ABSTRACT

Diarylethene-containing ligands and their coordination compounds are described. The ligands display photochromism with UV excitation, while the coordination compounds display photochromism with both excitation in the UV region and excitation into lower energy absorption bands characteristic of the coordination compounds, through which the excitation wavelengths for the photocyclization can be extended from \( \lambda \leq 340 \text{ nm} \) to wavelengths beyond 470 nm. Switching of the luminescence properties of the compounds has also been achieved through photochromic reactions.
Fig. 1

\[ \text{Scheme 1} \]

\[ \text{Scheme 2} \]

Fig. 2

\[ \text{Graph 1} \]
Fig. 6

![Normalized Emission Intensity vs Wavelength](image1)

Fig. 7

![Absorbance vs Wavelength](image2)
PHOTOCHROMIC DIARYLETHENE-CONTAINING COORDINATION COMPOUNDS AND THE PRODUCTION THEREOF

FIELD OF THE INVENTION

This invention is related to the design and the photochromic behavior of novel photochromic ligands and their coordination compounds. The design of these photochromic ligands and their coordination compounds is based on the cis-diarylethene structure, which forms part of a mono- or poly-cyclic ring structure that contains one or more donor heteroatom(s) for coordination to an acceptor atom to form photochromic coordination compounds.

BACKGROUND OF THE INVENTION

Photochromism is defined as "a reversible transformation of a single chemical species being induced in one or both directions by absorption of electromagnetic radiation, with two states having different distinguishable absorption spectra." Thus, photochromic compounds are compounds that possess at least two isomeric forms which have different physical properties, such as absorption properties, refractivity, and the like, and can be transformed from one form to another by light excitations at prescribed wavelengths.

Photochromism has been extensively studied due to its potential use for optical recording and other optical functioning devices. To be practically used as optical recording materials, both isomeric forms must be thermally stable and possess excellent durability for reversible photochromic reactivity. Diarylethene is one class of photochromic compounds which possesses these properties, and therefore is a suitable class of compounds for the construction of optical functioning devices. The cis-configuration of both aryl groups in the diarylethenes studied is generally fixed by an upper cycloalkene structure, such as fluorinated alicyclic group, aromatic group, anhydride and maleimide group. Apart from the difference in absorption characteristics and the like between the two forms and their thermal stabilities, the availability of desirable excitation wavelengths that can be tuned and selected for the photochromic reactions also represents an important aspect in the design of materials for optical functioning devices. It has been shown that with the more π-conjugated upper cycloalkene structures, such as maleimide derivatives, in the diarylethene compounds, the photocyclization proceeded with lower energy excitation in the visible region.


The present invention relates to the use of coordination compounds to perturb the properties of the diarylethenes in photochromic compounds. Described below is a report of the design, synthesis and studies of cis-diarylethene-containing ligands, with the upper cycloalkene being part of a mono- or poly- cyclic ring structure that contains one or more donor heteroatom(s), such as phenanthrolines, pyridines, diazines, triazines, polypyrarines, porphyrs and phthalocyanines and the like, for coordination compound formation.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a new class of diarylethene-containing coordination compounds capable of displaying perturbed and sensitized photochromic properties. The invented photochromic compound is a coordination compound that contains a diarylethene with one or more donor atoms coordinated to an acceptor atom of the coordination compound. Any diarylethene in which the ethine group in a heterocyclic moiety, monocyclic or poly cyclic, with any donor atom(s) capable of forming a coordination compound can be used in the present invention. There is no restriction on the nature of the aryl groups and they can be heterocyclic groups such as, for instance, thienyl groups. Likewise, any acceptor atoms which can be coordinated with the ethine-containing heterocyclic ligand moiety can be employed.

In a preferred form, the photochromic coordination compound is expressed by the following general formula (I):

![Chemical Structure](image)

where unit B represents a mono- or poly-cyclic ring structure, such as phenanthroline, pyridine, diazine, triazine, polypyrarine, porphyrin and phthalocyanine and the like, that contains one to four donor heteroatom(s) X, such as nitrogen, oxygen, sulfur, phosphorus, selenium, etc., n is integer from 0 to 3, [M] represents the coordination unit containing an acceptor atom M, such as rhenium(I), zinc(II), ruthenium(II), osmium(II), rhodium(III), iridium(III), gold(III), copper(I), copper(II), platinum(II), palladium(II), iron(II), cobalt(III), chromium(III), cerium(III), b Titanium(III), and the like, R1 and R2 individually represent alkyl groups and alkoxy groups, and R3 to R6 individually represent atoms or groups selected from the group of hydrogen atom, halogen atom, hydroxyl group, alkyl group, alkoxy group, cyanogroup, nitro group, alky Carbonyl group, alkoxy Carbonyl group, perfluoroalkyl group, ary1 group, cycloalkyl group, arylcarboxyl group, aryloxy carbonyl group, mono- or dialkoxyaminocarbonyl group, alkylcarboxylate group, arylcarboxylic acid group, aryloxy group, aryloxy carbonyl group, aryloxy carbonyl group, arylcarboxylate group, and the like. In general, any alkyl or alkoxy group contains 1 to about 20 carbon atoms, any cycloalkyl group contains 3 to 8 carbon atoms, and any aryl group contains 6 to about 20 carbon atoms.

A non-limiting list of examples of diarylethene compounds containing a heterocyclic ethine-containing...
ligand moiety includes 5,6-dithienyl-1,10-phenanthroline, 2,3,7,8,12,13,17,18-octatetraethyl-5,10,15,20-tetraphenyl porphyrin, 6,7- dithienyl-dipyrido[3,2-a:2',3'-c]phenazine and the like.

[0010] A non-limiting list of coordination units includes chlorotricarbonylironium(I), dihalotizarozone(II), dichloroplutonium(II), bipyridylplutonium(II) bis(bipyridyl)ruthenium(II), diphosphinocopper(I), bipyridylcopper(I) and the like.

[0011] One of the advantages of the formation of coordination compounds from their pure organic counterparts (free ligands) in this invention is the extension of the excitation wavelength for the photocyclization of the diarylthene moiety from λ<sub>ex</sub>=340 nm to lower energy, so that the photocromatic forward reaction can proceed with visible light excitation by utilization of the low-energy absorptions characteristic of coordination compounds. In addition, the photocromatic reactions can be utilized to switch the photoluminescence properties characteristic of the coordination compounds.

**BRIEF DESCRIPTION OF THE DRAWINGS**

[0012] FIG. 1 shows a representative synthetic route for a diarylthene-containing ligand and its coordination compounds using 5,6-dithienyl-1,10-phenanthroline and its chlorotricarbonylironium(I) and dihalotizarozone(II) compounds as illustrative examples.

[0013] FIG. 2 shows the overlaid electronic absorption spectra of the open form (—) and the close form (——) of a diarylthene-containing nitrogen donor ligand (L1).

[0014] FIG. 3 shows the overlaid electronic absorption spectra of the open form (—) and the close form (——) of a diarylthene-containing coordination compound (I).

[0015] FIG. 4 shows the photocromatic reactions of (a) a diarylthene-containing ligand and (b) its coordination compound using 5,6-dithienyl-1,10-phenanthroline and its chlorotricarbonylironium(I) compound as illustration.

[0016] FIG. 5 shows the overlaid corrected emission spectra of the open form (—) and the close form (——) of (I) in benzene solution at 298 K.

[0017] FIG. 6 shows the overlaid corrected emission spectra of the open form (—) and the close form (——) of (I) in EtOH-MeOH (4:1 v/v) glass at 77 K.

[0018] FIG. 7 shows the absorption spectral changes of complex (4) in benzene upon excitation at λ<sub>ex</sub>=300 nm.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

**EXAMPLE 1**

[0019] The ligand (L1) is synthesized by the Suzuki cross-coupling reactions of 2,5 equivalents of 2,5-dimethyl-3-thienylboronic acid and 5,6-dibromo-1,10-phenanthroline in the presence of the palladium catalyst, Pd(PPh<sub>3</sub>)<sub>4</sub>, and sodium carbonate in a heterogeneous mixture of water and THF according to the synthetic route depicted in FIG. 1. Excitation of (L1) with 313 nm light resulted in the formation of the close form, corresponding to the photocyclization product. The overlaid electronic absorption spectra of the open and close forms of (L1) in benzene solution are shown in FIG. 2.

[0020] Upon coordination to a chlorotricarbonylironium(I) complex, the open form of the corresponding complex (I) undergoes photocyclization with the excitation of both the intraligand absorptions at λ<sub>ex</sub>=340 nm and the metal-to-ligand charge transfer (MLCT) absorption characteristic of this coordination compound up to λ<sub>ex</sub>=480 nm. The electronic absorption data of (L1) and complex (I) are summarized in Table 1. The close forms of these compounds are found to undergo thermal backward reactions. The half-lives of the close forms have been determined and summarized in Table 2. The quantum yields for both photocyclization and photo-cycloreversion of (L1) and its rhenium complex (I) are summarized in Table 3.

**TABLE 1**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Configuration</th>
<th>λ&lt;sub&gt;exc&lt;/sub&gt;/nm (eV)</th>
<th>Absorption (in benzene)</th>
<th>λ&lt;sub&gt;abs&lt;/sub&gt;/nm (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L1)</td>
<td>Open form</td>
<td>1.86</td>
<td>304 (8670)</td>
<td>1.86</td>
</tr>
<tr>
<td>(L1)</td>
<td>Close form</td>
<td>1.86</td>
<td>366 (2440)</td>
<td>1.86</td>
</tr>
<tr>
<td>(I)</td>
<td>Open form</td>
<td>1.86</td>
<td>338 (4920)</td>
<td>1.86</td>
</tr>
<tr>
<td>(I)</td>
<td>Close form</td>
<td>1.86</td>
<td>390 (56670)</td>
<td>1.86</td>
</tr>
</tbody>
</table>

**TABLE 2**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Half-life (t&lt;sub&gt;1/2&lt;/sub&gt;) at 20°C</th>
<th>Half-life (t&lt;sub&gt;1/2&lt;/sub&gt;) at 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L1)</td>
<td>143 hours</td>
<td>222 mins</td>
</tr>
<tr>
<td>(I)</td>
<td>77.7 hours</td>
<td>79.3 mins</td>
</tr>
</tbody>
</table>

**TABLE 3**

<table>
<thead>
<tr>
<th>Photochemical Quantum Yield</th>
<th>Photocyclization</th>
<th>Photo-cycloreversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>φ&lt;sub&gt;313&lt;/sub&gt;</td>
<td>φ&lt;sub&gt;440&lt;/sub&gt;</td>
</tr>
<tr>
<td>(L1)</td>
<td>0.486</td>
<td>0</td>
</tr>
<tr>
<td>(I)</td>
<td>0.552</td>
<td>0.648</td>
</tr>
</tbody>
</table>

*Values reported are corrected to the ratio of the photocromatic active form, i.e. with respect to the anti-parallel configuration.

**TABLE 4**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium (T/K)</th>
<th>Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L1)</td>
<td>Benzene (98K)</td>
<td>363 &lt;eV&gt; 644 &lt;eV&gt;</td>
</tr>
<tr>
<td>Glass (77)</td>
<td>577 &lt;eV&gt;</td>
<td>577 &lt;eV&gt;</td>
</tr>
</tbody>
</table>

[0021]

[0022]

[0023] The photoluminescence properties of both the open and close forms were measured. FIGS. 5 and 6 display the overlaid emission spectra of the open form and the close form of complex (I) in benzene at 298 K and in EtOH-MeOH glass (4:1 v/v) at 77 K. The emission of complex (I) was found to change from metal-to-ligand charge transfer (MLCT) phosphorescence to ligand-centered (LC) phosphorescence upon photocyclization of the open form to the close form. These demonstrate the change of emission properties upon photocromatic reactions. Table 4 summarized the emission data of ligand (L1) and complex (I).
TABLE 4-continued

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium (TDK)</th>
<th>Emission ( \lambda_{\text{max}} \text{ (nm)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Open form</td>
</tr>
<tr>
<td>(1)</td>
<td>Benzene (298)</td>
<td>586 (0.36)</td>
</tr>
<tr>
<td>(2)</td>
<td>Glutathione (77)</td>
<td>535 (7.2)</td>
</tr>
</tbody>
</table>

* Excitation wavelength at ca. 355 nm. Emission maxima are corrected values.
* E0.16-MeOH (41, v/v)
* Non-emissive

EXAMPLE 2

Upon coordination of (1.1) to a dithiolatozinc(II) complex, the open forms of the corresponding complexes (2), (3), and (4) undergo photocyclization with excitation at \( \lambda \leq 340 \text{ nm} \). FIG. 7 shows the absorption spectral changes of complex (4) upon excitation at \( \lambda = 300 \text{ nm} \). The electronic absorption maxima of both the open and the close forms of complexes (2), (3) and (4) are summarized in Table 5.

TABLE 5

<table>
<thead>
<tr>
<th>Complex</th>
<th>Configuration</th>
<th>Absorption maximum (in benzene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2)</td>
<td>Open form</td>
<td>302, 326, 378</td>
</tr>
<tr>
<td>(2)</td>
<td>Close form</td>
<td>386, 382, 536, 576</td>
</tr>
<tr>
<td>(3)</td>
<td>Open form</td>
<td>302, 326, 382</td>
</tr>
<tr>
<td>(3)</td>
<td>Close form</td>
<td>386, 382, 538</td>
</tr>
<tr>
<td>(4)</td>
<td>Open form</td>
<td>302, 336, 396</td>
</tr>
<tr>
<td>(4)</td>
<td>Close form</td>
<td>386, 384, 542, 584</td>
</tr>
</tbody>
</table>

[0025] Those skilled in the art will recognize that various changes and modifications can be made in the invention without departing from the spirit and scope thereof. The various embodiments described were for the purpose of further illustrating the invention and were not intended to limit it.

1. A photochomic coordination compound comprising a diarylethene with one or more donor atoms coordinated to an acceptor atom of the coordination unit.

2. A photochomic compound which is a diarylethene-containing coordination compound in which the diarylethene contains part of a mono- or poly-cyclic ring structure with one or more donor atom(s) or heteroatom(s) coordinated to a coordination unit \([M]\), which contains an acceptor atom, \( M \), expressed by the general formula (I):

![Diagram](image_url)

where unit B represents a mono- or poly-cyclic ring structure that contains one to four heteroatom(s) \( X \), \( n \) is integer from 0 to 3, \([M]\) represents a coordination unit containing an acceptor atom \( M \), \( R_1 \) and \( R_4 \) individually represent an alkyl group or an alkoxy group, and \( R_2 \) to \( R_4 \) individually represent atoms or groups selected from the group of hydrogen atom, halogen atom, hydroxyl group, alkyl group, alkoxy group, cyano group, nitro group, alkylcarbonyl group, alkoxyalkyl group, perfluoroalkyl group, ary group, cycloalkyl group, arylcarbonyl group, arylalkoxy group, alkoxyalkoxy group, alkoxy group, alkoxyalkyl, group, and arylalkoxyalkoxy group.

3. A photochomic compound in accordance with claim 2, wherein unit B is selected from the group consisting of phenanthroline, pyridine, diazine, triazine, polypyridine, porphyrin and phthalocyanine; and acceptor atom \( M \) is selected from the group consisting of rhenium(I), zinc(II), ruthenium(II), osmium(II), rhodium(III), iridium(III), gold(III), copper(I), copper(II), platinum(II), palladium(II), irid(II), cobalt(III), chromium(III), cadmium(II) and boro-n(III).

4. A photochomic compound in accordance with claim 2, wherein the donor atom or heteroatom is not selected from the group consisting of carbon, nitrogen, oxygen, sulfur, phosphorus and selenium.

5. A photochomic compound in accordance with claim 2, wherein unit B is a phenanthroline.

6. A photochomic compound in accordance with claim 2, wherein unit B is a porphyrin.

7. A photochomic compound in accordance with claim 6, wherein \( R_1 \) and \( R_4 \) represent methyl groups, and \( R_2 \) and \( R_4 \) represent hydrogen atoms.

8. A photochomic compound in accordance with claim 7, wherein \( R_2 \) and \( R_4 \) represent hydrogen atoms.

9. A photochomic compound in accordance with claim 7, wherein \( R_2 \) and \( R_4 \) represent methyl groups.

10. A photochomic compound in accordance with claim 7, wherein \( R_2 \) and \( R_4 \) represent bromine atoms.

11. A photochomic compound in accordance with claim 5, wherein \( M \) represents rhenium(I).

12. A photochomic compound in accordance with claim 5, wherein \( M \) represents zinc(II).

13. A photochomic compound in accordance with claim 5, wherein \( M \) represents platinum(II).

14. A photochomic compound in accordance with claim 5, wherein \( R_1 \) and \( R_4 \) represent methyl groups, and \( R_2 \) and \( R_4 \) represent hydrogen atoms.

15. A photochomic compound in accordance with claim 14, wherein \( M \) represents zinc(II).

16. A photochomic compound in accordance with claim 14, wherein \( M \) represents platinum(II).

* * * *