Ligand *trans-effect*: using an old concept as a novel approach to bis(dipolar) NLO-phores

Claire Fave,[a] **Muriel Hissler,**[a] **Katell Sénéchal,**[a] **Isabelle Ledoux,**[b] **Joseph Zyss**[b] **and Régis Réau***[a]

[a] *Phosphore et Matériaux Moléculaires, UMR 6509 CNRS-Université de Rennes 1, Institut de Chimie, Campus de Beaulieu, 35042 Rennes Cedex, France. E-mail: regis.reau@univ-rennes1.fr*

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

In plane parallel arrangement and enhancement of NLO-activity are observed upon coordination of heteroditopic dipoles containing a phosphole ring on square-planar d8-palladium centre.

A recent strategy in nonlinear optics (NLO) involves gathering together identical one dimensional (1D) donor(D)–acceptor(A) substituted chromophores leading to molecular multi(dipolar) systems.[1] This approach however dictates that noncentrosymmetric organisation of dipolar NLO-phores is achieved at the molecular level. For bis(dipolar) derivatives, which are the simplest multi(chromophoric) systems, noncentrosymmetric structures have been obtained by coordination of 1D-chromophores to tetrahedral metal ions[1e] or by connection of two substituted β-naphthols[1f–i] (V-shaped molecules **A**, Scheme 1). We propose herein a new strategy based on the *trans-effect*, a long-standing concept in coordination chemistry.[2] The most useful application of this principle is for the preparation of specific isomers of d8-square planar complexes.[3a–e] In accordance with Pearson's antisymbiotic effect,[2b] heteroditopic P,N-donors can control the orientation of a second chelating

ligand in the coordination sphere of a Pd(II)-complex.[3c–g] Anticipating that this *trans-effect* could overcome the natural anti-parallel alignment tendency of 1D-dipolar chromophores at a molecular level, we envisaged the synthesis of in-plane bis(dipolar) assemblies **B** (Scheme 1) by stereoselective coordination of P,N-chromophores on a d8-square-planar Pd-centre.

2-(2-Pyridyl)phospholes act as tightly bonded 1,4-chelates toward Pd(II) centres and, owing to the different electronic nature of the donor sites, they undergo stereoselective coordination.[3f–h] We have shown that phospholes possess a highly polarisable dienic π-system[4] and theoretical studies[5] have suggested that this weakly aromatic P-heterocycle is a potentially interesting π-bridge for the engineering of NLO-phores. The metal-coordinated pyridyl group will act as an electron-withdrawing substituent,[6] thus, in order to obtain the classical dipolar D–π–A NLO-phore structure,[5,6c–e] electron-donating substituents (dibutylaminophenyl, methoxythienyl) were introduced at the C5-carbon atom of the P-ring. The target 2-(2-pyridyl)phospholes **2a,b** were prepared via a 'zirconocene'-promoted intramolecular coupling of diynes **1a,b** and subsequent addition of PhPBr₂ (Scheme 1).[4,7] These compounds were isolated in fairly good yields as air stable solids after purification by flash column chromatography on basic alumina (**2a**, 73% yield; **2b**, 55% yield). They exhibit classical NMR spectroscopic data[4,7] (Table 1) and have been characterised by high resolution mass spectrometry and elemental analyses. The UV/visible spectra of phospholes **2a,b** in CH₂Cl₂ solution show a broad absorption in the visible region attributed to the π–π* transition of the extended conjugated system (Table 1). The absorption maxima are comparable for both derivatives and, as expected, are shifted to longer wavelengths (Δλ_max: 20–35 nm) than those recorded for the corresponding derivatives featuring no methoxy[3h] or dibutylamino electron-donor end groups. The NLO properties of the donor–acceptor substituted phospholes **2a,b** were determined by the electric-field-induced second harmonic generation (EFISH, 1.91 μm) and the nonresonant hyperpolarisabilities were estimated using the two-level model.[8] The EFISH measurements revealed that phospholes **2a,b** exhibit moderate NLO-activities (Table 1), which are consistent with the weak acceptor character of the non-coordinated pyridine group.[5a,6b] Note that the NLO response of phosphole **2a** is slightly superior to that of **2b**.

2-(2-Pyridyl)phospholes **2a,b** reacted in CH₂Cl₂ solution with (CH₃CN)₄Pd²⁺, 2 BF₄⁻ giving rise, almost quantitatively, to complexes **3a,b** isolated as air stable solids (Scheme 1).
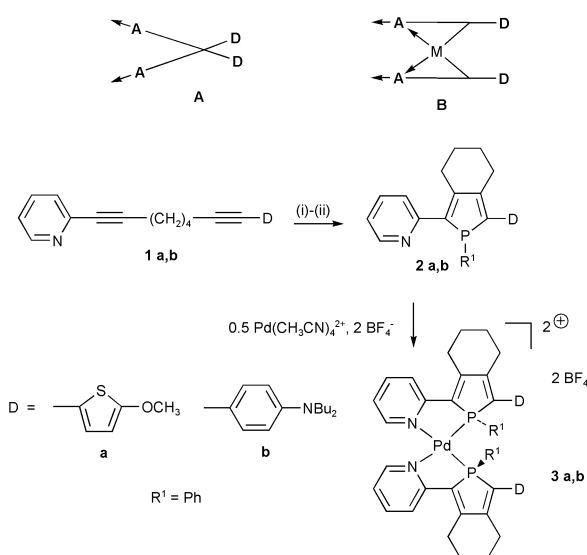
Scheme 1 (i) Cp₂ZrCl₂, 2 BuLi, THF, −78 to 25 °C; (ii) PhPBr₂, THF, −78 to 25 °C.

Table 1 ³¹P{¹H} NMR, linear and nonlinear optical data for compounds **2a,b** and **3a,b**

Compound	δ ³¹P{¹H}[a] (ppm)	λ_{max}[a] (nm)	ε (L mol⁻¹ cm⁻¹)	$\mu\beta$[b]; $\mu\beta(0)$ (10⁻⁴⁸ e.s.u)	β[c] (10⁻³⁰ e.s.u)
2a	+11.5	415	18000	170; 130	
2b	+10.2	417	17800	120; 90	31[d]
3a	+70.2	420 (550)	11900 (3200)		170
3b	+68.9	452 (640)	14400 (3100)		180

[a] Measured in CH₂Cl₂. [b] EFISH measurements in CH₂Cl₂ (10⁻² mol L⁻¹) at 1.91 μm. [c] HLS measurements in CH₂Cl₂ at 1.91 μm. [d] Calculated from the experimental HLS value recorded at 1340 nm: $\beta_{1.91} = \beta_{1.34} (R_{1.34}/R_{1.91})$; $R_\omega = \omega_o^2/(\omega_o^2 - \omega^2) (\omega_o^2 - 4\omega^2)$.

Complexes **3a,b** were characterised by high-resolution mass spectrometry and gave satisfactory elemental analyses. The $^{31}P\{^1H\}$ NMR spectra of the crude reaction mixtures contained only one sharp resonance, indicating the formation of only one geometric isomer. The large ^{31}P NMR coordination downfield chemical shifts (> 50 ppm, Table 1) are consistent with the formation of five-membered P,N-palladacycles.[3f,g] Only one set of ^1H and $^{13}C\{^1H\}$ NMR signals are recorded for the 2-pyridylphosphole ligands indicating that complexes **3a,b** possess a highly symmetric structure. The NMR data of the 2-pyridylphosphole moieties of **3a** and **3b** are comparable[9] and very similar to those of a related *cis*-(2-pyridyl-5-thienylphosphole)$_2$Pd^{2+} complex, recently characterised by an X-ray diffraction study.[3g]

The ionic nature of complexes **3a,b** precludes EFISH experiments and hence their first molecular hyperpolarisibilities were measured by means of harmonic light scattering (HLS) experiments. A fundamental wavelength of 1.91 μm was used in order to circumvent problems associated with enhancement of β by two-photon absorption fluorescence since **3a,b** exhibit low-energy UV-vis absorptions (Fig. 1). Complexes **3a,b** exhibit fairly high nonlinear optical activities with β values reaching 170–180 $\times$ 10^{-30} e.s.u. These large values clearly indicate that the *trans-effect* has imposed a parallel organisation of P,N-dipoles **2a,b** in the Pd-coordination sphere. As expected, the square-planar metal centre acts as a template imposing a noncentrosymmetric assembly of identical 1D-chromophores **2a,b**. Furthermore, the metal plays a puzzling role since a considerable enhancement of the NLO-activities is observed upon complexation (Table 1). The β value of derivative **2b** at 1.91 μm (31$\times$ 10^{-30} e.s.u) was deduced from the experimental HLS at 1.34 μm (35 $\times$ 10^{-30} e.s.u.) using the two-level dispersion approximation.[10] The molecular hyperpolarisibility of complex **3b** (180 $\times$ 10^{-30} e.s.u.) is much higher than the sum over the contribution of two sub-chromophores **2b**. In a first approach, this effect could be related to an increase of the acceptor character of the pyridine groups and/or to a modification of the phosphole dienic π-system polarisability[4] upon coordination. However, it is very likely that the origin of this large β enhancement is due to the appearance of new contributions to the second-order molecular hyperpolarisability. This assumption is supported by the UV-vis spectra of complexes **3a,b** that show two maxima (Fig. 1). Phospholes can be regarded as classical phosphines[7b,c] acting predominantly as σ-donors whereas the π-acceptor ability of pyridine is well-kwown.[6] It is thus very probable that the low energy UV-vis absorptions are due to charge transfers from the metal or the phosphorus-metal fragments to the pyridine ligands.[11] A simple vector model shows that these metal-to-ligand (MLCT) or ligand-to-metal-to-ligand charge transfers (LMLCT) will coherently contribute to the second harmonic generation (molecule **B**, Scheme 1).

In conclusion, we have described the first NLO-phores based on phosphole rings and we have shown that coordination chemistry offers a simple synthetic methodology for controlling the in-plane pa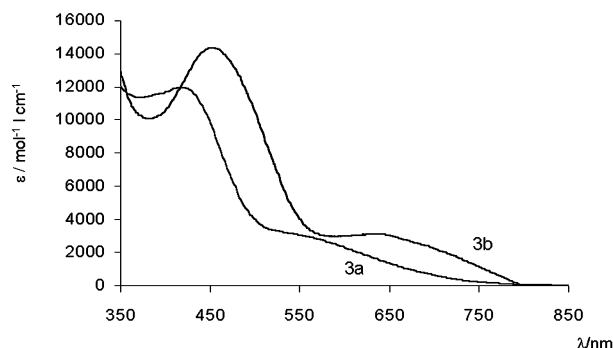rallel arrangement of 1D-P,N-dipoles in a molecular assembly. The elucidation of the origin of the dramatic increase of the NLO-activity observed upon coordination and the non-centrosymmetric macroscopic organisation of these new NLO-phores are under active investigation.

Notes and references

1 (*a*) E. Kelderman, W. A. J. Starmans, J. P. M. van Duynhoven, W. Verboom, J. F. J. Engbersen, D. N. Reinhoudt, L. Derhaeg, T. Verbiest, K. Clays and A. Persoons, *Chem. Mater.*, 1994, **6**, 412; (*b*) H. S. Nalwa, T. Watanabe and S. Miyata, *Adv. Mater.*, 1995, **7**, 754; (*c*) E. D. Rekaï, J-B. Baudin, L. Julien, I. Ledoux, J. Zyss and M. Blanchard-Desce, *Chem. Eur. J.*, 2001, **7**, 4395; (*d*) S. Yokoyama, T. Nakahama, A. Otomo and S. Mashiko, *J. Am. Chem. Soc.*, 2000, **122**, 3174; (*e*) T. Thami, P. Bassoul, M. A. Petit, J. Simon, A. Fort, M. Barzoukas and A. Villaeys, *J. Am. Chem. Soc.*, 1992, **114**, 915; (*f*) M. S. Wong, J.-F. Nicoud, C. Runser, A. Fort, M. Barzoukas and E. Marchal, *Chem. Phys. Lett.*, 1996, **253**, 141; (*g*) H. J. Deussen, C. Boutton, N. Thorup, T. Geisler, E. Hendrickx, K. Bechgaard and A. Persoons, *Chem. Eur. J.*, 1998, **4**, 240; (*h*) P. J. A. Kenis, O. F. J. Noordman, H. Schönherr, E. G. Kerver, B. H. M. Snellik-Ruël, G. J. van Hummel, S. Karkema, C. P. J. M. van des Vorst, J. Hare, S. J. Picken, J. F. J. Engbersen, N. F. van Hulst, G. J. Vansco and D. N. Reinhoudt, *Chem. Eur. J.*, 1998, **4**, 1225; (*i*) H. J. Deussen, E. Hendrickx, C. Boutton, D. Krog, K. Clays, K. Bechgaard, A. Persoons and T. Bjornholm, *J. Am. Chem. Soc.*, 1996, **118**, 684.

2 (*a*) A. Pidcock, R. E. Richards and L. M. Venanzi, *J. Chem. Soc. (A)*, 1966, 1701; (*b*) R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712.

3 (*a*) J. Buey, S. Coco, L. Diez, P. Espinet, J. M. Martin-Alvarez, J. A. Miguel, S. Garcia-Granda, A. Tesouro, I. Ledoux and J. Zyss, *Organometallics*, 1998, **17**, 1750; (*b*) P. Braunstein, C. Frison and X. Morise, *Angew. Chem., Int. Ed.*, 2000, **39**, 286; (*c*) P. Espinet and K. Soulantica, *Coord. Chem. Rev.*, 1999, **193–195**, 499; (*d*) P. Braunstein and F. Naud, *Angew. Chem., Int. Ed.*, 2001, **40**, 680; (*e*) G. Helchem and A. Pfaltz, *Acc. Chem. Res.*, 2000, **33**, 336; (*f*) M. Sauthier, B. Le Guennic, V. Deborde, L. Toupet, J.-H. Halet and R. Réau, *Angew. Chem., Int. Ed.*, 2001, **40**, 228; (*g*) M. Sauthier, F. Leca, L. Toupet and R. Réau, *Organometallics*, 2002, **21**, 1591; (*h*) C. Hay, M. Sauthier, V. Deborde, M. Hissler, L. Toupet and R. Réau, *J. Organomet. Chem.*, 2002, **643–644**, 494.

4 (*a*) D. Le Vilain, C. Hay, V. Deborde, L. Toupet and R. Réau, *Chem. Commun.*, 1999, 345; (*b*) C. Hay, F. Fischmeister, M. Hissler, L. Toupet and R. Réau, *Angew. Chem., Int. Ed.*, 2000, **39**, 1812; (*c*) C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulászi and R. Réau, *Chem. Eur. J.*, 2001, **19**, 4222.

5 (*a*) I. D. L. Albert, T. J. Marks and M. A. Ratner, *J. Am. Chem. Soc.*, 1997, **119**, 6575; (*b*) D. Delaire, A. Dransfeld, M. T. Nguyen and L. G. Vanquickenborne, *J. Org. Chem.*, 2000, **65**, 2631.

6 (*a*) B. J. Coe, J. A. Harris, K. Clays, A. Persoons, K. Wostyn and B. S. Brunschwig, *Chem. Commun.*, 2001, 1548; (*b*) O. Maury, J.-P. Guégan, T. Renouard, A. Hilton, P. Dupau, N. Sandon, L. Toupet and H. Le Bozec, *New J. Chem.*, 2001, **25**, 1553; (*c*) T. Renouard and H. Le Bozec, *Eur. J. Inorg. Chem.*, 2000, **1**, 229; (*d*) S. Di Bella, *Chem. Soc. Rev.*, 2001, **30**, 355; (*e*) P. G. Lacroix, *Eur. J. Chem.*, 2001, 339.

7 (*a*) P. J. Fagan, W. A. Fagan and J. C. Calabrese, *J. Am. Chem. Soc.*, 1994, **116**, 1880; (*b*) F. Mathey, *Chem. Rev.*, 1988, **88**, 437; (*c*) L. D. Quin in *Comprehensive Heterocyclic Chemistry*, ed. A. R. Katritzky, Pergamon, Oxford, England, 1996, 757.

8 According to the two-state model, the nonresonant hyperpolarisability can be estimated as $\beta_0 = \beta_w (\omega_o^2 - \omega^2)(\omega_o^2 - 4\omega^2)/\omega_o^2$ where β_w is the value measured at 2ω with the fundamental laser at 2ω.[6c–e]

9 Selected $^{13}C\{^1H\}$ NMR data for complexes **3a,b** (75.469 MHz, CDCl$_3$). **3a**: δ 157.4 (m, C$_2$, py), 153.3 (m, P$C C$phos), 152.6 (s, C$_6$ py), 151.1 (d, J = 18.1 Hz, PCC phos), 141.1 (s, C$_4$ py), 125.3 (s, C$_5$ py), 124.2 (s, C$_3$ py); **3b**: δ 153.6 (m, C$_2$ py), 152.8 (m, PCC phos), 151.7 (s, C$_6$ py); 151.1 (d, J = 17.3 Hz, PCC phos), 140.9 (s, C$_4$ py), 134.9 (d, J = 54.9 Hz, PC phos), 132.5 (d, J = 52.9 Hz, PC phos), 124.8 (s, C$_5$ py), 123.7 (m, C$_3$, py).

10 Note that care must be taken when comparing HLS β values obtained under different experimental conditions: P. Kaatz and D. P. Shelton, *J. Phys. Chem.*, 1996, **100**, 8157 and ref. 6a.

11 Theoretical calculations in order to elucidate the origin of these transitions are in progress. Note that a negative solvatochromism was observed for these transitions.

Fig. 1 UV-visible spectra of complexes **3a** and **3b**.