New bipyridyl ligands bearing azo- and imino-linked chromophores. Synthesis and nonlinear optical studies of related dipolar zinc complexes†

Adam Hilton,[a] Thierry Renouard,[a] Olivier Maury,[a] Hubert Le Bozec,*[a] Isabelle Ledoux[b] and Joseph Zyss[b]

[a] *Laboratoire de Chimie de Coordination et Catalyse, UMR 6509 CNRS-Université Rennes 1, Campus de Beaulieu, 35042 Rennes cedex, France. E-mail: lebozec@univ-rennes1.fr*

[b] *Laboratoire de Physique Quantique Moléculaire, ENS Cachan, 61 avenue du président Wilson, 94235 Cachan, France*

Received (in Cambridge, UK) 8th October 1999, Accepted 10th November 1999

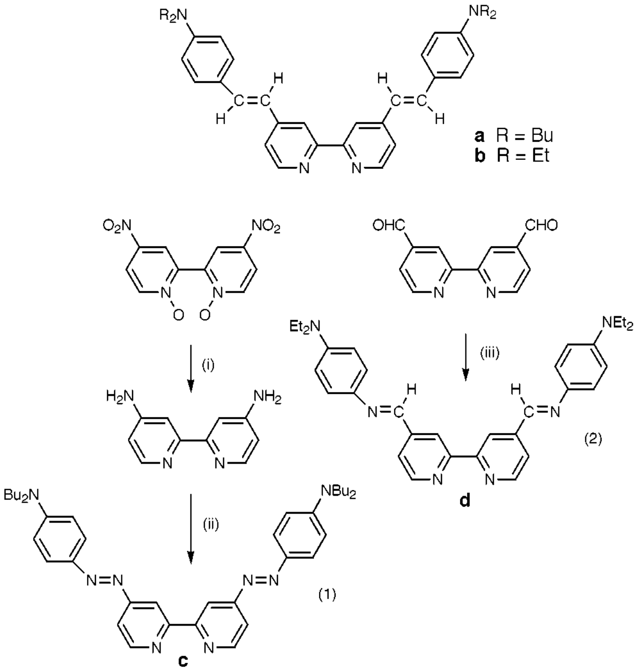
The synthesis and optical properties of 4,4′-bis(dialkylaminophenylazo)-2,2′-bipyridine and 4,4′-bis(dialkylaminophenylimino)-2,2′-bipyridine ligands are described; the corresponding dipolar bipyridyl zinc dichloride complexes have been prepared and their second order nonlinear optical properties determined by electric field-induced second harmonic generation (EFISH) at 1.34 μm.

Poled polymers containing second order nonlinear (NLO) molecules are particularly promising for electrooptic device applications. Usually, dipolar chromophores have to be aligned by using electric field poling near the glass transition temperature (T_g) of the polymer.[1] Besides this approach, which requires high temperature treatment, new mild optical poling techniques have been developed recently. The so-called 'photo-assisted electrical' poling[2] and the 'all optical' poling[3] can be used at room temperature for the macroscopic noncentrosymmetric organisation of dipolar and octupolar chromophores, respectively. These methods require the presence of chromophores featuring a photoisomerisable moiety and use the 'flexibility' of the molecule to break the centrosymmetry of the material.

We have previously reported that metalloorganic complexes containing π-donor substituted 4,4′-alkenyl-2,2′-bipyridyl ligands[4] such as **a** and **b** (Scheme 1), show large dipolar or octupolar microscopic nonlinearities.[5] As the C=C double bond is known to be poorly photoisomerisable as compared, for example, to the N=N double bond,[6] we sought to design new potentially photoisomerisable bipyridines by introducing nitrogen atoms into the transmitter. Herein we report the synthesis and characterisation of new bipyridines bearing azo- as well as imino-linked donor groups. We also describe the preparation of the corresponding dipolar zinc(II) complexes; the influence of the nature of the π-bridge on the linear and nonlinear properties of these complexes is also reported.

The synthesis of the azo-containing bipyridyl ligand **c** was readily accomplished in two steps from 4,4′-dinitro-2,2′-bipyridine-1,1′-dioxide[7] [Scheme 1, eqn. (1)]: 4,4′-diamino-2,2′-bipyridine was first prepared in quantitative yield by using hydrazine hydrate in the presence of Pd/C.[8] This mild and efficient method contrasts favourably with the well-known but poorly yielding (20%) procedure using Fe/AcOH as the reducing agent.[9] Finally, the diazotation of 4,4′-diamino-2,2′-bipyridine with sodium nitrite and subsequent coupling with *N,N*-dibutylaniline afforded derivative **c**, which was isolated (yield 25%) as dark red microcrystals after chromatographic workup. Imino-containing bipyridine **d** was synthesised in excellent yield (95%) by a Schiff base condensation reaction between *N,N*-diethyl-1,4-phenylenediamine and 4,4′-diformyl-2,2′-bipyridine[10] [Scheme 1, eqn. (2)]. Attempts to isolate the 'reverse' imino-bipyridine from the reaction of 4,4′-diamino-2,2′-bipyridine and diethylaminobenzaldehyde failed, confirming the already observed deactivation of the amino and carbonyl functions in the presence of acceptor and donor groups, respectively.[11] Ligands **c** and **d** were characterised by ^{1}H NMR and high resolution mass spectrometry. Their optical spectra and those of the related aminostyryl derivatives **a** and **b** are displayed in Fig. 1. Most importantly, a large bathochromic shift of the ICT band is observed on exchanging the C=C bond for an N=N ($\Delta\lambda_{max}$ = 71 nm) or N=C ($\Delta\lambda_{max}$ = 36 nm) bond. This effect has been already described for other chromophores: Ulman *et al.*[12] reported a bathochromic shift of 40 nm between 4-dimethylamino-4′-dimethylsulfonylazobenzene and the corresponding stilbene derivative, while Whitall *et al.* described a 20 nm shift between an imino-benzene and the corresponding stilbene ruthenium complex.[11a] In the latter case the shift was accompanied by a strong decrease of the molar extinction coefficient ε, an hypsochromic effect which is not observed in our case.

Tetrahedral zinc complexes **1a**–**d** (Scheme 2) were readily prepared upon room temperature treatment of the ligands **a**–**d** with $ZnCl_2$ in dichloromethane.[5a] In their UV-vis spectra (Fig. 1, Table 1), a red-shift of the intense ILCT (intraligand charge-transfer) band is observed ($\Delta\lambda_{max}$ = 45–60 nm), as expected from the inductive acceptor strength of the Lewis acid.[13] As in the free ligand, λ_{max} is sensitive to the nature of the X=Y transmitter and follows the order N=N > N=C > C=C.



Scheme 1 (i) Pd/C (10%), $N_2H_4\cdot H_2O$, EtOH, reflux, 8 h, 100%; (ii) $NaNO_2$, $Bu_2NC_6H_5$ in THF, 0–5 °C, 2 h, 25%; (iii) $Et_2NC_6H_4NH_2$, $MgSO_4$, THF, reflux, 12 h, 95%.

---

† Electronic supplementary information (ESI) available: experimental procedures and spectroscopic data. See http://www.rsc.org/suppdata/cc/1999/2521/

Table 1 Linear and nonlinear data for the free ligands and their $ZnCl_2$ complexes

Ligand	$\lambda_{max}{}^a$/nm	ε/mol^{-1} cm^{-1}	Complex	$\lambda_{max}{}^a$/nm	ε/mol^{-1} cm^{-1}	$\mu\beta^b/10^{-48}$ esu^c	$\mu\beta_0{}^b/10^{-48}$ esu^c
a	397	57000	**1a**	455	62000	1420	660
b	401	65000	**1b**	459	62000	1830	850
c	471	63000	**1c**	516	63000	2160	700
d	433	52000	**1d**	491	55000	1610	620

[a] Solution in CH_2Cl_2. [b] Solution in $CHCl_3$; the precision of the measurement is about 10%. [c] Correlation between esu and SI units: $\beta(\mathrm{SI}) = 4.172 \times 10^{-10}\ \beta$ (esu).

The molecular hyperpolarisabilities $\mu\beta$ of **1a–d** were measured in chloroform using electric field-induced second harmonic generation (EFISH) at 1340 nm, and the nonresonant $\mu\beta_0$ values were calculated using the two-level model (Table 1).[14] The results show that these complexes have good nonlinear optical activities, which are sensitive to the nature of both the transmitter and donor groups. For a given bridge, such as in **1a** and **1b**, dibutylaminophenyl is more efficient than the diethylaminophenyl group, a variation already observed for octupolar complexes.[5d] For a given donor, a slight increase in $\mu\beta$ is also observed on replacing CH by N. However, comparison of the zero-frequency $\mu\beta_0$ values reveals that the increase in nonlinearity seems to be mainly due to resonant enhancement.

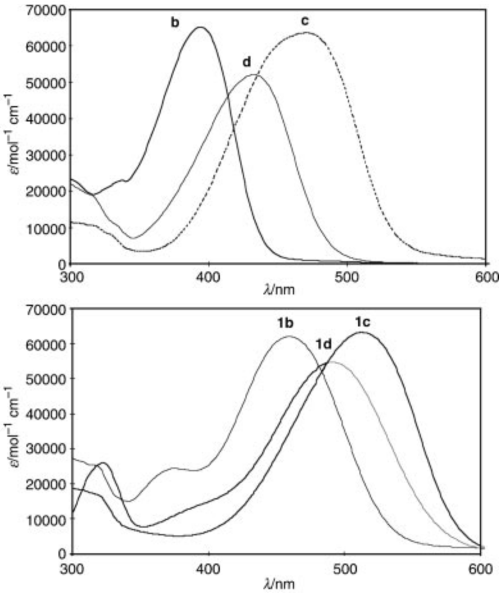
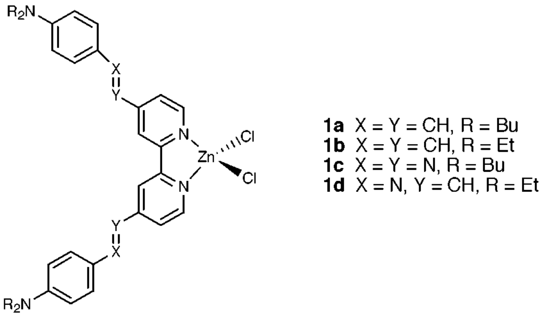


Fig. 1 UV-Vis spectra of the free bipyridine ligands (top) and related complexes (bottom).



1a X = Y = CH, R = Bu
1b X = Y = CH, R = Et
1c X = Y = N, R = Bu
1d X = N, Y = CH, R = Et

Scheme 2 (L-L)$ZnCl_2$ complexes.

In conclusion we have described the synthesis of new bipyridyl ligands bearing imino and azo substituents. The NLO activity of the chromophore **1c**, which contains the most suitable photoisomerisable azo ligand, can be favourably compared with that of the prototypical azo dye DR1 (λ_{max} = 480 nm, $\mu\beta_0 = 450 \times 10^{-48}$ esu).[15] Research is now in progress to study the photoassisted electrical poling of such dipoles in polymer films. Finally, these ligands provide access to D_3 octupolar complexes which will be promising candidates for the 'all optical' poling method.

We thank the CNRS (Programme Matériaux), the CNET and the Conseil Régional de Bretagne for financial support.

Notes and references

1 T. J. Marks and M. A. Ratner, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 155 and references therein.
2 Z. Sekkat and M. Dumont, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect B*, 1992, **2**, 359; R. Loucif-Saibi, K. Nakatani, J. A. Delaire, M. Dumont and Z. Sekkat, *Chem. Mater.*, 1993, **5**, 229.
3 J. M. Nunzi, F. Charra, C. Fiorini and J. Zyss, *Chem. Phys. Lett.*, 1994, **219**, 349.
4 A. Juris, S. Campagna, I. Bidd, J. M. Lehn and R. Ziessel, *Inorg. Chem.*, 1988, **27**, 4007; M. Bourgault, T. Renouard, B. Lognoné, C. Mountassir and H. Le Bozec, *Can. J. Chem.*, 1997, **75**, 318.
5 For dipolar molecules see: (*a*) M. Bourgault, K. Baum, H. Le Bozec, G. Pucetti, I. Ledoux and J. Zyss, *New J. Chem.*, 1998, 517. For octupolar molecules see: (*b*) C. Dhenaut, I. Ledoux, I. D. W. Samuel, J. Zyss, M. Bourgault and H. Le Bozec, *Nature*, 1995, **374**, 339; (*c*) T. Renouard, H. Le Bozec, I. Ledoux and J. Zyss, *Chem. Commun.*, 1999, 871. For a review see: (*d*) H. Le Bozec and T. Renouard, *Eur. J. Inorg. Chem.*, in press.
6 V. Wing-Wah Yam, V. Chor-Yue Lau and L. X. Wu, *J. Chem. Soc., Dalton Trans.*, 1998, 1461.
7 P. Wehman, G. C. Dol, E. R. Morrman, P. C. J. Kamer and P. W. N. M. van Leeuwen, *Organometallics*, 1994, **13**, 4856. **CAUTION!** During a nitration reaction, a strong explosion occurred.
8 H. Camren, M.-Y. Chang, L. Zen and E. McGuire, *Synth. Commun.*, 1996, **26**, 1247.
9 G. Maerker and F. H. Case, *J. Am. Chem. Soc.*, 1958, **80**, 2745.
10 P. Dupau, T. Renouard and H. Le Bozec, *Tetrahedron Lett.*, 1996, **37**, 7503.
11 (*a*) I. R. Whittall, M. G. Humphrey, A. Persoons and S. Houbrechts, *Organometallics*, 1996, **15**, 1935; (*b*) S. S. P. Chou, D. J. Sun, H. C. Lin and P. K. Yang, *Chem. Commun.*, 1996, 1045.
12 A. Ulman, C. S. Willand, W. Köhler, D. R. Robello, Q. J. Williams and L. Handley, *J. Am. Chem. Soc.*, 1990, **112**, 7083.
13 D. R. Kanis, P. G. Lacroix, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10 089.
14 J. L. Oudar, *J. Chem. Phys.*, 1977, **67**, 446; I. Ledoux and J. Zyss, *Chem. Phys.*, 1982, **63**, 203.
15 C. W. Dirk, H. E. Katz, M. L. Schilling and L. A. King, *Chem. Mater.*, 1990, **2**, 700.

Communication 9/08197F