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Towards new chiroptical switches

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Contents

Abstract

We have synthesized a new chiroptical ligand system, where a 4,5-diaza-fluorene type ligand and a methoxy-benzo-xanthene unit are coupled by a double bond. The ligand exists in two enantiomeric forms, namely P- and M-helical arrangement, as shown by X-ray analysis. By irradiation, the ligand can change its helicity (M↔P) by rotation around the double bond. A complexation between the new ligand and a photoactive metal center (ruthenium, osmium or rhenium) has extended the molecular structure by a chemical bounded photosensitizer. A calculation using MOPAC 97 and the semi-empirical AM1 method estimated the thermodynamic stability of the pure enantiomeric form of the ligand 3. The estimated rotational barrier found was 24 kcal mol^{-1}. Such an energy barrier is high enough to separate the two enantiomeric forms at room temperature. The preparation of the ligand system as well as the metal complexes is described. None of the metal complexes prepared shows any detectable emission at room temperature in aerated acetonitrile solutions. This is an indication that the different sensitizers in its excited state are quenched effectively by the coupled switching unit. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Energy transfer; Polypyridine complexes; Molecular switch; Molecular device; Chiral complexes; Metal complexes

1. Introduction

The design and construction of molecular-level devices is of great scientific interest because it enables the development of new concepts and offer interesting applications in the field of nanotechnology [1]. A molecular-level device can be defined as an assembly of molecular components that can achieve specific functions such as light-induced energy or electron transfer processes, conformational changes or bond breaking–making processes. Special care must be devoted to the design of systems able to perform light

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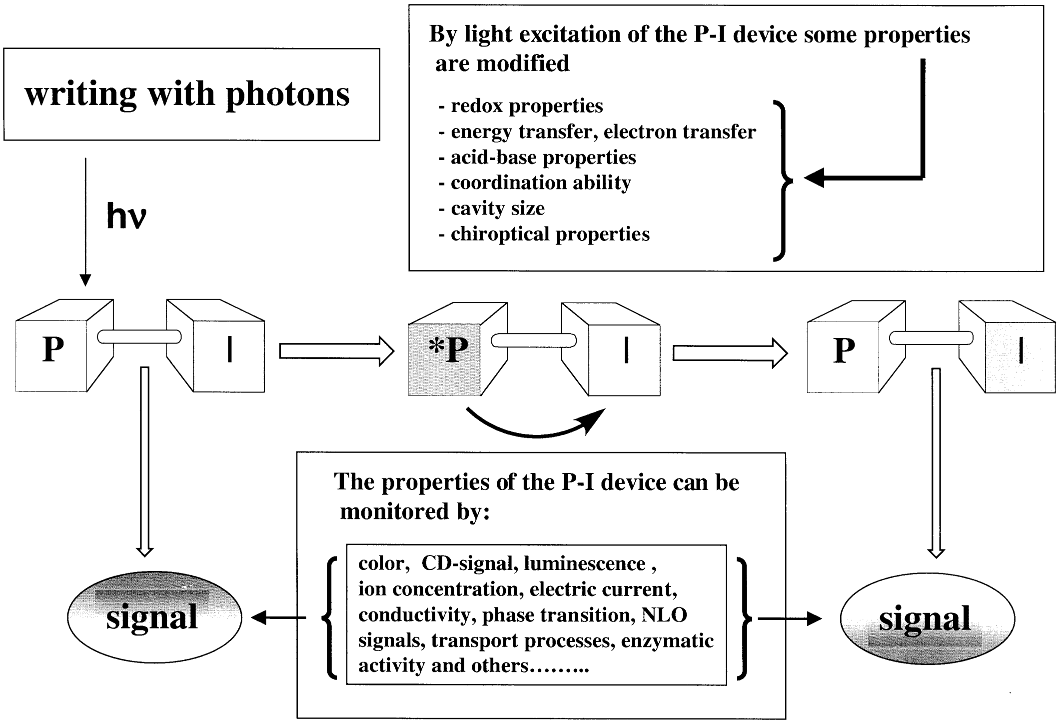


Fig. 1. A molecular device for information storage.

induced functions, since they can be used in signal generation, processing and storage [2]. Our target, described herein, is the synthesis and study of a new family of light-driven molecular switches. The general requirements for a photon driven molecular device can be summarized as following (see Fig. 1). The devices are constituted by a photsensitizer (P) attached to a bistable unit, (I), which is capable to use the energy of the excited state of the photosensitizer to switch between the different states. The modification of the P–I device by light excitation can be for example, a change in redox properties, an electron or energy transfer, a change in acid–base properties, a change in coordination geometry and/or a change in cavity size and a change in chiroptical properties of such a system [3]. The changes are easily monitored among others by measuring its color, CD-spectra, emission properties, the conductivity for electric current or NLO signals of the device. Such devices have a great potential for different applications. The photoactive molecules can be used for example for reversible optical data storage systems [4].

2. The design of a new switching molecule

2.1. An example of a photonic switching system

Recently, we have published a new photonic device constituted by two anthracene moieties linked to a rhenium complex [5]. The switch is based on a photo-induced molecular transformation, in the present case an intra-molecular cyclization. It is well known that two anthracene molecules form a dimer by irradiation with light in the visible region [6]. The inverse process (bond breaking) occurs upon irradiation with UV light. A chelate site was introduced by linking, through an ester linkage, the anthracene unit to a bipyridine ligand, which was coordinated, to a Re^{I} metal center. The rhenium complex acts as a sensor for the opening and closing reaction of the two anthracene moietys (see Fig. 2).

If the anthracene units are not dimerised, after irradiation of Re^{I}, an energy-transfer process to the anthracene units take place, which strongly quenches the luminescencence of the rhenium center. If the anthracene units are dimerised, they lose the capability to act as an intra-molecular quencher. In this case, a bright emission from the rhenium center is observed. Moreover, the observed quenching and restored emission were constant over a long number of closing and opening cycles.

2.2. Overcrowded alkenes as molecular switches

Overcrowded bistricyclic aromatic enes (Fig. 3) have been extensively studied as molecular switches since their ‘helicity’ can be inverted by means of circularly polarized light (CPL) and such a change can be easily monitored by means of CD techniques[7]. Besides, it has been proven that a light induced change in helicity of

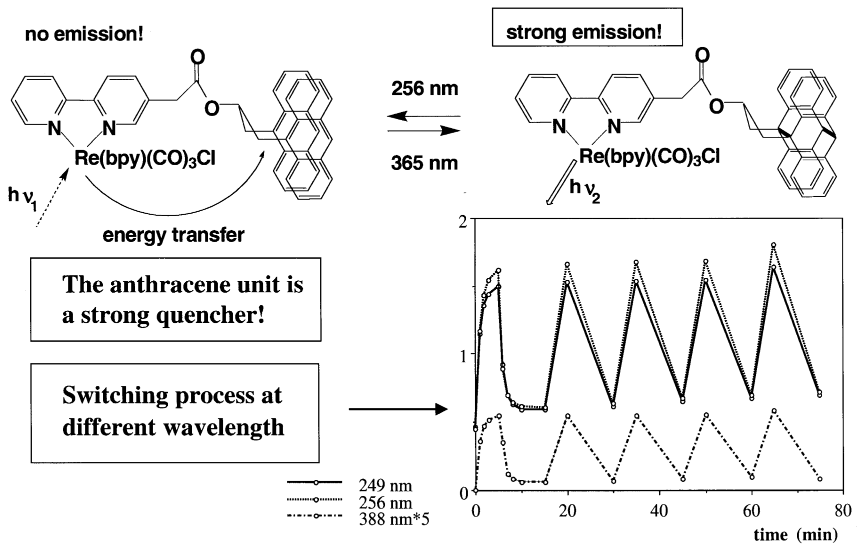


Fig. 2. An example of a photonic switch.

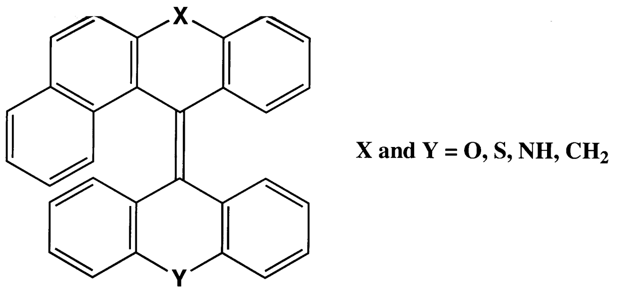


Fig. 3. A general scheme of the chiroptical switches developed by of Feringa et al.

these molecules can induce changes in the handedness and pitch of liquid crystalline materials when they are used as dopant agents [8]. These kind of systems have been used for these purposes either as pure diastereomeric form through a photodestruction process or as a racemic MP mixture through a photoenrichment process as it has been shown by Feringa et al. [9].

2.3. A new chiroptical switching ligand and its metal complexes

In this paper, we will present the preliminary results about the synthesis of the first overcrowded polycyclic aromatic ene based on a 4,5-diaza-fluorene moiety which fulfills the steric requirements to provide overcrowding in the fjord region and, therefore, helical conformation. Moreover, the introduction of the 4,5-diaza-fluorene moiety can open the door to new photochromic studies based on the use of metallic centers as build-in sensitizer for the helicity photomodulation of the system (see Fig. 4). By irradiation into the ^{1}MLCT band of the sensitizer an energy transfer can occur from the metal center to the double bond of the switching unit. Due to the energy transfer to the double bond a free rotation around the bond can be induced and, therefore, a change in the helicity (M or P) of the system could be observed. Such a photosensitized switching process can be performed at about 450 nm and not as often described in literature in the near UV-region. Therefore, an improvement of photoresistance can be achieved.

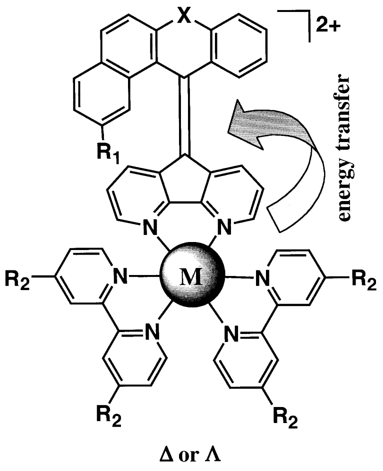


Fig. 4. The new chiroptical switching metal complex. The functions X, R_1, R_2, M, and Δ/Λ can be individually modified.

Optimization of our new chiroptical system can be performed in several ways. A change of the position X from an oxygen atom to a sulfur- or carbon atom changes not only the electronic situation, but also the sterical stress in the fjord region [10]. The same effect can be observed by an increase of the size of the substituent R_1. A change of the metal center M opens an other possibility of modification of the sensitizer part (M = Ru, Os, Ir, Re, Rh or Fe). A variation of the substituents R_2 (donor or acceptor groups) on the two bipyridine type ligands makes sure, that a directed energy transfer from the metal center to the diaza-fluorene ligand or to the attached double bond, respectively, occurs. Another, but nevertheless interesting modification can be studied. In the case of a metal complex (Octahedron), like $[Ru(bpy)_3]^{2+}$, our compounds exists in four different isomeric forms (pairs of diastereomeres), namely Δ(M/P) and Λ(M/P), respectively. We have developed in our laboratories different techniques to build up only one of the two chiral metal complexes in a pure form [11]. Adapted to our switching system, the P and the M helical arrangement are no longer mirror images. They change from an enantiomeric mixture to diastereomeric one.

Since we are at the beginning of our studies, only preliminary results about the photophysical and electrochemical properties of Ru(II), Os(II) and Re(I) complexes with the above mentioned ligand, are given.

3. Synthesis

3.1. Preparation of the switching ligand

Our interest was mainly focussed on the inclusion of a chelating center over the general structure shown in Fig. 3, in this sense, the first choice was the use of a diaza-fluorene moiety. The latest is due to its availability as a 4,5-diaza-9-azo-fluorene which can be a valuable framework in a synthesis based on the two-fold extrusion method, the so-called Barton coupling, which is a general way to obtain the central double bond in overcrowded alkenes (Scheme 1) [12].

The synthesis of compounds **1** and **2** has been achieved following published procedures [13]. It is well known that the Barton-reaction affords an episulfide type compound, which lead to the desired alkene after sulfur removal, this final step being the most difficult [14]. In our case, heating the starting materials, under reflux conditions, in toluene for 72 h, leads to the alkene type compound in a straightforward fashion without any trace of the episulfide intermediate. Different attempts based upon temperature/time tuning, never allowed us to isolate this episulfide type molecule. The structure of compound **3** was confirmed by X-ray analysis (Fig. 5).

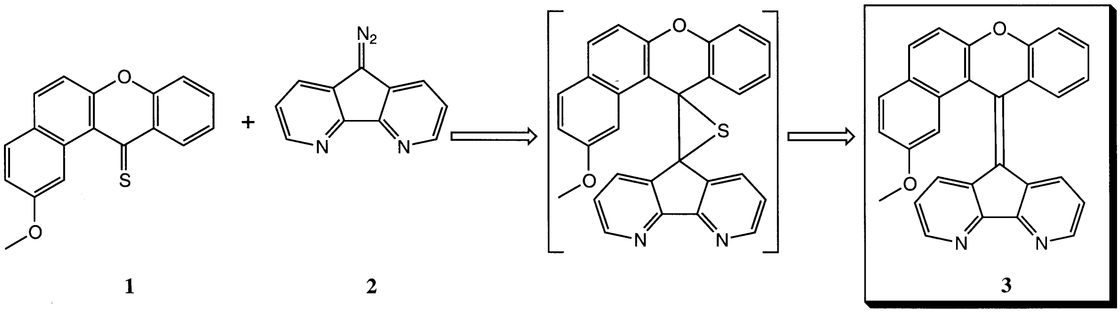
3.2. Structural characterization

Details of the X-ray analysis are given in [15]. As was expected, this structure shows helical conformation due to overcrowding in the fjord region. The main features of this system are based on an ‘anti’ conformation [16] around the newly formed double bond, this double bond being slightly twisted from planarity (pure twisting 1.2°).

The central six membered ring adopts a boat like conformation to define a dihedral angle of 44.2° between the aromatic systems of the ‘top half’ structure. The dihedral angle between the aromatic rings in the diaza-fluorene moiety is only slightly bent from planarity (14.7°). On the other hand, the double bond carbons are strongly pyramidalized, the values of this pyramidalization have been measured as 7.44 and −3.43° for the ‘top half’ carbon and ‘bottom half’ one, respectively, [16].

The ^1H-NMR spectrum in $CDCl_3$ (Fig. 6) shows the completely asymmetric pattern as the main feature for the protons of the diaza-fluorene moiety. In this spectrum one can see how protons 3 and 2 are strongly upfield shifted when compared with its homologous 4 and 5. This can be rationalized by attending to the strong shielding effect due to the aromatic rings located close to these protons. This effect can also be seen in the resonance of the methoxy group protons. In this case these protons are shifted upfield up to 0.6 ppm when compared with the xanthione based precursors. These features are consistent with a system in which ‘bottom half’ and ‘top half’ present strong through space interactions as it has been shown previously by X-ray analysis and, therefore, overcrowding in this region seems to be proved.

So far, the helical structure of compound **3** has been established by means of X-ray and NMR techniques, but more important than this last point is to understand the thermal behavior of the system. This arises from the fact that if thermic energy, under certain limits, can



Scheme 1. Synthetic protocol for the preparation of **3**.

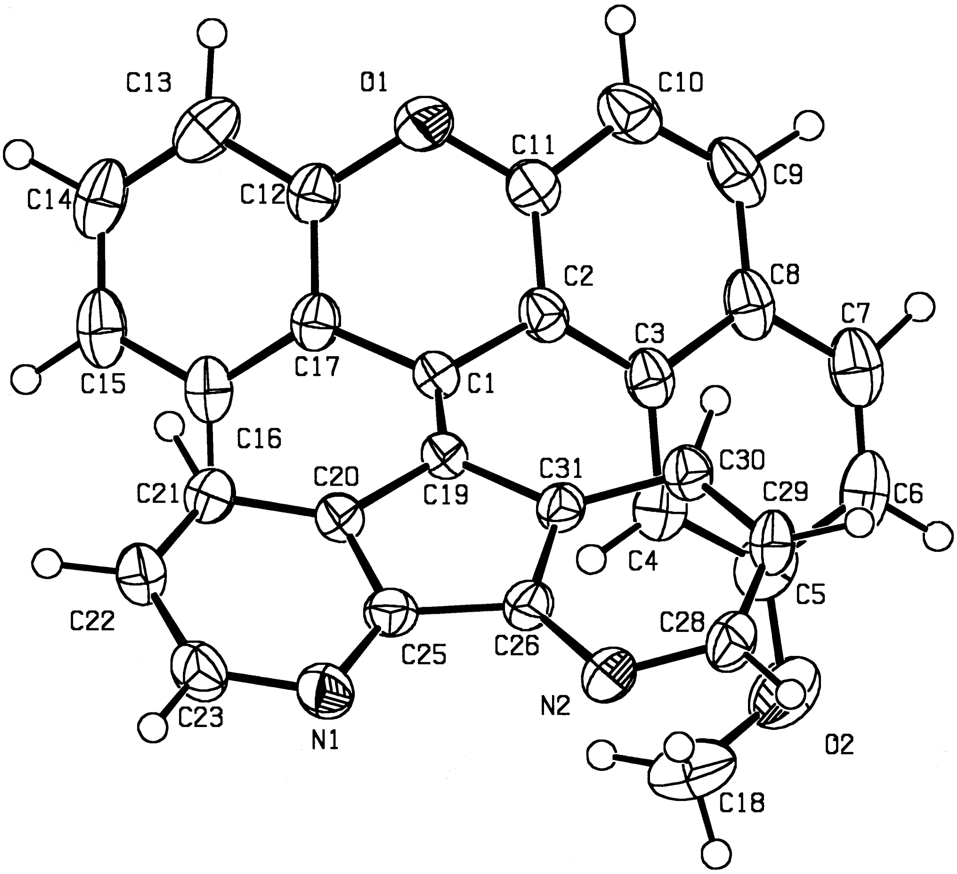


Fig. 5. ORTEP representation of the X-ray structure of the compound **3**.

invert the helical handedness of the system, then the concept of M and P will be lost and, therefore, the tuning will not be possible. On the other hand, this kind of M–P mixture can only be resolved when the thermal rotation barrier energy around the double bond is bigger than 20–21 kcal mol^{-1} [10]. In order to estimate this inversion rotational barrier, semi-empirical calculations were carried out [17]. Fig. 7 shows the Chem3D representation of the structures obtained employing MOPAC 97 and the semi-empirical method AM1[18,19].

The study showed a global minimum whose structure was identical to the one obtained by X-ray as well as two more local minimums. The study also afforded three transition states which were assigned to the two different 'edge passages' and to the perpendicular–birradical structure which can be assigned as the true transition state through which the thermal rotation takes place[17]. From this study the thermal rotational inversion barrier can be estimated as 24 kcal mol^{-1}.

3.3. Synthesis of the metal complexes

$[Ru(bpy)_2(3)](PF_6)_2$, $[Os(bpy)_2(3)](PF_6)_2$, and $Re(3)(CO)_3Cl$ were prepared by refluxing the ligand **3** with the appropriate metal source ($Ru(bpy)_2Cl_2$, $Os(bpy)_2Cl_2$ and $Re(CO)_5Cl$, respectively), for several hours using methoxyethanol for the ruthenium and osmium complexes and toluene for the rhenium complex formation [20]. The ruthenium and osmium complexes were purified, after counterion exchange, by recrystallization from acetone–hexane a mixture and a second recrystallization from methanol. For the rhenium complex the purification was achieved by recrystallization in a toluene–acetone mixture.

4. Ground-state properties of the new compounds

4.1. Absorption spectra and emission properties

The UV–vis absorption spectra are collected in Table 1; spectra of the ligand **3** and the metal complexes are shown in Fig. 8. The absorption spectrum of the ligand **3** shows a broad peak at 360 nm corresponding to a ligand centered (^{1}LC) transition, mainly located in the methoxy-benzo-xanthene part of the molecule. At about 300 nm a transition associated with the diaza-fluorene part can be observed. In the UV-part of the spectra of the ruthenium and osmium complexes exhibit an intense

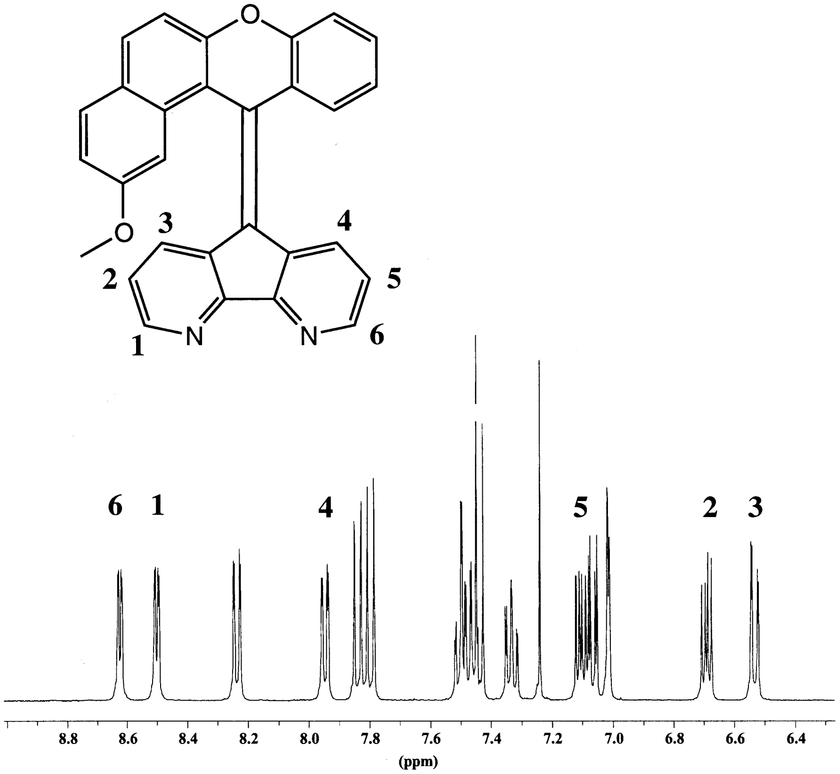


Fig. 6. ^{1}H-NMR of the aromatic part of compound **3** and assignment of the diazafluorene protons.

absorption band (280 nm) which can be attributed to a ^{1}LC transition from the bpy ligand. Moderately intense metal-to-ligand charge transfer (^{1}MLCT) bands are observed for both complexes in the 400–500 nm region. In the osmium containing complex, spin-orbit coupling gives rise to broad and weak absorption at wavelengths higher than 600 nm, corresponding to the spin-forbidden, formally ^{3}MLCT transition. The rhenium complex

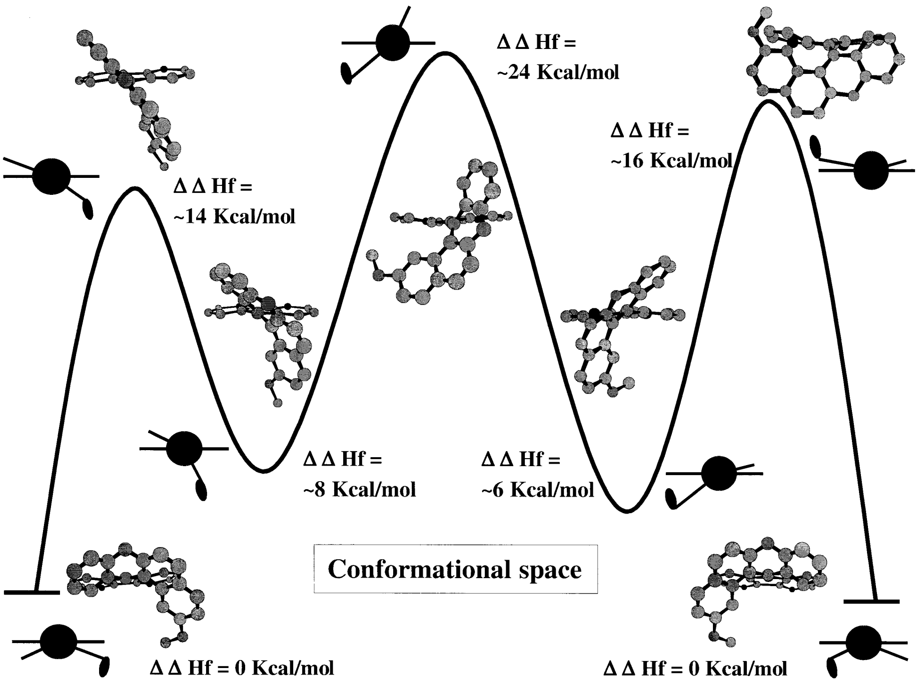


Fig. 7. CHEM3D representations of the calculated inversion process.

Table 1
UV–vis absorption and electrochemical data

Compound	Oxidation [a]	Reduction [a]	λ_{max} (nm) (ε) [b]
Ligand **3**	–	–	367 (15 400), 303 (17 600)
$[Ru(bpy)_2(\mathbf{3})]^{2+}$	+1.33(irr.)	−1.50/−1.73	450 (17 300), 424 (19 500), 286 (55 100)
$[Ru(bpy)_3]^{2+}$	+1.26	−1.33/−1.52/−1.76	452 (14 500), 345 (sh), 323 (sh), 285 (87 100)
$[Os(bpy)_2(\mathbf{3})]^{2+}$	+0.81	−1.44/−1.72	584 (3800), 482 (12 300), 427 (17 400), 290 57 800)
$[Os(bpy)_3]^{2+}$	+0.83	−1.28	580 (3800), 480 (14 500), 447 (sh), 289 (77 300)
$Re(\mathbf{3})(CO)_3Cl$	–	–	397 (18 500), 323 (21 000)

[a] Redox potentials are quoted in *V* versus SCE (with $[Ru(bpy)_3]^{2+}$ as internal standard) in MeCN at RT, supporting electrolyte was $[TBA]PF_6$. The complexes were measured as PF_6^- salts.

[b] Spectra were measured in MeCN (RT; sh = shoulder).

$Re(\mathbf{3})(CO)_3Cl$ shows a large absorption maximum at 370 nm attributed to a ^{1}MLCT transition.

A possible irradiation window that allows a proper energy transfer from the ruthenium metal center to the double bond in the switching part is indicated in Fig. 8.

All metal complexes have no detectable emission in aerated acetonitrile solutions at room temperature.

4.2. Redox behavior

The results obtained from electrochemical experiments are collected in Table 1, where, data concerning the parent complexes $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ are listed also for comparison purposes. The ruthenium complex has an irreversible metal centered oxidation peak at +1.33 V whereas, the corresponding reversible electrochemical process for the osmium complex lies at +0.81 V. The parent compounds have electrochemical processes at +1.26 and +0.84 V, respectively. Each of the two complexes shows two ligand centered, reversible reduction waves for the two bipyridine ligands at −1.50 and −1.73 V for the ruthenium complex and at −1.44 and −1.72 V for the osmium complex, respectively. In the range of +0.3 to −1.4 V irreversible reduction and oxidation processes can be observed, mainly due to the switching unit in the metal complexes and the presence of the methoxy substituent in the rotating part of the molecule.

5. Conclusion

We have achieved the synthesis of a new molecular system, capable of acting as a chiroptical switch. It consists of a switching part and a chemical bounded photosensitizer. The switching part was build up by a methoxy substituted benzo-xanthene unit connected via a double bond to a chelating ligand (4,5-diaza-fluorene). The new ligand system was bounded to different metal complexes (M = Ru, Os, and Re) which can act as photosensitizers. ^{1}H-NMR- and ^{13}C-NMR-spectroscopy, mass-spectroscopy (ESI) and X-ray analysis have provided the structural evidence of the prepared compounds. Calculation of the energy barrier for the rotation from the M- to the P-helix in the non-coordinated ligand has shown that the activation energy of 24 kcal mol^{-1} is high enough for the preparative isolation of a pure enantiomeric form. Different activities concerning the chiral resolution of the ligand **3** and the measurement of the photophysical properties of the ligand **3** and their metal complexes are under investigation.

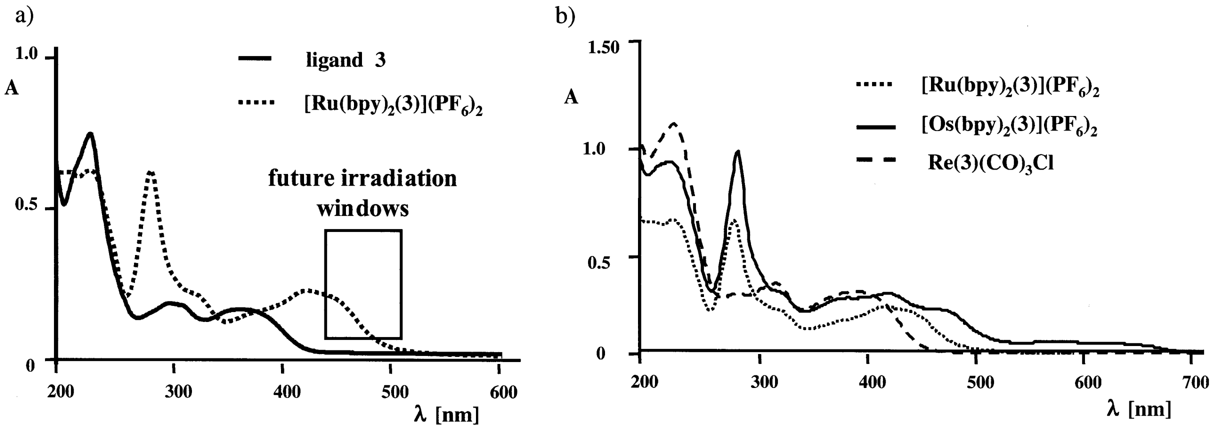


Fig. 8. UV–vis spectra of the ligand **3** and the metal complexes $[Ru(bpy)_2(\mathbf{3})](PF_6)_2$, $[Os(bpy)_2(\mathbf{3})](PF_6)$, and $Re(\mathbf{3})(CO)_3Cl$.

Acknowledgements

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