United States Patent
Yam et al.

PHOTOCHROMIC DIARYLETHENE CONTAINING COORDINATION COMPOUNDS AND THE PRODUCTION THEREOF

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Field of Classification Search ............... 359/241; 548/101, 402; 549/59

See application file for complete search history.

References Cited

U.S. PATENT DOCUMENTS

* cited by examiner

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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 λ≤340 nm to wavelengths beyond 470 nm. Switching of the luminescence properties of the compounds has also been achieved through photochromic reactions.

5 Claims, 7 Drawing Sheets
Fig. 1

\[
\begin{align*}
&\text{Br}_2 \\
&\text{CH}_3\text{COOH} \\
&\text{Br}_2 \\
&\text{Pd(PPh}_3\text{)}_4 \\
&\text{THF} / 2\text{M Na}_2\text{CO}_3 \\
&\text{Zn(OOCCH}_3\text{)}_2 \\
&\text{CH}_2\text{Cl}_2 \\
&\end{align*}
\]

(1)
Fig. 4

(a)

open form

313 nm

365, 540 nm

close form

(b)

open form

313, 440 nm

365, 540 nm

close form

Fig. 5

Normalized Emission Intensity

Wavelength / nm

550 600 650 700 750 800 850
Fig. 6

Normalized Emission Intensity vs. Wavelength (nm)

Fig. 7

Absorbance vs. Wavelength (nm)
Fig. 8

\[
2.5 \begin{array}{c}
\text{B(OH)}_2 \\
\text{Br} \\
\text{Br} \\
\text{N} - \text{N}
\end{array}
\begin{array}{c}
\text{R} \\
\text{R} \\
\text{R}
\end{array}
\begin{array}{c}
\text{R} \\
\text{R} \\
\text{R}
\end{array}
\xrightarrow{\text{Pd(PPh}_3)_4}
\text{THF / 2M Na}_2\text{CO}_3(aq)
\]

\[
\begin{array}{c}
\text{R} = \begin{array}{c}
\text{OMe} \\
\text{Me}
\end{array} \\
\text{(L2), Me (L3)}
\end{array}
\]

Fig. 9

(a) and (b) show the absorbance and normalized emission intensity spectra over a range of wavelengths from 400 to 800 nm.
Fig. 10

\[ \text{B(OH)}_2 + \text{Br} \rightarrow \text{Pd(PPh}_3\text{)}_4 \]
THF / 2M Na\textsubscript{2}CO\textsubscript{3}(aq)

\[ \text{MeI, NH}_4\text{PF}_6 \]
MeCN / K\textsubscript{2}CO\textsubscript{3}

\[ \text{PF}_6^- \]

(L4)

Fig. 11

Absorbance vs. Wavelength / nm

Absorbance

Wavelength / nm
PHOTOCROMIC DIARYLETHENE CONTAINING COORDINATION COMPOUNDS AND THE PRODUCTION THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

This application is a divisional of U.S. Ser. No. 11/598,131, filed Nov. 13, 2006 now U.S. Pat. No. 7,755,826, which is a continuation-in-part of U.S. Ser. No. 10/883,677, filed Jul. 6, 2004, now U.S. Pat. No. 7,555,775, issued on Apr. 8, 2008, which claims the benefit of U.S. Provisional Patent Application No. 60/673,017, filed Jul. 7, 2005, the entirety of which are incorporated herein by reference.

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 atom(s) or donor heteroatom(s), such as phosphorus, sulfur, oxygen, nitrogen, etc.

BACKGROUND OF THE INVENTION

Photochromism is described 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 with different physical properties, such as absorption properties, reflectivity, and the like, and can be transformed from one form to another by light excitations at prescribed wavelengths.

Photochromism has been intensively 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 possess these properties, and therefore is a suitable class of compounds for the construction of optical functioning devices. The cis-conformation of both aryl groups in the diarylethene is generally fixed by an upper cycloalkene structure, such as fluorinated allyl 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 the more n-conjugated upper cycloalkene structures, such as maleimide derivatives, in the diarylethene compounds, the photocyclization proceeds with lower energy excitation in the visible region.


The photochromic compounds of this invention can be used in the same way as described in these references.

SUMMARY OF THE INVENTION

The present invention relates to the use of coordination compounds to perturb the properties of the diarylenes 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 atom(s) or donor heteroatom(s), such as phosphorus, nitrogen, sulfur, oxygen, etc. These ligands have different physical properties, such as absorption properties, reflectivity, and the like, and can be transformed from one form to another by light excitations at prescribed wavelengths.

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

![Diagram](image)

where unit B represents a mono- or poly-cyclic ring structure, such as phenanthroline, pyridine, imidazole, pyrazole, thiazole, pyrrole, dioxane, triazine, polypyrindine, porphyrin and phthalocyanine and the like, that contains one or more donor atom(s) X, such as carbon, or donor heteroatom(s) X, such as nitrogen, oxygen, sulfur, phosphorus, selenium, i.e., is integer from 0 to 3, [M] represents the coordination unit containing an acceptor atom M, such as iron(II), Ni(II), Rh(III), Iridium(III), Gold(III), gold(I), silver(I), copper(I), copper(II), platinum(II), palladium(II), iron(II), cobalt(III), chromium(III), cadmium(II), boron(II) and the like, R₁ and R₂ individually represent alkyl groups and alkoxy groups, and R₃ to R₅ individually represent atoms or groups selected from the group of hydrogen atom, halogen atom, hydroxyl group, alkyl group, alkoxy group,
alkylnyl group, cyano group, nitro group, alkylcarbonyl group, alkoxycarbonyl group, perfluoroalkyl group, aryl group, cycloalkyl group, arylcarbonyl group, aryloxycar- bonyl group, mono- or dialkylaminocarbonyl group, alkylcarbonyloxy group, aryloxycar- bonyloxy group, arylcarbonyloxy group, aryloxycarbonyloxy group, and the like. In general, any alkylox or alkoxy group contains 1 to about 20 carbon atoms, any cycloalkyl group contains 2 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 ethene-containing ligand moiety includes 5,6-dithienyl-1,10-phenanthroline, 2,3,7,8,12,13, 17,18-octaphthenyl-5,10,15,20-tetraphenyl porphyrin, 6,7-dithienyl-dipyrind[3,2-a:2',3'-c]phenazine and the like.

A non-limiting list of coordination units includes chlororoticarborhenium(I), dithiolatozinc(II), dihydroplatinum(II), bipyridylplatinum(II), bis[bipyridyl]ruthenium(II), diphenoxophine(I), bipyridylecopper(I), and the like.

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 diarylethene moiety from λ=340 nm to lower energy, so that the photochromic forward reaction can proceed with visible light excitation by utilization of the low-energy absorptions characteristic of coordination compounds. In addition, the photochromatic reactions can be utilized to switch the photoluminescence properties characteristic of the coordination compounds.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a representative synthetic route for a diarylethene-containing ligand and its coordination compounds using 5,6-dithienyl-1,10-phenanthroline and its chlororoticarborhenium(I) and dithiolatozinc(II) compounds as illustrative examples.

FIG. 2 shows the overlaid electronic absorption spectra of the open form (-) and the close form (- -) of a diarylethene-containing nitrogen donor ligand (L1).

FIG. 3 shows the overlaid electronic absorption spectra of the open form (-) and the close form (- -) of a diarylethene-containing coordination compound (1).

FIG. 4 shows the photochromic reactions of (a) a diarylethene-containing ligand and (b) its coordination compound using 5,6-dithienyl-1,10-phenanthroline and its chlororoticarborhenium(I) compound as illustration.

FIG. 5 shows the overlaid corrected emission spectra of the open form (-) and the close form (- -) of (1) in benzene solution at 298 K.

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

FIG. 7 shows the absorption spectral changes of complex (4) in benzene upon excitation at λ=300 nm.

FIG. 8 shows a representative synthetic route for diarylethene-containing ligands and their coordination compounds using 1-(aryl)-bis-(2,5-dimethyl-3-thienyl)-2-(2-pyridyl)imidazoles and their chlororoticarborhenium(I) compounds as illustrative examples.

FIG. 9 shows (a) the absorption and (b) emission spectral changes of complex (6) in degassed chloroform solution (7.16x10^{-3} M) upon MLCT excitation at λ=410 nm.

FIG. 10 shows a representative synthetic route for a diarylethene-containing ligand and its coordination compounds using 1,3-dimethyl-4,5-bis-(2,5-dimethyl-3-thienyl)-imidazolium hexafluorophosphate and its diiodopalladium(II) compounds as illustrative examples.

FIG. 11 shows the absorption spectral changes of complex (7) in dichloromethane solution (1.21x10^{-4} M) upon excitation at λ=310 nm.

FIG. 12 shows a representative synthetic route for diarylethene-containing ligand and its coordination compounds using 5-ethyl-2,3-bis-(2-methyl-3-benzoyl)-2H[4]-thiophene and its bis(triethylphosphine)platinum(II) compounds as illustrative examples.

FIG. 13 shows the absorption spectral changes of complex (8) in dichloromethane solution (3.10x10^{-10} M) upon excitation at λ=400 nm.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

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(PPh3)4, 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.

Upon coordination to a chlororoticarborhenium(I) complex, the open form of the corresponding complex (1) undergoes photocyclization with the excitation of both the intraligand absorptions at λ=340 nm and the metal-to-ligand charge transfer (MLCT) absorption characteristic of this coordination compound up to λ=480 nm. The electronic absorption data of (L1) and complex (1) 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 photocycleversion of (L1) and its rheno complex (1) are summarized in Table 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Configuration</th>
<th>λ_{max}/nm</th>
<th>ΔH_{mol}/kJ mol^{-1}</th>
<th>ΔS_{mol}/J K^{-1} mol^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L1)</td>
<td>Open form</td>
<td>304 (8670)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(L1)</td>
<td>Close form</td>
<td>366 (24540), 510 (4030), 540 (3860)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>Open form</td>
<td>338 (4930), 369 (4690)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>Close form</td>
<td>390 (36670), 546 (5390), 580 (5050)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Half-life (t_{1/2}) at 20°C</th>
<th>Half-life (t_{1/2}) at 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L1)</td>
<td>143 hours</td>
<td>222 mins</td>
</tr>
<tr>
<td>(1)</td>
<td>77.7 hours</td>
<td>79.3 mins</td>
</tr>
</tbody>
</table>
TABLE 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Phi_{13}$</th>
<th>$\Phi_{400}$</th>
<th>$\Phi_{560}$</th>
<th>$\Phi_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L1)</td>
<td>0.486</td>
<td>0</td>
<td>0.123</td>
<td>0.029</td>
</tr>
<tr>
<td>(1)</td>
<td>0.352</td>
<td>0.648</td>
<td>0.028</td>
<td>0.009</td>
</tr>
</tbody>
</table>

Values reported are corrected to the ratio of the photometric active form, i.e., with respect to the anti-parallel conformation.

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 (1) in benzene at 298 K and in EtOH-MeOH glass (4:1 v/v) at 77 K. The emission of complex (1) 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 photophysical reactions. Table 4 summarized the emission data of ligand (L1) and complex (1).

TABLE 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>Medium (TK)</th>
<th>Emission $\lambda_{em}$ (nm), $\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L1)</td>
<td>Benzene (298)</td>
<td>383 (0.1) 464 (0.1) 577 (5.2)</td>
</tr>
<tr>
<td>(1)</td>
<td>Glass (77')</td>
<td>595 (0.26) 626 (0.1) 620 (6.4)</td>
</tr>
</tbody>
</table>

$^a$Excitation wavelength at ca. 355 nm. Emission maxima are corrected values.
$^b$EtOH-MeOH (4:1 v/v).
$^c$Non-emissive.

Example 2

Upon coordination of (L1) to a dithioloazinc(II) complex, the open forms of the corresponding complexes (2), (3) and (4) undergo photocyclization with excitation at $\lambda=340$ nm. FIG. 7 shows the absorption spectral changes of complex (4) upon excitation at $\lambda=300$ 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 benzen) $\lambda_{max}$ (nm)</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>366, 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>366, 382, 536</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>366, 384, 542, 584</td>
</tr>
</tbody>
</table>

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.

Example 3

The ligands, 1-[4-methoxyphenyl]-bis-(2,5-dimethyl-3-thiényl)-2-(2-pyridyl)imidazo [1,2-d] and 1-[4-(methylpheno-
TABLE 7

<table>
<thead>
<tr>
<th>Compound</th>
<th>Configuration</th>
<th>Absorption maximum (in dichloromethane) $\lambda_{max}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L4)</td>
<td>Open form</td>
<td>235</td>
</tr>
<tr>
<td>(L4)</td>
<td>Close form</td>
<td>350, 580</td>
</tr>
<tr>
<td>(7)</td>
<td>Open form</td>
<td>240, 305</td>
</tr>
<tr>
<td>(7)</td>
<td>Close form</td>
<td>345, 540</td>
</tr>
</tbody>
</table>

Example 5

5-Trimethylsilylthyl-2,3-bis-(2-methyl-3-benzoyl-3,2-b-thienyl)thiophene is synthesized by the Sonogashira coupling reaction of trimethylsilylacetylene and the mono-derivative of 2,3-bis-(2-methyl-3-benzoyl-3,2-b-thienyl)thiophene, which is also prepared from the Suzuki cross-coupling reaction of 2.5 equivalents of 2-methyl-3-benzoyl[3,2-b-thienyl]boronic acid and 2,3-dihydrothiophene in the presence of the palladium catalyst, Pd(PPh3)4, and sodium carbonate in a heterogeneous mixture of water and THF according to the procedure similar to that of (1.1). Subsequent deprotection of the trimethylsilyl group using potassium carbonate in dichloromethane solution gives the target ligand ethynyl-2,3-bis-(2-methyl-3-benzoyl-3,2-b-thienyl)thiophene (L5). The synthetic route is shown in FIG. 12. Excitation of the ligand with $\lambda$=352 nm light resulted in the formation of the close form, corresponding to the photocyclization product.

Upon reaction with dichlorobis(triethylphosphine)platinum(II), the open form of the corresponding complex (8) undergoes photocyclization with the excitation up to $\lambda$≤430 nm. The electronic absorption data of ligand (L5) and complex (8) are summarized in Table 8. The representative electronic absorption spectral changes of complex (8) in dichloromethane solution upon photo-irradiation are shown in FIG. 13.

Table 8

<table>
<thead>
<tr>
<th>Compound</th>
<th>Configuration</th>
<th>Absorption maximum (in dichloromethane) $\lambda_{max}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(L5)</td>
<td>Open form</td>
<td>290, 294, 304, 314dh</td>
</tr>
<tr>
<td>(L5)</td>
<td>Close form</td>
<td>300, 382, 554</td>
</tr>
<tr>
<td>(8)</td>
<td>Open form</td>
<td>296, 296, 304, 318dh</td>
</tr>
<tr>
<td>(8)</td>
<td>Close form</td>
<td>372, 560</td>
</tr>
</tbody>
</table>

What is claimed is:

1. A photochronic 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):

2. A photochronic 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):

where unit B represents a mono- or poly-cyclic ring structure wherein the diarylethene moiety is a five-membered ring having at least one nitrogen and that contains one or more donor atom(s) or heteroatom(s) X. n is integer from 0 to 3. [M] represents a coordination unit containing an acceptor atom M and excludes magnesium phthalocyanine, zinc phthalocyanine, metallophyrins and metalloporphyrins. R, and R, individually represent an alkyl group or an alkylo group, and R to R, individually represent atoms or groups selected from hydroxyl group, halogen group, hydroxyl group, alkyl group, alkylo group, alkynyl group, cyanogroup, nitro group, alkylcarbonyl group, alkoxycarbonyl group, perfluoroalkyl group, aryloalkyl group, cycloalkyl group, arylcarbonyl group, aryloxyaroyl group, mono- or dialkylaminoarylcarbonyl group, alkylcarboxyloxy group, aryloxyaroyl group, or arylcarboxyloxy group.

3. A photochronic compound in accordance with claim 1, wherein the donor atom or heteroatom X is carbon, nitrogen, oxygen, sulfur, phosphorus or selenium.

4. A photochronic compound in accordance with claim 2, wherein B is a phthalocyanine.

5. A photochronic compound in accordance with claim 1, wherein M represents rhodium(I).

* * * * *