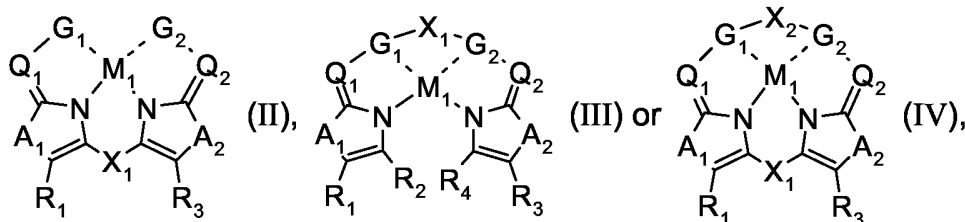
Conventional optical recording materials therefore satisfy high demands only to some extent, or do not satisfy all demands to an entirely satisfactory degree at the same time.

- On the other hand, J. Org. Chem. 67/16, 5753-5772 [2002] describes the synthesis of a number of bis(o-azaheteroaryl)methanes and their coordination properties with respect to divalent transition metals, heteroaryl being 1,3-azol-2-yl, 1,3-benzazol-2-yl and azinyl and the transition metals being Zn, Cu, Co, Ni, Hg and Pd. *Inter alia* 2:1 salt complexes of bis(benzothiazol-2-yl)methane and bis(benzoxazol-2-yl)-methane with copper(II) chloride and nickel(II) sulfate, and cobalt(II) chloride and palladium(II) nitrate are disclosed, whereas bis(thiazol-2-yl)methane yields, with deprotonation, neutral 2:1 chelates with Zn(II), Cu(II), Ni(II) and Co(II). All substances are strongly coloured.

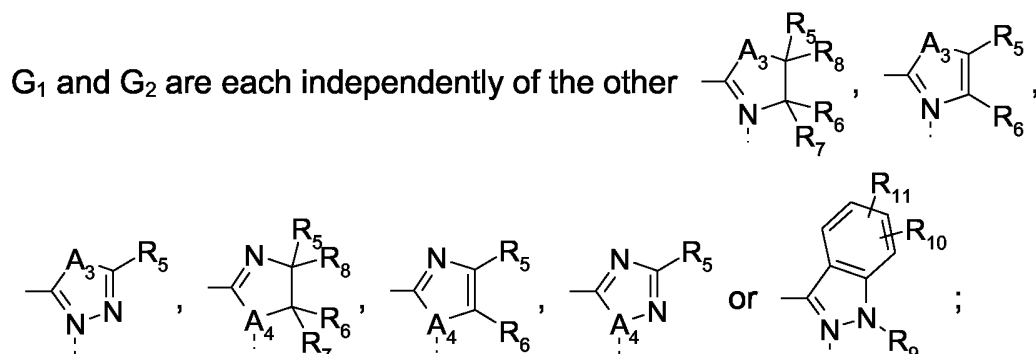
WO 04/079 732 is a patent application according to Art. 54(3) EPC and Rule 64.3 PCT, which is directed to metal complexes comprising two individual ligands.

- The aim of the invention is an optical recording medium having high information density, sensitivity and data reliability. Such a recording medium should be robust, durable and easy to use. Furthermore, it should be inexpensive to manufacture as a mass-produced product and should require equipment that is as small and inexpensive as possible.
- The invention therefore relates to an optical recording medium comprising a substrate, a recording layer and optionally one or more reflecting layers, wherein

the recording layer comprises a compound of formula

$$\begin{array}{c}
 \text{Q}_1-\text{G}_1-\text{X}_1 \\
 \diagup \quad \diagdown \\
 \text{A}_1 \quad \text{N} \quad \text{M}_1 \quad \text{N} \quad \text{A}_2 \\
 \diagdown \quad \diagup \quad \diagdown \quad \diagup \\
 \text{R}_1 \quad \text{R}_2 \quad \text{G}_2-\text{Q}_2 \quad \text{R}_3
 \end{array}
 \quad (\text{I}),$$


or a tautomer of a compound of formula (I), (II), (III) or (IV), wherein



X₁ and X₂ are each independently from the other a direct bond or a chain consisting
 5 of from 1 to 8 members each selected independently from the group consisting of
 CR₁₂=CR₁₃, C=CR₁₂R₁₃, CR₁₂R₁₃, C=O, C=S, C=N(R₁₄), N(R₁₄), O or S, preferably
 a direct bond or a chain consisting of 1, 2, 3 or 4 members, most preferred a direct
 bond or a chain CR₁₂R₁₃, C=O, C=S, C=N(R₁₄), N(R₁₄), O or S;

A₁, A₂ and A₃ are CR₁₅R₁₆, $\bigcirc$ R₁₇, N(R₁₄), O, S, Se, N=C(R₁₈) or CR₁₉=CR₂₀, and

10 A₄ is O, S or Se;

M₁ is a transition metal of groups 9 to 12, preferably Co, Cu, Ni, Pd or Zn,
 especially Co, Cu or Ni, or is SiR₂₁R₂₂, GeR₂₁R₂₂, PR₂₁R₂₂ or AlR₂₁;

Q₁ and Q₂ are each independently of the other C(R₂₃), N or P;

15 R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₁₉ and R₂₀ are each independently of the others
 hydrogen, R₁₀, or C₆-C₁₂aryl, C₄-C₁₂heteroaryl, C₇-C₁₂aralkyl or C₅-C₁₂heteroaralkyl
 each unsubstituted or substituted by one or more, where applicable identical or
 different, radicals R₁₀; or

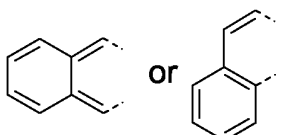
20 R₅ or R₆, preferably R₆, is the position of X₁ in formula (I) or (III) or the position of
 X₂ in formula (IV), with the proviso that when X₁ or X₂ is a direct bond or a chain
 with a length of less than 3 atoms, its position at G₁ or G₂ is not R₅;

R₉, R₁₄ and R₁₈ are each independently of the others C₁-C₂₄alkyl, C₃-C₂₄cycloalkyl,

C₂-C₂₄alkenyl, C₃-C₂₄cycloalkenyl, C₁-C₄alkyl-[O-C₁-C₄alkylene]_m or C₁-C₄alkyl-[NH-C₁-C₄alkylene]_m, each of which is unsubstituted or substituted by one or more, where applicable identical or different, radicals R₂₄; or C₆-C₁₂aryl, C₄-C₁₂heteroaryl, C₇-C₁₂aralkyl or C₅-C₁₂heteroaralkyl, each of which is unsubstituted or substituted
 5 by one or more, where applicable identical or different, radicals R₁₀;

or R₉ is the position of X₁ in formula (I) or (III) or the position of X₂ in formula (IV);
 and/or R₁₄ is COR₉, COOR₉, CONR₁₂R₁₃, C(R₉)=NR₁₈, C(OR₉)=NR₁₈ or
 C(NR₁₂R₁₃)=NR₁₈;

or R₁ and R₂, R₃ and R₄, R₅ and R₆, R₅ and R₁₈, R₅ and R₁₉, R₁ and R₃ in
 10 formula (II) or (IV), R₃ and R₅ in formula (I), R₅ of G₁ and R₅ of G₂ in formula (III) or (IV) and/or R₆ of G₁ and R₆ of G₂ in formula (III) or (IV), together in pairs, are C₃-C₆alkylene or C₃-C₆alkenylene, each of which is unsubstituted or substituted by one or more, where applicable identical or different, radicals R₂₄ and/or R₃₂ and may be uninterrupted or interrupted by O, S or N(R₁₄), or 1,4-buta-1,3-dienylene,

15  , each of which is unsubstituted or substituted by one or more,

where applicable identical or different, radicals R₁₀ and in which 1 or 2 carbon atoms may have been replaced by nitrogen;

R₁₀ and R₁₁ are each independently of the other C(R₂₃)=NR₂₅, C(R₂₃)=NR₂₆ or R₂₈;
 or R₁₀ is the position of X₁ in formula (I) or (III) or the position of X₂ in formula (IV);

20 R₁₂ and R₁₃ are each independently from the other hydrogen, R₁₀ or C₆-C₁₂aryl, C₄-C₁₂heteroaryl, C₇-C₁₂aralkyl or C₅-C₁₂heteroaralkyl each unsubstituted or substituted by one or more, where applicable identical or different, radicals R₁₀; or

R₁₂ and R₁₃ together are C₂-C₇alkylene or C₂-C₇alkenylene, preferably C₃-C₆alkylene or C₃-C₆alkenylene, most preferred C₄-C₅alkylene or

25 C₄-C₅alkenylene, each of which is unsubstituted or substituted by one or more, where applicable identical or different, radicals R₂₄ and/or R₃₂;

R_{15} and R_{16} are each independently from the other C_1 - C_5 alkyl which is unsubstituted or substituted by one or more, where applicable identical or different, radicals R_{24} ,

R_{17} is C_2 - C_7 alkylene, preferably C_4 - C_5 alkylene, each of which is unsubstituted or substituted by one or more, where applicable identical or different, radicals R_{24} and may be uninterrupted or interrupted by O, S or N(R_{14}),

R_{21} and R_{22} are each independently of the others hydroxy, C_1 - C_{12} alkoxy, C_3 - C_{12} cycloalkoxy, C_1 - C_{12} alkylthio, C_1 - C_{12} alkyl, C_3 - C_{12} cycloalkyl, C_2 - C_{12} alkenyl, C_3 - C_{12} cycloalkenyl, C_6 - C_{12} aryl, C_4 - C_{12} heteroaryl, C_7 - C_{12} aralkyl or C_5 - C_{12} heteroaralkyl, each of which is unsubstituted or substituted by one or more, where applicable identical or different, halogen, hydroxy, C_1 - C_{12} alkoxy or C_3 - C_{12} cycloalkoxy radicals;

R_{23} is hydrogen, cyano, hydroxy, C_1 - C_{12} alkoxy, C_3 - C_{12} cycloalkoxy, C_1 - C_{12} alkylthio, C_3 - C_{12} cycloalkylthio, amino, NHR_{29} , $NR_{30}R_{31}$, R_{32} , halogen, nitro, formyl, $N=N-R_{32}$, $C(R_{33})=CR_{26}R_{27}$, $C(R_{33})=NR_{25}$, $COO-R_{30}$, carboxy, carbamoyl, $CONH-R_{30}$, $CONR_{30}R_{31}$, $N=CR_{25}R_{34}$, or C_1 - C_{12} alkyl, C_3 - C_{12} cycloalkyl, C_2 - C_{12} alkenyl or C_3 - C_{12} cycloalkenyl each unsubstituted or substituted by one or more, where applicable identical or different, halogen, hydroxy, C_1 - C_{12} alkoxy or C_3 - C_{12} cycloalkoxy radicals;

R_{24} is halogen, hydroxy, $O-R_{30}$, $O-CO-R_{30}$, $S-R_{30}$, NH_2 , $NH-R_{30}$, $NR_{30}R_{31}$, NH_3^+ , $NH_2R_{30}^+$, $NHR_{30}R_{31}^+$, $NR_{29}R_{30}R_{31}^+$, $NR_{30}-CO-R_{29}$, $NR_{30}COOR_{29}$, cyano, formyl, $COO-R_{30}$, carboxy, carbamoyl, $CONH-R_{30}$, $CONR_{30}R_{31}$, ureido, $NH-CO-NHR_{29}$, $NR_{30}-CO-NHR_{29}$, phosphato, $PR_{30}R_{29}$, $POR_{30}OR_{29}$, $P(=O)OR_{30}OR_{29}$, $OPR_{30}R_{29}$, $OPR_{30}OR_{29}$, $OP(=O)R_{30}OR_{29}$, OPO_3R_{30} , $OP(=O)OR_{30}OR_{29}$, SO_2R_{30} , sulfato, sulfo or C_1 - C_{12} alkoxy or C_1 - C_{12} cycloalkoxy each unsubstituted or mono- or poly-substituted by halogen;

R_{26} and R_{27} are each independently of the other $NR_{30}R_{31}$, CN, $CONH_2$, $CONHR_{25}$, $CONR_{25}R_{34}$ or $COOR_{34}$;

R₂₈ is halogen, nitro, cyano, thiocyanato, hydroxy, O-R₂₅, O-CO-R₂₅, S-R₂₅, CHO, COR₃₄, CHOR₂₅OR₃₅, CR₃₄OR₂₅OR₃₅, R₃₆, N=N-R₃₆, N=CR₂₅R₃₄, N=CR₂₆R₂₇, NH₂, NH-R₂₅, NR₂₅R₃₄, NH₃⁺, NH₂R₂₅⁺, NHR₂₅R₃₄⁺, NR₂₅R₃₄R₃₅⁺, CONH₂, CONHR₂₅, CONR₂₅R₃₄, SO₂R₂₅, SO₂NH₂, SO₂NHR₂₅, SO₂NR₂₅R₃₄, COOH, COOR₂₅,

- 5 OCOOR₂₅, NHCOR₂₅, NR₂₅COR₃₅, NHCOOR₂₅, NR₂₅COOR₃₅, ureido, NR₂₅-CO-NHR₃₅, B(OH)₂, B(OH)(OR₂₅), B(OR₂₅)OR₃₅, phosphato, PR₂₅R₃₅, POR₂₅OR₃₅, P(=O)OR₂₅OR₃₅, OPR₂₅R₃₅, OPR₂₅OR₃₅, OP(=O)R₂₅OR₃₅, OP(=O)OR₂₅OR₃₅, OPO₃R₂₅, sulfato, sulfo, or C₁-C₁₂alkyl, C₃-C₁₂cycloalkyl, C₂-C₁₂alkenyl, C₃-C₁₂cycloalkenyl, C₁-C₁₂alkylthio, C₃-C₁₂cycloalkylthio,
- 10 C₂-C₁₂alkenylthio, C₃-C₁₂cycloalkenylthio, C₁-C₁₂alkoxy, C₃-C₁₂cycloalkoxy C₂-C₁₂alkenyloxy or C₃-C₁₂cycloalkenyloxy each unsubstituted or substituted by one or more, where applicable identical or different, radicals R₂₄;

R₂₉, R₃₀ and R₃₁ are each independently of the others C₁-C₁₂alkyl, C₃-C₁₂cycloalkyl, C₂-C₁₂alkenyl, C₃-C₁₂cycloalkenyl, C₆-C₁₂aryl, C₄-C₁₂heteroaryl, C₇-C₁₂aralkyl or

- 15 C₅-C₁₂heteroaralkyl; or

R₃₀ and R₃₁ together with the common nitrogen are pyrrolidine, piperidine, piperazine or morpholine, each of which is unsubstituted or mono- to tetra-substituted by C₁-C₄alkyl;

R₃₂ is C₆-C₁₂aryl, C₄-C₁₂heteroaryl, C₇-C₁₂aralkyl or C₅-C₁₂heteroaralkyl, each of

20 which is unsubstituted or substituted by one or more, where applicable identical or different, radicals R₂₈;

R₃₃ is hydrogen, R₂₈, or C₆-C₁₂aryl, C₄-C₁₂heteroaryl, C₇-C₁₂aralkyl or C₅-C₁₂heteroaralkyl each unsubstituted or substituted by one or more, where applicable identical or different, radicals R₂₈;

- 25 R₂₅, R₃₄ and R₃₅ are each independently of the others R₃₆, or C₁-C₁₂alkyl, C₃-C₁₂cycloalkyl, C₂-C₁₂alkenyl or C₃-C₁₂cycloalkenyl each unsubstituted or substituted by one or more, where applicable identical or different, halogen, hydroxy, C₁-C₁₂alkoxy or C₃-C₁₂cycloalkoxy radicals; or

R₁₉ and R₂₅ together, R₂₃ and R₂₅ together and/or R₂₅ and R₃₅ together are C₂-C₁₂alkylene, C₃-C₁₂cycloalkylene, C₂-C₁₂alkenylene or C₃-C₁₂cycloalkenylene, each of which is unsubstituted or substituted by one or more, where applicable identical or different, halogen, hydroxy, C₁-C₁₂alkoxy or C₃-C₁₂cycloalkoxy radicals;

5 or

R₂₅ and R₃₄ together with the common nitrogen are pyrrolidine, piperidine, piperazine or morpholine, each of which is unsubstituted or mono- to tetra-substituted by C₁-C₄alkyl; or carbazole, phenoxazine or phenothiazine, each of which is unsubstituted or substituted by one or more, where applicable identical or
10 different, radicals R₃₇;

R₃₆ is C₆-C₁₂aryl, C₄-C₁₂heteroaryl, C₇-C₁₂aralkyl or C₅-C₁₂heteroaralkyl, each of which is unsubstituted or substituted by one or more, where applicable identical or different, radicals R₃₇;

R₃₇ is nitro, SO₂NHR₃₀, SO₂NR₃₀R₃₁, or C₁-C₁₂alkyl, C₃-C₁₂cycloalkyl, C₁-C₁₂alkylthio, C₃-C₁₂cycloalkylthio, C₁-C₁₂alkoxy or C₃-C₁₂cycloalkoxy each unsubstituted or
15 substituted by one or more, where applicable identical or different, radicals R₂₄; and

m is a number from 1 to 10.

When R₅ forms a bridge with R₆, R₅ preferably does not at the same time form a bridge with R₁₈ or R₁₉.

20 It will be understood that acidic groups, such as carboxy, sulfo, sulfato and phosphato, may also be in the form of a salt, for example an alkali metal, alkaline earth metal, ammonium or phosphonium salt, such as Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Cu²⁺, Ni²⁺, Fe²⁺, Co²⁺, Zn²⁺, Sn²⁺, La³⁺, ammonium, methylammonium, ethylammonium, isopropylammonium, TMPrimene 81-R, TMRosin Amine D, penta-
25 decylammonium, TMPrimene JM-T, dicyclohexylammonium, tetramethylammonium, tetraethylammonium, tetrabutylammonium, benzyltrimethylammonium, benzyltriethylammonium, methyltrioctylammonium, tridodecylmethylammonium, tetra-

butylphosphonium, tetraphenylphosphonium, butyltriphenylphosphonium or ethyltriphenylphosphonium, or any of the cations B-1 to B-169 mentioned in US-6 225 024, to which individually reference is expressly made here.

5 Halogen is chlorine, bromine, fluorine or iodine, preferably fluorine or chlorine, especially fluorine on alkyl (for example trifluoromethyl, α,α,α -trifluoroethyl or perfluorinated alkyl groups, such as heptafluoropropyl) and chlorine on aryl, heteroaryl or on the aryl moiety of aralkyl or on the heteroaryl moiety of hetero-aralkyl.

10 Alkyl, cycloalkyl, alkenyl or cycloalkenyl can be straight-chain or branched, or monocyclic or polycyclic. Alkyl is, for example, methyl, straight-chain C_2 - C_{24} alkyl or preferably branched C_3 - C_{24} alkyl. Alkenyl is, for example, straight-chain C_2 - C_{20} alkenyl or preferably branched C_3 - C_{24} alkenyl, in particular vinyl, allyl, $C(R_{23})=CHR_{27}$ or $C(R_{23})=CR_{26}R_{27}$. The invention therefore relates especially also to compounds of formula (I), (II), (III) or (IV) containing branched C_3 - C_{24} alkyl or
15 branched C_3 - C_{24} alkenyl, and also to optical recording materials comprising such compounds. C_1 - C_{24} Alkyl is therefore, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, n-hexyl, n-octyl, 1,1,3,3-tetramethylbutyl, 2-ethylhexyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, heneicosyl, docosyl or
20 tetracosyl. C_3 - C_{24} Cycloalkyl is, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, trimethylcyclohexyl, menthyl, thujyl, bornyl, 1-adamantyl or 2-adamantyl.

C_2 - C_{20} Alkenyl and C_3 - C_{20} cycloalkenyl are C_2 - C_{20} alkyl and C_3 - C_{20} cycloalkyl that is
25 mono- or poly-unsaturated, wherein two or more double bonds may be isolated or conjugated, for example vinyl, allyl, 2-propen-2-yl, 2-buten-1-yl, 3-buten-1-yl, 1,3-butadien-2-yl, 2-cyclobuten-1-yl, 2-penten-1-yl, 3-penten-2-yl, 2-methyl-1-buten-3-yl, 2-methyl-3-buten-2-yl, 3-methyl-2-buten-1-yl, 1,4-pentadien-3-yl, 2-cyclopenten-1-yl, 2-cyclohexen-1-yl, 3-cyclohexen-1-yl, 2,4-cyclohexadien-1-yl, 1-p-menthen-8-yl, 4(10)-thujen-10-yl, 2-norbornen-1-yl, 2,5-norbornadien-1-yl, 7,7-dimethyl-2,4-

norcaradien-3-yl or the various isomers of hexenyl, octenyl, nonenyl, decenyl, dodecenyl, tetradecenyl, hexadecenyl, octadecenyl, eicosenyl, heneicosenyl, docosenyl, tetracosenyl, hexadienyl, octadienyl, nonadienyl, decadienyl, dodecadienyl, tetradecadienyl, hexadecadienyl, octadecadienyl or eicosadienyl.

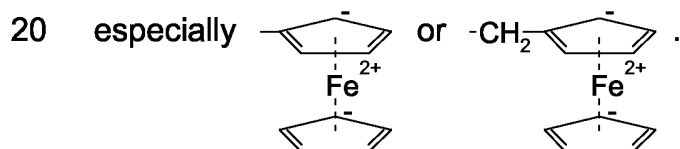
- 5 C_7 - C_{12} Aralkyl is, for example, benzyl, 2-benzyl-2-propyl, β -phenyl-ethyl, 9-fluorenyl, α,α -dimethylbenzyl, ω -phenyl-butyl or ω -phenyl-hexyl. When C_7 - C_{12} aralkyl is substituted, both the alkyl moiety and the aryl moiety of the aralkyl group can be substituted, the latter alternative being preferred.

C_6 - C_{12} Aryl is, for example, phenyl, naphthyl, biphenyl or 2-fluorenyl.

- 10 C_4 - C_{12} Heteroaryl is an unsaturated or aromatic radical having $4n+2$ conjugated π -electrons, for example 2-thienyl, 2-furyl, 2-pyridyl, 2-thiazolyl, 2-oxazolyl, 2-imidazolyl, isothiazolyl, triazolyl or any other ring system consisting of thiophene, furan, pyridine, thiazole, oxazole, imidazole, isothiazole, triazole, pyridine and benzene rings and unsubstituted or substituted by from 1 to 6 ethyl, methyl, ethylene and/or methylene substituents, for example benzotriazolyl, and in the case
15 of N-heterocycles where applicable also those in the form of their N-oxides.

C_5 - C_{12} Heteroaralkyl is, for example, C_1 - C_8 alkyl substituted by C_4 - C_{11} heteroaryl.

Furthermore, aryl and aralkyl can also be aromatic groups bonded to a metal, for example in the form of metallocenes of transition metals known *per se*, more

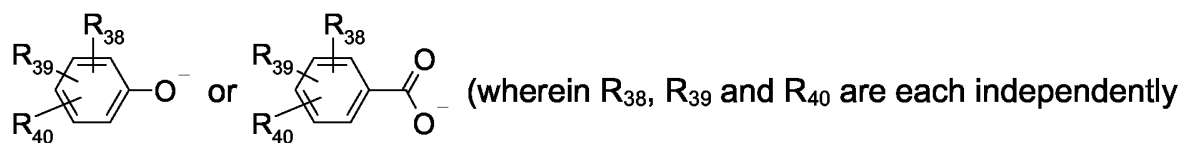


The transition metal M_1 is preferably in the form of a doubly positively charged cation, for example Co^{2+} , Cu^{2+} , Ni^{2+} , Pd^{2+} or Zn^{2+} , especially Co^{2+} , Cu^{2+} or Ni^{2+} .

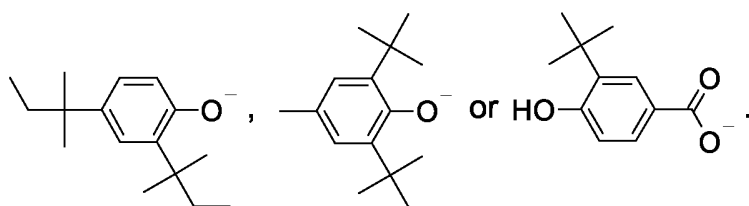
The compound of formula (I), (II), (III) or (IV) may also be a cation which has been neutralised with an inorganic, organic or organometallic anion, for example when

- one or more ammonium groups are present or when the transition metal has one or more excess positive charges, such as in Co^{3+} . The inorganic, organic or organometallic anion may be, for example, the anion of a mineral acid, of the conjugated base of an organic acid (for example an alcoholate, phenolate, carboxylate, sulfonate or phosphonate) or an organometallic complex anion, for example fluoride, chloride, bromide, iodide, perchlorate, periodate, nitrate, hydrogen carbonate, $\frac{1}{2}$ carbonate, $\frac{1}{2}$ sulfate, $\text{C}_1\text{-C}_4$ alkyl sulfate, hydrogen sulfate, $\frac{1}{3}$ phosphate, $\frac{1}{2}$ hydrogen phosphate, dihydrogen phosphate, $\frac{1}{2}$ $\text{C}_1\text{-C}_4$ alkanephosphonate, $\text{C}_1\text{-C}_4$ alkane- $\text{C}_1\text{-C}_{12}$ alkylphosphonate, di- $\text{C}_1\text{-C}_4$ alkylphosphinate, tetrafluoroborate, hexafluorophosphate, hexafluoroantimonate, acetate, trifluoroacetate, heptafluorobutyrate, $\frac{1}{2}$ oxalate, methanesulfonate, trifluoromethanesulfonate, benzenesulfonate, tosylate, p-chlorobenzenesulfonate, p-nitrobenzenesulfonate, phenolate, benzoate or a negatively charged metal complex.
- The person skilled in the art will readily recognise that it is also possible to use other anions with which he is familiar. It will be self-evident to him that $\frac{1}{x}$ of an inorganic, organic or organometallic anion having x negative charges, for example $\frac{1}{2} \cdot \text{SO}_4^{2-}$, is a multiply charged anion which neutralises several singly charged cations or a cation having x charges, as the case may be.

- Phenolates or carboxylates are, for example, of formula



- of the others hydrogen, R_{28} , or $\text{C}_6\text{-C}_{12}$ aryl, $\text{C}_4\text{-C}_{12}$ heteroaryl, $\text{C}_7\text{-C}_{12}$ aralkyl or $\text{C}_5\text{-C}_{12}$ heteroaralkyl each unsubstituted or substituted by one or more, where applicable identical or different, radicals R_{28} , for example anions of $\text{C}_1\text{-C}_{12}$ alkylated, especially tert- $\text{C}_4\text{-C}_8$ alkylated, phenols and benzoic acids, such as



Preference is given to compounds of formula (I), (II), (III) or (IV) wherein

A_1 and A_2 are each independently of the other N(R_{14}), O, S or Se and A_3 is

$C(C_1-C_5\text{alkyl})_2$, $C(C_4-C_5\text{alkylene})$, N(R_{14}), O, S, Se, $N=C(R_{18})$ or unsubstituted or

- 5 R_{19} -substituted $CH=CH$, especially wherein A_1 , A_2 and A_3 are each independently of the others O, S or N(R_{14}) and/or Q_1 and Q_2 are $C(R_{23})$ or N;

G_1 and G_2 are each independently of the other

or

especially at least one of G_1 and G_2 is

R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 and R_{19} are each independently of the others

- 10 hydrogen, R_{10} , or C_6-C_{12} aryl or C_7-C_{12} aralkyl each unsubstituted or substituted by one or more, where applicable identical or different, radicals R_{10} ;

R_9 , R_{14} and R_{18} are each independently of the others unsubstituted or R_{10} -substituted C_1-C_8 alkyl; or

R_9 is the position of X_1 in formula (I) or (III) or the position of X_2 in formula (IV);

- 15 R_{10} and R_{28} are each independently of the other halogen, nitro, cyano, $O-R_{25}$, formyl, $CH=C(CN)_2$, $CH=C(CN)CONH_2$, $CH=C(CN)CONHR_{25}$, $CH=C(CN)CONR_{25}R_{34}$, $CH=C(CN)COOR_{25}$, $CH=C(COOR_{25})COOR_{34}$, $CONH_2$, $CONHR_{25}$, $CONR_{25}R_{34}$, $SO_2C_1-C_{12}$ alkyl, SO_2NH_2 , SO_2NHR_{25} , $SO_2NR_{25}R_{34}$, $COOH$, $COOR_{25}$, $NHCOR_{25}$, $NR_{25}COR_{35}$, $NHCOOR_{25}$, $NR_{25}COOR_{35}$, ureido,

$P(=O)OR_{25}OR_{35}$, sulfo, or C_1 - C_{12} alkyl, C_1 - C_{12} alkylthio or C_1 - C_{12} alkoxy each unsubstituted or substituted by one or more, where applicable identical or different, radicals R_{24} ;

R_{23} is hydrogen, cyano, halogen, nitro, formyl, $N=N-R_{32}$, $C(R_{19})=CR_{26}R_{27}$,

- 5 $C(R_{19})=NR_{25}$, $COO-R_{30}$, carboxy, carbamoyl, $CONH-R_{30}$, $CONR_{30}R_{31}$, or C_1 - C_{12} alkyl unsubstituted or substituted by one or more halogen substituents;

R_{24} is halogen, hydroxy, $O-R_{30}$, amino, $NH-R_{30}$, $NR_{30}R_{31}$, $NR_{30}-CO-R_{29}$,

$NR_{30}COOR_{29}$, cyano, $COO-R_{30}$, carboxy, $CONH-R_{30}$, $CONR_{30}R_{31}$, sulfato, sulfo, or C_1 - C_{12} alkoxy unsubstituted or mono- or poly-substituted by halogen;

- 10 R_{25} , R_{34} and R_{35} are each independently of the others C_1 - C_{12} alkyl unsubstituted or substituted by one or more, where applicable identical or different, halogen, hydroxy or C_1 - C_{12} alkoxy radicals, or unsubstituted C_6 - C_{12} aryl or C_7 - C_{12} aralkyl; or

R_{25} and R_{34} together with the common nitrogen are morpholine, or piperidine N-substituted by C_1 - C_4 alkyl;

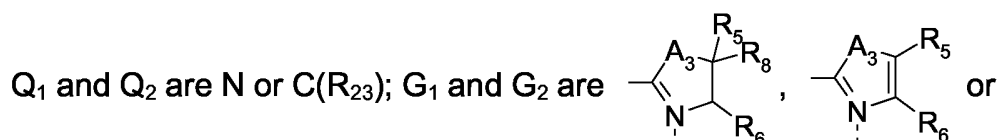
- 15 R_{29} , R_{30} and R_{31} are each independently of the others C_1 - C_{12} alkyl, C_2 - C_{12} alkenyl, C_6 - C_{12} aryl or C_7 - C_{12} aralkyl; or

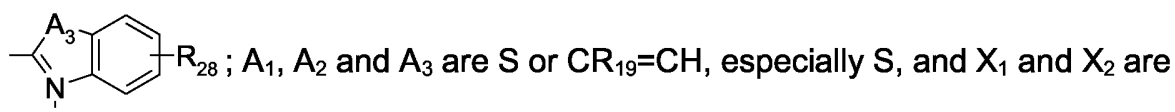
R_{30} and R_{31} together with the common nitrogen are morpholine, or piperidine N-substituted by C_1 - C_4 alkyl;

- 20 R_{36} is unsubstituted or substituted C_6 - C_{12} aryl or C_7 - C_{12} aralkyl, especially a metallocenyl radical; and/or

m is a number from 1 to 4, or a tautomer thereof.

Special preference is given to compounds of formula (I), (II), (III) or (IV), wherein





direct bonds or C₁-C₃alkylene bridges;

R₅ and R₈ are independently from each other hydrogen or R₂₈;

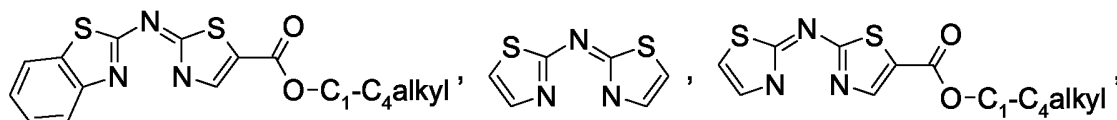
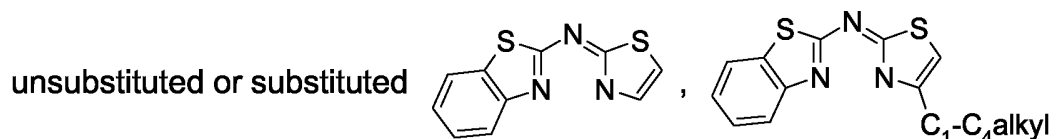
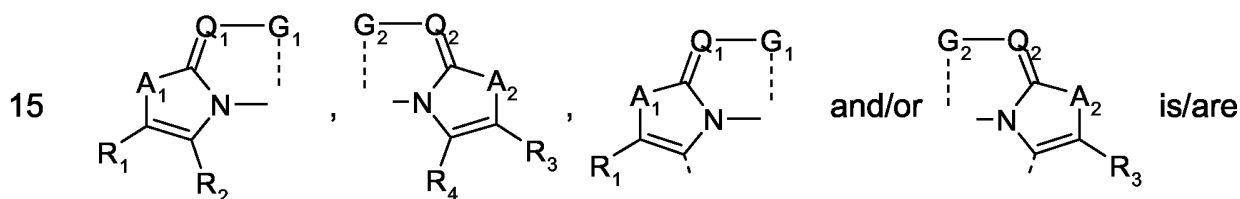
R₂, R₄ and R₆ are independently from each other hydrogen or unsubstituted or
5 substituted C₁-C₄alkyl, in particular unsubstituted or substituted methyl or ethyl;

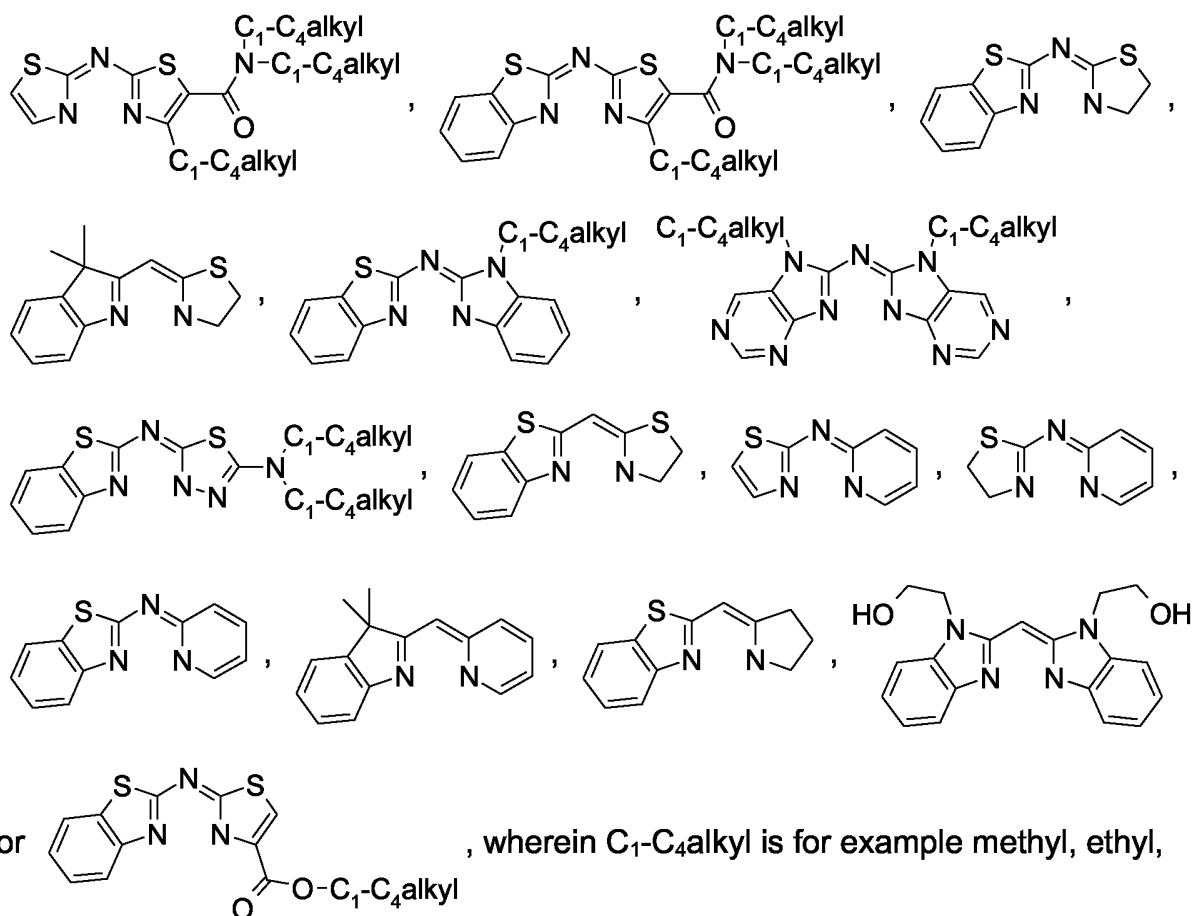
R₂₃ is hydrogen, cyano, COO-R₃₀ or C₁-C₁₂alkyl; and

R₂₈ is unsubstituted or substituted C₁-C₁₂alkyl, O-R₂₅ or an electron withdrawing
10 group, especially C₁-C₁₂alkyl either unsubstituted or substituted by halogen,
hydroxy or O-R₂₅, for example CH₂OH or CF₃, CH=C(CN)₂, COOR₂₅, COR₃₄, CHO,
ureido, CONR₃₀R₃₁, SO₂R₃₀, P(=O)OR₂₅OR₃₅, halogen, nitro or cyano.

Those preferred meanings apply both individually and in any combination. The
compounds of formula (I), (II), (III) or (IV) generally exhibit more advantageous
properties, the more preferred individual features they have.

Also preferred are compounds of formula (I), (II), (III) or (IV) wherein





isopropyl, 2-butyl, isobutyl or tert.-butyl, preferably methyl.

The recording layer advantageously comprises a compound of formula (I), (II), (III) or (IV) or a mixture of such compounds as main component, for example at least 30 % by weight, preferably at least 60 % by weight, especially at least 80 % by

10 weight. Further customary constituents are possible, for example other chromophores (for example those disclosed in WO 01/75873, or others having an absorption maximum at from 300 to 1000 nm), stabilisers, ¹O₂-, triplet- or luminescence-quenchers, melting-point reducers, decomposition accelerators or any other additives that have already been described in optical recording media.

15 Preferably, stabilisers or fluorescence-quenchers are added if desired.

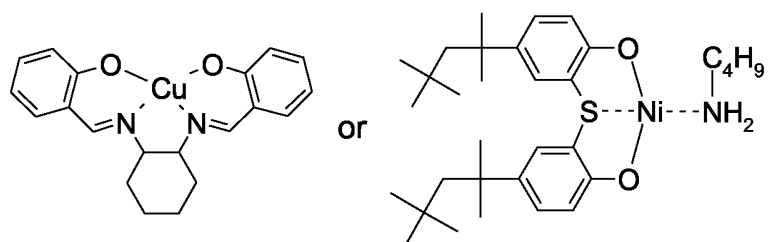
When the recording layer comprises further chromophores, the amount of such chromophores should preferably be small, so that the absorption thereof at the wavelength of the inversion point of the longest-wavelength flank of the absorption

of the entire solid layer is a fraction of the absorption of the pure compound of formula (I), (II), (III) or (IV) in the entire solid layer at the same wavelength, advantageously at most $\frac{1}{3}$, preferably at most $\frac{1}{5}$, especially at most $\frac{1}{10}$. The absorption maximum is preferably higher than 425 nm, especially higher than 500 nm.

Stabilisers, $^1\text{O}_2$ -, 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-dimethylamino-dithiobenzil)nickel [CAS N° 38465-55-3], [®]Irgalan Bordeaux EL, [®]Cibafast N or similar compounds, hindered phenols and derivatives thereof (optionally also as counter-ions X), such as [®]Cibafast AO, o-hydroxyphenyl-triazoles or -triazines or other UV absorbers, such as [®]Cibafast W or [®]Cibafast P or hindered amines (TEMPO or HALS, also as nitroxides or NOR-HALS, optionally also as counter-ions X), and also as cations diimmonium, Paraquat[™] 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-phenyleneamine-ammonium hexafluorophosphate, hexafluoroantimonate or perchlorate. The latter are available from Organica (Wolfen / DE); [®]Kayasorb brands are available from Nippon Kayaku Co. Ltd., and [®]Irgalan and [®]Cibafast brands are available from Ciba Spezialitäten-chemie AG.

Many such structures are known, some of them also in connection with optical recording media, for example from US-5 219 707, JP-A-06/199045, JP-A-07/76169, JP-A-07/262604 or JP-A-2000/272241. They may be, for example, salts of the metal complex anions disclosed above with any desired cations, for example the cations disclosed above, or metal complexes, illustrated, for example, by a

compound of formula



The person skilled in the art will know from other optical information media, or will easily identify, which additives in which concentration are particularly well 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
5 medium of formula (I), (II), (III) or (IV).

The optical recording materials according to the invention exhibit excellent spectral properties of the solid amorphous recording layer. The refractive index is extraordinarily high, in some cases even above 2.5. By virtue of an aggregation tendency in the solid that is surprisingly low for such compounds, the absorption
10 band is narrow and intense, the absorption band being especially steep on the long-wavelength side. Crystallites are unexpectedly and very advantageously not formed or are formed only to a negligible extent. The reflectivity of the layers in the range of the writing and reading wavelength is very high in the unwritten state.

The thermal stability is also surprisingly improved, as compared with previously
15 known compounds. Thus, the danger of data being accidentally altered by heat or multiple reading with a low intensity laser is minimized, while the decomposition behaviour remains as desired sharp when using a laser of higher (writing) energy, enabling marks to be recorded surprisingly efficiently.

By virtue of those excellent layer properties it is possible to obtain a rapid optical
20 recording having high sensitivity, high reproducibility and geometrically very precise mark boundaries, the refractive index and the reflectivity changing substantially, which gives a high degree of contrast. The differences in the mark lengths and the interval distances ("jitter") are very small, which enables a high storage density to be obtained using a relatively thin recording channel with a narrow track spacing
25 ("pitch"). In addition, the recorded data are played back with an astonishingly low error rate, so that error correction requires only a small amount of storage space.

By virtue of the fully unexpected excellent solubility, including in apolar solvents, solutions can be used even in high concentrations without troublesome precipitation, for example during storage, so that problems during spin-coating are

largely eliminated.

Recording and playback can take place at the same wavelength, therefore advantageously requiring a simple optical system with a single laser source of advantageously from 350 to 500 nm, preferably from 370 to 450 nm. Especially
5 preferred is the UV range from 370 to 390 nm, especially approximately 380 nm, or especially at the edge of the visible range of from 390 to 430 nm, more especially approximately 405 ± 5 nm. In the field of compact, blue or violet laser diodes (such as Nichia GaN 405 nm) with an optical system of high numerical aperture, the marks can be so small and the tracks so narrow that up to about 20 to 25 Gb per
10 recording layer is achievable on a 120 mm disc. At 380 nm it is possible to use indium-doped UV-VCSELs (Vertical-Cavity Surface-Emitting Laser), which laser source already exists as a prototype [Jung Han *et al.*, see MRS Internet J. Nitride Semicond. Res. 5S1, W6.2 (2000)].

The invention therefore relates also to a method of recording or playing back data,
15 wherein the data on an optical recording medium according to the invention are recorded or played back at a wavelength of from 350 to 500 nm.

The recording medium is based on the structure of known recording media and is, for example, analogous to those mentioned above. It may be composed, for example, of a transparent substrate, a recording layer comprising at least one of
20 the compounds of formula (I), (II), (III) or (IV), a reflector layer and a covering layer, the writing and readout being effected through the substrate.

Suitable substrates are, for example, glass, minerals, ceramics and thermosetting and thermoplastic plastics. Preferred supports are glass and homo- or co-polymeric plastics. Suitable plastics are, for example, thermoplastic polycarbonates,
25 polyamides, polyesters, polyacrylates and polymethacrylates, polyurethanes, polyolefins, polyvinyl chloride, polyvinylidene fluoride, polyimides, thermosetting polyesters and epoxy resins. Special preference is given to polycarbonate substrates which can be produced, for example, by injection-moulding. The substrate can be in pure form or may comprise customary additives, for example

UV absorbers or dyes, as proposed e.g. in JP-A-04/167239 as light stabilisation for the recording layer. In the latter case it may be that in the range of the writing wavelength (emission wavelength of the laser) the dye added to the support substrate has no or at most only very low absorption, preferably up to a maximum of about 20% of the laser light focussed onto the recording layer.

The substrate is advantageously transparent over at least a portion of the range from 350 to 500 nm, so that it is permeable to, for example, at least 80% of the incident light of the writing or readout wavelength. The substrate is advantageously from 10 μm to 2 mm thick, preferably from 100 to 1200 μm thick, especially from 600 to 1100 μm thick, with a preferably spiral guide groove (track) on the coating side, a groove depth of from 10 to 200 nm, preferably from 80 to 150 nm, a groove width of from 100 to 400 nm, preferably from 150 to 250 nm, and a spacing between two turns of from 200 to 600 nm, preferably from 350 to 450 nm. Grooves of different cross-sectional shape are known, for example rectangular, trapezoidal or V-shaped. Analogously to the known CD-R and DVD-R media, the guide groove may additionally undergo a small periodic or quasi-periodic lateral deflection (wobble), so that synchronisation of the speed of rotation and the absolute positioning of the reading head (pick-up) are made possible. Instead of, or in addition to, the deflection, the same function can be performed by markings between adjacent grooves (pre-pits).

The recording medium is applied, for example, by application of a solution by spin-coating, the objective being to produce a layer that is as amorphous as possible, the thickness of which layer is advantageously from 0 to 40 nm, preferably from 1 to 20 nm, especially from 2 to 10 nm, on the surface ("land") and, depending upon the geometry of the groove, advantageously from 20 to 150 nm, preferably from 50 to 120 nm, especially from 60 to 100 nm, in the groove.

Reflecting materials suitable for the reflector layer include especially metals, which provide good reflection of the laser radiation used for recording and playback, for example the metals of Main Groups 13–15 and of the Sub-Groups 3–12 of the

Periodic 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 and the lanthanide metals Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu and alloys thereof are especially suitable. On account of its high reflectivity and ease of production special preference is given to a reflective layer of aluminium, silver, gold or an alloy thereof (for example a white gold alloy), especially aluminium on economic and ecological grounds. The reflector layer is advantageously from 5 to 200 nm thick, preferably from 10 to 100 nm thick, especially from 40 to 60 nm thick, but reflector layers of greater thickness, for example 1 mm thick or even more, are also possible.

Materials suitable for the covering layer include chiefly plastics, which are applied in a thin layer to the reflector layer either directly or with the aid of adhesion promoters. It is advantageous to select mechanically and thermally stable plastics having good surface properties, which can be modified further, for example written on. The plastics may be thermosetting plastics and thermoplastic plastics. Directly applied covering layers are preferably radiation-cured (e.g. using UV radiation) coatings, 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-C₄alkyl groups in at least two ortho-positions of the amino groups, and oligomers with dialkylmaleinimidyl groups, e.g. dimethylmaleinimidyl groups. For covering layers that are applied using adhesion promoters it is preferable to use the same materials as those used for the substrate layer, especially polycarbonates. The adhesion promoters used are preferably likewise radiation-curable monomers and oligomers. Instead of the covering layer applied using an adhesion promoter there may also be used a second substrate comprising a recording and reflector layer, so that the recording medium is playable on both sides. Preference is given to a symmetrical structure, the two parts being joined together at the reflector side by an adhesion promoter directly or by way of an intermediate layer.

In such a structure, the optical properties of the covering layer, or the covering materials, are essentially unimportant *per se* provided that, where applicable, curing thereof e.g. by UV radiation is achieved. The function of the covering layer is to ensure the mechanical strength of the recording medium as a whole and, if
5 necessary, the mechanical strength of thin reflector layers. If the recording medium is sufficiently robust, for example when a thick reflector layer is present, it is even possible to dispense with the covering layer altogether. The thickness of the covering layer depends upon the thickness of the recording medium as a whole, which should preferably be a maximum of about 2 mm thick. The covering layer is
10 preferably from 10 μm to 1 mm thick.

The recording media according to the invention may also have additional layers, for example interference layers or barrier layers. It is also possible to construct recording media having a plurality of (for example from two to ten) recording layers. The structure and the use of such materials are known to the person skilled in the art.
15 Where present, interference layers are preferably 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-A-0 353 393 of TiO_2 , Si_3N_4 , ZnS or silicone resins.

The recording media according to the invention can be produced by processes
20 known *per se*, it being possible for various methods of coating to be employed depending upon the materials used and their function.

Suitable coating methods are, for example, immersion, pouring, brush-coating, blade-application and spin-coating, as well as vapour-deposition methods carried out under a high vacuum. When, for example, pouring methods are used, solutions
25 in organic solvents are generally employed. 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-0 401 791.

The recording layer is applied preferably by the application of a dye solution by spin-coating, solvents that have proved satisfactory being especially alcohols, e.g.

2-methoxyethanol, isopropanol or n-butanol, hydroxyketones, for example diacetone alcohol or 3-hydroxy-3-methyl-2-butanone, hydroxy esters, for example lactic acid methyl ester or isobutyric acid methyl ester, or preferably fluorinated alcohols, for example 2,2,2-trifluoroethanol or 2,2,3,3-tetrafluoro-1-propanol, and
5 mixtures thereof. Further suitable solvents are well-known in the art and disclosed, for example, in EP-A-0 483 387.

The application of the metallic reflector layer is preferably effected by sputtering or by vapour-deposition *in vacuo*. Such techniques are known and are described in specialist literature (e.g. J.L. Vossen and W. Kern, "Thin Film Processes", Academic Press, 1978). The operation can advantageously be carried out continuously
10 and achieves good reflectivity and a high degree of adhesiveness of the metallic reflector layer.

Recording is carried out in accordance with known methods by writing pits (marks) of fixed or variable length by means of a modulated, focussed laser beam guided at
15 a constant or variable speed over the surface of the recording layer. Readout of information is carried out according to methods known *per se* by registering the change in reflection using laser radiation, for example as described in "CD-Player und R-DAT Recorder" (Claus Biaesch-Wiepke, Vogel Buchverlag, Würzburg 1992). The person skilled in the art will be familiar with the requirements.

20 The information-containing medium according to the invention is especially an optical information material of the WORM type. It can be used, for example, analogously to CD-R (compact disc - recordable) or DVD-R (digital video disc - recordable) in computers, and also as storage material for identification and security cards or for the production of diffractive optical elements, for example
25 holograms.

Alternatively, however, there are also recording media which differ substantially from CD-R and DVD-R and in which recording and playback take place not through the substrate but through the covering layer ("in-groove recording"). Accordingly, the respective roles of the covering layer and the substrate, especially the

geometry and the optical properties, are reversed in comparison with the structure described above. Analogous concepts are described a number of times in Proceedings SPIE-Int. Soc. Opt. Eng. 1999, 3864 for digital video recordings in conjunction with a blue GaN laser diode. For such recording media, which are especially suitable for a high storage density and have correspondingly small marks ("pits"), precise focussing is important, so that the manufacturing process, while essentially analogous, is considerably more awkward.

The compounds of formula (I), (II), (III) or (IV) according to the invention, however, also meet the increased demands of an inverse layer structure surprisingly well.

- 10 Preference is therefore given to an inverse layer structure having the layer sequence substrate, reflector layer, recording layer and covering layer. The recording layer is therefore located between the reflector layer and the covering layer. A thin covering layer approximately from 50 to 400 μm in thickness is especially advantageous (typically 100 μm at a numerical aperture of 0.85).
- 15 The recording and reflector layers in an inverse layer structure have in principle the same functions as indicated above. As with the groove geometry, they therefore usually have dimensions within the ranges indicated above.

- The inverse layer structure requires particularly high standards, which the compounds used according to the invention fulfil astonishingly well, for example
- 20 when the recording layer is applied to the metallic reflector layer and especially when a covering layer is applied to the recording layer, the covering layer being required to provide the recording layer with adequate protection against rubbing, photo-oxidation, fingerprints, moisture and other environmental effects and advantageously having a thickness in the range of from 0.01 to 0.5 mm, preferably
- 25 in the range of from 0.05 to 0.2 mm, especially in the range of from 0.08 to 0.13 mm.

The covering layer preferably consists of a material that exhibits a transmission of 80% or above at the writing or readout wavelength of the laser. Suitable materials

for the covering layer include, for example, those materials mentioned above, but especially polycarbonate (such as Pure Ace[®] or Panlite[®], Teijin Ltd), cellulose triacetate (such as Fujitac[®], Fuji Photo Film) or polyethylene terephthalate (such as Lumirror[®], Toray Industry), special preference being given to polycarbonate.

- 5 Especially in the case of directly applied covering layers, radiation-cured coatings, such as those already described above, are advantageous, for example SD 347[™] (Dainippon Ink).

The covering layer can be applied directly to the solid recording layer by means of a suitable adhesion promoter. In another embodiment, there is applied to the solid
10 recording layer an additional, thin separating layer of a metallic, crosslinked organometallic or preferably dielectric inorganic material, for example in a thickness of from 0.001 to 10 μm , preferably from 0.005 to 1 μm , especially from 0.01 to 0.1 μm , for example from 0.05 to 0.08 μm in the case of dielectric separating layers and from 0.01 to 0.03 μm in the case of metallic separating layers. Separating
15 layers and corresponding methods are disclosed in WO 02/082 438, to which reference is expressly made here. If desired, such coatings can be applied, for example, in the same thickness also between the support material and the metallic reflector layer or between the metallic reflector layer and the optical recording layer. This may be advantageous in certain cases, for example when a silver reflector is
20 used in combination with sulfur-containing additives in the recording layer.

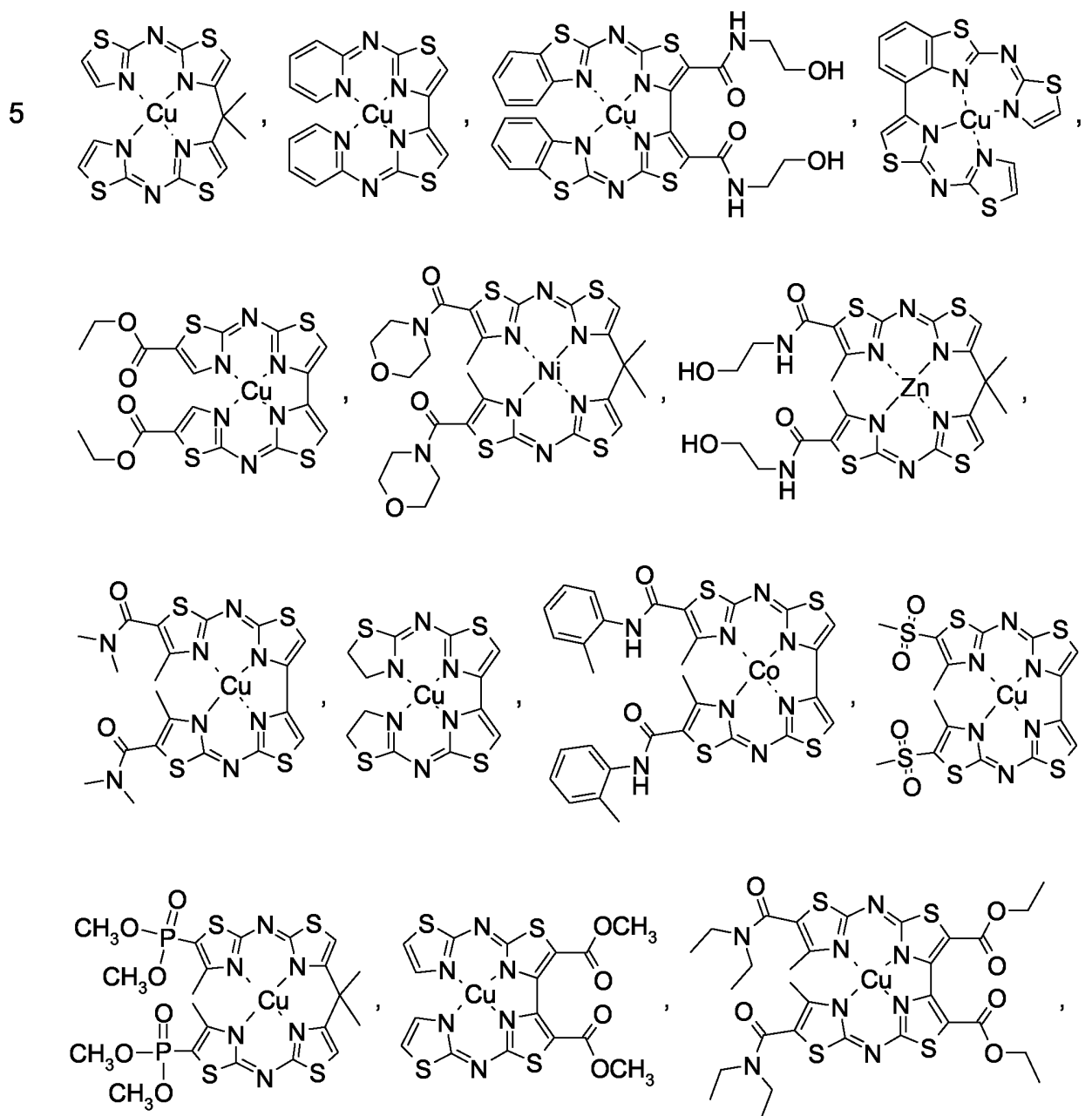
In a special variant, there is applied to the solid recording layer an additional, thin separating layer of a metallic, crosslinked organometallic or dielectric inorganic material, for example in a thickness of from 0.001 to 10 μm , preferably from 0.005 to 1 μm , especially from 0.01 to 0.1 μm . On account of their high reflectivity,
25 metallic separating layers should advantageously be a maximum of 0.03 μm thick. Separating layers and corresponding methods are disclosed in WO 02/082 438, to which reference is expressly made here.

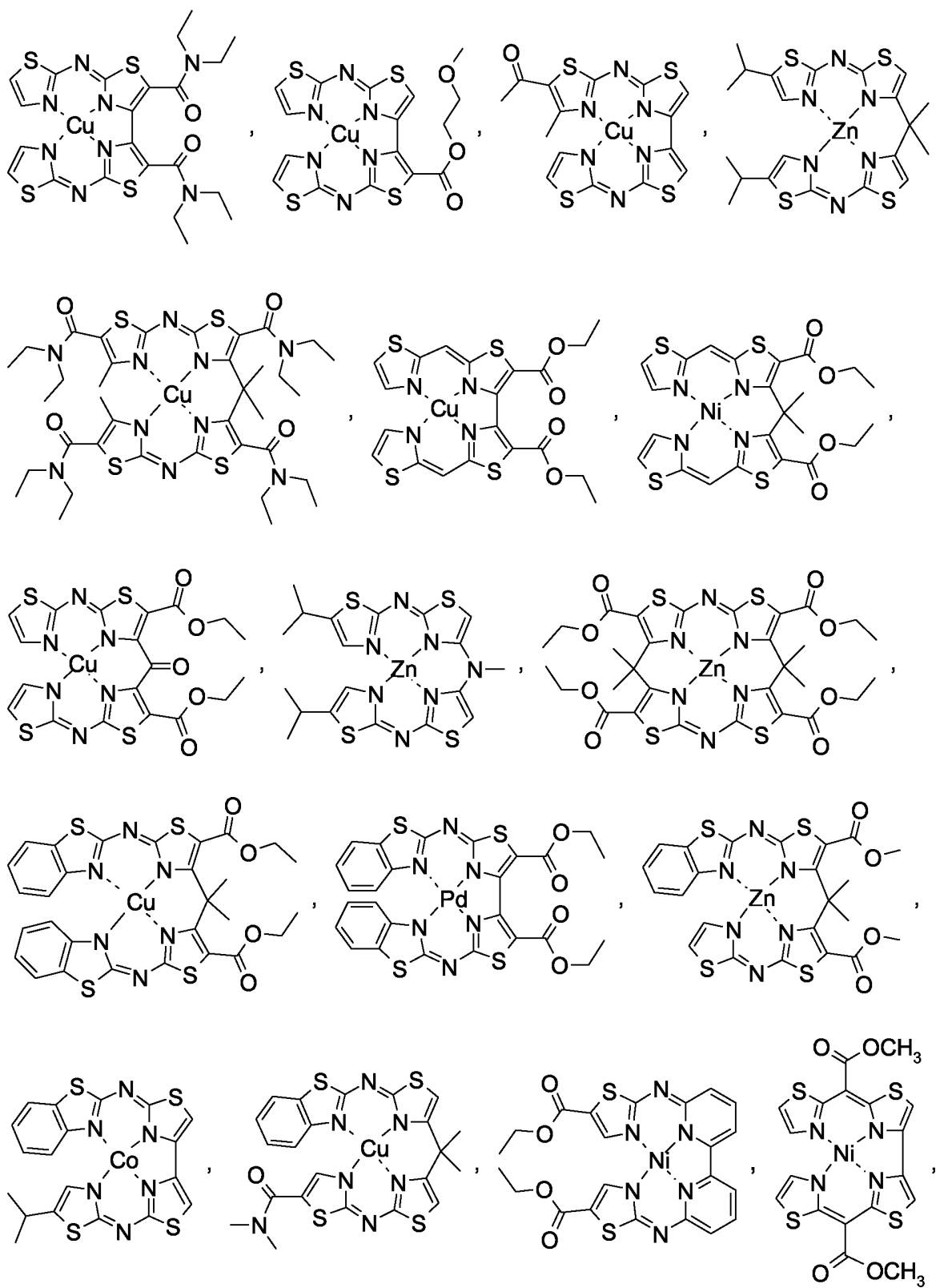
The compounds of formula (I), (II), (III) or (IV) used according to the invention are new, but easy to be made from known compounds by known methods, such as in

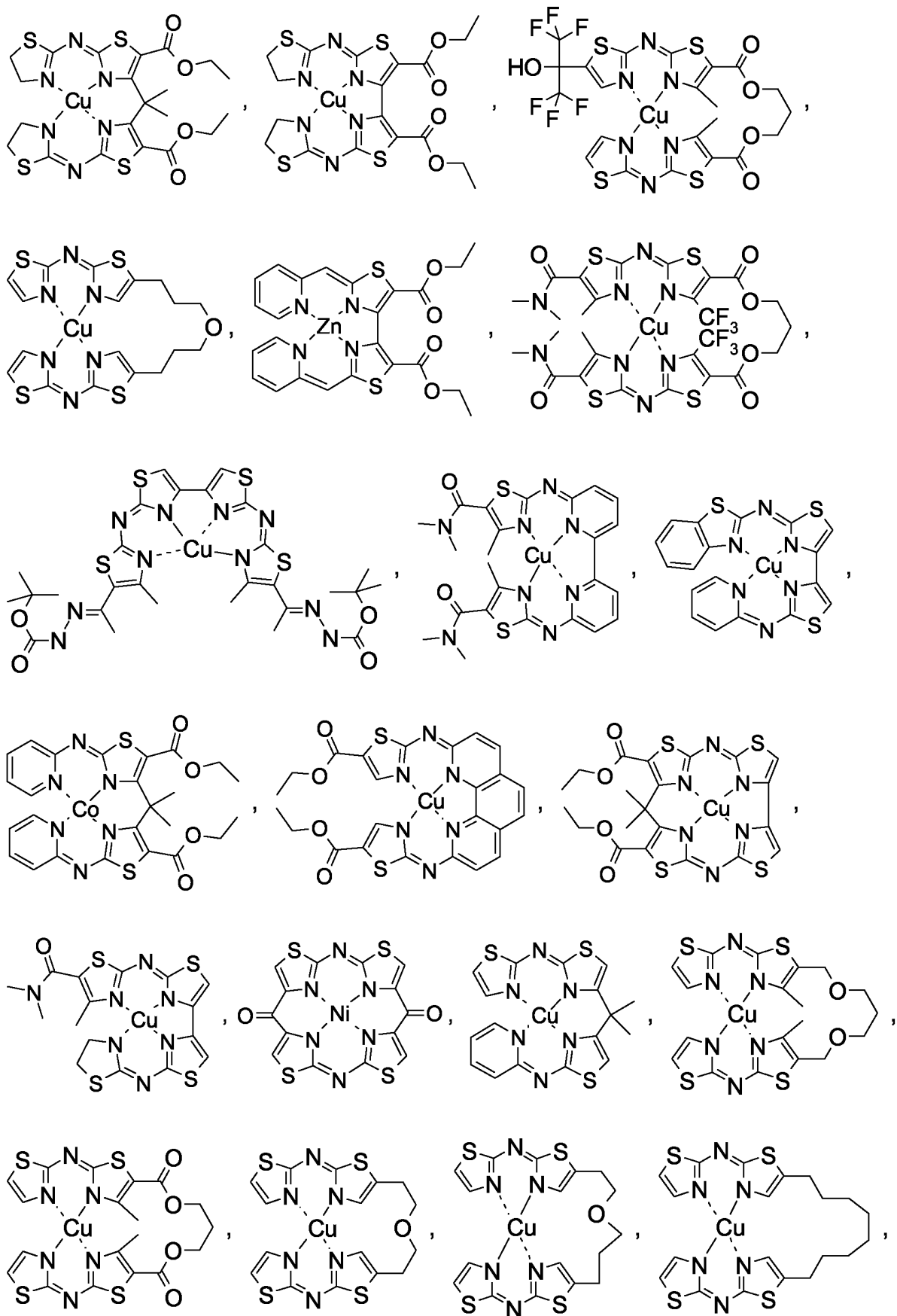
analogy to J. Org. Chem. 67/16, 5753-5772 [2002].

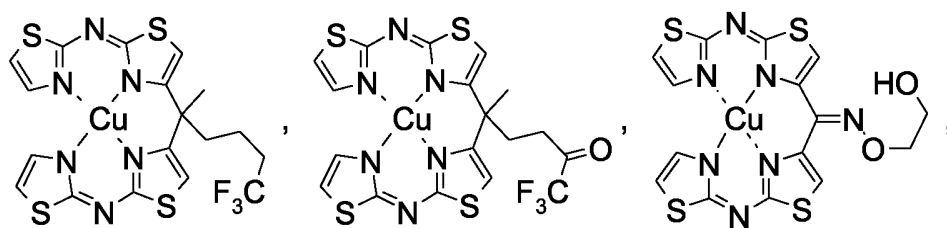
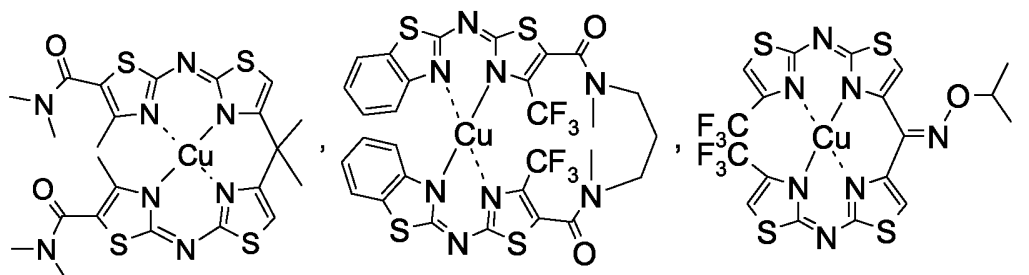
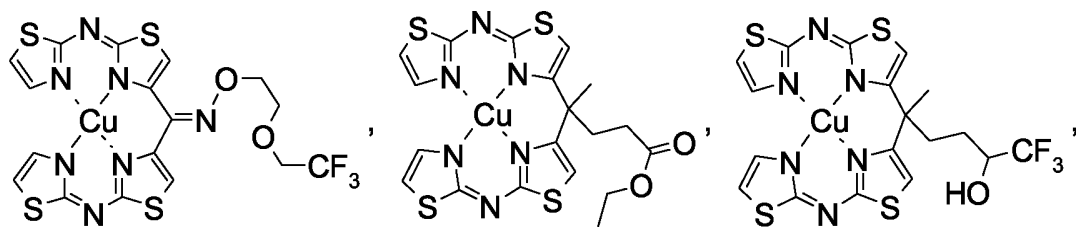
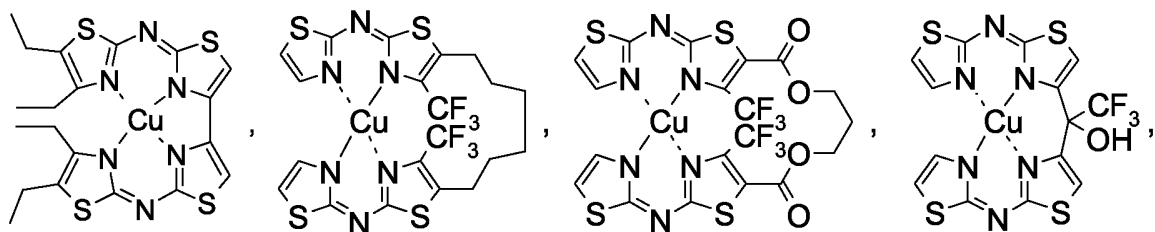
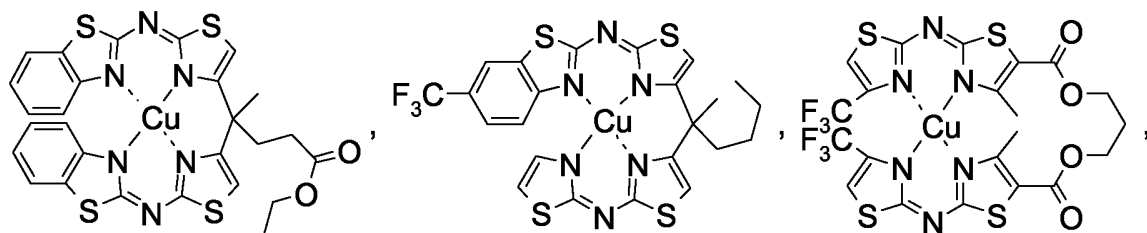
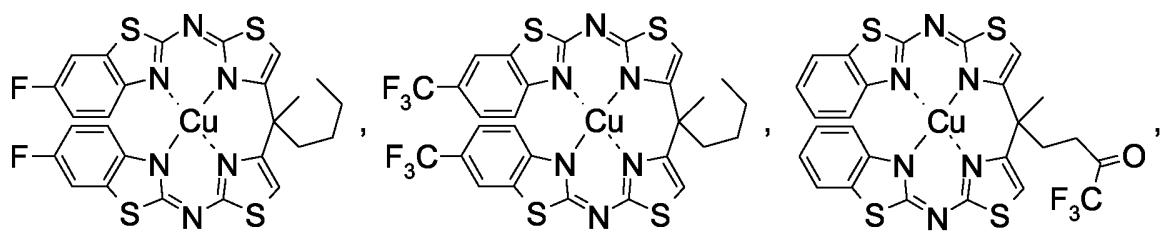
The invention therefore relates also to a compound of formula (I), (II), (III) or (IV).

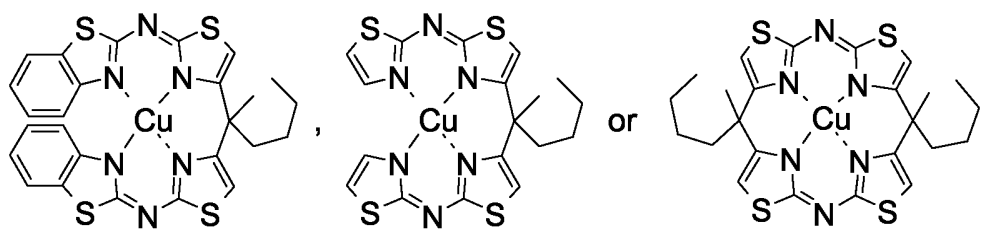
Examples of suitable compounds of formula (I), (II), (III) or (IV), to which the invention is however in no way restricted, are:







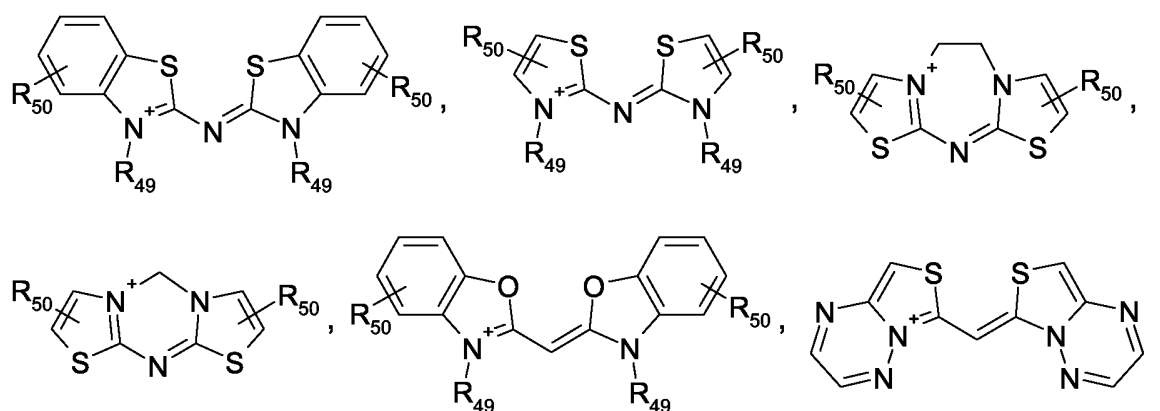




Instead of pure compounds it is also possible to use mixtures thereof.

In addition to comprising one or more compounds of formula (I), (II), (III) or (IV) and optionally customary additives, the optical recording media according to the invention may also comprise other chromophores, preferably metal-free chromophores. Other chromophores may, if desired, be added in an amount of from 1 to 200 % by weight, based on the total of the compounds of formula (I), (II), (III) or (IV). The amount of other chromophores is preferably from 5 to 100 % by weight, especially from 10 to 50 % by weight, based on the total of the compounds of formula (I), (II), (III) or (IV). Chromophores can be dyes or UV absorbers, preferably having an absorption maximum of from 350 to 400 nm or at from 600 to 700 nm, for example around 380 or 630 nm.

Especially preferred additional metal-free chromophores are cyanines, azacyanines, merocyanines and oxonols and also rhodamines, for example those disclosed in WO 04/006 878, WO 02/082 438 or EP-A-1 083 555, and also

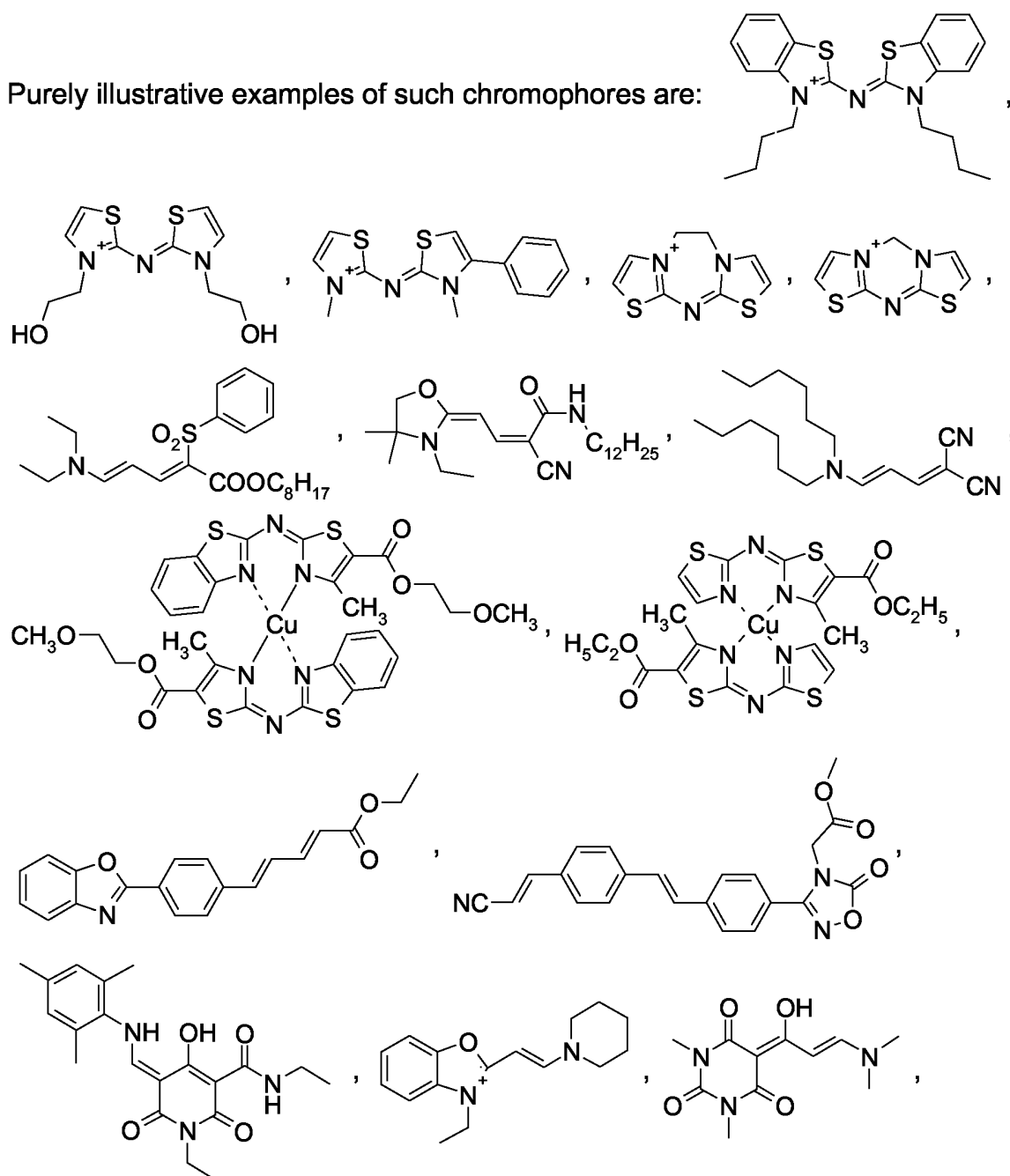


wherein R_{49} is C_1 - C_{24} alkyl or C_2 - C_{24} alkenyl, each of which can be unsubstituted or substituted, and R_{50} is any substituent. R_{49} may be, for example, methyl, ethyl, vinyl, allyl, isopropyl, n-butyl, 2-isopropoxy-ethyl, n-pentyl, 3-methyl-butyl,

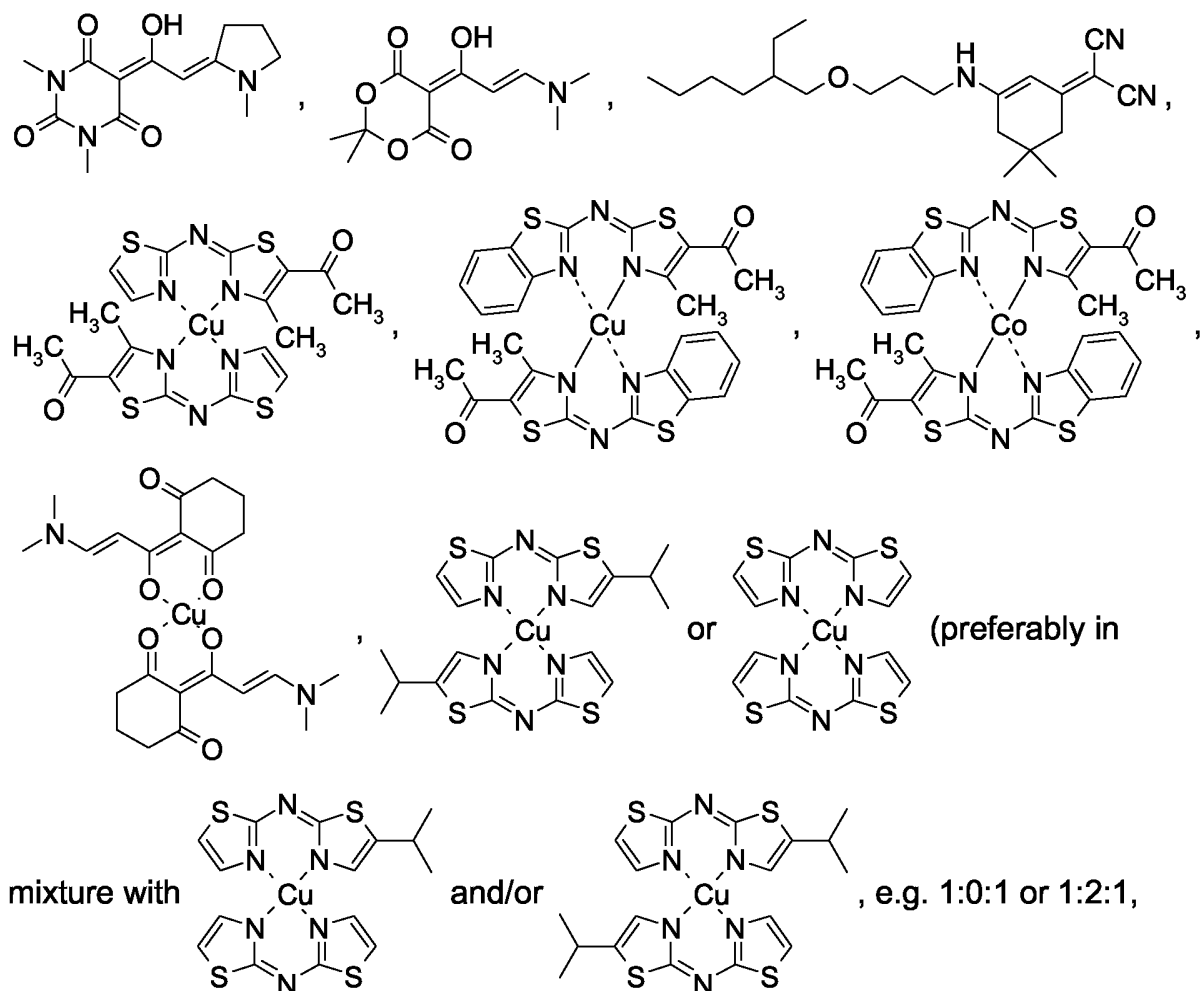
3,3-dimethyl-butyl, 2-ethyl-hexyl, 2-cyano-ethyl, furan-2-yl-methyl or 2-hydroxy-methyl; R_{50} is, for example, C_6 - C_{10} aryl, C_1 - C_{24} alkyl or C_2 - C_{24} alkenyl.

The instant compounds may also advantageously be used in mixtures with the compounds disclosed in WO 04/079 732, especially those of formula (II), (III), (IV) or (V) of WO 04/079 732, as well as those disclosed in WO 05/012 228.

Purely illustrative examples of such chromophores are:



- 30 -



- 5 what significantly improves the solubility and ensures an amorphous solid state, even enabling its use without addition of any instant compound though with poorer performance).

10 The instant compounds enable high quality recordings with high sensitivity and especially high modulation, with good read and light stability. It is easy to force either planarity or out of plane distortion through variations of the length of the bridges X_1 and/or X_2 and of the further substituents, thus tuning the hue and lowering the tendency to crystallisation.

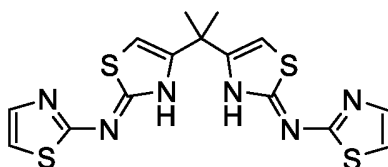
The following examples illustrate the invention but do not limit the scope thereof (unless otherwise indicated, "%" always refers to % by weight):

- 15 Example 1: a) 12.72 g Bromine is added in small portions to a solution of 5.12 g 3,3-dimethyl-2,4-pentanedione in 30 ml of acetic acid over a period of 30 minutes while maintaining the temperature at $\sim 10^\circ\text{C}$ by external cooling. After stirring for

6 hours, acetic acid is removed from the reaction mixture by distillation. 20 ml of methyl tert.-butylether are added to the resulting brown liquid and the solution is dried over K_2CO_3 . The solvent is evaporated, and the residue is chromatographed on silica gel with n-hexane/ethyl acetate (4:1) as eluent. 1.88 g 1,5-dibromo-3,3-dimethyl-2,4-pentanedione are obtained as a brown liquid.

1H -NMR (δ , $CDCl_3$): 4.05 (s, 4H); 1.36 (s, 6H).

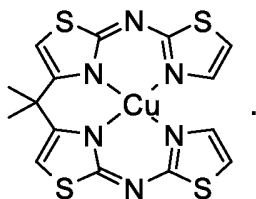
b) A solution of 684 mg 1,5-dibromo-3,3-dimethyl-2,4-pentanedione in 5 ml of ethanol is added under reflux to a solution of 1.274 g N-(2-thiazolyl)thiourea in 15 ml of ethanol and the mixture is refluxed for 3 h. After cooling to $0^\circ C$, the reaction mixture is neutralized with 10% aqueous sodium hydroxide. The precipitate (602 mg) is filtrated, and then the organic layer is extracted with ethyl acetate and dried over anhydrous sodium sulfate. The solvent is evaporated, and the residue is chromatographed on silica gel with n-hexane/ethyl acetate (2:1) as eluent. Further 148 mg compound of formula



are obtained as a pale gray solid (totally 750 mg).

1H -NMR (δ , $DMSO-d_6$): 7.29 (d, 2H); 6.95 (d, 2H); 6.58 (s, 2H); 1.64 (s, 6H); 12.01 (broad, 2H).

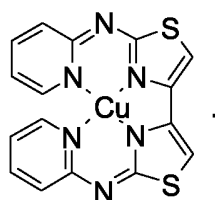
c) A solution of 98 mg copper acetate in 10 l of ethanol is added dropwise under reflux to a solution of 203 mg of this pale gray solid in 10 ml of tetrahydrofuran, and the mixture is refluxed for 2 h. After cooling to about $23^\circ C$, a dark brown solid precipitates in the course of the removal of the solvent by vacuum evaporation, which solid is collected by filtration (82 mg). The filtrate is condensed and the residue is chromatographed on silica gel with dichloromethane/acetone (20:1) as eluent to give further 70 mg of the metal complex, leading to totally 152 mg of dark brown powder of the formula:



Example 2: a) 1.0 g N-(2-pyridyl)thiourea is dissolved in 10 ml of hot ethanol, and then 0.80 g 1,4-dibromo-2,3-butanedione is added. The mixture is heated to reflux. After stirring for 1h, a saturated aqueous solution of sodium acetate is added to the reaction mixture. The resulting white solid is collected by filtration and washed with water and methanol. After drying, 0.80 g of pink solid is obtained.

$^1\text{H-NMR}$ (δ , DMSO-d_6): 11.41 (s, 2H), 8.31 (dd, 2H), 7.71 (ddd, 2H), 7.15 (s, 2H), 7.10 (d, 2H), 6.93 (ddd, 2H).

b) A solution of 85 mg $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in 7 ml hot ethanol is added dropwise to a solution of 150 mg of this pink solid in a mixture of 20 ml of tetrahydrofurane and 20 ml of ethanol. After completion of addition, the mixture is stirred under reflux for 1.5 h. Condensation of the mixture and subsequent washing with ethanol leads to 0.18 g of a green solid of formula:



Example 3: 0.31 mg of the product according to example 1 are dissolved in 50 ml of dichloromethane. The spectrum of the dye solution is measured with a spectrophotometer (U-3300™, Hitachi). The maximal absorption (λ_{max}) is at the wavelength of 346 nm.

Example 4: 12 mg of the product according to example 1 are dissolved in 1.00 ml of 2,2,3,3-tetrafluoro-1-propanol. The dye solution is then spin-coated at 800 rev/min to a 1.2 mm thick, flat polycarbonate plate (diameter 120 mm); the rotational speed is then increased to 2000 rev/min, so that the excess solution is spun off and a

uniform solid layer is formed. Using an optical measuring system (ETA-RT™, STEAG ETA-Optik), the layer thickness and the complex refractive index are determined. At 405 nm, the dye layer has a layer thickness of 45 nm, a refractive index n of 1.909 and an extinction coefficient k of 0.011. Marks of lower reflectivity
5 are written into the recording layer using a pulsed dye laser (15 ns pulse length) at a wavelength of 405 nm and an energy density of 0.8 kJ/m².

Example 5: 0.37 mg of the product according to example 2 are dissolved in 50 ml of dichloromethane. The spectrum of the dye solution is measured with a spectrophotometer (U-3300, Hitachi). The maximal absorption ($\lambda_{\max}$) is at the
10 wavelength of 325 nm.

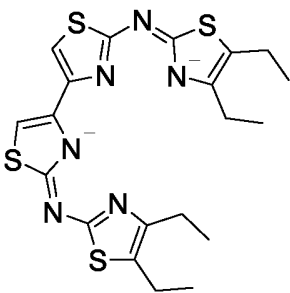
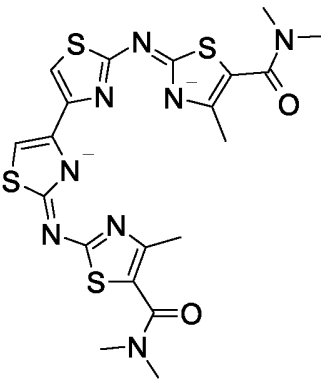
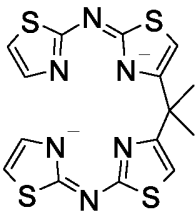
Example 6: 12 mg of the compound according to example 2 are dissolved in 1.00 ml of 2,2,3,3-tetrafluoro-1-propanol. The dye solution is then spin-coated at 800 rev/min to a 1.2 mm thick, flat polycarbonate plate (diameter 120 mm); the rotational speed is then increased to 2000 rev/min, so that the excess solution is
15 spun off and a uniform solid layer is formed. Using an optical measuring system (ETA-RT™, STEAG ETA-Optik), the layer thickness and the complex refractive index were determined. At 405 nm, the dye layer has a layer thickness of 41 nm, a refractive index n of 1.986 and an extinction coefficient k of 0.101. Marks of lower reflectivity are written into the recording layer using a pulsed dye laser (15 ns pulse
20 length) at a wavelength of 405 nm and an energy density of 0.8 kJ/m².

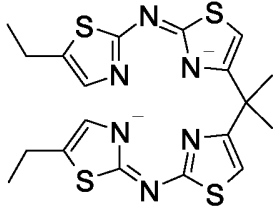
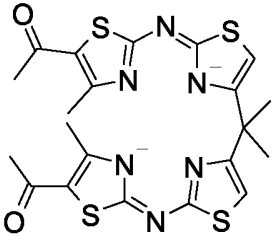
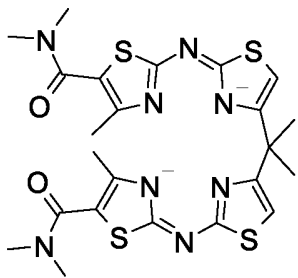
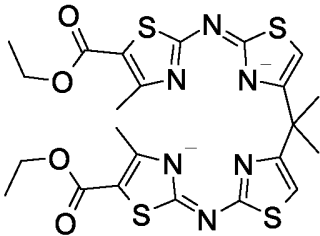
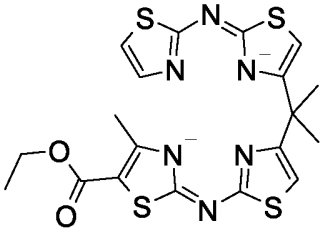
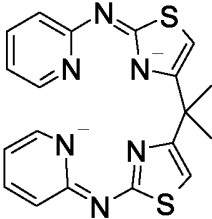
Example 7: In a vacuum-coating apparatus (Twister™, Balzers Unaxis), a 30 nm thick silver reflector layer is applied onto a 1.1 mm thick grooved polycarbonate disc (diameter 120 mm, groove pitch 400 nm, groove depth 80 nm, groove width 170 nm). 0.12 g of the product of example 1 are dissolved in 10 ml of 2,2,3,3-
25 tetrafluoro-1-propanol and filtered through a 0.2 µm Teflon™ filter. The dye solution is applied onto the reflector layer by the spin-coating method in order to form a uniform solid layer after drying in an oven for 15 min at 70°C. A 40 nm thick dielectric layer (SiON) is successively applied by RF-sputtering in a vacuum-coating apparatus (Sprinter™, Balzers Unaxis). A polycarbonate film covered on

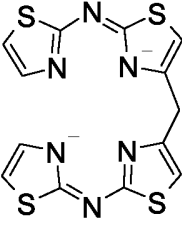
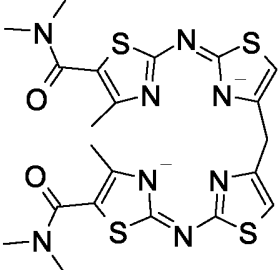
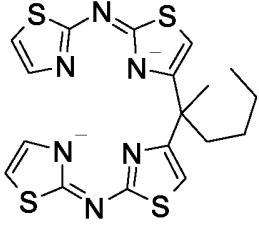
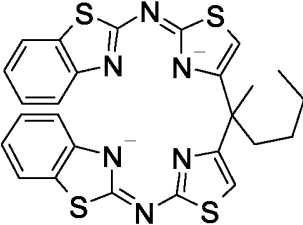
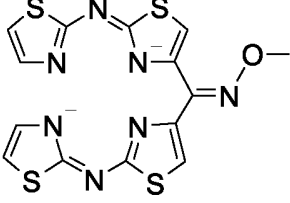
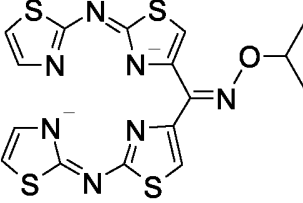
one side with a pressure-sensitive adhesive (total thickness 100 μm , Lintec Corp., Japan) is finally bonded onto the dielectric layer. Using a commercial disc testing equipment (ODU-1000TM for Blu-ray[®] Disc, Pulstec, Japan) based on a 407 nm laser diode and an objective lens numerical aperture of 0.85, marks are recorded on the disc with a linear speed of 5.28 m/s and a laser power of 7 mW. The recorded area is then read back with 0.35 mW laser power.

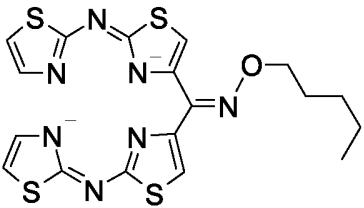
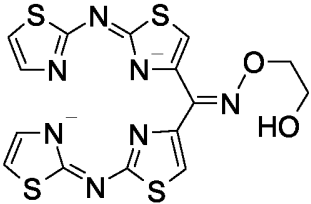
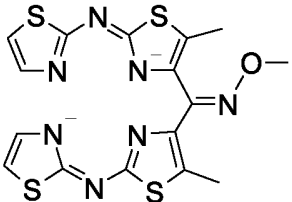
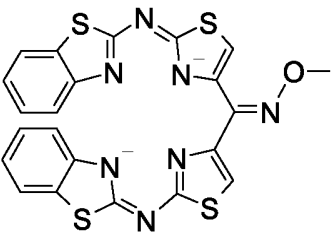
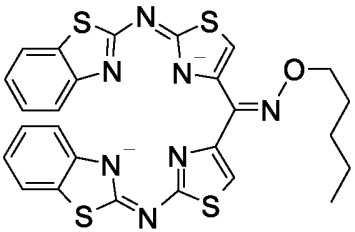
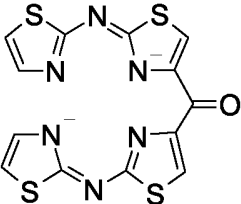
Example 8: It is proceeded in close analogy with example 7, with the difference that the compound of example 2 is spin-coated instead of the compound of example 1.

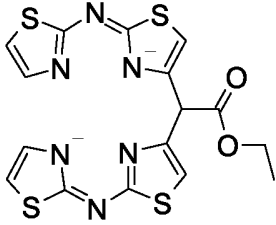
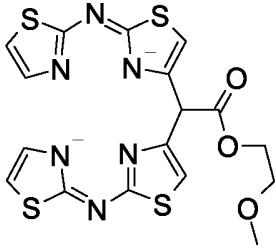
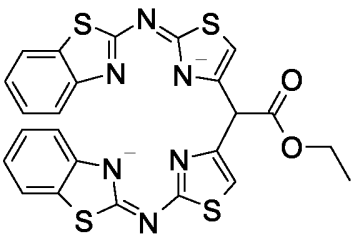
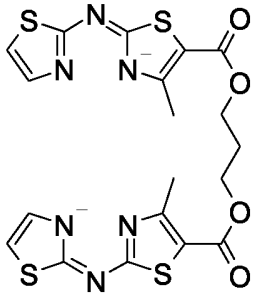
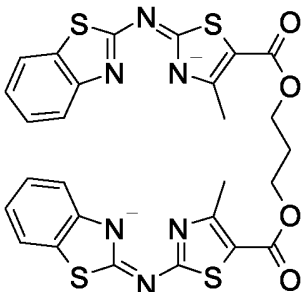
Examples 9-36: The following compounds are prepared and measured in close analogy to examples 1-5:

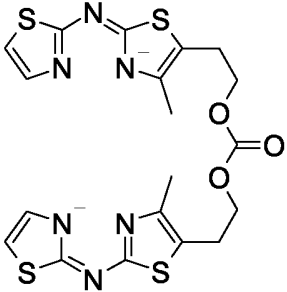
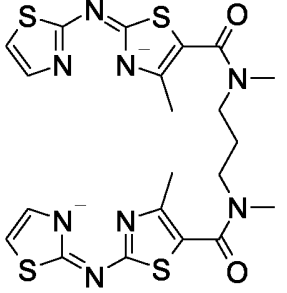
Example	Metal	Ligand	λ_{max} [nm]	Solvent	n	k
9	Cu^{2+}		360	CH_2Cl_2	2.125	0.124
10	Cu^{2+}		360	CH_2Cl_2	2.111	0.159
11	Zn^{2+}		343	THF		

Example	Metal	Ligand	$\lambda_{\max}$ [nm]	Solvent	n	k
12	Cu^{2+}		349	CH_2Cl_2	1.975	0.014
13	Cu^{2+}		378	CH_2Cl_2	2.090	0.576
14	Cu^{2+}		357	CH_2Cl_2	1.955	0.032
15	Cu^{2+}		367	CH_2Cl_2	2.220	0.238
16	Cu^{2+}		353	CH_2Cl_2	2.133	0.167
17	Cu^{2+}		314	CH_2Cl_2		

Example	Metal	Ligand	$\lambda_{\max}$ [nm]	Solvent	n	k
18	Cu^{2+}		346	CH_2Cl_2		
19	Cu^{2+}		358	CH_2Cl_2	2.093	0.083
20	Cu^{2+}		346	CH_2Cl_2	1.981	0.015
21	Cu^{2+}		350	CH_2Cl_2	2.066	0.027
22	Cu^{2+}		345	CH_2Cl_2	2.035	0.065
23	Cu^{2+}		346	CH_2Cl_2	2.104	0.090

Example	Metal	Ligand	$\lambda_{\max}$ [nm]	Solvent	n	k
24	Cu^{2+}		345	CH_2Cl_2	2.055	0.050
25	Cu^{2+}		344	CH_2Cl_2	2.064	0.051
26	Cu^{2+}		351	CH_2Cl_2	2.033	0.022
27	Cu^{2+}		351	CH_2Cl_2	1.841	0.196
28	Cu^{2+}		351	CH_2Cl_2		
29	Cu^{2+}		437	CH_2Cl_2		

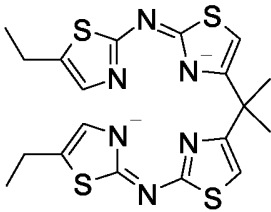
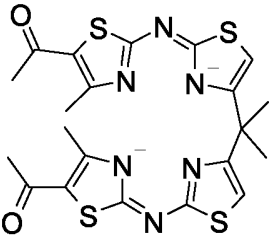
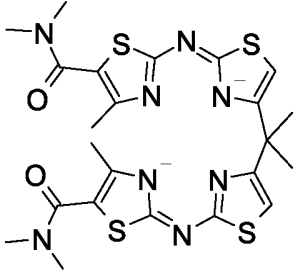
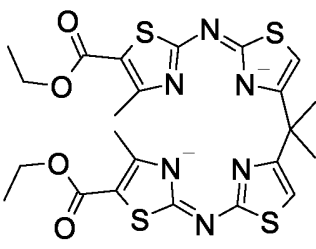
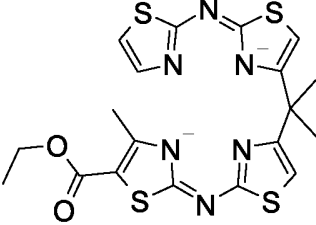
Example	Metal	Ligand	$\lambda_{\max}$ [nm]	Solvent	n	k
30	Cu^{2+}		345	CH_2Cl_2	1.956	0.061
31	Cu^{2+}		344	CH_2Cl_2	1.966	0.116
32	Cu^{2+}		351	CH_2Cl_2	1.772	0.161
33	Cu^{2+}		381	CH_2Cl_2	2.333	0.273
34	Cu^{2+}		389	CH_2Cl_2		

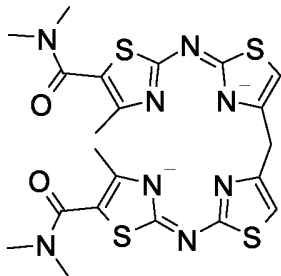
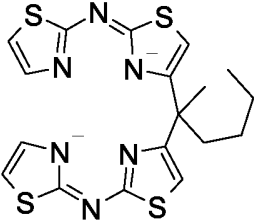
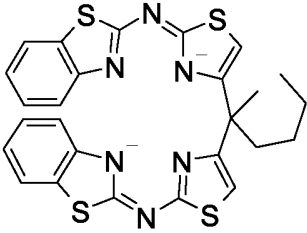
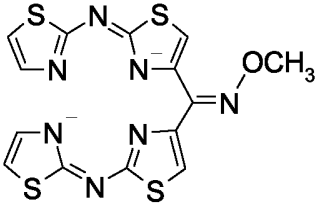
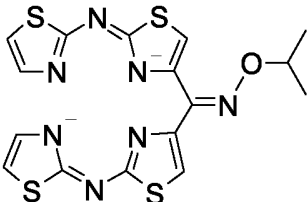
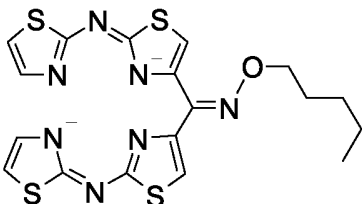
Example	Metal	Ligand	$\lambda_{\max}$ [nm]	Solvent	n	k
35	Cu^{2+}		369	CH_2Cl_2	2.033	0.031
36	Cu^{2+}		370	CH_2Cl_2	1.903	0.036

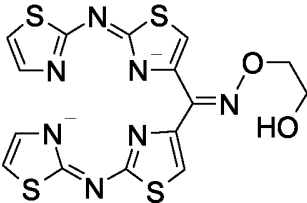
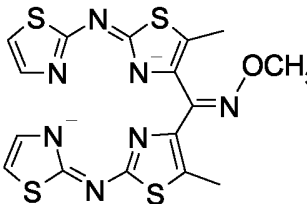
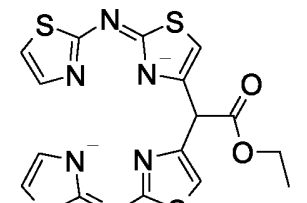
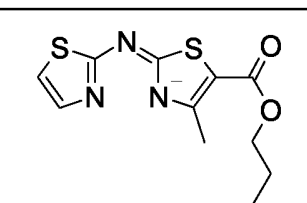
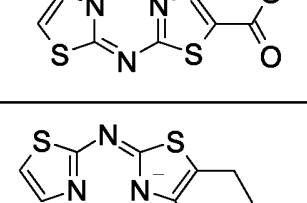
Examples 37-53: 10 mg of the compounds according to examples 12, 13, 14, 15, 16, 19, 20, 21, 22, 23, 24, 25, 26, 30, 33, 35 and 36 are dissolved each in 1.00 ml of 2,2,3,3-tetrafluoro-1-propanol. Each dye solution is then spin-coated at 800

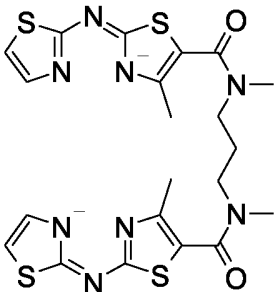
5 rev/min to a 1.2 mm thick, flat polycarbonate plate (diameter 120 mm); the rotational speed is then increased to 2000 rev/min, so that the excess solution is spun off and a uniform solid layer is formed. Using an static test-system for optical data storage media (MEDIA TEST-I™, TOPTICA Photonics), pit marks are formed with a writing laser (pulse length from 25 ns to 300 ns, laser power from 1 to 14

10 mW) at a wavelength of 399 nm. The reflectivity change before/after pit mark formation is measured with a read laser at a wavelength of 422 nm. Modulation is defined as the ratio of the reflectivity (R) change before and after the pit mark formation: Modulation [expressed in %] = $(R_{\text{before}} - R_{\text{after}}) / R_{\text{before}}$. Sensitivity is defined as the threshold write laser power when the modulation starts to rise up.

Example	Metal	Ligand	Sensitivity [mW]	Max. Modulation [%]
37 (12)	Cu^{2+}		6.5	32
38 (13)	Cu^{2+}		2.5	51
39 (14)	Cu^{2+}		3.5	42
40 (15)	Cu^{2+}		1.0	56
41 (16)	Cu^{2+}		3.0	52

Example	Metal	Ligand	Sensitivity [mW]	Max. Modulation [%]
42 (19)	Cu^{2+}		3.5	42
43 (20)	Cu^{2+}		8.0	28
44 (21)	Cu^{2+}		3.5	36
45 (22)	Cu^{2+}		5.5	39
46 (23)	Cu^{2+}		4.0	47
47 (24)	Cu^{2+}		5.5	32

Example	Metal	Ligand	Sensitivity [mW]	Max. Modulation [%]
48 (25)	Cu^{2+}		4.5	38
49 (26)	Cu^{2+}		5.5	38
50 (30)	Cu^{2+}		5.5	32
51 (33)	Cu^{2+}		1.5	48
52 (35)	Cu^{2+}		6.0	24

Example	Metal	Ligand	Sensitivity [mW]	Max. Modulation [%]
53 (36)	Cu ²⁺		8.5	6

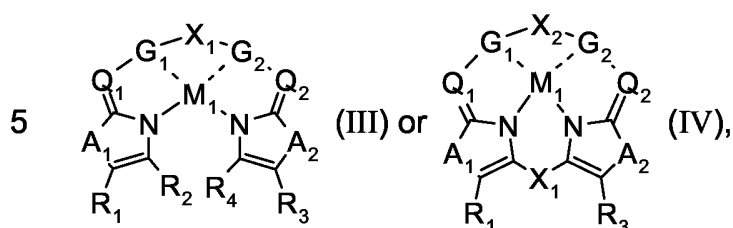
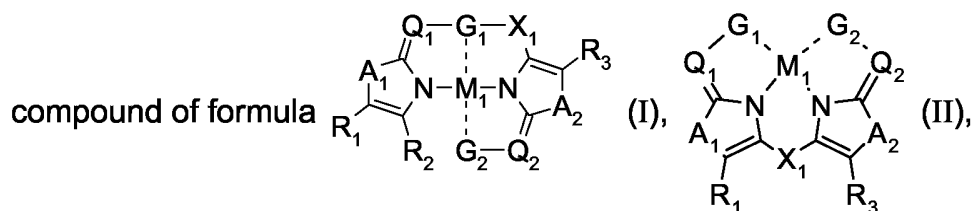
Example 54: 9 mg of the compound according to example 20 and 1 mg of the compound according to example 33 are dissolved in 1.00 ml of 2,2,3,3-tetrafluoro-1-propanol. The mixed dye solution is then spin-coated at 600 rev/min to a 1.2 mm thick, flat polycarbonate plate (diameter 120 mm); the rotational speed is then increased to 2000 rev/min, so that the excess solution is spun off and a uniform solid layer is formed. Pit marks are formed and the reflectivity is measured with an static test-system for optical data storage media (MEDIA TEST-I™, TOPTICA Photonics) in the same way as in examples 37-53. In order to test the read-stability, which is defined as the ratio of the reflectivity (R) change before and after the laser exposure, the reflectivity change is then also measured during laser exposure at low laser power (wavelength 399 nm, laser power 0.5 mW, pulse duration time 1 msec): Read-stability [expressed in %] = $(R_{\text{before}} - R_{\text{after}}) / R_{\text{before}}$.

Example	Dyes	Amount	Sensitivity [mW]	Max. Modulation [%]	Read-stability [%]
54	Example 20 Example 33	90% 10%	4.0	45	9

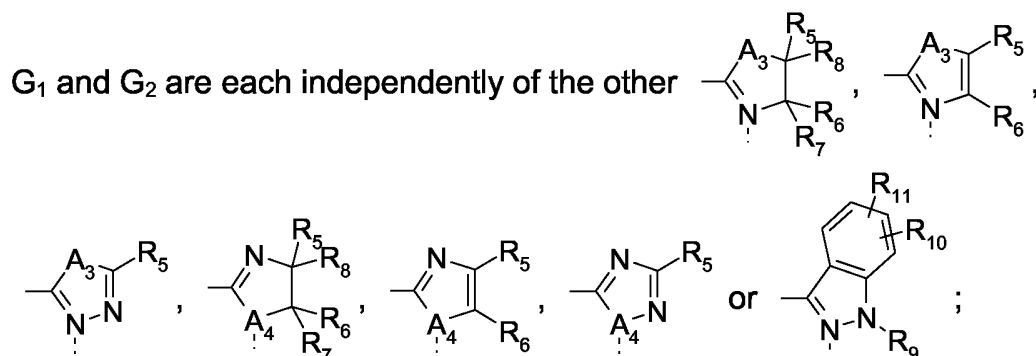
Further examples: It is proceeded in close analogy with above examples, with the difference that Zn or Cu are replaced by each other or by Co, Ni or Pd, respectively. One can also use mixtures of compounds comprising different two or more metals, such as Cu and Zn, Cu and Co, Cu and Ni, Cu and Pd, Co and Ni, Co and Pd, Co and Zn, Ni and Pd, Ni and Zn, or Cu, Co and Zn.

Claims:

1. An optical recording medium comprising a substrate, a recording layer and optionally one or more reflecting layers, wherein the recording layer comprises a



or a tautomer of a compound of formula (I), (II), (III) or (IV), wherein



10 X_1 and X_2 are each independently from the other a direct bond or a chain consisting of from 1 to 8 members each selected independently from the group consisting of $CR_{12}=CR_{13}$, $C=CR_{12}R_{13}$, $CR_{12}R_{13}$, $C=O$, $C=S$, $C=N(R_{14})$, $N(R_{14})$, O or S , preferably a direct bond or a chain consisting of 1, 2, 3 or 4 members, most preferred a direct bond or a chain $CR_{12}R_{13}$, $C=O$, $C=S$, $C=N(R_{14})$, $N(R_{14})$, O or S ;

A_1 , A_2 and A_3 are $CR_{15}R_{16}$, $C \begin{smallmatrix} \curvearrowright \\ R_{17} \end{smallmatrix}$, $N(R_{14})$, O , S , Se , $N=C(R_{18})$ or $CR_{19}=CR_{20}$, and

15 A_4 is O , S or Se ;

M_1 is a transition metal of groups 9 to 12, preferably Co , Cu , Ni , Pd or Zn ,

especially Co, Cu or Ni, or is $\text{SiR}_{21}\text{R}_{22}$, $\text{GeR}_{21}\text{R}_{22}$, $\text{PR}_{21}\text{R}_{22}$ or AlR_{21} ;

Q_1 and Q_2 are each independently of the other $\text{C}(\text{R}_{23})$, N or P;

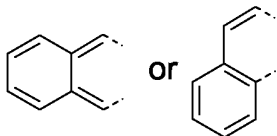
R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_{19} and R_{20} are each independently of the others hydrogen, R_{10} , or $\text{C}_6\text{-C}_{12}\text{aryl}$, $\text{C}_4\text{-C}_{12}\text{heteroaryl}$, $\text{C}_7\text{-C}_{12}\text{aralkyl}$ or $\text{C}_5\text{-C}_{12}\text{heteroaralkyl}$ each unsubstituted or substituted by one or more, where applicable identical or different, radicals R_{10} ; or

R_5 or R_6 , preferably R_6 , is the position of X_1 in formula (I) or (III) or the position of X_2 in formula (IV), with the proviso that when X_1 or X_2 is a direct bond or a chain with a length of less than 3 atoms, its position at G_1 or G_2 is not R_5 ;

10 R_9 , R_{14} and R_{18} are each independently of the others $\text{C}_1\text{-C}_{24}\text{alkyl}$, $\text{C}_3\text{-C}_{24}\text{cycloalkyl}$, $\text{C}_2\text{-C}_{24}\text{alkenyl}$, $\text{C}_3\text{-C}_{24}\text{cycloalkenyl}$, $\text{C}_1\text{-C}_4\text{alkyl-[O-C}_1\text{-C}_4\text{alkylene]}_m$ or $\text{C}_1\text{-C}_4\text{alkyl-[NH-C}_1\text{-C}_4\text{alkylene]}_m$, each of which is unsubstituted or substituted by one or more, where applicable identical or different, radicals R_{24} ; or $\text{C}_6\text{-C}_{12}\text{aryl}$, $\text{C}_4\text{-C}_{12}\text{heteroaryl}$, $\text{C}_7\text{-C}_{12}\text{aralkyl}$ or $\text{C}_5\text{-C}_{12}\text{heteroaralkyl}$, each of which is unsubstituted or substituted
15 by one or more, where applicable identical or different, radicals R_{10} ;

or R_9 is the position of X_1 in formula (I) or (III) or the position of X_2 in formula (IV); and/or R_{14} is COR_9 , COOR_9 , $\text{CONR}_{12}\text{R}_{13}$, $\text{C}(\text{R}_9)=\text{NR}_{18}$, $\text{C}(\text{OR}_9)=\text{NR}_{18}$ or $\text{C}(\text{NR}_{12}\text{R}_{13})=\text{NR}_{18}$;

or R_1 and R_2 , R_3 and R_4 , R_5 and R_6 , R_5 and R_{18} , R_5 and R_{19} , R_1 and R_3 in
20 formula (II) or (IV), R_3 and R_5 in formula (I), R_5 of G_1 and R_5 of G_2 in formula (III) or (IV) and/or R_6 of G_1 and R_6 of G_2 in formula (III) or (IV), together in pairs, are $\text{C}_3\text{-C}_6\text{alkylene}$ or $\text{C}_3\text{-C}_6\text{alkenylene}$, each of which is unsubstituted or substituted by one or more, where applicable identical or different, radicals R_{24} and/or R_{32} and may be uninterrupted or interrupted by O, S or $\text{N}(\text{R}_{14})$, or 1,4-butadienylene,

25  , each of which is unsubstituted or substituted by one or more,

where applicable identical or different, radicals R_{10} and in which 1 or 2 carbon atoms may have been replaced by nitrogen;

R_{10} and R_{11} are each independently of the other $C(R_{23})=NR_{25}$, $C(R_{23})=NR_{26}$ or R_{28} ; or R_{10} is the position of X_1 in formula (I) or (III) or the position of X_2 in formula (IV);

- 5 R_{12} and R_{13} are each independently from the other hydrogen, R_{10} or C_6-C_{12} aryl, C_4-C_{12} heteroaryl, C_7-C_{12} aralkyl or C_5-C_{12} heteroaralkyl each unsubstituted or substituted by one or more, where applicable identical or different, radicals R_{10} ; or

R_{12} and R_{13} together are C_2-C_7 alkylene or C_2-C_7 alkenylene, preferably C_3-C_6 alkylene or C_3-C_6 alkenylene, most preferred C_4-C_5 alkylene or

- 10 C_4-C_5 alkenylene, each of which is unsubstituted or substituted by one or more, where applicable identical or different, radicals R_{24} and/or R_{32} ;

R_{15} and R_{16} are each independently from the other C_1-C_5 alkyl which is unsubstituted or substituted by one or more, where applicable identical or different, radicals R_{24} ,

- 15 R_{17} is C_2-C_7 alkylene, preferably C_4-C_5 alkylene, each of which is unsubstituted or substituted by one or more, where applicable identical or different, radicals R_{24} and may be uninterrupted or interrupted by O, S or N(R_{14}),

R_{21} and R_{22} are each independently of the others hydroxy, C_1-C_{12} alkoxy, C_3-C_{12} cycloalkoxy, C_1-C_{12} alkylthio, C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_2-C_{12} alkenyl,

- 20 C_3-C_{12} cycloalkenyl, C_6-C_{12} aryl, C_4-C_{12} heteroaryl, C_7-C_{12} aralkyl or C_5-C_{12} heteroaralkyl, each of which is unsubstituted or substituted by one or more, where applicable identical or different, halogen, hydroxy, C_1-C_{12} alkoxy or C_3-C_{12} cycloalkoxy radicals;

R_{23} is hydrogen, cyano, hydroxy, C_1-C_{12} alkoxy, C_3-C_{12} cycloalkoxy, C_1-C_{12} alkylthio,

- 25 C_3-C_{12} cycloalkylthio, amino, NHR_{29} , $NR_{30}R_{31}$, R_{32} , halogen, nitro, formyl, $N=N-R_{32}$, $C(R_{33})=CR_{26}R_{27}$, $C(R_{33})=NR_{25}$, $COO-R_{30}$, carboxy, carbamoyl, $CONH-R_{30}$, $CONR_{30}R_{31}$, $N=CR_{25}R_{34}$, or C_1-C_{12} alkyl, C_3-C_{12} cycloalkyl, C_2-C_{12} alkenyl or

C₃-C₁₂cycloalkenyl each unsubstituted or substituted by one or more, where applicable identical or different, halogen, hydroxy, C₁-C₁₂alkoxy or C₃-C₁₂cycloalkoxy radicals;

5 R₂₄ is halogen, hydroxy, O-R₃₀, O-CO-R₃₀, S-R₃₀, NH₂, NH-R₃₀, NR₃₀R₃₁, NH₃⁺, NH₂R₃₀⁺, NHR₃₀R₃₁⁺, NR₂₉R₃₀R₃₁⁺, NR₃₀-CO-R₂₉, NR₃₀COOR₂₉, cyano, formyl, COO-R₃₀, carboxy, carbamoyl, CONH-R₃₀, CONR₃₀R₃₁, ureido, NH-CO-NHR₂₉, NR₃₀-CO-NHR₂₉, phosphato, PR₃₀R₂₉, POR₃₀OR₂₉, P(=O)OR₃₀OR₂₉, OPR₃₀R₂₉, OPR₃₀OR₂₉, OP(=O)R₃₀OR₂₉, OPO₃R₃₀, OP(=O)OR₃₀OR₂₉, SO₂R₃₀, sulfato, sulfo or C₁-C₁₂alkoxy or C₁-C₁₂cycloalkoxy each unsubstituted or mono- or poly-substituted
10 by halogen;

R₂₆ and R₂₇ are each independently of the other NR₃₀R₃₁, CN, CONH₂, CONHR₂₅, CONR₂₅R₃₄ or COOR₃₄;

R₂₈ is halogen, nitro, cyano, thiocyanato, hydroxy, O-R₂₅, O-CO-R₂₅, S-R₂₅, CHO, COR₃₄, CHOR₂₅OR₃₅, CR₃₄OR₂₅OR₃₅, R₃₆, N=N-R₃₆, N=CR₂₅R₃₄, N=CR₂₆R₂₇, NH₂,
15 NH-R₂₅, NR₂₅R₃₄, NH₃⁺, NH₂R₂₅⁺, NHR₂₅R₃₄⁺, NR₂₅R₃₄R₃₅⁺, CONH₂, CONHR₂₅, CONR₂₅R₃₄, SO₂R₂₅, SO₂NH₂, SO₂NHR₂₅, SO₂NR₂₅R₃₄, COOH, COOR₂₅, OCOOR₂₅, NHCOR₂₅, NR₂₅COR₃₅, NHCOOR₂₅, NR₂₅COOR₃₅, ureido, NR₂₅-CO-NHR₃₅, B(OH)₂, B(OH)(OR₂₅), B(OR₂₅)OR₃₅, phosphato, PR₂₅R₃₅, POR₂₅OR₃₅, P(=O)OR₂₅OR₃₅, OPR₂₅R₃₅, OPR₂₅OR₃₅, OP(=O)R₂₅OR₃₅,
20 OP(=O)OR₂₅OR₃₅, OPO₃R₂₅, sulfato, sulfo, or C₁-C₁₂alkyl, C₃-C₁₂cycloalkyl, C₂-C₁₂alkenyl, C₃-C₁₂cycloalkenyl, C₁-C₁₂alkylthio, C₃-C₁₂cycloalkylthio, C₂-C₁₂alkenylthio, C₃-C₁₂cycloalkenylthio, C₁-C₁₂alkoxy, C₃-C₁₂cycloalkoxy C₂-C₁₂alkenyloxy or C₃-C₁₂cycloalkenyloxy each unsubstituted or substituted by one or more, where applicable identical or different, radicals R₂₄;

25 R₂₉, R₃₀ and R₃₁ are each independently of the others C₁-C₁₂alkyl, C₃-C₁₂cycloalkyl, C₂-C₁₂alkenyl, C₃-C₁₂cycloalkenyl, C₆-C₁₂aryl, C₄-C₁₂heteroaryl, C₇-C₁₂aralkyl or C₅-C₁₂heteroaralkyl; or

R₃₀ and R₃₁ together with the common nitrogen are pyrrolidine, piperidine,

piperazine or morpholine, each of which is unsubstituted or mono- to tetra-substituted by C₁-C₄alkyl;

R₃₂ is C₆-C₁₂aryl, C₄-C₁₂heteroaryl, C₇-C₁₂aralkyl or C₅-C₁₂heteroaralkyl, each of which is unsubstituted or substituted by one or more, where applicable identical or
5 different, radicals R₂₈;

R₃₃ is hydrogen, R₂₈, or C₆-C₁₂aryl, C₄-C₁₂heteroaryl, C₇-C₁₂aralkyl or C₅-C₁₂heteroaralkyl each unsubstituted or substituted by one or more, where applicable identical or different, radicals R₂₈;

R₂₅, R₃₄ and R₃₅ are each independently of the others R₃₆, or C₁-C₁₂alkyl,
10 C₃-C₁₂cycloalkyl, C₂-C₁₂alkenyl or C₃-C₁₂cycloalkenyl each unsubstituted or substituted by one or more, where applicable identical or different, halogen, hydroxy, C₁-C₁₂alkoxy or C₃-C₁₂cycloalkoxy radicals; or

R₁₉ and R₂₅ together, R₂₃ and R₂₅ together and/or R₂₅ and R₃₅ together are C₂-C₁₂alkylene, C₃-C₁₂cycloalkylene, C₂-C₁₂alkenylene or C₃-C₁₂cycloalkenylene,
15 each of which is unsubstituted or substituted by one or more, where applicable identical or different, halogen, hydroxy, C₁-C₁₂alkoxy or C₃-C₁₂cycloalkoxy radicals; or

R₂₅ and R₃₄ together with the common nitrogen are pyrrolidine, piperidine, piperazine or morpholine, each of which is unsubstituted or mono- to tetra-substituted by C₁-C₄alkyl; or carbazole, phenoxazine or phenothiazine, each of
20 which is unsubstituted or substituted by one or more, where applicable identical or different, radicals R₃₇;

R₃₆ is C₆-C₁₂aryl, C₄-C₁₂heteroaryl, C₇-C₁₂aralkyl or C₅-C₁₂heteroaralkyl, each of which is unsubstituted or substituted by one or more, where applicable identical or
25 different, radicals R₃₇;

R₃₇ is nitro, SO₂NHR₃₀, SO₂NR₃₀R₃₁, or C₁-C₁₂alkyl, C₃-C₁₂cycloalkyl, C₁-C₁₂alkylthio, C₃-C₁₂cycloalkylthio, C₁-C₁₂alkoxy or C₃-C₁₂cycloalkoxy each unsubstituted or

substituted by one or more, where applicable identical or different, radicals R_{24} ; and

m is a number from 1 to 10.

2. An optical recording medium according to claim 1, wherein X_1 and X_2 are each independently from the other a direct bond or a chain $CR_{12}R_{13}$, $C=O$, $C=S$,

5 $C=N(R_{14})$, $N(R_{14})$, O or S.

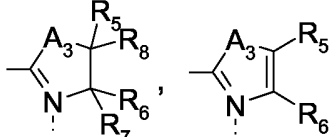
3. An optical recording medium according to claim 1 or 2, wherein the recording layer comprises a compound of formula (I), (II), (III) or (IV) wherein

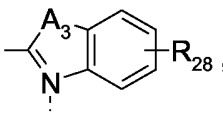
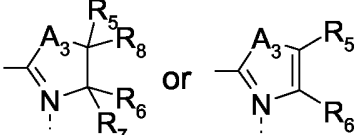
A_1 and A_2 are each independently of the other $N(R_{14})$, O, S or Se and A_3 is

$C(C_1-C_5\text{alkyl})_2$, $C(C_4-C_5\text{alkylene})$, $N(R_{14})$, O, S, Se, $N=C(R_{18})$ or unsubstituted or

10 R_{19} -substituted $CH=CH$, especially wherein A_1 , A_2 and A_3 are each independently of the others O, S or $N(R_{14})$ and/or Q_1 and Q_2 are $C(R_{23})$ or N;

G_1 and G_2 are each independently of the other




, especially at least one of G_1 and G_2 is
 
;

R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 and R_{19} are each independently of the others

15 hydrogen, R_{10} , or C_6-C_{12} aryl or C_7-C_{12} aralkyl each unsubstituted or substituted by one or more, where applicable identical or different, radicals R_{10} ;

R_9 , R_{14} and R_{18} are each independently of the others unsubstituted or R_{10} -substituted C_1-C_8 alkyl; or

R_9 is the position of X_1 in formula (I) or (III) or the position of X_2 in formula (IV);

20 R_{10} and R_{28} are each independently of the other halogen, nitro, cyano, $O-R_{25}$, formyl, $CH=C(CN)_2$, $CH=C(CN)CONH_2$, $CH=C(CN)CONHR_{25}$,

CH=C(CN)CONR₂₅R₃₄, CH=C(CN)COOR₂₅, CH=C(COOR₂₅)COOR₃₄, CONH₂,
 CONHR₂₅, CONR₂₅R₃₄, SO₂C₁-C₁₂alkyl, SO₂NH₂, SO₂NHR₂₅, SO₂NR₂₅R₃₄, COOH,
 COOR₂₅, NHCOR₂₅, NR₂₅COR₃₅, NHCOOR₂₅, NR₂₅COOR₃₅, ureido,
 P(=O)OR₂₅OR₃₅, sulfo, or C₁-C₁₂alkyl, C₁-C₁₂alkylthio or C₁-C₁₂alkoxy each unsub-
 5 stituted or substituted by one or more, where applicable identical or different,
 radicals R₂₄;

R₂₃ is hydrogen, cyano, halogen, nitro, formyl, N=N-R₃₂, C(R₁₉)=CR₂₆R₂₇,
 C(R₁₉)=NR₂₅, COO-R₃₀, carboxy, carbamoyl, CONH-R₃₀, CONR₃₀R₃₁, or C₁-C₁₂alkyl
 unsubstituted or substituted by one or more halogen substituents;

10 R₂₄ is halogen, hydroxy, O-R₃₀, amino, NH-R₃₀, NR₃₀R₃₁, NR₃₀-CO-R₂₉,
 NR₃₀COOR₂₉, cyano, COO-R₃₀, carboxy, CONH-R₃₀, CONR₃₀R₃₁, sulfato, sulfo, or
 C₁-C₁₂alkoxy unsubstituted or mono- or poly-substituted by halogen;

R₂₅, R₃₄ and R₃₅ are each independently of the others C₁-C₁₂alkyl unsubstituted or
 substituted by one or more, where applicable identical or different, halogen,
 15 hydroxy or C₁-C₁₂alkoxy radicals, or unsubstituted C₆-C₁₂aryl or C₇-C₁₂aralkyl; or

R₂₅ and R₃₄ together with the common nitrogen are morpholine, or piperidine N-
 substituted by C₁-C₄alkyl;

R₂₉, R₃₀ and R₃₁ are each independently of the others C₁-C₁₂alkyl, C₂-C₁₂alkenyl,
 C₆-C₁₂aryl or C₇-C₁₂aralkyl; or

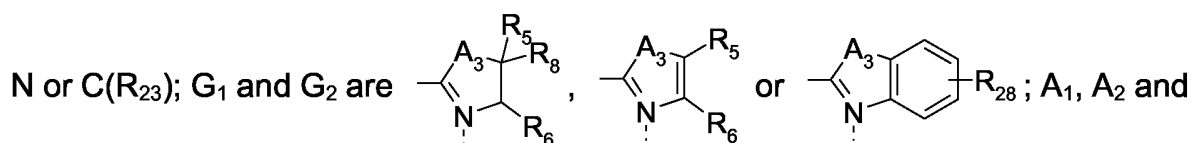
20 R₃₀ and R₃₁ together with the common nitrogen are morpholine, or piperidine N-
 substituted by C₁-C₄alkyl;

R₃₆ is unsubstituted or substituted C₆-C₁₂aryl or C₇-C₁₂aralkyl, especially a
 metallocenyl radical; and/or

m is a number from 1 to 4, or a tautomer thereof.

25 4. An optical recording medium according to claim 1, 2 or 3, wherein the recording

layer comprises a compound of formula (I), (II), (III) or (IV), wherein Q_1 and Q_2 are



A_3 are S or $CR_{19}=CH$, especially S, and X_1 and X_2 are direct bonds or C_1 - C_3 alkylene bridges;

5 R_5 and R_8 are independently from each other hydrogen or R_{28} ;

R_2 , R_4 and R_6 are independently from each other hydrogen or unsubstituted or substituted C_1 - C_4 alkyl, in particular unsubstituted or substituted methyl or ethyl;

R_{23} is hydrogen, cyano, $COO-R_{30}$ or C_1 - C_{12} alkyl; and

10 R_{28} is unsubstituted or substituted C_1 - C_{12} alkyl, $O-R_{25}$ or an electron withdrawing group;

or a tautomer thereof.

5. An optical recording medium according to claim 1, 2, 3 or 4, wherein the recording layer is substantially amorphous.

15 6. An optical recording medium according to claim 1, 2, 3, 4 or 5, additionally comprising a covering layer, wherein substrate, reflector layer, recording layer and covering layer are arranged in that order.

7. An optical recording medium according to claim 1, 2, 3, 4, 5 or 6, which in addition to comprising a compound of formula (I) comprises a metal-free chromophore.

20 8. A method of recording or playing back data, wherein the data on an optical recording medium according to claim 1, 2, 3, 4, 5, 6 or 7 are recorded or played back with a laser of wavelength from 350 to 500 nm.

9. A method according to claim 8, wherein the data are in the form of marks of different reflectivity.

10. A compound of formula (I), (II), (III) or (IV) according to claim 1, or a tautomer thereof.

5 11. A spin-coating solution comprising a compound of formula (I), (II), (III) or (IV) according to claim 10 or tautomer thereof dissolved in a solvent.

12. The use of a compound of formula (I), (II), (III) or (IV) according to claim 1 or tautomer thereof, or of a spin-coating solution according to claim 10, for the preparation of an optical recording medium.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/053782

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B57/10 G11B7/24

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)
IPC 7 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 066 653 A (CROUNSE ET AL) 3 January 1978 (1978-01-03) compounds V, VI	10
A	WO 03/063151 A (CIBA SPECIALTY CHEMICALS HOLDING INC; FEILER, LEONHARD; SCHMIDHALTER,) 31 July 2003 (2003-07-31) see the generic formula III	1-12
A	JP 2004 090564 A (FUJI PHOTO FILM CO LTD) 25 March 2004 (2004-03-25) compound 26	10
A	WO 02/082438 A (CIBA SPECIALTY CHEMICALS HOLDING INC; LEHMANN, URS; BUDRY, JEAN-LUC; S) 17 October 2002 (2002-10-17) cited in the application first compound on page 31	1-12
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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Date of the actual completion of the international search

2 November 2005

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/053782

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 376 664 B1 (CHAN MICHAEL K ET AL) 23 April 2002 (2002-04-23) the whole document -----	10
A	A.ABBOTTO ET AL.: "Metal Chelation Aptitudes of Bis(o-azaheteroaryl)methanes as tuned by Heterocycle Charge Demands" J.ORG.CHEM., vol. 67, 2002, pages 5753-5772, XP002319909 cited in the application the whole document -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2005/053782

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US 6376664	B1	23-04-2002	NONE	