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Nonlinear Optics

Efficient Photoswitching of the Nonlinear Optical Properties of Dipolar Photochromic Zinc(II) Complexes**

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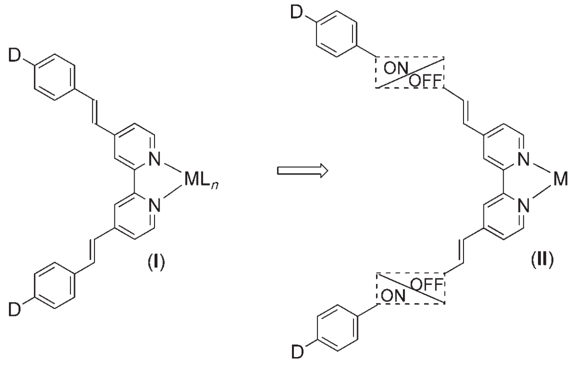
A current challenge is the development of efficient strategies for the design of switchable nonlinear optical (NLO) materials.[1] As most molecules with large first hyperpolarizability values β comprise π systems that are unsymmetrically end-capped with donor and acceptor moieties, various strategies have been explored to alter the electron-donor (or acceptor) capacity of the end groups using external stimuli such as redox methods[2] and protonation/deprotonation reactions.[3] Another elegant approach to the reversible switching of NLO properties is the use of photochromic compounds.[1b,4] Among them, dithienylethene (DTE) derivatives are the most promising because of their good fatigue resistance, the remarkable thermal stability of both isomers, and the rapid response time, which are prerequisite conditions for practical applications.[5] Typically, DTE derivatives undergo reversible interconversion between an unconjugated open form and a π-conjugated closed form when irradiated in the UV and visible spectral ranges, respectively.

In recent years, considerable effort has been devoted to the development of transition-metal complexes as NLO chromophores, and their large second-order nonlinearities have been demonstrated.[6] The photoswitching of their NLO properties has not been reported to date, although recent studies have highlighted the potential of metal-containing DTE ligands for luminescence or electron-transfer photoswitching.[7]

We previously described the use of 4,4′-bis(dialkylaminostyryl)-2,2′-bipyridine compounds for the molecular engineering of noncentrosymmetric dipolar[8] (Scheme 1, type **I**) or octupolar metal complexes.[9] With the aim of photoswitching the NLO properties, we designed a new type of 4,4′-bis(ethenyl)-2,2′-bipyridine ligand functionalized by phenyl- and dimethylaminophenyl DTE groups. These ligands allowed us to prepare the corresponding photochromic dipolar (bipyridyl)zinc(II) complexes (Scheme 1, type **II**). Herein, we report the synthesis and photochromic properties of these new compounds, as well as the efficiently phototriggered enhancement of the NLO activity of dipolar complexes.



Scheme 1. Target photochromic complexes.

The target bipyridine derivatives **1a**(o) (D = H, (o) indicates open form) and **1b**(o) (D = NMe$_2$) were readily prepared in 55–60 % yield by a double Horner–Wadsworth–Emmons condensation between the bisphosphonate bipyridine and the aryl-substituted DTE aldehydes **6** (Scheme 2). The latter compounds were obtained by a multistep procedure. The two thienyl fragments were prepared independently and were successively connected to C_5F_8 (see the Supporting Information for details).

For both ligands, the photocyclization process was confirmed by ^{1}H NMR spectroscopy experiments. The colorless solutions of **1a**(o) and **1b**(o) in CD_2Cl_2 turn blue and green, respectively, upon UV irradiation. The ^{1}H NMR spectra of the closed forms **1a**(c) and **1b**(c) show the characteristic upfield shift of the two thiophene protons, while the methyl proton signals are shifted downfield. Integration of the methyl-group resonances indicates approximately 95 % conversion to the ring-closed isomers. The photocyclization and photocycloreversion processes were also monitored by absorption spectroscopy (Figure 1, Table 1). The UV/Vis spectra (CH_2Cl_2) of **1a**(o) and **1b**(o) show an intense band at 343–348 nm, which is tentatively assigned to intraligand (IL) $\pi\rightarrow\pi^*$ transitions of the bipyridyl moieties with some mixing of $\pi\rightarrow\pi^*$ transitions of the DTE units. Irradiation of CH_2Cl_2 solutions at 365 nm resulted in a new broad band at

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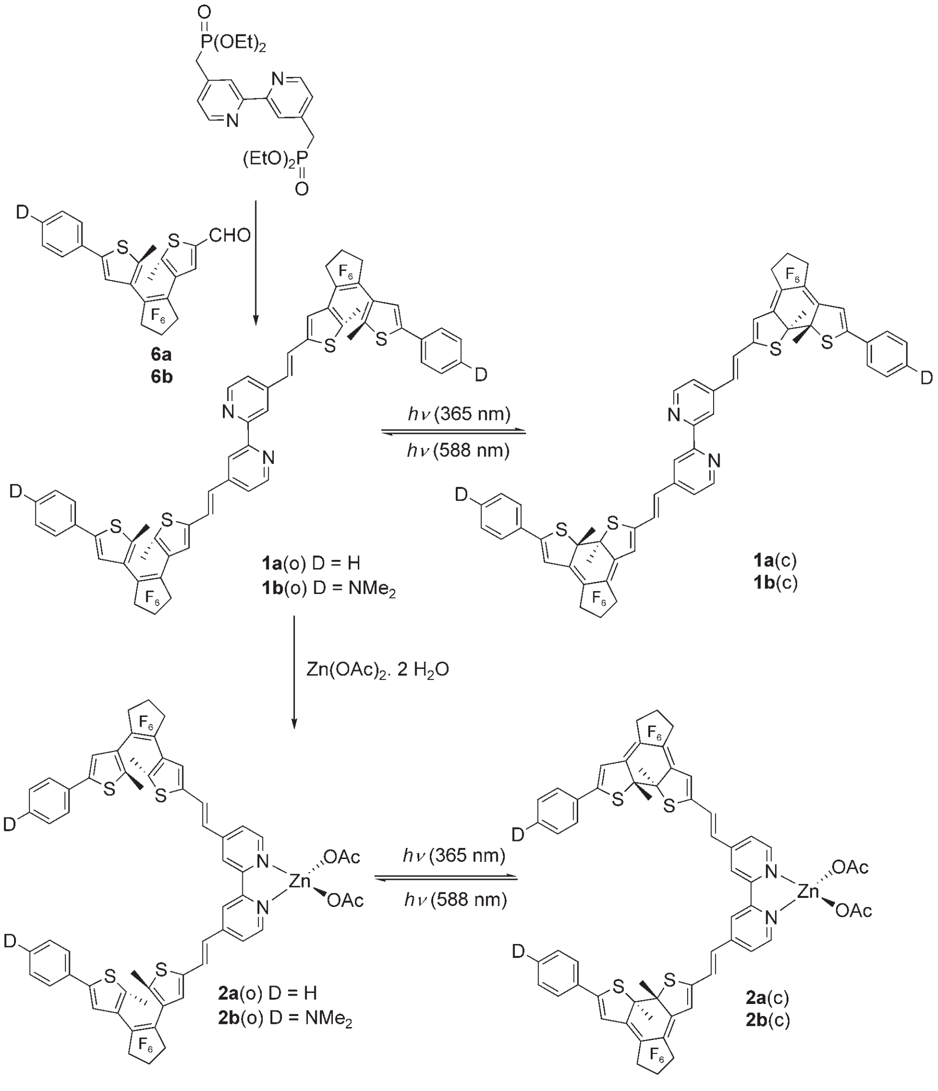

Scheme 2. Synthesis and photochromic reactions of ligands and complexes. D = H (**1a**, **2a**, **6a**), D = NMe_2 (**1b**, **2b**, **6b**).

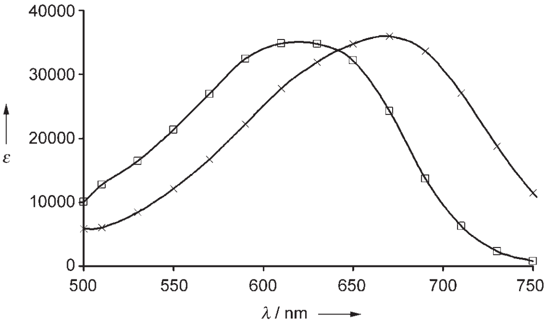

Figure 1. Absorption spectra (visible region) of the PSS closed-ring isomers **1a**(c) (——□——) and **1b**(c) (——×——) in CH_2Cl_2, from which the influence of the terminal group D (H vs. NMe_2) is apparent.

623 nm, which is attributed to the IL $S_0 \rightarrow S_1$ transition of the closed form **1a**(c), the red shift arising from the formation of a π-conjugated system. Replacement of the H end group with the strongly donating NMe_2 group induces an additional 46-nm red shift for the IL band, which appears at 669 nm for **1b**(c) (Figure 1).[10] Excitation at 588 nm, in the absorption band of the closed forms **1a**(c) and **1b**(c), led to the quantitative regeneration of the open isomers. The quantum yields for the ring-closure process (**1a**(o) $\phi = 0.45$, **1b**(o) $\phi = 0.24$) were found to be much higher than those for the reverse process (**1a**(c) $\phi = 8.4 \times 10^{-3}$, **1b**(c) $\phi = 1.9 \times 10^{-3}$), as has been observed for related systems.[7f,g] No emission was detected for **1a**,**b**(o) and **1a**,**b**(c) in solution at room temperature.

The corresponding bipyridyl zinc(II) bis(acetato) complexes **2a**(o) and **2b**(o) (Scheme 2) were prepared quantitatively upon treatment of $Zn(OAc)_2 \cdot 2H_2O$ with one equivalent of ligand **1a**(o) or **1b**(o) in dichloromethane at room temperature (Scheme 2). The zinc complexes displayed identical photochromic behavior, confirming that complexation of the bipyridyl ligands to Zn^{II} did not alter the photoconversion process. Upon illumination at 365 nm, new absorption bands at 629 nm and 687 nm appeared, originating from the formation of the closed isomers **2a**(c) and **2b**(c), respectively (Figure 2, Table 1). Complexation to $Zn(OAc)_2$ induces a typical bath-

Table 1: UV/Vis absorption data.

Compound[a]	λ_{abs} [nm] (ε [$M^{-1}cm^{-1}$]) open form	E_{max} [ev]	λ_{abs} [nm] (ε [$M^{-1}cm^{-1}$]) closed form	E_{max} [ev]
1a	343 (75600)	3.61	347 (62000)	3.57
			396 (22000)	3.13
			623 (35000)	1.99
1b	348 (89000)	3.56	347 (54000)	3.57
			395 (24000)	3.14
			438 (17800)	2.83
			669 (36000)	1.85
2a	357 (55000)	3.47	342 (60000)	3.62
			400 (25000)	3.1
			629 (32000)	1.97
2b	360 (76000)	3.44	343 (46000)	3.61
			394 (26500)	3.14
			450 (17200)	2.75
			687 (34560)	1.80

[a] Determined in CH_2Cl_2.

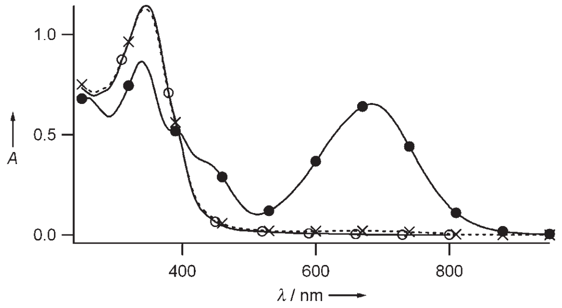

Figure 2. UV/Vis absorption change of **2b** in $CHCl_3$ (1.5×10^{-5} M) upon irradiation. ——○—— open form, ——●—— photostationary state (PSS) after irradiation at 365 nm, -----×----- PSS after irradiation at 588 nm (reverse reaction).

ochromic shift ($\Delta\lambda = 6$–18 nm) of the intraligand charge-transfer (ILCT) bands, as has been observed for related bis(acetato) zinc(II) complexes.[11]

Upon photoexcitation at 588 nm, the (c) isomers completely reverted to the corresponding (o) isomers without any decomplexation (Figure 2). According to ^{1}H NMR spectroscopy, the degree of cyclization showed slightly lower conversion efficiencies than those of the ligands (92 % for **2a** and 87 % for **2b**), whereas the quantum yields for the photocyclization of **2a**(o) ($\phi = 0.24$) and **2b**(o) ($\phi = 0.16$) were again much higher than those for the photocycloreversion (**2a**(c) $\phi = 2.4\times10^{-3}$, **2b**(c) $\phi = 0.6\times10^{-3}$).

The NLO figure of merit $\mu\beta$ (where μ is the dipole moment and β the quadratic hyperpolarizability coefficient) was evaluated by electric-field induced second harmonic generation (EFISH) measurement for the open and photostationary state (PSS) closed forms of **2a,b** in concentrated dichloromethane solution (10^{-3} M) with a nonresonant incident wavelength of 1.91 μm. The static $\mu\beta_0$ values extrapolated at zero frequency were calculated using the two-level model.[12]

As indicated in Table 2, the $\mu\beta_0$ values for the open forms are very small, in agreement with the absence of π conjugation between the two thiophene rings of the DTE fragment. Note that the larger NLO activity of **2b**(o) relative to **2a**(o) can be tentatively explained by a dipolar contribution of the dimethylaminophenylthienyl perfluoropentene fragment, the perfluoropentene moiety acting as a weak electron-accepting group. Upon conversion to the closed form in the photostationary state, the NLO activity of complexes **2a** and **2b** increased dramatically, from $75–160\times10^{-48}$ to $1020–1800\times10^{-48}$ esu. As expected, the largest NLO enhancement is obtained with compound **2b**(c), which features the strongly electron-donating dimethylamino substituent. Interestingly, **2a**(c) also displays quite a large NLO response even in the absence of any apparent strongly electron-donating group. Thus, the substantial enhancement of $\mu\beta_0$ clearly reflects the efficient delocalization of the π-electron system in the closed forms and demonstrates efficient on/off switching of the NLO responses.

Table 2: Quadratic nonlinear optical data in CH_2Cl_2.[a]

Compound	$\mu\beta$ [10^{-48} esu] open form	$\mu\beta$ [10^{-48} esu] closed form	$\mu\beta_0$ [10^{-48} esu] open form	$\mu\beta_0$ [10^{-48} esu] closed form
2a	90[b]	2020[c]	75[b]	1020[c]
2b	200[b]	4220[c]	160[b]	1800[c]

[a] Determined at $\lambda_{inc} = 1907$ nm. [b] Error ±20%. [c] Error ±5%.

In summary, we have prepared and studied the first photochromic metal complexes that allow efficient switching of the nonlinear optical properties. Owing to the ubiquity of 2,2′-bipyridine derivatives in coordination chemistry, this work opens attractive perspectives for the construction of photochromic multipolar NLO molecules and materials.

Experimental Section

Spectroscopic-grade chloroform and dichloromethane were used for all optical measurements. Photoisomerization experiments and kinetics were performed using a Hamamatsu UV Spot Light Source (Xe–Hg lamp) as an excitation light source equipped with bandpass filters (0.63 mW cm^{-2} at 365 nm, 18.6 mW cm^{-2} at 588 nm) and an optical fiber, while simultaneous probing was performed with a continuous Xe lamp (450 W) and a CCD camera coupled with a spectrometer (Princeton Instruments). The values of $\mu\beta$ for the chromophores were measured using the EFISH technique. The amplified nanosecond Nd^{3+}:YAG laser at 1.06 μm and a repetition rate of 10 Hz pumps a hydrogen Raman cell to obtain a larger wavelength (1.907 μm) for which both the fundamental and harmonic frequencies are far away from the resonance of the investigated molecule.

Full details of the experimental procedures and compound characterization are given in the Supporting Information.

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[1] a) B. J. Coe, *Chem. Eur. J.* **1999**, *5*, 2464; b) J. A. Delaire, K. Nakatani, *Chem. Rev.* **2000**, *100*, 1817; c) I. Asselberghs, K. Clays, A. Persoons, M. D. Ward, J. McCleverty, *J. Mater. Chem.* **2004**, *14*, 2831; d) M. Samoc, N. Gautier, M. P. Cifuentes, F. Paul, C. Lapinte, M. G. Humphrey, *Angew. Chem.* **2006**, *118*, 7536; *Angew. Chem. Int. Ed.* **2006**, *45*, 7376.
[2] Selected examples: a) B. J. Coe, S. Houbrechts, I. Asselberghs, A. Persoons, *Angew. Chem.* **1999**, *111*, 377; *Angew. Chem. Int. Ed.* **1999**, *38*, 366; b) M. Malaun, Z. R. Reeves, R. L. Paul, J. C. Jeffery, J. A. McCleverty, M. D. Ward, I. Asselberghs, K. Clays, A. Persoons, *Chem. Commun.* **2001**, 49; c) F. Paul, K. Costuas, I. Ledoux, S. Deveau, J. Zyss, J.-F. Halet, C. Lapinte, *Organometallics* **2002**, *21*, 5229; d) I. Asselberghs, K. Clays, A. Persoons, M. McDonagh, M. D. Ward, J. A. McCleverty, *Chem. Phys. Lett.* **2003**, *368*, 408.
[3] a) I. Asselberghs, I. Zhao, K. Clays, Y. Rubin, *Chem. Phys. Lett.* **2002**, *364*, 279; b) B. J. Coe, J. L. Harries, M. Helliwell, L. A. Jones, I. Asselberghs, K. Clays, B. S. Brunschwig, J. A. Harris, J. Garin, J. Orduna, *J. Am. Chem. Soc.* **2006**, *128*, 12192; c) I. Asselberghs, G. Hennrich, K. Clays, *J. Phys. Chem. A* **2006**, *110*, 6271.
[4] a) S. L. Gilat, S. H. Kawai, J.-M. Lehn, *Chem. Eur. J.* **1995**, *1*, 275; b) K. Nakatani, J. A. Delaire, *Chem. Mater.* **1997**, *9*, 2682; c) L. Sanguinet, J.-L. Pozzo, V. Rodriguez, F. Adamietz, F. Castet, L. Ducasse, B. Champagne, *J. Phys. Chem. B* **2005**, *109*, 11139;

d) M. Giraud, A. Léaustic, R. Guillot, P. Yu, P. G. Lacroix, K. Nakatani, R. Pansu, F. Maurel, *J. Mater. Chem.* **2007**, *17*, 4414.

[5] M. Irie, *Chem. Rev.* **2000**, *100*, 1685.

[6] B. J. Coe in *Comprehensive Coordination Chemistry II*, *Vol. 9* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier Pergamon, Oxford, **2004**, p. 621.

[7] a) A. Fernàndez-Acebes, J.-M. Lehn, *Chem. Eur. J.* **1999**, *5*, 3285; b) S. Fraysse, C. Coudret, J.-P. Launay, *Eur. J. Inorg. Chem.* **2000**, 1581; c) K. Matsuda, K. Takayama, M. Irie, *Chem. Commun.* **2001**, 363; d) H. Tian, B. Z. Chen, H. Tu, K. Müllen, *Adv. Mater.* **2002**, *14*, 918; e) B. Z. Chen, M. Z. Wang, Y. Q. Wu, H. Tian, *Chem. Commun.* **2002**, 1060; f) V. W.-W. Yam, C.-C. Ko, N. Zhu, *J. Am. Chem. Soc.* **2004**, *126*, 12734; g) R. T. F. Jukes, V. Adamo, F. Hartl, P. Belser, L. De Cola, *Inorg. Chem.* **2004**, *43*, 2779; h) P. H.-M. Lee, C.-C. Ko, N. Zhu, V. W.-W. Yam, *J. Am. Chem. Soc.* **2007**, *129*, 6058.

[8] a) M. Bourgault, K. Baum, H. Le Bozec, G. Pucetti, I. Ledoux, J. Zyss, *New J. Chem.* **1998**, *22*, 517; b) O. Maury, J.-P. Guégan, T. Renouard, A. Hilton, P. Dupau, N. Sandon, L. Toupet, H. Le Bozec, *New J. Chem.* **2001**, *25*, 1553.

[9] a) O. Maury, L. Viau, K. Sénéchal, B. Corre, J.-P. Guégan, T. Renouard, I. Ledoux, J. Zyss, H. Le Bozec, *Chem. Eur. J.* **2004**, *10*, 4454; b) O. Maury, H. Le Bozec, *Acc. Chem. Res.* **2005**, *38*, 691.

[10] Two new weaker bands between 400 and 500 nm were also observed and ascribed to $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions, respectively.[7g]

[11] F. Tessore, D. Roberto, R. Ugo, P. Mussini, S. Quici, I. Ledoux-Rak, J. Zyss, *Angew. Chem.* **2003**, *115*, 472; *Angew Chem. Int. Ed.* **2003**, *42*, 456.

[12] J. L. Oudar, *J. Chem. Phys.* **1977**, *67*, 446.