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(54) **Title:** INDANDIONE BASED AZO METAL COMPLEX DYES AND THEIR USE IN OPTICAL LAYERS FOR OPTICAL DATA RECORDING

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

INDANDIONE BASED AZO METAL COMPLEX DYES AND THEIR USE IN OPTICAL LAYERS FOR OPTICAL DATA RECORDING

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

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

Recently, organic dyes have attracted considerable attentions in the field of diode-laser optical data storage. WORM type optical data recording media like commercial recordable compact discs (CD-R) and recordable digital versatile discs (DVD-R) can contain in the recording layer dyes based on phthalocyanine, hemicyanine, cyanine and metallized azo structures. These dyes are suitable in their respective fields with the laser wavelength criteria. Other general requirements for dye media are strong absorption, high reflectance, high recording sensitivity, enhancement of photosensitivity, low thermal conductivity as well as light and thermal stabilities, durability for storage or non-toxicity. Important criteria are also good read-out stability, which means high number of cycles at a given intensity of laser-light, and sufficient solubilities of the dyes in the organic solvents generally applied in the spin coating process.

At the recorded region of such an organic dye type optical data recording medium, the optical properties have been changed not only by a change in the optical characteristics and a decrease in the layer thickness resulting from the thermal decomposition of the dye, but also by a deformation of the substrate.

This recording principle is the same for CD-R and DVD-R, the difference remaining the spot size and the wavelength of the laser light used. CD-R are writable at a wavelength of from 770 to 830 nm and DVD-R, by using more recent compact high-performance

red diode lasers, at a wavelength from 600 to 700 nm achieving then a 6- to 8 fold improvement in data packing density in comparison with conventional CDs.

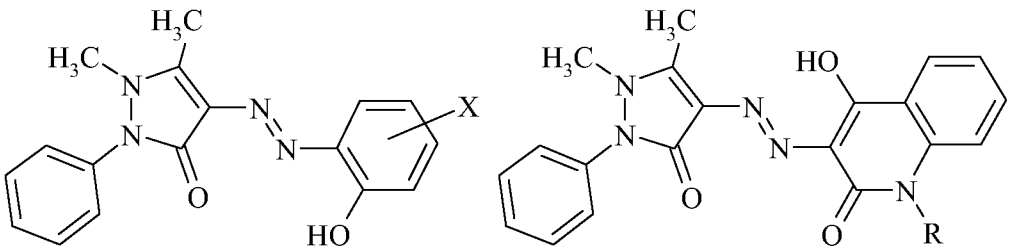
However, considering factors such as the recent spread of electronic networks (e.g. Internet) and the emergence of high definition television (HDTV) broadcasting, inexpensive and convenient recording media, capable of recording image information at even larger capacity, are required. While DVD-R's sufficiently serve as high-capacity recording media at present, demand for larger capacity and higher density has increased.

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

The construction of such optical data recording media is known in the art. The optical recording medium comprises preferably a substrate with a guide groove for laser beam tracking, a recording layer, also called optical layer, containing an organic dye as the main component, a reflective layer and a protective layer. When recording/readout is carried out through the substrate, a transparent substrate is employed. As such a transparent substrate, one made of a resin such as polycarbonate, polymethacrylate or amorphous polyolefin, one made of glass or one having a resin layer made of radiation curable resin, i.e. photopolymerizable resin, formed on glass, may, for example, be employed. Advanced optical data recording media may comprise further layers, such as protective layers, adhesive layers or even additional optical recording layers.

For blue diode-laser optical data storage a variety of dye compounds has been proposed in the literature.

Amino antipyrine based dyes of the below general formulae are known from DE-A-1076078 and US 2,993,884:



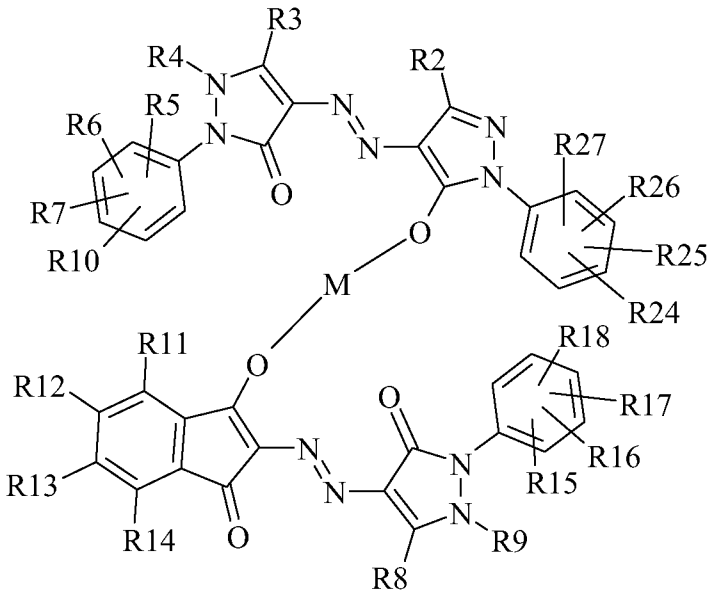
Unfortunately the dye compounds described so far still show disadvantages which impede their satisfactory use as dyes for optical data storage.

There is a still a need for an optical data recording medium that is capable of recording data at high density with improved recording characteristics and with improved read-out stabilities.

Surprisingly the object was achieved by using asymmetric metal complex dyes based on amino antipyrine, pyrazolone and indandione.

In the following text "halogen" represents F, Cl, Br and I, preferably F, Cl or Br, more preferably F or Cl, even more preferably Cl, if not otherwise stated; "alkyl" represents linear and branched alkyl; and "alkoxy" represents linear and branched alkoxy; if not otherwise stated.

Subject of the invention is a compound of formula (I),



(I)

wherein

M represents a divalent metal atom, preferably selected from main groups 1 to 5 or from transition groups 1 or 2 or 4 to 8 of the Periodic Table of the Chemical Elements;

R^2, R^3 and R^8 are independently from each other selected from the group consisting of

hydrogen, halogen, CN, CF_3, NO_2, C_{1-10} alkoxy, C_{1-10} alkyl, C_{5-10} cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, and

unsubstituted phenyl or substituted phenyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

unsubstituted benzyl or substituted benzyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

$NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21};

R^4 and R^9 are independently from each other selected from the group consisting of

C_{1-10} alkyl, C_{5-10} cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, and

unsubstituted phenyl or substituted phenyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

unsubstituted benzyl or substituted benzyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$;

R^5, R^6, R^7, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of

hydrogen, OH, halogen, CN, CF_3, NO_2, C_{1-10} alkoxy, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, and

unsubstituted phenyl or substituted phenyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

unsubstituted benzyl or substituted benzyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2 R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

$NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$;

R^{21} and R^{22} are independently from each other selected from the group consisting of hydrogen, C_{1-10} alkyl, C_{6-10} aryl;

R^{23} is OH or C_{1-10} alkoxy.

In a preferred aspect, subject of the invention is a compound of formula (I), wherein

M is selected from the group consisting of Ni, Cu, Co, Zn, Fe, Pd, Pt, Mn;

R^2, R^3 and R^8 are independently from each other selected from the group consisting of hydrogen, CH_3, C_2H_5, C_3H_7, preferably $CH(CH_3)_2$, C_4H_9, preferably n-butyl, phenyl, CN, CF_3;

R^4 and R^9 are independently from each other selected from the group consisting of C_{1-4} alkyl,

unsubstituted benzyl or substituted benzyl with 1 to 3, preferably 1 or 2, more preferably 1, substituents being independently from each other selected from the group consisting of halogen, C_{1-4} alkyl and NO_2;

R^5, R^6, R^7, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of hydrogen, halogen, CN, CF_3, C_{1-4}-alkyl, C_{1-4}-alkoxy, NO_2 and SO_2-$NR^{21}R^{22}$;

with R^{21} and R^{22} being independently from each other selected from the group consisting of hydrogen and C_{1-4} alkyl;

and with halogen being preferably F, Cl or Br, more preferably F or Cl.

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

M is selected from the group consisting of Ni, Cu, Co, Zn and Mn;

R^2, R^3 and R^8 are independently from each other selected from the group consisting hydrogen, CH_3, C_2H_5, C_3H_7, preferably $CH(CH_3)_2$, and C_4H_9, preferably n-butyl;

R^4 and R^9 are independently from each other CH_3 or C_2H_5;

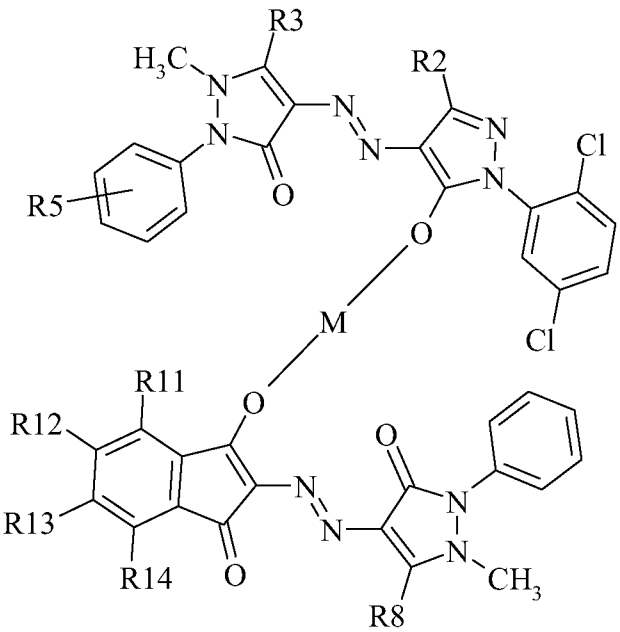
R^5, R^6, R^7, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of hydrogen, Cl, Br, CN, CH_3, C_2H_5 and NO_2.

In a particularly preferred aspect of the invention, R^5, R^6, R^7, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from hydrogen or Cl;

more particular preferred R^6, R^7, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{24} and R^{25} are hydrogen and R^5 is hydrogen or Cl and R^{26} and R^{27} are Cl;

and in another more particularly preferred aspect of the invention, R^6, R^7, R^{10}, R^{15}, R^{16}, R^{17}, R^{18}, R^{24}, R^{25} are hydrogen, R^5 is hydrogen or Cl, R^{11}, R^{12}, R^{13}, R^{14}, R^{26} and R^{27} are Cl.

In an even more preferred aspect, the subject of the invention is a compound of formula (II),



(II)

wherein M is selected from Ni, Zn, Cu, Co and Mn;

R^2, R^3 and R^8 are independently from each other selected from the group consisting of hydrogen, CH_3, C_2H_5, $CH(CH_3)_2$ and n-butyl;

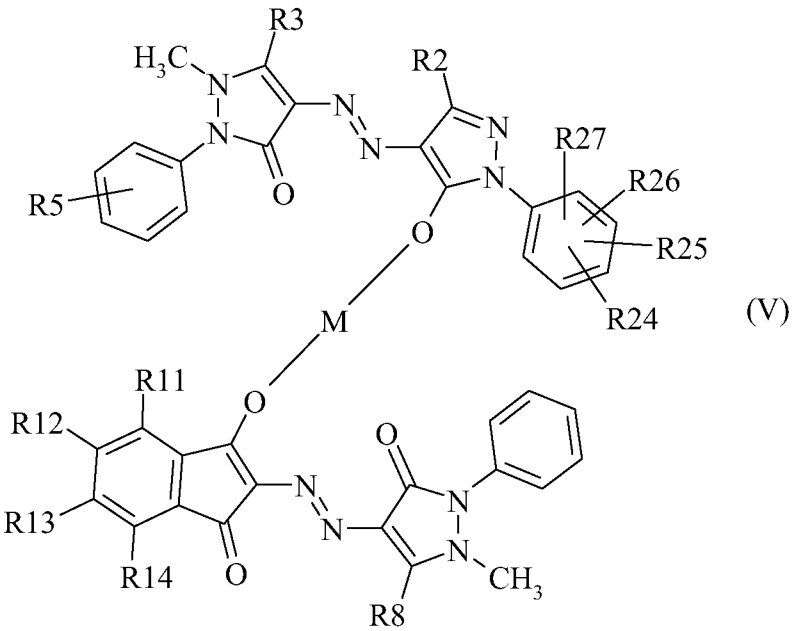
R^5, R^{11}, R^{12}, R^{13} and R^{14} are independently from each other selected from the group consisting of hydrogen, Cl, CH_3 and C_2H_5;

preferably the subject of the invention is a compound of formula (II), wherein M is selected from Ni, Zn, Cu and Co, especially from Cu and Co; more especially M represents Cu;

R^2, R^3 and R^8 are independently from each other selected from the group consisting of CH_3, C_2H_5 and $CH(CH_3)_2$;

R^5, R^{11}, R^{12}, R^{13} and R^{14} are independently from each other selected from the group consisting of hydrogen and Cl.

In another even more preferred aspect, the subject of the invention is a compound of formula (V),



wherein M is selected from Ni, Zn, Cu, Co and Mn;

R^2, R^3 and R^8 are independently from each other selected from the group consisting of hydrogen, CH_3, C_2H_5, $CH(CH_3)_2$ and n-butyl;

R^5, R^{11}, R^{12}, R^{13} and R^{14} are independently from each other selected from the group consisting of hydrogen, Cl, CH_3 and C_2H_5;

R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of hydrogen, F and CF_3, with the proviso, that at least one of the substituents R^{24}, R^{25}, R^{26} and R^{27} is not hydrogen;

preferably the subject of the invention is a compound of formula (V), wherein

M is selected from the group consisting of Ni, Zn, Cu and Co, especially from Ni, Cu and Co; more especially M represents Cu or Ni; even more especially Cu;

R^2, R^3 and R^8 are independently from each other selected from the group consisting of CH_3, C_2H_5 and $CH(CH_3)_2$;

R^5, R^{11}, R^{12}, R^{13} and R^{14} are independently from each other selected from the group consisting of hydrogen and Cl;

R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of hydrogen, F and CF_3, with the proviso, that at least one of the substituents R^{24}, R^{25}, R^{26} and R^{27} is not hydrogen.

Especially preferably in the case of formula (I), (II) or (V), preferably in the case of formula (II) or (V), M is selected from Ni, Zn, Cu and Co, preferably from Cu and Co; even more preferably M represents Cu;

R^2, R^3 and R^8 are independently from each other selected from the group consisting of CH_3, C_2H_5 and $CH(CH_3)_2$;

R^5 represents hydrogen or Cl;

R^{11}, R^{12}, R^{13} and R^{14} are same and represent either hydrogen or Cl;

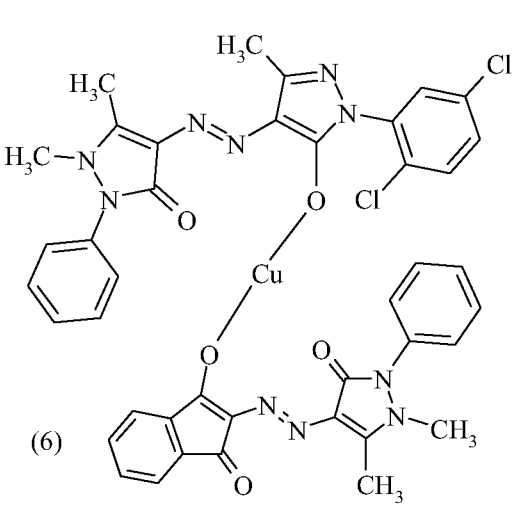
and in case of formula (V)

R^{24}, R^{25}, R^{26} and R^{27} are same and represent either F; or

R^{24}, R^{25}, R^{26} are same and represent hydrogen, and R^{27} represents CF_3; with R^{27} preferably located at the meta- or para-position.

In a particular preferred aspect, subject the invention is a compound, according to the formula (I) or (II), of the formula (6), (7), (8) or (9), more particular preferably of formula (6);

in another particular preferred aspect, subject the invention is a compound, according to the formula (I) or (V), of the formula (40), (41), (42), (43), (44), (45), (46) or (47) , more particular preferably of formula (40), (42) or (44).



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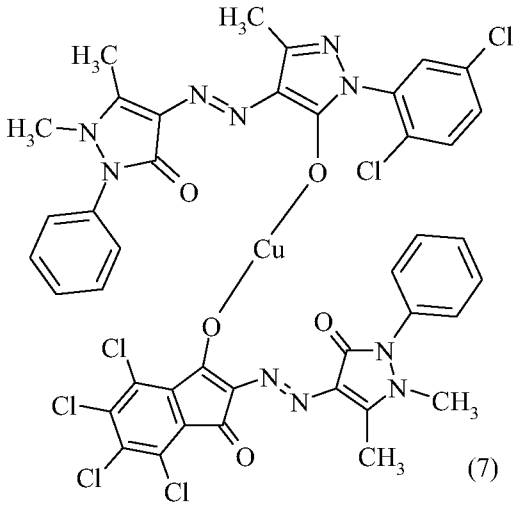

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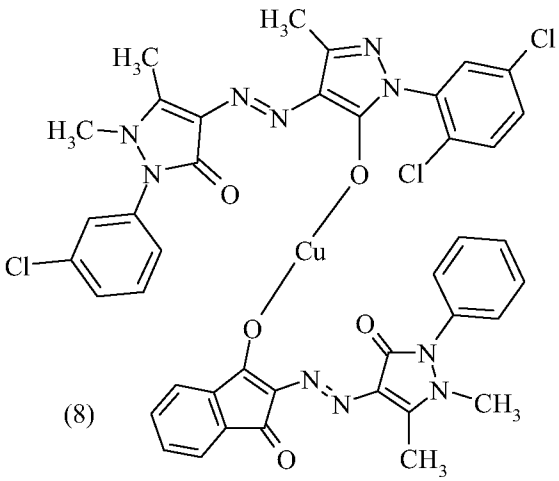

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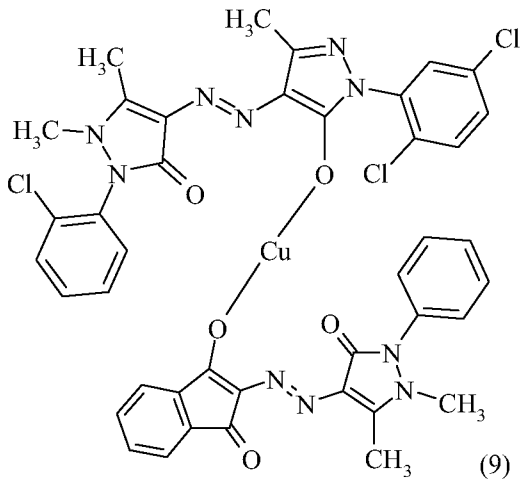

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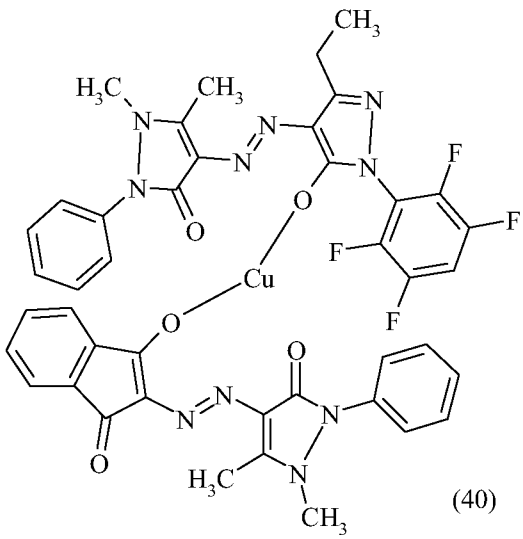

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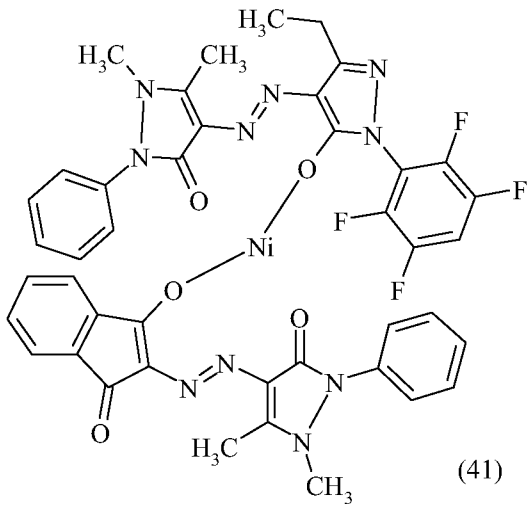

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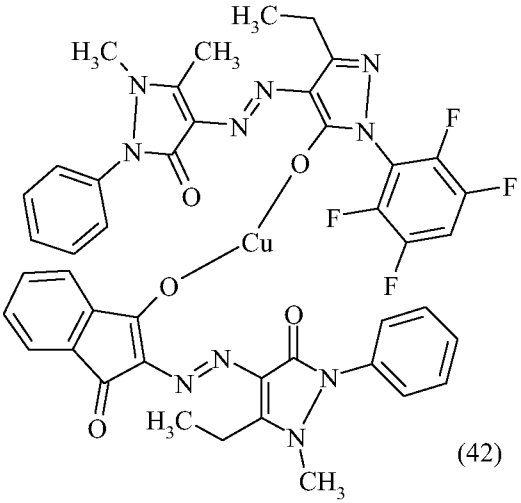

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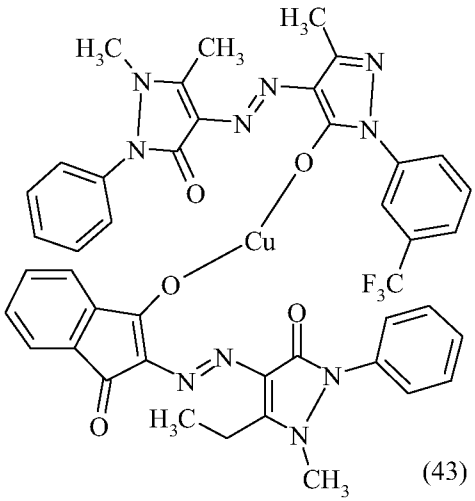

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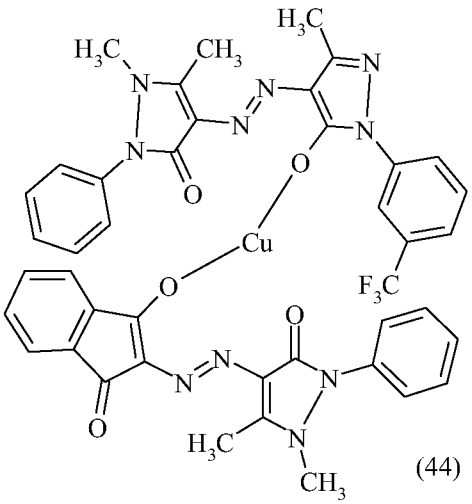

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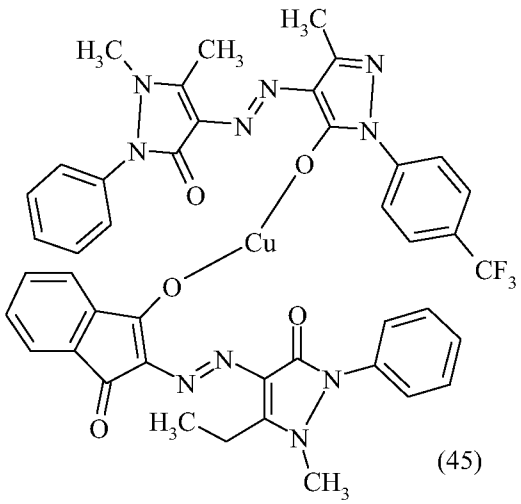

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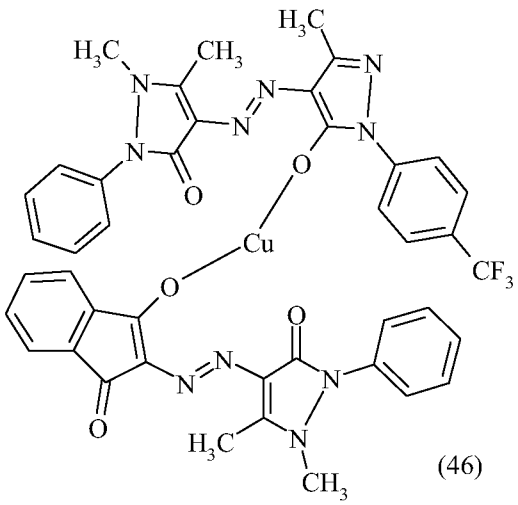

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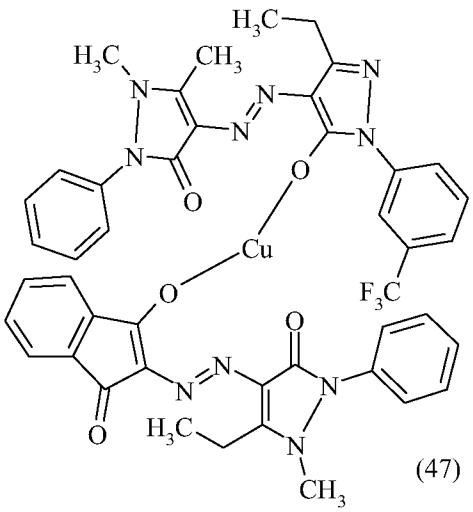
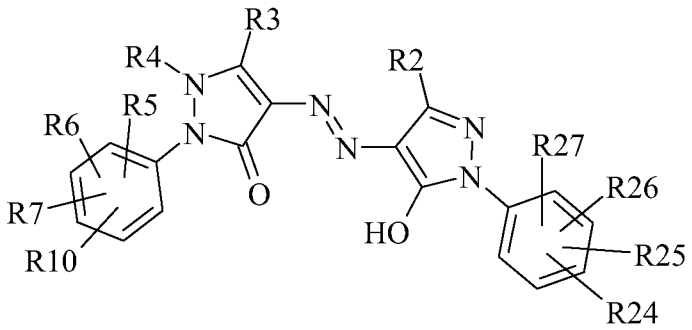


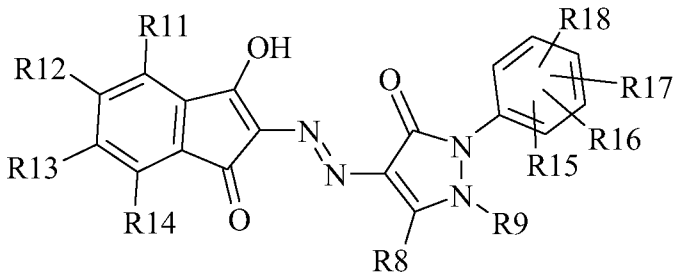
(47)

Preparation of the inventive compounds of formula (I), (II) and (V)

The compounds of formula (I) are prepared by complexing reaction of one equivalent of a compound of formula (III) and one equivalent of a compound of formula (IV) with one equivalent of a divalent metal salt,



(III)



(IV)

wherein

R^2, R^3 and R^8 are independently from each other selected from the group consisting of

hydrogen, halogen, CN, CF_3, NO_2, C_{1-10} alkoxy, C_{1-10} alkyl, C_{5-10} cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, and

unsubstituted phenyl or substituted phenyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

unsubstituted benzyl or substituted benzyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy,

$NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

$NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21};

R^4 and R^9 are independently from each other selected from the group consisting of

C_{1-10} alkyl, C_{5-10} cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, and

unsubstituted phenyl or substituted phenyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

unsubstituted benzyl or substituted benzyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$;

R^5, R^6, R^7, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of

hydrogen, OH, halogen, CN, CF_3, NO_2, C_{1-10} alkoxy, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, and

unsubstituted phenyl or substituted phenyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

unsubstituted benzyl or substituted benzyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy,

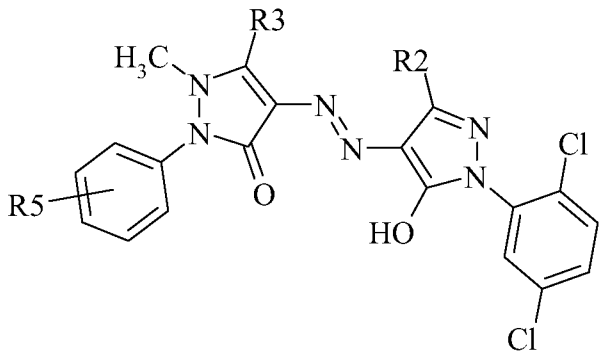
$NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2 R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

$NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$;

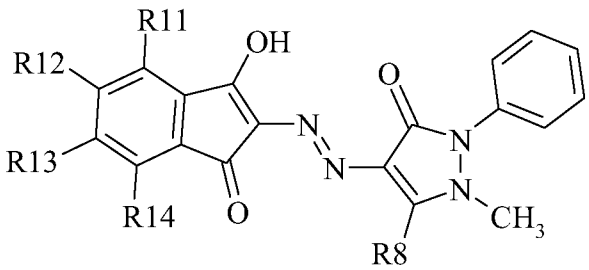
R^{21} and R^{22} are independently from each other selected from the group consisting of hydrogen, C_{1-10} alkyl, C_{6-10} aryl;

R^{23} is OH or C_{1-10} alkoxy.

The compounds of formula (II) are prepared by complexing reaction of one equivalent of a compound of formula (IIIb) and one equivalent of a compound of formula (IVb) with a one equivalent of a divalent metal salt,



(IIIb)



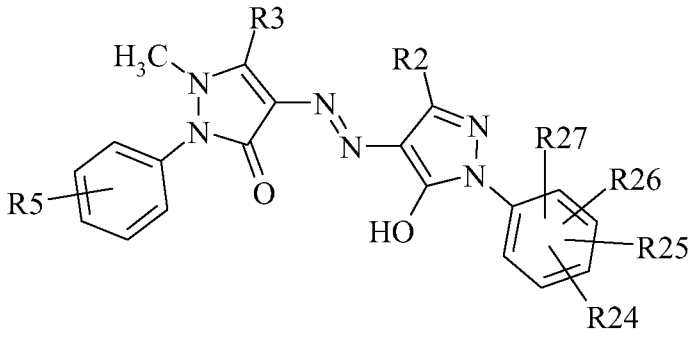
(IVb)

wherein

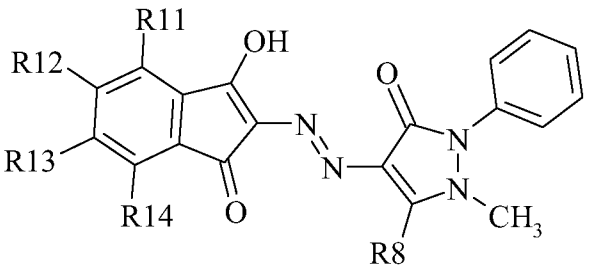
R^2, R^3 and R^8 are independently from each other selected from the group consisting of hydrogen, CH_3, C_2H_5, $CH(CH_3)_2$ and n-butyl;

R^5, R^{11}, R^{12}, R^{13} and R^{14} are independently from each other selected from the group consisting of hydrogen, Cl, CH_3 and C_2H_5.

The compounds of formula (V) are prepared by complexing reaction of one equivalent of a compound of formula (IIIc) and one equivalent of a compound of formula (IVc) with a one equivalent of a divalent metal salt,



(IIIc)



(IVc)

wherein

R^2, R^3 and R^8 are independently from each other selected from the group consisting of hydrogen, CH_3, C_2H_5, $CH(CH_3)_2$ and n-butyl;

R^5, R^{11}, R^{12}, R^{13} and R^{14} are independently from each other selected from the group consisting of hydrogen, Cl, CH_3 and C_2H_5;

R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of hydrogen, F and CF_3, with the proviso, that at least one of the substituents R^{24}, R^{25}, R^{26} and R^{27} is not hydrogen.

The compounds of formula (III), (IV), (IIIb), (IVb), (IIIc) and (IVc) are called azo ligands.

The divalent metal salt is a derived from a metal preferably selected from the group consisting of Ni, Cu, Co, Zn, Fe, Pd, Pt, Mn. Salts of the divalent metal are preferably sulfates, halides (preferably fluoride, chloride, bromide, iodide, more preferably chloride and bromide, especially chlorides) and acetates and their respective hydrates.

More preferred metal salts are derived from Ni, Cu, Co, Zn, and Mn. More preferred metal salts are for example nickel-, copper-, cobalt-, zinc-, or manganese sulfate; nickel-, copper-, cobalt-, zinc-, or manganese chloride or nickel-, copper-, cobalt-, zinc-, or manganese acetate and their respective hydrates, especially the metal salt is selected from the group consisting of $Cu(SO_4)$, $Cu(SO_4)*5\ H_2O$, $CuCl_2$, $Ni(OAc)_2*4\ H_2O$, $NiCl_2*6\ H_2O$, $Co(SO_4)$, $CoSO_4*7H_2O$ and $Zn(OAc)_2*4\ H_2O$; preferably from the group consisting of $Ni(OAc)_2*4\ H_2O$, $Cu(SO_4)*5\ H_2O$, $Cu(SO_4)$, $Co(SO_4)$, $CoSO_4*7H_2O$ and $Zn(OAc)_2*4\ H_2O$, more preferably from $Cu(SO_4)$ and $Cu(SO_4)\ *5\ H_2O$.

Preparation of compounds of formula (III) (IV), (IIIb), (IVb), (IIIc) and (IVc)

The compounds of formula (III) (IV), (IIIb), (IVb), (IIIc) and (IVc) are prepared by azo coupling reaction of the respective diazo component and the respective coupling agent. The diazo component is prepared by diazotization reaction of the respective amine compound. These amine compounds and the coupling agents are known substances.

It is possible to use more than one amine compound and/or more than one coupling agent resulting in the respective mixture of azo ligands.

The azo coupling reaction may be carried out in water, non-aqueous solvents and in mixtures thereof. Suitable non-aqueous solvents are alcohols such as methanol, ethanol, propanol, butanol, pentanol, etc., dipolar aprotic solvents such as acetone, DMF, DMSO, NMP and water-immiscible solvents such as toluene or chlorobenzene.

Preferably the azo coupling reaction is carried out in water.

The azo coupling is preferably carried out in a stoichiometric ratio of coupling agent and diazo component. The azo coupling is generally done at temperatures between -30°C to 100°C, preference being given to temperatures of -10°C to 30°C, and particular preference to temperatures of -5°C to 20°C.

The azo coupling may be carried out in an acidic as well as an alkaline medium. Preference is given to pH <10, particular preference to pH from between 3 to 9.0.

Preparation of the compounds of formula (I), (II) and (V)

Preferably, the compounds of formula (I), (II) and (V) are prepared by complexing reaction of a solution of one equivalent of a metal salt with a boiling solution of one equivalent of the azo ligand of formula (III), (IIIb) or (IIIc) respectively and one equivalent of the azo ligand of formula (IV), (IVb) or (IVc) respectively. It is possible to use more than one azo ligand of formula (III), (IIIb) or (IIIc) respectively, as well as more than one azo ligand of formula (IV), (IVb) or (IVc) respectively. Preferably in this case the combined amounts of the azo ligands should preferably be equal to two equivalents of the metal salt. Of course it is also possible to use more than one metal salt, preferably a mixture of 2 or 3 metal salts, in the required stoichiometric amounts with regard to the azo ligands; and a combination of these measures is also possible.

The complexing reaction usually results in a precipitate, the precipitate is isolated following standard methods, preferably by filtration.

The solvents that can be used in the complexing reaction are water, solvents and mixtures thereof. The solvents are preferably selected from the group consisting of C_{1-8} alcohols, nitriles, preferably acetonitrile, acetone, aromatic solvents such as toluene or chlorobenzene, DMF, DMSO, NMP.

More preferred solvents used for the complexing reaction are C_{1-8} alcohols, especially ethanol, and acetonitrile.

It is also possible to add the metal salt already at an earlier stage of the synthesis of the compounds of formula (I), (II) and (V) or their precursors, preferably before, during or after the azo coupling reaction, more preferably after the azo coupling reaction to the resulting suspension or solution of the azo ligands.

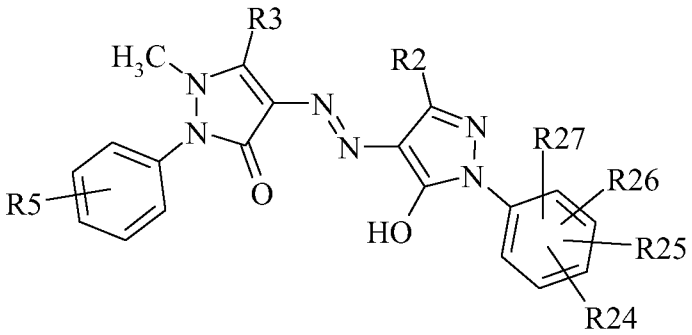
Even more preferably the azo ligands are isolated and dried after synthesis, and the complexing reaction is carried out in a separate step.

A further subject of the invention is therefore a process for the preparation of the compounds of formula (I), as well as of the compounds of formula (I) in all the

preferred aspects of the formula (I) as described above, by a complexing reaction of the azo ligands of formula (III) and (IV), with a metal salt; and further a process for the preparation of the compounds of formula (II), as well as of the compounds of formula (II) in all the preferred aspects of the formula (II) as described above, by a complexing reaction of the azo ligands of formula (IIIb) and (IVb), with a metal salt; and further a process for the preparation of the compounds of formula (V), as well as of the compounds of formula (V) in all the preferred aspects of the formula (V) as described above, by a complexing reaction of the azo ligands of formula (IIIc) and (IVc), with a metal salt;

with the azo ligands preferably prepared by a azo coupling reaction of the respective diazo components and the respective coupling agents.

Another subject of the invention is a compound of the formula (IIIc), wherein



(IIIc)

R^2 and R^3 are independently from each other selected from the group consisting of hydrogen, CH_3, C_2H_5, $CH(CH_3)_2$ and n-butyl;

R^5 is selected from the group consisting of hydrogen, Cl, CH_3 and C_2H_5;

R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of hydrogen, F and CF_3, with the proviso, that at least one of the substituents R^{24}, R^{25}, R^{26} and R^{27} is not hydrogen;

preferably, another subject of the invention is a compound of formula (IIIc), wherein

R^2 and R^3 are independently from each other selected from the group consisting of CH_3, C_2H_5 and $CH(CH_3)_2$;

R^5 is selected from the group consisting of hydrogen and Cl;

R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of hydrogen, F and CF_3, with the proviso, that at least one of the substituents R^{24}, R^{25}, R^{26} and R^{27} is not hydrogen;

more preferably, another subject of the invention is a compound of formula (IIIc), wherein

R^2 and R^3 are independently from each other selected from the group consisting of CH_3, C_2H_5 and $CH(CH_3)_2$;

R^5 represents hydrogen or Cl;

R^{24}, R^{25}, R^{26} and R^{27} are same and represent either F; or

R^{24}, R^{25}, R^{26} are same and represent hydrogen, and R^{27} represents CF_3; with R^{27} preferably located at the meta- or para-position;

even more preferably, another subject of the invention is a compound of formula (IIIc), wherein

R^2 is CH_3 or C_2H_5;

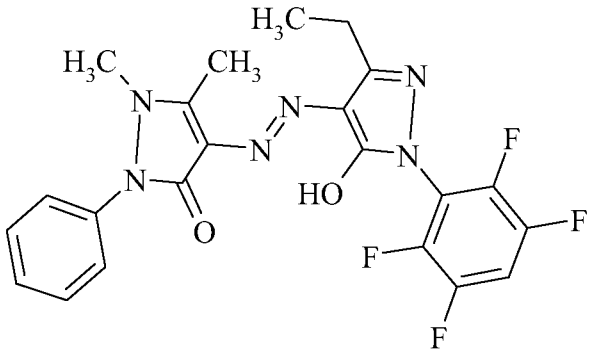
R^3 is CH_3;

R^5 represents hydrogen;

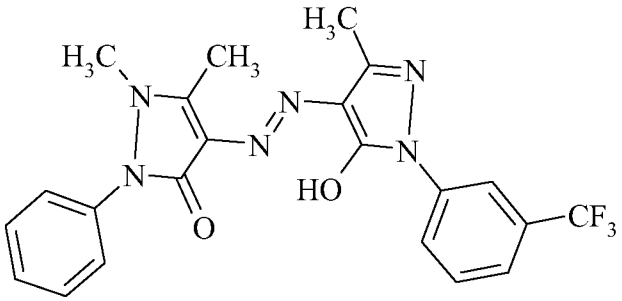
R^{24}, R^{25}, R^{26} and R^{27} are same and represent either F; or

R^{24}, R^{25}, R^{26} are same and represent hydrogen, and R^{27} represents CF_3; with R^{27} preferably located at the meta- or para-position;

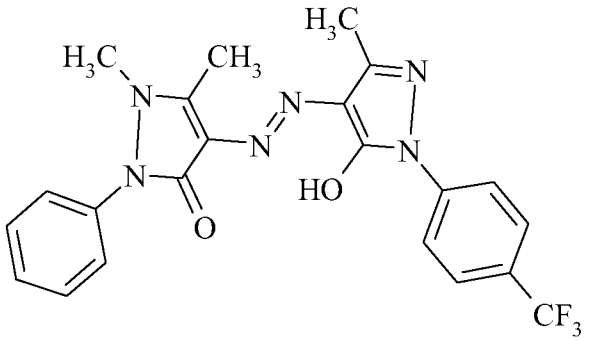
especially preferably, another subject of the invention is a compound according to formula (IIIc), of the formula (30), (31), (32) or (33).



(30)



(31)



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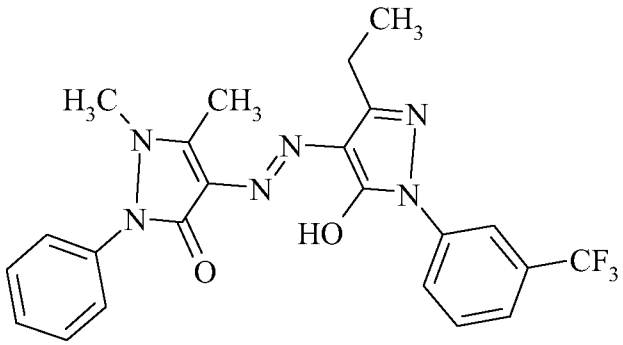


(33)

A further subject of the invention is the use of a compound of the formula (IIIc) in all its preferred embodiments, or of the formula (30), (31), (32) or (33), as an azo ligand, preferably in azo metal complex dyes; the azo metal complex dyes preferably being used in optical layers, preferably for optical data recording.

A further subject of the invention is the use of the compounds of formula (I), (II) or (V) and the use of the compounds of formula (I), (II) or (V) in all the preferred aspects of the formula (I), (II) or (V) as described above, in an optical layer, preferably for optical data recording.

A further subject of the invention is the use of the compounds of formula (I), (II) or (V) and the use of the compounds of formula (I), (II) or (V) in all the preferred aspects of

the formula (I), (II) or (V) as described above, as a dye in an optical layer, preferably for optical data recording.

A further subject of the present invention is an optical layer comprising at least one compound of formula (I), (II) or (V) and the use of said optical layer for optical data recording media. An optical layer according to the invention may also comprise a mixture of two or more, preferably of two or three, more preferably of two compounds of formula (I), (II) or (V). A further subject of the invention therefore is an optical data recording medium comprising an optical layer comprising at least one compound of formula (I), (II) or (V).

Further, the invention relates to a method for producing optical layers on a substrate comprising the following steps

(a) providing a substrate,

(b) dissolving at least one compound of formula (I), (II) or (V) in an organic solvent to form a solution,

(c) coating the solution (b) on the substrate (a),

(d) evaporating the solvent to form an optical layer (also called dye layer or recording layer).

(a) Substrate

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

Suitable substrates are, for example, glass, minerals, ceramics and thermosetting or thermoplastic plastics. Preferred supports are glass and homo- or co-polymeric plastics. Suitable plastics are, for example, thermoplastic polycarbonates, polyamides, polyesters, polyacrylates and polymethacrylates, polyurethanes, polyolefins, polyvinyl chlorides, polyvinylidene fluorides, polyimides, thermosetting polyesters and epoxy resins. The most preferred substrates are polycarbonates (PC) or polymethylmethacrylates (PMMA).

The substrate can be in pure form or may also comprise customary additives, for example UV absorbers as light-stabilizers for the optical layer.

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

(b) Organic solvents

Organic solvents are selected from C_{1-8} alcohols, halogen substituted C_{1-8} alcohols, C_{1-8} ketones, C_{1-8} ethers, halogen substituted C_{1-4} alkanes, nitriles, preferably acetonitrile, or amides, or mixtures thereof.

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

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

Preferred halogen substituted C_{1-4} alkanes are for example chloroform, dichloromethane or 1-chlorobutane.

Preferred amides are for example dimethylformamide or dimethylacetamide.

(c) Coating methods

Suitable coating methods are, for example, immersion, pouring, brush-coating, blade-application and spin-coating, as well as vapor-deposition methods carried out under a high vacuum. When pouring methods are used, solutions in organic solvents are generally used. When solvents are employed, care should be taken that the supports used are insensitive to those solvents. The optical layer is preferably applied by spin-coating with a dye solution.

(d) Optical layer (also called dye layer or recording layer)

The optical layer is preferably arranged between the transparent substrate and the reflecting layer. The thickness of the recording layer is from 10 to 1000 nm, preferably from 30 to 300 nm, more preferably from 70 to 250 nm, especially about 80 nm, for example from 60 to 120 nm.

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

Further customary components are stabilizers, for example $^1O_2$-, triplet- or luminescence quenchers, melting-point reducers, decomposition accelerators or any other additives that have already been described in optical data recording media. Preferably, stabilizers or fluorescence-quenchers are added if desired.

Stabilizers, $^1O_2$-, triplet- or luminescence-quenchers are, for example, metal complexes of N- or S-containing enolates, phenolates, bisphenolates, thiolates or bisthiolates, hindered phenols and derivatives thereof such as o-hydroxyphenyl-triazoles or -triazines or other UV absorbers, such as hindered amines (TEMPO or HALS, as well as nitroxides or NOR-HALS), and also as cations diimmonium, Paraquat™ or Orthoquat salts, such as ®Kayasorb IRG 022, ®Kayasorb IRG 040, optionally also as radical ions, such as N,N,N',N'-tetrakis(4-dibutylaminophenyl)-p-phenylene amine-ammonium hexafluorophosphate, hexafluoroantimonate or perchlorate. The latter are available from Organica (Wolfen/DE); ®Kayasorb brands are available from Nippon Kayaku Co. Ltd.

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

Preparation of the optical data recording medium

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

(e) applying a metal layer (also called reflective layer) onto the optical layer,

(f) applying a second polymer based layer to complete the disk (cover layer or protective layer).

(e) Reflective layer

The application of the metallic reflective layer is preferably effected by sputtering, vapor-deposition in vacuum or by chemical vapor deposition (CVD). The sputtering technique is especially preferred for the application of the metallic reflective layer.

Reflecting materials suitable for the reflective layer include especially metals, which provide good reflection of the laser radiation used for recording and playback, for example the metals of Main Groups III, IV and V and of the Sub-groups of the Periodic Table of the Elements. Al, In, Sn, Pb, Sb, Bi, Cu, Ag, Au, Zn, Cd, Hg, Sc, Y, La, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu and alloys thereof are especially suitable. Special preference is given to a reflective layer of aluminum, silver, copper, gold or an alloy thereof, on account of their high reflectivity and ease of production.

(f) Cover layer (also called protective layer)

Materials suitable for the cover layer include plastics, which are applied in a thin layer to the support or the uppermost layer either directly or with the aid of adhesive layers. The material of the cover layer may for example be the same as the material of the substrate. It is advantageous to select mechanically and thermally stable plastics having good surface properties, which may be modified further.

The plastics may be thermosetting plastics and thermoplastic plastics. Preference is given to radiation-cured (e.g. using UV radiation) protective layers, which are particularly simple and economical to produce. A wide variety of radiation-curable materials are known. Examples of radiation-curable monomers and oligomers are acrylates and methacrylates of diols, triols and tetrols, polyimides of aromatic

tetracarboxylic acids and aromatic diamines having C_1-C_4alkyl groups in at least two ortho-positions of the amino groups, and oligomers with dialkylmaleinimidyl groups, e.g. dimethyl maleinimidyl groups.

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

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

The optical data recording media according to the invention may also have additional layers, for example interference layers. It is also possible to construct optical data recording media having a plurality of (for example two) recording layers. The structure and the use of such materials are known to the person skilled in the art. Preferred, if present, are interference layers that are arranged between the recording layer and the reflecting layer and/or between the recording layer and the substrate and consist of a dielectric material of $Ti0_2$, Si_3N_4, ZnS or silicone resins.

These optical data recording media according to the invention can be produced by processes known in the art.

Readout methods

The structure of the optical data recording medium according to the invention is governed primarily by the readout method; known function principles include the measurement of the change in the transmission or, preferably, in the reflection, but it is

also known to measure, for example, the fluorescence instead of the transmission or reflection.

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

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

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

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

The readout of information is carried out according to methods known in the art by registering the change in absorption or reflection using laser radiation.

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

The compounds of formula (I), (II) and (V) provide for particularly preferable properties when used in optical layers for optical data recording media according to the invention. They possess the required optical characteristics, demonstrated when used in the form of a solid film:

- an advantageously homogeneous, amorphous and low-scattering optical layer,
- a high refractive index at the longer wavelength flank of the absorption band, which preferably achieves n values of the refractive index of from 1.0 to 3.0 in the range of from 350 to 500 nm,
- a high sensitivity under laser radiation of high power density and good playback characteristics in the desired spectral range,
- an enhanced photosensitivity and stability (in daylight and under laser radiation of low power density) compared to dyes already known in the art,
- an uniform script width and a high contrast,
- an absorption maximum λmax in the preferred range between 390 nm and 470 nm as being preferred for blue laser applications, more precisely from 400 to 460 nm,
- a decomposition point DP in the preferred temperature range between 220°C and 300°C, more precisely 230°C to 290°C,
- a sufficient heat release (HR).

Recording performance of a compound is related to specific parameters measured on disc like:

- a low simulated bit error rate (SbER),
- a low inner parity error rate (PI error),
- a high reflectivity (R),

- a low laser recording power (Pw or OPC: optimum power control),
- good readout stability at several laser reading powers,
- an appropriate partial response signal to noise ratio (PRSNR).

The absorption edge is surprisingly steep even in the solid phase.

The compounds of formula (I), (II) and (V) also show a narrow decomposition temperature of 240-300°C, fitting with the thermal requirements. Additionally, these compounds show a high solubility in organic solvents, which is ideal for the spin-coating process to manufacture optical layers.

Examples

UV-vis

For UV-vis spectra, λ max and ε values of a compound are determined by using an UV-vis spectrophotometer, the compound was dissolved in CH_2Cl_2, DMSO or in tfp. The values are obtained by balancing the measurements performed on compound solutions at three different concentrations.

Thermal Decomposition: Decomposition point (DP) and heat release (HR)

For the determination of DP and HR, the compound is incorporated into a sealed aluminum pan. Analysis conditions are as following: Temperature range from 25 to 400°C, heating rate 10°C/min, nitrogen flow of 50 ml/min. Values are determined by single measurement.

Partial response signal to noise ratio (PRSNR)

A definition and the measuring techniques of PRSNR are described in a book available from DVD Format Logo Licensing Co., Ltd. for example, Annex H of Version 0.9, PART 1 Physical Specifications, DVD Specifications for High Density Read-Only Disk.

Simulated bit error rate (SbER)

A definition and the measuring techniques of SbER are described in a book available from DVD Format Logo Licensing Co., Ltd. for example, Annex H of Version 0.9, PART 1 Physical Specifications, DVD Specifications for High Density Read-Only Disk.

PRSNR and SbER are measured in a state in which information has been recorded in the adjacent tracks.

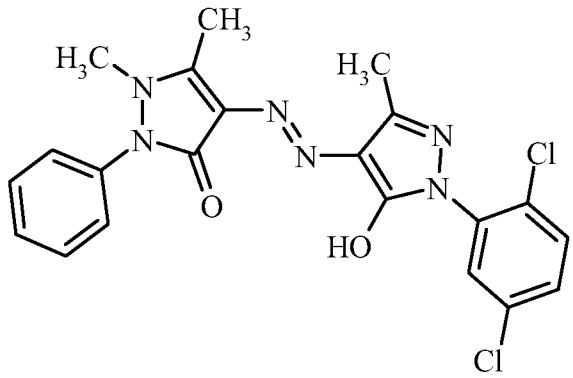
Reflectivity (R)

A definition and the measuring techniques for the light reflectivity (R) is described in a book available from DVD Format Logo Licensing Co., Ltd. for example, Annex D of Version 0.9, PART 1 Physical Specifications, DVD Specifications for High Density Read-Only Disk.

Example 1

Diazotization and coupling

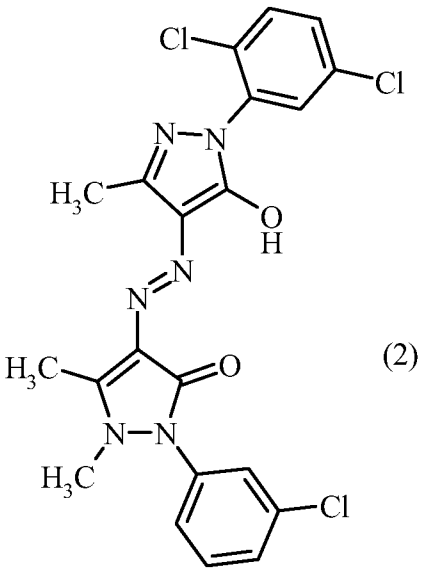
A mixture of 20.7 g of 4-aminoantipyrine, 130 ml of water and 32 g of concentrated hydrochloric acid (30% w/w) was gradually admixed with 24.9 ml of sodium nitrite (33% w/v) at 0°C. After 1 hour of reaction at 0°C, the orange diazotization solution was added drop wise to an alkaline solution of 24.7 g of 2,5-dichloropyrazolone while maintaining pH at 7.5-9 with sodium hydroxide (30% w/w). The suspension was stirred 3 hours, then filtered with suction. The filtrate was washed with water and dried. 46.0 g of compound of formula (1) was obtained.



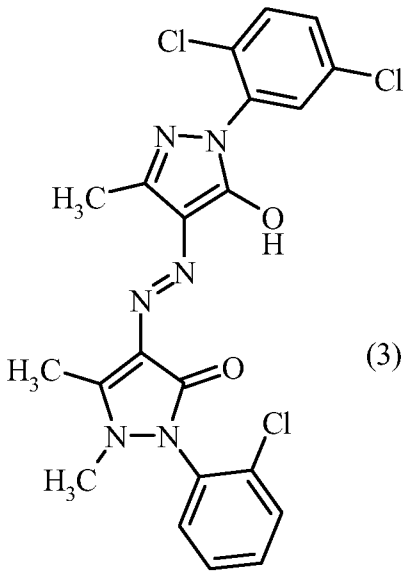
(1)

Examples 2 and 3

The diazotization and coupling according to example 1 was repeated with the respective coupling agent in a stoichiometric ratio with regard to the diazo component to yield the compounds of formula (2) and (3).



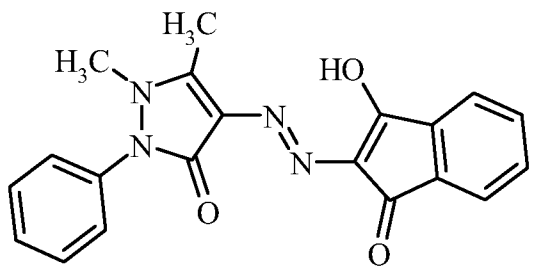
(2)



(3)

Example 4

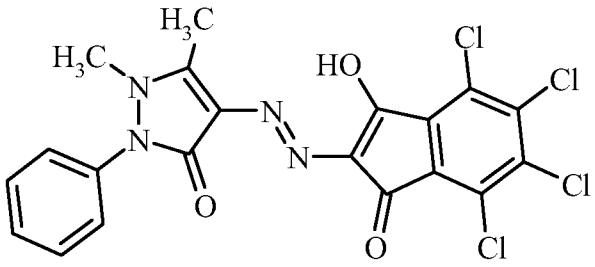
A mixture of 10.4 g of 4-aminoantipyrine, 50 ml of water and 16.1 g of concentrated hydrochloric acid (34% w/v) was gradually admixed with 12.4 ml of sodium nitrite (33% w/v) at 0°C; After 1 hour of reaction at 0°C, the orange diazotization solution was added dropwise to an alkaline solution of 7.5 g of 1,3-indandione, 200ml of water and 15.9g of sodium carbonate to attain pH at 7.5-8. The suspension was stirred 30 minutes, and 17ml of acetic acid is added to adjust to pH 5. Then the suspension is filtered with suction. The filtrate was washed with water and dried. 17.8 g of compound of the formula (4) were obtained.



(4)

Example 5

Compound of formula (5) was prepared according to example 4 using tetrachloroindandione in place of 1,3-indandione in a stoichiometric ratio with regard to the 4-aminoantipyrine.



(5)

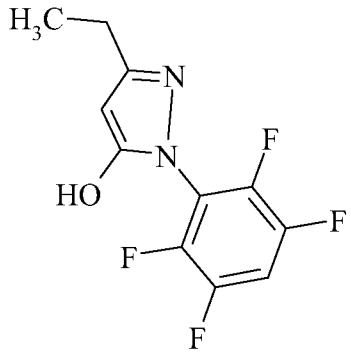
Examples 6 to 9

3.8 g of compound of formula (1), prepared according to example 1, and 3.0 g of compound of formula (4), prepared according to example 4, are suspended in 100 ml of ethanol together with 1.5 g of sodium acetate. After heating up to reflux, a solution of 2.1 g of copper sulfate penta hydrate in 35 ml of water is added for over one hour, whereupon a dark orange suspension of the copper complex dye results. The suspension is cooled down to room temperature and the resulting precipitate is stirred for one hour, filtered and the residue washed salt free with deionized water and dried. 7.0 g of compound of formula (6) is obtained.

The complexing reaction was repeated with one equivalent of azo ligand 1 and one equivalent of azo ligand 2 and with the respective metal salt, details are given in Table (A1) and (A2), to yield metal complex dye compounds of formulae (7) to (9) of examples 7 to 9.

Example 20

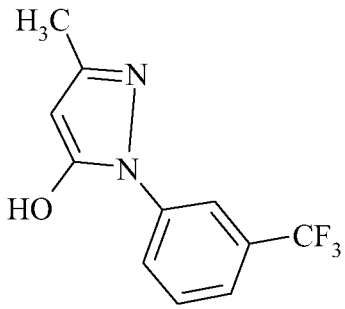
10 g of (2,3,5,6-tetrafluorophenyl) hydrazine are mixed with 8.1 g of ethyl propionylacetate (ethyl 3-oxovalerate) in 120 ml of acetic acid under nitrogen atmosphere. The whole mixture is then stirred under reflux for 12 hours. After reaction completion, the dark yellow solution is cooled to 25°C until a precipitate is obtained. This suspension is then filtered, washed with water until no acetic acid remains and the presscake is dried under vacuum. 13.0 g of compound of formula (20) are then obtained as yellowish product.



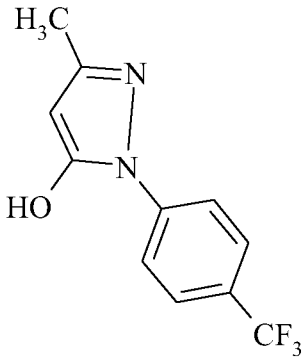
(20)

Examples 21, 22 and 23

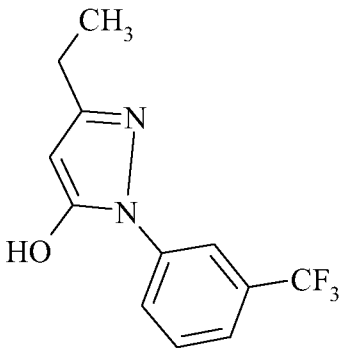
The compounds of formula (21), (22) and (23) were synthesized according to the procedure described in example (20), using the corresponding 3-trifluoromethylphenyl hydrazine and 4-trifluoromethylphenyl hydrazine and the corresponding ethyl-propionylacetate (ethyl 3-oxovalerate) and ethyl-acetoacetate.



(21)



(22)



(23)

Example 30

Diazotization and coupling

A mixture of 10.0 g of 4-aminoantipyrine, 50 ml of water and 18.7 g of concentrated hydrochloric acid (34% w/v) was gradually admixed with 11.4 ml of sodium nitrite

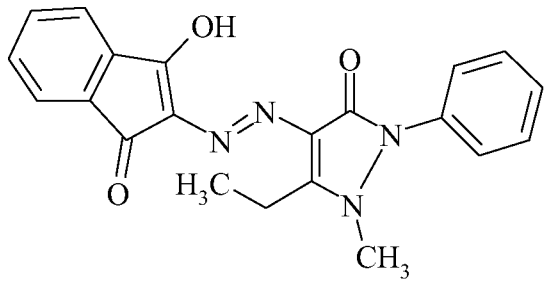
(33% w/v) at 0°C. After 1 hour of reaction at 0°C, the orange diazotization solution was added dropwise to an alkaline solution of 12.9 g of compound of formula (20), prepared according to example 20, 200ml of water and 15.9g of sodium carbonate to attain pH at 7.5 to 8. The suspension was stirred 30 minutes, and 18 ml of acetic acid is added to adjust to pH 5. Then the suspension is filtered with suction. The filtrate was washed with water and dried. 21.2 g of the compound of formula (30) were obtained.

Examples 31, 32 and 33

The diazotization and coupling reaction according to example (30) was repeated with the respective compounds of formulae (21), (22) and (23), prepared according to examples 21, 22 and 23, in a stoichiometric ratio with regard to the diazo component 4-aminoantipyrine to yield the compounds of formula (31), (32) and (33).

Example 34

A mixture of 10.4 g of 1-phenyl-2-methyl-3-ethyl-4-aminopyrazolone-5, 50 ml of water and 16.1 g of concentrated hydrochloric acid (34% w/v) was gradually admixed with 11.3 ml of sodium nitrite (33% w/v) at 0°C. After 1 hour of reaction at 0°C, the orange diazotization solution was added dropwise to an alkaline solution of 7.6 g of 1,3-indandione, 200ml of water and 15.9g of sodium carbonate to attain pH at 7.5 to 8. The suspension was stirred 30 minutes, and 17ml of acetic acid is added to adjust to pH 5. Then the suspension is filtered with suction. The filtrate was washed with water and dried. 17.5 g of the compound of formula (34) were obtained.



(34)

Examples 40 to 47

The complexing reaction according to example 6 was repeated with one equivalent of azo ligand 1 and one equivalent of azo ligand 2 and with the respective metal salt,

details are given in Table (A1) and (A2), to yield metal complex dye compounds of formulae (40) to (47) of examples 40 to 47.

Table (A1)

Ex.	M	used metal salt	[g]	azo ligand 1 of formular	[g]	azo ligand 2 of formular	[g]	yield [g]
6	Cu	$Cu(SO_4)*5H_2O$	2.1	(1)	3,8	(4)	3,0	7,0
7	Cu	$Cu(SO_4)*5H_2O$	2.1	(1)	3,8	(5)	4,1	7,2
8	Cu	$Cu(SO_4)*5H_2O$	1.8	(2)	3,5	(4)	2,6	5,3
9	Cu	$Cu(SO_4)*5H_2O$	1.9	(3)	3,8	(4)	2,8	6,1
40	Cu	$Cu(SO_4)*5H_2O$	1,8	(30)	3,5	(4)	2,7	6,0
41	Ni	Ni(OAc)2*5H2O	2,0	(30)	3,5	(4)	2,7	5,8
42	Cu	$Cu(SO_4)*5H_2O$	1,8	(30)	3,5	(34)	2,8	6,2
43	Cu	$Cu(SO_4)*5H_2O$	2,2	(31)	3,6	(34)	3,3	6,7
44	Cu	$Cu(SO_4)*5H_2O$	2,2	(31)	3,6	(4)	3,2	6,8
45	Cu	$Cu(SO_4)*5H_2O$	2,1	(32)	3,4	(34)	3,1	6,9
46	Cu	$Cu(SO_4)*5H_2O$	2,1	(32)	3,4	(4)	3,0	6,1
47	Cu	$Cu(SO_4)*5H_2O$	2,1	(33)	3,5	(34)	3,2	5,7

Table (A2)

Ex.	λ max [nm]	ε (λ max) [l/g/cm]	DP [°C]	HR [W/g]
6	447	56	258	20
7	444	60	254	12
8	448	58	265	10
9	448	55	253	11
40	445	60	274	15
41	440	65	287	4
42	446	63	249	5
43	449	56	245	5
44	444	56	254	7
45	443	59	248	6
46	447	68	252	6
47	448	68	246	5

Application Example 1

The optical and thermal properties of the compounds of formula (I), (II) and (V) were studied. The compounds of formula (I), (II) and (V) show high absorption at the desired wavelengths. In addition, the shapes of the absorption spectra, that still remain critical

to the disc reflectivity and formation of clean mark edges, are composed of one major band, comprised in a range of from 350 to 500 nm.

More precisely, n values of the refractive index were evaluated between 1.0 and 2.7. Light stabilities were found comparable to commercial dyes which are already stabilized with quenchers for the use in optical data recording.

Sharp threshold of thermal decomposition within the required temperature range characterizes the compounds of formula (I), (II) and (V), which are desirable for the application in optical layers for optical data recording.

Application example 2 Optical layer and optical data recording medium

1.4% by weight of a compound of formula (6), prepared according to Example 6, are dissolved in 2,2,3,3-tetrafluoro-l-propanol and the solution is filtered through a Teflon filter of pore size 0.2 µm and applied by spin-coating at 1000 rpm to the surface of a 0.6 mm thick, grooved polycarbonate disc of 120 mm diameter. The excess solution is spun off by increasing the rotational speed. On evaporation of the solvent, the dye remains behind in the form of a uniform, amorphous solid layer, the optical layer. After drying the optical layer in a circulating-air oven at 70°C (10 min) in a vacuum coating apparatus, a 100 µm thick silver layer is then applied to the recording layer by atomisation. Then a 6 µm thick protective layer of a UV curable photopolymer (650-020, DSM) is applied thereto by means of spincoating. Finally, a second substrate is provided to combine with the resin protection layer using an attachment layer. This completes the manufacturing of a high-density recordable optical disc, the optical data recording medium.

The testing conditions are the following ones:

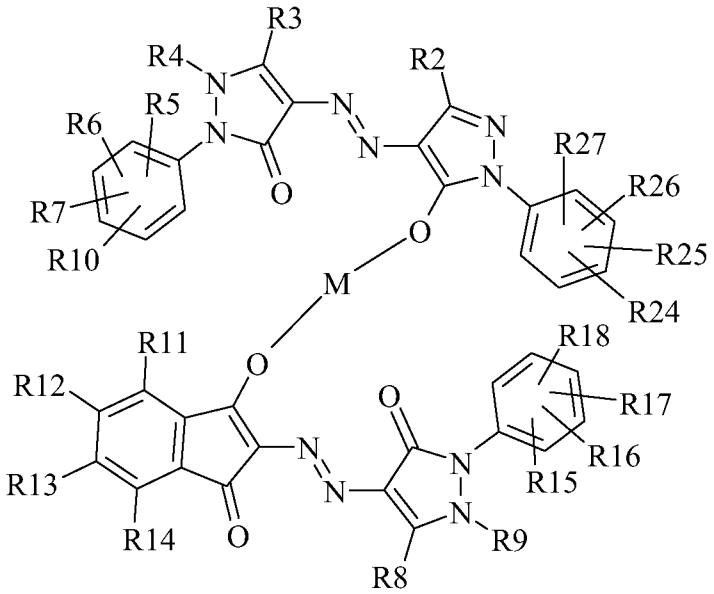
- Numerical aperture (NA) of the optical head: 0.65
- Wavelength of a laser light for recording and reproduction: 405 nm
- Constant linear velocity (CLV): 6.61 m/sec.
- Track pitch: 400 nm
- Wobble amplitude of the groove track: 14 nm
- Groove depth: 90 nm.

Results of the evaluation tests of the compound of formula (6) of example 6 and of other compounds of other examples are summarized in table (B):

Table (B)				
Example	**Pw**	**SbER**	**PRSNR**	**reflectivity**
	[mW]		**[db]**	**[%]**
6	6.6	9.80E-10	30	22.7
40	6.6	2.50E-08	28	23.6
42	6.7	4.10E-10	37	24.7
44	6.3	1.80E-09	35	21.5

Claims

1. A compound of formula (I), wherein



(I)

M represents a divalent metal atom;

R^2, R^3 and R^8 are independently from each other selected from the group consisting of

hydrogen, halogen, CN, CF_3, NO_2, C_{1-10} alkoxy, C_{1-10} alkyl, C_{5-10} cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, and

unsubstituted phenyl or substituted phenyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

unsubstituted benzyl or substituted benzyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

$NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21};

R^4 and R^9 are independently from each other selected from the group consisting of

C_{1-10} alkyl, C_{5-10} cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, and

unsubstituted phenyl or substituted phenyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

unsubstituted benzyl or substituted benzyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$;

R^5, R^6, R^7, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of

hydrogen, OH, halogen, CN, CF_3, NO_2, C_{1-10} alkoxy, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, and

unsubstituted phenyl or substituted phenyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

unsubstituted benzyl or substituted benzyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2 R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

$NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$;

R^{21} and R^{22} are independently from each other selected from the group consisting of hydrogen, C_{1-10} alkyl, C_{6-10} aryl;

R^{23} is OH or C_{1-10} alkoxy.

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

M is selected from the group consisting of Ni, Cu, Co, Zn, Fe, Pd, Pt, Mn;

R^2, R^3 and R^8 are independently from each other selected from the group consisting of hydrogen, CH_3, C_2H_5, C_3H_7, C_4H_9, phenyl, CN, CF_3;

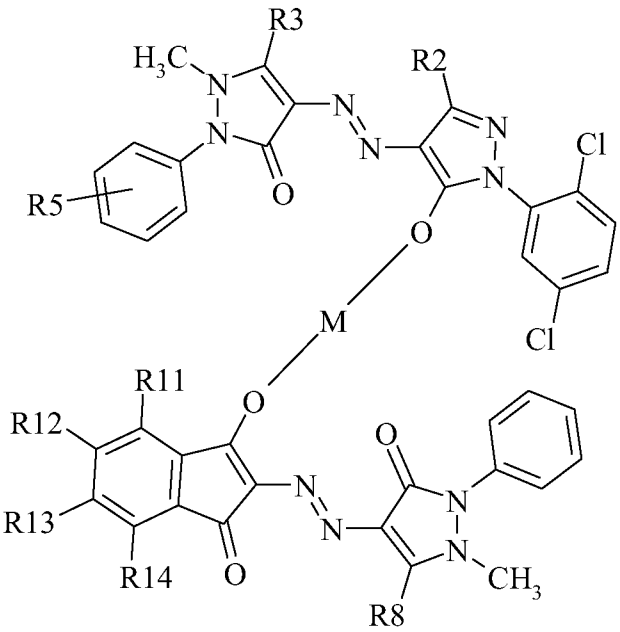
R^4 and R^9 are independently from each other selected from the group consisting of C_{1-4} alkyl,

unsubstituted benzyl or substituted benzyl with 1 to 3 substituents being independently from each other selected from the group consisting of halogen, C_{1-4} alkyl and NO_2;

R^5, R^6, R^7, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of hydrogen, halogen, CN, CF_3, C_{1-4}-alkyl, C_{1-4}-alkoxy, NO_2 and SO_2-$NR^{21}R^{22}$;

with R^{21} and R^{22} being independently from each other selected from the group consisting of hydrogen and C_{1-4} alkyl.

3. A compound according to claim 1 or 2 of formula (II), wherein



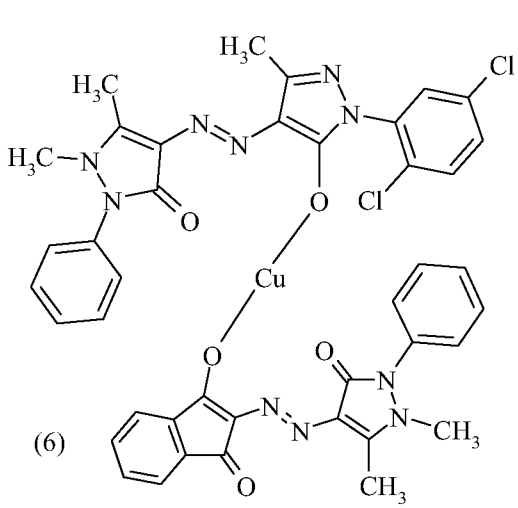
(II)

M is selected from Ni, Zn, Cu, Co and Mn;

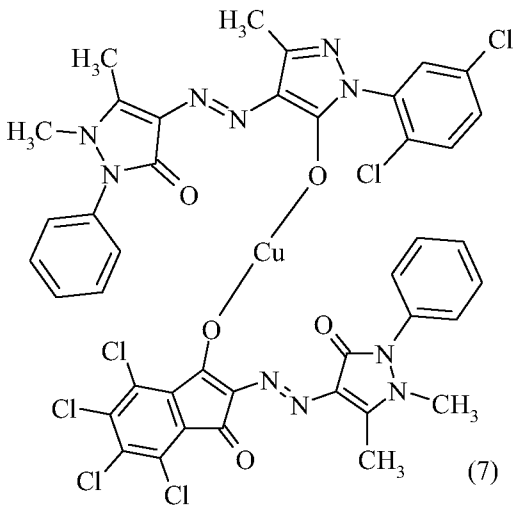
R^2, R^3 and R^8 are independently from each other selected from the group consisting of hydrogen, CH_3, C_2H_5, $CH(CH_3)_2$ and n-butyl;

R^5, R^{11}, R^{12}, R^{13} and R^{14} are independently from each other selected from the group consisting of hydrogen, Cl, CH_3 and C_2H_5.

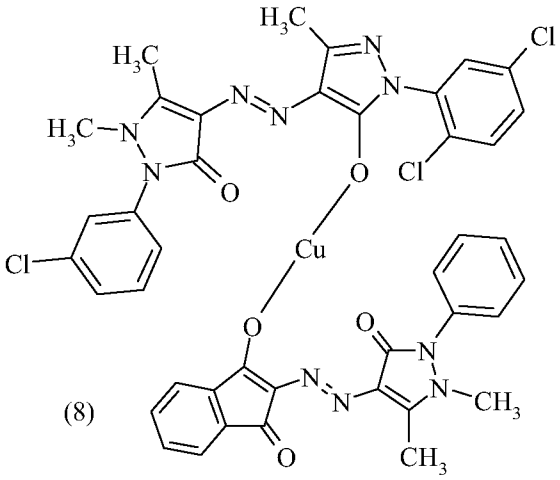
4. A compound according to any one of claims 1 to 3 of the formula (6), (7), (8) or (9).



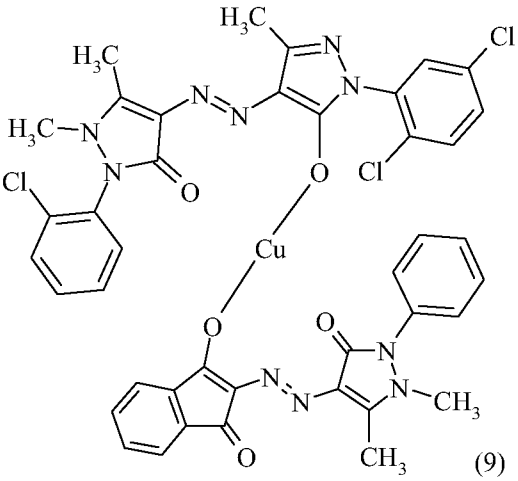
(6)



(7)

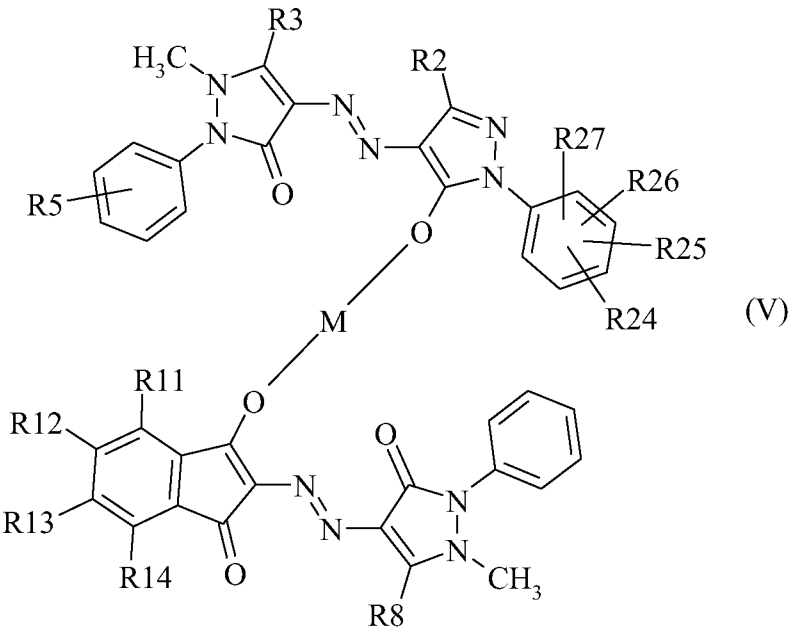


(8)



(9)

5. A compound according to claim 1 or 2 of formula (V), wherein



(V)

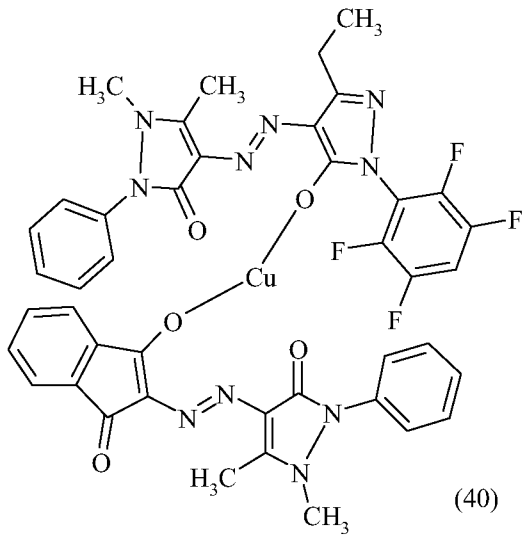
M is selected from Ni, Zn, Cu, Co and Mn;

R^2, R^3 and R^8 are independently from each other selected from the group consisting of hydrogen, CH_3, C_2H_5, $CH(CH_3)_2$ and n-butyl;

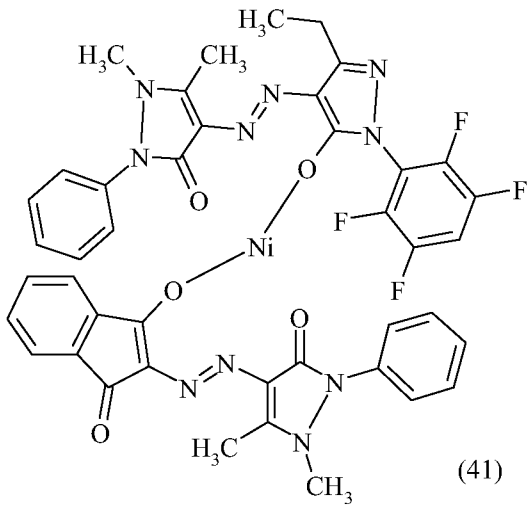
R^5, R^{11}, R^{12}, R^{13} and R^{14} are independently from each other selected from the group consisting of hydrogen, Cl, CH_3 and C_2H_5;

R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of hydrogen, F and CF_3, with the proviso, that at least one of the substituents R^{24}, R^{25}, R^{26} and R^{27} is not hydrogen.

6. A compound according to any one of claims 1, 2 or 5 of the formula (40), (41), (42), (43), (44), (45), (46) or (47).



(40)



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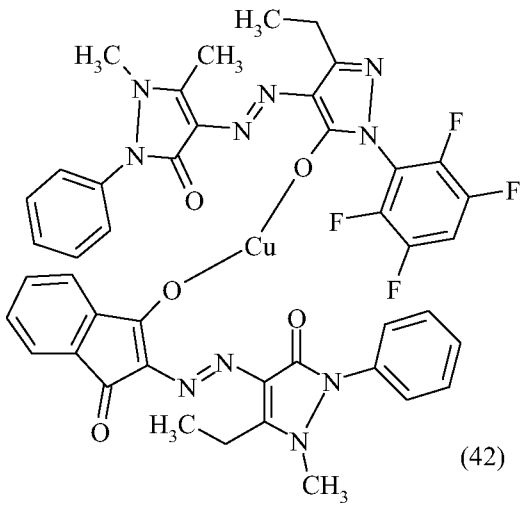
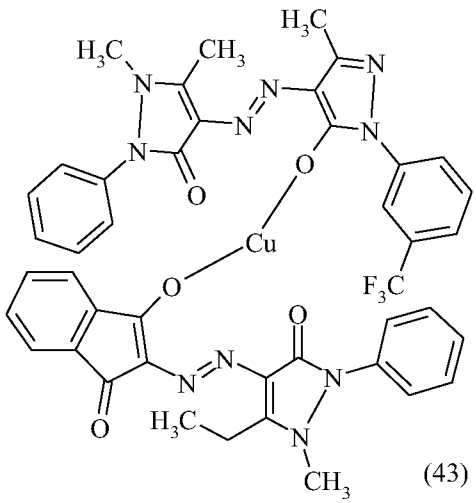
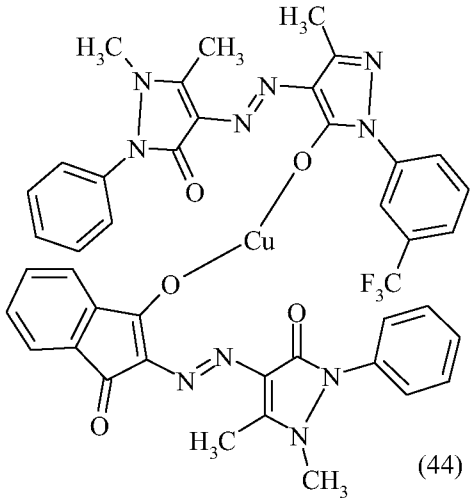


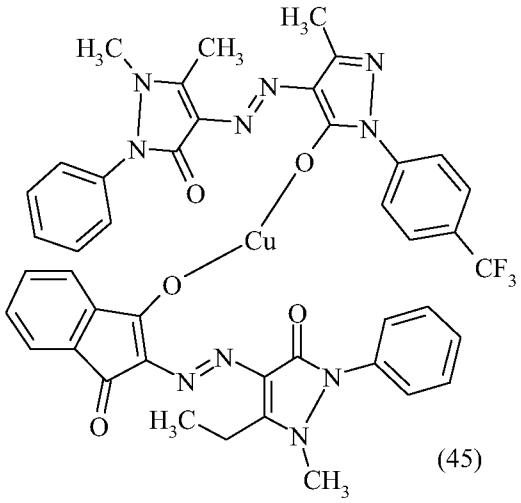
(42)



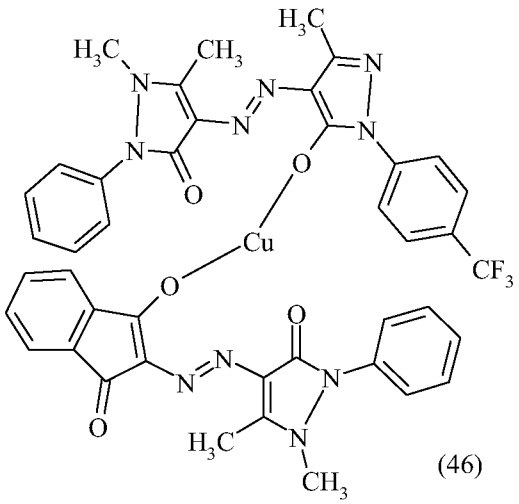
(43)



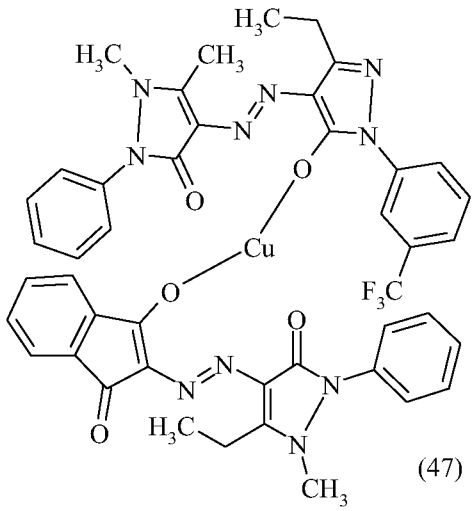
(44)



(45)



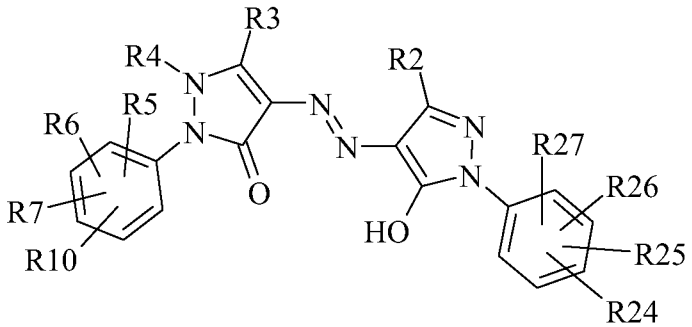
(46)



(47)

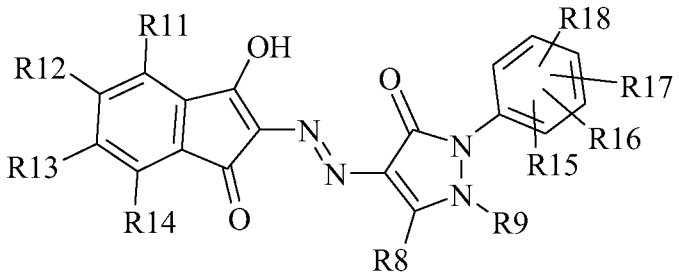
5

7. A process for the preparation of a compound of formula (I) as defined in claim 1 or 2 by complexing reaction of one equivalent of a compound of formula (III) and one equivalent of a compound of formula (IV) with one equivalent of a divalent metal salt,



(III)

10



(IV)

wherein

R^2, R^3 and R^8 are independently from each other selected from the group consisting of

hydrogen, halogen, CN, CF_3, NO_2, C_{1-10} alkoxy, C_{1-10} alkyl, C_{5-10} cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, and

unsubstituted phenyl or substituted phenyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

unsubstituted benzyl or substituted benzyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

$NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21};

R^4 and R^9 are independently from each other selected from the group consisting of C_{1-10} alkyl, C_{5-10} cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, and

unsubstituted phenyl or substituted phenyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy,

$NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

unsubstituted benzyl or substituted benzyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$;

R^5, R^6, R^7, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of

hydrogen, OH, halogen, CN, CF_3, NO_2, C_{1-10} alkoxy, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, and

unsubstituted phenyl or substituted phenyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

unsubstituted benzyl or substituted benzyl with 1 to 4 substituents being independently from each other selected from the group consisting of OH, halogen, CN, CF_3, NO_2, C_{1-10} alkyl, C_{5-10}-cycloalkyl, the alkyl and cycloalkyl groups being optionally substituted by halogen, C_{1-10} alkoxy, $NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2 R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$, and

$NR^{21}R^{22}$, S-C_{1-10} alkyl, O-C_{6-10}-aryl, S-C_{6-10}-aryl, SO_2-$NR^{21}R^{22}$, CO-R^{23}, SO_2R^{23}, CO-$NR^{21}R^{22}$, NH-CO-R^{21}, NH-SO_2-R^{21} or C_{1-10} alkyl-$NR^{21}R^{22}$;

R^{21} and R^{22} are independently from each other selected from the group consisting of hydrogen, C_{1-10} alkyl, C_{6-10} aryl;

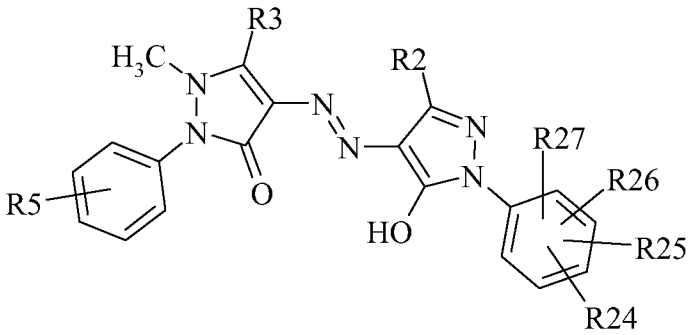
R^{23} is OH or C_{1-10} alkoxy.

8. A process according to claim 7, wherein the compounds of formula (III) and (IV) are prepared by azo coupling reaction.

9. A process according to claim 7 or 8, wherein the divalent metal salt is a derived from a metal selected of the group consisting of Ni, Cu, Co, Zn, Fe, Pd, Pt, Mn.

10. A process according to one or more of claim 7 to 9, wherein the divalent metal salt is selected of the group consisting $Cu(SO_4)$, $Cu(SO_4)*5\ H_2O$, $CuCl_2$, $Ni(OAc)_2*4\ H_2O$, $NiCl_2*6\ H_2O$, $Co(SO_4)$, $CoSO_4*7H_2O$, $Zn(OAc)_2*4\ H_2O$

11. A compound of the formula (IIIc), wherein



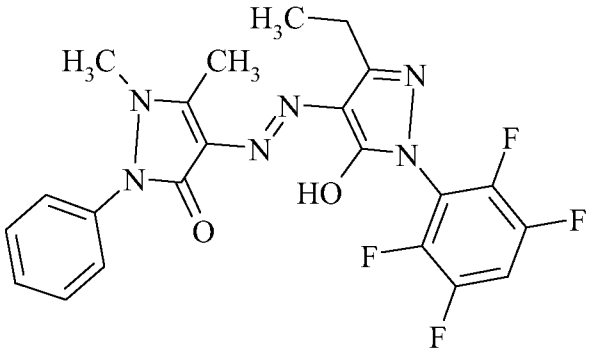
(IIIc)

R^2 and R^3 are independently from each other selected from the group consisting of hydrogen, CH_3, C_2H_5, $CH(CH_3)_2$ and n-butyl;

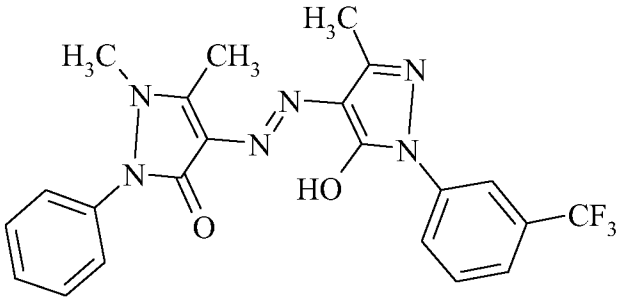
R^5 is selected from the group consisting of hydrogen, Cl, CH_3 and C_2H_5;

R^{24}, R^{25}, R^{26} and R^{27} are independently from each other selected from the group consisting of hydrogen, F and CF_3, with the proviso, that at least one of the substituents R^{24}, R^{25}, R^{26} and R^{27} is not hydrogen;

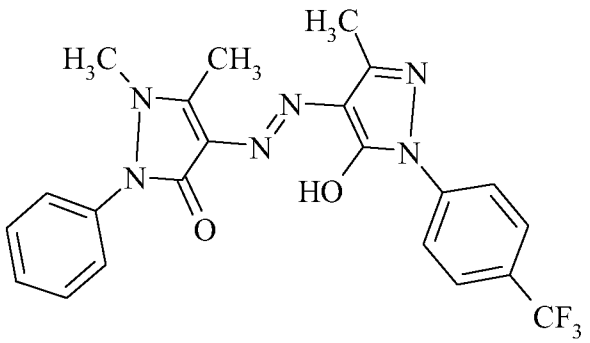
12. A compound according to claim 11 of the formula (30), (31), (32) or (33).



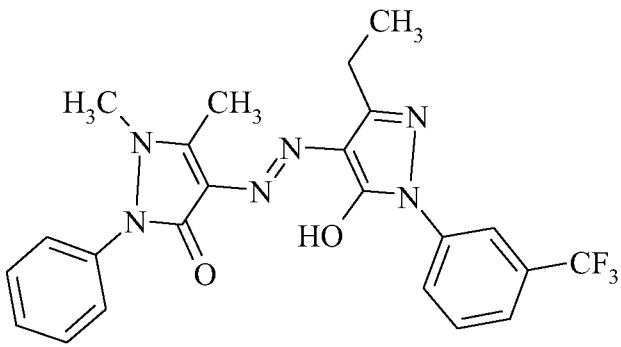
(30)



(31)



(32)



(33)

13. The use of a compound of the formula (IIIc) according to claim 11, or of the formula (30), (31), (32) or (33) according to claim 12, as an azo ligand.

14. The use according to claim 13, of a compound of the formula (IIIc) according to claim 11, or of the formula (30), (31), (32) or (33) according to claim 12, as an azo ligand in azo metal complex dyes.

15. The use of a compound of formula (I), as defined in claim 1 or 2, or of a compound of formula (II), as defined in claim 3 or 4, or of a compound of formula (V), as defined in claim 5 or 6, in an optical layer for optical data recording.

16. The use according to claim 15 of a compound of formula (I), as defined in claim 1 or 2, or of a compound of formula (II), as defined in one or more of claims 3 or 4, or of a compound of formula (V), as defined in one or more of claims 5 or 6, as a dye in an optical layer for optical data recording.

17. An optical layer comprising at least one compound of formula (I), as defined in claim 1 or 2, or of formula (II), as defined in claim 3 or 4, or of formula (V), as defined in claim 5 or 6.

18. A method for producing an optical layer as defined in claim 17, comprising the following steps

(a) providing a substrate,

(b) dissolving at least one compound of formula (I), as defined in claim 1 or 2, or of formula (II), as defined in claim 3 or 4, or of formula (V), as defined in claim 5 to 6, in an organic solvent to form a solution,

(c) coating the solution (b) on the substrate (a),

(d) evaporating the solvent to form an optical layer.

19. A method according to claim 18, wherein the substrate is polycarbonate (PC) or polymethylmethacrylate (PMMA).

20. A method according to claim 18 or 19, wherein the organic solvent is selected from C_{1-8} alcohol, halogen substituted C_{1-8} alcohols, C_{1-8} ketone, C_{1-8} ether, halogen substituted C_{1-4} alkane, or amides.

21. An optical data recording medium comprising an optical layer as defined in claim 17.