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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*

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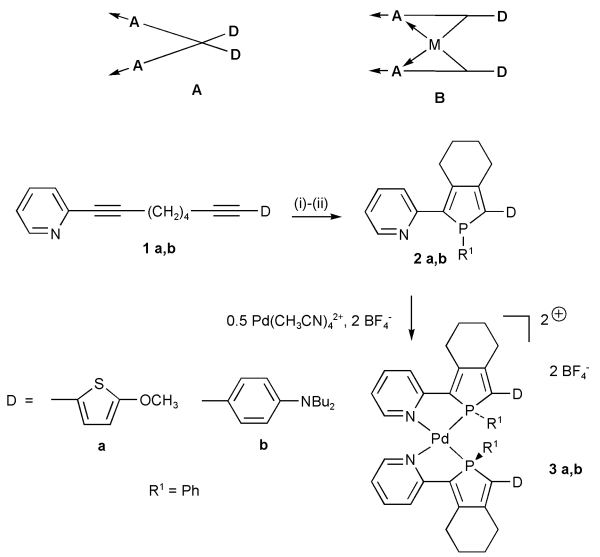
In plane parallel arrangement and enhancement of NLO-activity are observed upon coordination of heteroditopic dipoles containing a phosphole ring on square-planar d^8-palladium centre.

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 d^8-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 d^8-square-planar Pd-centre.



Scheme 1 (i) Cp_2ZrCl_2, 2 BuLi, THF, −78 to 25 °C; (ii) $PhPBr_2$, THF, −78 to 25 °C.

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 $PhPBr_2$ (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 CH_2Cl_2 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 ($\Delta\lambda_{max}$: 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 CH_2Cl_2 solution with $(CH_3CN)_4Pd^{2+}$, 2 BF_4^- giving rise, almost quantitatively, to complexes **3a**,**b** isolated as air stable solids (Scheme 1).

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

Compound	δ $^{31}P\{^1H\}$[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 CH_2Cl_2. [b] EFISH measurements in CH_2Cl_2 (10^{-2} mol L^{-1}) at 1.91 μm. [c] HLS measurements in CH_2Cl_2 at 1.91 μm. [d] Calculated from the experimental HLS value recorded at 1340 nm: $\beta_{1.91} = \beta_{1.34}(R_{1.34}/R_{1.91})$; $R_\omega = \omega_o^2/(\omega_o^2 - \omega^2)(\omega_o^2 - 4\omega^2)$.

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Complexes **3a**,**b** were characterised by high-resolution mass spectrometry and gave satisfactory elemental analyses. The $^{31}P\{^{1}H\}$ 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 ^{1}H and $^{13}C\{^{1}H\}$ 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)$_2Pd^{2+}$ 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 parallel 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.

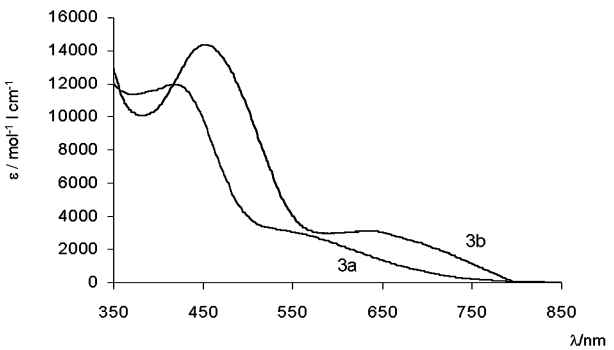

Fig. 1 UV-visible spectra of complexes **3a** and **3b**.

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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 ω.[6c–e]

9 Selected $^{13}C\{^{1}H\}$ NMR data for complexes **3a**,**b** (75.469 MHz, $CDCl_3$). **3a**: δ 157.4 (m, C_2, py), 153.3 (m, PC*C*phos), 152.6 (s, C_6 py), 151.1 (d, J = 18.1 Hz, PC*C* 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, PC*C* phos), 151.7 (s, C_6 py); 151.1 (d, J = 17.3 Hz, PC*C* phos), 140.9 (s, C_4 py), 134.9 (d, J = 54.9 Hz, P*C* phos), 132.5 (d, J = 52.9 Hz, P*C* 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.