Account/Revue

Photochromic bipyridyl metal complexes: Photoregulation of the nonlinear optical and/or luminescent properties

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A B S T R A C T

The combination of transition metals and ligands featuring photochromic units is receiving much attention and opens up new perspectives for the design of metal-based photoswitchable molecules. This account summarizes some of our recent works made in the area of photochromic organometallic and coordination compounds, which have been used for the photomodulation of the quadratic non-linear optical (NLO) properties, as well as of the photoregulation of the emission properties of the resulting systems. For this purpose, we have designed new chromophores combining dithienylethene (DTE)-based bipyridine ligands with different metallic fragments (Re^I, Fe^{II}, Ru^{II}, Ir^{III}, Cu^I, Zn^{II}), giving rise to multi-photochromic metal complexes containing from two to six DTE units, and studied the photocontrol of both NLO and luminescence properties.

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R É S U M É

La chimie des complexes de métaux à ligands photochromes s'est considérablement développée durant cette dernière décennie. Elle a ouvert de nouvelles perspectives vers la conception de structures moléculaires et supramoléculaires multifonctionnelles, et plus particulièrement de dispositifs photo-commutables pour l'optique non linéaire (ONL) et la luminescence. Cette revue résume les travaux récents réalisés par notre équipe dans le domaine de la photomodulation de l'activité ONL quadratique et/ou de la luminescence au moyen de complexes organométalliques et de coordination photochromes. Nous décrivons la synthèse de complexes multi-photochromes associant des ligands bipyridines fonctionnalisés par des unités dithiényléthènes (DTE) et différents ions métalliques (Re^I, Fe^{II}, Ru^{II}, Ir^{III}, Cu^I, Zn^{II}), ainsi que leurs applications pour la photo-commutation des propriétés ONL et de luminescence.

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1. Introduction

A current challenge is the development of efficient strategies for the design of switchable non-linear optical (NLO) materials. The ability to switch "ON/OFF" the NLO activity of a molecule is of relevance for the development of molecular photonic devices those properties can be switched by modifying one of the component parts [1]. To achieve an efficient switching effect, the molecule must be stable in the two ON and OFF states and the response time must be relatively fast. As most molecules with large quadratic hyperpolarizability values comprise π-systems end-capped with donor and acceptor moieties, various strategies have been proposed and categorized into three types (Fig. 1) [1a]: types (I) and (II) include the alteration of either the electron-donor or the electron-acceptor capacity of the end groups by using external stimuli, such as redox and protonation/deprotonation. Type (III) includes the

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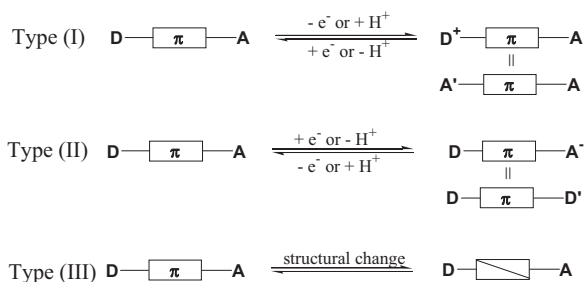 *E-mail address:* lebozec@univ-rennes1.fr (H. Le Bozec).

Fig. 1. Schematic representations of strategies for switching NLO responses.

alteration of the π-bridge using an external trigger, such as light, and in this category photochromic compounds seem to be promising candidates for the design of photoswitchable NLO materials [2].

Photochromism, which refers to the reversible colour change of a compound with light irradiation, is attracting much attention for the construction of molecular devices, and there has been a growing interest in the synthesis, properties and applications of organic photochromic materials during the last decade [1b,3]. Among them, dithienylethene (DTE) derivatives are the most promising because of their good fatigue resistance, remarkable thermal stability of both isomers and rapid response time [3a]. Typically, DTE undergo reversible interconversion between a non-conjugated open form and a π-conjugated closed form when irradiated in the UV and visible spectral ranges, respectively (Scheme 1), and changes in the π-conjugated chain of DTE derivatives can be successfully used to control donor-acceptor interactions. Recently, the combination of transition metals and ligands featuring diarylethene units has received much attention and opened up new perspectives for the design of metal-based photoswitchable molecules [4]. For example, versatile diarylethene-containing polyimine ligands and their transition metal complexes have been synthesized and their photochromic behaviour has been widely exploited for the photomodulation of luminescence and electronic properties [5–10].

Our research group has been involved for the past 15 years in the NLO properties of bipyridyl metal complexes [11]. We have previously shown that compounds, such as donor-substituted bipyridines are excellent building blocks for the construction of either dipolar compounds [12] or non-dipolar (octupolar) metal complexes of D_3 [13] and D_{2d} [14] symmetry (Fig. 2). We have shown that the NLO response is mainly dictated by the intense intra-ligand charge-transfer (ILCT) transition from

the donor group to the acceptor pyridine ring, and the role of the metal fragment is that of an inductive acceptor. These works have also underlined the role of the metallic core not only as a template but also for its participation in the quadratic non-linear optical responses, and suggested that other factors, such as the geometry of the complexes and the low-energy MLCT transitions, which may also contribute to the global NLO activity.

The scope of this account is to discuss some of the recent work made in the area of photochromic organometallic and coordination compounds, which have been used for the photomodulation of the quadratic non-linear optical (NLO) properties, as well as of the photoregulation of the emission properties of the resulting systems. For this purpose, we have designed new chromophores combining DTE-based bipyridines with different metallic fragments, giving rise to multi-photochromic metal complexes containing from two to six DTE units, and studied the photocontrol of both NLO and luminescence properties.

## 2. Design and photochromic properties of bis-DTE 2,2′-bipyridine derivatives

2.1. Synthesis

The synthesis of bipyridine derivatives $\mathbf{L^{a-d}}$ (R = H; D = H, OMe, NMe$_2$, NBu$_2$) [15,16] and $\mathbf{L'^c}$ (R = Me; D = NMe$_2$) [17] was achieved by functionalization of the 4,4′ positions of 4,4′-dimethyl-2,2′-bipyridine and 4,4′,6,6′-tetramethyl-2,2′-bipyridine, respectively (Scheme 2). Dilithiation with LDA in THF at −78 °C, followed by reaction with chlorotrimethylsilane and subsequent chlorination with hexachloroethane afforded the resulting bis-chloromethyl derivatives in good yields Finally, the treatment of diethylphosphonatomethyl-2,2′-bipyridines, readily obtained through an Arbuzov reaction, with aldehydes a–d under normal Wadsworth–Emmons conditions afforded the target bipyridine derivatives $\mathbf{L^{a-d}}_{(o,o)}$ and $\mathbf{L'^c}_{(o,o)}$ in their open forms in 50–60% yield after purification by recrystallization.

All compounds $\mathbf{L}$ and $\mathbf{L'}_{(o,o)}$ show good transparencies in the visible region whatever the nature of the end D group: the UV–visible spectra in dichloromethane show an intense absorption at 340–350 nm which is tentatively assigned to (IL) π → π* transitions of the bipyridyl moieties with some mixing of the DTE units.

2.2. Photochromic properties

For all bipyridyl derivatives, the photocyclization process was confirmed by ¹H NMR experiments: the
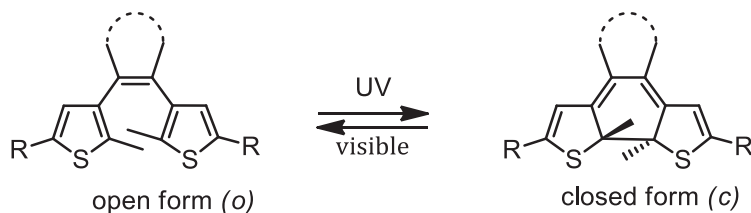
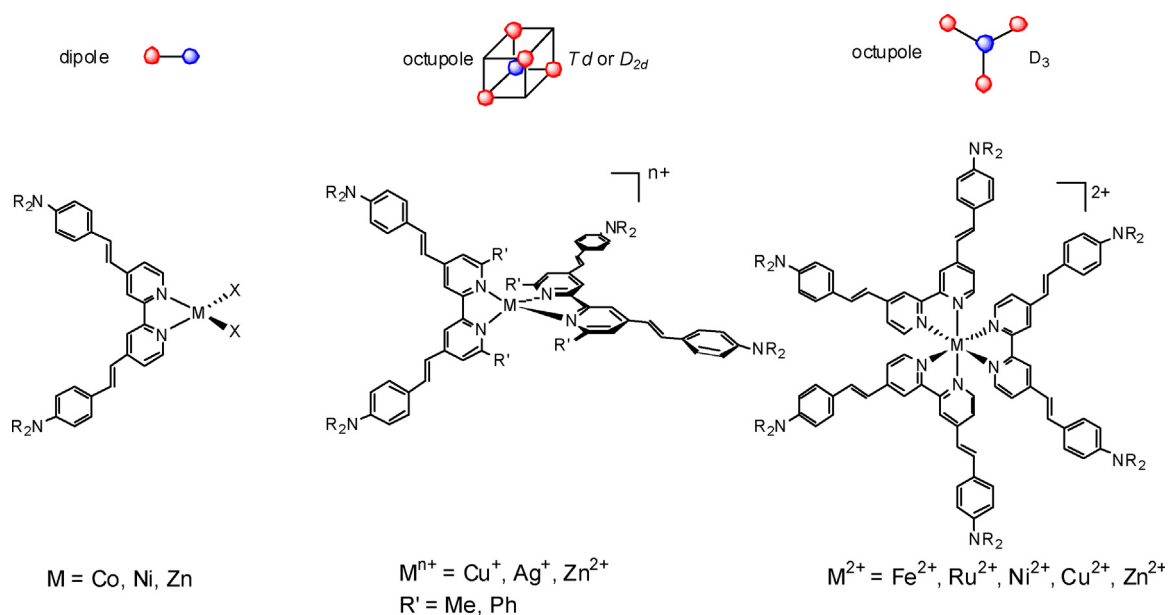Scheme 1. Photochromic interconversion of a dithienylethene (DTE) unit.

Fig. 2. Representative examples of bipyridyl metal NLO chromophores.

Table 1
Main electronic absorption data for bipyridyl ligands in the open and closed (PSS) forms, % conversion at the PSS and photochromic quantum yields.

Compound	λ_{abs}/nm[a] open	λ_{abs}/nm[a,b] closed (PSS)	% Conv[c]	Φ Ring-closure[b] $(o,o) \rightarrow (o,c)/(o,c) \rightarrow (c,c)$
L[a]	343	623	> 95	0.83/0.16
L[b]	345	629	> 95	0.65/0.15
L[c]	348	669	> 95	0.58/0.043
L[d]	346	679	> 95	0.12/0.012
L′[c]	340	668	> 95	–

[a] At 298 K in CH_2Cl_2.
[b] Irradiation at λ = 365 nm.
[c] Determined by ^1H NMR spectroscopy.

colorless (or pale yellow) solution of **L**[a–d]$_{(o,o)}$ and **L′**[c]$_{(o,o)}$ in CD_2Cl_2 turns to blue-green, upon UV irradiation at 365 nm. Their ^1H NMR spectra show the characteristic upfield shift by ca. 0.5–0.6 ppm of the two thiophene protons, meanwhile, the methyl signals are shifted downfield by ca. 0.2 ppm. Integration of the methyl groups indicates a nearly quantitative conversion to the fully ring-closed isomers. The photocyclization and photocycloreversion processes were also followed by absorption spectroscopy [15–17] (Fig. 3). Irradiation of CH_2Cl_2 solutions at 365 nm resulted in the increase of a new broad band located between 620 and 670 nm (Table 1), which is attributed to the intra-ligand (ILc) $\pi \rightarrow \pi^*$ transition of the closed form of the DTE units, the red-shift arising from the formation of a π-conjugated system. The influence of the electron-donor end group D is reflected by the bathochromic shift of the absorption band within the series NBu_2 > NMe_2 > OMe > H. For example, replacement of the H end group with the strong donating NBu_2 group induces an additional 56-nm red shift of the ILc band (Table 1). Excitation in the absorption band of the closed forms leads to the quantitative regeneration of the open isomers, showing the reversibility of the process.

In order to gain further insight into the mechanistic closing process operating for the biphotochromic compound of these series, we have investigated quantitatively the photo-induced formation of the **(c,c)** species in solution under light irradiation [18]. We have measured the
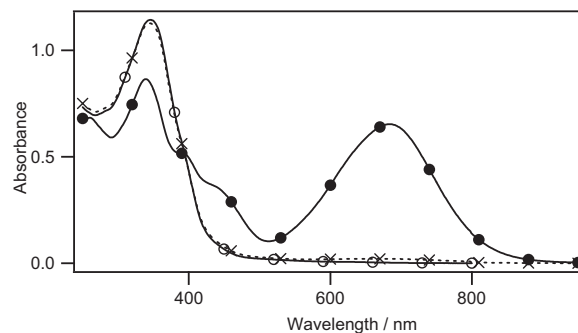
Fig. 3. UV–vis absorption change of **L**[c] in $CHCl_3$ (1.5×10^5 M) upon irradiation. —○— open form, —●— PSS after irradiation at 365 nm, –×– PSS after backward irradiation at 588 nm.
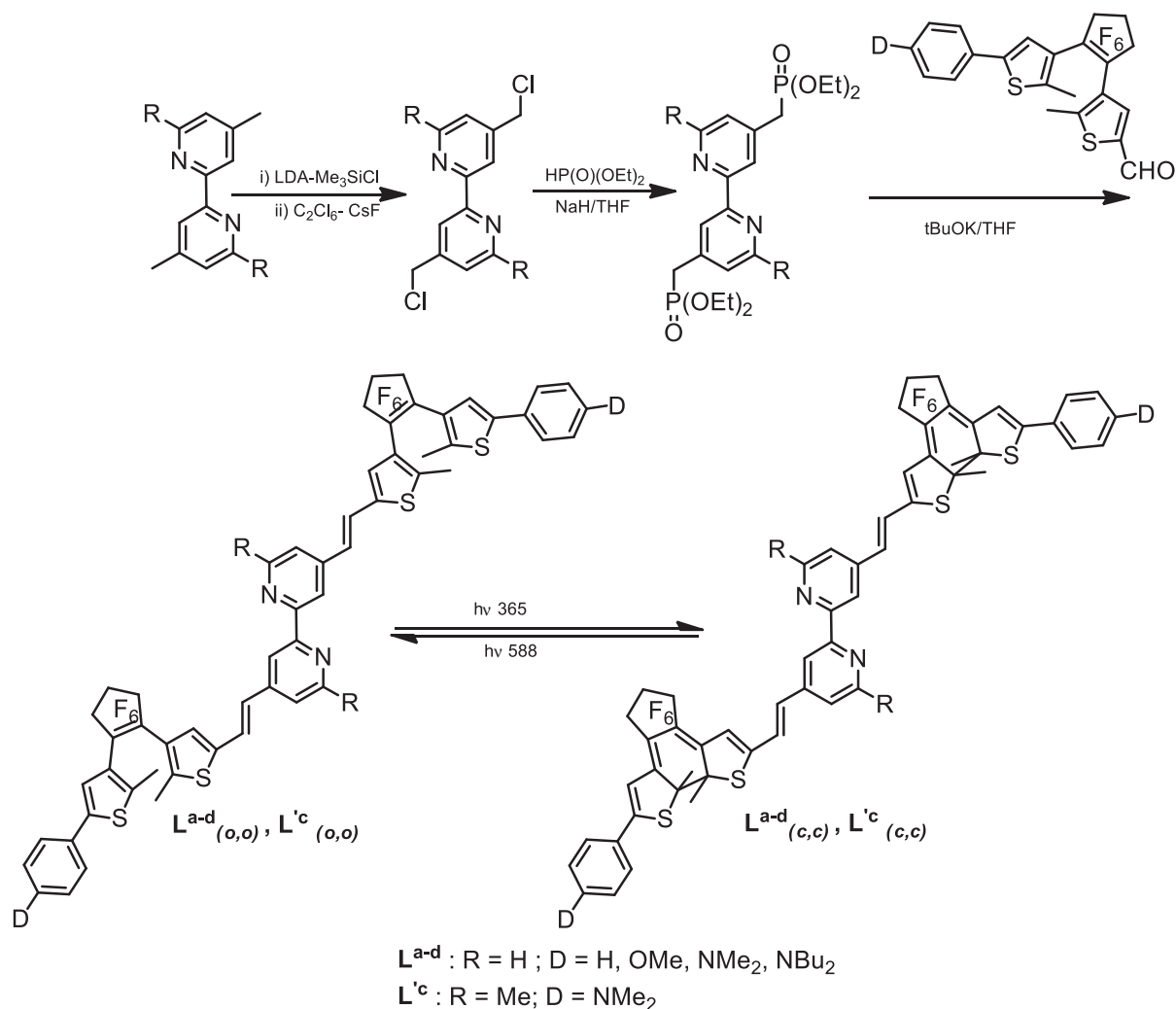
Scheme 2. Synthesis of the photochromic bipyridine ligands and their photocyclization properties.

photochromic quantum yields by means of absorption spectroscopy and photokinetic models. All the spectroscopic experiments were conducted in CH_2Cl_2 solutions under continuous irradiation at λ = 365 nm (resp. λ = 588 or 650 nm) to promote the cyclization (resp. retrocyclization) reactions. This study revealed two different sets of quantum yields, the first one related to the (*o,o*)→(*o,c*) reaction being systematically larger by one order of magnitude than the second one describing the second ring-closure (*o,c*)→(*c,c*) (Fig. 4, Table 1). It thus becomes clear that although both photochromic reactions (*o,o*)→(*o,c*) and (*o,c*)→(*c,c*) can actually take place, the efficiency of the reaction is strongly reduced for the second step, and we believe that this can be the consequence of a strong cross-talk between a given open-DTE unit in the excited state and its neighbour. Concerning the ring opening, the quantum yields were found identical for both retrocyclization processes, which tend to confirm the weak electronic coupling between the closed-DTE units through the twisted bipyridyl central bridge. Their values were found to be lower than 10^{-2}, namely, much smaller

than those related to cyclization as usually reported for non-constraint DTE units. Systematic analyses of the ligands show a monotonous decrease of the quantum yields with increasing electron-donating ability of the end group D, namely H < OMe < NMe$_2$ < NBu$_2$.

3. Photochromic, NLO and luminescence properties of metal complexes featuring one bis-DTE 2,2′-bipyridine ligand

3.1. Synthesis

Fig. 5 depicts the structures of the Zn(II), Re(I), Ru(II) and Ir(III) complexes featuring a. *bis*-DTE bipyridine ligand. The Zn(II) complexes **1 a–d** were readily obtained after room temperature treatment of $L^{a-d}_{(o,o)}$ with one equivalent of zinc diacetate dihydrate or zinc dichloride in dichloromethane [15,16]. Reaction of $L^{c}_{(o,o)}$ with Re(CO)$_5$Br under refluxing anhydrous toluene afforded *fac*-$L^{c}_{(o,o)}$**Re**(CO)$_3$Br **2c** as brown crystals. The ruthenium complex [($L^{c}_{(o,o)}$)(dmbipy)$_2$Ru](PF$_6$)$_2$ **3c** (dmbipy = 4,4′-dimethyl-2,2′-bipyridine)
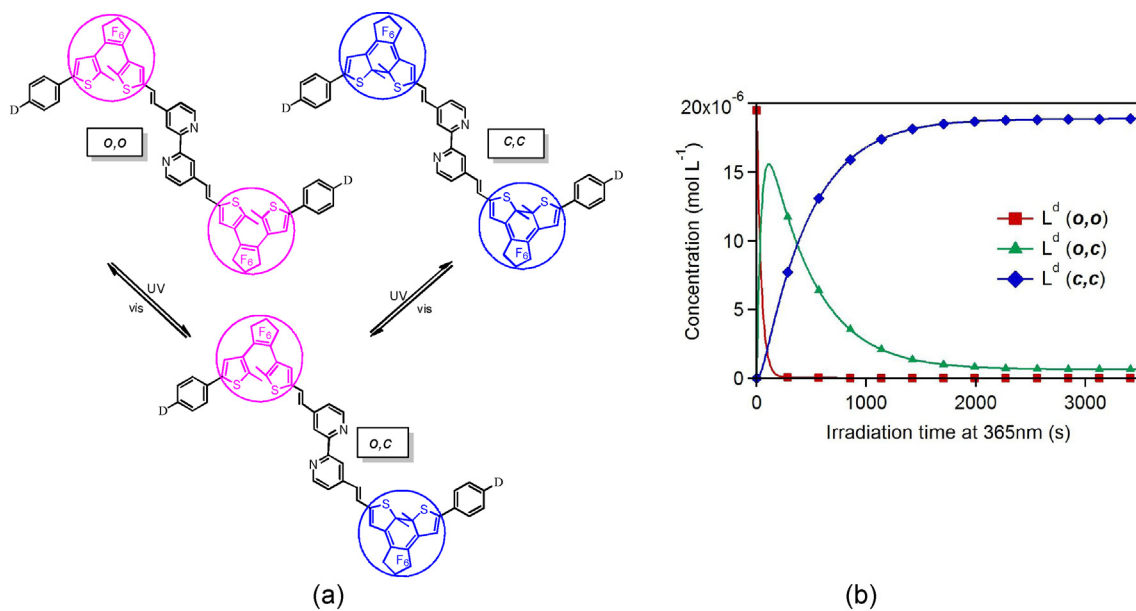
Fig. 4. (a) Stepwise ring-closure and ring opening reactions of the photochromic bipyridines. (b) Time-evolution of the concentration of the three interconverting isomers of **L^d**.
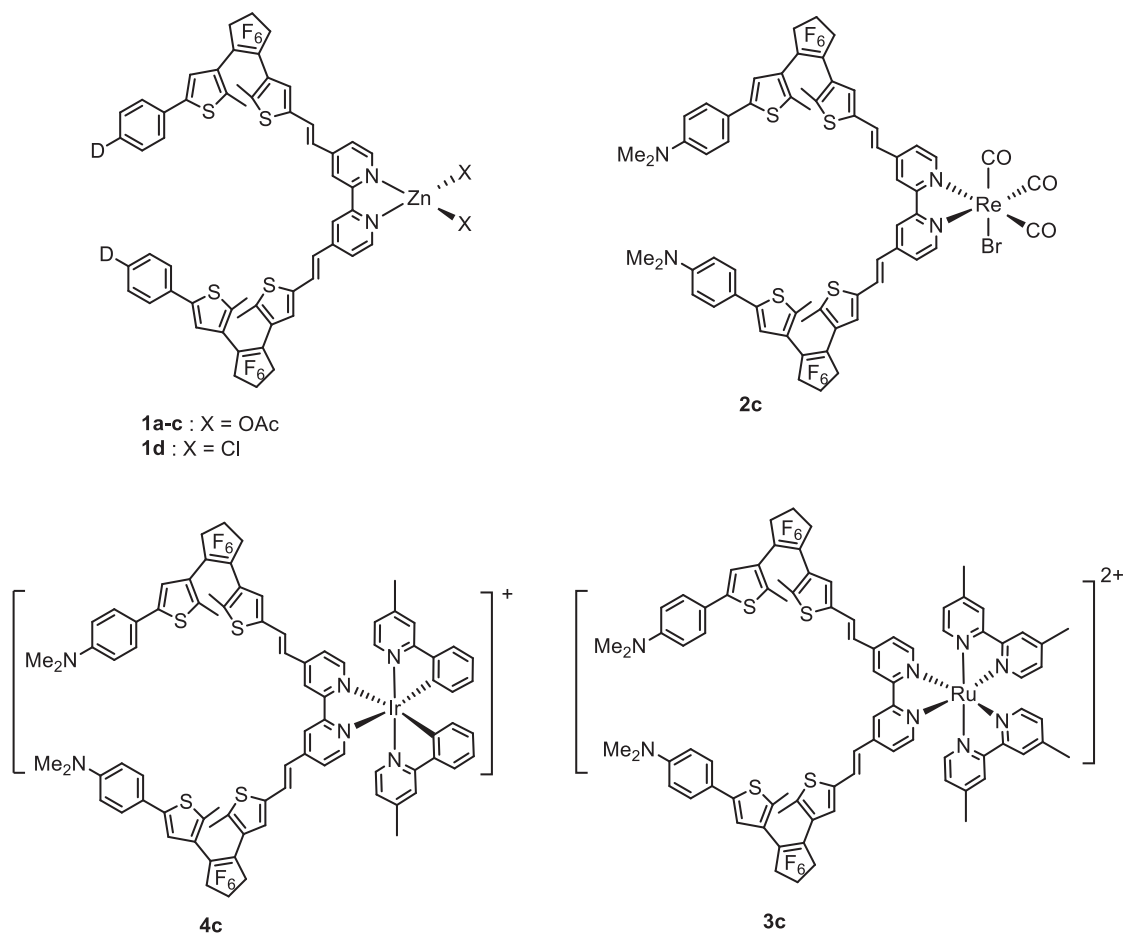

Fig. 5. Chemical structures of photochromic bipyridine Zn(II), Re(I), Ru(II) and Ir(III) complexes.
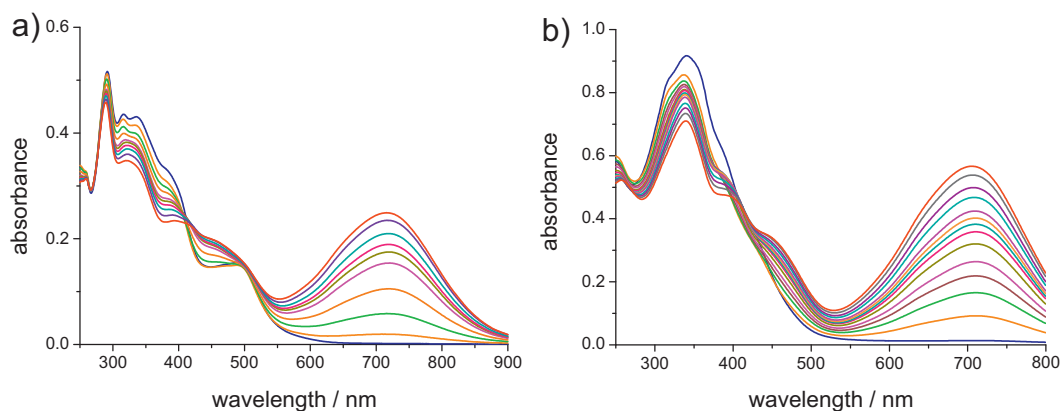
Fig. 6. UV-vis absorption spectra changes of (a) **3c** and (b) **2c** in dichloromethane upon irradiation at 350 nm.

Table 2
Main electronic absorption data for bipyridyl metal complexes in the open and closed (PSS) forms and % conversion at the PSS.

Complex	λ_{abs}/nm[a] open	λ_{abs}/nm[a] closed (PSS)	% conv[b]
1a	357	629	95%
1b	355	646	95%
1c	360	687	90%
1d	351	714	90%
2c	340, 380 (sh),410 (sh)	705	65%
3c	338, 377 (sh), 491	716	65%
4c	341, 397 (sh)	715	79%

[a] At 298 K in CH$_2$Cl$_2$.
[b] Determined by ^{1}H NMR spectroscopy.

was obtained from the corresponding *cis*-(dmbipy)$_2$RuCl$_2$ upon treatment first with 2 equiv of silver triflate in methanol, then, the reaction with ligand $\mathbf{L^c_{(o,o)}}$ in dichloromethane at room temperature, followed by anion-exchange from triflate with hexafluorophosphate [16]. The cationic Ir(III) complex 4c was readily synthesized upon treatment of the corresponding μ-chloro dimer [Ir(N^C-ppy-Me)$_2$(μ-Cl)]$_2$ with $\mathbf{L^c_{(o,o)}}$ in the presence of AgPF$_6$ [19]. All complexes were fully characterized by means of ^{1}H and ^{13}C NMR and UV–visible spectroscopy.

The UV–visible spectra of the Zn complexes (in CH$_2$Cl$_2$) all show an intense band around 360 nm similar to that of the ligands, and slightly red-shifted by complexation

(Table 2). The electronic absorption spectra of the Re, Ru and Ir complexes also show intense IL absorptions near 340 nm and 380–400 nm. In addition, the Ru complex displays another broad band in the visible at 490 nm corresponding to MLCT dπ(Ru) → π*(bipy) transitions, whereas the Re and Ir complexes show a moderately intense absorption shoulder at ca. 400–410 nm, which can be assigned as the dπ(M) → π*(bipy) transitions.

3.2. Photochromic properties

For Zn complexes **1a–d**, upon illumination at 365 nm, new absorption bands between 629 and 715 nm appear, originating from the formation of the corresponding closed isomers. As shown in Table 2, the absorption maxima of the closed-ring forms are dependent on the nature of the donor groups and metallic fragments: complexation of ligands $\mathbf{L^{a-c}}$ to Zn(OAc)$_2$ induces a small bathochromic shift ($\Delta\lambda$ = 6–18 nm) of the IL bands, whereas complexation to ZnCl$_2$ (**1d** vs **1c**) induces a much larger bathochromic shift ($\Delta\lambda$ = 35 nm) than Zn(OAc)$_2$, in agreement with the higher Lewis acidity of ZnCl$_2$ vs Zn(OAc)$_2$ [15,16,18]. According to ^{1}H NMR analysis, integration of the methyl groups indicates a photocyclization yield of ca. 90%, showing that complexation to the Zn(II) ion does not perturb the photochromic properties of the bipyridyl ligands. Similarly to the free bipyridine ligands, photokinetics studies show that the photochromic ring-closure/opening reactions

Table 3
EFISH μβ values and HLS β values determined at λ_{inc} = 1910 nm in CH$_2$Cl$_2$.

Compound	EFISH[a] open μβ$_{1.91}$[a,b]	EFISH[a] after UV irr. μβ$_{1.91}$[a,c]	HLS open <β$_{1.91}$>[d,e]	HLS after UV irr. < β$_{1.91}$>[d,e]	λ_{em}/nm (τ/μs)[f] Open	% Ring closing
1c	200	4220	–	–	–	90
1d	113	5650	–	–	–	65
2c	240	2920	229	965	652, 725(22)	65
3c	–	–	325	1113	680, 753(13)	62
4c	–2190	–2000	–	–	650, 717(23)	79

[a] 10^{48} esu.
[b] Error ± 20%.
[c] Error ± 5%.
[d] 10^{30} esu.
[e] Error ± 15%.
[f] At 77 K in EPA (ether/isopentane/ethanol 2:2:1, v/v); λ_{exc} = 400 nm.
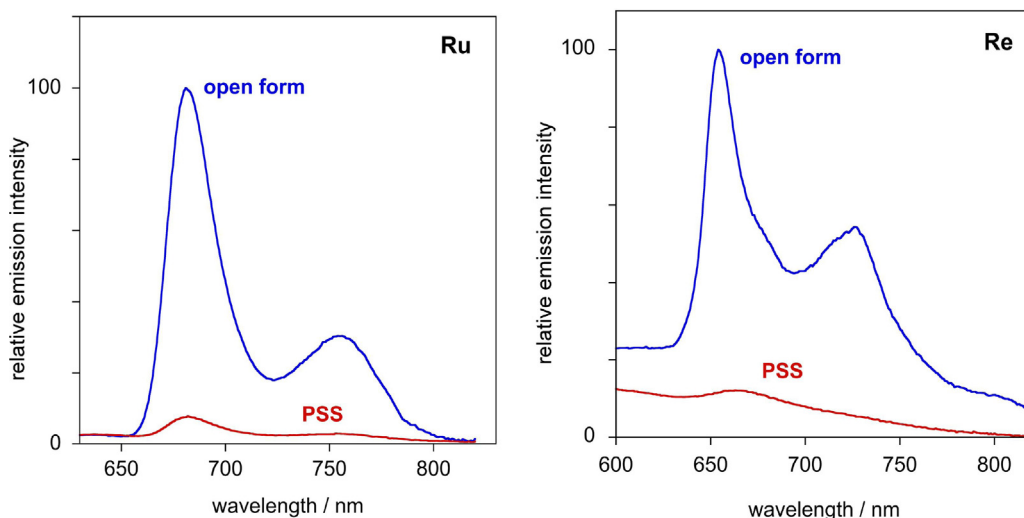
Fig. 7. *Left*: Emission spectrum of **3c** at 77 K in EPA (blue line) and the corresponding spectrum recorded for the photostationary state (red line). *Right*: Corresponding spectra of **2c** and its PSS.

occur in a stepwise fashion with a decrease in the quantum yields [18]. Photocyclizations of the Re(I), Ru(II) and Ir(III) complexes **2–4c** by irradiation with UV light at 350 nm, also give rise to lower-energy absorptions between 705 and 716 nm, corresponding to the ring-closed isomers (see Fig. 6) [16,19]. Thus, a substantial bathochromic shift of the IL band ($\Delta\lambda$ = 36–47 nm) is also observed upon complexation of $\mathbf{L^c}$ to these organometallic fragments. According to ^{1}H NMR, the ratio of the methyl signals between the closed and open-DTE units (ring closing) in the photostationary states (PSS) is lower (60–79%) than those found for the Zn(II) complexes. It is also interesting to note that the photochromic reaction can be triggered by irradiation of the Re, Ru and Ir complexes into the low-energy MLCT bands. This MLCT photosensitization suggests the intermediacy of the triplet state [3]IL(DTE) in the photocyclization process. Finally, for all the complexes, excitation at 650 nm, in the absorption band of the closed forms leads to the quantitative regeneration of the open isomers, indicating the fully reversible closed-to-open photoisomerization.

3.3. Photoregulation of the quadratic NLO properties

The second-order NLO responses of the dipolar Zn and Re complexes were determined in CH_2Cl_2 (concentration = 10^{-3} M) by the EFISH technique, working with an incident wavelength of 1.91 μm [15,16]. The values of EFISH $\mu\beta_{1.91}$, before and after UV irradiation, are reported in Table 3. The $\mu\beta_{1.91}$ values of **1c–d** and **2c** are quite weak, as expected by the absence of conjugation between the amino donor group and the bipyridyl metal acceptor moieties. A dramatic increase of the second-order NLO activity is observed after UV irradiation and subsequent accumulation of the ring-closed isomers: in the case of L^dZnCl_2 **1d**, the second-order NLO response is increased almost 50-fold after only 65% of ring closing [23]. Furthermore, it is also interesting to note that this latter EFISH $\mu\beta_{1.91}$ value is even higher than that found for

$L^cZn(OAc)_2$ **2c** in the PSS (90% of ring closing) as expected by the higher Lewis acidity of $ZnCl_2$ vs $Zn(OAc)_2$. A similar, but somewhat less dramatic, behavior is observed for the Re(I) complex with an increase of $\mu\beta_{1.91}$ from 240 to 2920×10^{48} esu in the PSS (65% of ring closing). The lower efficiency of the Re(I) complex in comparison with that of the corresponding Zn(II) complexes has already been shown in dipolar donor-substituted styryl bipyridine metal chromophores [12], and can be explained by the presence of two vectorially opposed charge-transfer transitions (MLCT and ILCT) which contribute to a lowering of the total NLO response. The large enhancement of $\mu\beta_{1.91}$ values after ring-closure clearly reflects the delocalization of the π-electron system in the closed forms and, as expected, the largest NLO enhancement is observed with the complex featuring the harder $ZnCl_2$ Lewis acid associated with the better NBu_2 donor group, in agreement with the higher red-shift of the intra-ligand transition which dominates the second-order NLO response. This efficient ON/OFF switching markedly contrasts with the absence of photomodulation of the NLO response observed for the *bis*-cyclometallated phenylpyridine Ir(III) complex **3c** featuring the same photochromic bipyridyl ligand $\mathbf{L^c}$ (Table 3) [19]. Whereas for the Zn(II) and Re(I) complexes the ILCT mainly contributes to the NLO response, for the Ir(III) complex the EFISH hyperpolarizability is dominated by L'LCT/MLCT processes, and thus, the nature of the π-conjugated substituents on the bipyridine ligand does not influence so much the $\mu\beta$ values.

The Harmonic Light Scattering (HLS) technique was also used for the molecular first hyperpolarizability β measurements of the dicationic Ru complex **3c**, and for comparison of the neutral Re complex **2c** [16]. The HLS technique can be used also for ionic molecular species and for non-dipolar molecules, such as octupolar molecules. The measurements were performed in dichloromethane at a fundamental wavelength of 1.91 μm (Table 3). It has already been shown that the large β responses of bipyridine ruthenium chromophores, such as octupolar
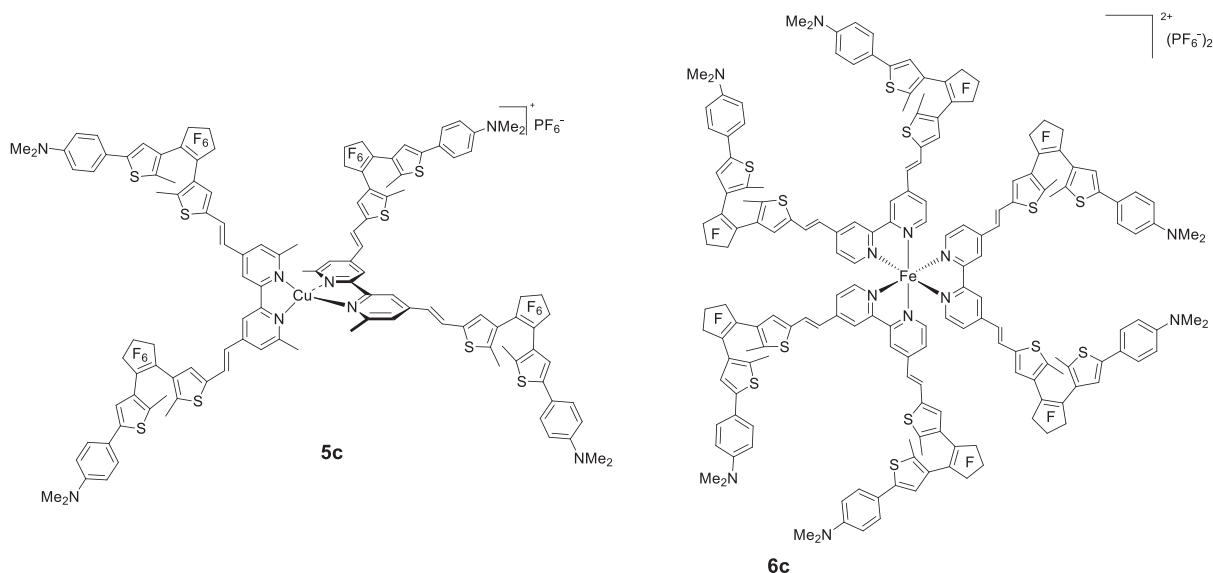
Fig. 8. Chemical structure of the Cu(I) and Fe(II) complex salts (open forms).

D$_3$ tris-chelate ruthenium complexes are dominated by low-lying ILCT or MLCT excitations, depending on the electron-donating or -accepting nature of the substituents on the bipyridyl ligands [13,20]. It turned out that **3c** in its open form also shows a fairly large $<\beta_{HLS}>$ value, larger than that of the Re complex, which can be reasonably attributed to the low-lying MLCT $d\pi(Ru) \rightarrow \pi^*(bipy)$ transition. Upon photocyclisation of the DTE, $<\beta_{HLS}>$ is found to increase by a factor of ca. 3.4, a result which is consistent with an NLO response mainly controlled by the red-shifted ILCT transition.

3.4. Photoregulation of the luminescence properties

In contrast to the free ligand **L^c**, which is non-emissive at room temperature in fluid solution and even in frozen glasses at 77 K, the corresponding Re(I), Ru(II) and Ir(III) complexes **2–4c** in their open forms emit at 77 K (EPA), displaying structured luminescence spectra with vibronic progressions of 1400–1500 cm^{-1}, typical of aromatic and/or C=C bond vibrations [16,19]. The emission character-istics are summarized in Table 3 and the emission spectra of **2c** and **3c** and their PSS are shown in Fig. 7. The long lifetimes (13–23 μs), low-energy, and structured spectra are indicative of emission from a triplet IL state pre-dominantly localized on the bpy–C=C–Ar moiety, rather than from the MLCT state. Following conversion of solutions of **2–4c** to the PSS at room temperature and re-freezing to 77 K, a substantial quenching of the 77 K luminescence is observed. The quenching can be attributed to intramolecular energy transfer from the triplet emissive state to the IL state of the closed-ring DTE part of the molecule: there is extensive overlap of the emission bands of the Re and Ru and Ir chromophores ($\lambda^{max}_{em} = 650$–680 nm) with the low-energy absorption band of the acceptor photochromic unit in its closed form ($\lambda^{max}_{abs} = 705$–716 nm). Thus, the combination of the photochro-mic DTE-based bipyridine ligand **L^c** with luminescent Re and Ru organometallic fragments allows the photoregula-tion of the emission and NLO properties of the resulting

Table 4
Experimental electronic absorption data for complexes in the open and closed (PSS) forms and measured quadratic hyperpolarizabilities (β) by HLS for the copper and iron derivatives.

Compound[a]	λ_{abs}/nm (ε/M^{-1} cm^{-1})[a] Open	λ_{abs}/nm Closed (PSS)	HLS open $<\beta_{1.91}>$[b]	HLS after UV irr. $<\beta_{1.91}>$[b]
5c	344(166000) 511(24000)	343(119000) 399(sh) 450(47000) 701(95000)	266 ± 52	1672 ± 160[c]
6c	331(206000) 387(sh) 583(42000)	339(170000) 392(sh) 599(sh) 715(103000)	250 ± 50	2000 ± 200[d]

[a] Measured in CH$_2$Cl$_2$.
[b] 10^{30} esu.
[c] 65% Ring closing determined by ^{1}H NMR.
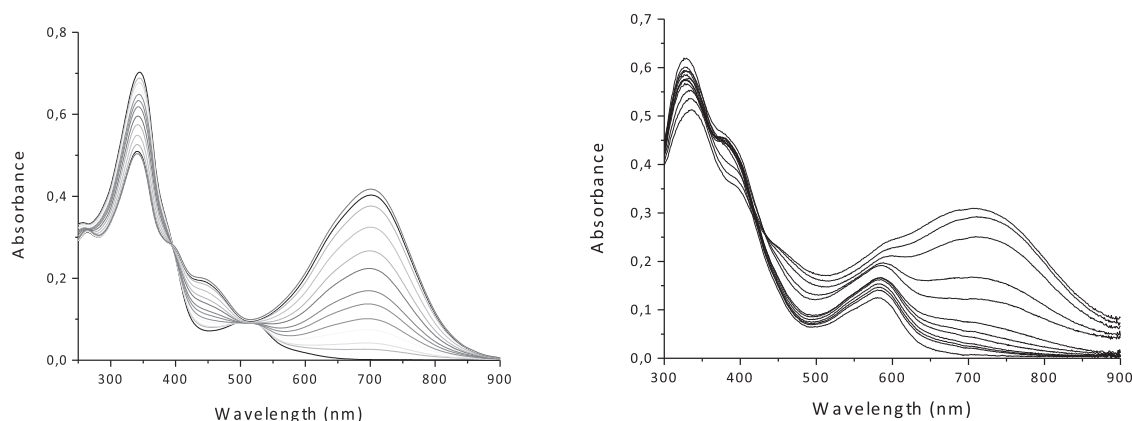[d] 60% Ring closing determined by ^{1}H NMR.

Fig. 9. UV-vis absorption spectra changes of (left) **5c** and (right) **6c** in CH$_2$Cl$_2$ upon irradiation at 350 nm.

system. This study demonstrates for the first time that the photocontrol of two optical properties, linear and non-linear,could be achieved by using the same photochromic ligand.

4. Photochromic and NLO properties of octupolar multi DTE-based metal complexes.

Having demonstrated the photoswitching of the quadratic NLO responses of dipolar metal complexes, we sought to study for the first time the photoregulation of the NLO properties of tetrahedral (T_d, D_{2d}) and octahedral (D_3) octupolar chromophores. To this end, we have very recently designed new series of bis(bipyridyl) copper(I) complexes [17] and tris(bipyridyl) metal complexes featuring four and six DTE photochromic DTE units [21], respectively (Fig. 8). To the best of our knowledge, only a very few numbers of single molecules containing four DTE have been synthesised up to now [22], and only one example of star-shaped DTE-substituted molecule, in which six photochromic DTE units are connected around a central benzene core has been reported [23].

4.1. Synthesis and photochromic properties

The Cu(I) complex **5c** was formed almost quantitatively after mixing 2 equiv of $\mathbf{L'^c}_{(o,o)}$ with [Cu(MeCN)$_4$]PF$_6$ at room temperature in dichloromethane–acetonitrile solution. The tris(bipyridyl) iron(II) **6c** was prepared in good yield by refluxing in ethanol the metallic precursors FeCl$_2$·4H$_2$O with 3 equiv of bipyridines $\mathbf{L^c}_{(o,o)}$, followed by an anionic metathesis with sodium hexafluorophosphate. The ^{1}H and ^{13}C NMR spectra were in agreement with the proposed structures, and theoretical calculations confirmed both series of complexes belong to the D_{2d} and D_3 symmetry, respectively.

The UV–visible spectra of the fully open forms of **5c** and **6c** (in CH$_2$Cl$_2$) show like the free ligands an intense band around 340 nm assigned to (IL) $\pi \rightarrow \pi^*$ transition of the bipyridyl moieties with some mixing of the DTE units, and another band in the visible at 511 nm and 583 nm, corresponding to the dπ(Cu) $\rightarrow \pi^*$(bipy) and dπ(Fe) $\rightarrow \pi^*$(bipy) MLCT transitions, respectively (Fig. 9,

Table 4). The photocyclization process for both complexes was monitored by UV–vis (Fig. 9) and ^{1}H NMR spectroscopy in dichloromethane. Upon irradiation at 350 nm, the red solution of **5c** and the violet solution of **6c** turn green, due to the ring-closure of the DTE units with a photostationary state (PSS) > 90% for the Cu(I) complex and > 60% for the Fe(II) complex. New broad bands emerge in the visible at 701 and 715 nm, respectively, which are attributed to intra-ligand (IL) transitions located on the closed-DTE centers. These results have been rationalized with the help of TD-DFT calculations, and the computed TD-DFT electronic spectra are in good agreement with experimental ones [17,21]. Upon irradiation at 650 nm, the quantitative regeneration of the fully open isomers is observed, indicating the fully reversible closed-to-open photoisomerization.

4.2. Quadratic NLO studies

The Harmonic Light Scattering (HLS) technique was used for the molecular first hyperpolarizability β measurements of the Cu(I) and Fe(II) complexes. Measurements were carried out in dichloromethane (10^{-4} M) with an incident wavelength of 1.91 μm. Complexes **5c** and **6c** in their open forms shows fairly large $<β_{HLS}>$ values of 250–300 × 10^{30} esu (Table 4), which can be reasonably attributed to the low-energy MLCT dπ(M) $\rightarrow \pi^*$(bipy) transitions (M = Cu, Fe). A substantial enhancement of the second-order NLO activity is then observed after UV irradiation and subsequent accumulation of the ring-closed isomer, a result which is consistent with an NLO response mainly controlled by the red-shifted Intra-Ligand transition with a 6–8-fold enhancement of the dynamic first hyperpolarizability after only 60–65% of ring closing to reach extremely large $β_{HRS}$ values exceeding 1600 × 10^{30} esu. Theoretical calculations of the dynamic (1907 nm) and static first hyperpolarizabilities of the fully open and fully closed structures of **5c** and **6c** also predict a large enhancement of the non-linear response by a factor between 8 and 12, when switching all the four and six DTE units, respectively [17,21]. This agreement confirms that the increase of the NLO response is related to the additional IL transitions rather than in variations of the MLCT bands.

5. Conclusions

In this account, we summarize our successful strategies toward the synthesis of photochromic organometallic and coordination compounds based on metal-bipyridyl chemistry. We have shown that coordination chemistry is a versatile tool for the design of multi-photochromic molecules incorporating from two to six dithienylethene (DTE) units, and their access can be easily achieved by combining bipyridyl ligands with different metal ions. These metal systems, which can be either dipolar or octupolar, allowing the photomodulation of optical properties, such as quadratic non-linear optics and phosphorescence. This study also demonstrates for the first time that the photocontrol of two optical properties, linear and non-linear, could be achieved by using the same photochromic ligand. This coordination chemistry approach should open up new perspectives for the design of multi-photochromic metallo-switches with improved switching efficiency and NLO contrast upon varying the metal ion. Finally, the integration of such photochromic molecules into polymeric matrices in order to develop switchable NLO materials and devices should be another interesting issue. We are currently working in that direction.

Acknowledgements

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