

Photochromic Dithienylethene-Phenanthroline Ligands and their Corresponding Ru(II) Complexes

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Abstract: Dithienylethene-phenanthroline ligands as new photochromic systems are described. The photochemical and photophysical properties are strongly influenced by the substituents on the thiophene moiety. The photochromic properties are lost, if one or two methyl groups in position 2 and/or 2' of the target molecules (**2o**, **3o**, **4o**) are replaced by isopropyl groups. Replacement of a methyl group by a phenyl group in position 5 and/or 5' shifts the absorption maxima from 514 nm to 575 nm for the free ligand (**1c**, **2c**) and from 530 nm to 613 nm for the corresponding ruthenium complex (**Ru(1c)**, **Ru(2c)**) in its closed form. Unfortunately, the photochromic unit in its closed form can be reopened by a back reaction in the dark at room temperature. Complex **Ru(2o)** shows an emission with a maximum at 608 nm. The emission is quenched if the metal complex is in its closed form (**Ru(2c)**). Fatigue resistance is better for complex **Ru(2o)** than for the free ligand (**2o**).

Keywords: Energy transfer · Molecular switch · Photochromism · Ruthenium complex · T-junction

1. Introduction

Photochromism is a reversible transformation of a single chemical species, being induced in one or both directions by electromagnetic radiation, between two states having different distinguishable absorption spectra. Reversibility of such a bi-stable system is one important criterion for a possible application. The back reaction can occur thermally (T-type) or photochemically (P-type). Photochromic systems can be classified into several categories depending on the chemical transformation induced by light: pericyclic reaction, *cis/trans* isomerisation, group transfer and others. The dithienylethene type photochromic system can be closed by a 1,6-electrocyclic reaction like in spiropyrans and fulgides [1].

Organic dithienylethene derivatives have been extensively studied in recent times [2][3]. Properties like ring opening–closing processes, thermal stability, photofatigue resistance, absorption spectra, quantum yield, response time, and others have been frequently reported [2]. On the other hand, dithienylethene derivatives involving metal complexes are rare [4–22]. Most of the dithienylethene switches described in literature need UV light to perform the photocyclisation reaction [2][3]. By introduction of a metal complex, electronic absorption properties are drastically changed by the appearance of the ¹MLCT

transition. It allows the use of visible light to close the switch photochemically by an energy transfer process from the excited metal centre to the dithienylethene moiety (Fig. 1). Therefore, photofatigue resistance can be increased because visible light is usually less destructive than UV light. Moreover, visible light is also employed to reopen the switch, and such a photochromic system works exclusively with Vis-light.

[Ru(bpy)₃]²⁺ type metal complexes can act as sensitizers, and can therefore be used to induce the desired closing reaction by an energy transfer process. In the present work, a phenanthroline-type ligand has been com-

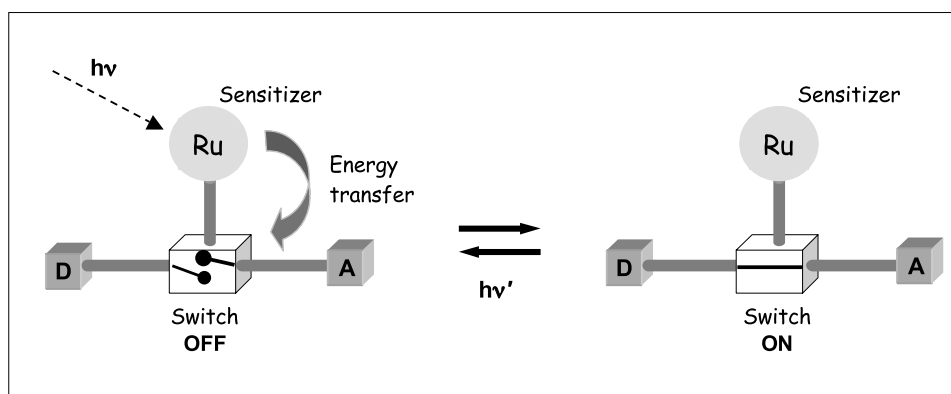


Fig. 1. Schematic illustration of a photochemically active switch driven by a photoinduced energy transfer process. D corresponds to a donor and A to an acceptor unit.

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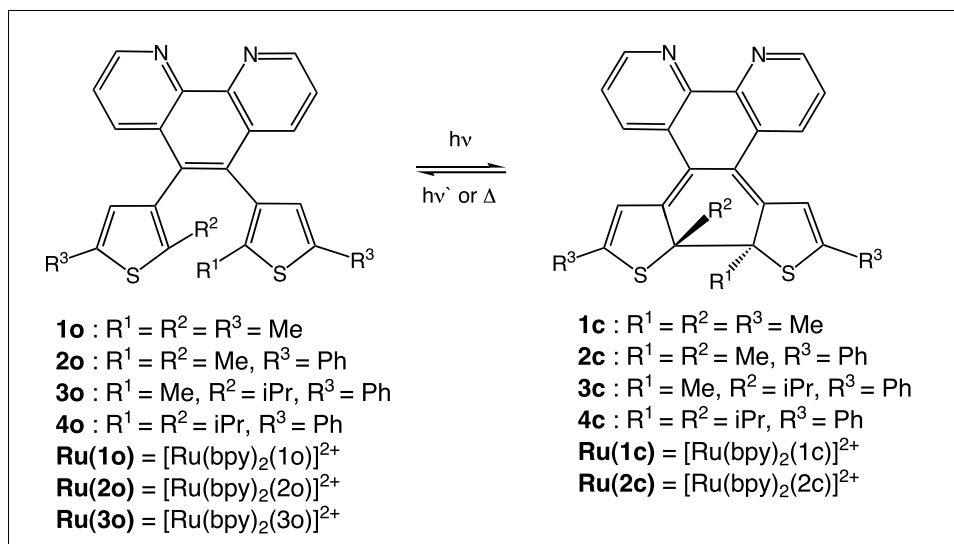


Fig. 2. Photochromism of the prepared ligands and complexes

bined with the dithienylethene moiety to introduce a coordinating unit and take up the following tasks: Firstly, nitrogen atoms in position 1 and 10 can coordinate to the ruthenium centre and secondly, the double bond between carbon 5 and 6 can perform the electrocyclic reaction.

In this regard, a new family of ligands (Fig. 2) and their corresponding metal com-

plexes [Ru(bpy)₂(L)]²⁺ (L = **1o**, **2o**, **3o**) have been synthesised and characterised.

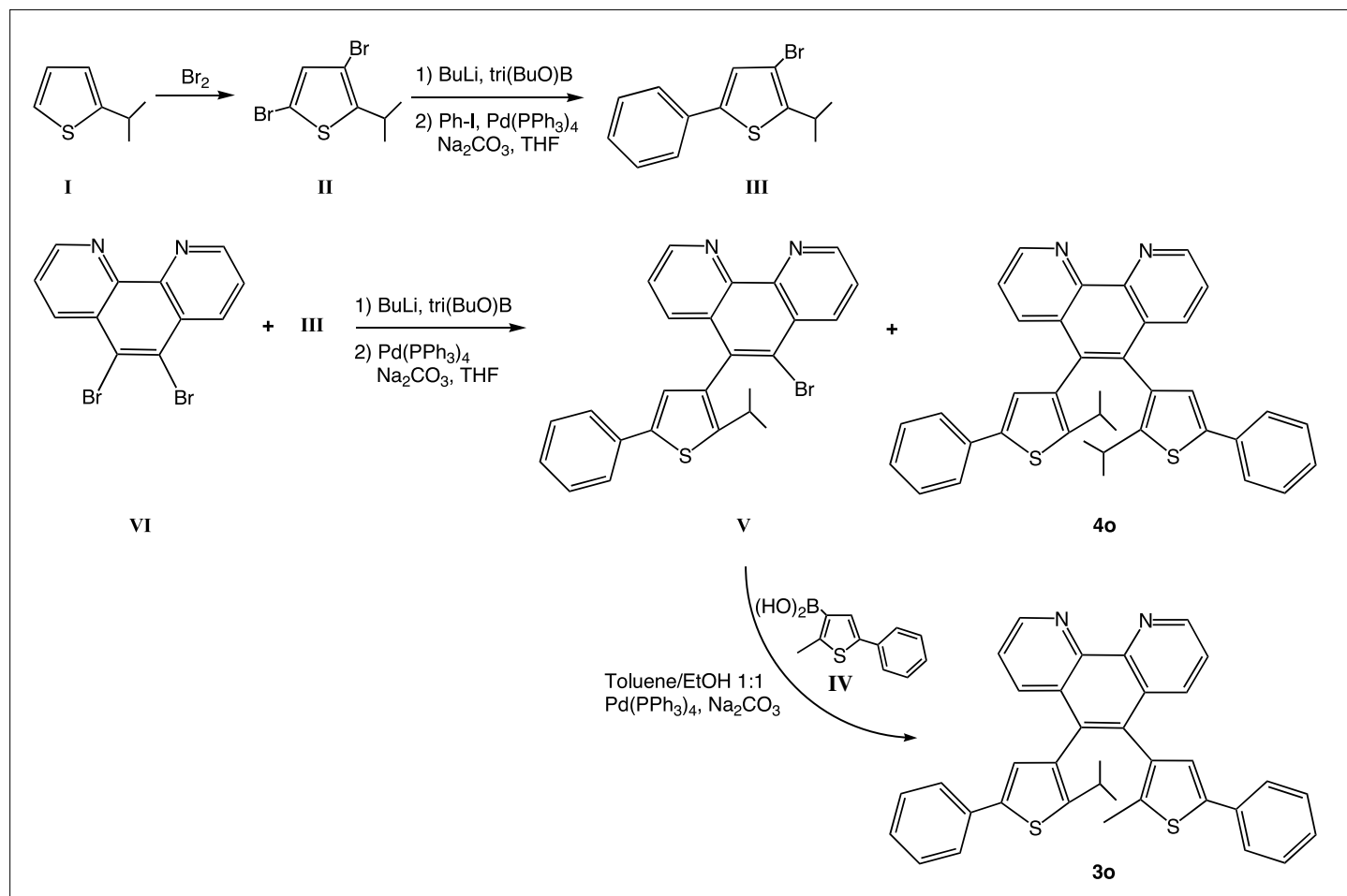
2. Results and Discussion

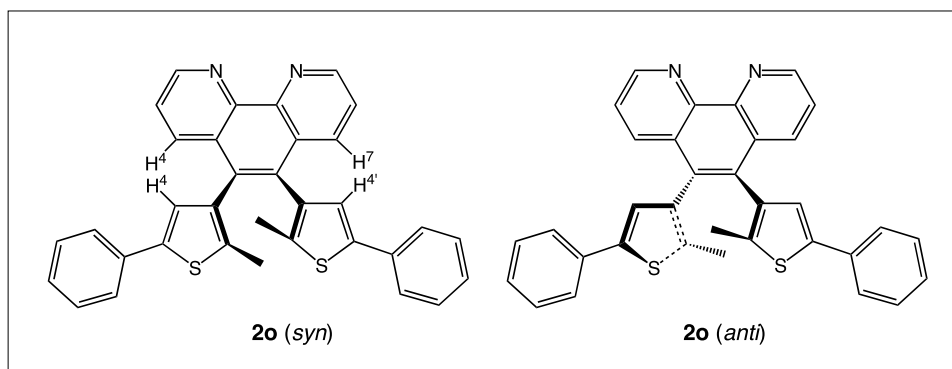
2.1. Synthesis

The synthesis of ligands and complexes **1o**, **2o**, **Ru(1o)** and **Ru(2o)** have already

been published [4]. To obtain ligands **3o** and **4o**, 5,6-dibromo-1,10-phenanthroline was prepared by the method described by Mlochowski (Scheme) [23]. The corresponding thienyl moieties were synthesised by bromination of 2-methylthiophene and 2-isopropylthiophene and 2-isopropylthiophene and 2-isopropylthiophene each followed by Suzuki coupling with iodobenzene [4]. 5,6-Dibromo-1,10-phenanthroline (**VI**) was coupled by a Suzuki reaction, first with 2-isopropyl-3-bromo-5-phenylthiophene (**III**) and then with 2-methyl-5-phenylthiophene-3-boronic acid (**IV**) to obtain ligand **3o**. Ligand **4o** was prepared by a double coupling of 2-isopropyl-3-bromo-5-phenylthiophene (**III**) with 5,6-dibromo-1,10-phenanthroline (**VI**). The synthesis of the metal complex **Ru(3o)** was performed by following the protocol described in literature [4]. The precursor compound Ru(bpy)₂Cl₂·2 H₂O and **3o** were heated to reflux in methoxyethanol to yield the complex **Ru(3o)**. We did not prepare the metal complex **Ru(4o)**. The prepared amount of ligand **4o** was so small that a further synthetic step was not possible.

During the preparation of the dithienylethene switches two conformers, *syn* and *anti* were detected (Fig. 3). In most of the cases described in literature, the thiophene moiety can rotate freely to yield one

Scheme. Protocol for the synthesis of photochromic ligands **3o** and **4o**

Fig. 3. *Syn* and *anti* isomers of ligand **2o**

set of signals by $^1\text{H-NMR}$ [2][3]. By introduction of a bulky substituent, free rotation is no longer possible and the molecules show two sets of signals by $^1\text{H-NMR}$ [25–28], attributed to the *syn* (photochromic inactive) [29] and *anti* isomers (photochromic active) [29] as observed for the new ligands **1o**, **2o**, **3o** and **4o**. Interconversion between both isomers seems to be blocked at room temperature because of steric hindrance between protons H^4 and $\text{H}^{4'}$ in the thiophene part and protons H^4 and H^7 in the phenanthroline unit [5].

The ratio *syn/anti* can be influenced by R^1 and R^2 [30], but not by R^3 (Table 1). $^1\text{H-NMR}$ analysis does not allow peak attribution for the isomers *syn* and *anti* though it does give their ratio.

The photochemical transformation of the photochromic unit from its open to the closed form was performed by irradiation

at 254 nm for the ligands **1o** and **2o**. The ligands **3o** and **4o** are photochemically inactive and cannot be closed by such an irradiation process. Irradiation at 450 nm closed the photochromic unit in the metal complexes **Ru(1o)** and **Ru(2o)**. The metal complex **Ru(3o)** is photochemically inactive and exists only in its open form.

The incorporation of the photochromic ligands **1o** and **2o** in a metal complex opens a new photochemical pathway for the closing process, which is not observed in the free ligands. Therefore, the closing process can be performed at relatively milder energetic conditions and as a result, the photofatigue resistance increases strongly.

By introduction of an isopropyl group in R^2 , ligand **3o** and complex **Ru(3o)** become photo-inert; that is why we have not synthesised the complex **Ru(4o)** containing two isopropyl groups. Two explanations can

underline this behaviour. Firstly, the closed form of the switching unit is thermally unstable [31–34] and only a small part of the system is present in its closed form. Secondly, the *syn/anti* ratio of the ligand **3o** was 7/1 and during synthesis, probably the thermodynamically more stable, but photochemically inactive *syn* conformer was produced as the main compound (Table 1).

2.2. Absorption Spectra UV/vis

Absorption maxima and extinction coefficients are reported in Table 2. The absorption spectra of the ligands **1o–4o** are similar. The photochromic units of the ligands **1o** and **2o** can be closed photochemically and the metal complexes **Ru(1o)** and **Ru(1c)** have overlapping peaks in their UV/vis spectra. Therefore, only the photochromic systems, **2o/2c** and **Ru(2o)/Ru(2c)**, will be discussed.

2.2.1. Ligand **2o/2c**

The UV-spectrum of the open form of ligand **2** shows three transitions in the range 230–300 nm, which can be attributed to the phenanthroline and thiophene moieties (Fig. 4). During irradiation at 254 nm, two new bands arise at 389 nm and 575 nm attributable to the closed form of the photochromic switch. Substituents in position 5 at the thiophene unit in its closed form (**1c**, **2c**, **Ru(1c)**, and **Ru(2c)**), influence strongly the energetically lowest absorption band [31][35–39]. For example, the absorption maximum is shifted from 513 nm for **1c** (methyl substituent) to 575 nm for **2c** (phenyl substituent). An extension of the π -system can explain such behaviour.

2.2.2. Metal Complex **Ru(2o)/Ru(2c)**

The absorption spectrum of metal complex **Ru(2o)** shows a band at 285 nm in the UV region (Fig. 5). It can be attributed to the $\pi \rightarrow \pi^*$ transition in 2,2'-bipyridine or 1,10-phenanthroline ligands of the metal complex. In the vicinity of 450 nm, an intense band appears ($^1\text{MLCT}$ -transition). After the closing process **Ru(2c)**, performed by irradiation at 450 nm, two new bands can be observed as was the case with the free ligand. However, the bands are shifted with respect to the free ligand; from 389 nm \rightarrow 415 nm and from 575 nm \rightarrow 613 nm. The band at 285 nm has the same intensity in the open and closed forms.

2.3. Emission Spectra

Complex **Ru(2o)** shows an emission at 608 nm (Fig. 6) with the excitation wavelength of 450 nm. The emissive band can be attributed to the $^3\text{MLCT}$ state of the metal complex. If the switching unit is photochemically closed, the intensity of the emission is only decreased by around 17 % but regains the initial intensity in the dark

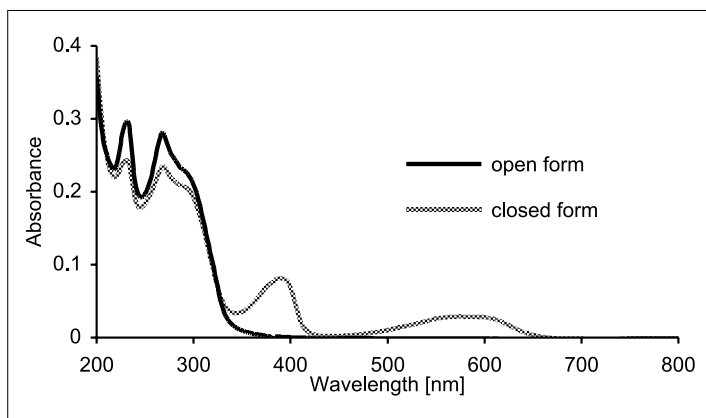
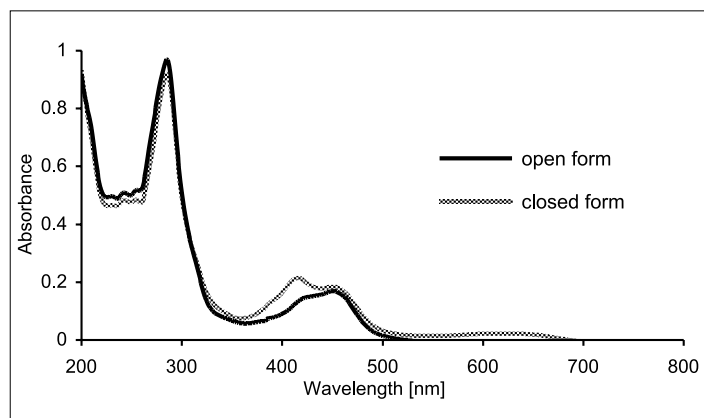
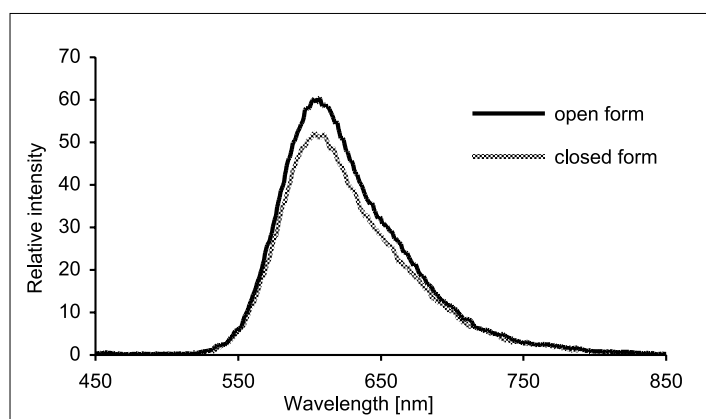
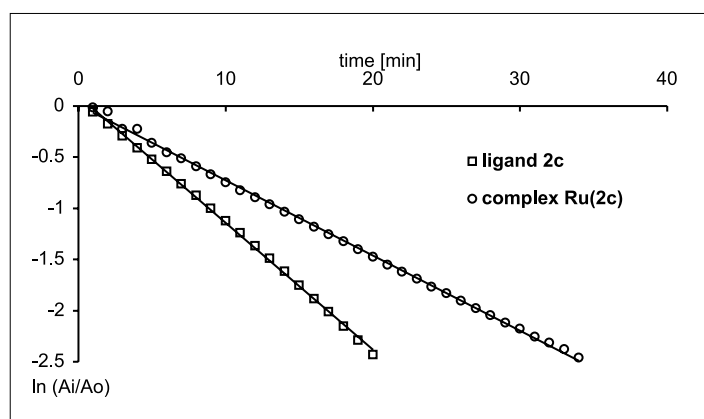
Table 1

Ligands:	1o	2o	3o	4o
<i>syn/anti</i> ratio	1:1	1:1	7:1	6:1

Table 2

Compounds	λ_{max} (nm) [$10^4 \epsilon_{\text{max}}$ ($\text{M}^{-1} \text{cm}^{-1}$)] ^a
Ligand	
1o	232 (5.5), 267 (2.7)
1c	226 (3.6), 267 (2.2), 360(1.6), 514 (0.2)
2o	231 (2.8), 268 (2.6), 294 (2.1)
2c	230 (2.3), 268 (2.1), 294 (1.8), 389 (0.6), 575 (0.3)
3o	228 (2.6), 272 (2.3), 282 (2.2)
4o	229 (2.4), 271 (2.2), 285 (2.1)
Complexes	
Ru(1o)	285 (6.5), 420 (1.2), 450 (1.5)
Ru(1c)	285 (6.7), 346 (1.0), 420 (1.2), 450 (1.4), 530 (0.2).
Ru(2o)	285 (9.6), 421 (1.4), 450 (1.7)
Ru(2c)	285 (9.1), 415 (2.1), 450 (1.8), 613 (0.2)
Ru(3o)	286 (9.2), 420 (1.4), 452 (1.7)

^aMeCN at 293K. Solution concentration: 10^{-5} M.

Fig. 4. UV/vis spectra of ligands **2o** and **2c**Fig. 5. UV/vis spectra of complexes **Ru(2o)** and **Ru(2c)**Fig. 6. Emission spectra of complexes **Ru(2o)** and **Ru(2c)**; excitation wavelength = 450 nmFig. 7. Thermal stability of ligand **2c** and metal complex **Ru(2c)**

at room temperature, because the switching unit is thermally reversible. The photostationary state of the closed form (**Ru(2c)**) at room temperature is estimated to be in the range of 20–30%.

The observation that the switching unit of the metal complex **Ru(2o)** can be closed by an irradiation at 450 nm, together with the measured emission behaviour, indicates that the energy levels of both triplet states of the ruthenium complex and the switching unit must be similar. By comparison with other photochromic systems [8], we can predict that the metal complex in its pure closed form is non-emissive.

2.4. Thermal Stability

Thermal stability deals with the conversion from closed to open form (and *vice versa*) proceeding spontaneously if the solution of the closed form is kept in the dark.

A thermal process which opens the closed form can be observed for ligands **1c**, **2c**, and their metal complexes **Ru(1c)** and **Ru(2c)** (Fig. 7). By measuring the decrease in the intensity of the characteristic band in the visible part of the UV/vis spectrum of ligand **2c**, centred at 575 nm, the mentioned opening reaction can be observed. This thermal process has its driving force

in the partial loss of aromaticity [40–45], if the double bond between the carbon 5 and 6 in the phenanthroline moiety changes to two exo-double bonds at the same position in the closed form. The reaction rate is determined by applying a first order reaction model. The rate constant and half-lifetime are 0.12 min^{-1} and 5.6 min, respectively at room temperature. Complex **Ru(2c)** shows a similar behaviour to ligand **2c**. The absorption band at 613 nm was chosen to follow the back reaction. The corresponding values are 0.074 min^{-1} for the rate constant and 9.5 min for the half-lifetime. The complex **Ru(2c)** is more stable than the free ligand **2c** by a factor of 1.7.

2.5. Fatigue Resistance

Photochromic reactions are always accompanied by undesirable side reactions. Consequently, after a certain number of cycles, photochromic properties are altered. This photochromic resistance is essential for practical application.

Fatigue resistance can be measured as following: In deaerated acetonitrile solution, the dithienylethene derivative is irradiated till 90% of the photostationary state is reached and the coloured closed form is completely bleached. This sequence is repeated several times. After each cycle,

absorbance of the coloured compound is measured.

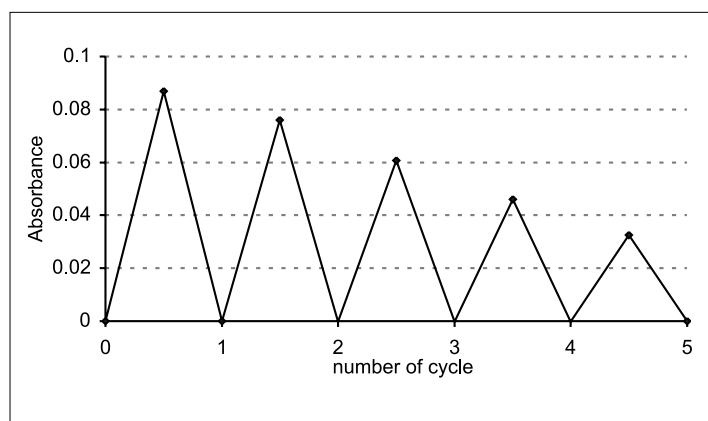
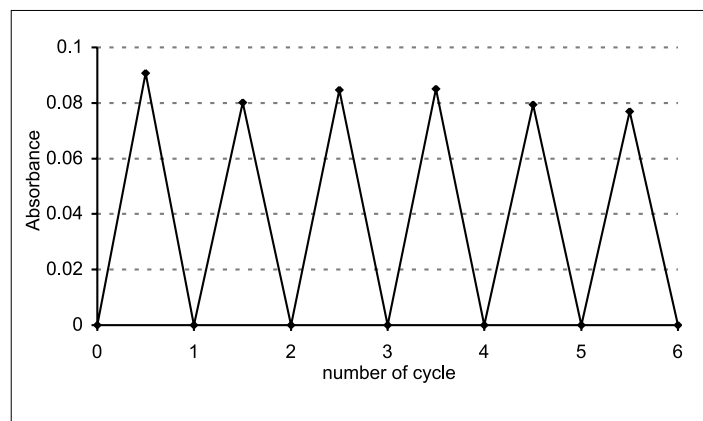
Ligand **2o** is closed by irradiation at 254 nm and reopened with visible light at 600 nm and shows a deterioration of the photochromic properties after the first cycle. Fatigue resistance is therefore considered lower than other published molecules (Fig. 8) [2].

On the other hand, complex **Ru(2o)** closed by irradiation at 450 nm and reopened with visible light at 600 nm shows quasi-constant photochromic properties after a few cycles (Fig. 9).

By using an irradiation wavelength of 450 nm, the fatigue resistance has been enhanced. The alternative path of energy transfer from the excited $^3\text{MLCT}$ state of the ruthenium metal complex to the triplet state of the switching unit occurs under much milder condition compared to the corresponding irradiation at 254 nm and no other photochemical side reaction lowers the fatigue resistance.

3. Conclusions

A new series of dithienylethene-phenanthroline ligands and their ruthenium complexes ($[\text{Ru}(\text{bpy})_2(\text{ligand})](\text{PF}_6)_2$) has been prepared and studied. Ligand **2o** and

Fig. 8. Photofatigue resistance of ligand **2o**Fig. 9. Photofatigue resistance of metal complex **Ru(2o)**

complex **Ru(2o)** have the most promising photochromic properties, which are limited by the presence of two isomers *syn* and *anti*, because only the *anti* conformer is photochemically active and undergoes the photocyclisation reaction. Moreover, an interconversion between the two isomers *syn* and *anti* is sterically blocked.

Complex **Ru(2o)** has a better fatigue resistance and is thermally more stable than the free ligand **2o**. The complex **Ru(2o)** shows an emission whereas its closed form is non-emissive.

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