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Photochromic Metal Complexes: Photoregulation of both the Nonlinear Optical and Luminescent Properties

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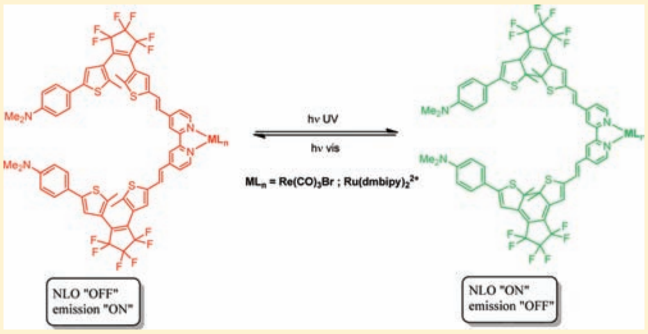
ABSTRACT: A series of dithienylethene (DTE)-containing 2,2′-bipyridine ligands and their zinc(II) diacetate, zinc(II) dichloro, rhenium(I) tricarbonyl bromo, and ruthenium(II) bis(bipyridine) complexes have been designed and synthesized, and their photochromic, photophysical, and quadratic nonlinear optical properties have been studied. Upon UV irradiation at 350 nm, the ligands and complexes undergo ring closure of the DTE units, with a good to excellent photocyclization yield. In the case of the Re(I) and Ru(II) complexes, the photocyclization of the DTE units can also be triggered using visible light, upon excitation into the metal-to-ligand charge-transfer (MLCT) bands at 400 and 490 nm, respectively. Molecular quadratic nonlinear optical (NLO) responses of the complexes have been determined by using either the electrical field induced second harmonic generation (EFISH) or harmonic light scattering (HLS) technique at 1910 nm. These studies reveal a large increase of the second-order NLO activity after UV irradiation and subsequent formation of the ring-closed isomers. This efficient enhancement clearly reflects the delocalization of the π-electron system and the formation of strong push–pull chromophores in the closed forms. The combination of the photochromic DTE-based bipyridine ligand with luminescent Re(I) and Ru(II) fragments also allows the photoregulation of the emission, leading to an efficient quenching of the ligand-based 77 K luminescence and demonstrating that the photocontrol of two optical properties, linear and nonlinear, could be achieved by using the same photochromic ligand.



INTRODUCTION

The ability to switch on and off the NLO activity of a molecule is of relevance to the development of molecular photonic devices, where switching can be achieved by modifying one of the component parts of the molecule.[1,2] Since π-conjugated connections between donor and acceptor end groups are a central requirement for obtaining large quadratic nonlinearities, one strategy to achieve an efficient switching effect concerns the alteration of the π bridge in response to an external trigger such as light. In this category, photochromic compounds are promising candidates for the design of photoswitchable NLO materials.[3−6] Diarylethene (DTE) derivatives are widely used as the photochromic units, and changes in the π-conjugated chain of DTE derivatives can be successfully used to control donor–acceptor interactions.[7] Typically, the DTE unit undergoes reversible interconversion between a nonconjugated open form and a π-conjugated closed form when irradiated in the UV and visible spectral ranges, respectively. 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.[8] For example, versatile diarylethene-containing polyimine ligands and their transition-metal complexes[9−15] have been synthesized and their photochromic behavior has been widely exploited for the photomodulation of luminescence and electronic properties.

We have been involved for several years in the use of 4,4′-disubstituted-2,2′-bipyridines as precursors to dipolar and octupolar metal complexes for nonlinear optics.[16,17] In order to carry out the photoswitching of the NLO properties, we recently prepared a new type of 4,4′-bis(ethenyl)-2,2′-bipyridine ligand functionalized by a 4-(dimethylamino)-phenyldithienylethene (DTE) group and the corresponding zinc bis(acetate) complex (Scheme 1).[18] The excellent photochromic property of this complex was exploited to design the first example of metal-containing photochromic ligands allowing an efficient switching of the quadratic NLO properties.

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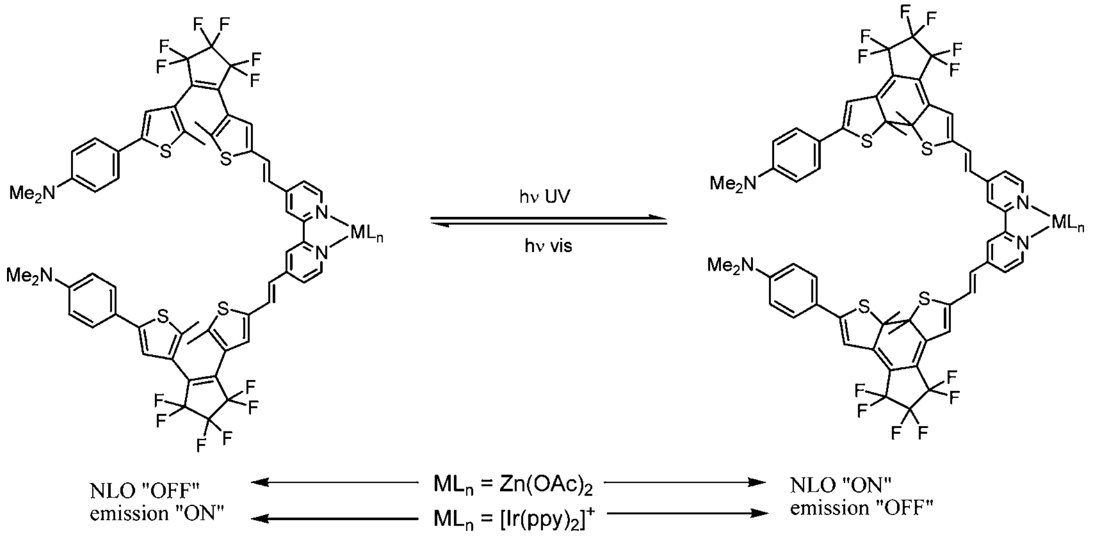
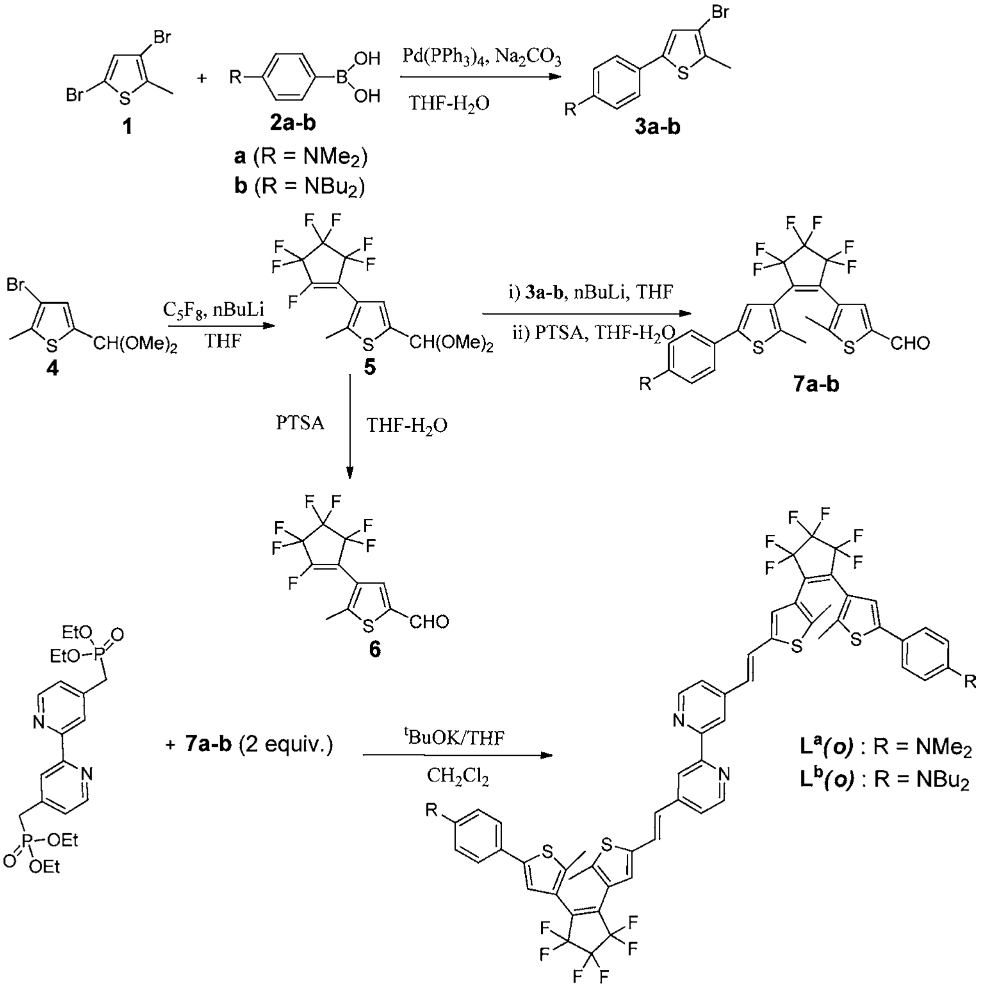
Scheme 1



Scheme 2. Stepwise Synthesis of Photochromic Bipyridyl Ligands



In contrast, by complexation of the same photochromic bipyridine ligand to the luminescent bis-cyclometalated Ir(III) center, an efficient photoregulation of the emission was found, whereas no significant modification of the quadratic NLO response could be observed accompanying photocyclization,[19] due to the weaker contribution of the ILCT vs MLCT transitions to the quadratic hyperpolarizability. These observations prompted us to extend our study to another series of chromophores combining DTE-based bipyridines $L^{a,b}$ (**a**, NMe_2; **b**, NBu_2) with different metallic fragments, namely the stronger Lewis acid $ZnCl_2$ as well as the $Ru(bipy)_2^{2+}$ and $Re(CO)_3Br$ moieties, known for their luminescent properties.

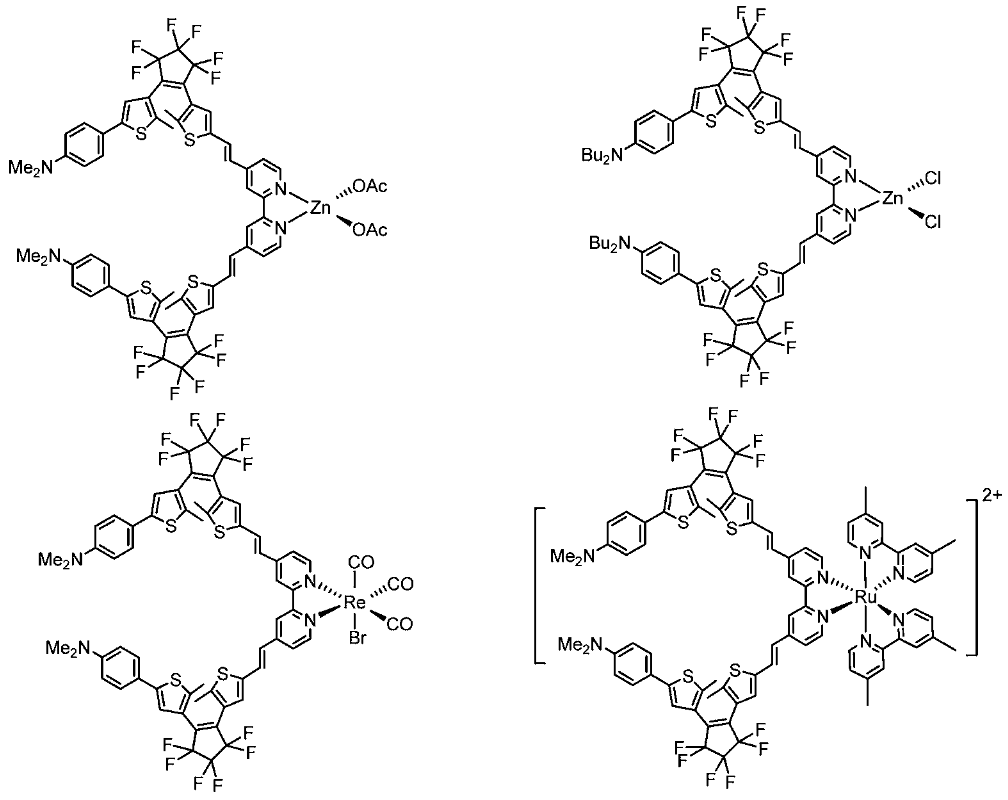


Figure 1. Chemical structures of photochromic bipyridine Zn(II), Re(I), and Ru(II) complexes.

In particular, it was appealing to study the role of the metal center on the photochromic and NLO activity and, in addition, to investigate the photoregulation of the emission properties of the resulting system, as the use of a single photochromic metal complex for photocontrol of both NLO and luminescence properties, which could be of interest for the elaboration of multifunctional molecular materials and hence for optical data storage, has not been reported yet.[15] We describe herein the synthesis, photochromic, and luminescence properties of these complexes, together with the quadratic hyperpolarizability of the open and photocyclized forms, measured by the EFISH and HLS techniques.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Ligands and Complexes. The synthesis of the target bipyridines $\mathbf{L}^{\mathbf{a,b}}(\boldsymbol{o})$ was performed according to Scheme 2. The aryl-substituted DTE aldehydes **7a,b** were first obtained by a multistep procedure: the two thienyl fragments were prepared independently and then successively connected to the perfluorocyclopentene ring. The 3-bromo-2-methyl-5-aryl thiophene compounds **3a,b** were prepared in 75−98% yield by the Suzuki coupling of **1** with the commercially available arylboronic acids **2a,b**. The second thienyl derivative **4**,[3] bearing a protecting dimethylacetal group, was reacted with octafluorocyclopentene (C_5F_8) using a commonly used procedure to afford **5** in 70% yield. Due to partial deprotection of the carbonyl group during the chromatographic workup, the characterization of this synthon was made on the corresponding fully deprotected compound **6**. Reaction of **3a,b** with **5** in the presence of *n*-butyllithium afforded, after subsequent treatment with *p*-toluenesulfonic acid (PTSA) in wet tetrahydrofuran, the desired aldehydes **7a,b** in 50−55% yield. Finally, treatment of diethylphosphonatomethyl-2,2′-bipyridine[17d] with aldehydes **7a,b** under normal Wadsworth-Emmons conditions afforded the target bipyridine ligands $\mathbf{L}^{\mathbf{a,b}}(\boldsymbol{o})$ in 55−60% yield after purification by recrystallization.

$\mathbf{L}^{\mathbf{a,b}}(\boldsymbol{o})$ were characterized by ^{1}H and ^{13}C NMR, UV−visible spectroscopy, and high-resolution mass spectrometry and gave satisfactory elemental analysis. The ^{1}H NMR spectra display classical chemical shifts for the vinyl-bipyridine protons with a $^3J_{\mathrm{H-H}}$ vinylic coupling constant of ca. 16 Hz typical for an *E* configuration about the double bond. The DTE moieties exhibit two very close resonance signals for the methyl protons at ca. 2 ppm and two singlets for the methine protons of the thiophene rings, as expected for the asymmetrical nature of this fragment. Ligands $\mathbf{L}^{\mathbf{a,b}}(\boldsymbol{o})$ show good transparencies in the visible region, whatever the nature of the R group: the UV−visible spectra in dichloromethane show an intense absorption at 340−350 nm which is tentatively assigned to (IL) $\pi \rightarrow \pi^*$ transitions of the bipyridyl moieties with some mixing of the DTE units.

The corresponding Zn(II) complexes $(\mathbf{L}^{\mathbf{a}}(\boldsymbol{o}))\mathrm{Zn(OAc)_2}$ and $(\mathbf{L}^{\mathbf{a,b}}(\boldsymbol{o}))\mathrm{ZnCl_2}$ (Figure 1) were readily obtained after room-temperature treatment of $\mathbf{L}^{\mathbf{a,b}}(\boldsymbol{o})$ with 1 equiv of zinc diacetate dihydrate or zinc dichloride in dichloromethane. Reaction of $\mathbf{L}^{\mathbf{a}}(\boldsymbol{o})$ with $\mathrm{Re(CO)_5Br}$ in refluxing anhydrous toluene afforded *fac*-$(\mathbf{L}^{\mathbf{a}}(\boldsymbol{o}))\mathrm{Re(CO)_3Br}$ as brown crystals in 82% yield. The ruthenium complex $[(\mathbf{L}^{\mathbf{a}}(\boldsymbol{o}))(\mathrm{dmbipy})_2\mathrm{Ru}](\mathrm{PF_6})_2$ (dmbipy = 4,4′-dimethyl-2,2′-bipyridine) was obtained in 60% yield from the corresponding *cis*-$(\mathrm{dmbipy})_2\mathrm{RuCl_2}$ upon treatment first with 2 equiv of silver triflate in methanol and then reaction with ligand $\mathbf{L}^{\mathbf{a}}(\boldsymbol{o})$ in dichloromethane at room temperature, followed by anion exchange from triflate with hexafluorophosphate. The complexes $(\mathbf{L}^{\mathbf{a}}(\boldsymbol{o}))\mathrm{Zn(OAc)_2}$, $(\mathbf{L}^{\mathbf{b}}(\boldsymbol{o}))\mathrm{ZnCl_2}$, $(\mathbf{L}^{\mathbf{a}}(\boldsymbol{o}))\mathrm{Re(CO)_3Br}$, and $[(\mathbf{L}^{\mathbf{a}}(\boldsymbol{o}))(\mathrm{dmbipy})_2\mathrm{Ru}](\mathrm{PF_6})_2$ are soluble in chlorinated solvents (CH_2Cl_2, $CHCl_3$) and were fully characterized by means of ^{1}H and ^{13}C NMR and UV−visible spectroscopy and gave satisfactory microanalyses (see the Experimental Section). Conversely, the very low solubility of $(\mathbf{L}^{a}(\boldsymbol{o}))\mathrm{ZnCl}_2$, bearing the dimethylamino end group, prevented its complete spectroscopic characterization or further photochromic and NLO studies. In all cases, that the *E* configuration of the double bond is retained upon complexation of the ligand is clearly established on the basis of the large olefinic protons coupling constant ($^3J_{\mathrm{H-H}} \approx 16$ Hz), showing that there is no isomerization of the C═C linker.

The UV−visible spectra of the zinc complexes (in CH_2Cl_2) all show an intense band around 360 nm similar to that of the ligands, which is slightly red-shifted by complexation (Table 1).

Table 1. Electronic Absorption Data for Ligands and Complexes in the Open and Closed (PSS) forms, Emission Data in the Open Form, and Percentage Conversion at Photostationary State

compd	λ_{abs}/nm (ε/M^{-1} cm^{-1})^a open	λ_{abs}/nm^a closed (PSS)	λ_{em}/nm (τ/μs)^b open	ring closing/%^{c}
$\mathbf{L}^{a}$^{d}	348 (89 000)	347, 395, 438, **669**		95
$\mathbf{L}^{a}$	346 (76 300)	339, 400, 441, **679**		95
$(\mathbf{L}^{a})\mathrm{Zn(OAc)}_2$^{d}	360 (76 000)	343, 394, 450, **687**		90
$(\mathbf{L}^{b})\mathrm{ZnCl}_2$	351 (53 000)	342, 390 (sh), 463, **714**		85
$(\mathbf{L}^{a})\mathrm{Re(CO)}_3\mathrm{Br}$	340 (110 000), 380 (sh), 410 (sh)	336, 387, 443, **705**	652, 725 (22)	65
$[(\mathbf{L}^{a})(\mathrm{dmbipy})_2\mathrm{Ru}](\mathrm{PF}_6)_2$	338 (78 000), 377 (sh), 491 (27 000)	336, 387, 443 (sh), **716**	680, 753 (13)	62

[a] At 298 K in CH_2Cl_2. [b] At 77 K in diethyl ether/isopentane/ethanol (2/2/1, v/v). [c] Determined by ^{1}H NMR spectroscopy. [d] From ref 18.

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

Photochromic Properties of Ligands and Complexes. For each ligand and complex, the photocyclization process was monitored by ^{1}H NMR and UV−vis spectroscopy in dichloromethane. We have already described the photochromic behavior of ligand $\mathbf{L}^{a}$ and its zinc diacetato complex,[18,20] which undergo ring closure of both DTE units. Similarly, upon irradiation at 350 nm, the yellow solutions of $\mathbf{L}^{b}(\boldsymbol{o})$ and $(\mathbf{L}^{b}(\boldsymbol{o}))\mathrm{ZnCl}_2$ turn green, with the emergence of a new broad bands at 679 and 714 nm, respectively, attributed to the intraligand (IL) S_0 → S_1 transition of the closed DTE form. Their ^{1}H NMR spectra show the characteristic downfield shift of the methyl signals by ca. 0.2 ppm and an upfield shift by ca. 0.5−0.6 ppm of the two thiophene protons. According to ^{1}H NMR analysis, integration of the methyl groups indicates a photocyclization yield of 95% and 85% for $\mathbf{L}^{b}(\boldsymbol{o})$ and $(\mathbf{L}^{b}(\boldsymbol{o}))\mathrm{ZnCl}_2$, respectively, showing that complexation to the Zn(II) ion does not perturb the photochromic properties of $\mathbf{L}^{b}$. We only notice a much slower conversion rate for the zinc complex as compared to the free ligand (the irradiation time, under our experimental conditions, to achieve the PSS is 600 s for $\mathbf{L}^{a}$, 1500 s for $(\mathbf{L}^{a})\mathrm{Zn(OAc)}_2$, 1500 s for $\mathbf{L}^{b}$, and 2500 s for $(\mathbf{L}^{b})\mathrm{ZnCl}_2$[20]). As shown in Table 1, the absorption maxima of the closed-ring forms are dependent on the nature of the donor groups and metallic fragments. Replacement of NMe_2 with the more strongly donating NBu_2 end group induces a small red shift ($\Delta\lambda$ = 10 nm) of the IL band, and complexation to $ZnCl_2$ induces a much larger bathochromic shift ($\Delta\lambda$= 35 nm) than for $\mathrm{Zn(OAc)}_2$, in agreement with the higher Lewis acidity of $ZnCl_2$ vs $\mathrm{Zn(OAc)}_2$.

Photocyclizations of $(\mathbf{L}^{a}(\boldsymbol{o}))\mathrm{Re(CO)}_3\mathrm{Br}$ and $[(\mathbf{L}^{a}(\boldsymbol{o}))(\mathrm{dmbipy})_2\mathrm{Ru}](\mathrm{PF}_6)_2$ are also accomplished by irradiation with UV light at 350 nm, giving rise to lower-energy absorptions at 705 and 716 nm, respectively, corresponding to the ring-closed isomers (Figure 2). Thus, a substantial bathochromic shift of the IL band ($\Delta\lambda$ = 36−47 nm) is also observed upon complexation of $\mathbf{L}^{a}$ to the Re(I) and Ru(II) organometallic fragments. The ratio of the methyl signals between the closed and open DTE units (ring closing) in the photostationary states (PSS) is lower (60−65%) than those found for the zinc(II) complexes according to ^{1}H NMR.[21] It is

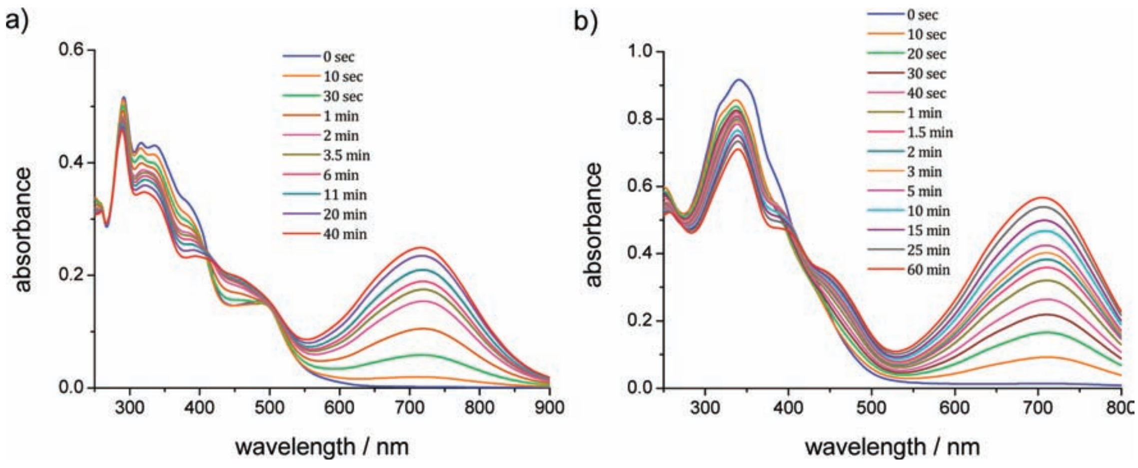


Figure 2. UV−vis absorption spectra changes of (a) $[(\mathbf{L}^{a})(\mathrm{dmbipy})_2\mathrm{Ru}](\mathrm{PF}_6)_2$ and (b) $(\mathbf{L}^{a})\mathrm{Re(CO)}_3\mathrm{Br}$ in dichloromethane upon excitation at 350 nm.

also interesting to note that the photochromic reaction can be triggered by irradiation of the rhenium and ruthenium complexes into the low-energy MLCT bands at 400 and 490 nm, respectively. This MLCT photosensitization has been previously established for a cyclometalated iridium(III) complex containing a similar DTE-based bipyridine ligand and suggests the intermediacy of the triplet state ^{3}IL(DTE) in the photocyclization process.[10a] Finally, for all ligands and 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.

Nonlinear Optical Properties. The second-order NLO responses of the new, neutral, dipolar zinc and rhenium complexes were determined in CH_2Cl_2 (concentration 10^{-3} M) by the EFISH technique, working with an incident wavelength of 1.91 μm. The EFISH $\mu\beta_{1.91}$ values, before and after UV irradiation, are reported in Table 2, along with that previously reported[18] for $(\mathbf{L}^a)Zn(OAc)_2$. The static $\mu\beta_0$ values extrapolated at zero frequency were calculated by using the two-level model.[22] As evidenced in Table 2, the EFISH $\mu\beta_{1.91}$ values of $(\mathbf{L}^b\boldsymbol{(o)})ZnCl_2$ and $(\mathbf{L}^a\boldsymbol{(o)})Re(CO)_3Br$ are very weak and quite similar to that of $(\mathbf{L}^a\boldsymbol{(o)})Zn(OAc)_2$, 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 $(\mathbf{L}^b)ZnCl_2$ the second-order NLO response is increased almost 14-fold after only 35% of ring closing, while a 21-fold enhancement is observed after 65% of ring closing which consists mainly of a mixture of open−closed and closed−closed isomers in a ca. 2:1 ratio.[23] Furthermore, it is also interesting to note that this latter EFISH $\mu\beta_0$ value is even higher than that previously reported for $(\mathbf{L}^a)Zn(OAc)_2$ in the PSS (90% of ring closing), as expected from the higher Lewis acidity of $ZnCl_2$ vs $Zn(OAc)_2$. A similar, but somewhat less dramatic, behavior is observed for the rhenium(I) complex, with an increase of $\mu\beta_0$ from 187 × 10^{-48} to 1148 × 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[24] and could 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.

Table 2. EFISH $\mu\beta$ Values Determined at λ_{inc} 1910 nm of Zn(II) and Re(I) Complexes in CH_2Cl_2

	EFISH^a open		EFISH^a after UV irr		
compd	$\mu\beta_{1.91}$^{a,b}	$\mu\beta_0$^{a,b}	$\mu\beta_{1.91}$^{a,c}	$\mu\beta_0$^{a,c}	ring closing/%^{d}
$(\mathbf{L}^a)Zn(OAc)_2$^{e}	200	160	4220	1800	90
$(\mathbf{L}^b)ZnCl_2$	113	105	3850	1460	35
			5650	2143	65
$(\mathbf{L}^a)Re(CO)_3Br$	240	187^f	2920	1148	65

^{a}In units of 10^{-48} esu. ^{b}Error ±20%. ^{c}Error ±5%. ^{d}Determined by ^{1}H NMR spectroscopy. ^{e}From ref 18. ^{f}calculated by using the two-level model and λ_{MLCT} value

The large enhancement of $\mu\beta_0$ 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 intraligand (IL) transition which dominates the second-order NLO response. This efficient on/off switching markedly contrasts with the absence of switching of the NLO response observed for the cyclometalated phenylpyridine Ir(III) complex featuring the same photochromic bipyridyl ligand $\mathbf{L}^a$ (Scheme 1), in which the EFISH response was found to be mainly controlled by a MLCT/L′LCT process from the cyclometalated phenylpyridine Ir(III) moiety to the π^* orbitals of the bipyridine, and not by an intraligand transition.[19]

The harmonic light scattering (HLS) technique was also used for the molecular first-hyperpolarizability β measurements of the dicationic ruthenium complex and for comparison of the neutral Re complex. Unlike EFISH, HLS can be used also for ionic molecular species and for nondipolar molecules such as octupolar molecules. The measurements were performed in dichloromethane at a fundamental wavelength of 1.91 μm, and the values of $\langle\beta_{1.91}\rangle$ and static hyperpolarizabilities $\langle\beta_0\rangle$[25] are given in Table 3. Much attention has been given to the large β responses of bipyridine ruthenium chromophores, such as octupolar D_3 tris-chelate ruthenium complexes, which are dominated by low-lying ILCT or MLCT excitations, depending on the electron-donating or -accepting nature of the substituents on the bipyridyl ligands.[17,26] It turned out that $[(\mathbf{L}^a)(dmbipy)_2Ru](PF_6)_2$ in its open form also shows a fairly large $\langle\beta\rangle$ value, larger than that of the rhenium complex, which can be reasonably attributed to low-energy MLCT $d\pi(Ru) \rightarrow \pi^*(bipy)$ transitions. Upon photocyclization of the DTE, $\langle\beta_0\rangle$ is found to increase by a factor of ca. 2, a result which is consistent with an NLO response mainly controlled by the red-shifted IL transition.

Table 3. β_{HLS} Values of Re(I) and Ru(II) in CH_2Cl_2

	HLS open		HLS after UV irr		
compd	$\langle\beta_{1.91}\rangle^{a,b}$	$\langle\beta_0\rangle^{a,b}$	$\langle\beta_{1.91}\rangle^{a,b}$	$\langle\beta_0\rangle^{a,b}$	ring closing/%
$(\mathbf{L}^a)Re(CO)_3Br$	229	178^c	965	380^d	65
$[(\mathbf{L}^a)Ru(dmbipy)_2](PF_6)_2$	325	223^c	1113	419^d	62

^{a}In units of 10^{-30} esu. ^{b}Error ±15%. ^{c}Calculated by using the two-level model and λ_{MLCT} values. ^{d}Calculated by using the two-level model and $\lambda_{IL(DTE)}$ values.

Luminescent Properties. None of the ligands and complexes display detectable luminescence in solution at room temperature when excited in the UV or visible bands. This behavior contrasts with that of the DTE-free counterparts: the free and Zn complexed 4-(dimethylamino)styrylbipyridine ligands are emissive at room temperature in fluid solutions.[17d] It is likely that the luminescence is inhibited by the competitive photocyclization pathway of the DTE unit. The rate constant for cyclization at room temperature will greatly exceed the rather slow radiative rate constant of the triplet state (typically around 10^5 s^{-1} for Ru and Re complexes). In frozen glasses upon UV irradiation, we do not observe by UV−vis spectroscopy any formation of closed-DTE species. As the photocyclization is inhibited under these experimental conditions, this allows the phosphorescence process to compete effectively. At 77 K (EPA), only the rhenium and ruthenium

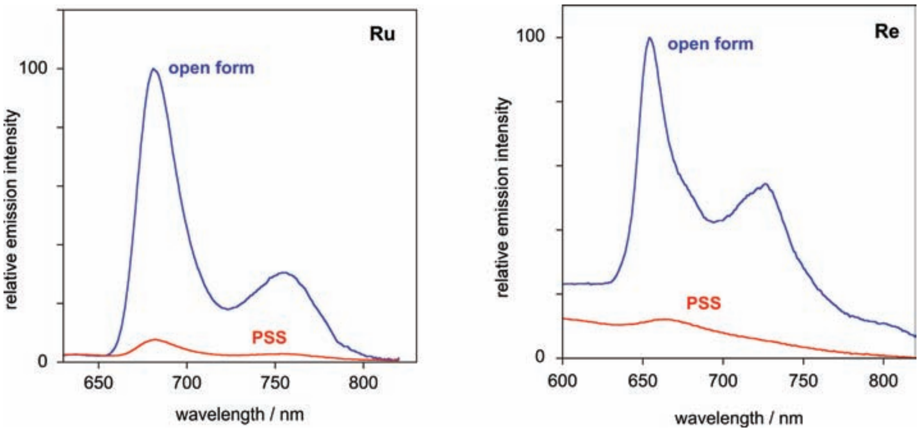


Figure 3. (left) Emission spectrum of $[(\mathbf{L}^a(\boldsymbol{o}))(\text{dmbipy})_2\text{Ru}](\text{PF}_6)_2$ at 77 K in diethyl ether/isopentane/ethanol (2/2/1 v/v) (blue line) upon excitation into the lowest energy absorption band (490 nm) and the corresponding spectrum recorded for the photostationary state (red line). (right) Corresponding spectra of $(\mathbf{L}^a(\boldsymbol{o}))\text{Re}(\text{CO})_3\text{Br}$ and its PSS.

complexes emit, displaying structured luminescence spectra with vibronic progressions of 1400−1500 cm^{-1}, typical of aromatic and/or C═C bond vibrations. The emission characteristics are summarized in Table 1, and the emission spectra of $(\mathbf{L}^a(\boldsymbol{o}))\text{Re}(\text{CO})_3\text{Br}$ and $[(\mathbf{L}^a(\boldsymbol{o}))(\text{dmbipy})_2\text{Ru}](\text{PF}_6)_2$ and their PSS are shown in Figure 3. The long lifetimes (22 and 13 μs for the Re and Ru complexes, respectively), low energy, and structured spectra are indicative of emission from a triplet state predominantly localized on the bpy−C═C−Ar moiety, rather than from the MLCT state.

Following conversion of solutions of $(\mathbf{L}^a(\boldsymbol{o}))\text{Re}(\text{CO})_3\text{Br}$ and $[(\mathbf{L}^a(\boldsymbol{o}))(\text{dmbipy})_2\text{Ru}](\text{PF}_6)_2$ to the PSS at room temperature and refreezing to 77 K, a substantial reduction of the 77 K luminescence is observed (Figure 3). 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 chromophores ($\lambda_{\text{max}}{}^{\text{em}}$ 652 and 680 nm, respectively) with the low-energy absorption band of the acceptor photochromic unit in its closed form ($\lambda_{\text{max}}{}^{\text{abs}}$ 725 and 753 nm). A similar quenching of the luminescence upon DTE closure was observed in the previously mentioned cyclometalated iridium complex featuring the same photochromic ligand.[19]

■ CONCLUSION

We have presented in this work a full investigation of the synthesis, characterization, and linear and nonlinear optical properties of a series of Zn(II), Re(I), and Ru(II) complexes which incorporate the DTE photochromic unit into the bipyridine ligand. We have demonstrated that, like the free DTE-containing bipyridyl ligands, the corresponding complexes undergo reversible ring-closure reactions under light irradiation, with photocyclization yields ranging from 62 to 90%. The combination of the photochromic DTE-based bipyridine ligand **L** with luminescent Re and Ru organometallic fragments allows the photoregulation of the emission and NLO properties of the resulting system. This study demonstrates for the first time that the photocontrol of two optical properties, linear and nonlinear, could be achieved by using the same photochromic ligand.

■ EXPERIMENTAL SECTION

General Information. All manipulations were performed using Schlenk techniques under an Ar atmosphere. All solvents were dried and purified by standard procedures. Spectroscopic grade dichloromethane was used for all optical measurements. Compound **4** was prepared according to a reported procedure, namely by bromination of 5-methyl-thiophene-2-carboxaldehyde, and was subsequently converted into its dimethyl acetal **4**-$(\text{OMe})_2$ for further use.[3] NMR spectra were recorded on Bruker DPX 200, AV 300, and AV 500 MHz spectrometers. ^{1}H and ^{13}C chemical shifts are given versus SiMe_4 and were determined by reference to residual ^{1}H and ^{13}C solvent signals. Attribution of carbon atoms was based on HMBC, HMQC, and COSY experiments. High-resolution mass spectra (HRMS) were performed on a MS/MS ZABSpec TOF at the CRMPO (Centre de Mesures Physiques de l'Ouest) in Rennes. Elemental analyses were performed at the CRMPO.

Optical Spectroscopy. UV−vis irradiations were performed either with a Rayonet RPR 100 photochemical reactor equipped with 16 RPR 3500 Å lamps or with a LS series Light Source of ABET Technologies, Inc. (150 W xenon lamp), with "350FS 10-25", "450FS 20-25", and "650FS 10-25" single-wavelength light filters. UV/vis absorption spectra were recorded using a UVIKON 9413 or Biotek Instruments XS spectrophotometer using quartz cuvettes of 1 cm path length (spectroscopic grade dichloromethane was used for all optical measurements). Steady-state luminescence spectra were measured using a Jobin Yvon FluoroMax-2 spectrofluorimeter, fitted with a red-sensitive Hamamatsu R928 photomultiplier tube. The spectra shown are corrected for the wavelength dependence of the detector, and the quoted emission maxima refer to the values after correction. Lifetimes were obtained by multichannel scaling following excitation with a microsecond-pulsed xenon lamp and detection of the light emitted at right angles using an R928 photomultiplier tube, after passage through a monochromator.

Second-Order NLO Properties. *EFISH Measurements.* The molecular quadratic hyperpolarizabilities were measured by the solution-phase dc electric field induced second harmonic (EFISH) generation method, which can provide direct information on the

$$\gamma_{\text{EFISH}} = (\mu\beta_\lambda/5kT) + \gamma(-2\omega;\, \omega,\, \omega,\, 0) \qquad (1)$$

intrinsic molecular NLO properties through eq 1, [22]where $\mu\beta_\lambda/5kT$ is the dipolar orientational contribution and $\gamma(-2\omega;\omega,\omega,0)$, a third-order term corresponding to the mixing of two optical fields at ω and of the DC poling field at $\omega = 0$, is the electronic cubic contribution to γ_{EFISH} ,which is usually negligible with respect to $\mu\beta_\lambda/5kT$. β_λ is the projection along the dipole moment axis of the vectorial component of the tensor of the quadratic hyperpolarizability, working with an incident wavelength λ. All EFISH measurements were carried out in CH_2Cl_2 solutions at a concentration of 1×10^{-3} M, working with a nonresonant incident wavelength of 1.907 μm.

HLS Measurements. The HLS technique[27,28] involves the detection of the incoherently scattered second harmonic light generated by a solution of the molecule under irradiation with a laser of wavelength λ, leading to the measurement of the mean value of the $\beta \times \beta$ tensor product, $\langle \beta_{HLS} \rangle$. All HLS measurements were carried out in CH_2Cl_2 solution at a concentration of 1×10^{-3} M, working with a low-energy, nonresonant incident radiation of 1.91 μm. The 1.91 μm fundamental beam was emitted by a high-pressure (30 bar), 50 cm long Raman cell pumped by a Nd^{3+}:YAG laser operating at 1.06 μm and providing a 10 Hz repetition rate, with pulses of 15 ns duration. Only the backscattered 1.91 μm Raman emission was collected by use of a dichroic mirror, in order to eliminate most of the residual 1.06 μm pump photons. Our reference sample was a concentrated (10^{-3} M) solution of ethyl violet, its β value being calibrated at 1.91 μm with respect to that of the *N*-4-nitrophenylprolinol (NPP) reference dipolar molecule, leading to $\beta = 170 \times 10^{-30}$ esu for ethyl violet at 1.91 μm. The HLS photons at 955 nm were focused onto the photomultiplier tube using two collecting lenses (we used a Hamamatsu R632-01 photomultiplier tube). The signal detected was then sampled and averaged using a boxcar and processed by a computer. The reference beam was collected at a 45° incidence angle by a glass plate and focused onto a highly nonlinear NPP powder, which was used as the frequency doubler. The variation of the scattered second harmonic intensity from the solution was recorded on the computer as a function of the reference second harmonic signal provided by the NPP powder, which scales as the square of the incoming fundamental intensity. Values for β were then inferred from the slopes of the resulting lines. The dispersion-free hyperpolarizabilities β_0 are inferred from experimental ones using a two-level dispersion model according to ref 22.

Synthesis. *3-Bromo-2-methyl-5-(p-dimethylaminophenyl)-thiophene (**3a**).* In a Schlenk flask, the boronic acid **2a** (1.66 g, 10 mmol) and 3,5-dibromo-2-methylthiophene **1** (3.86 g, 15 mmol) were added to a solution of Na_2CO_3 (8 g, 75 mmol) and $Pd(PPh_3)_4$ (0.58 g, 0.5 mmol) in H_2O/THF (40 mL/40 mL). The reaction mixture was refluxed overnight. The resultant mixture was extracted into 2 × 25 mL of chloroform. The organic layer was first washed with an aqueous solution of NaCl and then with water (25 mL) and finally dried over magnesium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (pentane/dichloromethane, 75/25) to give **3a** as a white powder (2.2 g, 75%). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 7.42 (d, ^3J = 8.7 Hz, 2H, C_6H_4), 7.15 (s, 1H, thio), 6.70 (d, ^3J = 8.7 Hz, 2H, C_6H_4), 3.00 (s, 6H, NMe_2), 2.50 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ (ppm) 150.5, 142.5, 131.7, 126.8, 123.6, 122.4, 112.9, 109.9, 40.9, 15.2. Anal. Calcd for $C_{13}H_{14}BrNS$: C, 52.71; H, 4.76; N, 4.73; S, 10.82. Found: C, 52.88; H, 4.85; N, 4.82; S, 10.41.

*3-Bromo-2-methyl-5-(p-dibutylaminophenyl)thiophene (**3b**).* Following the procedure for **3a**, the title compound **3b** was obtained as a yellow powder (2.4 g, 80%) from the boronic acid **2b** (2 g, 8 mmol), 3,5-dibromo-2-methylthiophene (**1**; 2.7 g, 10.5 mmol), and $Pd(PPh_3)_4$ (0.36 g, 0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 (d, ^3J = 9.0 Hz, 2H, C_6H_4-), 6.92 (s, 1H, thio), 6.64 (d, ^3J = 9.0 Hz, 2H, C_6H_4-), 3.30 (m, 4H, CH_2N), 2.41 (s, 3H, CH_3), 1.60 (m, 4H, CH_2CH_2N), 1.38 (sext, ^3J = 7.6 Hz, 4H, CH_2CH_3), 0.99 (t, ^3J = 7.4 Hz, 6H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ (ppm) 147.8, 142.3, 130.9, 126.5, 122.7, 120.6, 111.6, 109.35, 50.8, 29.4, 20.4, 14.7, 14.0. Anal. Calcd for $C_{19}H_{26}BrNS$: C, 59.99; H, 6.89; N, 3.68; S, 8.43. Found: C, 59.77; H, 6.79; N, 3.85; S, 8.41. HRMS: m/z 380.1041 $[M + H]^+$, calcd for $C_{19}H_{27}NBrS$ 380.1042.

*5-Methyl-4-(perfluorocyclopent-1-enyl)thiophene-2-carbaldehyde (**6**).* ^{n}BuLi (2.4 M in hexane, 15.6 mmol, 6.5 mL) was added dropwise to a stirred solution of **4** (3.00 g, 12 mmol) in 100 mL of THF at −78 °C under a nitrogen atmosphere. After 60 min, the reaction mixture was transferred into a Schlenk tube containing a solution of perfluorocyclopentene (4.8 mL, 36 mmol) in 20 mL of THF. The reaction mixture was stirred for 1 h at −78 °C and then warmed to room temperature and stirred for an additional 16 h. After addition of 200 mL of water, THF was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated in vacuo. The residue was extracted with 50 mL of THF. PTSA (1.2 mmol, 228 mg) and a few drops of water were added. The reaction mixture was stirred for 16 h at 40 °C. After addition of water (100 mL), THF was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated in vacuo, and the residue was chromatographed with silica gel. Elution with a 2/3 dichloromethane/pentane mixture afforded **6** as orange crystals (1.9 g, 50%). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 9.87 (s, 1H, CHO), 7.76 (s, 1H, thio), 2.58 (d, $^6J_{H-F}$ = 3 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ (ppm) 180.1, 151.4, 140.0, 133.8, 119.2, 13.7. Anal. Calcd for $C_{11}H_5OF_7S$: C, 41.52; H, 1.58; S, 10.08. Found: C, 41.27; H, 1.69; S, 10.37. HRMS: m/z 317.9924 $[M]^+$, calcd for $C_{11}H_5F_7O_5S$ 317.9949.

*4-(3,3,4,4,5,5-Hexafluoro-2-(2-methyl-5-N,N-dimethylaminophenylthiophenyl-3)cyclopent-1-enyl)-5-methylthiophene-2-carbaldehyde (**7a**).* To a solution of 3-bromo-2-methyl-5-phenylthiophene **3a** (2.10 g, 7.12 mmol) in 50 mL of THF, which was cooled to −78 °C, was added dropwise ^{n}BuLi (2.32 M in hexane, 4.6 mL, 10.7 mmol). After the reaction mixture was stirred at −78 °C for 1 h, a solution of **5** (2.6 g, 7.12 mmol) in 50 mL of THF was added. After it was stirred at −78 °C for 1 h and at room temperature for 16 h, the reaction mixture was hydrolyzed with water, and the solvent was removed in vacuo. The residue was extracted with CH_2Cl_2 (2 × 30 mL) and then dried over $MgSO_4$. After evaporation of the solvent, the residual orange oil was dissolved in 20 mL of THF, and then PTSA (85 mg, 0.44 mmol) and a few drops of water were added. After the mixture was stirred at 40 °C for 16 h, the solvent was removed and the oil was purified by column chromatography (SiO_2, pentane/ethyl acetate 95/5) to give yellow-green microcrystals (1.80 g, 50%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.88 (s, 1H, CHO), 7.80 (s, 1H, thio), 7.42 (d, ^3J = 8.8 Hz, 2H, C_6H_4-), 7.07 (s, 1H, thio), 6.74 (d, ^3J = 8.8 Hz, 2H, C_6H_4-), 3.02 (s, 6H, NMe_2), 2.08 (s, 3H, Me), 1.93 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (125.77 MHz, $CDCl_3$): δ (ppm) 182.16 (CHO), 152.00, 150.35, 143.81, 141.64, 139.14, 138.14, 136.43, 134.09, 126.74, 126.61, 125.02, 121.30, 119.45, 116.03, 112.45, 111.16, 40.41, 15.49, 14.45. Anal. Calcd for $C_{24}H_{19}NF_6OS_2$: C, 55.91; H, 3.71; N, 2.72; S, 12.44. Found: C, 55.41; H, 3.61; N, 2.70; S, 12.49. HRMS: m/z 515.0813 $[M]^+$, calcd for $C_{24}H_{19}NF_6OS_2$ 515.0812.

*4-(3,3,4,4,5,5-Hexafluoro-2-(2-methyl-5-N,N-dibutylaminophenylthiophen-3-yl)cyclopent-1-enyl)-5-methylthiophene-2-carbaldehyde (**7b**).* Following the procedure for **7a**, the title compound **7b** was obtained as yellow-green microcrystals (0.5 g, 64%) from **3b** (0.5 g, 1.31 mmol), ^{n}BuLi (1.6 M in hexane, 1 mL, 1.57 mmol), and **5** (0.48 g, 1.31 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) 9.88 (s, 1H, CHO), 7.83 (s, 1H, thio), 7.39 (d, ^3J = 9.0 Hz, 2H, C_6H_4-), 7.08 (s, 1H, thio), 6.67 (d, ^3J = 9.0 Hz, 2H, C_6H_4-), 3.34 (m, 4H, CH_2N), 2.11 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 1.62 (m, 4H, CH_2CH_2N), 1.40 (sext, ^3J = 7.5 Hz, 4H, $-CH_2CH_3$), 1.01 (t, ^3J = 7.3 Hz, 6H, $-CH_2CH_3$). $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2): δ (ppm) 182.01, 151.97, 148.19, 144.09, 141.79, 139.03, 144.09, 141.79, 139.03, 136.29, 126.59, 124.89, 119.90, 118.92, 111,67, 50.65, 29.38, 20.26, 15,21, 14.17, 13.70. Anal. Calcd for $C_{30}H_{31}NOF_6S_2$: C, 60.08; H, 5.21; N, 2.34; S, 10.69. Found: C, 60.31; H, 5.34; N, 2.29; S, 10.55. HRMS: m/z 599.1748, $[M]^+$ calcd for $C_{30}H_{31}NOF_6S_2$ 599.1746.

*4,4′-Bis((E)-2-(4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-p-N,N-dimethylaminophenylthiophen-3-yl)cyclopent-1-nyl)-5-methylthiophen-2-yl)vinyl)-2,2′-bipyridine (**L^a(o)**).* A THF solution (25 mL) of **7a** (0.20 g, 0.37 mmol) was added to 4,4′-bis-(diethylphosphonomethyl)-2,2′-bipyridine (0.076 g, 0.17 mmol) and ^{t}BuOK (0.081 g, 0.72 mmol) at 0 °C. The reaction mixture was stirred for 2.5 h at room temperature. After addition of water, the organic layer was washed with brine and water, dried over $MgSO_4$, filtered, and concentrated. Crystallization in a CH_2Cl_2/pentane mixture afforded **L^a** as a green powder (0.15 g, 75%). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 8.66 (d, ^3J = 5 Hz, 2H, Py^6), 8.50 (s, 2H, Py^3), 7.55 (d, ^3J = 16

Hz, 2H, ═CH), 7.40 (d, ^3J = 8.6 Hz, 4H, C_6H_4−), 7.35 (d, ^3J = 5 Hz, 2H, Py^5), 7.20 (s, 2H, thio), 7.10 (s, 2H, thio), 6.82 (d, ^3J = 16 Hz, 2H, ═CH), 6.70 (d, ^3J = 8.6 Hz, 4H, C_6H_4−), 3.00 (s, 12H, NMe$_2$), 2.04 (s, 6H, CH$_3$), 2.03 (s, 6H, CH$_3$). ^{13}C{^{1}H} NMR (125.77 MHz, CDCl$_3$): δ (ppm) 156.43, 150.26, 149.63, 145.06, 143.25, 142.69, 139.59, 139.15, 127.69, 126.58, 126.08, 125.92, 125.56, 125.45, 121.62, 120.75, 119.79, 118.04, 112.48, 40.44, 14.85, 14.48. HRMS: *m/z* 1179.24920 [M + H]$^+$, calcd for $C_{60}H_{47}N_4F_{12}S_4$ 1179.2492. Anal. Calcd for $C_{60}H_{46}F_{12}N_4S_4$: C, 61.11; H, 3.93; N, 4.75; S, 10.88. Found: C, 60.91; H, 4.15; N, 4.56; S, 10.73.

Spectroscopic Data of the Photocyclized L^a(c). ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ (ppm) 8.69 (d, ^3J = 5 Hz, 2H, Py^6), 8.57 (s, 2H, Py^3), 7.54 (d, ^3J = 16 Hz, 2H, ═CH), 7.52 (d, ^3J = 8.6 Hz, 4H, C_6H_4−), 7.40 (d, ^3J = 3.7 Hz, 2H, Py^5), 6.82 (d, ^3J = 16 Hz, 2H, ═CH), 6.73 (d, ^3J = 8.6 Hz, 4H, C_6H_4−), 6.62 (s, 2H, thio), 6.53 (s, 2H, thio), 3.10 (s, 12H, N*Me*$_2$), 2.18 (s, 6H, CH$_3$), 2.16 (s, 6H, CH$_3$).

4,4′-Bis((E)-2-(4-(3,3,4,4,5,5-hexafluoro-2-(2-methyl-5-p-N,N-dibutylaminophenylthiophen-3-yl)cyclopent-1-nyl)-5-methylthiophen-2-yl)vinyl)-2,2′-bipyridine (L^b(o)). To a THF solution at 0 °C (80 mL) of **7b** (0.50 g, 0.83 mmol) and 4,4′-bis(diethylphosphonomethyl)-2,2′-bipyridine (0.173 g, 0.38 mmol) was added ^{t}BuOK (0.17 g, 1.52 mmol). The reaction mixture was then stirred for 5 h at room temperature. After addition of water, the organic layer was washed with brine and water, dried over MgSO$_4$, filtered, and concentrated. Recrystallization in a CH$_2$Cl$_2$/pentane mixture afforded **L^b** as a brown powder (0.425 g, 83%). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ (ppm) 8.67 (d, ^3J = 5 Hz, 2H, Py^6), 8.56 (s, 2H, Py^3), 7.55 (d, ^3J = 16.2 Hz, 2H, ═CH), 7.41 (m, 6H, C_6H_4 + Py^5), 7.23 (s, 2H, thio), 7.11 (s, 2H, thio), 6.92 (d, ^3J = 16.2 Hz, 2H, ═CH), 6.67 (d, ^3J = 9.0 Hz, 4H, C_6H_4−), 3.35 (m, 8H, CH$_2$N), 2.03 (s, 6H, CH$_3$), 1.98 (s, 6H, CH$_3$), 1.61 (quint, ^3J = 7.5 Hz, 8H, CH$_2$CH$_2$−N), 1.40 (sext, ^3J = 7.5 Hz, 8H, −CH$_2$CH$_3$), 0.99 (t, 12H, ^3J = 7.5 Hz, −CH$_2$CH$_3$). ^{13}C{^{1}H} NMR (125.77 MHz, CD$_2$Cl$_2$): δ (ppm) 156.29, 149.50, 148.02, 144.99, 143.56, 142.96, 139.72, 138.95, 127.62, 126.53, 126.07, 125.73, 125.37, 125.27, 120.61, 120.05, 119.15, 117.83, 111.64, 50.63, 29.32, 20.24, 14.59, 14.18, 13.70. HRMS: *m/z* 1346.4312, [M]$^+$ calcd for $C_{72}H_{70}N_4F_{12}S_4$ 1346.4292. Anal. Calcd for $C_{72}H_{70}F_{12}N_4S_4\cdot0.5CH_2Cl_2$: C, 62.64; H, 5.15; N, 4.03; S, 9.23. Found: C, 62.38; H, 5.06; N, 4.12; S, 8.98.

Spectroscopic Data of the Photocyclized L^b(c). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ (ppm) 8.70 (d, ^3J = 5.0 Hz, 2H, Py^6), 8.59 (s, 2H, Py^3), 7.50 (m, 6H, ═CH + C_6H_4−), 7.41 (d, ^3J = 6.0 Hz, 2H, Py^5), 6.79 (d, ^3J = 15.5 Hz, 2H, ═CH), 6.69 (d, ^3J = 9.0 Hz, 4H, C_6H_4−), 6.60 (s, 2H, thio), 6.54 (s, 2H, thio), 3.39 (m, 8H, CH$_2$N), 2.17 (s, 6H, CH$_3$), 2.16 (s, 6H, CH$_3$), 1.64 (m, 8H, C*H*$_2$CH$_2$N), 1.42 (m, 8H, −C*H*$_2$CH$_3$), 1.01 (t, ^3J = 7.0 Hz, 12H, −CH$_2$C*H*$_3$).

(L^a(o))Zn(OAc)$_2$. To a CH$_2$Cl$_2$ solution (40 mL) of **L^a** (0.322 g, 0.27 mmol) was added Zn(OAc)$_2$·2H$_2$O (0.060 g, 0.27 mmol). The reaction mixture was stirred for 16 h at room temperature. The solvent was then evaporated, and crystallization of the residue in a CH$_2$Cl$_2$/pentane mixture afforded a brown powder (0.35 g, 95%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 8.75 (br d, 2H, Py^6), 8.24 (s, 2H, Py^3), 7.62 (d, ^3J = 16 Hz, 2H, ═CH), 7.52 (s, 2H, Py^5), 7.46 (d, ^3J = 8 Hz, 4H, C_6H_4−), 7.35 (s, 2H, thio), 7.15 (s, 2H, thio), 6.84 (d, ^3J = 16 Hz, 2H, ═CH), 6.73 (d, ^3J = 8 Hz, 4H, C_6H_4−), 3.00 (s, 12H, N*Me*$_2$), 2.07 (s, 6H, CH$_3$), 2.05 (s, 6H, CH$_3$), 2.03 (s, 6H, OC(O)C*H*$_3$). ^{13}C{^{1}H} NMR (75 MHz, CD$_2$Cl$_2$): δ (ppm) 180.0, 150.4, 149.6, 144.6, 143.5, 139.3, 138.9, 129.4, 128.7, 126.4, 126.1, 125.3, 123.8, 122.8, 121.1, 119.5, 117.9, 112.3, 40.11, 21.8, 14.8, 14.3. Anal. Calcd for $C_{64}H_{52}F_{12}N_4O_4S_4Zn\cdot H_2O$: C, 55.67; H, 3.94; N, 4.06; S, 9.41. Found: C, 55.47; H, 3.87; N, 3.85; S, 9.32.

Spectroscopic Data of the Photocyclized (L^a(c))Zn(OAc)$_2$. ^{1}H NMR (200 MHz, CDCl$_3$): δ (ppm) 8.91 (br d, 2H, Py^6), 8.16 (s, 2H, Py^3), 7.63 (s, 2H, Py^5), 7.58 (d, ^3J = 16 Hz, 2H, ═CH), 7.51 (d, ^3J = 8 Hz, 4H, C_6H_4−), 6.70 (d, ^3J = 8 Hz, 4H, C_6H_4−), 6.68 (d, ^3J = 16 Hz, 2H, ═CH), 6.63 (s, 2H, thio), 6.60 (s, 2H, thio), 3.10 (s, 12H, NMe$_2$), 2.17 (s, 6H, Me), 2.16 (s, 6H, Me), 2.10 (s, 6H, OC(O)CH$_3$).

(L^b(o))ZnCl$_2$. To a CH$_2$Cl$_2$ solution (20 mL) of **L^b** (0.130 g, 0.096 mmol) was added ZnCl$_2$ (0.013 g, 0.095 mmol). The reaction mixture was stirred for 16 h at room temperature. The solvent was then evaporated, and the residue was successively washed with pentane and diethyl ether to afford a black powder (0.125 g, 89%). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ (ppm) 8.71 (d, ^3J = 5.5 Hz, 2H, Py^6), 8.29 (s, 2H, Py^3), 7.75 (d, ^3J = 5.5 Hz, 2H, Py^5), 7.70 (d, ^3J = 16.0 Hz, 2H, ═CH), 7.41 (d, ^3J = 8.8 Hz, 4H, C_6H_4−), 7.38 (s, 2H, thio), 7.11 (s, 2H, thio), 6.95 (d, ^3J = 16.0 Hz, 2H, ═CH), 6.67 (d, ^3J = 8.8 Hz, 4H, C_6H_4−), 3.33 (m, 8H, CH$_2$N), 2.08 (s, 6H, CH$_3$), 2.00 (s, 6H, CH$_3$), 1.61 (m, 8H, C*H*$_2$CH$_2$N), 1.39 (sext, ^3J = 7.6 Hz, 8H, −C*H*$_2$CH$_3$), 0.99 (t, ^3J = 7.3 Hz, 12H, −CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (125.77 MHz, CD$_2$Cl$_2$): δ (ppm) 149.73, 149.21, 148.84, 148.11, 145.15, 143.80, 139.00, 138.57, 129.96, 129.76, 126.58, 126.32, 125.19, 123.40, 123.15, 119.95, 119.06, 118.41, 111.64, 50.66, 29.68, 20.25, 14.82, 14.30, 13.73. Anal. Calcd for $C_{72}H_{70}N_4F_{12}S_4ZnCl_2\cdot CH_2Cl_2$: C, 55.89; H, 4.63; N, 3.57; S, 8.18. Found: C, 55.58; H, 4.48; N, 3.65; S, 8.03.

Spectroscopic Data of the Photocyclized (L^b(c))ZnCl$_2$. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ (ppm) 8.74 (d, ^3J = 5.5 Hz, 2H, Py^6), 8.29 (s, 2H, Py^3), 7.76 (d, ^3J = 4.7 Hz, 2H, Py^5), 7.63 (d, ^3J = 15.8 Hz, 2H, ═CH), 7.52 (d, ^3J = 8.9 Hz, 4H, C_6H_4−), 6.77 (d, ^3J = 15.9 Hz, 2H, ═CH), 6.70 (d, ^3J = 8.9 Hz, 4H, C_6H_4−), 6.68 (s, 2H, thio), 6.64 (s, 2H, thio), 3.41 (m, 8H, C*H*$_2$N), 2.21 (s, 6H, CH$_3$), 2.18 (s, 6H, CH$_3$), 1.63 (m, 8H, C*H*$_2$CH$_2$N), 1.41 (sext, ^3J = 7.4 Hz, 8H, −C*H*$_2$CH$_3$), 1.02 (t, ^3J = 7.3 Hz, 12H, −CH$_2$C*H*$_3$).

(L^a(o))Re(CO)$_3$Br. In a Schlenk tube, under an argon atmosphere, Re(CO)$_5$Br (0.71 g, 0.176 mmol) and **L^a** (0.210 g, 0.178 mmol) were dissolved in toluene (20 mL) and refluxed at 110 °C overnight in the dark. The solvent was evaporated, and the resulting dark yellow residue was dissolved in CH$_2$Cl$_2$. After filtration through Celite, crystallization in CH$_2$Cl$_2$/pentane mixture afforded a brown powder (220 mg, 82% yield). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ (ppm) 8.80 (d, ^3J = 5.7 Hz, 2H, Py^6), 8.26 (s, 2H, Py^3), 7.56 (d, ^3J = 16 Hz, 2H, ═CH), 7.47 (d, ^3J = 8.9 Hz, 4H, C_6H_4−), 7.41 (s, 2H, thio), 7.29 (m, 2H, Py^5), 7.16 (s, 2H, thio), 6.74 (d, ^3J = 8.9 Hz, 4H, C_6H_4−), 6.66 (d, ^3J = 16 Hz, 2H, ═CH), 2.99 (s, 12H, NMe$_2$), 2.14 (s, 6H, CH$_3$), 2.09 (s, 6H, CH$_3$). ^{13}C{^{1}H} NMR (125.77 MHz, CD$_2$Cl$_2$): δ (ppm) 197.27, 189.39, 155.99, 152.12, 150.39, 147.31, 145.26, 143.53, 139.24, 138.91, 129.73, 129.39, 126.44, 125.34, 123.13, 123.02, 121.21, 119.90, 119.78, 112.30, 40.08, 14.81, 14.32. HRMS: *m/z* 1526.1040 [M]$^+$, calcd for $C_{63}H_{46}N_4O_3F_{12}{}^{79}BrS_4{}^{185}Re$ 1526.097 43; *m/z* 1498.1085 [M − CO]$^+$, calcd for $C_{62}H_{46}N_4O_2F_{12}{}^{79}BrS_4{}^{185}Re$ 1498.102 52. Anal. Calcd for $C_{63}H_{46}BrF_{12}N_4O_3ReS_4\cdot0.5CH_2Cl_2$: C, 48.52; H, 3.01; N, 3.56; S, 8.16. Found: C, 48.50; H, 3.09; N, 3.49; S, 8.16.

Spectroscopic Data of the Photocyclized (L^a(c))Re(CO)$_3$Br. ^{1}H NMR 400 MHz (CD$_2$Cl$_2$): δ (ppm) 8.90 (d, ^3J = 5.7 Hz, 2H, Py^6), 8.30 (s, 2H, Py^3), 7.64 (d, ^3J = 16 Hz, 2H, ═CH), 7.56 (d, ^3J = 8.9 Hz, 4H, C_6H_4−), 7.38 (d, ^3J = 6.4 Hz, 2H, Py^5), 6.75 (m, 6H, C_6H_4− + ═CH), 6.74 (s, 2H, thio), 6.67 (s, 2H, thio), 3.12 (s, 12H, NMe$_2$), 2.23 (s, 6H, CH$_3$), 2.22 (s, 6H, CH$_3$).

[(L^a(o))(dmbipy)$_2$Ru](PF$_6$)$_2$. In a Schlenk tube, under an argon atmosphere, AgOTf (54 mg, 0.21 mmol) and Ru(4,4′-diMe-2,2′-bpy)$_2$Cl$_2$ (55.7 mg, 0.103 mmol) were dissolved in MeOH (8 mL) for 5 h at room temperature in the dark. To the resulting red solution were added **L^a** (120 mg, 0.102 mmol) and CH$_2$Cl$_2$ (8 mL). After the mixture was stirred overnight at room temperature in the dark, a large excess of NaPF$_6$ was added, this mixture was stirred for 6 h, and then the solvent was evaporated. The residue was suspended in the mixture of EtOH (5 mL) and H$_2$O (50 mL), filtered, and washed with H$_2$O and then with diethyl ether. Crystallization in a CH$_2$Cl$_2$/pentane mixture afforded a dark brown powder (99.0 mg, 60% yield). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ (ppm) 8.48 (m, 2H, Py$^{3\text{-DTEbpy}}$), 8.27 (m, 4H, Py$^{3\text{-Mebpy}}$), 7.67 (d, ^3J = 16 Hz, 2H, ═CH), 7.62−7.53 (m, ^{6}H, Py$^{6\text{-Mebpy+bpyDTE}}$), 7.45 (d, ^3J = 8.8 Hz, 4H, C_6H_4−), 7.44 (m, 2H, Py$^{5\text{-bpyDTE}}$), 7.36 (s, 2H, thio), 7.27 (m, 4H, Py$^{5\text{-Mebpy}}$), 7.13 (s, 2H, thio), 6.96 (d, ^3J = 16 Hz, 2H, ═CH), 6.76 (d, ^3J = 8.8 Hz, 4H, C_6H_4−), 3.01 (s, 12H, NMe$_2$), 2.62 (s, 6H, CH$_3$$^{\text{Mebpy}}$), 2.61 (s, 6H, CH$_3$$^{\text{Mebpy}}$), 2.04 (s, 6H, CH$_3$$^{\text{DTE}}$), 1.97 (s, 6H, CH$_3$$^{\text{DTE}}$). ^{13}C{^{1}H} NMR (125.77 MHz, CD$_2$Cl$_2$): δ (ppm) 157.14, 156.37, 156.22, 151.10, 150.75, 150.51, 150.27, 150, 146.01, 144.78, 143.42, 139.50, 138.95, 129.59, 128, 126.43, 126.12, 125, 124.81, 123.65, 123.20, 121.52, 120.68, 119.58, 112.46, 40.27, 21.11, 14.78, 14.27. HRMS: *m/z* 824.172 36, [M]$^{2+}$ calcd for $C_{84}H_{70}N_8F_{12}S_4{}^{102}Ru$ 824.1735; *m/z*

1793.309 45 $[M^{2+},PF_6^{-}]^+$, calcd for $C_{84}H_{70}N_8F_{12}PS_4{}^{102}Ru$ 1793.3102. Anal. Calcd for $C_{84}H_{70}F_{24}N_8P_2RuS_4 \cdot CH_2Cl_2$: C, 50.45; H, 3.59; N, 5.54; S, 6.34. Found: C, 50.39; H, 3.67; N, 5.43; S, 6.33.

*Spectroscopic Data of the Photocyclized [(**L**^{a}**(c)**)(dmbipy)$_2$Ru]-(PF$_6$)$_2$.* ^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) 8.48 (m, Py$^{3\text{-bpyDTE}}$), 8.27 (m, Py$^{3\text{-Mebpy}}$), 7.67−7.60 (m, =CH, Py$^{6\text{-Mebpy+DTEbpy}}$), 7.52 (m, C_6H_4−), 7.45 (m, Py$^{5\text{-DTEbpy}}$), 7.27 (m, 4H, Py$^{5\text{-Mebpy}}$), 6.77−6.63 (m, thio + C_6H_4− + =CH), 3.10 (s, 12H, NMe_2), 2.62 (m, 2 $CH_3{}^{\text{Mebpy}}$), 2.18 (s, 6H, $CH_3{}^{\text{DTE}}$), 2.15 (s, 6H, $CH_3{}^{\text{DTE}}$), 2.04 (s, 6H, $CH_3{}^{\text{DTE}}$), 1.97 (s, 6H, $CH_3{}^{\text{DTE}}$).

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Notes

The authors declare no competing financial interest.

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