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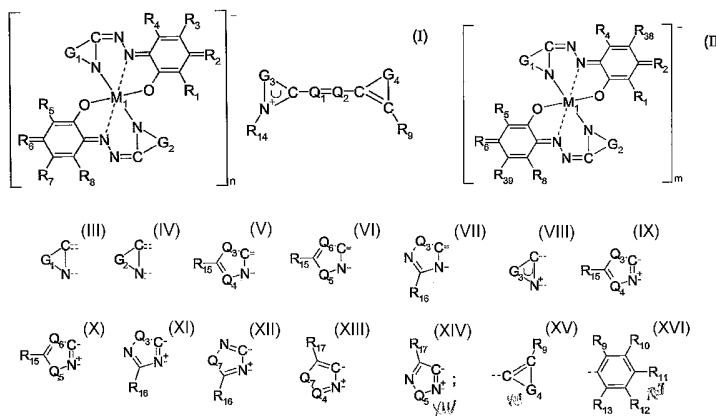
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(54) Title: HIGH-CAPACITY OPTICAL STORAGE MEDIA



(57) Abstract: The invention accordingly relates to an optical recording medium comprising a substrate, a reflecting layer and a recording layer, wherein the recording layer comprises a compound of formula (I) or a mesomeric or tautomeric form thereof, wherein M_1 is a metal cation in the oxidation state +3, a hydroxy or halogeno metal group wherein the metal is in the oxidation state +4, or an oxo metal group wherein the metal is in the oxidation state +5; (III) and (IV) are each independently of the other (V), (VI) or (VII); (VIII) is (IX), (X), (XI), (XII), (XIII) or (XIV); (XV) is (XVI) or C_{2-8} heteroaryl unsubstituted or mono- or poly-substituted by R_{10} , R_{11} , R_{12} and/or R_{13} ; Q_1 is N or CR_{18} , Q_2 is N or CR_{19} , Q_3 , Q_5 and Q_7 are each independently of the other CR_{20} , R_{21} , O, S or NR_{22} , Q_4 is CR_{16} or N and Q_6 is CR_{17} or N; and R_2 and/or R_6 are O, S or NR_{33} . Please see the disclosure for the other substituents which are less relevant. The compounds of formula (I) are novel and also claimed, as well as the compound of formula (II), or a mesomer or tautomer thereof, wherein R_{38} is halogen, CF_3 , NO_2 , CN, COR_{22} , $COOR_{23}$, SO_3R_{23} , NCO or SCN, G_1 , G_2 , M_1 , R_1 , R_2 , R_4 , R_5 , R_6 , R_8 , R_{22} and R_{23} are as defined in formula (I), M_2^{m+} is a cation with m positive charges, and m is an integer 1, 2 or 3. The optical recording media are remarkably suitable for DVD±R (658 nm), especially at high recording speeds.



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

High-capacity optical storage media

The field of the invention is the optical storage of information on write-once storage media, the information pits being differentiated by the different optical properties of a colorant at written and unwritten sites. This technology is usually termed "WORM"
5 (for example "CD-R", "DVD-R", "DVD+R"); those terms have been retained herein.

By the use of compact high-performance diode lasers that emit in the range of from 630 to 690 nm, it is possible in principle to achieve a 4- to 5-fold improvement in data packing density and a 6- to 8-fold increase in storage capacity in comparison with media having a blue or green layer, in that the track pitch (distance between
10 two turns of the information track) and the size of the pits can be reduced, for example, to approximately half the value in comparison with conventional CDs.

This imposes extraordinarily high demands on the recording layer to be used, however, such as high refractive index, uniformity of script width at different length pulse durations and also high light stability in daylight with, at the same time, high
15 sensitivity to high-energy laser radiation especially at high recording speeds. The known recording layers possess those properties only to an unsatisfactory extent.

JP-A-02/55 189 and JP-A-03/51 182 disclose optical storage media in which the recording layer consists substantially of a cyanine dye and an O-coordinated, homocyclic azo metal complex.

20 US-6 168 843, US-6 242 067 and JP-A-2000/198 273 disclose storage media suitable for recording using a laser of wavelength 635–650 nm that consist of mixtures of cyanine or phthalocyanine dyes with para-amino- and nitro- or halo-substituted, homocyclic azo metal complexes, which are also O-coordinated.

Those azo metal complexes may additionally be substituted by hydroxy.

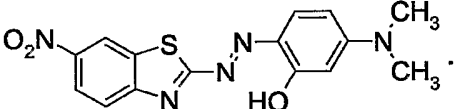
25 Comparison Example 2 of US-6 242 067 discloses, however, that hydroxy substitution results in insufficient solubility. In addition, the sensitivity of compounds according to US-6 168 843 is sufficient only for single (1×), or in the case of compounds according to US-6 242 067 double (2×), DVD-recording speed.

- 2 -

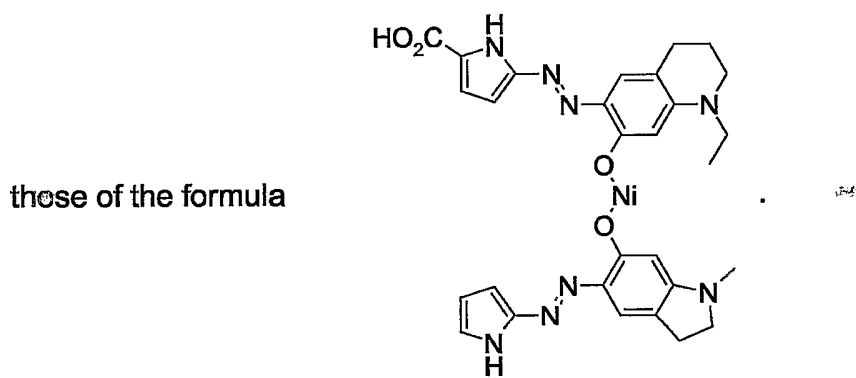
WO-03/098 617 and WO-03/098 618 disclose pentacyclic rhodamines, in combination with which *inter alia* also O-coordinated, homocyclic azo metal complexes are mentioned.

- 5 US-4 686 143 discloses writable optical information media that can be written at 780 nm and comprise metal complexes of monoazo compounds having an aromatic ring and an N-heteroaromatic ring. The N-heteroaromatic ring may be unsubstituted or substituted by an electron acceptor substituent and both rings may be substituted by an electron donor substituent, illustrated, for example, by the

ligand "NBTADMAP" of the formula



- 10 JP-A-2002/002 118 likewise discloses for use at 780 nm writable optical information media comprising metal complexes of heterocyclic azo compounds, for example



- 15 JP-A-2002/293 031 proposes the combination of metal complexes from JP-A-02/55 189 and JP-A-03/51 182 with those of US-6 168 843, US-6 242 067 and JP-A-2000/198 273.

JP-A-11/213 442 discloses an optical recording medium of geometry suitable for use in the range from 620 to 690 nm, comprising a metal complex of a heterocyclic

azo ligand of the formula $\text{A} \begin{array}{c} \text{C} \\ \text{N} \end{array} \text{C}=\text{N}=\text{N}=\text{C} \begin{array}{c} \text{B} \\ \text{C} \end{array} \text{X}$. While A may be substituted by both

an electron-donating or an electron-attracting group, however, B may only be

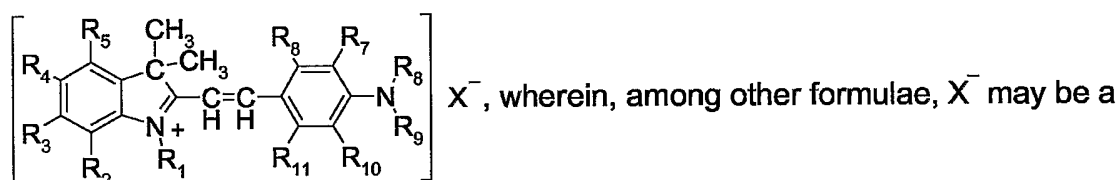
- 3 -

substituted by an electron-donating group.

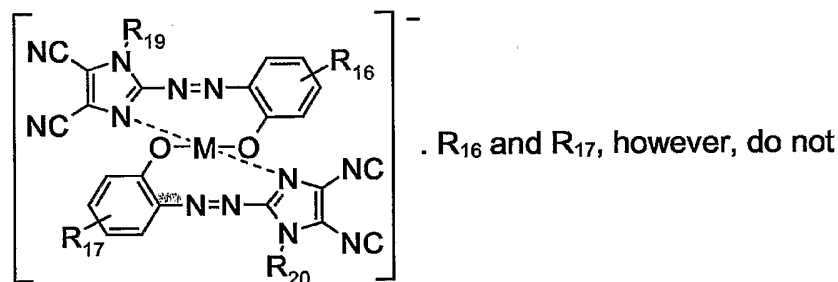
EP-A-1 125 987 similarly discloses cyanine azo metal complexes. The examples wherein one ligand is a heterocyclic group all have a diethylamino group in para position to the azo group. This is also the case in formula 16 of EP-A-1 174 472.

- 5 A leitmotif in all those publications is that a dialkylated amino group in the para-position to the azo group is essential for good performance in optical information media.

EP-A-1 170 339 discloses styryl dyes of the generic formula



10 complex of structure



comprise any deprotonated group. Furthermore, the only example of such complex (chemical formula 8), while lacking embodiment, shows protonated heterocyclic rings (R₁₉/R₂₀) with the metal in the oxidation state +1 (see comparative example).

- 15 WO 2004/088 649 is a patent application according to Art. 54(3) EPC and Rule 64.3 PCT, which is directed to a broad choice of metal complex dyes.

However, the properties of the known recording media still leave something to be desired, especially in respect of the quality of recordings using a laser of a wavelength around 658 ± 5 nm (DVD-R or DVD+R, hereafter DVD±R).

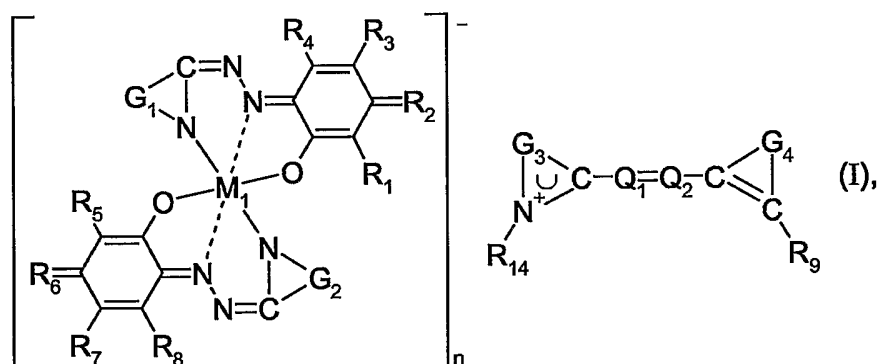
- 20 The aim of the present invention is to provide an optical recording medium, the recording layer of which has high storage capacity combined with excellent other

- 4 -

properties. Such a recording medium should be both writable and readable at the same wavelength in the range of from 600 to 700 nm (preferably from 630 to 690 nm). The main features of the recording layer according to the invention are the very high initial reflectivity in the said wavelength range of the laser diodes, which
 5 can be modified with great sensitivity; the high refractive index; the good uniformity of the script width at different pulse durations; the excellent light and multiple read stability; and the good solubility in polar solvents, as well as excellent compatibility with laser sources of different wavelengths both for recording and for playback.

Very surprisingly, by the use of certain salts of styryl or azo cations with metal
 10 complex anions having particular substituents as recording layer or as an additive to the recording layer, it has been possible to provide an optical recording medium having properties that are astonishingly better than those of the recording media known hitherto. The refractive index in the solid layer is astonishingly very high. The layers are unexpectedly neither hygroscopic nor moisture-sensitive and
 15 possess a high environmental, light and multiple read stability. The instant cations surprisingly provide a high solubility, which is not expected in view of the metal complex anion's general physicochemical properties.

The invention accordingly relates to an optical recording medium comprising a substrate, a reflecting layer and a recording layer, wherein the recording layer
 20 comprises a compound of formula



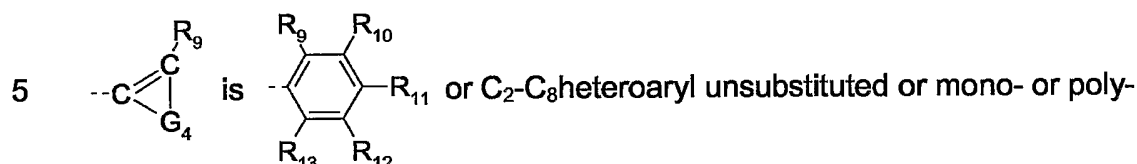
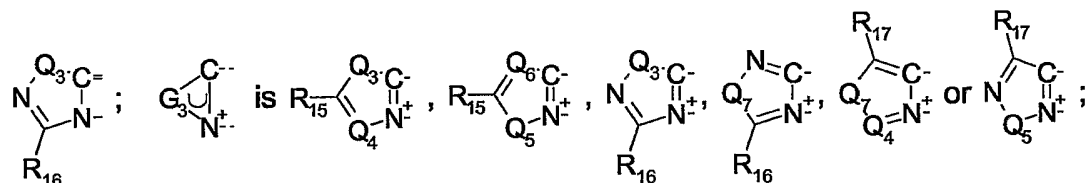
or a mesomeric or tautomeric form thereof, wherein

M_1 is a metal cation in the oxidation state +3, a hydroxy or halogeno metal group

- 5 -

wherein the metal is in the oxidation state +4, or an oxo metal group wherein the metal is in the oxidation state +5;

$G_1-\overset{\cdot\cdot}{C} \begin{smallmatrix} \cdot\cdot \\ | \\ N^{\cdot\cdot} \end{smallmatrix}$ and $G_2-\overset{\cdot\cdot}{C} \begin{smallmatrix} \cdot\cdot \\ | \\ N^{\cdot\cdot} \end{smallmatrix}$ are each independently of the other $R_{15}-\overset{Q_3}{C} \begin{smallmatrix} \cdot\cdot \\ | \\ Q_4-N^{\cdot\cdot} \end{smallmatrix}$, $R_{15}-\overset{Q_6}{C} \begin{smallmatrix} \cdot\cdot \\ | \\ Q_5-N^{\cdot\cdot} \end{smallmatrix}$ or

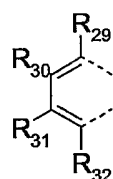


substituted by R₁₀, R₁₁, R₁₂ and/or R₁₃;

Q₁ is N or CR₁₈, Q₂ is N or CR₁₉, Q₃, Q₅ and Q₇ are each independently of the other CR₂₀R₂₁, O, S or NR₂₂, Q₄ is CR₁₆ or N and Q₆ is CR₁₇ or N;

- 10 R₁, R₃, R₄, R₅, R₇, R₈, R₉, R₁₀, R₁₁, R₁₂, R₁₃, R₁₅, R₁₆, R₁₇, R₁₈ and R₁₉ are each independently of all others H, halogen, OR₂₃, SR₂₃, NR₂₂R₂₄, NR₂₂COR₂₅, NR₂₂COOR₂₆, NR₂₂CONR₂₆R₂₇, NR₂₂CN, OSiR₂₂R₂₅R₂₈, COR₂₂, CR₂₂OR₂₅OR₂₈, NO₂, CN, COOR₂₃, CONR₂₆R₂₇, SO₂R₂₂, SO₂NR₂₆R₂₇, SO₃R₂₆, PO(OR₂₂)(OR₂₅); C₁-C₆alkyl, C₂-C₆alkenyl, C₂-C₆alkynyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkenyl or C₂-C₅heterocycloalkyl each unsubstituted or mono- or poly-substituted by halogen,
- 15 OR₂₃, SR₂₃, NR₂₂R₂₄, NR₂₂COR₂₅, NR₂₂COOR₂₃, NR₂₂CONR₂₆R₂₇, NR₂₂CN, COR₂₂, CR₂₂OR₂₅OR₂₈, NO₂, CN, COOR₂₃, CONR₂₆R₂₇ and/or SO₂R₂₆; or C₇-C₁₁aralkyl, C₆-C₁₀aryl or C₁-C₈heteroaryl each unsubstituted or mono- or poly-substituted by C₁-C₄alkyl, halogen, OR₂₃, SR₂₃, NR₂₂R₂₄, COR₂₂, NO₂, CN and/or COOC₁-C₄alkyl;
- or

- 6 -

R₁₅ and R₁₆ or R₁₅ and R₁₇ are together in pairs , thus forming a phenyl

ring together with the two adjacent carbons to which they are bound;

R₂ and/or R₆ are O, S or NR₃₃;

- R₁₄ is C₁-C₁₂alkyl, C₃-C₁₂cycloalkyl, C₁-C₁₂heterocycloalkyl, C₂-C₁₂alkenyl,
 5 C₃-C₁₂cycloalkenyl, C₄-C₁₂heterocycloalkenyl, C₇-C₁₂aralkyl, C₁-C₉heteroaryl,
 C₂-C₁₁heteroaralkyl, C₆-C₁₂aryl or C₁-C₁₂alkyl interrupted by from one to five non-
 successive oxygen and/or sulfur atoms and/or by from one to five identical or
 different groups NR₂₂, each unsubstituted or mono- or poly-substituted by halogen,
 OR₂₃, SR₂₃, NR₂₂R₂₄, NR₂₂COR₂₅, NR₂₂COOR₂₆, NR₂₂CONR₂₆R₂₇, NR₂₂CN,
 10 OSiR₂₂R₂₅R₂₈, COR₂₂, CR₂₂OR₂₅OR₂₈, NO₂, CN, COOR₂₃, CONR₂₆R₂₇, SO₂R₂₂,
 SO₂NR₂₆R₂₇, SO₃R₂₆ or PO(OR₂₂)(OR₂₅);

- R₂₀ and R₂₁ are each independently of the other C₁-C₁₂alkyl, C₂-C₁₂alkenyl,
 C₂-C₁₂alkynyl, C₇-C₁₂aralkyl, C₃-C₁₂cycloalkyl, C₃-C₁₂cycloalkenyl or C₂-C₁₁hetero-
 cycloalkyl each unsubstituted or mono- or poly-substituted by halogen, OR₂₃, SR₂₃,
 15 NR₂₂R₂₄, NR₂₂COR₂₅, NR₂₂COOR₂₃, NR₂₂CONR₂₆R₂₇, NR₂₂CN, COR₂₂,
 CR₂₂OR₂₅OR₂₈, NO₂, CN, COOR₂₃, CONR₂₆R₂₇ and/or SO₂R₂₆; or

- R₂₀ and R₂₁ are together C₂-C₁₂alkylen, C₂-C₁₂alkenylen, C₂-C₁₂cycloalkylen or
 C₂-C₁₂cycloalkenylen, one to five non-successive carbon atoms of which can be
 replaced by oxygen and/or sulfur atoms and/or by identical or different groups
 20 NR₂₂, C₂-C₁₂alkylen, C₂-C₁₂alkenylen, C₂-C₁₂cycloalkylen or C₂-C₁₂cycloalkenylen
 being each unsubstituted or mono- or poly-substituted by halogen, OR₂₃, SR₂₃,
 NR₂₂R₂₄, NR₂₂COR₂₅, NR₂₂COOR₂₃, NR₂₂CONR₂₆R₂₇, NR₂₂CN, COR₂₂,
 CR₂₂OR₂₅OR₂₈, NO₂, CN, COOR₂₃, CONR₂₆R₂₇ and/or SO₂R₂₆;

- R₂₂, R₂₅ and R₂₈ are each independently of the others hydrogen; C₁-C₄alkyl,
 25 C₂-C₄alkenyl, C₂-C₄alkynyl, [C₂-C₃alkylene-O]_k-R₃₄ or [C₂-C₃alkylene-NR₃₅]_k-R₃₄

- 7 -

each unsubstituted or mono- or poly-substituted by halogen; or benzyl;

each R_{23} , independently of any other R_{23} , is R_{24} or R_{33} , preferably H;

R_{24} , R_{26} and R_{27} are each independently of the others H; C_1 - C_6 alkyl, C_2 - C_6 alkenyl, C_2 - C_6 alkynyl, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkenyl or C_2 - C_5 heterocycloalkyl each
 5 unsubstituted or mono- or poly-substituted by halogen, OR_{23} , SR_{23} , $NR_{22}R_{28}$, CN and/or $COOR_{22}$; or C_6 - C_{10} aryl, C_7 - C_{11} aralkyl or C_1 - C_8 heteroaryl each unsubstituted or mono- or poly-substituted by C_1 - C_4 alkyl, halogen, OR_{23} , SR_{23} , $NR_{22}R_{25}$, COR_{22} , $CR_{22}OR_{25}OR_{28}$, NO_2 , CN and/or $COOR_{28}$;

or $NR_{22}R_{24}$, $NR_{22}R_{25}$, $NR_{25}R_{28}$ or $NR_{26}R_{27}$ is a five- or six-membered heterocycle
 10 which may contain a further N or O atom and which can be mono- or poly-substituted by methyl or ethyl;

R_{29} , R_{30} , R_{31} and R_{32} are each independently of the other H, C_1 - C_4 alkyl, halogen, OR_{23} , SR_{23} , $NR_{22}R_{24}$, COR_{22} , NO_2 , CN and/or $COOC_1$ - C_4 alkyl;

R_{33} is COR_{24} , $CONR_{26}R_{27}$, CN, $SO_2NR_{26}R_{27}$ or SO_2R_{26} ;

15 R_{34} and R_{35} are each independently of the other methyl, ethyl, vinyl and/or allyl;

it being possible once or more times radicals of the same or different substituents each selected from the group consisting of R_1 , R_3 , R_4 , R_5 , R_7 , R_8 , R_9 , R_{10} , R_{11} , R_{12} , R_{13} , R_{14} , R_{15} , R_{16} , R_{17} , R_{18} , R_{19} , R_{20} , R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{28} , R_{29} , R_{30} , R_{31} , R_{32} , R_{34} and R_{36} to be bonded to one another in pairs by way of a direct bond or an -O-,
 20 -S- or -N(R_{35})- bridge, optionally forming a dimer, trimer or oligomer comprising two or more identical or different moieties of formula (I);

k is an integer 1, 2, 3 or 4; and n is an integer 1, 2 or 3.

Substituents, including a plurality of substituents having the same label, are generally independent from each other. n depends on the number of charges in the
 25 substituents of the compound of formula (I), so that eventual positive charges

- 8 -

resulting for example from N-substitution of C₁-C₈heteroaryl groups are compensated and the compound of formula (I) is neutral. Preferred are compounds of formula (I), wherein n is 1, as well as alternatively compounds of formula 1, wherein n is 2 and one of G₃, R₉, R₁₀, R₁₁, R₁₂, R₁₃ or R₁₄, preferably R₉, R₁₀, R₁₁,
 5 R₁₂ or R₁₃, comprises a positively charged N-substituted C₁-C₅heteroaryl group.

M₁ is a cation in the oxidation state +3, a hydroxy or halogen metal cation wherein the metal is in the oxidation state +4, or an oxo metal cation wherein the metal is in the oxidation state +5, of an at least trivalent metal of groups 3 to 15 (formerly groups IIIA to VB), preferably Al³⁺, As³⁺, Au³⁺, Bi³⁺, Ce³⁺, Co³⁺, Cr³⁺, Dy³⁺, Er³⁺,
 10 Eu³⁺, Fe³⁺, Gd³⁺, Ho³⁺, Ir³⁺, La³⁺, Lu³⁺, Mn³⁺, Mo³⁺, Nb³⁺, Nd³⁺, Pm³⁺, Pr³⁺, Rh³⁺, Ru³⁺, Sb³⁺, Sc³⁺, Sm³⁺, Ta³⁺, Tb³⁺, Ti³⁺, [TiCl]³⁺, [TiOH]³⁺, Tm³⁺, V³⁺, [VO]³⁺, W³⁺, Y³⁺, Yb³⁺, [ZrCl]³⁺ or [ZrOH]³⁺, most preferred Co³⁺ or Cr³⁺.

Alkyl, alkenyl or alkynyl may be straight-chain or branched. Alkenyl is alkyl that is mono- or poly-unsaturated, wherein two or more double bonds may be isolated or
 15 conjugated. Alkynyl is alkyl or alkenyl that is doubly-unsaturated one or more times, wherein the triple bonds may be isolated or conjugated with one another or with double bonds. Cycloalkyl or cycloalkenyl is monocyclic or polycyclic alkyl or alkenyl, respectively.

C₁-C₁₂Alkyl can therefore be, for example, methyl, ethyl, n-propyl, isopropyl,
 20 n-butyl, sec-butyl, isobutyl, tert-butyl, 2-methyl-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, n-hexyl, heptyl, n-octyl, 1,1,3,3-tetramethylbutyl, 2-ethylhexyl, nonyl, decyl, undecyl or dodecyl.

C₃-C₁₂Cycloalkyl can therefore be, for example, cyclopropyl, cyclopropyl-methyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclohexyl-methyl, trimethylcyclohexyl, thujyl,
 25 norbornyl, bornyl, norcaryl, caryl, menthyl, norpinyl, pinyl, 1-adamantyl or 2-adamantyl.

C₂-C₁₂Alkenyl is, for example, vinyl, allyl, 2-propen-2-yl, 2-buten-1-yl, 3-buten-1-yl, 1,3-butadien-2-yl, 2-penten-1-yl, 3-penten-2-yl, 2-methyl-1-buten-3-yl, 2-methyl-

- 9 -

3-buten-2-yl, 3-methyl-2-buten-1-yl, 1,4-pentadien-3-yl, or any isomer of hexenyl, octenyl, nonenyl, decenyl or dodecenyl.

C₃-C₁₂Cycloalkenyl is, for example, 2-cyclobuten-1-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 camphenyl.

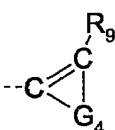
C₂-C₁₂Alkynyl is, for example, 1-propyn-3-yl, 1-butyln-4-yl, 1-pentyn-5-yl, 2-methyl-3-butyln-2-yl, 1,4-pentadiyn-3-yl, 1,3-pentadiyn-5-yl, 1-hexyn-6-yl, cis-3-methyl-2-penten-4-yn-1-yl, trans-3-methyl-2-penten-4-yn-1-yl, 1,3-hexadiyn-5-yl, 1-octyn-8-yl, 1-nonyn-9-yl, 1-decyn-10-yl or 1-dodecyn-12-yl.

C₇-C₁₂Aralkyl is, for example, benzyl, 2-benzyl-2-propyl, β -phenyl-ethyl, 9-fluorenyl, α,α -dimethylbenzyl, ω -phenyl-butyl, ω -phenyl-octyl, ω -phenyl-dodecyl or 3-methyl-5-(1',1',3',3'-tetramethyl-butyl)-benzyl. When C₇-C₁₂aralkyl is substituted, both the alkyl moiety and the aryl moiety of the aralkyl group can be substituted, the latter alternative being preferred.

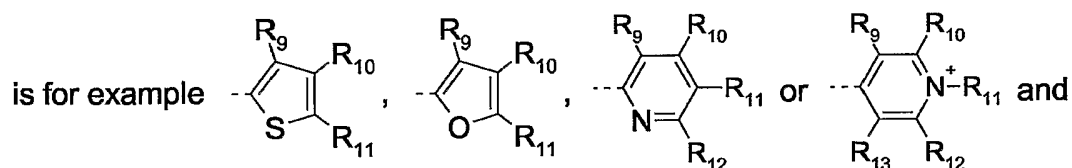
C₆-C₁₂Aryl is, for example, phenyl, naphthyl or biphenyl, always preferred phenyl.

Halogen is chlorine, bromine, fluorine or iodine, preferably chlorine or bromine on aryl or heteroaryl and fluorine on alkyl.

C₁-C₉Heteroaryl is an unsaturated or aromatic radical having 4n+2 conjugated π -electrons, for example 2-thienyl, 2-furyl, 1-pyrazolyl, 2-pyridyl, 2-thiazolyl, 2-oxazolyl, 2-imidazolyl, isothiazolyl, triazolyl, tetrazolyl or any other ring system consisting of thiophene, furan, thiazole, oxazole, imidazole, isothiazole, thiadiazole, triazole, pyridine, pyrazine, pyrimidine, pyridazine and benzene rings and unsubstituted or substituted by from 1 to 6 ethyl substituents, for example methyl, ethylene and/or

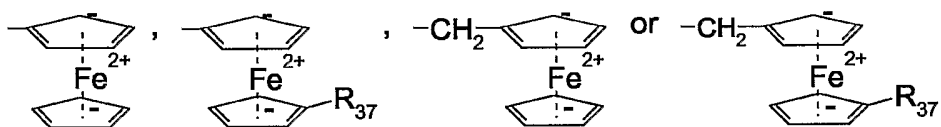
25 methylene substituents. Heterocyclic  substituted by R₁₀, R₁₁, R₁₂ and R₁₃

- 10 -



provides highly surprisingly an improved sensitivity (with sufficient thermal interference control) at high recording speeds, as compared with aryl groups.

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 especially



wherein R_{37} is CH_2OH , $\text{CH}_2\text{OR}_{24}$ or COOR_{24} .

$\text{C}_3\text{-C}_{12}$ Heterocycloalkyl is an unsaturated or partially unsaturated ring system radical, for example epoxy, oxetan, aziridine; tetrazolyl, pyrrolidyl, piperidyl, piperazinyl, imidazolyl, pyrazolidinyl, pyrazolyl, morpholinyl, quinuclidinyl; or some other $\text{C}_4\text{-C}_{12}$ heteroaryl that is mono- or poly-hydrogenated.

5- to 12-membered rings are, for example, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl, preferably cyclopentyl and especially cyclohexyl.

The quinoid structure with double bonds to R_2 and R_6 is of course only one mesomeric form of the compound of formula (I), but it is the most likely structure in view of the spectroscopic data. There may alternatively also be drawn a phenylazo with a single bond to R_2 or R_6 and a negative charge on R_2 or R_6 , which may further be protonated through tautomerism. Nevertheless, the electronic delocalisation through mesomerism is an essential feature of the invention and advantageously stabilizes the anion through additional bonds with the metal. Thus, R_2 and/or R_6 are preferably O, S, N-CN or N-SO₂CF₃, especially preferred O.

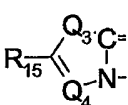
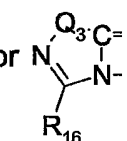
Either in combination with preferred R_2 and/or R_6 or independently thereof, R_3

- 11 -

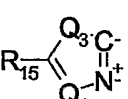
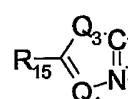
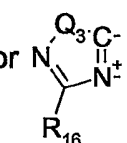
and/or R_7 are much preferably H, halogen, CF_3 , NO_2 , CN, COR_{22} , $COOR_{23}$, SO_3R_{23} , NCO or SCN, most preferably H. Independently from the counter ion's structure, these preferred substituents surprisingly lead to an improved light and multiple read stability when used in optical recording media, either as the main recording dye or
 5 as an additive for other recording dyes, too.

It is especially preferred that, either in combination with preferred R_2 , R_3 , R_6 and/or R_7 or independently thereof, preferably in the heterocycle comprising G_1 or G_2 , at least one of R_{15} and R_{17} , especially R_{15} , is CF_3 , NO_2 , CN, COR_{22} , $COOR_{23}$, $CR_{22}OR_{25}OR_{28}$, $CONR_{26}R_{27}$, SO_2R_{22} , SO_3R_{23} , $SO_2NR_{26}R_{27}$ or $PO(OR_{22})(OR_{25})$,
 10 most preferred CF_3 , NO_2 , CN, COR_{22} , $COOR_{23}$, SO_2R_{22} and/or SO_3R_{23} . Though both R_{15} and R_{17} may be such preferred groups, preferably only one of them is a preferred group and the other is hydrogen or C_1 - C_4 alkyl, or R_{15} and R_{17} are together butadienylen either unsubstituted or substituted, preferably unsubstituted or substituted by CF_3 , NO_2 , CN, COR_{22} , $COOR_{23}$ and/or SO_3R_{23} .

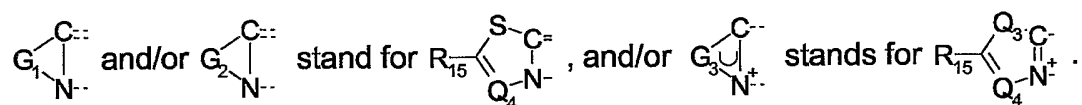
15 Preferably, either in combination with preferred R_2 , R_3 , R_6 , R_7 , R_{15} and/or R_{17} or independently thereof, especially in the heterocycle comprising G_3 , R_{16} is H or F, or together with R_{15} is butadienylen either unsubstituted or substituted, preferably unsubstituted or substituted by one or more C_1 - C_4 alkyl, halogen, OR_{23} , SR_{23} , $NR_{22}R_{25}$, CF_3 , NO_2 , CN, COR_{22} , $COOR_{23}$, SO_2R_{22} and/or SO_3R_{23} .

20 Q_3 is preferably S or $CR_{20}R_{21}$, more preferably S in  or  standing

for  and/or , and/or $CR_{20}R_{21}$, in particular C_3 - C_6 alkyliden or C_3 - C_6 cycloalkyliden, (even more preferably 1-cyclohexyliden or especially 2-butyliden — that is, $CR_{20}R_{21}$ wherein R_{20} and R_{21} together = 1,5-pentylen or R_{20} = methyl / R_{21} = ethyl,

respectively), in   or  standing for . Most preferably,

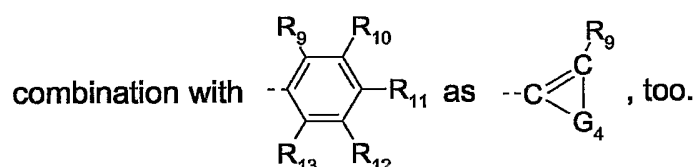
- 12 -



Q₅ and Q₇ are preferably S. These preferences are independent of the preferred R₂, R₃, R₆, R₇, R₁₅, R₁₆ and/or R₁₇; however, the preferences disclosed herebefore for R₂, R₃, R₆, R₇, R₁₅, R₁₆ and/or R₁₇ are fully applicable with particular benefits in

5 the case of preferred $G_1 \begin{array}{c} \text{C} \\ | \\ \text{N} \end{array}$ and/or $G_2 \begin{array}{c} \text{C} \\ | \\ \text{N} \end{array}$, Q₅ and Q₇, too.

All above-mentioned preferences are fully applicable especially in further



The preferences for the cationic and anionic sub-structures contained in formula (I) are independent of each other. However, it is preferable to combine preferred cations with preferred anions.

Further preference is given to compounds of formula (I) wherein R₄ is hydrogen, hydroxy, C₁-C₄alkoxy or C₁-C₄alkyl; R₁₅ is nitro or cyano, preferably nitro; and/or R₂₂ or R₂₄ are methyl, ethyl, n-propyl, isopropyl, n-butyl, 2-butyl, isobutyl, tert-butyl, 3-pentyl, n-amyl, tert-amyl, neopentyl, 2,2-dimethyl-but-4-yl, cyclopropyl, cyclopropylmethyl, cyclobutyl, cyclobutylmethyl, cyclopentyl, cyclopentylmethyl or cyclohexyl, each unsubstituted or mono- or poly-substituted by fluorine. R₂₀ and R₂₁ are preferably both methyl, both ethyl or R₂₀ ethyl and R₂₁ methyl, or both together 1,5-pentylene. Alkyl, alkenyl, alkynyl, cycloalkyl and heterocycloalkyl are generally preferably C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl and epoxyalkyl, respectively. All these further preferences are fully applicable with particular benefits in the case of

preferred R₂, R₃, R₆, R₇, R₁₅, R₁₆ and/or R₁₇ as well as $G_1 \begin{array}{c} \text{C} \\ | \\ \text{N} \end{array}$ and/or $G_2 \begin{array}{c} \text{C} \\ | \\ \text{N} \end{array}$, Q₅ and Q₇, too.

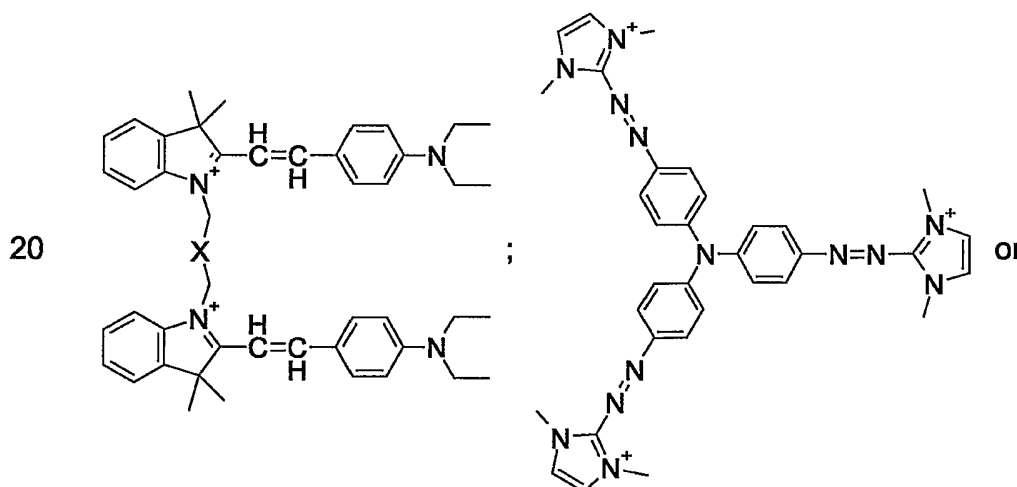
- 13 -

When R_{22} , R_{25} and R_{28} are bonded to one another in pairs by way of a direct bond or an -O-, -S- or -NR₃₅- bridge, they are preferably so bonded that a five- or six-membered ring is formed.

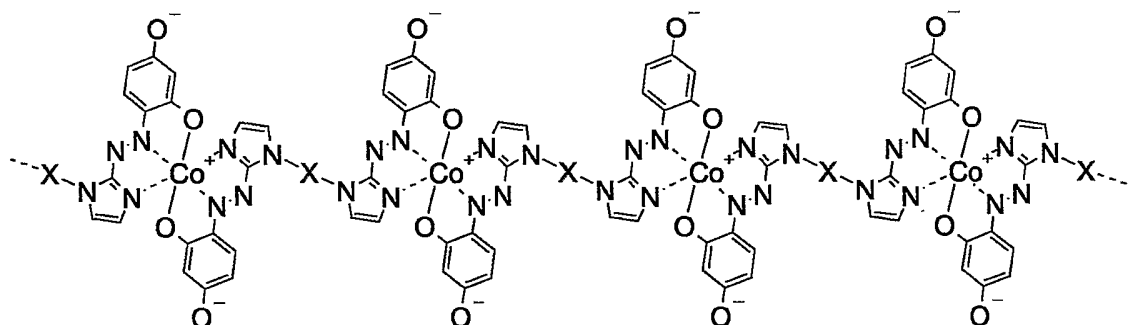
Another aspect of the invention are compounds of formula (I) wherein two cations or two ligands of the anion are bridged, for example by way of direct bonds or -O-, -S- or -NR₃₅- bridges between any substituents in formula (I), it being possible for the bridged ligands to be complexed either with the same metal cation or optionally with different metal cations, there being formed in the latter case oligomers which are, of course, also to be regarded as being subjects of the invention. Bridgings by way of O or N atoms of the cation or anion, either those in the chromophore or those on substituents, are especially advantageous.

Dimers and trimers can be made purposefully in close analogy to methods which are known *per se*. They may be either symmetrical or preferably asymmetrical, comprising 2 or 3 different moieties of formula (I) linked together by bonds and/or bridges. Oligomer are constituted for example of 4 to 12 moieties of formula (I) all linked together.

Such dimer, trimer or higher formation is illustrated by the following examples (which are on no account limiting) wherein X may be, for example, -CH₂-, -CH₂-CH₂-, -CH₂-O-CH₂- or -CH₂-NH-CH₂- :



- 14 -



Of course, in oligomers the stoichiometry should be such that the resulting compound of formula (I) is not charged. Such and similar oligomers can also prepared unintentionally together with the monomeric compounds, in which case

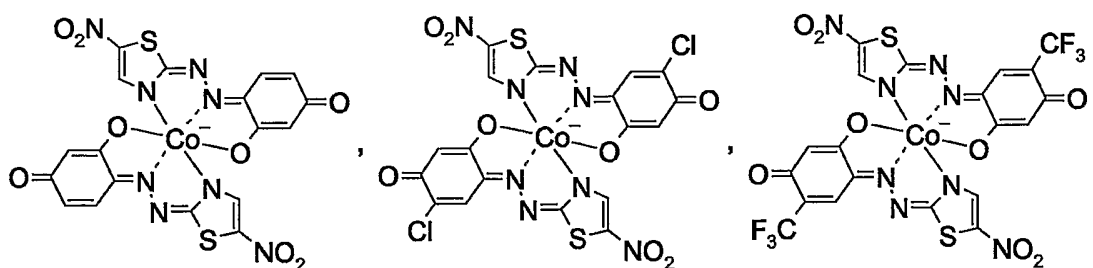
5 they can be separated by known methods. The formation of monomers or oligomers can be favoured by usual means through control of the reaction conditions, in particular the respective concentrations of the reagents and the sequence and speed of addition.

The recording medium according to the invention, in addition to comprising the compounds of formula (I), may additionally comprise salts, for example ammonium

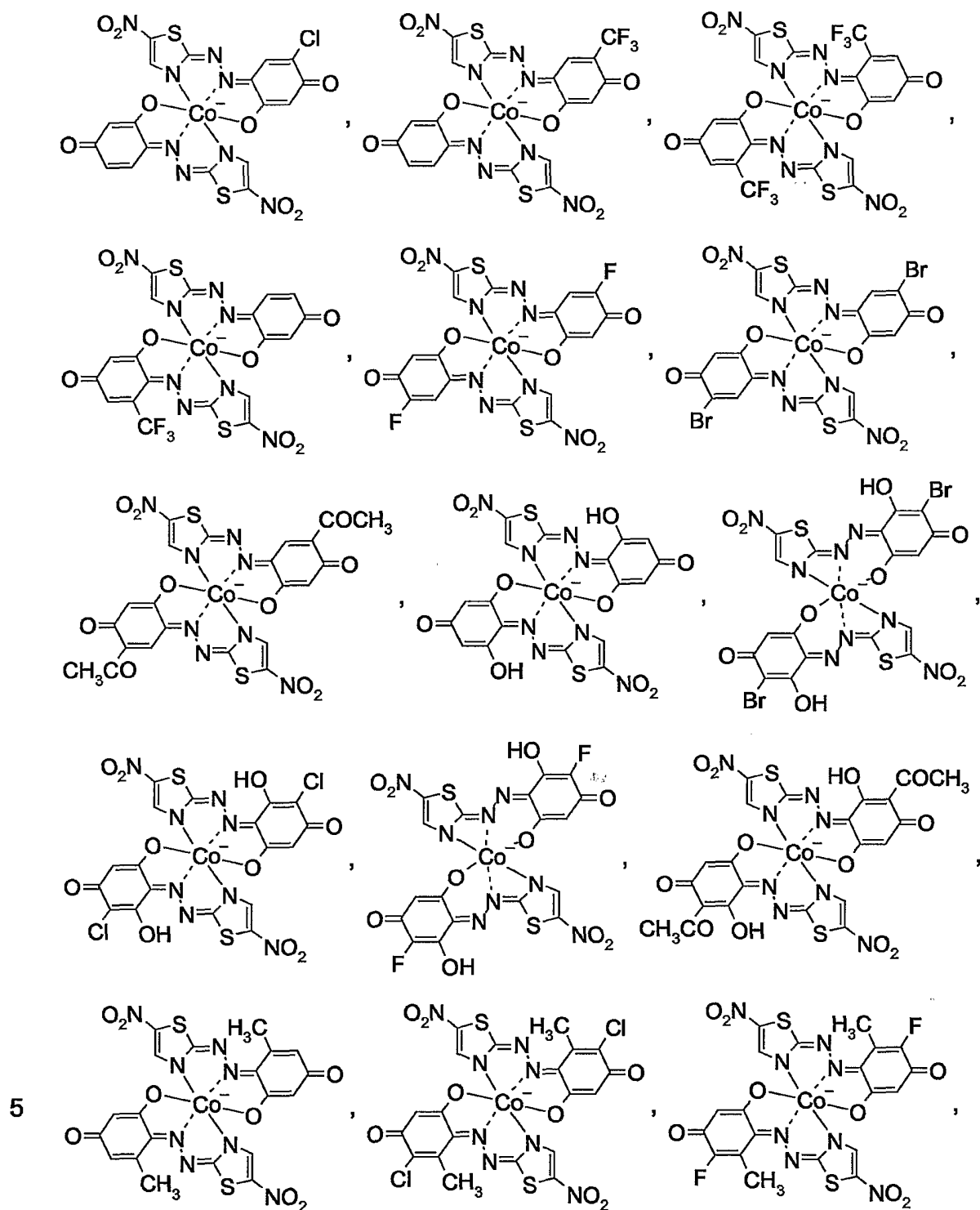
10 chloride, pentadecylammonium chloride, sodium chloride, sodium iodide, sodium sulfate, sodium hydrogen sulfate, sodium methyl sulfate, sodium methylsulfonate, sodium tosylate, sodium acetate, sodium hexafluorophosphate, cobalt(II) acetate or cobalt(II) chloride, the ions of which may, for example, originate from the

15 components used.

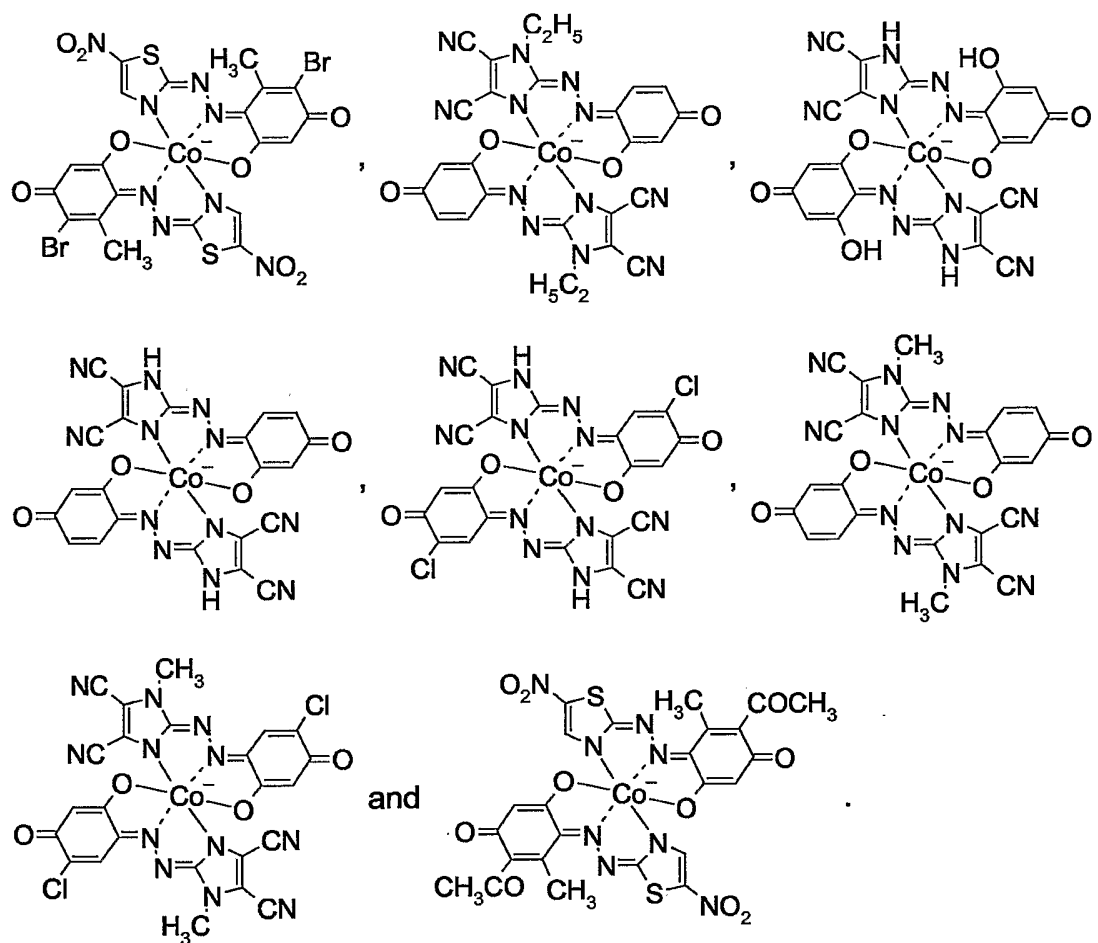
Interesting anions of formula (I) are especially those of the following formulae (all six bonds to the metal have similar length according to the X-ray data):



- 15 -



- 16 -



- Interesting compounds of formula (I), wherein one or more of R₁ to R₄ is different from the corresponding R₅ to R₈ and/or wherein G₁ is different from G₂ may be prepared simply by mixed synthesis, two different ligands being metallated at the same time. The compounds of formula (I) having asymmetric ligands can either be isolated by customary methods, such as chromatography, or preferably used in admixture with the compounds of formula (I) having two identical ligands.
- 10 Acta Poloniae Pharmaceutica 49/5, 55-61 [1992] discloses the complexation of metal ions with Atidarez-β and Atidarez-γ. It is disclosed that strong bases and acids lead to decomposition and that tentatives to isolate metal complexes through extraction with various organic solvents failed.

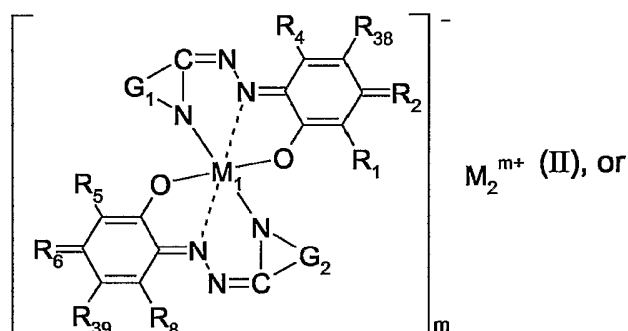
The compounds of formula (I) are new. Some of their components are known, in

- 17 -

particular the styryl cation part, for example from US-6 103 331. The metal complex anions are partially new but can be prepared in close analogy to known metal complexes by methods known *per se*. The final salts of formula (I) are simply prepared by mixing each a soluble salt of the cation and anion. Hence, the invention also

5 pertains to a compound of formula (I) or a tautomeric or mesomeric form thereof.

Also new is a compound of formula



a mesomer or tautomer thereof, wherein

R_{38} is halogen, CF_3 , NO_2 , CN , COR_{22} , $COOR_{23}$, SO_3R_{23} , NCO or SCN ,

R_{39} is R_7 as defined in formula (I), preferably H , halogen, CF_3 , NO_2 , CN , COR_{22} ,
 10 $COOR_{23}$, SO_3R_{23} , NCO or SCN ,

G_1 , G_2 , M_1 , R_1 , R_2 , R_4 , R_5 , R_6 , R_8 , R_{22} and R_{23} are as defined in formula (I),

M_2^{m+} is a cation with m positive charges, and m is an integer 1, 2 or 3.

M_2^{m+} is for example a proton, a suitable metal, ammonium or phosphonium cation or a positively charged organic or organometallic chromophore as mentioned
 15 above.

The compounds of formula (II) are especially useful as stabilizers in the recording layer of optical recording media, particularly in combination either with the instant compounds of formula (I) or with any other, known dyes such as those mentioned herein below.

20 The substrate, which acts as support for the layers applied thereto, is

- 18 -

advantageously semi-transparent ($T \geq 10\%$) or preferably transparent ($T \geq 90\%$).
The support can be from 0.01 to 10 mm thick, preferably from 0.1 to 5 mm thick.

The recording layer is preferably arranged between the transparent substrate and the reflecting layer. The thickness of the recording layer is from 10 to 1000 nm, preferably from 30 to 300 nm, especially about 80 nm, for example from 60 to 120 nm. The absorption of the recording layer is typically from 0.1 to 1.0 at the absorption maximum (up to 1.5 in dual layer). The layer thickness is very especially so chosen in known manner in dependence upon the respective refractive indices in the non-written state and in the written state at the reading wavelength that in the non-written state constructive interference is obtained, but in the written state destructive interference is obtained, or *vice versa*.

The reflecting layer, the thickness of which can be from 10 to 150 nm, preferably has high reflectivity ($R \geq 45\%$, especially $R \geq 60\%$), coupled with low transparency ($T \leq 10\%$). In further embodiments, for example in the case of media having a plurality of recording layers, the reflector layer may likewise be semi-transparent, that is to say may have comparatively high transparency (for example $T \geq 50\%$) and low reflectivity (for example $R \leq 30\%$).

The uppermost layer, for example the reflective layer or the recording layer, depending upon the layer structure, is advantageously additionally provided with a protective layer having a thickness of from 0.1 to 1000 μm , preferably from 0.1 to 50 μm , especially from 0.5 to 15 μm . Such a protective layer can, if desired, serve also as adhesion promoter for a second substrate layer applied thereto, which is preferably from 0.1 to 5 mm thick and consists of the same material as the support substrate.

The reflectivity of the entire recording medium is preferably at least 15%, especially at least 40%.

The main features of the recording layer according to the invention are the very high initial reflectivity in the said wavelength range of the laser diodes, which can

- 19 -

be modified with great sensitivity; the high refractive index; the especially narrow absorption band in the solid state; the good uniformity of the script width at different pulse durations; as well the good light stability and the good solubility in polar solvents.

- 5 The recording medium according to the invention is neither writable nor readable using the infra-red laser diodes of customary CD apparatus in accordance with the requirements of the Orange Book Standard. As a result, the risk of damage in the event of an erroneous attempt at writing using an apparatus not capable of high resolution is largely averted, which is of advantage. The use of dyes of formula (I)
- 10 results in advantageously homogeneous, amorphous and low-scatter recording layers having a high refractive index, and the absorption edge is surprisingly especially steep even in the solid phase. Further advantages are high light stability in daylight and under laser radiation of low power density with, at the same time, high sensitivity under laser radiation of high power density, uniform script width,
- 15 high contrast, and also good thermal stability and storage stability.

At a high recording speed (for example 2×, 4×, 8× or 16×, preferably 8× or 16×, corresponding to a range of about 20 to 60 m·s⁻¹), the results obtained are surprisingly better than with previously known recording media. The marks are more precisely defined relative to the surrounding medium, and thermally induced

20 deformations do not occur. The error rate (PI Sum 8) and the statistical variations in mark lengths (jitter) are also low both at normal recording speed and at elevated recording speed, so that an error-free recording and playback can be achieved over a wide range of speeds. There are virtually no rejects even at high recording speed, and the reading of written media is not slowed down by the correction of errors. The

25 advantages are obtained over the entire range from 600 to 700 nm (preferably from 630 to 690 nm), but are especially marked at from 640 to 680 nm, more especially from 650 to 670 nm, particularly at 658 ± 5 nm.

Suitable substrates are, for example, glass, minerals, ceramics and thermosetting or thermoplastic plastics. Preferred supports are glass and homo- or co-polymeric

30 plastics. Suitable plastics are, for example, thermoplastic polycarbonates, poly-

- 20 -

amides, polyesters, polyacrylates and polymethacrylates, polyurethanes, poly-olefins, polyvinyl chloride, polyvinylidene fluoride, polyimides, thermosetting polyesters and epoxy resins. The substrate can be in pure form or may also comprise customary additives, for example UV absorbers or dyes, as proposed e.g. in
5 JP 04/167 239 to provide light-stabilisation for the recording layer. In the latter case it may be advantageous for the dye added to the support substrate to have an absorption maximum hypsochromically shifted relative to the dye of the recording layer by at least 10 nm, preferably by at least 20 nm.

The substrate is advantageously transparent over at least a portion of the range
10 from 600 to 700 nm (preferably as indicated above), so that it is permeable to at least 90% of the incident light of the writing or readout wavelength. The substrate has preferably on the coating side a spiral guide groove having a groove depth of from 50 to 500 nm, a groove width of from 0.2 to 0.8 μm and a track pitch between two turns of from 0.4 to 1.6 μm , especially having a groove depth of from 100 to
15 200 nm (or from 20 to 60 nm in dual layer), a groove width of from $0.35 \pm 0.10 \mu\text{m}$ and a pitch between two turns of from 0.6 to 0.8 μm . The recording layer is advantageously of different thickness in and outside the groove, depending upon the depth of the groove; the thickness of the recording layer in the groove is usually about from 2 to 20 $\times$ greater than outside, typically 5-10 $\times$ greater in the groove than
20 outside. The recording layer can also be present exclusively in the groove.

The storage media according to the invention are therefore suitable especially advantageously for the optical recording of DVD media having the currently customary minimum pit length of 0.4 μm and track pitch of 0.74 μm . The increased recording speed relative to known media allows synchronous recording or, for
25 special effects, even accelerated recording of video sequences with excellent image quality.

The recording layer, instead of comprising a single compound of formula (I), may alternatively comprise a mixture of such compounds having, for example, 2, 3, 4 or 5 metal azo dyes according to the invention. By the use of mixtures, for example

- 21 -

mixtures of isomers or homologues as well as mixtures of different structures, often the solubility can be increased and/or the amorphous content improved. If desired, mixtures of ion pair compounds may have different anions, different cations or both different anions and different cations.

- 5 It is also judicious to use the instant compounds of formula (I) in admixtures with one or more salts of the cation of formula (I) with a suitable inorganic, organic or organometallic anion, and/or with one or more salts of the anion of formula (I) with a proton, a suitable metal, ammonium or phosphonium cation or a positively charged organic or organometallic chromophore. In many cases, the optical
- 10 properties still remain satisfactory while the solubility and amorphicity of the solid layer can be improved. Compounds of formula (II) provide a particular benefit.

Suitable anions are, for example, hydroxide, oxide, fluoride, chloride, bromide, iodide, perchlorate, periodate, carbonate, hydrogen carbonate, sulfate, hydrogen sulfate, phosphate, hydrogen phosphate, dihydrogen phosphate, tetrafluoroborate,

15 hexafluoroantimonate, acetate, oxalate, methanesulfonate, trifluoromethanesulfonate, tosylate, methyl sulfate, phenolate, benzoate or a negatively charged metal complex.

Metal, ammonium or phosphonium cations are, for example, Ca^{2+} , Co^{2+} , Co^{3+} , Cr^{3+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , K^+ , La^{3+} , Li^+ , Mg^{2+} , Na^+ , Ni^{2+} , Sn^{2+} , Zn^{2+} , methylammonium,

20 ethylammonium, pentadecylammonium, isopropylammonium, dicyclohexylammonium, tetramethylammonium, tetraethylammonium, tetrabutylammonium, benzyltrimethylammonium, benzyltriethylammonium, methyltrioctylammonium, tridodecylmethylammonium, tetrabutylphosphonium, tetraphenylphosphonium, butyltriphenylphosphonium or ethyltriphenylphosphonium, or protonated Primene

25 81R™ or Rosin Amine D™. Preference is given to H^+ , Na^+ , K^+ , NH_4^+ , primary, secondary, tertiary or quaternary ammonium and also to cationic chromophores, especially those mentioned below, as well as cations of the additional chromophores mentioned below (obtainable for example through quaternisation of N). Other metal cations, such as those disclosed hereinbefore for M_1 , are also suitable.

- 22 -

As positively charged organic chromophores there may be used any cations that absorb in the range of from 300 to 1500 nm, especially in the range of from 300 to 800 nm. The person skilled in the art will preferably select especially chromophore cations that have already been previously proposed for use in optical information media, for example cyanine, xanthene, dipyrromethene, styryl, triphenylmethine, azo, metal complex, quinone diimmonium, bipyridinium and other cations. Cyanine, xanthene (for example those of US-5 851 621, WO-03/098 617 or WO-03/098 618), dipyrromethene and azo metal complex cations are preferred. Further chromophores suitable for use in cationic form are known from WO-01/75873, but those examples are on no account to be regarded as a limiting selection.

For a further increase in stability it is also possible, if desired, to add known stabilisers in customary amounts, for example a nickel dithiolate described in JP 04/025 493 as light stabiliser.

The recording layer comprises a compound of formula (I) or a mixture of such compounds advantageously in an amount sufficient to have a substantial influence on the refractive index, for example at least 10% by weight, preferably at least from 30 to 70% by weight, especially at least from 40 to 60% by weight. The recording layer can especially valuably comprise a compound of formula (I) or a mixture of a plurality of such compounds as main component, or may consist exclusively or substantially of one or more compounds of formula (I).

Further customary constituents are possible, for example other chromophores (for example those having an absorption maximum at from 300 to 1000 nm), UV absorbers and/or other stabilisers, $^1\text{O}_2$ -, triplet- or luminescence-quenchers, melting-point reducers, decomposition accelerators or any other additives that have already been described in optical recording media, for example film-formers.

When the recording layer comprises further chromophores, such chromophores may in principle be any dyes that can be decomposed or modified by the laser radiation during the recording, or they may be inert towards the laser radiation. When the further chromophores are decomposed or modified by the laser radiation,

- 23 -

this can take place directly by absorption of the laser radiation or can be induced indirectly by the decomposition of the compounds of formula (I) according to the invention, for example thermally.

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

10 When further chromophores having optical properties that conform as far as possible to those of compounds of formula (I) are used, preferably this should apply in the range of the longest-wavelength absorption flank. Preferably the wavelengths of the inversion points of the further chromophores and of the compounds of formula (I) are a maximum of 40 nm, especially a maximum of 20 nm, more especially a maximum of 10 nm, apart. In that case the further chromophores and
15 the compounds of formula (I) should exhibit similar behaviour in respect of the laser radiation, so that it is possible to use as further chromophores known recording agents the action of which is synergistically enhanced or heightened by the compounds of formula (I).

20 When further chromophores or coloured stabilisers having optical properties that are as different as possible from those of compounds of formula (I) are used, they advantageously have an absorption maximum that is hypsochromically or bathochromically shifted relative to the dye of formula (I). In that case the absorption maxima are preferably at least 50 nm, especially at least 100 nm, apart. Examples thereof are UV absorbers that are hypsochromic to the dye of formula (I)
25 or coloured stabilisers that are bathochromic to the dye of formula (I) and have absorption maxima lying, for example, in the NIR or IR range. Other dyes can also be added for the purpose of colour-coded identification, colour-masking ("diamond dyes") or enhancing the aesthetic appearance of the recording layer. In all those cases, the behaviour of the further chromophores or coloured stabilisers towards
30 light and laser radiation should preferably be as inert as possible.

- 24 -

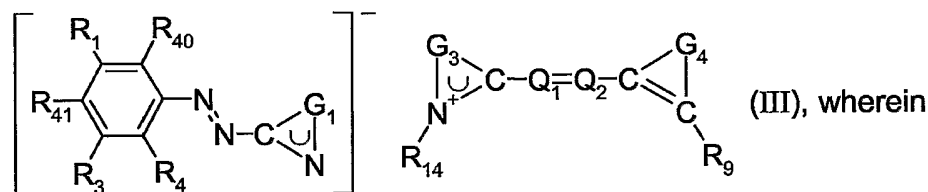
When another dye is added in order to modify the optical properties of the compounds of formula (I) the amount thereof is dependent upon the optical properties to be achieved. The person skilled in the art will find little difficulty in varying the ratio of additional dye to compound of formula (I) until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

- 5 When chromophores or coloured stabilisers are used for other purposes, the amount thereof should preferably be small so that their contribution to the total absorption of the recording layer in the range of from 600 to 700 nm is a maximum of 20%, preferably a maximum of 10%. In such a case, the amount of additional dye or stabiliser is advantageously a maximum of 50% by weight, preferably a
10 maximum of 10% by weight, based on the recording layer.

- Further chromophores which can optionally be used in the recording layer in addition to the compounds of formula (I) are, for example, cyanines also including zwitterions (EP-A-1 464 678) and metal complexes thereof (US-5 958 650), oxonol dyes (EP-A-833 314), azo dyes and azo metal complexes (JP-A-11/028865),
15 phthalocyanines (EP-A-232 427, EP-A-337 209, EP-A-373 643, EP-A-463 550, EP-A-492 508, EP-A-509 423, EP-A-511 590, EP-A-513 370, EP-A-514 799, EP-A-518 213, EP-A-519 419, EP-A-519 423, EP-A-575 816, EP-A-600 427, EP-A-676 751, EP-A-712 904, WO-98/14520, WO-00/09522, CH-693/01), porphyrins and azaporphyrins (EP-A-822 546, US-5 998 093), dipyrromethene
20 dyes and metal chelate compounds thereof (EP-A-822 544, EP-A-903 733), xanthene dyes and metal complex salts thereof (US-5 851 621) or quadratic acid compounds (EP-A-568 877), or oxazines, dioxazines, diazastyrils, formazans, anthraquinones or phenothiazines; this list is on no account exhaustive and the person skilled in the art will interpret the list as including further known dyes.
- 25 Especially preferred additional chromophores are especially cyanines and xanthenes. Of the cyanines, preference is given to benzoindocarbocyanines, and of the xanthenes especially rhodamines.

It is very especially preferred, however, that no additional chromophore is added, unless it is a coloured stabiliser or a compound of formula

- 25 -



one of R_{40} and R_{41} is $NR_{42}R_{43}$, $NR_{43}R_{44}$, $NR_{44}R_{45}$, OR_{42} , SR_{42} , OR_{44} or SR_{44} , and the other of R_{40} and R_{41} is O^- , S^- or N^-R_{46} ;

R_{42} and R_{43} are each independently of the other C_1 - C_{12} alkyl, C_2 - C_{12} alkenyl,

- 5 C_2 - C_{12} alkynyl, C_3 - C_{12} cycloalkyl, C_3 - C_{12} cycloalkenyl or C_2 - C_{11} heterocycloalkyl each unsubstituted or mono- or poly-substituted by halogen, OR_{47} , SR_{47} , $CR_{48}OR_{49}OR_{50}$, $NR_{48}R_{51}$, $NR_{48}COR_{49}$, $NR_{48}COOR_{47}$, $NR_{48}CONR_{52}R_{53}$, $NR_{48}CN$, COR_{48} , NO_2 , CN , $COOR_{47}$, $CONR_{52}R_{53}$ and/or SO_2R_{52} ; or

R_{42} and R_{43} are together C_2 - C_{12} alkylen, C_2 - C_{12} alkenylen, C_2 - C_{12} cycloalkylen or

- 10 C_2 - C_{12} cycloalkenylen, one to five non-successive carbon atoms of which can be replaced by oxygen and/or sulfur atoms and/or by identical or different groups NR_{46} , C_2 - C_{12} alkylen, C_2 - C_{12} alkenylen, C_2 - C_{12} cycloalkylen or C_2 - C_{12} cycloalkenylen being each unsubstituted or mono- or poly-substituted by halogen, OR_{47} , SR_{47} , $NR_{48}R_{51}$, $NR_{48}COR_{49}$, $NR_{48}COOR_{47}$, $NR_{48}CONR_{52}R_{53}$, $NR_{48}CN$, COR_{48} ,
15 $CR_{48}OR_{49}OR_{50}$, NO_2 , CN , $COOR_{47}$, $CONR_{52}R_{53}$ and/or SO_2R_{52} ;

R_{44} , R_{45} and R_{46} are each independently of the others H , COR_{51} , $CONR_{52}R_{53}$, CN , $SO_2NR_{52}R_{53}$ or SO_2R_{52} , preferably R_{44} and/or R_{45} are H and R_{46} is COR_{51} , $CONR_{52}R_{53}$, CN , $SO_2NR_{52}R_{53}$ or SO_2R_{52} ;

each R_{47} , independently of any other R_{47} , is R_{51} or R_{46} , preferably H ;

- 20 R_{48} , R_{49} and R_{50} are each independently of the others hydrogen; C_1 - C_4 alkyl, C_2 - C_4 alkenyl, C_2 - C_4 alkynyl, $[C_2$ - C_3 alkylene- O] $_p$ - R_{54} or $[C_2$ - C_3 alkylene- NR_{55}] $_p$ - R_{54} each unsubstituted or mono- or poly-substituted by halogen; or benzyl;

R_{51} , R_{52} and R_{53} are each independently of the others H ; C_1 - C_6 alkyl, C_2 - C_6 alkenyl, C_2 - C_6 alkynyl, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkenyl or C_2 - C_5 heterocycloalkyl each

- 26 -

unsubstituted or mono- or poly-substituted by halogen, OR₄₇, SR₄₇, NR₄₈R₅₀, CN and/or COOR₄₈; or C₆-C₁₀aryl, C₇-C₁₁alkyl or C₁-C₅heteroaryl each unsubstituted or mono- or poly-substituted by C₁-C₄alkyl, halogen, OR₄₇, SR₄₇, NR₄₈R₄₉, COR₄₈, CR₄₈OR₄₉OR₅₀, NO₂, CN and/or COOR₅₀;

- 5 or NR₄₈R₄₉, NR₄₈R₅₁, NR₄₉R₅₀ or NR₅₂R₅₃ is a five- or six-membered heterocycle which may contain a further N or O atom and which can be mono- or poly-substituted by methyl or ethyl;

R₅₄ and R₅₅ are each independently of the other methyl, ethyl, vinyl and/or allyl;

- 10 it being possible once or more times radicals of the same or different substituents each selected from the group consisting of R₁, R₃, R₄, R₄₀, R₄₁, R₄₂, R₄₅, R₄₆, R₄₇, R₄₈, R₄₉, R₅₀, R₅₁, R₅₂ and R₅₄ to be bonded to one another in pairs by way of a direct bond or an -O-, -S- or -N(R₅₅)- bridge; and

p is an integer from 1 to 4.

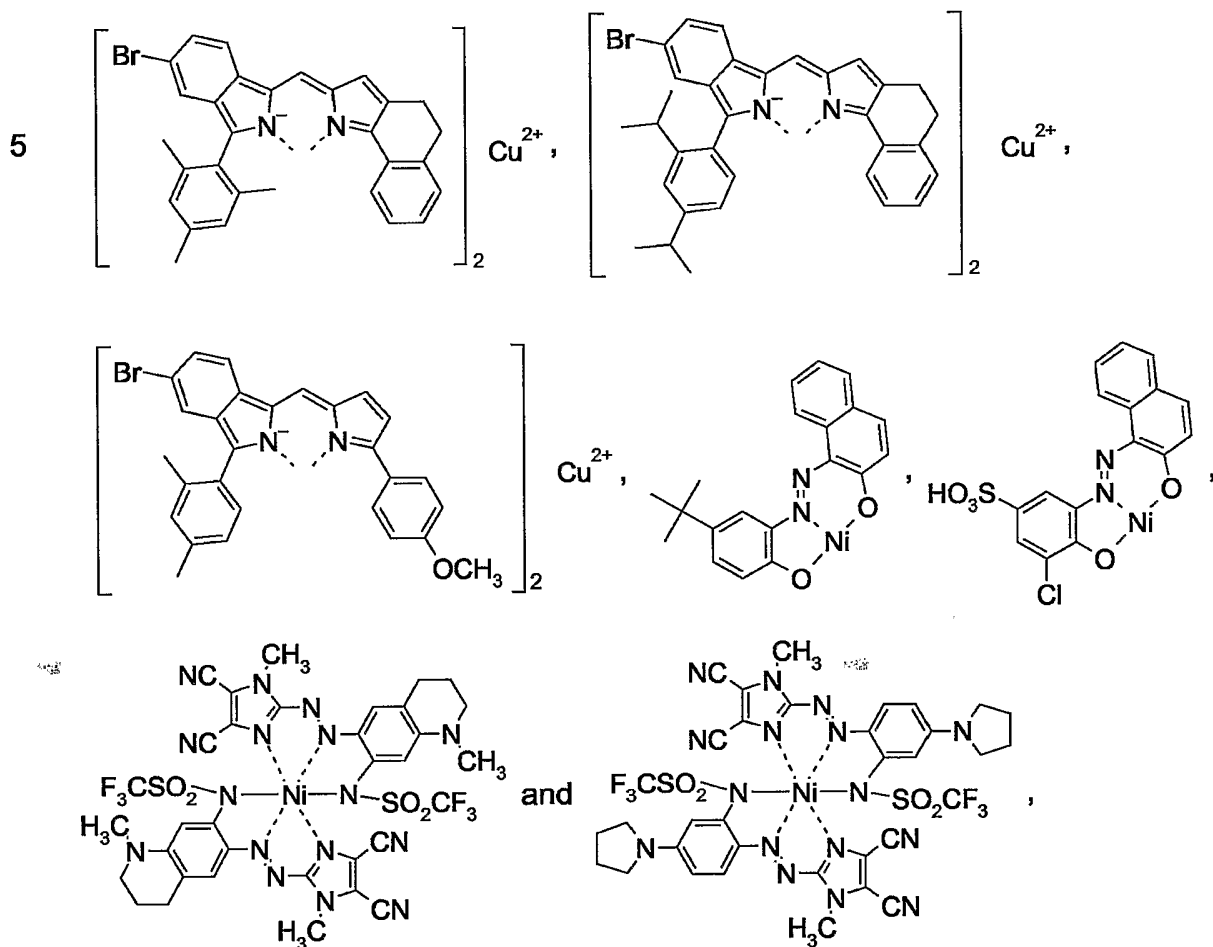
- 15 Stabilisers or fluorescence-quenchers are, for example, metal complexes of N- or S-containing enolates, phenolates, bisphenolates, thiolates or bithiolates or of azo, azomethine or formazan dyes, such as [®]Irgalan Bordeaux EL (Ciba Specialty Chemicals Inc.), [®]Cibafast N3 (Ciba Specialty Chemicals Inc.) or similar compounds, hindered phenols and derivatives thereof (optionally also as anions X⁻), such as [®]Cibafast AO (Ciba Specialty Chemicals Inc.), 7,7',8,8'-tetracyanoquino-
- 20 dimethane (TCNQ) and compounds thereof (optionally as an anion of a charge transfer complex), hydroxyphenyl-triazoles or -triazines or other UV absorbers, such as [®]Cibafast W or [®]Cibafast P (Ciba Specialty Chemicals Inc.) or hindered amines (TEMPO or HALS, also as nitroxides or NOR-HALS, optionally also as anions X⁻).

- 25 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 or JP-A-07/262604. They may be, for example, salts of the metal complex anions

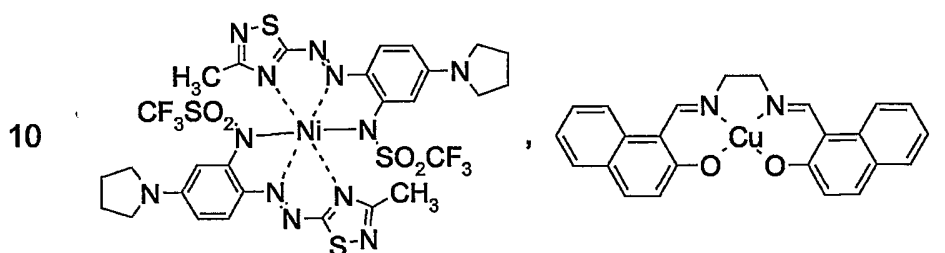
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disclosed above with any desired cations, for example the cations disclosed above.

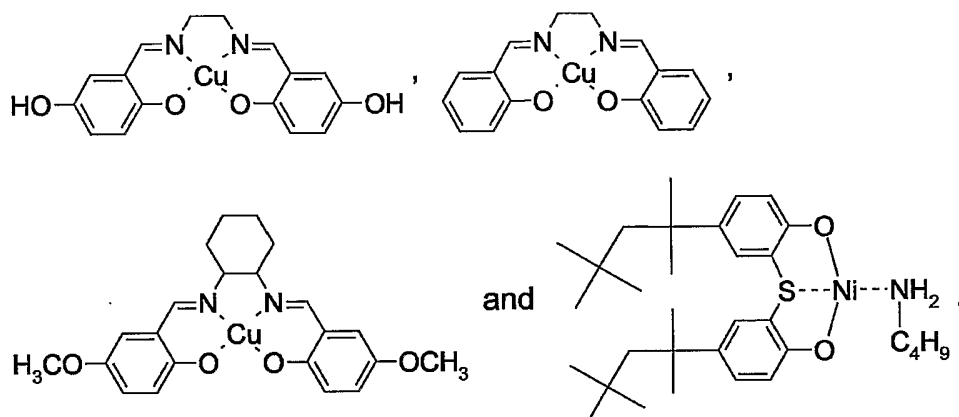
Also suitable are neutral metal complexes, for example those metal complexes disclosed in EP 0 822 544, EP 0 844 243, EP 0 903 733, EP 0 996 123, EP 1 056 078, EP 1 130 584 or US 6 162 520, for example



and other known metal complexes, illustrated, for example, by the compounds of formulae



- 28 -



Further suitable additives are organometallic compounds, such as for example ferrocenes, for example those of EP-A-0 600 427 or US-A-2003/0 224 293, which
 5 provide some stability while controlling the decomposition temperature.

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
 10 medium of formula (I). This range is also valid for the compounds of formula (II).

The recording medium according to the invention, in addition to comprising the compounds of formula (I) may additionally comprise salts, the ions of which may originate, for example, from the components used, such as those mentioned above. If present, the additional salts are preferably present in amounts of up to 20% by
 15 weight, based on the total weight of the recording layer.

Reflecting materials suitable for the reflective layer include especially metals, which provide good reflection of the laser radiation used for recording and playback, for example the metals of Groups 3–12, 13, 14 and 15 of the Periodic Table of the Chemical Elements. Ag, Al, Au, Bi, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Gd, Hf, Hg, Ho, In, Ir, La, Lu, Mo, Nb, Nd, Ni, Os, Pb, Pd, Pm, Pr, Pt, Rh, Ru, Sb, Sc, Sm, Sn, Ta, Tb, Ti, Tm, V, W, Y, Yb, Zn and Zr and alloys thereof are especially suitable.
 20 Special preference is given to a reflective layer of aluminium, silver, copper, gold or

- 29 -

an alloy thereof, on account of its high reflectivity and ease of production. It is suitable to check the compatibility of the reflecting layer with the recording layer compound, which is sometimes borderline at higher temperatures in a moist environment, depending on the chemical structure of the quinoid anion of the recording layer compound and the reflective layer's metal (potential redox reaction).

Materials suitable for the protective layer include chiefly plastics, which are applied in a thin layer to the support or to the uppermost layer either directly or with the aid of adhesive layers. It is advantageous to select mechanically and thermally stable plastics having good surface properties, which may be modified further, for example written on. The plastics may be thermosetting plastics or thermoplastic plastics. Preference is given to radiation-cured (e.g. using UV radiation) protective layers, which are particularly simple and economical to produce. A wide variety of radiation-curable materials is 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 having dialkylmaleinimidyl groups, e.g. dimethylmaleinimidyl groups.

The recording media according to the invention may also have additional layers, for example interference layers. It is also possible to construct recording media having a plurality of (for example two, three, four or five) recording layers. The structure and the use of such materials are known to the person skilled in the art (dual layer media are described more in detail below). 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 353 393 of TiO₂, Si₃N₄, ZnS or silicone resins.

The recording media according to the invention can be produced by processes 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,

- 30 -

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 in organic solvents are generally employed. When solvents are employed, care should be taken that the supports used are not sensitive to those solvents. Suitable
5 coating methods and solvents are described, for example, in EP-A-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, n-propanol, isopropanol, isobutanol, n-butanol, 1-methoxy-2-propanol, amyl alcohol or 3-methyl-1-butanol, or preferably fluorinated alcohols, for
10 example 2,2,2-trifluoroethanol or 2,2,3,3-tetrafluoro-1-propanol, and mixtures thereof. It will be understood that other solvents or solvent mixtures can also be used, for example those solvent mixtures described in EP-A-511 598 and EP-A-833 316. Ethers (dibutyl ether), ketones (2,6-dimethyl-4-heptanone, 5-methyl-2-hexanone), esters (e.g. the lactic acid esters known from WO-03/098 617) or
15 saturated or unsaturated hydrocarbons (toluene, xylene or as disclosed in WO-03/034 146 tert-butyl-benzene and similar compounds) can also be used, optionally also in the form of mixtures (e.g. dibutyl ether / 2,6-dimethyl-4-heptanone) or mixed components.

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

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

- 31 -

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

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

When the recording material is structured for a change in reflection, the following structures, for example, can be used: transparent support / recording layer (optionally multilayered) / reflective layer and, if expedient, protective layer (not necessarily transparent); or support (not necessarily transparent) / reflective layer /
15 recording layer and, if expedient, transparent protective layer. In the first case, the light is incident from the support side, whereas in the latter case the radiation is incident from the recording layer side or, where applicable, from the protective layer side. In both cases the light detector is located on the same side as the light source. The first-mentioned structure of the recording material to be used according
20 to the invention is generally preferred.

In particular, a dual layer disk where both recording layers can be recorded and read from the same side can be used: for example DVD+R Dual Layer or DVD-R Dual Layer featuring both 8.5 GB/side.

One way to manufacture such dual layer media called "2P Process" uses the
25 following embodiment: transparent substrate / recording material / semi-reflective layer / spacer layer applied by spin-coating and cured through a transparent stamper / second recording layer / reflective layer / adhesive layer / second half disk. Intermediate protective layers can be introduced when required.

- 32 -

Another way to manufacture dual layer media called "inverted stack" consists of making on one hand a half-disk with the following embodiment: transparent substrate / recording material / semi-reflective layer and on the other hand another half-disk with an inverted layer sequence: substrate / reflective layer / recording materials. The two half disks are then bonded together with an adhesive layer so that the two substrates form the two sides of the final disk. Intermediate protective layers can be introduced at various places when required, for example between the recording material and the adhesive layer. Such technique is described in WO-04/021 336 and in WO-04/042 717.

Of course, similar or analogue techniques can be used for media with a higher number of recording layers, too.

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

Suitable lasers are those having a wavelength of from 600 to 700 nm, for example commercially available lasers having a wavelength of 602, 612, 633, 635, 647, 650, 670 or 680 nm, especially semi-conductor lasers, such as GaAsAl, InGaAlP or GaAs laser diodes having a wavelength especially of about 635, 650 or 658 nm. The recording is effected, for example, point for point in a manner known *per se*, by modulating the laser in accordance with the mark lengths and focussing its radiation onto the recording layer. It is known from the specialist literature that other methods are currently being developed which may also be suitable for use.

The method according to the invention allows the storage of information with great reliability and stability, distinguished by very good mechanical and thermal stability and by high light stability and by sharp pit boundary zones. Special advantages include the high contrast, the low jitter and the surprisingly high signal/noise ratio,

- 33 -

so that excellent readout is achieved. The high storage capacity is especially valuable in the field of video and multimedia.

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

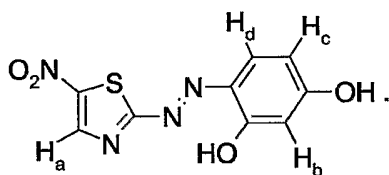
The information-containing medium according to the invention is especially an optical information material of the WORM type. It can be used, for example, as a playable DVD (digital versatile disk), as storage material for a computer or as an
10 identification and security card or for the production of diffractive optical elements, for example holograms.

The invention accordingly relates also to a method for the optical recording, storage and playback of information, wherein a recording medium according to the invention is used. The recording and/or the playback advantageously take place in a
15 wavelength range of from 600 to 700 nm, preferably as already indicated.

The following examples illustrate the invention in greater detail (all percentages are by weight, unless otherwise indicated):

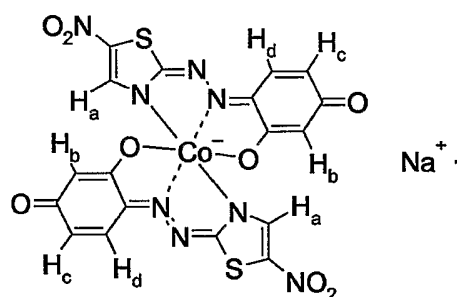
Example 1: 60.0 g of 97% 2-amino-5-nitrothiazole are dissolved, with stirring, in 880 ml of 50% (vol.) sulfuric acid at 23°C. The light-brown solution is cooled to
20 -10°C. In the course of 40 minutes, 100 ml of aqueous 4N sodium nitrite solution are added. The now dark blue-green solution is stirred at from -10 to -8°C for a further 15 minutes. During that time 48 g of resorcinol are dissolved in 400 ml of ethanol and cooled to -10 to -15°C. The resulting solution is then added slowly to the diazonium solution. Immediately a thick, dark-red precipitate is formed and the
25 temperature rises to about 0°C. The reaction mixture is then stirred for a further 2 hours at from 0 to 5°C, diluted with 500 ml of water and filtered with suction. The suction-filtered material is washed with 4 litres of water and dried for 24 hours at 60°C / 10³ Pa, yielding 78 g of red-brown product of formula:

- 34 -



¹H-NMR [ppm]: 8.87 (s, H_a); 6.46 (s, H_b); 6.49/6.52 (d, H_c); 7.71/7.74 (d, H_d).

Example 2: 25 g of the compound according to example 1 are introduced into 100 ml of dimethylacetamide and stirred at 23°C. Then 12.7 g of cobalt(II) acetate tetrahydrate are added. Both starting materials slowly dissolve and an almost black solution is formed which is stirred at room temperature for 3 hours. After that time a dark-red precipitate has formed, which is filtered with suction through a Büchner filter and washed with 20 ml of dimethylacetamide. The suction-filtered material is suspended, with stirring, in 1.2 litres of methanol. After the addition of 10 g of sodium acetate (anhydrous) the reaction mixture is heated to 60-65°C and clarified by filtration at that temperature. The filtrate is concentrated to 200 ml using a rotary evaporator and cooled to from 5 to 10°C, whereupon crystallisation begins. The precipitate is filtered with suction and washed with 50 ml of methanol of a temperature of 0-5°C. Drying at 50-55°C / 10³ Pa yields 15 g of an almost black product of formula:

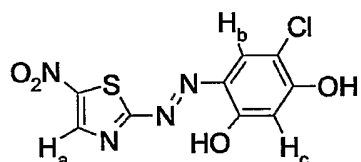


¹H-NMR [ppm]: 7.99 (s, H_a); 5.32 (s, H_b); 6.22/6.25 (d, H_c); 7.81/7.85 (d, H_d).

Example 3: 60.0 g of 2-amino-5-nitrothiazole are dissolved, with stirring, in 600 ml of 50% (vol.) sulfuric acid and 500 g of ice. The light-brown solution is cooled to -10°C. In the course of 108 minutes, 108 ml of aqueous 4N sodium nitrite solution are added. The now dark black-green solution is stirred at from -12 to -10°C for a further 1 hour. During that time, 64 g of 4-chlor-resorcinol are dissolved in 400 ml of

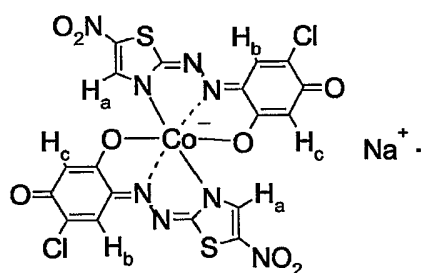
- 35 -

isopropanol and cooled to -5°C . The resulting solution is then added in the course of 10 minutes to the diazonium solution. The reaction mixture is then stirred for 15 h at from 0°C to room temperature and filtered with suction. The suction-filtered material is washed with 4 litres of water and dried for 24 hours at $50^{\circ}\text{C}/10^3\text{ Pa}$,
 5 yielding 90 g of red-brown product of formula:



$^1\text{H-NMR}$ [ppm]: 8.86 (s, H_a); 7.75 (s, H_b); 6.57 (s, H_c).

Example 4: 35 g of the compound according to example 3 are introduced into 620 ml of methanol and stirred at 23°C . Then 12.45 g of cobalt(II) acetate tetrahydrate are added. Both starting materials slowly dissolve and a dark violet solution is formed which is stirred for 15 h at room temperature. The solution is evaporated to about half the volume under vacuum (10^3 Pa) and cooled to 5°C . A dark violet precipitate has formed, which is filtered with suction through a Büchner filter and washed with methanol and isopropanol. Drying at $50^{\circ}\text{C}/10^3\text{ Pa}$ yields
 10 24 g of an almost black product of formula:

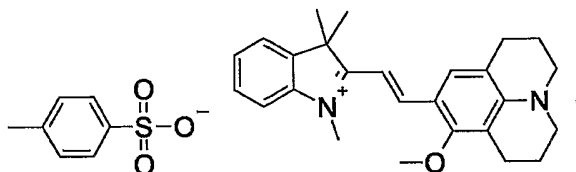


$^1\text{H-NMR}$ [ppm]: 8.31 (s, H_a); 8.03 (s, H_d); 5.37 (s, H_c).

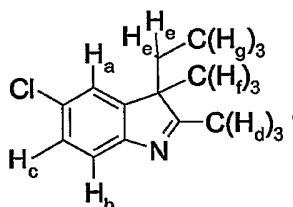
Example 5 (synthesis of indolium): 1.53 g of p-toluenesulfonic acid are dissolved, with stirring, in 10 ml of methanol. To the colorless solution, an orange solution of
 20 1.86 g of 8-methoxyjulolidine-9-aldehyde in 10 ml of methanol is added. 1.39 g of 1,3,3-trimethyl-2-methyleneindoline are then added to the now yellow-red solution, which turns violet and is stirred for 15 h at 23°C . The solvent is evaporated at

- 36 -

10³ Pa giving 4.67 g of a violet liquid. The product is dissolved in dichloromethane, filtered and the solvent is evaporated at 10³ Pa yielding 4 g of shining violet crystals of following formula, which are used directly for the next step (example 12):



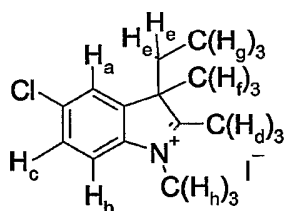
- 5 **Example 6:** 4.5 ml of 98% sulfuric acid are dissolved in 46 ml of ethanol under stirring, with some cooling in order to keep a temperature close to 25°C. 8 g of 4-chlor-phenylhydrazine hydrochloride are added, followed by 6.5 ml of 3-methyl-2-pentanone. The reaction media is then stirred at 75°C for 15 h. After cooling to 23°C, some ethanol is evaporated under reduced pressure, and 60 ml of 5% aqueous NaOH solution are slowly added. The aqueous phase is extracted with ethyl acetate, and this organic phase is evaporated under reduced pressure to 9.1 g of dark orange oil. The product of the following formula is used crude for the next step (examples 6 and 35):



- 15 ¹H-NMR [ppm]: 7.47 / 7.46 (d, H_a); 7.42 / 7.40 (d, H_b); 7.32-7.29 (dd, H_c); 2.15 (s, 3H_d); 2.00-1.71 (m, 2H_e); 1.23 (s, 3H_f); 0.26 (t, 3H_g).

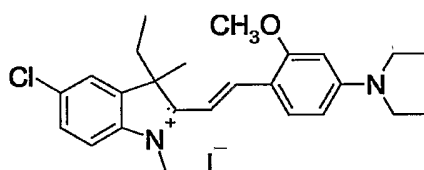
- Example 7:** The crude material according to example 6 is dissolved in 18 ml of chloroform, and 3.7 ml of methyl iodide are added. Then, the reaction medium is heated to reflux for 18 hours. It is then cooled to 0°C and filtrated at this temperature. The solid obtained is washed with cold acetone, yielding 11.2 g of a beige compound of formula:

- 37 -



¹H-NMR [ppm]: 8.0 (d, H_a); 7.99 / 7.96 (d, H_b); 7.76-7.73 (dd, H_c); 4.02 (s, 3H_h); 2,8 (s, 3H_d); 2.31-2.05 (m, 2H_e); 1.55 (s, 3H_f); 0.41 (t, 3H_g).

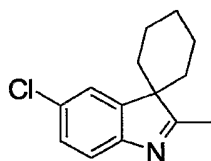
Example 8: 2,1 g of the compound according to example 7 are dissolved in 40 ml of methanol. 1,24 g of 2-methoxy-4-diethylamino-benzaldehyde are added. The solution is refluxed for 4.5 hours. After cooling down to 23°C, the solution is evaporated under reduced pressure to yield 3,5 g of a dark-green crude compound of formula:



¹H-NMR [ppm]: 8.37 / 8.32 (d, 1H); 8.05 / 8.02 (d, 1H); 7.87-7.86 (d, 1H); 7.66-7.57 (m, 2H); 7.22 / 7.16 (d, 1H); 6.63-6.60 (dd, 1H); 4.02 (s, 3H); 3.85 (s, 3H, OMe); 3.65-3.58 (q, 4H); 2.38-2.20 (m, 2H); 1.70 (s, 3H); 1.20 (t, 6H); 0.35 (t, 3H).

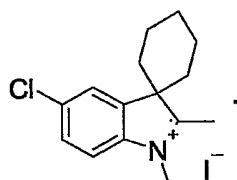
Example 9: 10 ml of 98% sulfuric acid are dissolved in 105 ml of ethanol under stirring, with some cooling in order to keep a temperature close to 25°C. 17.9 g of 4-chlor-phenylhydrazine hydrochloride are added, followed by 15.1 g of cyclohexyl methyl ketone. The pink-beige suspension obtained is then stirred for 15 h at 75°C. After cooling to 23°C, some ethanol is evaporated under reduced pressure, and 130 ml of 5% aqueous NaOH solution are slowly added. The aqueous phase is extracted with ethyl acetate, and this organic phase is evaporated under reduced pressure to obtain 24,8 g of a dark brown oily solid. The product of the following formula is used crude for the next step (example 10):

- 38 -



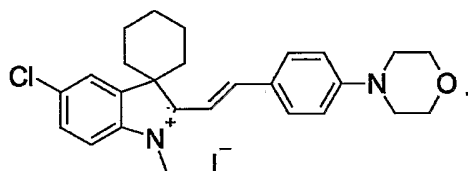
¹H-NMR [ppm]: 7.76 (d, 1H); 7.46 / 7.44 (d, 1H); 7.38-7.36 (dd, 1H); 2.21 (s, 3H); 1.90-1.09 (m, 11H).

Example 10: 23,3 g of the compound according to example 9 are dissolved in 40 ml chloroform. Then, 8.7 ml of methyl iodide are added. The solution is then heated to reflux for 4 hours, it becoming necessary to add 40 ml more of chloroform). The rest of the procedure is identical to example 7 and yields 18.4 g of a hell-beige solid of formula:



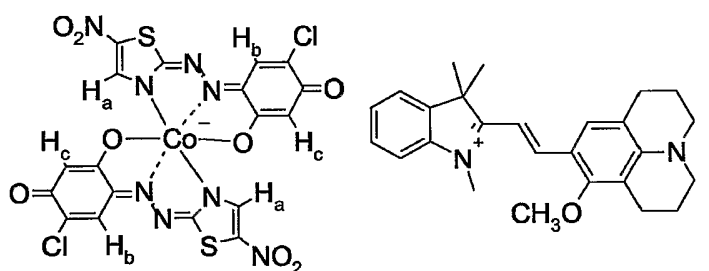
¹H-NMR [ppm]: 8.16 / 8.15 (d, 1H); 8.01 / 7.98 (d, 1H); 7.81-7.77 (dd, 1H); 3.96 (s, 3H); 2.80 (s, 3H); 2.09-1.23 (m, 11H).

Example 11: 2,25 g of the compound according to example 10 are dissolved in 40 ml of methanol. 1.15 g of p-morpholino-benzaldehyde are added and the solution is heated to reflux for 5 hours. After cooling down to 23°C, the solution is evaporated under reduced pressure to yield 3.4 g of a greenish crude compound of formula:



¹H-NMR [ppm]: 8.36 / 8.31 (d, 1H); 8.16 / 8.08 (m, 2H); 8.00-7.98 (d, 1H); 7.75-7.72 (dd, 2H); 7.30 / 7.25 (d, 1H); 7.13-7.10 (d, 2H); 4.04 (s, 3H); 3.77-3.72 (m, 4H); 3.51 (t, 4H); 2.30-1.44 (3m, 11H).

Example 12 (synthesis of salt): 1 g of the product according to example 4 is added to 20 ml of methanol at 23°C. A solution of 0.82 g of the product according to example 5 in 10 ml of methanol is added and the resulting solution is stirred for 15 h at 23°C, thus giving a violet suspension. Water is added to the suspension and the organic solvents are removed under vacuum (10^3 Pa). The product is filtered with suction through a Büchner filter and washed with water. Drying at 40°C/ 10^3 Pa yields 1.27 g of an almost black product of formula:

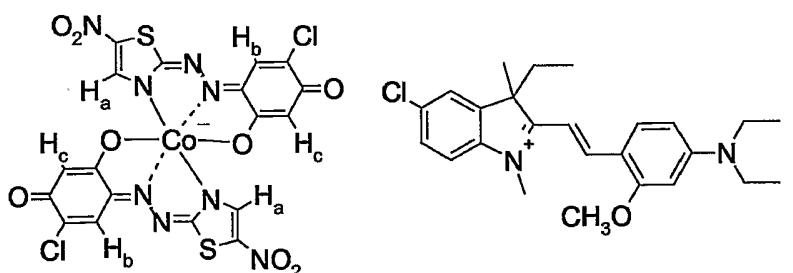


¹H-NMR [ppm]: 8.22 (d, 1 H); 8.16 (s, 2 H_a); 8.04 (s, 2 H_d); 7.81 (s, 1 H); 7.71 (d, 1 H); 7.62 (d, 1 H); 7.52 (d, 1 H); 7.42 (dd, 1 H); 7.10 (d, 1 H); 5.47 (s, 2 H_c); 3.87 (s, 3 H); 3.79 (s, 3 H); 3.43 (br. s, 4 H); 2.72 (m, 4 H); 1.89 (m, 4 H); 1.71 (s, 6 H).

	Microanalysis:	C	H	N	O	Na
	[%]	50.00	3.85	13.20	14.93	71 mg/kg
15	calc.:	50.63	3.57	13.42	13.80	0

 λ_{max} (solid film): 560 nm.

Example 13: The product is prepared according to the method of example 12 starting from 0.81 g of the product of example 4 and 0.64 g of the product of example 8. The product is a dark brown powder of formula:



- 40 -

¹H-NMR [ppm]: 8.35 (d, 1 H); 8.15 (s, 2 H_a); 8.04 (s, 2 H_b); 8.03 (d, 1 H); 7.86 (d, 1 H); 7.61 (d, 1 H); 7.60 (d, 1 H); 7.21 (d, 1 H); 6.61 (d, 1 H); 6.24 (d, 1 H); 5.47 (s, 2 H_c); 4.01 (s, 3 H); 3.84 (s, 3 H); 3.59 (t, 4 H); 2.15-2.35 (m, 2 H); 1.70 (s, 3 H); 1.20 (t, 6 H); 0.36 (t, 3 H).

5	Microanalysis:	C	H	N	Cl
	[%]	47.12	3.80	12.75	9.47
	calc.:	48.35	3.59	13.11	9.96

Example 14: 1.5 g of the compound according to example 12 are dissolved in 98.5 g of 1-methoxy-2-propanol and filtered through a 0.2 µm Teflon™ filter. The dye solution is then applied at 250 rev/min to a 1.2 mm thick, planar polycarbonate disc (diameter 120 mm) and the speed of rotation is increased to 1200 rev/min so that the excess of solution is spun off and a uniform solid layer is formed. After drying, the layer thickness and the complex refractive index of the solid layer are determined by means of spectral transmission and reflection measurements using an optical measuring system (ETA-RT™, Steag ETA-Optik GmbH). At 658 nm the dye layer has a refractive index n of 2.65 and an extinction coefficient k of 0.14. The photostability is determined with a calibrated xenon lamp (Hanau), the relative decrease in absorption -D₂₄ after 24 hours' irradiation is 29%.

Example 15: 1.5% by weight of the compound according to example 13 is dissolved in 2,2,3,3-tetrafluoropropanol and applied to a planar polycarbonate substrate by spin-coating. The film thickness and optical constants of the solid layer are determined by the same methods as in example 14. λ_{max} of the 50 nm thick solid film is at 587 nm, with a refractive index n of 2.95 and an extinction coefficient k of 1.32. At 658 nm the dye layer has a refractive index n of 2.47 and an extinction coefficient k of 0.06, the relative decrease in absorption -D₂₄ is 6%. Thus, the dye film is both highly photostable and possesses a surprisingly high refractive index.

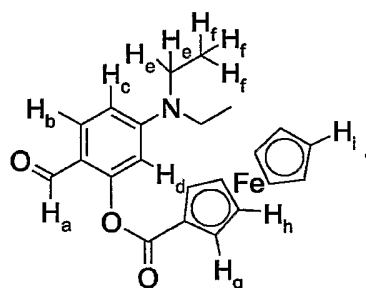
Example 16: It is proceeded in close analogy to example 15, with the difference that the compound according to example 4 is used instead of the compound according to example 13. λ_{max} of the 50 nm thick solid film is at 565 nm. At 658 nm

- 41 -

the dye layer has a refractive index n of 2.54 and an extinction coefficient k of 0.11, the relative decrease in absorption $-D_{24}$ is 8%.

Example 17: 1 g of 4-(diethylamino)salicylaldehyde and 1.4 g of potassium carbonate are suspended in 25 ml of acetone. 1.9 g of ferrocenecarboxylic acid chloride is added dropwise. Then the reaction is stirred at 23°C for 48 hours. The mixture is diluted with dichloromethane and washed with water. Drying of the organic phase over sodium sulphate and evaporation of the solvent lead to a brown-red oil that is purified by flash chromatography to obtain 0.7 g of a red compound of formula

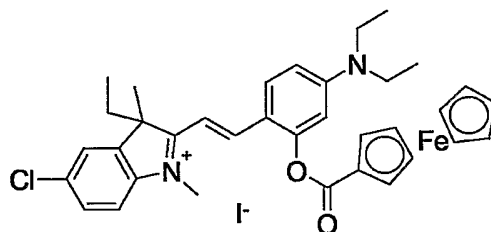
10



$^1\text{H-NMR}$ [ppm]: 9.84 (s, H_a); 7.67 (m, H_b); 6.71 (d, H_c); 6.42 (s, H_d); 4.96 (m, $2H_g$); 4.64 (m, $2H_h$); 4.38 (m, $5H_i$); 3.42 (m, $4H_e$); 1.14 (m, $6H_f$).

Example 18: 0.7 g of the compound according to example 17 and 0.59 g of the compound according to example 7 are dissolved in 25 ml of methanol. The solution is heated to reflux for 16 hours. After cooling down to 23°C, the solution is evaporated at 300 Pa to yield 1.3 g of a dark-blue crude compound of formula

15



that is used directly to form the compound of example 282.

Example 19: 5 g of 3,4,5-trifluorobenzyl bromide and 8 g of potassium iodide are suspended in 50 ml of acetone. The reaction is heated to reflux for 5 hours. After

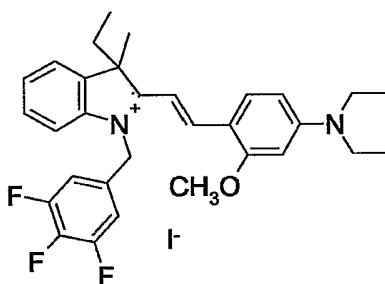
20

- 42 -

cooling down to 23°C, the mixture is diluted with water and extracted with dichloromethane. The organic phase is washed with a solution of sodium carbonate. Drying of the organic phase over sodium sulphate and evaporation of the solvent leads to 4 g of 3,4,5-trifluorobenzyl iodide as a yellow oil that is used directly for the next step.

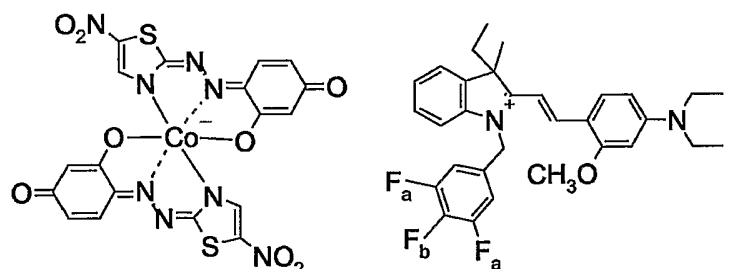
2.55 g of 3-ethyl-1,2,3-trimethyl-3H-indolium iodide are dissolved in 20 ml of methyl ethyl ketone. 4 g of 3,4,5-trifluorobenzyl iodide are added through a syringe. The mixture is heated to reflux for 15 hours.

3.35 g of 2-methoxy-4-diethylamino-benzaldehyde are added and the mixture is further heated to reflux for 7 hours. After cooling down to 10°C, the mixture is filtered and the solid is washed with cold acetone yielding 3.19 g of compound of formula



that is used directly to form the compound of example 20.

Example 20: The product is prepared according to the method of example 12, starting from 2.92 g of the product according to example 2 and 3.19 g of the product according to example 19. The product is a dark green powder of formula:



^{19}F -NMR [ppm]: -134 (s, F_a); -162 (s, F_b);

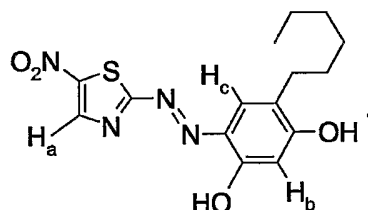
MS (-cACPI): 588 (M^- , A^-); (+cACPI): 507 (M^+ , C^+); λ_{max} (solid film): 550 nm.

- 43 -

See example 279 for the optical parameters of the solid compound.

Example 21: The product is prepared in the same way as example 1 starting from 4.35 g of 2-amino-5-nitrothiazole and 5.24 g of 4-hexylresorcinol yielding 7.6 g of a violet powder of formula:

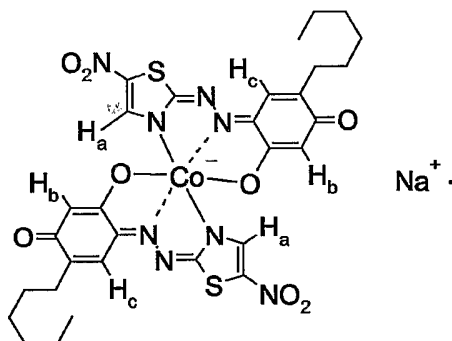
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$^1\text{H-NMR}$ [ppm]: 8.83 (s, H_a); 7.52 (s, H_c); 6.46 (s, H_b); 2.49 (m, 2 H); 1.46 (m, 2 H); 1.27 (m, 6 H); 0.84 (m, 3 H).

Example 22: The product is prepared in the same way as example 2 starting from 7 g of the product of example 21 and 2.49 g of cobalt(II) acetate yielding 3 g of a dark green powder of formula:

10

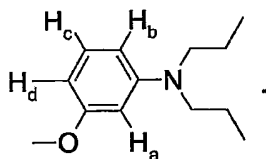


$^1\text{H-NMR}$ [ppm]: 7.89 (s, H_a); 7.62 (s, H_c); 5.30 (s, H_b); 2.37 (m, 2 H); 1.51 (m, 2 H); 1.33 (m, 6 H); 0.88 (m, 3 H).

Example 23: 28.52 g of m-anisidine and 50.5 g of tri-propyl phosphate are heated to 240°C for 2 hours. After cooling down to 150°C, 50 ml of 30% aqueous NaOH solution are added slowly. The mixture is poured on water and extracted with dichloromethane. Drying of the organic phase over sodium sulphate and evaporation of the solvent leads to 48.9 g of a brown oil that is purified by chromatography (hexane) yielding 27.65 g of a colourless oil of the formula:

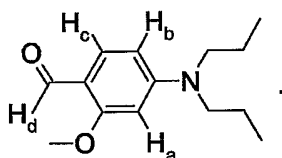
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- 44 -



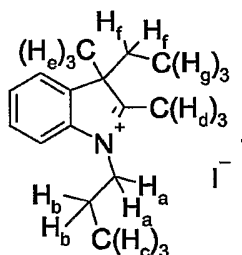
$^1\text{H-NMR}$ [ppm]: 7.02 (t, $J = 8.1$, H_c); 6.22 (m, H_d); 6.14 (m, H_b); 6.11 (s, H_a); 3.70 (s, 3 H); 3.19 (t, $J = 7.5$, 4 H); 1.51 (m, 4 H); 0.87 (t, $J = 10.8$, 6 H).

Example 24: 8.43 g of phosphorous trichloride are added dropwise to 30 ml of dimethylformamide (DMF) at -10°C . The mixture is stirred at 0°C for 20 minutes. A solution of 12.65 g of the product according to example 23 in 10 ml of DMF are added and the mixture is heated to 110°C for 2 hours. After cooling to 23°C , the mixture is poured on ice, neutralized with sodium bicarbonate and extracted with dichloromethane. Drying of the organic phase over sodium sulphate and evaporation of the solvent leads to 12.6 g of a brown viscous oil that is purified by chromatography (hexane ethyl acetate 5:1), yielding 10.55 g of a yellow solid of the formula



$^1\text{H-NMR}$ [ppm]: 9.98 (s, H_d); 7.48 (d, $J = 9$, H_c); 6.34 (d, $J = 9$, H_b); 6.12 (s, H_a); 3.85 (s, 3 H); 3.35 (t, $J = 7.5$, 4 H); 1.57 (m, 4 H); 0.90 (t, $J = 7.2$, 6 H).

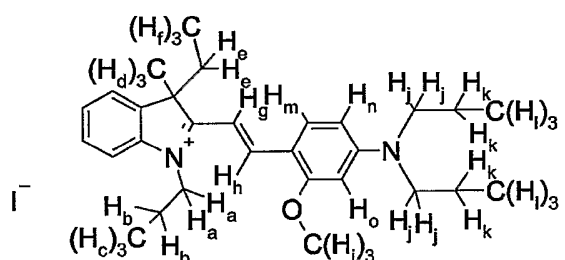
Example 25: 3.46 g of the compound according to example 51 and 5.2 g of propyl iodide are heated at 120°C in a closed vessel for 18 hours. After cooling to 23°C , the mixture is diluted with a 2:1 mixture of hexane and acetone, cooled to 0°C and filtered giving 5.15 g of a beige solid of the formula



- 45 -

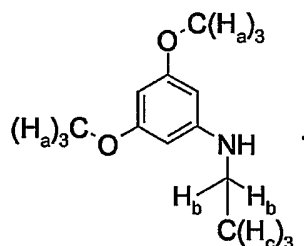
$^1\text{H-NMR}$ [ppm]: 8.03 (m, H); 7.80 (m, H); 7.65 (m, 2 H); 4.48 (t, $J = 7.5$ Hz);
2.87 (s, 3 H_d); 2.32–2.07 (m, 2 H_f); 1.87 (m, 2 H_b); 1.55 (s, 3 H_e);
1.00 (t, $J = 7.5$, 3 H_c); 0.35 (t, $J = 7.5$, 3 H_g).

Example 26: The product is prepared according to the method of example 11,
5 starting from 1.03 g of the product according to example 24 and 0.7 g of the
product according to example 25. The product, which is used directly to prepare the
product of example 246, is a dark violet powder of the formula



$^1\text{H-NMR}$ [ppm]: 8.35 (m, H); 8.04 (m, H); 7.68 (m, H_g and H_m); 7.47 (m, 2 H); 7.26
10 (m, H_n); 6.59 (m, H_n); 6.24 (m, H_o); 4.38 (m, 2 H_a); 4.00 (s, 3 H_i);
3.52 (m, 4 H_j); 2.33 (m, 2 H_e); 1.80 (m, 2 H_b); 1.70 (s, 3 H_o); 1.63
(m, 4 H_k); 1.03–0.83 (m, 6 H_i and 3 H_c); 0.35 (t, $J = 6.9$, 3 H_f).

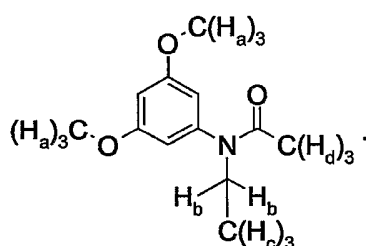
Example 27: 14.44 g of borane dimethylsulfide complex are added in 30 minutes to
a solution of 21.5 g of N-(3,5-dimethoxy-phenyl)-acetamide in 80 ml of tetrahydro-
15 furan (THF). The mixture is heated to 100°C. The solvent and the dimethylsulfide
are distilled. After cooling to 23°C, 40 ml of 20% aqueous HCl are added and the
mixture is heated to 100°C for 30 minutes. After cooling to 0°C, 25 ml of 30%
aqueous NaOH are added and the mixture is extracted with ethyl acetate. Drying of
the organic phase over sodium sulphate and evaporation of the solvent leads to
20 21.2 g of greenish crystals of the formula



- 46 -

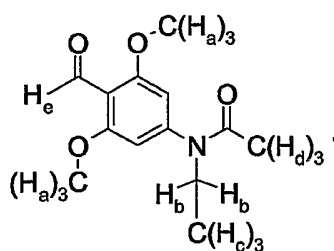
$^1\text{H-NMR}$ [ppm]: 5.72 (m, 3 H); 5.49 (broad s, NH); 3.63 (s, 6 H_a);
2.98 (q, $J = 7.2$, 2 H_b); 1.12 (t, $J = 7.2$, 3 H_c).

Example 28: 21 g of the product according to example 27 are dissolved in 80 ml of pyridine. 33.7 ml of acetic anhydride are added in 40 minutes and the mixture is stirred at 23°C for 30 minutes. The mixture is poured into water and extracted with dichloromethane. Drying of the organic phase over sodium sulphate and evaporation of the solvent leads to 13.3 g of grey crystals of the formula



$^1\text{H-NMR}$ [ppm]: 6.50 (m, H); 6.44 (m, 2 H); 3.75 (s, 6 H_a); 3.60 (q, $J = 6.9$, 2 H_b);
1.77 (s, 3 H_d); 1.00 (t, $J = 7.2$, 3 H_c).

Example 29: 13.3 g of the product according to example 28 are dissolved in 110 ml of dichloromethane and the solution is cooled to 0°C. 21.2 g of titanium tetrachloride are added in 20 minutes and the mixture is stirred at 0°C for 2 hours. The mixture is then cooled down to -78°C and 9 g of dichloromethyl methyl ether are added in 10 minutes. The mixture is stirred for 1 hour at -78°C and then warmed to 23°C. After pouring the solution on water, 20 ml of concentrated HCl are added. The organic phase is separated and evaporated under vacuum (10^3 Pa) giving a brown resin that is purified by chromatography yielding 16.1 g of a yellowish solid of the formula

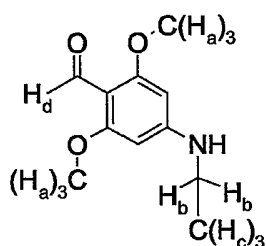


$^1\text{H-NMR}$ [ppm]: 10.31 (s, H_e); 6.70 (s, 2 H); 3.84 (s, 6 H_a); 3.70 (q, $J = 7.2$, 2 H_b);

- 47 -

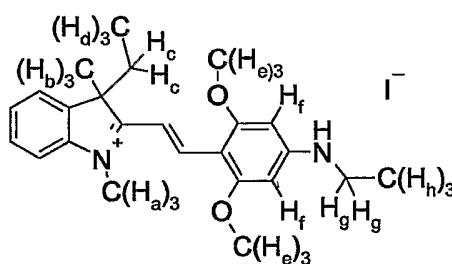
1.89 (s, 3 H_d); 1.04 (t, J = 7.2, 3 H_c).

Example 30: 2 g of the product according to example 29 and 0.44 mg of sodium methylate (as a 5.4 M solution in methanol) are dissolved in 21 ml of methanol. The solution is stirred at 23°C for 10 days. After pouring the solution into water, the mixture is extracted with methylene dichloride. Drying of the organic phase over sodium sulphate and evaporation of the solvent leads to 1.5 g of a beige solid of the formula



¹H-NMR [ppm]: 10.08 (s, H_d); 6.78 (m, NH); 5.78 (s, 2 H); 3.74 (s, 6 H_a);
3.16 (m, 2 H_b); 1.04 (t, J = 7.2, 3 H_c).

Example 31: It is proceeded according to the method of example 11, but starting from 0.32 g of the product according to example 30 and 0.21 g of 3-ethyl-1,2,3-trimethyl-3H-indolium iodide (prepared in a similar way as in example 7). The product is a dark violet powder of the formula



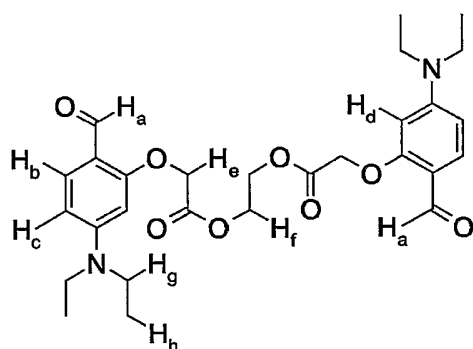
that is used directly to prepare the product of example 254.

¹H-NMR [ppm]: 8.42 (m, H); 7.95 (m, NH); 7.84-7.36 (m, 6 H_f); 6.00 (s, 2 H_f);
3.94 (s, 6 H_e); 3.76 (s, 3 H_a); 3.33 (m, 2 H_g); 2.30 (m, 2 H_c);
1.74 (s, 3 H_b); 1.20 (t, 3 H_h); 0.32 (t, 3 H_d).

- 48 -

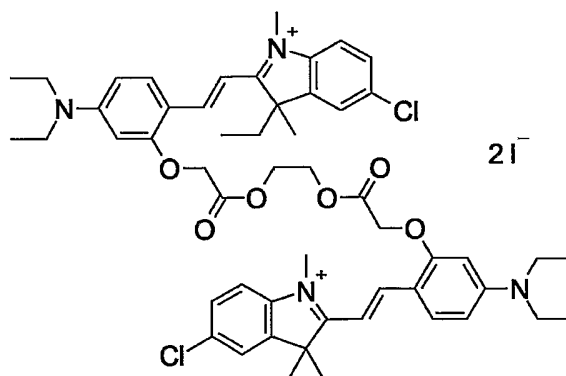
Example 32: 2 g of 1,2-bis-bromoacetoxy-ethane (prepared according to Phosphorus, Sulfur Silicon Relat. Elem. 143, 191 [1998]) and 2.79 g of 4-diethyl-amino-2-hydroxy-benzaldehyde are suspended in 20 ml methyl ethyl ketone. 2.24 g of potassium bromide and 70 mg of potassium iodide are added in portions and the

5 light brown suspension is heated to reflux for 24 h. The reaction mixture is cooled to 20°C, filtered and concentrated by rotary evaporation to yield 3.66 g of a brown residue which is purified by repeated crystallization from ethyl acetate / hexane to obtain the pure compound (oil) of formula



10 $^1\text{H-NMR}$ [ppm]: 10.07 (s, 2H_a); 7.51 (d, 2H_b); 6.37 (d, 2H_c); 6.08 (s, 2H_d); 4.95 (s, 4H_e); 4.37 (s, 4H_f); 3.41 (q, 8H_g); 1.10 (t, 12H_h).

Example 33: 0.42 g of the compound according to example 32 and 0.56 g of the compound according to example 7 are suspended in 15 ml of methanol and heated to reflux for 15 h. After evaporation, 0.92 g of the product of formula



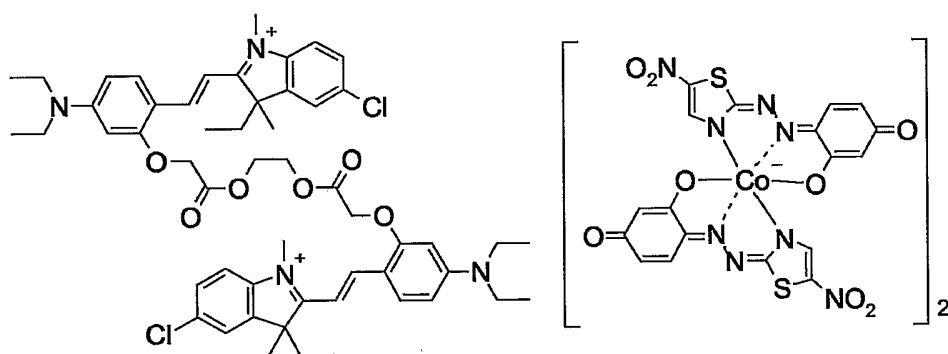
15

are obtained as a dark violet solid and used in example 34 without further purification.

- 49 -

¹H-NMR [ppm]: 8.4 (bd, 2H); 8.0 (m, 2H); 7.86 (d, 2H); 7.55-7.68 (m, 4H); 7.42 (broad s, 2H); 6.60 (d, 2H); 6.25 (s, 2H); 5.09 (s, 4H); 4.53 (s, 4H); 3.90 (s, 6H); 3.57 (q, 8H); 2.25-2.45 (m, 4H); 1.73 (s, 6H); 1.14 (t, 12H); 0.4 (t, 6H).

- 5 **Example 34:** A solution of 0.65 g of the cobalt complex according to example 2 in 12 g of 1-methoxy-2-propanol is added dropwise to a solution of 0.7 g of the product according to example 33 in 15 ml of methanol. The mixture is stirred 18 h at 23°C, then poured onto a 2:1 mixture of water and methanol. The precipitate is filtered on a sintered glass filter, washed with water and dried at 10³ Pa to yield
- 10 0.72 g of the greenish black product of formula



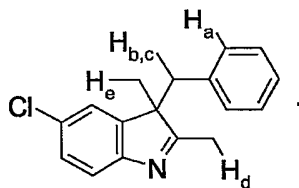
- ¹H-NMR [ppm]: 8.4 (bd, 2H); 8.0 (m, 6H); 7.80-7.92 (m, 6H); 7.55-7.68 (m, 4H); 7.42 (broad s, 2H); 6.60 (d, 2H); 6.25 (d, 4H); 6.21 (s, 2H); 5.31 (s, 4H); 5.07 (s, 4H); 4.51 (s, 4H); 3.89 (s, 6H); 3.58 (q, 8H); 2.25-2.45 (m, 4H); 1.73 (s, 6H); 1.14 (t, 12H); 0.34 (t, 6H).
- 15

$\lambda_{\max}$ (solid film): 544 nm.

See example 276 for the optical parameters of the solid compound.

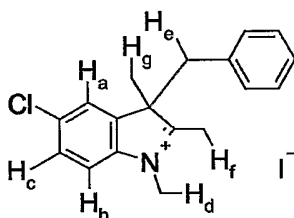
- Example 35:** 2.5 g of 3-methyl-4-phenyl-2-butanone (prepared according to Bull. Chem. Soc. Jpn. 62, 4072 [1989]) is reacted with 2.36 g of 4-chlorophenyl-hydrazine hydrochloride according to the method of example 6 to yield 3.7 g of the
- 20 crude, brownish yellow oil of formula

- 50 -



¹H-NMR [ppm]: 7.37-7.0 (m, 6 H); 6.82 (m, 2H_a); 3.18 /3.14 (d, H_b); 2.89 /2.85 (d, H_c); 2.34 (s, 3H_d); 1.39 (s, 3H_e).

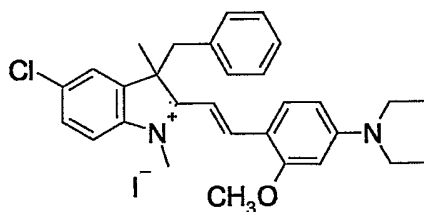
Example 36: 3.2 g of the compound according to example 35 are alkylated with methyl iodide according to the method of example 7 to yield 1.6 g of a beige powder of formula



that is used directly to form the compound of example 37.

¹H-NMR [ppm]: 7.91 (d, H_a); 7.76 / 7.73 (d, H_b); 7.67/ 7.64 (dd, H_c);
7.13-7.03 (m, 3H); 6.79-6.76 (m, 2H); 3.82 (s, 3H_d);
3.6-3.3 (m, 2H_e); 2.94 (s, 3H_f); 1.67 (s, 3H_g).

Example 37: 1.36 g of the compound according to example 36 are treated with 0.68 g of 2-methoxy-4-diethylamino-benzaldehyde according to the method of example 8 to yield 2.0 g of a crude dark powder of formula



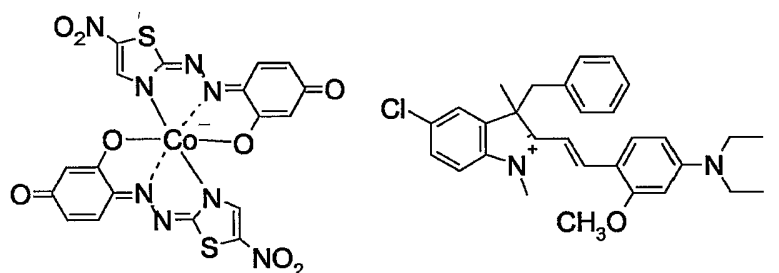
that is used directly for the next step (example 38).

¹H-NMR [ppm]: 8.50 /8.45 (d, 1H); 8.08 / 8.05 (d, 1H); 8.0 (d, 1H);
7.52 / 7.49 (d, 1H); 7.42 / 7.39 (d, 1H); 7.19 / 7.14 (d, 1H);

- 51 -

7.07-7.0 (m, 3H); 6.66-6.61 (m, 3H); 6.28 (d, 1H); 4.04 (s, 3H);
3.7-3.3 (m, 6H); 3.56 (s, 3H); 1.86 (s, 3H); 1.22 (t, 6H).

Example 38: According to the method of example 12, 2.0 g of the product according to example 37 are treated with 2.02 g of the cobalt complex according to example 2. After washing with water and drying, 2.56 g of a greenish black product of the following formula are obtained:



¹H-NMR [ppm]: 8.50 / 8.45 (d, 1H); 8.08 / 8.05 (d, 1H); 8.0 (d, 1H);
7.52 / 7.49 (d, 1H); 7.42 / 7.39 (d, 1H); 7.19 / 7.14 (d, 1H);
7.07-7.0 (m, 3H); 6.66-6.61 (m, 3H); 6.28 (d, 1H); 4.04 (s, 3H);
3.7-3.3 (m, 6H); 3.56 (s, 3H); 1.86 (s, 3H); 1.22 (t, 6H).

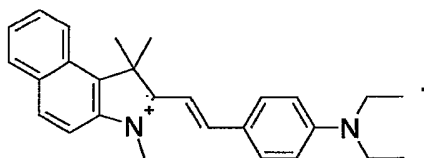
Microanalysis:	C	H	N	O
[%]	54.32	3.99	13.20	13.57
calc.:	53.57	4.20	12.74	14.40

$\lambda_{\max}$ (solid film): 552 nm.

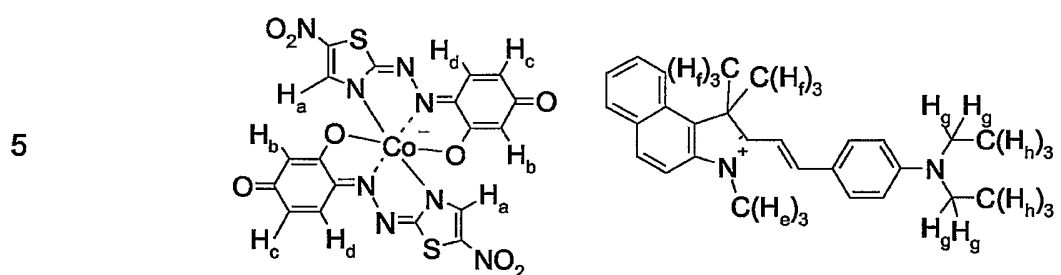
See example 275 for the optical parameters of the solid compound.

Example 39: 2.5 g of 1,1,2,3-tetramethyl-benzindolinium iodide are stirred at 23°C in 25 ml of methanol. 1.4 g of 4-diethylaminobenzaldehyde are added. The mixture is heated to 60°C and stirred at this temperature for 3 hours. The obtained violet solution containing the compound of the following formula is used directly to prepare the product of example 40:

- 52 -



Example 40: The product is prepared according to the method of example 12, starting from the product according to example 2 and the product according to example 39. The product is a dark green powder of formula



¹H-NMR [ppm]: 8.36 (m, 2 H); 8.17 (m, 2 H); 8.00 (m, 5 H); 7.83 (d, J = 5, 2 H_d);
 7.42 (broad s, 2H); 7.76 (m, 1 H); 7.63 (m, 1 H); 7.25 (d, J = 16,
 1 H); 6.87 (d, J = 9, 2 H); 6.22 (dd, J = 10, J = 15, 2 H_c); 5.31 (s,
 2 H_b); 5.07 (s, 4H); 4.07 (s, 3 H_e); 3.54 (q, J = 7, 4 H_g); 1.98 (s,
 6 H_f); 1.15 (t, J = 7, 6 H_h).

10

See example 201 for the optical parameters of the solid compound.

Example 41: 111 g of 4-fluoro-aniline are stirred in 500 ml of water and 212.5 ml of hydrochloric acid 37% are added. The mixture is cooled to -5°C. 252 ml of aqueous 4N sodium nitrite solution are added within 50 minutes. The reaction mixture is stirred for 2 hours at 0°C to 5°C. The orange solution is added within 30 minutes to a chilled solution of 74.8 g of imidazole in 750 ml of water. During this addition, the pH is kept at 10.5 by addition of 161.5 ml of a 30% aqueous solution of sodium hydroxyde while keeping the temperature between 0°C and 5°C. The reaction mixture is stirred overnight (18 h) at room temperature (23°C). The orange precipitate is filtered and washed with 5 liters of water.

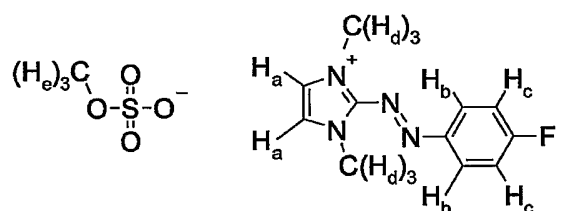
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20

The wet filter cake is stirred at room temperature in 700 ml of water. 266.5 ml of dimethylsulfate are added within 5 hours. During the addition, the pH is kept at 10

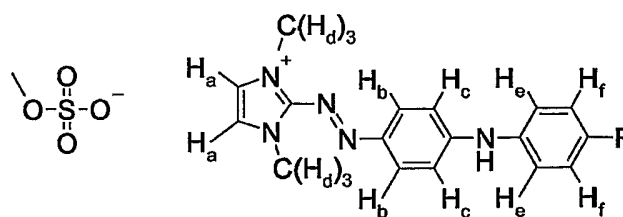
- 53 -

by adding 155 ml of a 30% aqueous solution of sodium hydroxyde while keeping the temperature between 25°C and 30°C. The reaction mixture is stirred for 2 hours at 23°C. 500 g of sodium chloride and 250 g of potassium chloride are added leading to the precipitation of the product. The reaction mixture is stirred overnight,
 5 filtered and washed with 1.5 liter of brine (20%). The filtered material is dried for 24 hours at 50°C / 10³ Pa, yielding 324 g of an orange product which is dissolved in 1 liter of methanol and filtered. The solution is diluted with 350 ml of dimethylformamide and the methanol is evaporated at 10³ Pa / 40°C. The precipitate is diluted with 350 ml of acetone, cooled to 5°C, filtered and washed with 500 ml of
 10 acetone. The filtered material is dried for 24 hours at 50°C / 10³ Pa, yielding 227.1 g of a reddish brown product of formula



¹H-NMR [ppm]: 8.22 (dd, J_{HH} = 6, J_{HF} = 9, 2 H_c); 8.13 (s, 2 H_a); 7.59 (m, 2 H_b);
 4.12 (s, 6 H_d); 3.37 (s, 3 H_e).

15 **Example 42:** 21.9 g of the compound according to example 41 are stirred at 23°C in 100 ml of methanol. 13.3 g of fluoroaniline and 19.6 g of sodium acetate are added. The reaction is stirred for 18 h and the methanol evaporated at 10³ Pa. The sticky residue is stirred in 200 ml of an 5% aqueous solution of sodium chloride. The solid formed is filtered and washed with 100 ml of an 5% aqueous solution of sodium
 20 chloride. The filtered material is dried for 24 hours at 50°C / 10³ Pa, yielding 26 g of an almost black product of formula

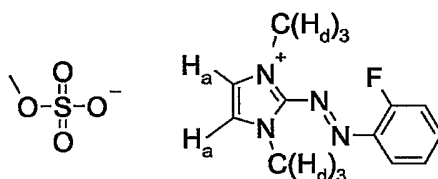


that is used directly to prepare the product of example 198.

- 54 -

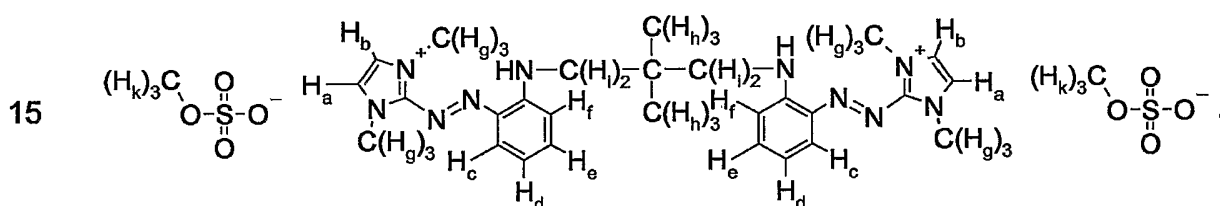
¹H-NMR [ppm]: 7.88 (d, J_{HF} = 9, 2 H_f); 7.73 (s, 2 H_a); 7.27 (m, 4 H);
7.08 (d, J = 9, 2 H); 3.96 (s, 6 H_d).

Example 43: The product is prepared according to the method of example 41,
starting from 12.4 g of 2-fluoroaniline and 7.4 g of imidazole. 27 g of the compound
5 of formula



are obtained, which is used directly to prepare the product of example 44.

Example 44: 4 g of triethylamine are added at 23°C to a stirred mixture of 2.04 g
2,2-dimethyl-1,3-diamino-propane, 100 g isopropanol and 14.3 g of the compound
10 according to example 43. The mixture is stirred for 6 hours at 60°C and 4 hours
while cooling down to 22°C. The reaction mass is filtered. The cake is washed with
30 ml of isopropanol and dried for 24 hours at 50°C / 10³ Pa, yielding 12 g of a
reddish violet product of the following formula that is used directly to prepare the
product of example 215:

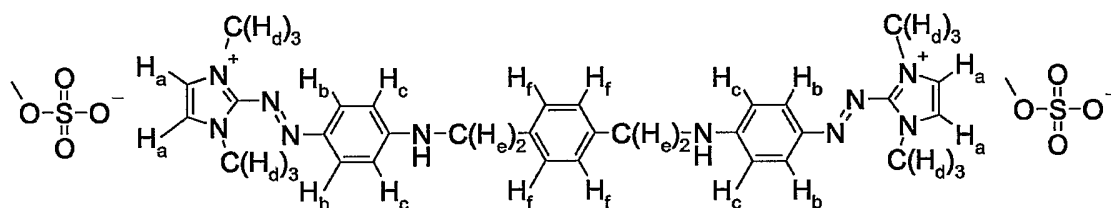


¹H-NMR [ppm]: 8.64 (broad s, 2 NH); 7.80 (s, 2 H_a and 2 H_b);
7.74 (dd, J = 3, J = 9, 2 H_c); 7.47 (ddd, J = 3, J = 9, J = 15, 2 H_e);
7.21 (d, J = 9, 2 H_f); 6.79 (ddd, J = 3, J = 9, J = 15 2 H_d);
3.97 (s, 12 H_g); 3.52 (d, J = 6, 4 H_i); 3.37 (s, 4 H_k); 1.07 (s, 6 H_h).

Example 45: 3.3 g of anhydrous sodium acetate and 2.72 g of α,α'-diamino-p-
xylene are added to a solution of 13.7 g of the compound according to example 41
20 in 270 ml of isopropanol at 23°C. The reaction mixture is stirred 18 h at 65-70°C.

- 55 -

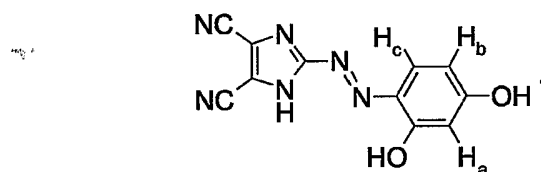
The isopropanol is evaporated at 40°C/10³ Pa and the residue is dissolved in 100 ml of water. 10 g of sodium chloride are added to precipitate the product. Filtration and washing with 100 ml of a 5% aqueous solution of sodium chloride affords a solid which is stirred in 40 ml of water for 10 minutes. Filtration and drying
 5 for 24 hours at 50°C/10³ Pa yields 5.5 g of dark reddish brown product of formula



that is used directly to prepare the product of example 232.

¹H-NMR [ppm]: 8.65 (broad s, 2 NH); 7.86 (d, J = 9, 4 H_b); 7.71(s, 4 H_a); 7.34/-
 7.38(m, 4 H_f); 6.87 (d, J = 9, 4H_c); 4.54(s, 4 H_e); 3.94 (s, 12 H_d).

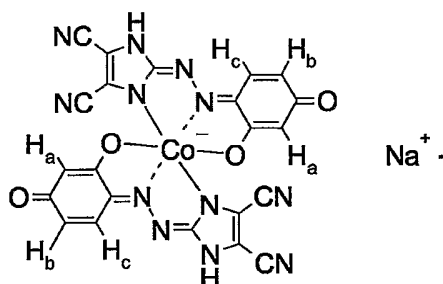
- 10 **Example 46:** The product is prepared in the same way as in example 1, starting from 26.6 g of 2-amino-4,5-dicyano-imidazole and 22 g of resorcinol. The product is an orange powder of formula:



- ¹H-NMR [ppm]: 10.99 (s, 2 OH); 7.63 (d, J = 6, H_c); 6.50 (dd, J = 3, J = 6, H_b);
 15 6.40 (d, J = 3, H_a); 4.8 (broad s, NH).

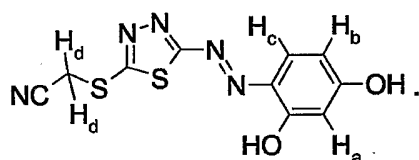
- Example 47:** 10.1 g of the compound according to example 46 are dissolved in 200 ml of 1-methoxy-2-propanol at 23°C. 3.3 g of anhydrous sodium acetate dissolved in 50 ml of methanol are added, followed by 5 g of cobalt(II) acetate tetrahydrate. The mixture is stirred for 3 hours, evaporated and the residue is
 20 dissolved in 100 ml of water. 10 g of sodium chloride are added and the solution kept 18 h at 5°C. The precipitate is filtered and washed with 20 ml of a 5% aqueous sodium chloride solution. Drying affords 9 g of an almost black product of formula

- 56 -



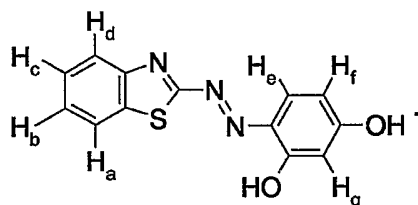
$^1\text{H-NMR}$ [ppm]: 11.5 (broad s, 2 NH); 7.98 (d, $J = 9$, H_c); 6.45 (dd, $J = 3$, $J = 9$ H_b); 6.04 (d, $J = 3$, H_a).

- Example 48:** The product is prepared in the same way as in example 1, starting from 14.6 g of (5-amino-1,3,4-thiadiazol-2-ylsulfanyl)-acetonitrile and 10 g of resorcinol. The product is an orange powder of formula



$^1\text{H-NMR}$ [ppm]: 11.13 (broad s, OH); 11.08 (s, OH); 7.70 (m, H_c); 6.48 (m, H_a and H_b); 4.57 (s, 2 H_d).

- Example 49:** The product is prepared in the same way as in example 1, starting from 15 g of 2-amino-benzthiazole and 12.1 g of resorcinol. The product is an orange powder of formula

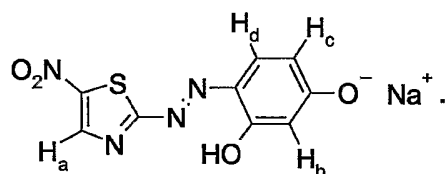


- $^1\text{H-NMR}$ [ppm]: 8.26 (m, H_a and H_d); 7.94 (d, $J = 9$, H_e); 7.66-7.78 (m, H_b and H_c); 6.73 (m, H_f and H_g).

Example 50: 33.3 g of the compound according to example 1 are dissolved, with stirring, in 550 ml of methanol at 23°C. To the red suspension, 10.25 g of sodium acetate are added. The now violet solution is stirred at room temperature for

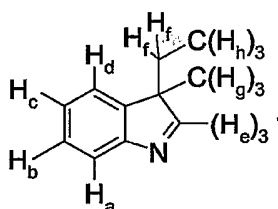
- 57 -

3 hours. The solution is filtered with suction, evaporated under vacuum yielding after drying for 12 hours at 50°C / 10³ Pa 30.76 g of a black powder of formula:



¹H-NMR [ppm]: 8.45 (s, H_a); 7.04/7.01 (d, H_d); 6.16/6.13 (d, H_c); 5.53/5.52 (d, H_b).

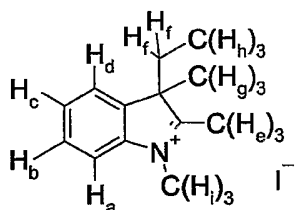
- 5 **Example 51:** 25 ml of 98% sulfuric acid are dissolved in 260 ml of ethanol under stirring, with some cooling in order to keep a temperature close to 25°C. 28.1 g of phenylhydrazine hydrochloride are added, followed by 38.3 ml of 3-methyl-2-pentanone. The reaction media is then stirred at 75°C for 3 h. After cooling to 23°C, some ethanol is evaporated under reduced pressure, and 200 ml of 5% aqueous
- 10 NaOH solution are slowly added. The aqueous phase is extracted with ethyl acetate, and this organic phase is evaporated under reduced pressure to 41.8 g of brown resin. The product of the following formula is used crude for the next step (example 52):



- 15 ¹H-NMR [ppm]: 7.43 / 7.40 (d, H_a); 7.34 / 7.33 (d, H_d); 7.33-7.31 (dd, H_b); 7.16-7.14 (dd, H_c); 2.15 (s, 3H_e); 1.98-1.69 (m, 2H_f); 1.21 (s, 3H_g); 0.26 (t, 3H_h).

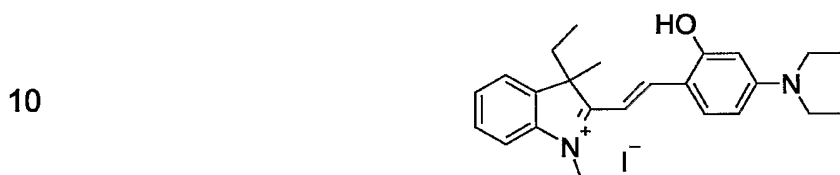
- Example 52:** The crude material according to example 51 is dissolved in 150 ml of chloroform, and 20 ml of methyl iodide are added. Then, the reaction medium is
- 20 heated to reflux for 4 hours. It is then cooled to 0°C and filtrated at this temperature. The solid obtained is washed with cold acetone, yielding 45 g of a beige compound of formula:

- 58 -



¹H-NMR [ppm]: 7.97-7.91 (dd, H_a); 7.82-7.76 (d, H_d); 7.69-7.61 (m, H_b and H_c); 4.03 (s, 3H_i); 2.80 (s, 3H_e); 2.28-2.03 (m, 2H_f); 1.53 (s, 3H_g); 0.41 (t, 3H_h).

- 5 **Example 53:** 8 g of the compound according to example 52 are dissolved in 200 ml of methanol. 4.8 g of 4-diethylamino-salicylaldehyde are added. The solution is refluxed for 4 hours and stirred for 18 hours at room temperature, then adjusted to a volume of 220 ml and used directly in example 54. An analytical sample is evaporated at 10³ Pa to yield a dark-violet crude compound of formula:

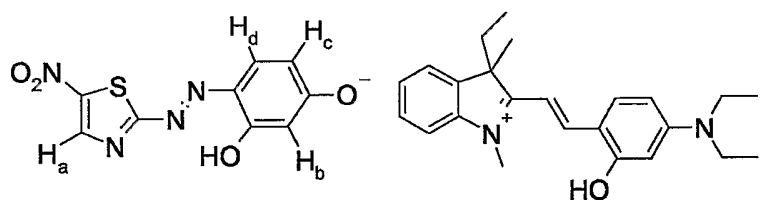


¹H-NMR [ppm]: 11.02 (br. S, OH); 8.42 / 8.37 (d, 1H); 7.98 / 7.95 (d, 1H); 7.68-7.61 (m, 2H); 7.55-7.50 (dd, 1H); 7.44-7.39 (dd, 1H); 7.23 / 7.18 (d, 1H); 6.55-6.51 (dd, 1H); 6.23 / 6.22 (d, 1H); 3.86 (s, 3H); 3.51-3.41 (m, 4H); 3.35 (s, 3H); 2.40-2.18 (m, 2H); 1.69 (s, 3H); 1.17 (t, 6H); 0.34 (t, 3H).

15

- Example 54** (synthesis of salt): 0.3 g of the product according to example 50 is added to 20 ml of methanol at 23°C. 8.8 ml of the solution of example 53 corresponding to 0.5 g of pure compound are added and the resulting solution is stirred for 2 h at 23°C, thus giving a violet suspension. 15 ml of water are added to the suspension and the product is filtered with suction through a Büchner filter and washed with a 1:1 mixture of methanol and water. Drying at 50°C / 10³ Pa yields 0.24 g of an almost black product of formula:
- 20

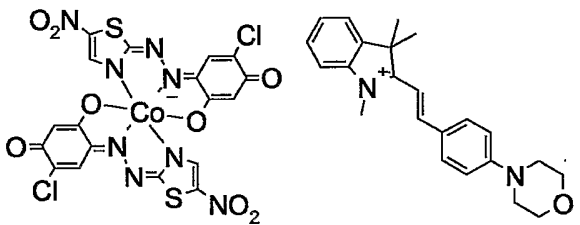
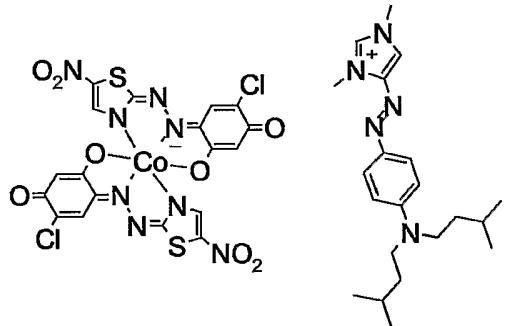
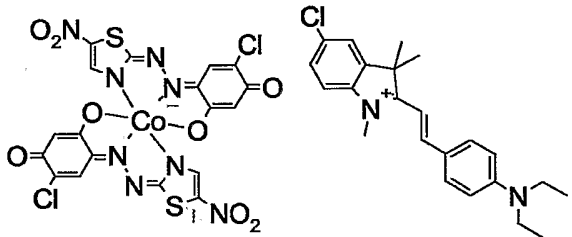
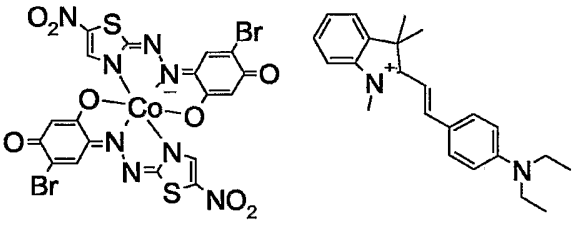
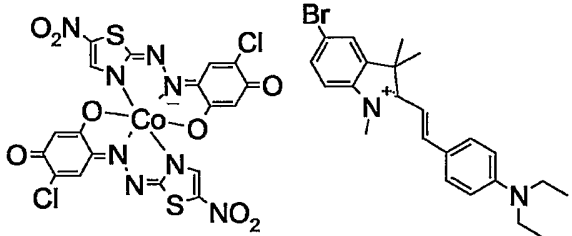
- 59 -



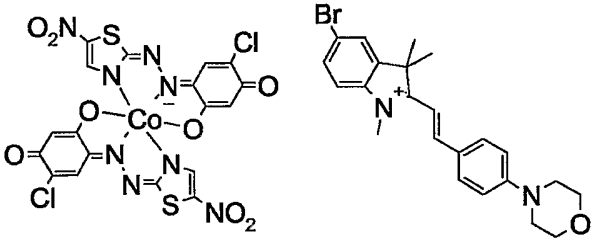
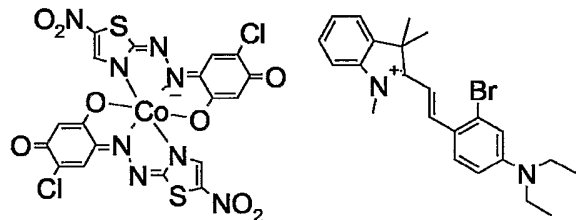
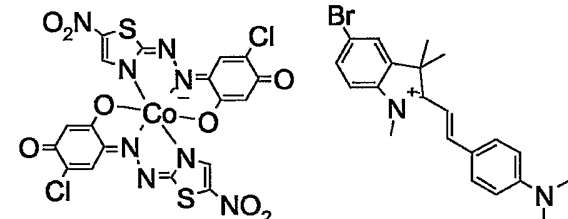
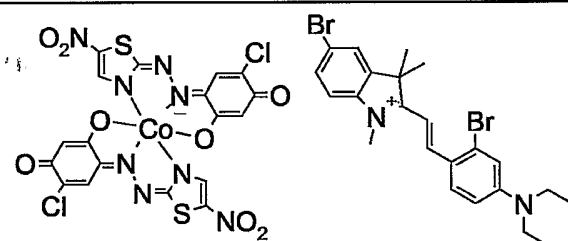
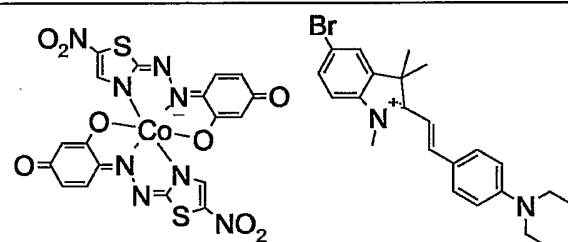
See example 288 for the optical parameters of a solid layer made from a mixture of this compound with the compound of example 88.

- Examples 55-293: Analogously to examples 14 and 15, the $\lambda_{\max}$ (solid film), the n - and k -values (using a Steag ETA-Optik) and the photostability (relative decrease in absorption $-D_{24}$ after 24 hours' irradiation with a calibrated xenon lamp / Hanau) of recording layers are determined, the following compounds being used:

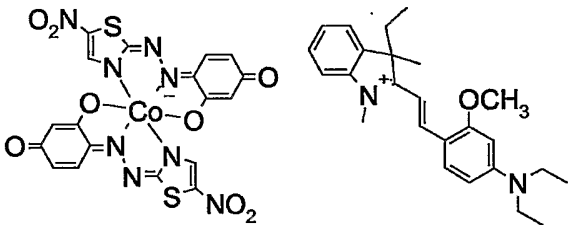
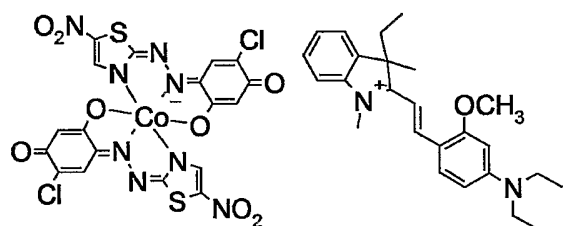
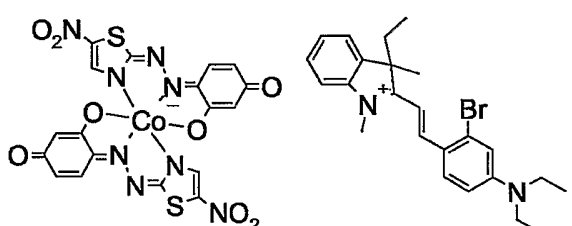
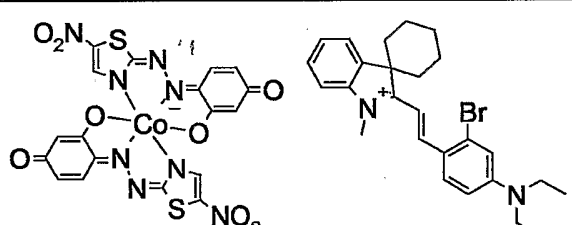
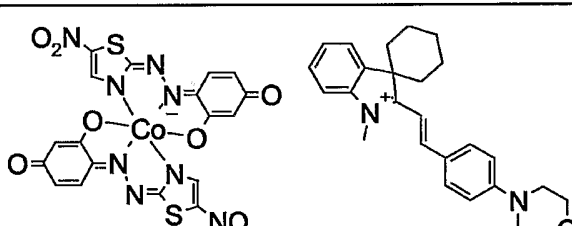
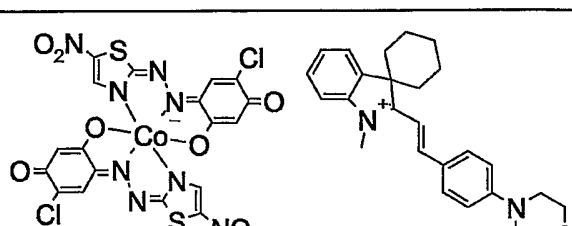
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
55		546	2.52	0.07	41
56		552	2.64	0.11	34
57		559	2.58	0.08	14

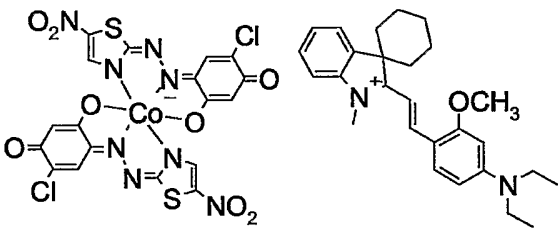
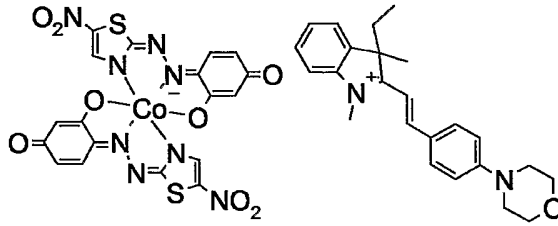
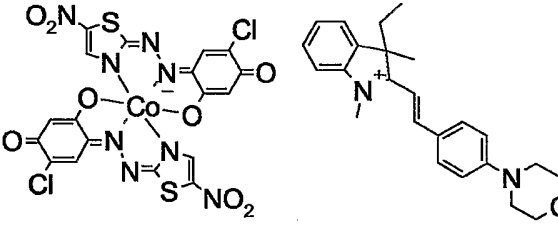
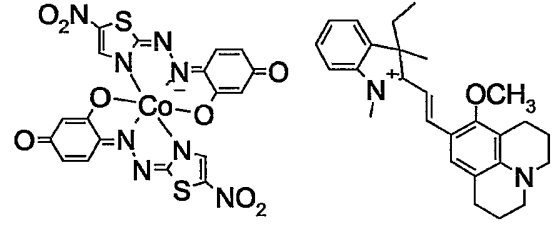
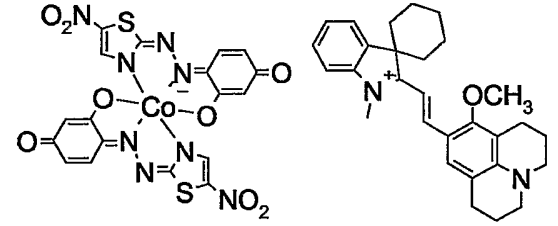
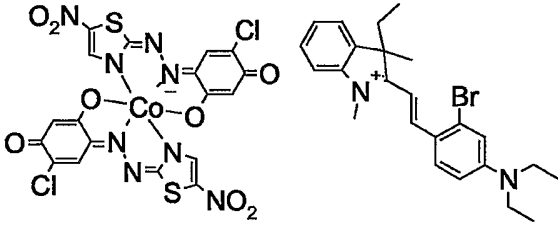
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}^{24}$ [%]
58		544	2.47	0.07	22
59		574	2.42	0.05	13
60		558	2.60	0.07	10
61		552	2.57	0.08	10
62		560	2.70	0.09	8

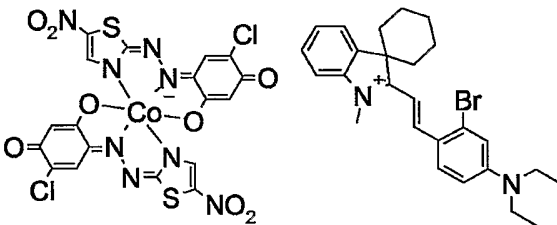
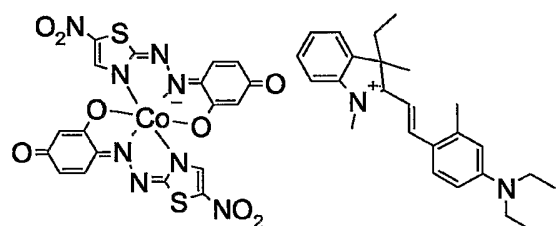
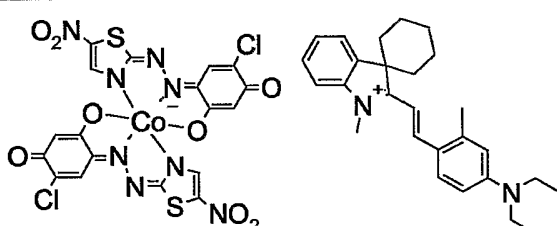
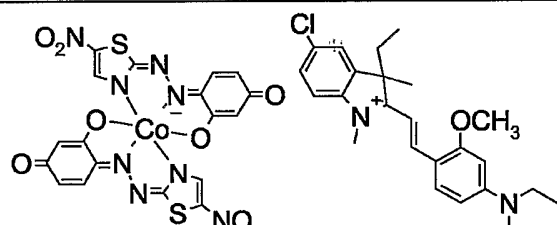
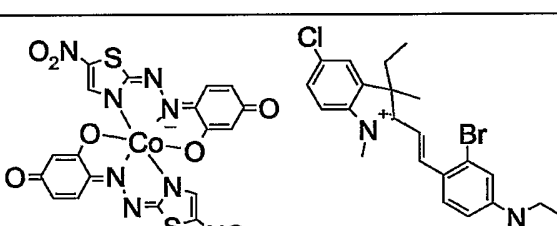
- 61 -

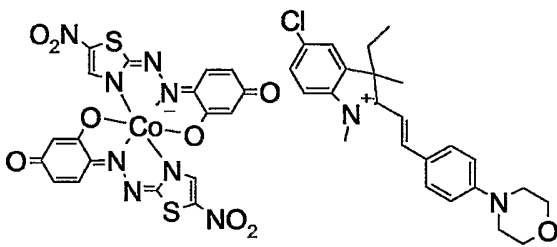
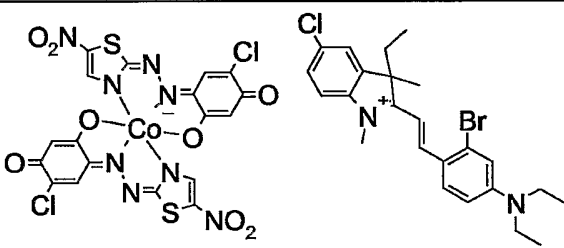
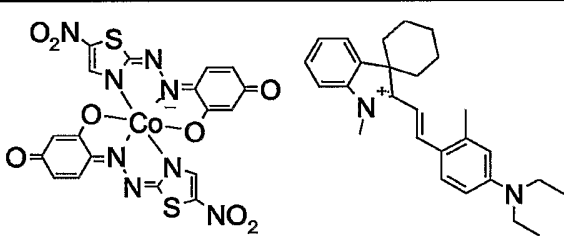
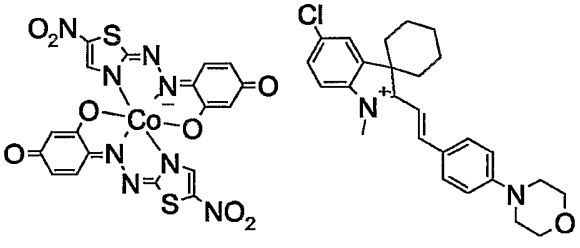
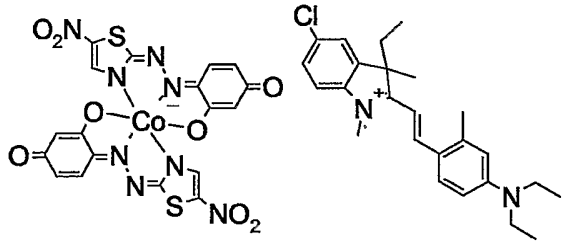
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}^{24}$ [%]
63		552	2.51	0.06	19
64		548	2.46	0.05	11
65		568	2.60	0.09	10
66		553	2.53	0.06	14
67		555	2.60	0.07	16

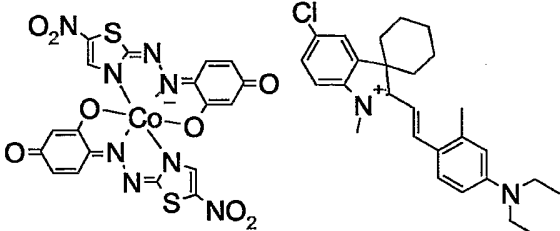
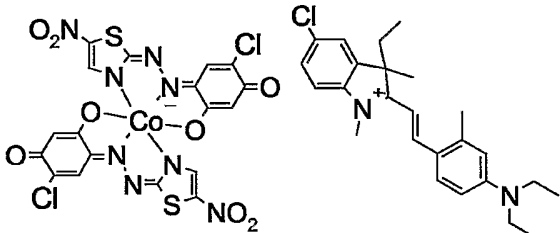
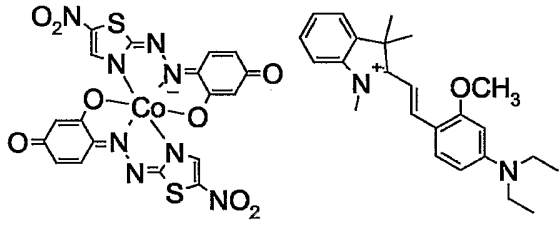
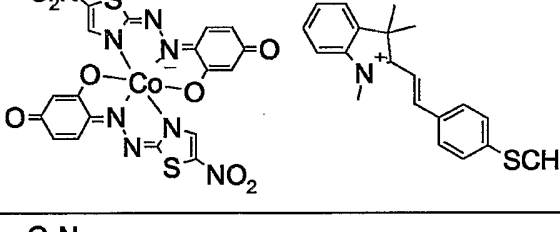
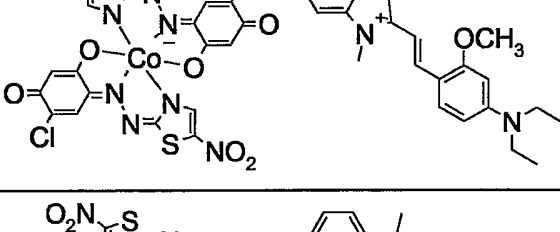
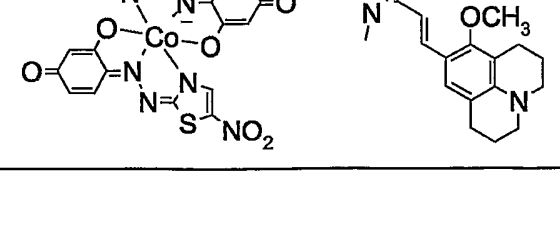
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
68		565	2.66	0.17	9
69		552	2.45	0.06	22
70		537	2.31	0.05	16
71		566	2.72	0.14	13
72		548	2.37	0.04	14

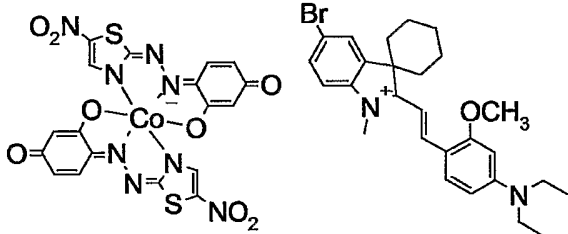
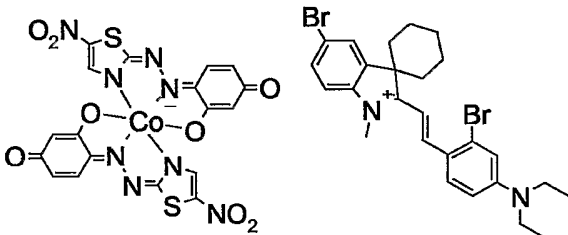
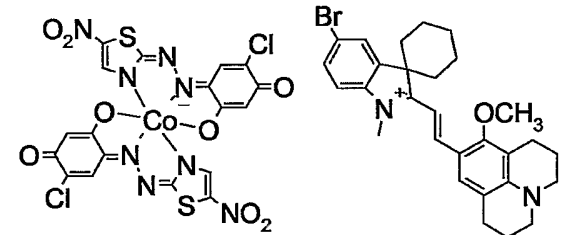
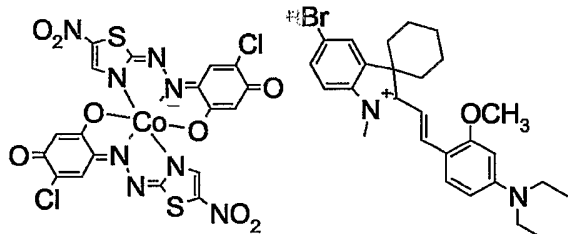
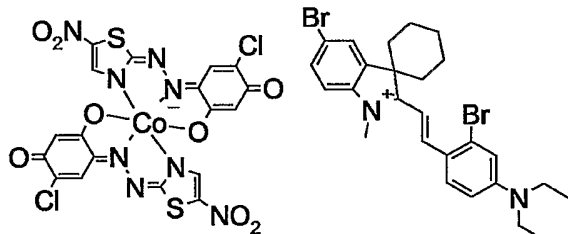
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
73		548	2.41	0.04	14
74		580	2.42	0.04	8
75		549	2.42	0.05	15
76		547	2.39	0.05	21
77		538	2.34	0.04	28
78		547	2.38	0.06	19

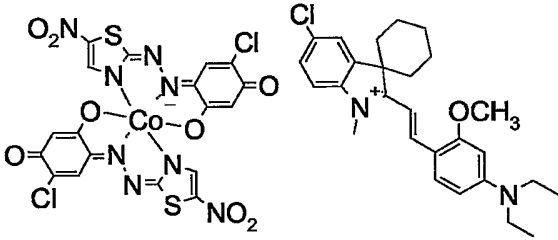
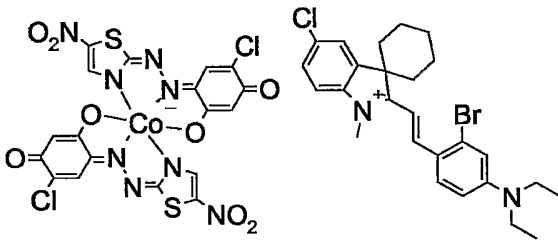
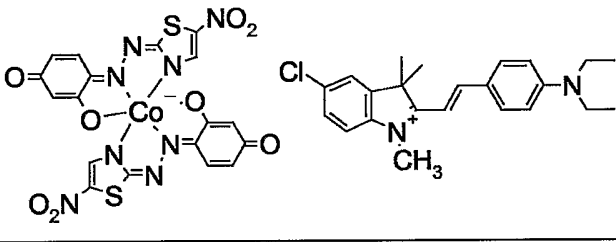
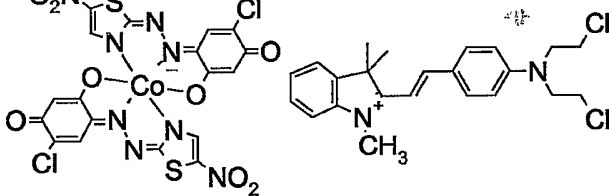
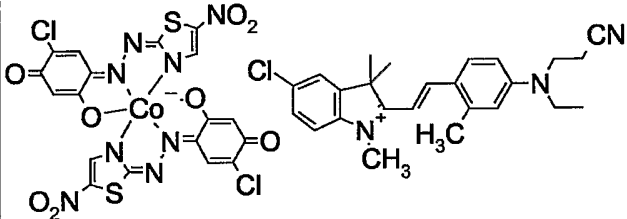
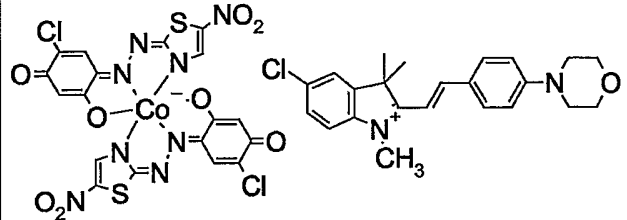
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}^{24}$ [%]
79		578	2.42	0.05	12
80		539	2.39	0.05	23
81		553	2.37	0.05	23
82		557	2.65	0.15	38
83		557	2.57	0.12	27
84		553	2.49	0.06	10

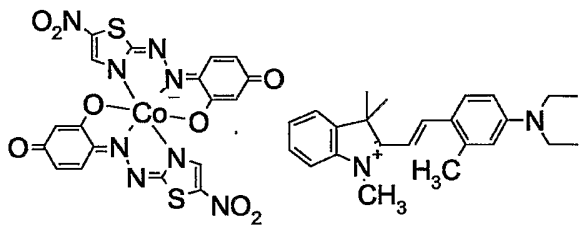
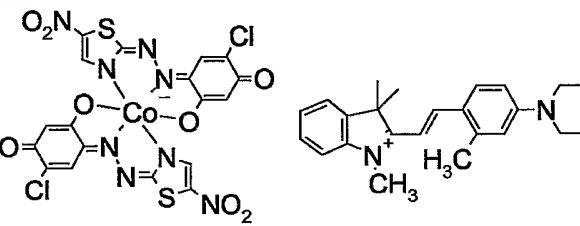
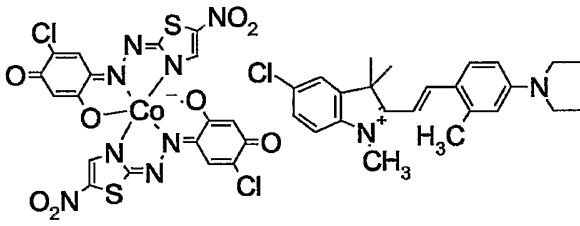
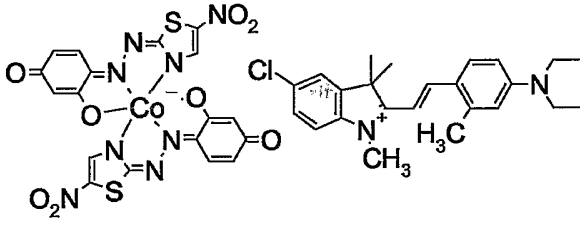
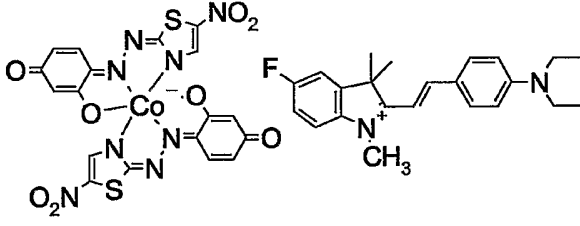
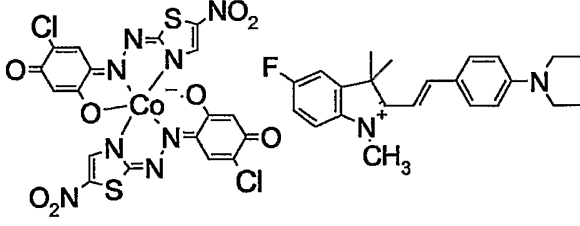
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}^{\lambda}$ [%]
85		551	2.41	0.05	11
86		555	2.51	0.05	13
87		559	2.51	0.06	10
88		552	2.47	0.05	19
89		555	2.48	0.04	18

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
90		552	2.46	0.03	30
91		558	2.54	0.04	14
92		554	2.50	0.05	18
93		545	2.49	0.03	29
94		561	2.67	0.09	16

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}^{24}$ [%]
95		559	2.63	0.09	15
96		561	2.65	0.09	15
97		543	2.42	0.03	13
98		523	2.23	0.03	24
99		547	2.48	0.05	12
100		552	2.62	0.14	37

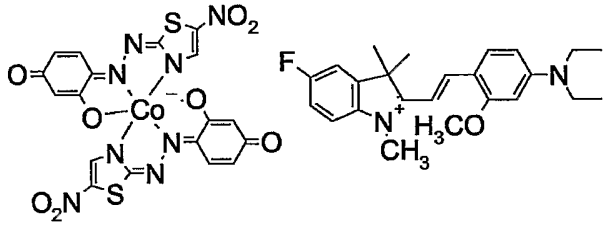
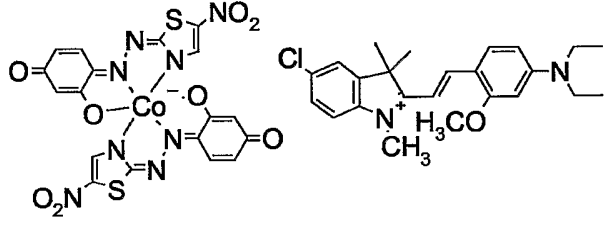
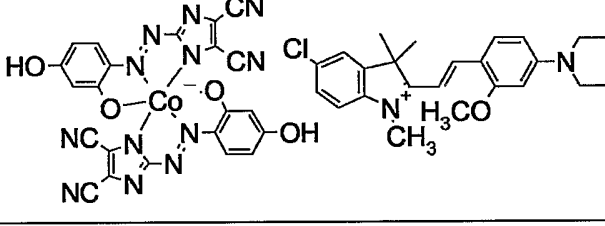
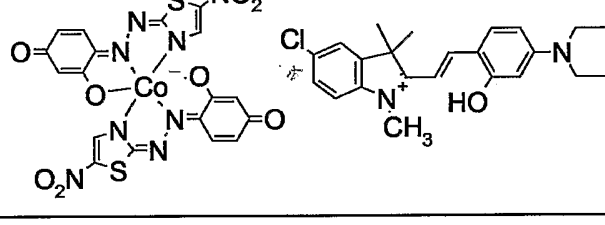
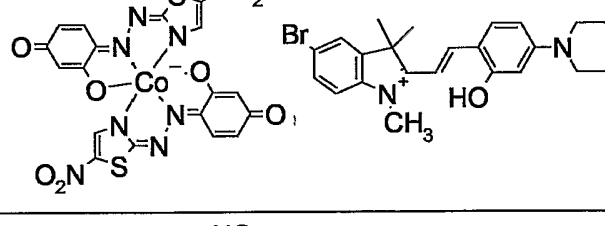
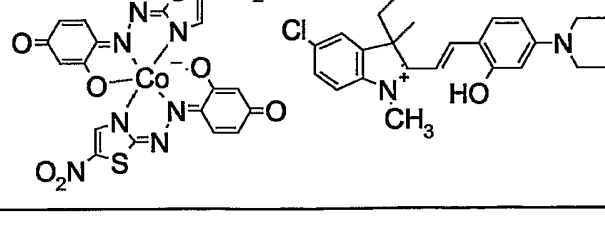
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
101		554	2.43	0.06	11
102		558	2.53	0.07	13
103		561	2.60	0.22	25
104		586	2.39	0.08	4
105		557	2.32	0.07	12

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}^{24}$ [%]
106		560	2.38	0.08	9
107		554	2.31	0.08	7
108		555	2.52	0.07	6
109		534	2.25	0.03	10
110		549	2.24	0.04	10
111		554	2.46	0.06	21

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
112		552	2.51	0.09	6
113		560	2.47	0.06	11
114		564	2.64	0.12	14
115		560	2.60	0.09	16
116		547	2.49	0.07	18
117		553	2.55	0.08	7

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
118		561	2.54	0.06	18
119		561	2.55	0.07	14
120		553	2.55	0.07	26
121		553	2.53	0.03	29
122		549	2.42	0.06	27
123		548	2.45	0.06	6

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
124		555	2.53	0.06	9
125		545	2.37	0.04	6
126		545	2.40	0.05	4
127		554	2.49	0.07	12
128		546	2.40	0.04	11
129		544	2.40	0.05	6

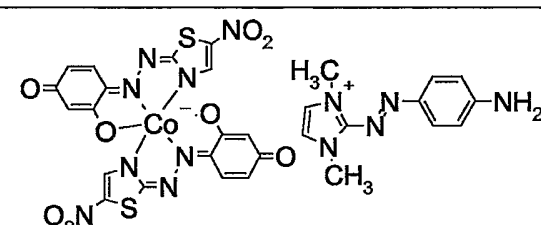
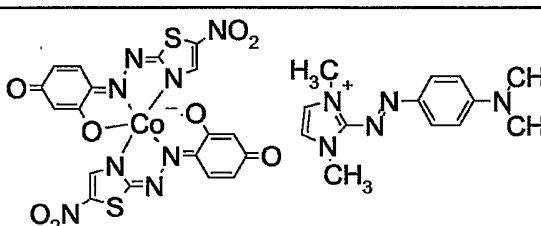
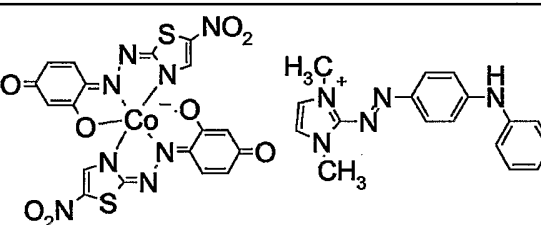
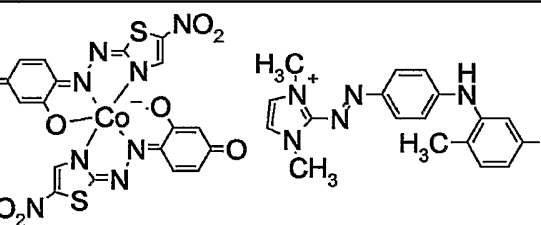
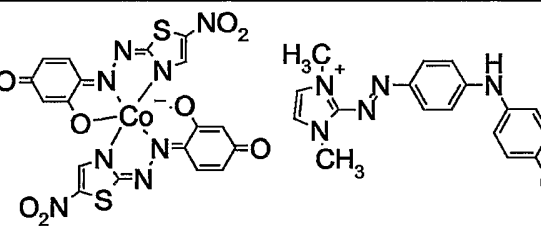
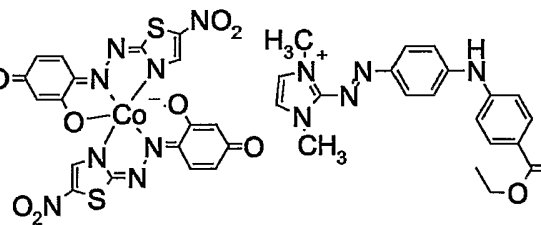
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
130		546	2.44	0.04	13
131		549	2.46	0.05	17
132		588	2.32	0.06	2
133		549	2.52	0.06	7
134		583	2.48	0.05	8
135		584	2.48	0.05	7

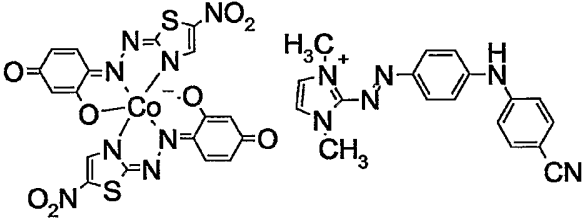
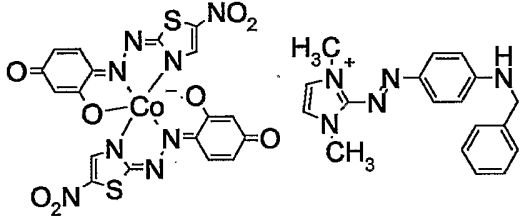
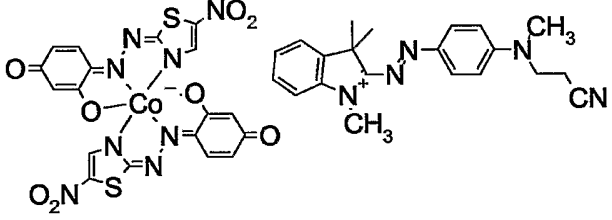
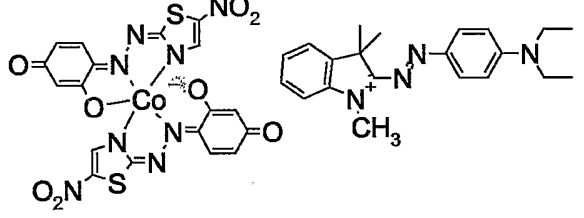
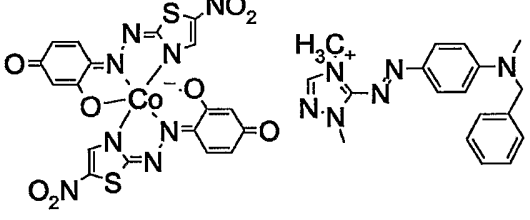
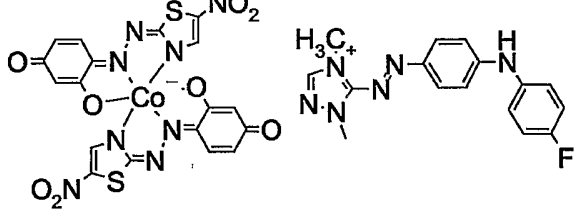
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}^{24}$ [%]
136		586	2.47	0.04	9
137		545	2.43	0.05	11
138		545	2.43	0.05	11
139		574	2.48	0.05	7
140		574	2.48	0.05	7
141		574	2.47	0.04	13

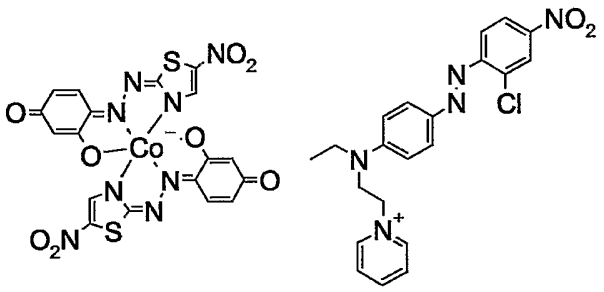
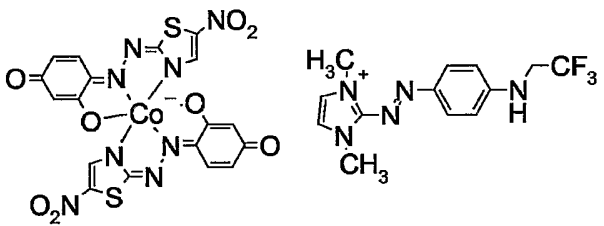
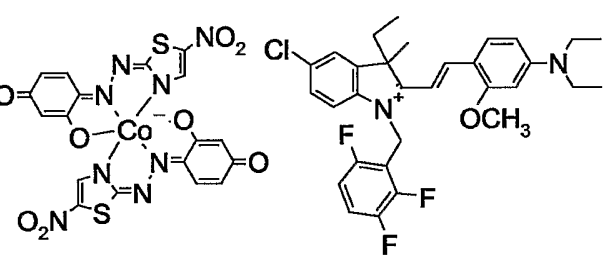
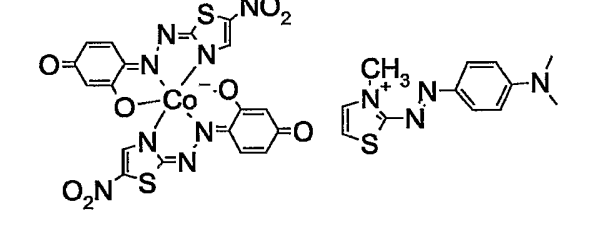
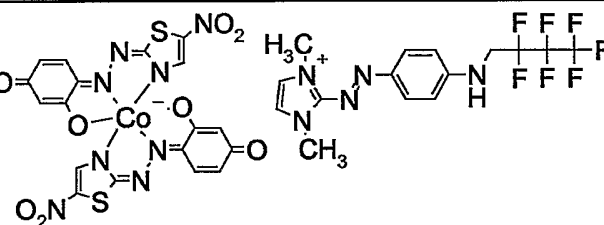
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
142		548	2.38	0.04	17
143		561	2.58	0.10	16
144		559	2.61	0.07	11
145		560	2.57	0.08	16
146		558	2.55	0.10	23
147		551	2.41	0.05	21

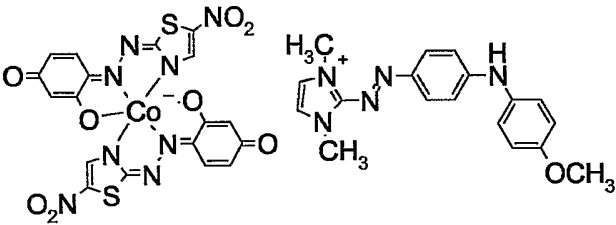
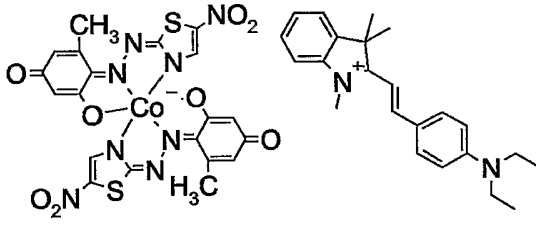
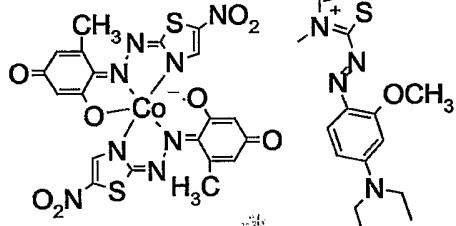
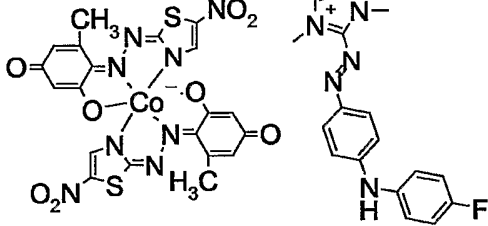
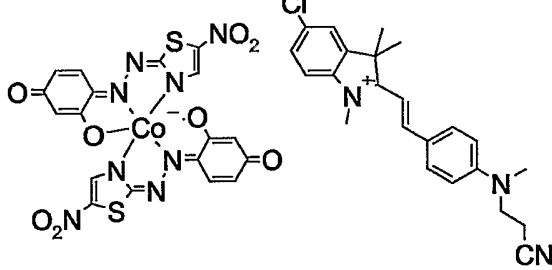
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}^{24}$ [%]
148		560	2.60	0.09	27
149		552	2.40	0.06	17
150		565	2.14	0.12	10
151		556	2.31	0.05	18
152		543	2.40	0.159	8
153		534	2.46	0.04	15

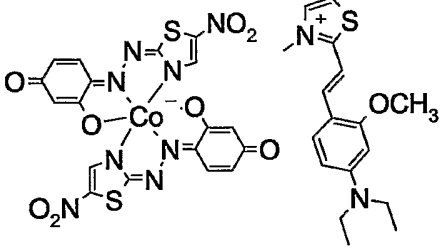
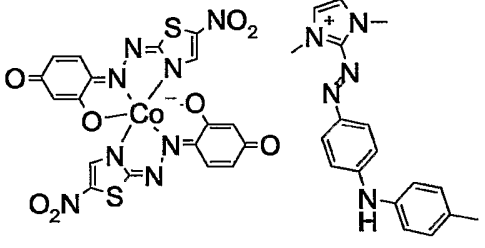
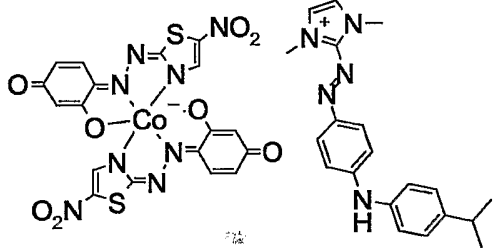
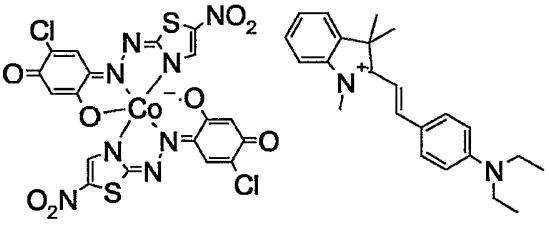
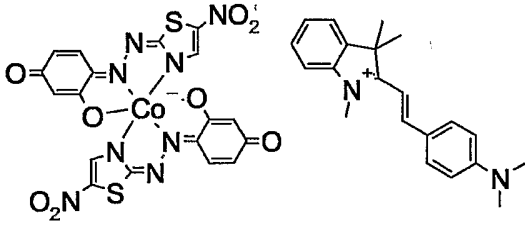
- 77 -

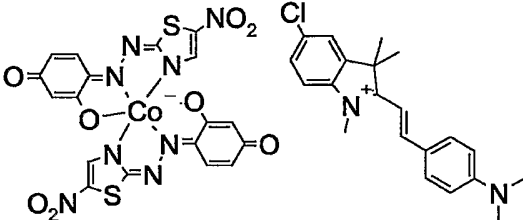
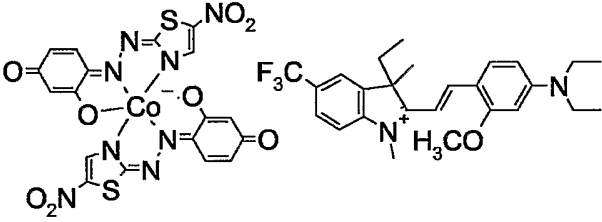
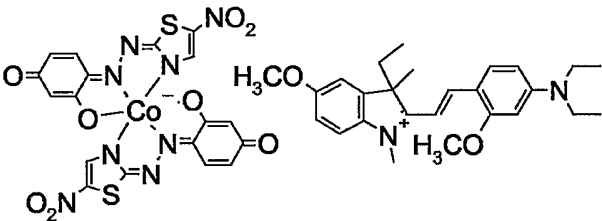
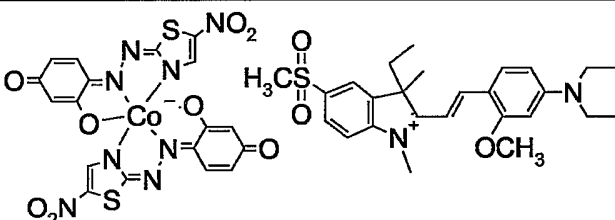
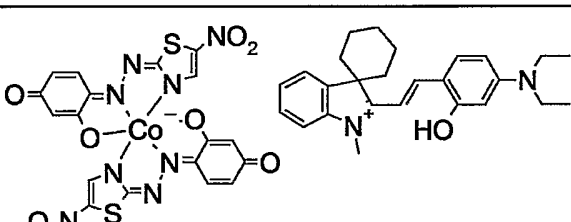
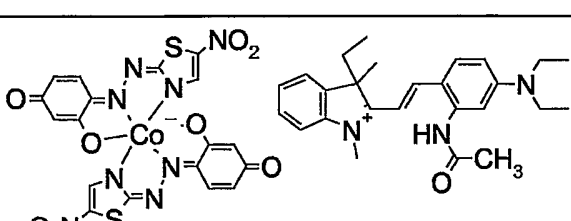
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
154		534	2.38	0.06	9
155		532	2.39	0.039	23
156		539	2.42	0.074	11
157		537	2.35	0.043	11
158		539	2.37	0.071	8
159		535	2.34	0.043	13

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
160		537	2.33	0.052	15
161		538	2.38	0.05	24
162		532	2.34	0.04	17
163		546	2.47	0.05	20
164		533	2.36	0.04	19
165		539	2.42	0.06	8

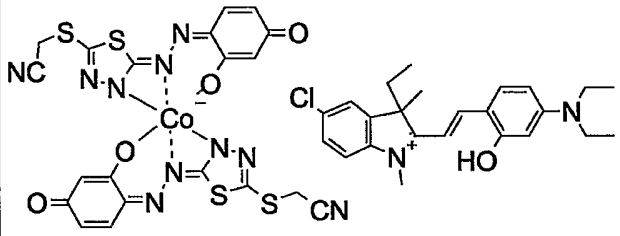
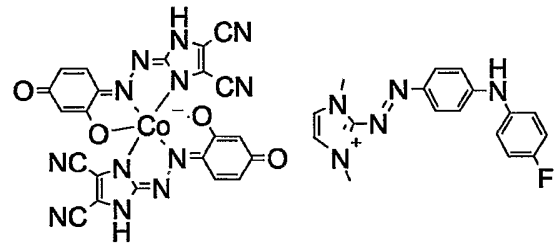
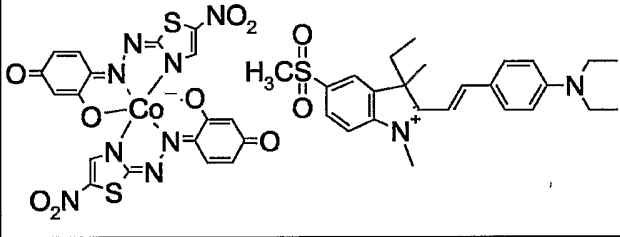
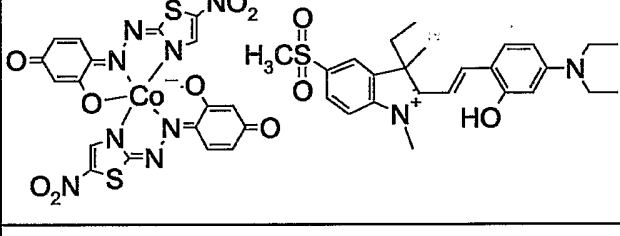
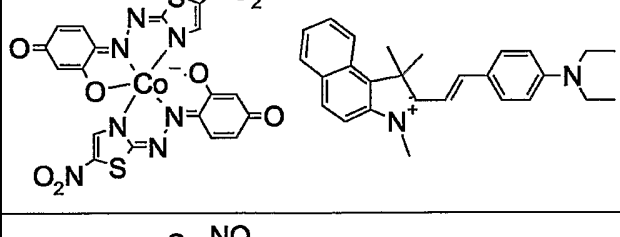
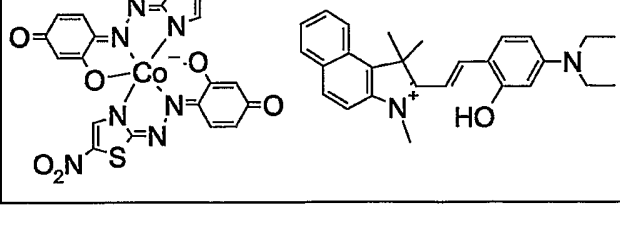
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	-D ₂₄ [%]
166		526	2.20	0.03	28
167		534	2.28	0.03	13
168		552	2.45	0.05	15
169		558	2.79	0.50	17
170	95 parts compound of example 165 5 parts compound of example 169	537	2.45	0.08	8
171		555	2.15	0.02	47

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
172		543	2.40	0.16	8
173	95 parts compound of example 165 5 parts compound of example 172	537	2.44	0.06	7
174		547	2.45	0.04	24
175		533	2.60	0.15	22
176		540	2.39	0.06	17
177		540	2.31	0.05	17

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}^{24}$ [%]
178		558	2.66	0.16	14
179		544	2.47	0.08	11
180		544	2.43	0.08	12
181		556	2.53	0.06	8
182		545	2.52	0.06	19
183	95 parts compound of example 182 5 parts compound of example 172	543	2.46	0.07	15
184	95 parts compound of example 182 5 parts compound of example 169	543	2.51	0.08	16

Example	Structure	λ_{max} [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
185		557	2.64	0.08	20
186		550	2.41	0.04	13
187		550	2.40	0.05	11
188		590	2.47	0.03	15
189		544	2.44	0.05	9
190		554	2.44	0.08	13

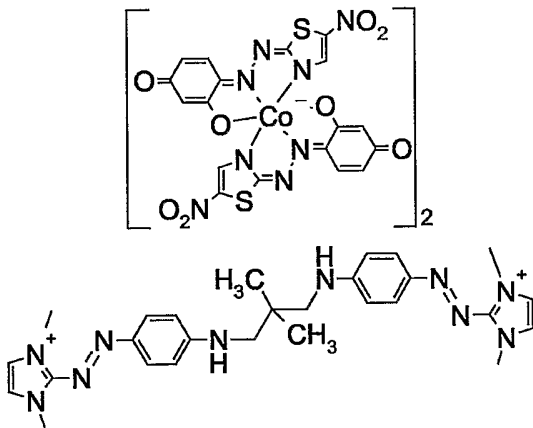
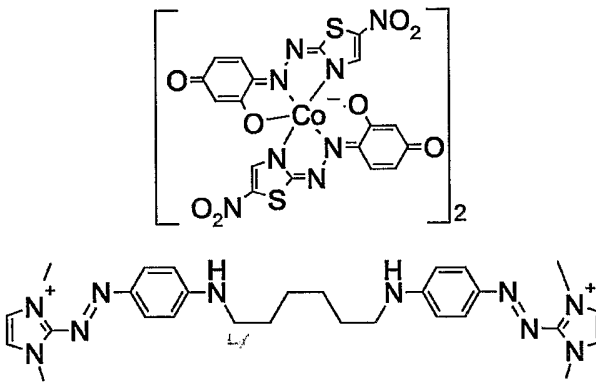
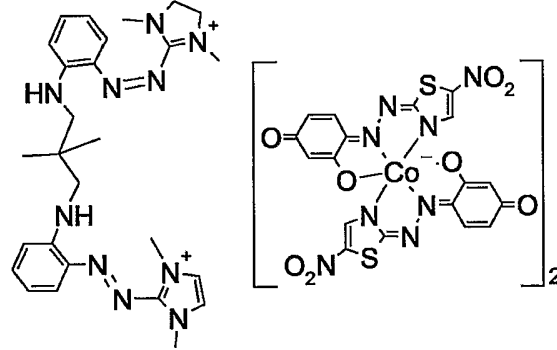
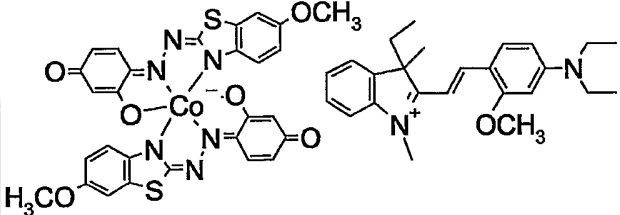
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
191		578	2.42	0.04	12
192		547	2.43	0.06	8
193		557	2.58	0.08	15
194		580	2.27	0.05	6
195		575	2.24	0.04	4
196		588	2.26	0.02	15

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
197		596	2.31	0.04	18
198		532	2.21	0.05	6
199		556	2.49	0.12	14
200		585	2.47	0.05	10
201		554	2.57	0.10	15
202		550	2.50	0.07	7

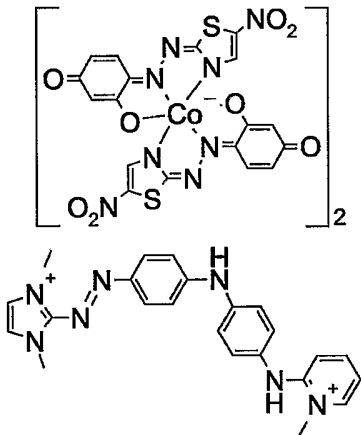
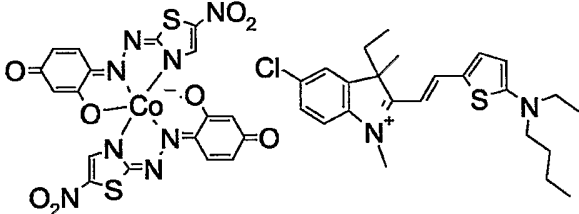
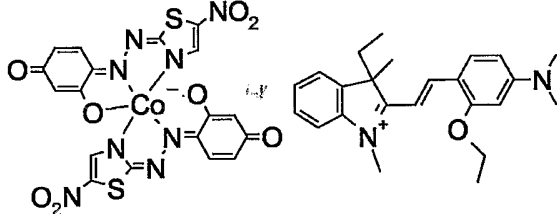
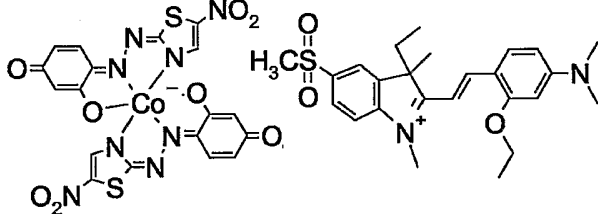
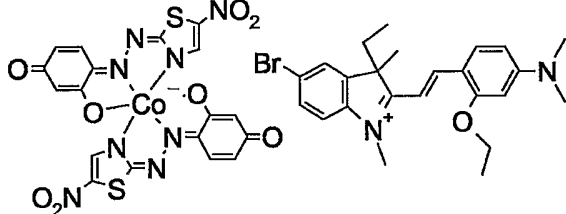
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
203		589	2.37	0.04	18
204		545	2.42	0.06	11
205		552	2.49	0.07	16
206		559	2.66	0.11	17
207		557	2.51	0.09	14

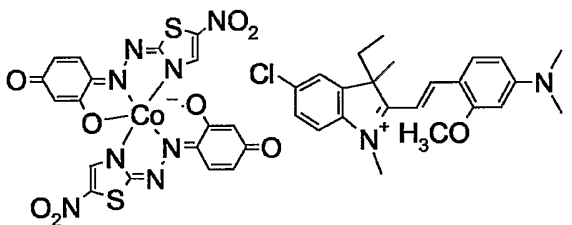
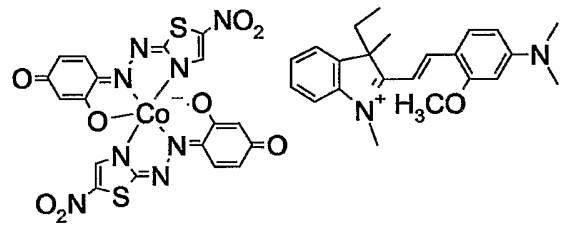
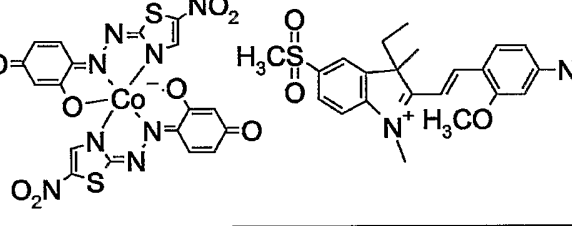
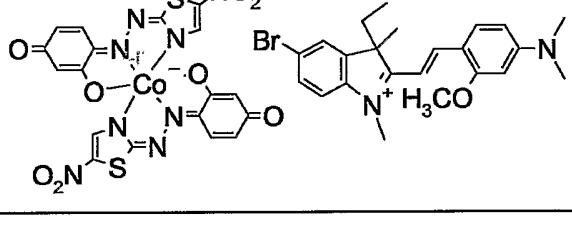
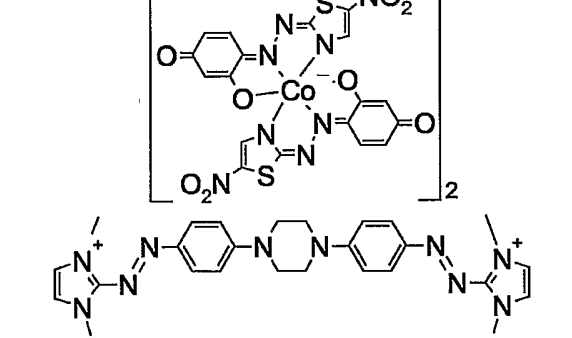
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
208		538	2.45	0.06	20
209		590	2.38	0.04	15
210		592	2.34	0.05	15
211		545	2.34	0.02	13
212		536	2.45	0.05	20

- 87 -

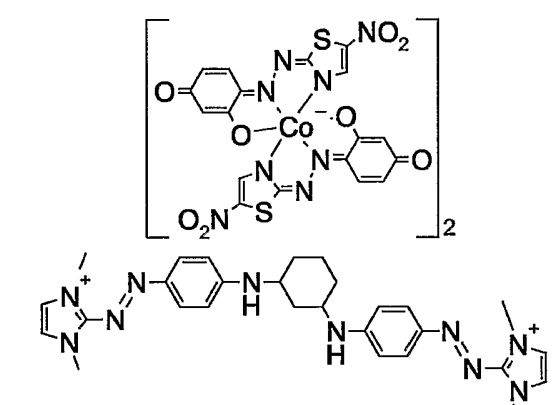
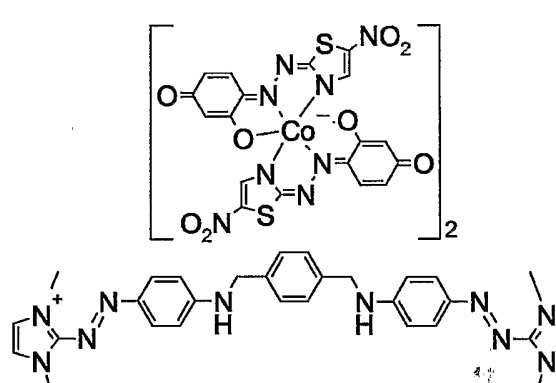
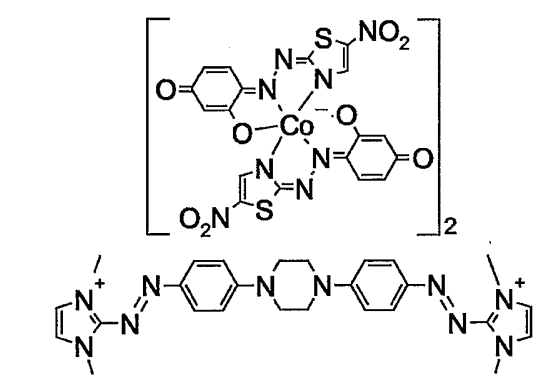
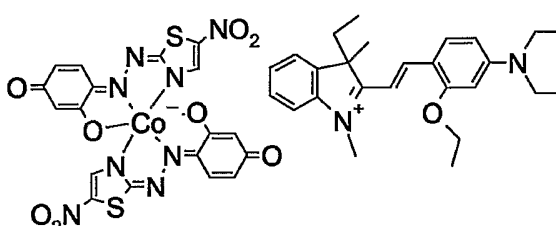
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
213		532	2.38	0.04	14
214		529	2.39	0.05	22
215		555	2.29	0.07	20
216		579	2.36	0.13	8

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
217		531	2.36	0.03	15
218		531	2.30	0.06	13
219		533	2.40	0.04	20
220		547	2.43	0.04	20

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
221		541	2.40	0.07	11
222		549	2.46	0.06	11
223		541	2.38	0.04	20
224		550	2.46	0.03	18
225		548	2.45	0.04	21

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
226		547	2.46	0.04	19
227		543	2.40	0.05	18
228		551	2.46	0.05	16
229		549	2.51	0.05	17
230		542	2.45	0.05	24

- 91 -

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}^{24}$ [%]
231		531	2.37	0.05	12
232		531	2.34	0.04	20
233		543	2.41	0.05	39
234		542	2.37	0.04	16

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
235		587	2.42	0.03	14
236		550	2.43	0.04	15
237		548	2.43	0.04	15
238		554	2.56	0.08	30
239		553	2.44	0.05	16

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
240		546	2.36	0.04	18
241		546	2.31	0.06	20
242		550	2.45	0.04	15
243		546	2.39	0.04	14
244		587	2.54	0.05	14
245		544	2.40	0.03	16

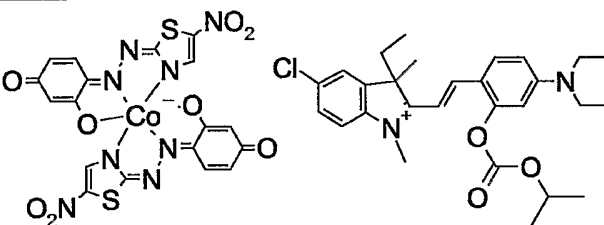
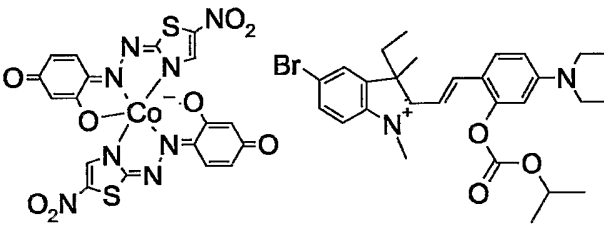
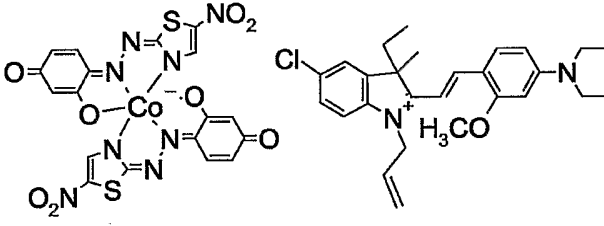
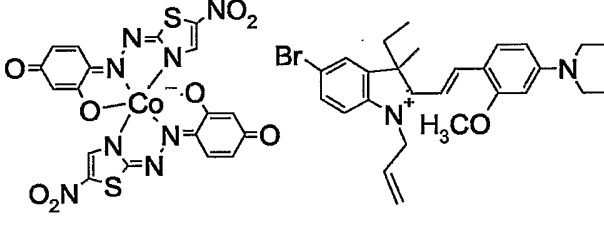
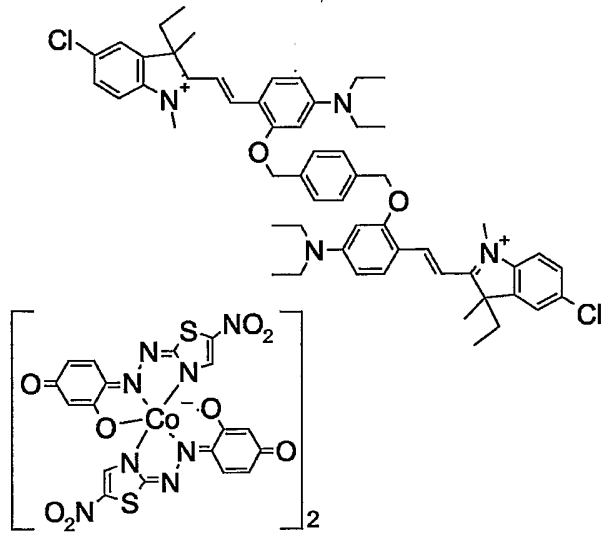
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
246		545	2.38	0.03	18
247		549	2.44	0.03	17
248		549	2.42	0.03	17
249		545	2.37	0.03	17
250		547	2.35	0.03	17
251		554	2.36	0.04	10

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
252		548	2.42	0.05	14
253		561	2.33	0.03	17
254		555	2.32	0.03	15
255		547	2.27	0.03	16
256		557	2.15	0.02	17
257		563	2.14	0.03	14

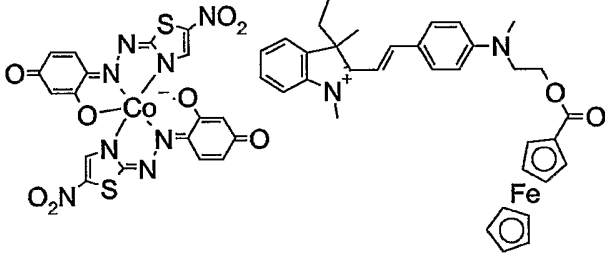
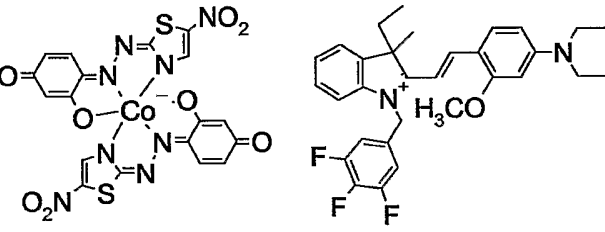
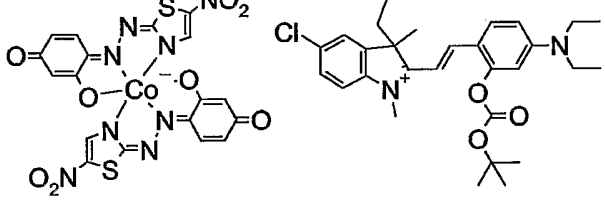
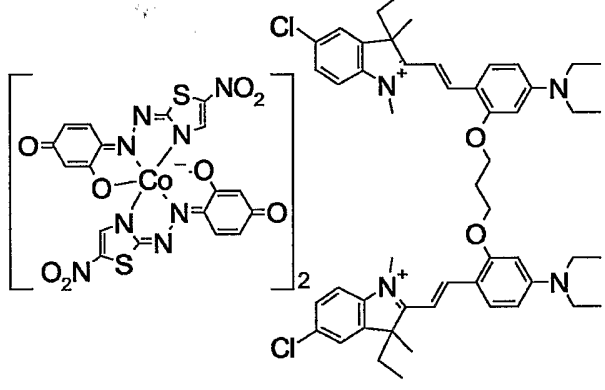
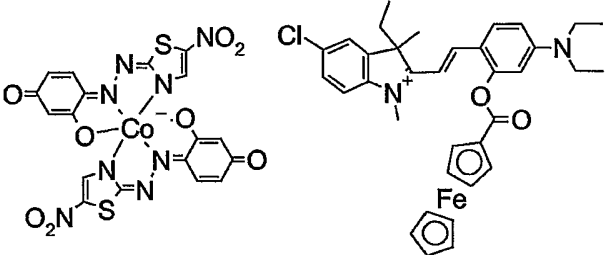
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
258		549	2.43	0.04	16
259		549	2.45	0.05	20
260		520	2.01	0.03	33
261		551	2.48	0.04	17
262		552	2.50	0.05	23
263		554	2.50	0.05	22

- 97 -

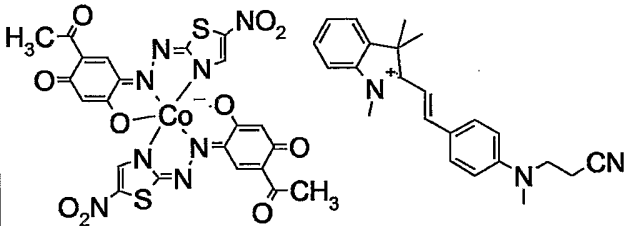
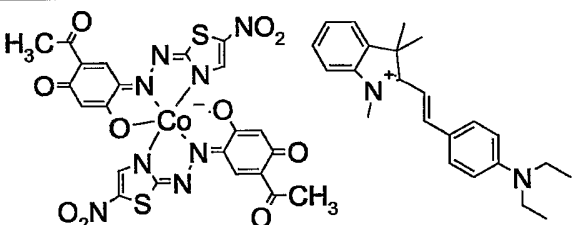
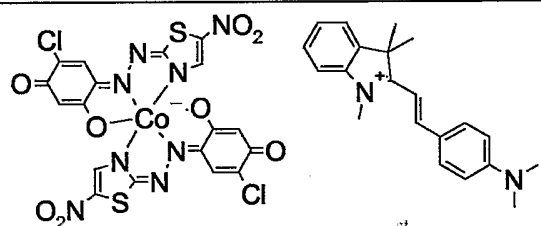
Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
264		555	2.53	0.05	22
265		545	2.45	0.03	19
266		548	2.46	0.03	21
267		554	2.51	0.05	17
268		555	2.45	0.04	15

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
269		548	2.42	0.04	19
270		552	2.44	0.03	20
271		554	2.48	0.04	19
272		554	2.55	0.05	18
273		550	2.40	0.05	18

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
274		550	2.41	0.06	16
275		552	2.44	0.05	16
276		544	2.35	0.04	20
277		553	2.44	0.05	15

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
278		540	2.30	0.05	21
279		550	2.25	0.03	13
280		548	2.46	0.05	10
281		552	2.39	0.04	14
282		550	2.39	0.05	25

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	$-D_{24}$ [%]
283		550	2.33	0.04	17
284		596	2.42	0.04	10
285		562	2.53	0.07	14
286		568	2.44	0.04	10
287		558	2.40	0.06	13
288	1 part compound of example 54 + 1 part compound of example 88	580	2.47	0.08	17
289	1 part compound of example 88 + 1 part compound of example 151	550	2.40	0.05	16

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	-D ₂₄ [%]
290	1 part compound of example 88 + 1 part compound of example 278	546	2.37	0.04	21
291		535	2.37	0.12	15
292		587	2.48	0.13	17
293		551	2.65	0.09	14

Example 294: 1.48 g of the compound according to example 13 are dissolved in 100 ml of 2,2,3,3-tetrafluoropropanol and filtered through a Teflon™ filter having a pore size of 0.2 μm. The dye solution is then applied at 250 rev/min to the surface of a 0.6 mm thick, grooved polycarbonate disc (groove depth 164 nm, groove width 380 nm, track pitch 0.74 mm) having a diameter of 120 mm. The excess of solution is spun off by increasing the speed of rotation. When the solvent is evaporated off, the dye remains behind in the form of a uniform, amorphous solid layer. Drying is carried out in a circulating-air oven at 70°C for 20 minutes. In a vacuum-coating apparatus (Twister™, Balzers Unaxis) a 120 nm thick silver layer is then applied to the recording layer by sputter coating. An adhesive layer of a UV-curable photo-polymer (LMD2277™, Vantico/Huntsman) is then applied thereto by spin-coating, and a second polycarbonate disc (0.6 mm thick, 120 mm diameter) is adhesively bonded thereto. The final disk has a reflectivity of 45% at 658 nm. On a commercial

- 103 -

test apparatus (DDU-1000™, Pulstec Japan), using a laser diode of wavelength 658 nm, marks are written into the active layer at speeds of $\sim 3.5 \text{ m} \cdot \text{s}^{-1}$ ($3.49 = 1 \times$) and $28 \text{ m} \cdot \text{s}^{-1}$ ($8 \times$). Then, on a commercial test apparatus (DVD Pro, Audio Dev), the following dynamic parameters are determined: data-to-clock (DTC) jitter, R14H, I14/I14H, asymmetry. After routine optimisation of the writing strategy, especially low values for DTC jitter are obtained.

Writing speed [$\text{m} \cdot \text{s}^{-1}$]	R14H [%]	I14/I14H	DTC Jitter [%]	Asymmetry [%]
3.5 (1 x)	45	0.61	8.7	10
28 (8 x)	45	0.71	9.4	0

The performance is excellent at both low ($1 \times$) and high ($8 \times$) recording speeds.

Examples 295-533: It is proceeded analogously to example 294, with the difference that the compound according to example 13 is replaced by the compounds of examples 55-293. The performance of each recording medium is tested at $1 \times$ ($3.5 \text{ m} \cdot \text{s}^{-1}$), $2 \times$ ($7 \text{ m} \cdot \text{s}^{-1}$), $4 \times$ ($14 \text{ m} \cdot \text{s}^{-1}$), $8 \times$ ($28 \text{ m} \cdot \text{s}^{-1}$) and $16 \times$ ($56 \text{ m} \cdot \text{s}^{-1}$) recording and playback speeds.

Example 534: 1.48 g of the compound according to example 88 are dissolved in 100 ml of 2,2,3,3-tetrafluoropropanol and filtered through a Teflon™ filter having a pore size of $0.2 \mu\text{m}$. The dye solution is then applied at 500 rev/min to the surface of a 0.6 mm thick, grooved polycarbonate disc (groove depth 165 nm, groove width 370 nm, track pitch 0.74 mm) having a diameter of 120 mm. The excess of solution is spun off by increasing the speed of rotation up to 3500 rev/min. When the solvent is evaporated off, the dye remains behind in the form of a uniform, amorphous solid layer. Drying is carried out in a circulating-air oven at 70°C for 20 minutes. In a vacuum-coating apparatus (Twister™, Balzers Unaxis) a 120 nm thick silver layer is then applied to the recording layer by sputter coating. An adhesive layer of a UV-curable photopolymer (LMD2277™, Vantico/Huntsman) is then applied thereto by spin-coating, and a second polycarbonate disc (0.6 mm thick, 120 mm diameter) is adhesively bonded thereto. The final disk has a reflectivity of 48% at 658 nm and

- 104 -

25 mm radius. On a commercial test apparatus (ODU-1000™, Pulstec Japan), using a laser diode of wavelength 658 nm and numerical aperture 0.65, marks are written into the active layer at speeds of $8.38 \text{ m} \cdot \text{s}^{-1}$ (2.4x), $27.92 \text{ m} \cdot \text{s}^{-1}$ (8x) and $55.84 \text{ m} \cdot \text{s}^{-1}$ (16x). Then, the following dynamic parameters are determined on the same drive: data-to-clock (DTC) jitter, R14H, I14/I14H, laser power. After routine optimisation of the writing strategy, especially low values for DTC jitter are obtained.

Writing speed [$\text{m} \cdot \text{s}^{-1}$]	R14H [%]	I14/I14H	DTC Jitter [%]	Laser power [mW]
8.38 (2.4 x)	48	0.60	7.6	11.0
55.84 (16 x)	52	0.74	7.9	48.0

The performance is excellent from low (2.4 ×) to high (16 ×) recording speeds.

The instant optical recording media according to examples 294-534 are compatible with both DVD+R and DVD-R formats. Excellent results, especially at high recording speeds, are obtained in particular with a groove depth of from 150 to 190 nm and a groove width of from 0.35 to 0.40 μm , preferably with a groove depth of from 160 to 180 nm and a groove width of from 0.36 to 0.39 μm , most preferred with a groove depth of from 165 to 172 nm and a groove width of from 0.37 to 0.38 μm ; preferably in combination with a groove side wall angle of from 60 to 85°, more preferably from 65 to 80°, most preferred from 70 to 75°.

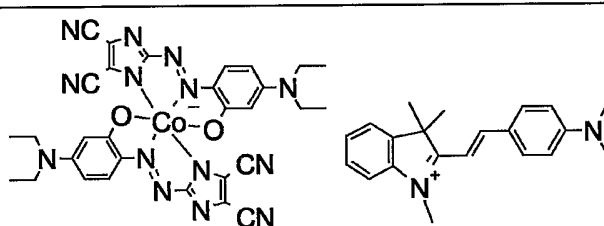
Examples 535-540: It is proceeded analogously to example 534, with the difference that the compound according to example 88 is replaced by the compounds of examples 68, 168, 188, 208, 268 or 280. The performance of each recording medium is tested at 2.4× ($8.38 \text{ m} \cdot \text{s}^{-1}$) and 16× ($56 \text{ m} \cdot \text{s}^{-1}$) recording speed. The same testing procedure as described in example 534 is followed except that the recording at 16× speed are made on a commercial DVD+/-R drive (BenQ 1620) and tested on another reference test equipment (DVD Pro, Audio Dev AB), showing a good performance from low (2.4 ×) to high (16 ×) recording speeds with sensitivities (laser power) appropriate for high speed recording :

- 105 -

Example	Compound according to example :	Reflectivity [%]	2.4× Modulation I14/I14H	16× DC-Jitter [%]	16× Optimum Laser power [mW]
535	68	44.5%	0.68	9.3%	48
536	168	51.5%	0.69	9%	49
537	188	54%	0.59	10%	45
538	208	47%	0.65	9%	52
539	268	47%	0.51	9%	44
540	280	47%	0.67	10.1%	49

Comparative Example: The $\lambda_{\max}$ (solid film), n- and k-values and the photostability of recording layers are determined as in examples 55-293, however using a layer consisting of the compound closely similar to that of example 8 of EP-A-1 170 339, but with the difference that both imidazoles are deprotonated and cobalt is in the higher oxidation state (+3) and hexacoordinated:

5

Example	Structure	$\lambda_{\max}$ [nm]	n_{658}	k_{658}	-D ₂₄ [%]
541		551	2.35	0.07	7

The same procedure as described in example 534 is then followed, except that the above comparative compound according to example 541 is compared with the instant compound according to example 88 on the same apparatus (ODU-1000, Pulstec Co, Japan) at 2.4× (8.38 m·s⁻¹) and 12× (42 m·s⁻¹) recording speed. The performance of both recording media is as follows:

10

- 106 -

Compound according to example :	2.4 x Optimum laser power [mW]	2.4 x DC-Jitter [%]	12 x DC-Jitter [%]	12 x I14/I14H Modulation
88 (instant)	15.75	6.4%	8.5%	0.71
541 (comparative)	17	9%	13%	0.49

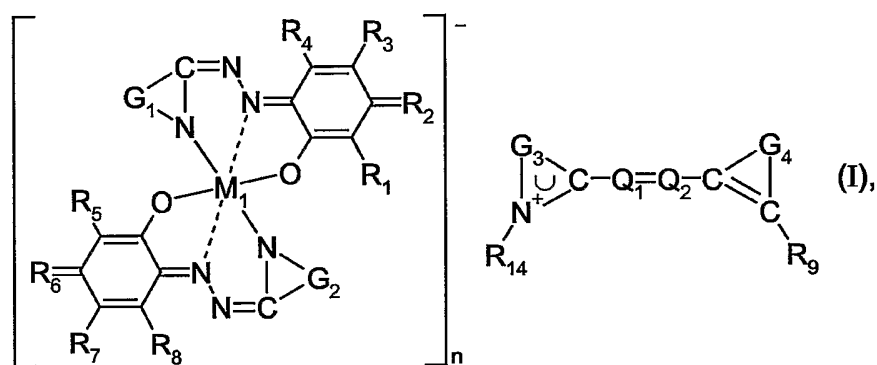
The compound closely similar to that of example 8 of EP-A-1 170 339 shows a much worse mark formation (higher jitter) from low (2.4 ×) to high (16 ×) recording speeds. Moreover, this compound is significantly less sensitive and clearly fails at high recording speed (too high jitter, much too low modulation).

- 5 The examples show clearly that the identity of the instant groups R₂ and their capability of forming a quinoid structure are essential for obtaining satisfactory sensitivity and recording properties, especially at high recording speeds.

- 107 -

Claims:

1. An optical recording medium comprising a substrate, a reflecting layer and a recording layer, wherein the recording layer comprises a compound of formula



5 or a mesomeric or tautomeric form thereof, wherein

M_1 is a metal cation in the oxidation state +3, a hydroxy or halogeno metal group wherein the metal is in the oxidation state +4, or an oxo metal group wherein the metal is in the oxidation state +5;

G_1 and G_2 are each independently of the other $R_{15}=\begin{matrix} Q_3 & C \\ & \diagup \quad \diagdown \\ & N^- \end{matrix}$, $R_{15}=\begin{matrix} Q_6 & C \\ & \diagup \quad \diagdown \\ & N^- \end{matrix}$ or

10 $\begin{matrix} Q_3 & C \\ \diagup & \diagdown \\ N^- & \end{matrix}$; G_3 is $R_{15}=\begin{matrix} Q_3 & C \\ & \diagup \quad \diagdown \\ & N^+ \end{matrix}$, $R_{15}=\begin{matrix} Q_6 & C \\ & \diagup \quad \diagdown \\ & N^+ \end{matrix}$, $\begin{matrix} Q_3 & C \\ \diagup & \diagdown \\ N^+ & \end{matrix}$, $\begin{matrix} N & C \\ \diagup & \diagdown \\ Q_7 & \end{matrix}$ or $\begin{matrix} R_{17} & C \\ \diagup & \diagdown \\ Q_4 & \end{matrix}$;

$\begin{matrix} R_9 \\ \diagup \\ C \\ \diagdown \\ G_4 \end{matrix}$ is $\begin{matrix} R_9 & R_{10} \\ \diagup & \diagdown \\ & \\ \diagdown & \diagup \\ R_{13} & R_{12} \end{matrix}$ or C_2 - C_8 heteroaryl unsubstituted or mono- or poly-

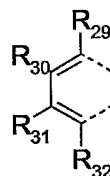
substituted by R_{10} , R_{11} , R_{12} and/or R_{13} ;

Q_1 is N or CR_{18} , Q_2 is N or CR_{19} , Q_3 , Q_5 and Q_7 are each independently of the other CR_{20} , R_{21} , O, S or NR_{22} , Q_4 is CR_{16} or N and Q_6 is CR_{17} or N;

- 108 -

- $R_1, R_3, R_4, R_5, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{15}, R_{16}, R_{17}, R_{18}$ and R_{19} are each independently of all others H, halogen, OR_{23} , SR_{23} , $NR_{22}R_{24}$, $NR_{22}COR_{25}$, $NR_{22}COOR_{26}$, $NR_{22}CONR_{26}R_{27}$, $NR_{22}CN$, $OSiR_{22}R_{25}R_{28}$, COR_{22} , $CR_{22}OR_{25}OR_{28}$, NO_2 , CN , $COOR_{23}$, $CONR_{26}R_{27}$, SO_2R_{22} , $SO_2NR_{26}R_{27}$, SO_3R_{26} , $PO(OR_{22})(OR_{25})$;
- 5 C_1 - C_6 alkyl, C_2 - C_6 alkenyl, C_2 - C_6 alkynyl, C_3 - C_6 cycloalkyl, C_3 - C_6 cycloalkenyl or C_2 - C_5 heterocycloalkyl each unsubstituted or mono- or poly-substituted by halogen, OR_{23} , SR_{23} , $NR_{22}R_{24}$, $NR_{22}COR_{25}$, $NR_{22}COOR_{23}$, $NR_{22}CONR_{26}R_{27}$, $NR_{22}CN$, COR_{22} , $CR_{22}OR_{25}OR_{28}$, NO_2 , CN , $COOR_{23}$, $CONR_{26}R_{27}$ and/or SO_2R_{26} ; or C_7 - C_{11} aralkyl, C_6 - C_{10} aryl or C_1 - C_8 heteroaryl each unsubstituted or mono- or poly-substituted by
- 10 C_1 - C_4 alkyl, halogen, OR_{23} , SR_{23} , $NR_{22}R_{24}$, COR_{22} , NO_2 , CN and/or $COOC_1$ - C_4 alkyl; or

R_{15} and R_{16} or R_{15} and R_{17} are together in pairs



, thus forming a phenyl

ring together with the two adjacent carbons to which they are bound;

R_2 and/or R_6 are O, S or NR_{33} ;

- 15 R_{14} is C_1 - C_{12} alkyl, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocycloalkyl, C_2 - C_{12} alkenyl, C_3 - C_{12} cycloalkenyl, C_4 - C_{12} heterocycloalkenyl, C_7 - C_{12} aralkyl, C_1 - C_9 heteroaryl, C_2 - C_{11} heteroaralkyl, C_6 - C_{12} aryl or C_1 - C_{12} alkyl interrupted by from one to five non-successive oxygen and/or sulfur atoms and/or by from one to five identical or different groups NR_{22} , each unsubstituted or mono- or poly-substituted by halogen,
- 20 OR_{23} , SR_{23} , $NR_{22}R_{24}$, $NR_{22}COR_{25}$, $NR_{22}COOR_{26}$, $NR_{22}CONR_{26}R_{27}$, $NR_{22}CN$, $OSiR_{22}R_{25}R_{28}$, COR_{22} , $CR_{22}OR_{25}OR_{28}$, NO_2 , CN , $COOR_{23}$, $CONR_{26}R_{27}$, SO_2R_{22} , $SO_2NR_{26}R_{27}$, SO_3R_{26} or $PO(OR_{22})(OR_{25})$;

- R_{20} and R_{21} are each independently of the other C_1 - C_{12} alkyl, C_2 - C_{12} alkenyl, C_2 - C_{12} alkynyl, C_7 - C_{12} aralkyl, C_3 - C_{12} cycloalkyl, C_3 - C_{12} cycloalkenyl or C_2 - C_{11} heterocycloalkyl each unsubstituted or mono- or poly-substituted by halogen, OR_{23} , SR_{23} ,
- 25 $NR_{22}R_{24}$, $NR_{22}COR_{25}$, $NR_{22}COOR_{23}$, $NR_{22}CONR_{26}R_{27}$, $NR_{22}CN$, COR_{22} , $CR_{22}OR_{25}OR_{28}$, NO_2 , CN , $COOR_{23}$, $CONR_{26}R_{27}$ and/or SO_2R_{26} ; or

- 109 -

R₂₀ and R₂₁ are together C₂-C₁₂alkylen, C₂-C₁₂alkenylen, C₂-C₁₂cycloalkylen or C₂-C₁₂cycloalkenylen, one to five non-successive carbon atoms of which can be replaced by oxygen and/or sulfur atoms and/or by identical or different groups NR₂₂, C₂-C₁₂alkylen, C₂-C₁₂alkenylen, C₂-C₁₂cycloalkylen or C₂-C₁₂cycloalkenylen
 5 being each unsubstituted or mono- or poly-substituted by halogen, OR₂₃, SR₂₃, NR₂₂R₂₄, NR₂₂COR₂₅, NR₂₂COOR₂₃, NR₂₂CONR₂₆R₂₇, NR₂₂CN, COR₂₂, CR₂₂OR₂₅OR₂₈, NO₂, CN, COOR₂₃, CONR₂₆R₂₇ and/or SO₂R₂₆;

R₂₂, R₂₅ and R₂₈ are each independently of the others hydrogen; C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, [C₂-C₃alkylene-O]_k-R₃₄ or [C₂-C₃alkylene-NR₃₅]_k-R₃₄
 10 each unsubstituted or mono- or poly-substituted by halogen; or benzyl;

each R₂₃, independently of any other R₂₃, is R₂₄ or R₃₃, preferably H;

R₂₄, R₂₆ and R₂₇ are each independently of the others H; C₁-C₆alkyl, C₂-C₆alkenyl, C₂-C₆alkynyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkenyl or C₂-C₅heterocycloalkyl each unsubstituted or mono- or poly-substituted by halogen, OR₂₃, SR₂₃, NR₂₂R₂₈, CN
 15 and/or COOR₂₂; or C₆-C₁₀aryl, C₇-C₁₁aralkyl or C₁-C₈heteroaryl each unsubstituted or mono- or poly-substituted by C₁-C₄alkyl, halogen, OR₂₃, SR₂₃, NR₂₂R₂₅, COR₂₂, CR₂₂OR₂₅OR₂₈, NO₂, CN and/or COOR₂₈;

or NR₂₂R₂₄, NR₂₂R₂₅, NR₂₅R₂₈ or NR₂₆R₂₇ is a five- or six-membered heterocycle which may contain a further N or O atom and which can be mono- or poly-
 20 substituted by methyl or ethyl;

R₂₉, R₃₀, R₃₁ and R₃₂ are each independently of the other H, C₁-C₄alkyl, halogen, OR₂₃, SR₂₃, NR₂₂R₂₄, COR₂₂, NO₂, CN and/or COOC₁-C₄alkyl;

R₃₃ is COR₂₄, CONR₂₆R₂₇, CN, SO₂NR₂₆R₂₇ or SO₂R₂₆;

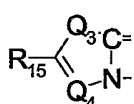
R₃₄ and R₃₅ are each independently of the other methyl, ethyl, vinyl and/or allyl;

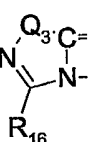
25 it being possible once or more times radicals of the same or different substituents each selected from the group consisting of R₁, R₃, R₄, R₅, R₇, R₈, R₉, R₁₀, R₁₁, R₁₂,

- 110 -

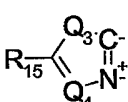
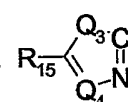
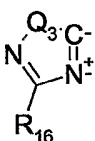
R_{13} , R_{14} , R_{15} , R_{16} , R_{17} , R_{18} , R_{19} , R_{20} , R_{22} , R_{23} , R_{24} , R_{25} , R_{26} , R_{28} , R_{29} , R_{30} , R_{31} , R_{32} , R_{34} and R_{36} to be bonded to one another in pairs by way of a direct bond or an -O-, -S- or -N(R_{35})- bridge, optionally forming a dimer, trimer or oligomer comprising two or more identical or different moieties of formula (I);

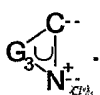
5 k is an integer 1, 2, 3 or 4; and n is an integer 1, 2 or 3.

2. An optical recording medium according to claim 1, wherein Q_3 is S in R_{15} 

or N  standing for  and/or , and/or Q_3 is $CR_{20}R_{21}$, preferably

C_3 - C_6 alkyliden or C_3 - C_6 cycloalkyliden, more preferably 1-cyclohexyliden or

2-butyliden, most preferred 2-butyliden, in R_{15}   or N  standing

10 for .

3. An optical recording medium according to claim 1 or 2, wherein R_2 and/or R_6 are O, S, N-CN or N-SO₂CF₃, preferably O.

4. An optical recording medium according to claim 1, 2 or 3, wherein R_3 and/or R_7 are H, halogen, CF₃, NO₂, CN, COR₂₂, COOR₂₃, SO₃R₂₃, NCO or SCN, preferably
15 H.

5. An optical recording medium according to claim 1, 2, 3 or 4, wherein in the heterocycle comprising G_1 or G_2 , at least one of R_{15} and R_{17} , especially R_{15} , is CF₃, NO₂, CN, COR₂₂, COOR₂₃, CR₂₂OR₂₅OR₂₈, CONR₂₆R₂₇, SO₂R₂₂, SO₃R₂₃, SO₂NR₂₆R₂₇ or PO(OR₂₂)(OR₂₅), most preferred CF₃, NO₂, CN, COR₂₂, COOR₂₃,
20 SO₂R₂₂ and/or SO₃R₂₃, or R_{15} and R_{17} are together butadienylen either unsubstituted or substituted, preferably unsubstituted or substituted by CF₃, NO₂, CN, COR₂₂, COOR₂₃ and/or SO₃R₂₃.

- 111 -

6. An optical recording medium according to claim 1, 2, 3, 4 or 5, wherein in the heterocycle comprising G_3 , R_{16} is H or F, or together with R_{15} is butadienylen either unsubstituted or substituted, preferably unsubstituted or substituted by one or more C_1 - C_4 alkyl, halogen, OR_{23} , SR_{23} , $NR_{22}R_{25}$, CF_3 , NO_2 , CN , COR_{22} , $COOR_{23}$, SO_2R_{22} and/or SO_3R_{23} .
7. An optical recording medium according to claim 1, 2, 3, 4, 5 or 6, wherein Q_5 and Q_7 are S.
8. An optical recording medium according to claim 1, 2, 3, 4, 5, 6 or 7, wherein M_1 is Al^{3+} , As^{3+} , Au^{3+} , Bi^{3+} , Ce^{3+} , Co^{3+} , Cr^{3+} , Dy^{3+} , Er^{3+} , Eu^{3+} , Fe^{3+} , Gd^{3+} , Ho^{3+} , Ir^{3+} , La^{3+} , Lu^{3+} , Mn^{3+} , Mo^{3+} , Nb^{3+} , Nd^{3+} , Pm^{3+} , Pr^{3+} , Rh^{3+} , Ru^{3+} , Sb^{3+} , Sc^{3+} , Sm^{3+} , Ta^{3+} , Tb^{3+} , Ti^{3+} , $[TiCl]^{3+}$, $[TiOH]^{3+}$, Tm^{3+} , V^{3+} , $[VO]^{3+}$, W^{3+} , Y^{3+} , Yb^{3+} , $[ZrCl]^{3+}$ or $[ZrOH]^{3+}$, preferably Co^{3+} or Cr^{3+} .
9. An optical recording medium according to claim 1, 2, 3, 4, 5, 6, 7 or 8, wherein n is 0 or 1.
10. A method for the optical recording or playback of information, wherein a recording medium according to claim 1, 2, 3, 4, 5, 6, 7, 8 or 9 is used and the recording and/or the playback take place in a wavelength range of from 600 to 700 nm, preferably from 630 to 690 nm, more especially from 640 to 680 nm, very especially from 650 to 670 nm, particularly at 658 ± 5 nm.
11. A method according to claim 10, wherein the groove depth is from 150 to 190 nm and the groove width is from 0.35 to 0.40 μm , preferably wherein the groove depth is from 160 to 180 nm and the groove width is from 0.36 to 0.39 μm , most preferred the groove depth is from 165 to 172 nm and the groove width is from 0.37 to 0.38 μm ; preferably in combination with a groove side wall angle of from 60 to 85°, more preferably from 65 to 80°, most preferred from 70 to 75°.
12. A method according to claim 10 or 11, wherein recording or playback of information takes place at a speed of from 20 to 60 $m \cdot s^{-1}$.

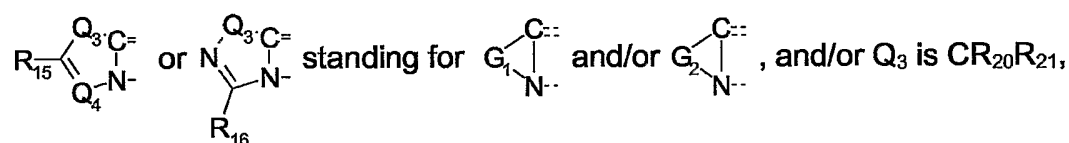
- 112 -

13. A compound of formula (I) according to claim 1, 2, 3, 4, 5, 6, 7, 8 or 9 or a tautomeric or mesomeric form thereof.

14. A compound of formula (I) according to claim 13, wherein n is 1 or wherein n is 2 and one of G₃, R₉, R₁₀, R₁₁, R₁₂, R₁₃ or R₁₄, preferably R₉, R₁₀, R₁₁, R₁₂ or R₁₃,

5 comprises a positively charged N-substituted C₁-C₅heteroaryl group.

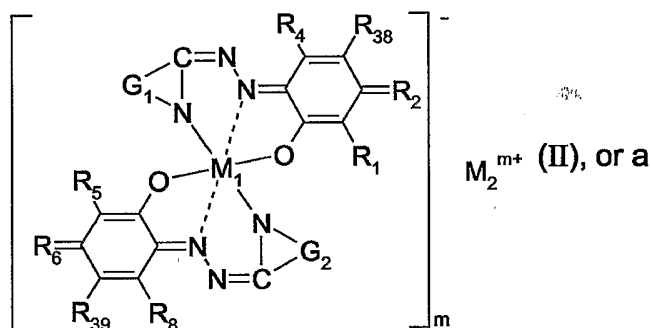
15. A compound of formula (I) according to claim 13 or 14, wherein Q₃ is S in



preferably C₃-C₆alkyliden or C₃-C₆cycloalkyliden, more preferably 1-cyclohexyliden or 2-butyliden, most preferred 2-butyliden.

10 16. A compound according to claim 13, 14 or 15, which is a dimer or trimer comprising two or three identical or different moieties of formula (I).

17. A compound of formula



mesomer or tautomer thereof, wherein

R_{38} is halogen, CF_3 , NO_2 , CN , COR_{22} , $COOR_{23}$, SO_3R_{23} , NCO or SCN ,

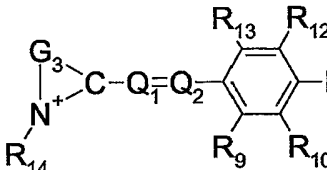
15 R₃₉ is R₇ as defined in formula (I), preferably H, halogen, CF₃, NO₂, CN, COR₂₂, COOR₂₃, SO₃R₂₃, NCO or SCN,

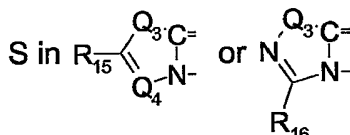
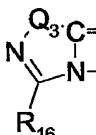
$G_1, G_2, M_1, R_1, R_2, R_4, R_5, R_6, R_8, R_{22}$ and R_{23} are as defined in formula (I),

M_2^{m+} is a cation with m positive charges, and m is an integer 1, 2 or 3.

- 113 -

18. A compound of formula (I) according to claim 16 or of formula (II) according to

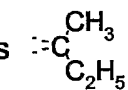
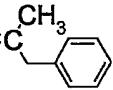
claim 17, wherein M_2^{m+} is a cation of formula  and Q_3 is

S in  or  standing for  and/or , and/or Q_3 is $CR_{20}R_{21}$,

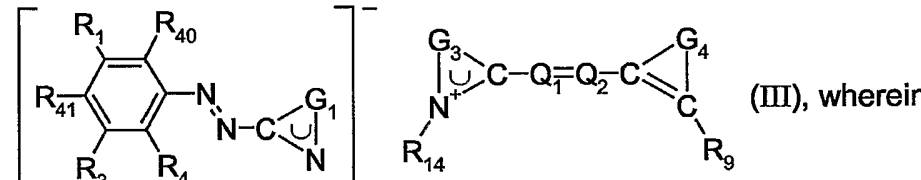
preferably C_3 - C_6 alkyliden or C_3 - C_6 cycloalkyliden, more preferably 1-cyclohexyliden
5 or 2-butyliden, most preferred 2-butyliden.

19. A compound of formula (II) according to claim 17 or 18, wherein n is 2 and one of G_3 , R_9 , R_{10} , R_{11} , R_{12} , R_{13} or R_{14} , preferably R_9 , R_{10} , R_{11} , R_{12} or R_{13} , comprises a positively charged N-substituted C_1 - C_5 heteroaryl group.

20. A compound according to claim 13, 14, 15, 16, 17, 18 or 19, wherein G_3

10 comprises  or  as Q_3 , and preferably R_{15} - $C=Q_4$ is part of a phenyl ring.

21. A composition comprising a compound of formula (I) according to claim 13, 14, 15 or 16 or a compound of formula (II) according to claim 17 or 18, and a compound of formula

15  (III), wherein

one of R_{40} and R_{41} is $NR_{42}R_{43}$, $NR_{43}R_{44}$, $NR_{44}R_{45}$, OR_{42} , SR_{42} , OR_{44} or SR_{44} , and the other of R_{40} and R_{41} is O^- , S^- or N^-R_{46} ;

R_{42} and R_{43} are each independently of the other C_1 - C_{12} alkyl, C_2 - C_{12} alkenyl, C_2 - C_{12} alkynyl, C_3 - C_{12} cycloalkyl, C_3 - C_{12} cycloalkenyl or C_2 - C_{11} heterocycloalkyl each

- 114 -

unsubstituted or mono- or poly-substituted by halogen, OR₄₇, SR₄₇, CR₄₈OR₄₉OR₅₀, NR₄₈R₅₁, NR₄₈COR₄₉, NR₄₈COOR₄₇, NR₄₈CONR₅₂R₅₃, NR₄₈CN, COR₄₈, NO₂, CN, COOR₄₇, CONR₅₂R₅₃ and/or SO₂R₅₂; or

- R₄₂ and R₄₃ are together C₂-C₁₂alkylen, C₂-C₁₂alkenylen, C₂-C₁₂cycloalkylen or
- 5 C₂-C₁₂cycloalkenylen, one to five non-successive carbon atoms of which can be replaced by oxygen and/or sulfur atoms and/or by identical or different groups NR₄₆, C₂-C₁₂alkylen, C₂-C₁₂alkenylen, C₂-C₁₂cycloalkylen or C₂-C₁₂cycloalkenylen being each unsubstituted or mono- or poly-substituted by halogen, OR₄₇, SR₄₇, NR₄₈R₅₁, NR₄₈COR₄₉, NR₄₈COOR₄₇, NR₄₈CONR₅₂R₅₃, NR₄₈CN, COR₄₈,
- 10 CR₄₈OR₄₉OR₅₀, NO₂, CN, COOR₄₇, CONR₅₂R₅₃ and/or SO₂R₅₂;

R₄₄, R₄₅ and R₄₆ are each independently of the others H, COR₅₁, CONR₅₂R₅₃, CN, SO₂NR₅₂R₅₃ or SO₂R₅₂, preferably R₄₄ and/or R₄₅ are H and R₄₆ is COR₅₁, CONR₅₂R₅₃, CN, SO₂NR₅₂R₅₃ or SO₂R₅₂;

each R₄₇, independently of any other R₄₇, is R₅₁ or R₄₆, preferably H;

- 15 R₄₈, R₄₉ and R₅₀ are each independently of the others hydrogen; C₁-C₄alkyl, C₂-C₄alkenyl, C₂-C₄alkynyl, [C₂-C₃alkylene-O-]_p-R₅₄ or [C₂-C₃alkylene-NR₅₅]_p-R₅₄ each unsubstituted or mono- or poly-substituted by halogen; or benzyl;

- R₅₁, R₅₂ and R₅₃ are each independently of the others H; C₁-C₆alkyl, C₂-C₆alkenyl, C₂-C₆alkynyl, C₃-C₆cycloalkyl, C₃-C₆cycloalkenyl or C₂-C₅heterocycloalkyl each
- 20 unsubstituted or mono- or poly-substituted by halogen, OR₄₇, SR₄₇, NR₄₈R₅₀, CN and/or COOR₄₈; or C₆-C₁₀aryl, C₇-C₁₁aralkyl or C₁-C₅heteroaryl each unsubstituted or mono- or poly-substituted by C₁-C₄alkyl, halogen, OR₄₇, SR₄₇, NR₄₈R₄₉, COR₄₈, CR₄₈OR₄₉OR₅₀, NO₂, CN and/or COOR₅₀;

- or NR₄₈R₄₉, NR₄₈R₅₁, NR₄₉R₅₀ or NR₅₂R₅₃ is a five- or six-membered heterocycle
- 25 which may contain a further N or O atom and which can be mono- or poly-substituted by methyl or ethyl;

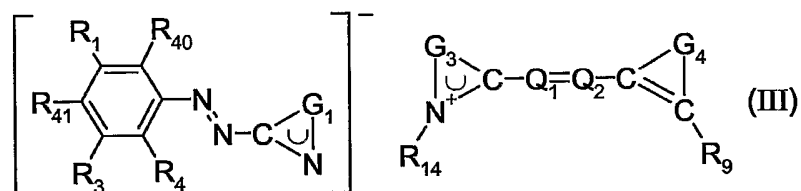
R₅₄ and R₅₅ are each independently of the other methyl, ethyl, vinyl and/or allyl;

- 115 -

it being possible once or more times radicals of the same or different substituents each selected from the group consisting of R_1 , R_3 , R_4 , R_{40} , R_{41} , R_{42} , R_{45} , R_{46} , R_{47} , R_{48} , R_{49} , R_{50} , R_{51} , R_{52} and R_{54} to be bonded to one another in pairs by way of a direct bond or an -O-, -S- or -N(R_{55})- bridge; and

5 p is an integer from 1 to 4.

22. A recording medium according to claim 1, 2, 3, 4, 5, 6, 7, 8 or 9, further comprising a compound of formula



according to claim 21.

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/EP2005/053215

A. CLASSIFICATION OF SUBJECT MATTER

C09B69/02 C09B45/34 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)

C09B G11B

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, 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.
Y	EP 1 170 339 A (KABUSHIKI KAISHA HAYASHIBARA SEIBUTSU KAGAKU KENKYUJO) 9 January 2002 (2002-01-09) cited in the application Formula 8, page 9 -----	1-20
Y	EP 0 837 458 A (EASTMAN KODAK COMPANY) 22 April 1998 (1998-04-22) Tetra Dye A8, Tab.3 -----	1-20
Y	EP 1 174 472 A (KABUSHIKI KAISHA HAYASHIBARA SEIBUTSU KAGAKU KENKYUJO) 23 January 2002 (2002-01-23) Formula 16, page 8 - paragr. '0024! ----- -/--	1-20

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

31 October 2005

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2005/053215

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 125 987 A (KABUSHIKI KAISHA HAYASHIBARA SEIBUTSU KAGAKU KENKYUJO) 22 August 2001 (2001-08-22) compounds 18,28,35,45 -----	1-20
Y	US 6 103 331 A (KANNO ET AL) 15 August 2000 (2000-08-15) cited in the application column 20, line 26 - line 35 -----	1-20
X	S.ZAREBA: "Thiadiazolyl azo derivatives as analytical reagents" ACTA POLONIAE PHARMACEUTICA, vol. 49, no. 5, 1992, pages 55-61, XP009044074 Schema I at page 60 -----	17
A	S.I.GUSEV ET AL.: "2'-(4-Phenyl-2-thiazolylazo)-4'-methyl-5'- ethylaminophenol and its analytical uses" ZHURNAL ANALITICHESKOJ KHIMII, vol. 40, no. 12, 1985, pages 2134-2137, XP009056275 formula on page 2136 -----	17
Y	EP 0 483 387 A (MITSUBISHI KASEI CORPORATION; MITSUBISHI CHEMICAL CORPORATION) 6 May 1992 (1992-05-06) example 18; table 11 -----	17-20
A	EP 0 649 133 A (EASTMAN KODAK COMPANY) 19 April 1995 (1995-04-19) Dye A, Tab.1 -----	17-20
Y	EP 0 649 884 A (EASTMAN KODAK COMPANY) 26 April 1995 (1995-04-26) Tab.2: mixtures 2,5; claim 5 -----	21,22
Y	EP 0 837 460 A (EASTMAN KODAK COMPANY) 22 April 1998 (1998-04-22) tables 5-7 -----	21,22
A	US 6 242 067 B1 (KAMBE EMIKO ET AL) 5 June 2001 (2001-06-05) the whole document -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2005/053215

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1170339	A	09-01-2002	JP 2002206061 A US 2002028918 A1	26-07-2002 07-03-2002
EP 0837458	A	22-04-1998	JP 10172178 A US 6361922 B1	26-06-1998 26-03-2002
EP 1174472	A	23-01-2002	WO 0162853 A1 US 2002178517 A1	30-08-2001 05-12-2002
EP 1125987	A	22-08-2001	TW 572969 B US 2001044074 A1	21-01-2004 22-11-2001
US 6103331	A	15-08-2000	GB 2329751 A	31-03-1999
EP 0483387	A	06-05-1992	CA 2063579 A1 DE 69112337 D1 DE 69112337 T2 WO 9118950 A1 KR 160944 B1 US 5330542 A	26-11-1991 28-09-1995 02-05-1996 12-12-1991 15-12-1998 19-07-1994
EP 0649133	A	19-04-1995	DE 69422132 D1 DE 69422132 T2 JP 3561009 B2 JP 7175166 A US 5426015 A	20-01-2000 25-05-2000 02-09-2004 14-07-1995 20-06-1995
EP 0649884	A	26-04-1995	DE 69422137 D1 DE 69422137 T2 JP 7186547 A US 5500325 A	20-01-2000 13-07-2000 25-07-1995 19-03-1996
EP 0837460	A	22-04-1998	JP 10152621 A US 5876821 A	09-06-1998 02-03-1999
US 6242067	B1	05-06-2001	JP 3441410 B2 JP 2000190642 A	02-09-2003 11-07-2000