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# The synthesis of tetrahedral bipyridyl metallo-octupoles with large second- and third-order nonlinear optical properties

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## ABSTRACT

Two new 4,4′-bis(donor)-6,6′-diphenyl- 2,2′-bipyridine ligands and their corresponding $D_{2d}$ ($Cu^I$, $Ag^I$, $Zn^{II}$) octupolar metal complexes were synthesized, and their linear and nonlinear optical properties were investigated. A single crystal X-ray structure was also determined for the bis[4,4′-bis(diethylaminostyryl)-6,6′-diphenyl-bipyridine]copper(I) complex, which revealed a distorded pseudo-tetrahedral geometry. Molecular second-order nonlinear optical properties were determined for the complexes using the Harmonic Light Scatterring technique at 1.91 μm. These metallo-chromophores display large first hyperpolarizabilities $\beta_{1.91}$ in the range of $211–340 \times 10^{-30}$ esu, which increase with the Lewis acidity of the metal ion. The two-photon absorption properties of the bipyridyl ligands and related complexes were determined using either the two-photon emission method for fluorescent compounds or the open aperture Z-scan technique for non emissive ones. The complexes display red-shifted two-photon absorption bands compared to their metal-ion free chromophores, as well as a large increase of the maximum two-photon absorption cross-sections.

## 1. Introduction

Molecular nonlinear optical (NLO) materials have been the focus of intensive investigations for several decades from both the fundamental and practical points of view for their possible applications in the domain of optoelectronics and photonics [1–4]. Among them, transition metal complexes are especially interesting because they offer, compared to organic molecules, additional advantages due to their structural, electronic and optical properties [5–12]. Greater design flexibility can be achieved by varying the metal, its oxidation state, the ligand environment and the geometry. In addition, many complexes are known to possess low-lying charge transfer transitions such as intraligand (ILCT), metal-to-ligand (MLCT) and ligand-to-metal (LMCT), which can be associated with large second-order nonlinearities β.

Metal complexes of nitrogen-heterocyclic ligands, such as pyridines and oligopyridines, represent an important class of NLO chromophores which have received much attention during the last fifteen years [13–19]. In this context, our research group has been involved in the NLO properties of bipyridyl metal complexes. We have previously shown that ligands such as donor-substituted bipyridyl are excellent building blocks for the construction of either dipolar compounds [20–22] or non-dipolar metal complexes of $D_3$ symmetry [23–25]. These studies have underlined the important role of both the metallic core and the bipyridyl substituents to enhance the quadratic nonlinear optical responses of such chromophores. These molecules are also attractive for third-order nonlinear applications, including two-photon absorption (TPA), and recent experimental and theoretical studies on tris(bipyridyl) metal complexes have revealed moderate to large TPA cross-sections $\sigma_2$ [26–30].

The design of tetrahedral ($T_d$) or pseudo-tetrahedral ($D_{2d}$) metal complexes with quadratic NLO and TPA properties has been scarcely studied, in comparison with octahedral $D_3$ metal complexes [13,31]. Bipyridyl ligands also allow the design of $D_{2d}$ octupoles by coordination of two bipyridines to metal ions, such as $Cu^I$, $Ag^I$ or $Zn^{II}$. This type of geometry has been extensively used to design new architectures that feature an original topology, such as catenates or knots [32]. The key feature to stabilize the tetrahedral geometry is the incorporation of either alkyl or aryl substituents at the

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6,6′-positions in the bipyridyl ligand. We have previously reported the first examples of pseudo-tetrahedral Cu(I), Ag(I) and Zn(II) complexes containing the 4,4′-dialkylaminostyryl-6,6′-dimethyl-2,2′-bipyridine ligand **a** (Scheme 1), which have been shown to display moderate to good second-order NLO responses β [24]. These preliminary results prompted us to prepare and study a series of complexes featuring bipyridine ligands with phenyl groups as substituents α to the nitrogen atoms. Here we describe the synthesis of ligands **b** and **c** and we show that the corresponding metal complexes represent a new class of $D_{2d}$ tetrahedral organometallic chromophores. The replacement of methyl by phenyl substituents is expected to give rise to stable pseudo-tetrahedral complexes with larger second- and third-order nonlinearities, as the consequence of extended conjugated π-systems.

In order to include the effect of varying the donor moiety, we have also incorporated on the 4,4′-positions a diphenylaminostyryl group, because its contains an enhanced π-conjugation which is also expected to increase the NLO responses. The effect of alkyl vs aryl substitution on the molecular hyperpolarizability has already been observed on push-pull derivatives, and explained by an enhanced π-conjugation in the case of diarylamino donor groups [33–36].

## 2. Experimental

### 2.1. Materials

All reactions were performed under argon with Schlenk techniques. All reagents and solvents were of commercial quality and were purified or dried and stored under nitrogen using standard procedures.

### 2.2. Measurements

NMR spectra ($^1$H, $^{13}$C) were recorded at room temperature on BRUKER DPX200 and DMX500 spectrometers operating at 200.12 and 500.13 MHz. UV–Visible spectra were recorded on a Cary 5000 spectrophotometer. Fluorescence experiments were performed in dilute dichloromethane solution ($\approx 10^{-5}$ mol L$^{-1}$) with a PTI spectrometer. High-resolution mass spectra were obtained on a Bruker Micro-TOF-Q II instrument or a ZabSpec TOF Micromass instrument at CRMPO, University of Rennes 1. Elemental analyses were performed by the CRMPO, University of Rennes 1.

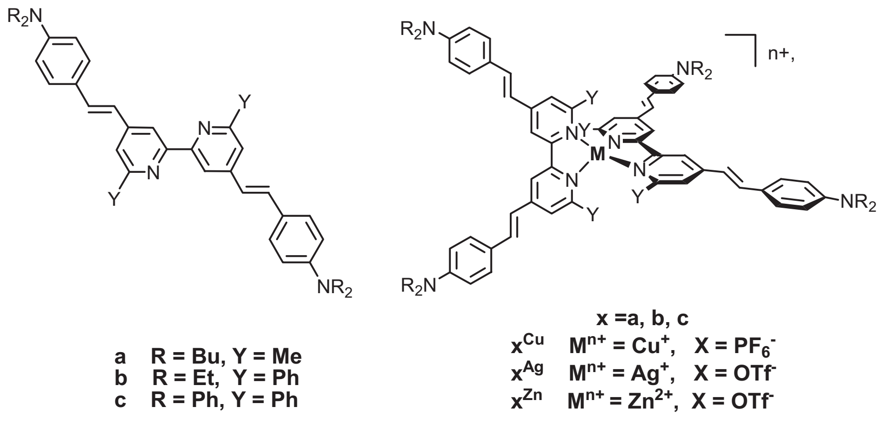
The Harmonic Light Scattering (HLS) technique was used for the molecular hyperpolarisability ($\beta$) measurements which were performed in dicholoromethane at a fundamental wavelength of 1.91 μm. Using this wavelength ensures that any contribution to the HLS signal from two-photon fluorescence becomes negligible, as its harmonic at 955 nm lies far from the fluorescence domain. The values of $\beta_{1.91}$ and the corresponding dipersion free hyperpolarizabilities $\beta_0$ for all the complexes are reported in Table 1. These “static” $\beta_0$ values are inferred from experimental ones using a two-level dispersion model according to Ref. [37]. Although this model is not valid for 2- or 3-dimensional charge transfer processes [38], it has been shown that in the case of purely octupolar systems, the 3-level dispersion equation is equivalent to the 2-level one owing to the degeneracy of the two excited states [39]. In the case of MLCT additional transition for copper complexes, the weak molar absorption coefficient associated to it makes its contribution to the $\beta$ values almost negligible. HLS measurements were carried out in concentrated dicholoromethane solution ($1–5 \times 10^{-2}$ mol L$^{-1}$) with a concentrated solution of ethyl-violet as reference ($\beta_{1.91} = 170 \times 10^{-30}$ esu).

The TPA cross sections ($\delta$) of fluorescent chromophores were determined using the relative two-photon excited fluorescence (TPEF) method [40,41]. These measurements were performed with a femtosecond mode-locked Ti: Sapphire laser (Spectra-Physics, Mai Tai: pulse duration: ~100 fs; repetition rate: 80 MHz; wavelength range: 690–1020 nm). A $10^{-4}$ M solution of fluorescein [41] in water at pH = 11 ($\delta_r = 38 \pm 9.7$ GM at 782 nm) was used as the reference (r). The value of $\delta$ for a sample (s) is given by:

$$\delta_S = \frac{S_S \Phi_r \eta_r c_r}{S_r \Phi_S \eta_S c_S}\delta_r$$

where $S$ is the detected two-photon excited fluorescence integral area, $c$ the concentration of the chromophores, and $\Phi$ is the fluorescence quantum yield of the chromophores. $\eta$ is the collection efficiency of the experimental set-up and accounts for the wavelength dependence of the detectors and optics as well as the difference in refractive indices between the solvents in which the reference and sample compounds are dissolved. The measurements were conducted in a regime where the fluorescence signal showed a quadratic dependence on the intensity of the excitation beam, as expected for two-photon-induced emission. The collection of the two-photon-induced fluorescence signal was performed at the same excitation wavelength (i.e. 782 nm) for fluorescein and compounds. The concentration of the compounds in $CH_2Cl_2$ was in the range of $0.5–3 \times 10^{-4}$ M. The laser intensity was in the range of $0.2–2 \times$ GW/cm$^2$. The experimental error on the reported cross section is 15–20%.

The two-photon absorption cross sections for the non-fluorescent compounds were measured at 800 nm and 900 nm by using open-aperture Z-scan method [42,43] with the same femtosecond laser used for TPEF. After passing through a beam expander (×4), the laser beam is focused using an $f = 10$ cm lens and passed through a quartz cell (1 mm optical path length). The position of the



**Scheme 1.** Chemical structures of representative bipyridyl pro-ligands **a**, **b** and **c** and corresponding pseudo-tetrahedral Copper(I), Silver(I) and Zinc(II) complexes.

**Table 1**
Crystal and structure refinement data of complex $\mathbf{b}^{\mathbf{Cu}}$.

| | | | |
|---|---|---|---|
| Empirical formula | C93.50 H95 Cl3 Cu F6 N8 P | $\theta$ range (°) | 2.60 to 27.00 |
| Formula weight | 1645.64 | Index range | $-12 \le h \le 17$ |
| Crystal system | Triclinic | | $-21 \le k \le 20$ |
| Space group | *P*-1 | | $-27 \le l \le 26$ |
| *a* (Å) | 13.8741(9) | Reflns collected | 30,637 |
| *b* (Å) | 16.4820(10) | Unique reflns | 18,285 |
| *c* (Å) | 21.2900(10) | Refinement method | Full-matrix |
| $\alpha$ (°) | 70.931(7) | on $F^2$ | Least-squares |
| $\beta$ (°) | 86.407(6) | Goodness-of-fit on $F^2$ | 0.919 |
| $\gamma$ (°) | 84.681(6) | $R_1$ $[I > 2\sigma(I)]$ | 0.0970 |
| $V$ (Å$^3$), Z | 4578.8(5)/2 | $wR_2$ $[I > 2\sigma(I)]$ | 0.2470 |
| $D_{\mathrm{calc}}$ | 1.194 g/cm$^{-3}$ | $R_1$ (all data) | 0.2175 |
| $\mu$ (mm$^{-1}$) | 0.403 | $wR_2$ (all data) | 0.2874 |
| $F$ (000) | 1722 | Residual (e Å$^{-3}$) | 1.349 and −0.720 |

sample cell is varied along the laser-beam direction (*z*-axis) using a Z-step motorized stage controlled by a computer. At constant incident excitation, the local power density within the sample is changed and the corresponding transmitted laser beam, $T(z)$, recorded with a silicon photodetector (Ophir PD300) is monitored in connection with the z-position of the cell. The on-axis peak intensity of the incident pulses at the focal point, $I_0$, ranged from 40 to 45 GW cm$^{-2}$. If we assume that the linear absorption of the sample is negligible at working wavelength and that the laser exhibits a Gaussian beam profile, the nonlinear absorption coefficient $\beta$ (Note that there is some confusion over the term $\beta$ in nonlinear optics, since it is sometimes used to describe the second-order polarizability, and occasionally for the two-photon absorption coefficient) can be calculated from the curve fitting to the experimental transmittance with the following equation (1):

$$T(z) = 1 - \frac{\beta l I_0}{2\left(1 + \left(\frac{z}{z_0}\right)^2\right)} \tag{1}$$

where $z_0$ corresponds to the diffraction length of the incident beam, $l$ the optical path length. The 2PA cross-section, $\delta$, (in units of 1 GM: $10^{-50}$ cm$^4$ s photon$^{-1}$ molecule$^{-1}$) is then determined by using the relationship:

$$\beta = \frac{\delta N_A d}{h\nu} 10^{-3}$$

where $h$ is the Planck constant, $\nu$ the frequency of the incident laser beam, $N_A$ the Avogadro constant and $d$ is the concentration of the chromophore (mol L$^{-1}$). The concentration of the compounds in $CH_2Cl_2$ was in the range of $1–3 \times 10^{-3}$ M. The rhodamine 6G in methanol [44] (16.2 ± 2.4 GM at 806 nm) was used for the calibration of our measurement technique.

It should be noted that the Z-scan measurement as nonlinear transmission method is strongly dependent on the local intensity at the focal point. Due to the variation of the focal beam size before and after the focal point and to self-focusing of the laser beam across the sample, the two-photon absorption cross sections measured with Z-scan method could differ significantly from those obtained with the fluorescence-based method

### 2.3. Synthesis

#### 2.3.1. Synthesis of ligand **b**

In a Schlenk flask, 6,6′-diphenyl-4,4′-dimethyl-[2,2′]-bipyridine **1** (150 mg, 0.44 mmol) and 4-diethylaminobenzaldehyde (372 mg, 1.78 mmol, 4 equiv.) were dissolved in dimethylformamide (15 mL) and tBuOK (200 mg, 1.78 mmol) was slowly added at room temperature. The solution, which immediately turned brown, was then heated at 90 °C overnight. Addition of water led to the formation of a pale brown mixture. Dimethylformamide was removed by trap-to-trap method, the mixture was extracted by dichloromethane, dried over $MgSO_4$, and the solvent was removed under vacuum. Recrystallization from a dichloromethane-pentane mixture gave **b** as a orange microcrystalline powder (230 mg, 79%). $^1H$ NMR ($CD_2Cl_2$, 500 MHz): $\delta$ ppm 8.68 (s, 2H, $H^{6,6'}$), 8.31 (d, $J = 8.3$ Hz, 4H, $C_6H_4$–), 7.92 (s, 2H, $H^{3,3'}$), 7.58 (m, 12H, $C_6H_5$– + –CH=CH–), 7.10 (d, $J = 16.3$ Hz, 4H, –CH=CH–), 6.75 (d, $J = 9.0$ Hz, 4H, $C_6H_5$–), 3.46 (q, $J = 7.1$ Hz, 8H, $CH_3\mathit{CH_2}$–), 1.24 (t, $J = 7.1$ Hz, 12H, $\mathit{CH_3}CH_2$–). $^{13}C$ NMR ($CDCl_3$, 400 MHz): $\delta$ ppm 156.8, 156.5, 148.1, 147.3, 140.0, 133.1, 128.7, 128.68, 128.64, 127.1, 123.7, 121.6, 117.0, 116.8, 111.6, 44.4, 12.6. Anal. found: C, 83.09; H, 7.05; N, 8.72. $C_{46}H_{46}N_4 \cdot 0.5H_2O$ Calc.: C, 83.22; H, 7.14; N, 8.44, *m*/*z* (Micro-TOF-Q II) 655.3793; ($[M+H]^+$, $C_{46}H_{47}N_4$ requires 655.3795).

#### 2.3.2. Synthesis of ligand **c**

Compound **c** was prepared according to the above procedure, from 6,6′-diphenyl-4,4′-dimethyl-[2,2′]-bipyridine (160 mg, 0.47 mmol), 4-diphenylaminobenzaldehyde (285 mg, 1.04 mmol, 2.2 equiv.) and tBuOK (214 mg, 1.9 mmol) in DMF (15 mL), (250 mg, 62%). $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ ppm 8.68 (s, 2H, $H^{6,6'}$), 8.24 (d, $J = 7.2$ Hz, 4H, $C_6H_4$–), 7.87 (s, 2H, $H^{3,3'}$), 7.58 (t, $J = 7.4$ Hz, 4H, $C_6H_5$–), 7.49 (m, 6H, $C_6H_5$–),), 7.32 (t, $J = 7.3$ Hz, 6H, $C_6H_5$–), 7.12 (m, 22H, $C_6H_5$–). $^{13}C$ NMR ($CDCl_3$, 500 MHz): $\delta$ ppm 157.0, 148.3, 147.3, 146.6, 139.7, 132.5; 130.2; 129.3; 128.9; 128.7; 128.0; 127.1; 124.8; 123.4; 123.0; 117.4; 117.0. Anal. found: C, 82.60; H, 5.32; N, 6.61. $C_{62}H_{46}N_4 \cdot 0.75CH_2Cl_2$ Calc.: C, 82.75; H, 5.26; N, 6.15; *m*/*z* (Micro-TOF-Q II) 847.3802, ($[M+H]^+$, $C_{62}H_{47}N_4$ requires 847.3795).

#### 2.3.3. General procedure for the preparation of bis(bipyridyl)metal complexes

Diphenylbipyridyl ligand (50 mg, 0.076 mmol) and the corresponding Metal salts (0.5 equiv) were mixed in dichloromethane (10 mL). After stirring overnight at room temperature, the dichloromethane was evaporated. The solid was purified further by recrystallization from a $CH_2Cl_2$/pentane mixture ($v/v = 1{:}10$).

*2.3.3.1. Complex [Cu(b)₂][PF₆] ($\mathbf{b}^{\mathbf{Cu}}$).* Dark-brown powder, 73% yield; $^1H$ NMR ($CD_2Cl_2$, 500 MHz): $\delta$ ppm 7.93 (s, 4H), 7.55 (m, 24H), 7.12 (m, 4H), 6.99 (m, 12H), 6.79 (d, $J = 8.0$ Hz, 8H), 3.49 (q, $J = 7.1$ Hz, 16H), 1.27 (t, $J = 7.1$ Hz, 24H). $^{13}C$ NMR ($CD_2Cl_2$, 500 MHz): $\delta$ ppm 156.6, 153.3, 150.2, 148.8, 147.5, 138.8, 135.3, 129.0, 127.5, 127.3, 122.6, 120.7, 118.9, 117.3, 111.5, 44.4, 12.4. Anal. found: C, 73.72; H, 7.13; N, 6.13. $C_{92}H_{92}CuF_6N_8P \cdot 2C_5H_{12}$ Calc.: C, 73.79; H, 7.03; N, 6.74; *m*/*z* (Zabspec-TOF) 1371.6741, ($[M+H]^+$, $C_{92}H_{92}N_8Cu$ requires 1371.67409).

*2.3.3.2. Complex [Ag(b)₂][OTf] ($\mathbf{b}^{\mathbf{Ag}}$).* Gold powder, 75% yield; $^1H$ NMR ($CD_2Cl_2$, 500 MHz): $\delta$ ppm 7.96 (s, 4H), 7.73 (s, 4H), 7.57 (m, 20H), 7.03 (m, 16H), 6.78 (s, 8H), 3.49 (q, $J = 7.1$ Hz, 16H), 1.27 (t, $J = 7.1$ Hz, 24H). $^{13}C$ NMR ($CD_2Cl_2$, 500 MHz): $\delta$ ppm 158.7, 153.8, 149.0, 140.5; 135.7, 129.1, 128.1, 127.0, 122.0, 119.5, 118.8, 118.0, 111.5, 44.5, 12.3. Anal. found: C, 72.59; H, 7.32; N, 5.78. $C_{93}H_{92}AgF_3N_8O_3S \cdot 3C_5H_{12}$ Calc.: C, 72.75; H, 7.24; N, 6.28. *m*/*z* (Zabspec-TOF) 1415.6526, ($[M+H]^+$, $C_{92}H_{92}N_8Ag$ requires 1415.64959).

*2.3.3.3. Complex [Zn(b)₂][OTf]₂ ($\mathbf{b}^{\mathbf{Zn}}$).* Violet powder, 70% yield; $^1H$ NMR ($CD_2Cl_2$, 500 MHz): $\delta$ ppm 8.62 (s, 4H), 7.83 (d, $J = 15.9$ Hz, 4H), 7.73 (d, $J = 8.0$ Hz, 8H), 7.64 (s, 4H), 7.31 (d, $J = 8.0$ Hz, 12H), 7.24 (d, $J = 7.1$ Hz, 4H), 7.15 (t, $J = 7.2$ Hz, 8H), 6.81 (d, $J = 6.4$ Hz, 8H), 3.49 (q, $J = 7.1$ Hz, 16H), 1.27 (t, $J = 7.1$ Hz, 24H). $^{13}C$ NMR ($CD_2Cl_2$, 500 MHz): $\delta$ ppm 158.8, 154.7, 150.9, 141.7, 138.1, 132.2, 131.6, 130.2, 128.1, 126.1, 123.3, 120.8, 117.9, 116.8, 112.7, 45.8, 13.6. Anal. found: C, 70.93; H, 8.02; N, 4.46. $C_{94}H_{92}F_6N_8O_6S_2Zn\cdot 6C_5H_{12}$ Calc.: C, 70.71; H, 7.85; N, 5.32.

*2.3.3.4. Complex [Cu(c)$_2$][PF$_6$] (**c**$^{\mathbf{Cu}}$).* Dark-brown powder, 73% yield; $^1$H NMR ($CD_2Cl_2$, 500 MHz): $\delta$ ppm 7.55 (d, 16H), 7.38 (m, 24H), 7.16 (m, 52H). $^{13}$C NMR ($CD_2Cl_2$, 500 MHz): $\delta$ ppm 149.3, 147.0, 146.9, 129.49, 129.47, 129.44, 128.5, 127.54, 127.46, 125.4, 124.0, 122.5, 122.0, 111.6. Anal. found: C, 74.27; H, 4.41; N, 5.94. $C_{128}H_{98}AgF_3N_8O_3S\cdot 1.5CH_2Cl_2$ Calc.: C, 74.25; H, 4.72; N, 5.52; *m/z* (Micro-TOF-Q II) 1755.6724, ([C$^+$], $C_{124}H_{92}N_8Cu$ requires 1755.6735).

*2.3.3.5. Complex [Ag(c)$_2$][OTf] (**c**$^{\mathbf{Ag}}$).* Gold powder, 75% yield; $^1$H NMR ($CD_2Cl_2$, 500 MHz): $\delta$ ppm 8.01 (s, 4H), 7.55 (s, 4H), 7.59 (m, 20H), 7.37 (m, 16H), 7.16 (m, 48H). $^{13}$C NMR ($CD_2Cl_2$, 500 MHz): $\delta$ ppm 149.3, 147.1, 135.1, 129.8, 129.6, 128.5, 127.54, 127.15, 125.4, 124.0, 122.3, 122.2, 120.3, 119.2, 118.6. Anal. found: C, 69.77; H, 4.94; N, 4.90. $C_{128}H_{98}AgF_3N_8O_3S\cdot 3CH_2Cl_2$ Calc.: C, 69.70; H, 4.48; N, 5.08.

*2.3.3.6. Complex [Zn(c)$_2$][OTf]$_2$ (**c**$^{\mathbf{Zn}}$).* Violet powder, 70% yield; $^1$H NMR ($CD_2Cl_2$, 500 MHz): $\delta$ ppm 8.87 (s, 4H), 7.93 (d, $J = 16.3$ Hz, 4H), 7.73 (d, $J = 8.5$ Hz, 8H), 7.69 (s, 4H), 7.35 (m, 30H), 7.17 (m, 42H). $^{13}$C NMR ($CD_2Cl_2$, 400 MHz): $\delta$ ppm 157.1, 152.8, 149.3, 149.1, 146.1, 139.0, 135.9, 130.5, 128.7, 128.3, 127.5, 126.1, 124.9, 123.4, 123.0, 120.6, 119.9, 119.6. Anal. found: C, 67.48; H, 4.01; N, 5.32. $C_{128}H_{98}AgF_3N_8O_3S\cdot 3CH_2Cl_2$ Calc.: C, 67.00; H, 4.27; N, 4.85; *m/z* (Micro-TOF-Q II) 878.3352, ([C$^{++}$], $C_{124}H_{92}N_8Zn$ requires 878.3362).

### *2.4. X-ray diffraction crystallography*

Single crystals suitable for X-ray crystal analysis were obtained by slow diffusion of pentane into a dichloromethane solution of **b**$^{\mathbf{Cu}}$ at room temperature. Crystals were removed from their mother solution, coated with oil and rapidly transferred to the diffractometer in order to prevent solvent evaporation. The samples were studied on a Xcalibur Oxford Diffraction automatic diffractometer with graphite monochromated Mo-K$\alpha$ radiation. The structure was solved with SIR-97, which revealed the non-hydrogen atoms of the structure. After anisotropic refinement all the hydrogen atoms were found with a Fourier difference synthesis. The whole structure was refined with SHELXL97 by the full-matrix least-squares techniques [use of F magnitude; *x*, *y*, *z*, (ij for C, N and O atoms, *x*, *y*, *z* in riding mode for H atoms)]. ORTEP views were realized with PLATON98 [45]. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 794182. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [of from Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. The crystal and structure refinement data of **b**$^{\mathbf{Cu}}$ are listed in Table 1.

## 3. Results and discussion

### *3.1. Synthesis and characterization*

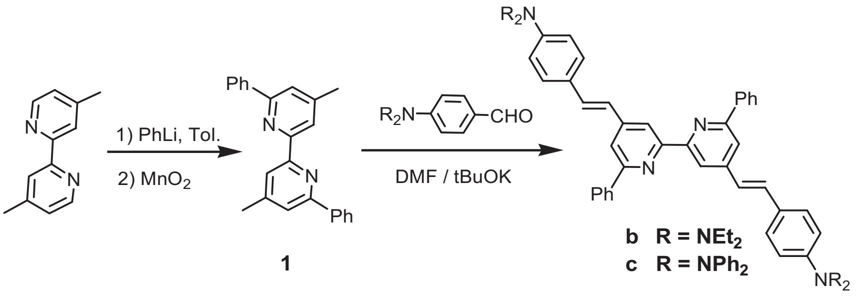
The 6,6′-diphenyl-4,4′-dimethyl-[2,2′]-bipyridine **1** was synthesized according to previously reported procedures [46]. The target bipyridine derivatives **b** and **c** were readily prepared by means of a double Knoevenagel condensation between **1** and the corresponding aldehyde derivatives, respectively, in the presence of *tert*-BuOK (Scheme 2). This coupling reaction afforded derivative **b** and **c** as orange microcrystals (average yield 80%), which were fully characterized by $^1$H and $^{13}$C NMR and UV/Vis spectroscopy.

Copper(I), silver(I) and zinc(II) complexes were obtained upon treatment of the ligands **b** and **c** (2 equiv.) with respectively [Cu(MeCN)$_4$]PF$_6$, AgOTf and Zn(OTf)$_2$ (1 equiv.) in dichloromethane solution at room temperature. The complexes were isolated in nearly quantitative yield and their structures were demonstrated by high resolution mass spectroscopy, $^1$H, $^{13}$C NMR spectroscopy, UV–visible and fluorescence spectroscopy. The $^1$H NMR spectra confirm the strong vicinal coupling constants of the olefinic protons ($J_{HH} \approx 16$ Hz) and no *E*/*Z* isomerization of the alkenyl fragments was detected.

### *3.2. Crystal structure of complex **b**$^{\mathbf{Cu}}$*

The complex **[Cu(b)$_2$][PF$_6$]** was also characterized in the solid state by X-ray diffraction method on single-crystals (See ESI for selected bond lengths and angles, crystal data and refinement parameters). Suitable crystals were obtained in a few days upon slow diffusion at room temperature of pentane into a $CH_2Cl_2$ solution of the complex. The **[Cu(b)$_2$][PF$_6$]** dark-brown complex crystallizes in the triclinic system with *P*-1 as the space group (Fig. 1). The crystal also contains dichloromethane molecules in addition to **[Cu(b)$_2$][PF$_6$]** complexes.

As expected and often observed, the cationic part of the structure is composed of a Cu(I) metal ion also coordinated to two ligands **b** with Cu–N distances varying between 2.015 and 2.057 Å. The coordination geometry around the metal center is pseudo tetrahedral with the NCuN angle varying between 82.8° and 131.9°. Both bipyridine units are in cis configuration with dihedral angles of 11.31 and 20.41° between the two pyridines. A relevant feature is the torsion angle between the two coordinated bipyridines which is ca 61.03°, so that the planes are far from being perpendicular. Four interligand $\pi$–$\pi$ stacking ($\approx$3.8 Å) between pyridines and the four phenyl rings flatten the coordination geometry around the copper center from tetrahedral coordination, which is a common feature in copper(I) complexes [47]. This strong distortion has been described earlier for several particularly interesting [Cu(NN)$_2$]$^+$ complexes [48,49]. For example, the X-ray structure of [Cu(dnpp)$_2$]PF$_6$ [50] described by McMillin and coworkers (dnnp = 2,9-dineopentyl-1,10-phenanthroline) reveals



**Scheme 2.** Synthesis of bipyridine derivatives **b** and **c**.

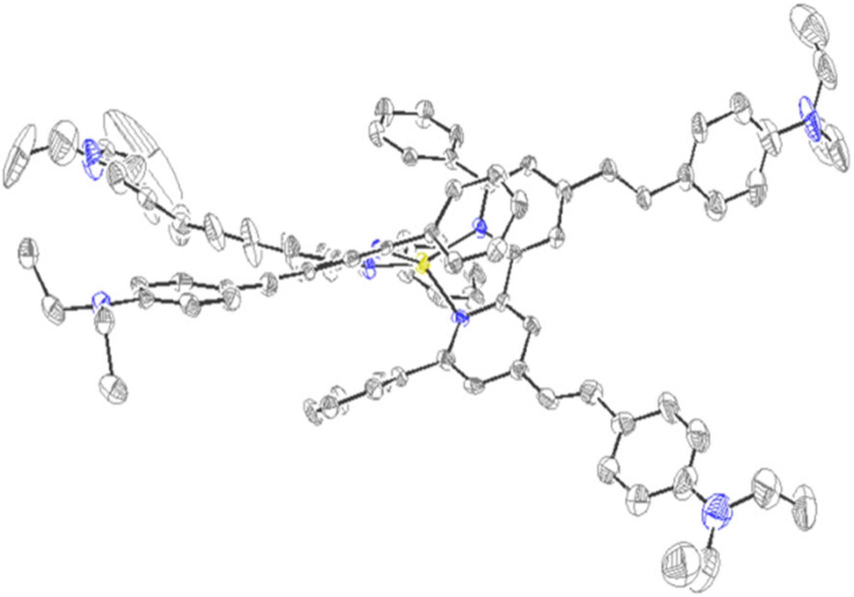


**Fig. 1.** ORTEP drawing of compound $\mathbf{b}^{\mathbf{Cu}}$ (50% probability thermal ellipsoids); for clarity H atoms, solvents and counter-anions were omitted.

that the dihedral angle between the least-squares planes of the dnpp ligands is only 63.4(1)°.

### *3.3. Optical properties*

#### *3.3.1. Linear optical properties*

The electronic absorption spectral data for all the ligands and the complexes recorded in dichloromethane are summarized in Table 2. Ligands **b** and **c** display intense intramolecular charge transfer bands (ICT) at $\lambda_{max} \approx 400$ nm. All complexes exhibit strong absorption bands in the visible region. These bands are sensitive to the nature of the donor group and the metallic core (Table 2). Two types of transitions can be observed: intraligand charge transfer (ILCT) and metal-to-ligand charge transfer (MLCT). In the case of silver(I) and zinc(II) complexes, UV-visible spectra exhibit one broad intense absorption band assigned to the ILCT transition. The electronic spectra of the copper(I) complexes also exhibit red-shifted intense absorptions ($\Delta\lambda_{abs}$(complex *vs.* ligand) = 26–28 nm) in the visible region assigned to intraligand charge transfer bands. In addition a typical MLCT transition [$\mathrm{Cu^I} \rightarrow \pi^*$(bpy)] is found at ca. 440 nm with smaller absorption coefficients and can be discerned in the spectra as a shoulder of the more intense ILCT band [51]. A more important red shift of ≈120 nm is observed for the zinc(II) series. The red shift of the ILCT transition induced by complexation can be correlated to the Lewis acidity of the metallic ion: the $\mathrm{Zn^{2+}}$ complex within each series does show the largest $\lambda_{ILCT}$ value, but those for the analogous $\mathrm{Cu^+}$ and $\mathrm{Ag^+}$ species are essentially indistinguishable, a feature already demonstrated for the tetrahedral series with the 4,4′-dialkenyl-6,6′-dimethyl-2,2′-bipyridine ligand [13].

Compounds **b**, **c** are fluorescent in dichloromethane at 298 K, with fluorescence quantum yield ranging from 0.15 to 0.64. The fluorescence quantum yield for compound **b** is consistent with the values previously described for donor-substituted bipyridyl ligands [52], but it increases dramatically to 0.64 for the ligand **c**. This enhancement effect of diphenylamino vs diethylamino has previously been observed by Cho and co-workers [53] for organic octupolar 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives. The corresponding metal complexes display different luminescent

**Table 2**
Optical and nonlinear optical data.

| Compound | $\lambda_{abs}$/nm[a] ($\varepsilon_{max}$)[b] | $\lambda_{em}$/nm | Stokes shift/cm$^{-1}$ | $\Phi_{em}$[c] | $\beta_{1.91}$[d]/10$^{-30}$ esu | $\beta_0$[e]/10$^{-30}$ esu | $\lambda_{TPA}$ nm | $\delta_{TPA}$/GM | $\lambda^{MAX}$ ($\delta^{MAX}$) | Method |
|---|---|---|---|---|---|---|---|---|---|---|
| **b** | 400 (71) | 495 | 4798 | 0.15 | – | – | 780 | 160 | 810 (171) | TPEF |
| $\mathbf{b}^{\mathbf{Cu}}$ | 426 (102)<br>438 (sh) | – | – | – | 268 | 203 | 800/900 | 2080/712 | | Z-scan |
| $\mathbf{b}^{\mathbf{Ag}}$ | 428 (122) | 550 | 5182 | 0.10 | 241 | 182 | 780 | 355 | 850 (677) | TPEF |
| $\mathbf{b}^{\mathbf{Zn}}$ | 527 (112) | 707 | 4831 | 0.005 | 401 | 258 | 900 | 500 | | Z-scan |
| **c** | 398 (45) | 502 | 5205 | 0.64 | – | – | 780 | 180[f] | 800 (200[f]) | TPEF |
| $\mathbf{c}^{\mathbf{Cu}}$ | 428 (79)<br>445 (sh) | – | – | – | 300 | 227 | 800/900 | 1931/988 | | Z-scan |
| $\mathbf{c}^{\mathbf{Ag}}$ | 431 (84) | 562 | 5408 | 0.33 | 283 | 214 | 780 | 210 | 800 (427) | TPEF |
| $\mathbf{c}^{\mathbf{Zn}}$ | 513 (101) | 712 | 5448 | 0.006 | 358 | 236 | 800/900 | 670/2093 | | Z-scan |
| **a** | 394 (67) | – | | – | – | – | 780 | 125 | 800 (141) | TPEF |

[a] In $CH_2Cl_2$.

[b] Units = $10^3$ Mol$^{-1}$ cm$^{-1}$.

[c] Fluorescence quantum yield with ±10% error.

[d] Measured by HLS at 1.91 μm in $CH_2Cl_2$ (precision ±10%) solution ($10^{-3}$ mol L$^{-1}$).

[e] Deduced from a two-level model.

[f] Addition of tetramethylguanidine (base).

behavior depending on the nature of the metal ion. Photoluminescence is observed for the silver(I) complexes $\mathbf{b^{Ag}}$ and $\mathbf{c^{Ag}}$ in diluted dichloromethane solution at room temperature (Table 2). They exhibit a broad, intense structureless emission band assigned to ligand-centered emission with large Stokes shifts (5182 and 5408 $cm^{-1}$, respectively). The complexation induces a red-shift of the emission wavelength when compared to that of free ligands **b** and **c** ($\Delta\lambda_{em}$(complex *vs.* ligand) = 55–60 nm). By contrast, copper(I) complexes $\mathbf{b^{Cu}}$ and $\mathbf{c^{Cu}}$ does not show any luminescence in dichloromethane, upon excitation either at the MLCT or the ILCT wavelength, whereas a very weak red-shifted photoluminescence is observed for the zinc(II) complexes $\mathbf{b^{Zn}}$ and $\mathbf{c^{Zn}}$ at ca. 710 nm.

### 3.3.2. Non linear optical properties

The Harmonic Light Scattering (HLS) technique was used for the molecular first hyperpolarizability $\beta$ measurements. The measurements were performed in dichloromethane at a fundamental wavelength of 1.91 µm. Using this wavelength ensures that any contribution to the HLS signal from two-photon fluorescence becomes negligible, as its harmonic at 955 nm lies far from the fluorescence domain. The values of $\beta_{1.91}$ and static hyperpolarizabilities $\beta_0$ are given in Table 2. These data clearly show the large quadratic NLO activity of these new multipolar chromophores. As previously observed for donor-substituted bipyridine metal complexes [54], the quadratic NLO response increases with the Lewis acidity of the metal center and the $\beta_0$ values roughly follow those found for the relative energies of the ILCT transitions which dominate the second-order nonlinear response, i.e. $Zn^{2+} > Cu^{+} \approx Ag^{+}$. All the complexes $\mathbf{b^{M}}$ and $\mathbf{c^{M}}$ (M = Cu, Ag, Zn) exhibit $\beta_{1.91}$ and $\beta_0$ values which are much larger than those of previously reported for pseudo-tetrahedral ($D_{2d}$) metal complexes featuring 4,4′-dibutylaminostyryl-6,6′-dimethyl-2,2′-bipyridine **a** (Scheme 1) ($\mathbf{a^{Cu}}$ $\beta_{1.91} = 113 \times 10^{-30}$ esu; $\mathbf{a^{Ag}}$ $\beta_{1.91} = 90 \times 10^{-30}$ esu; $\mathbf{a^{Zn}}$ $\beta_{1.91} = 245 \times 10^{-30}$ esu). This enhancement of the second-order NLO response can be reasonably attributed to an increase in the π-delocalization on the bipyridine ligands induced by the phenyl substituents, a feature that has also been observed in the case of iridium and ruthenium complexes featuring substituted phenanthroline ligands [55,56].

The two-photon absorption cross-sections were measured using either the TPEF (two-photon excited fluorescence) method for fluorescent compounds or using the open aperture Z-scan technique for non emissive ones. The ligands **b**,**c** exhibit similar TPA bands with maxima absorption wavelengths twice that of their linear absorption ones. This effect clearly indicates that the low-energy ILCT transition is two-photon active which is consistent with the noncentrosymmetric feature of the chromophores. Interestingly the maximum TPA cross sections are of the same order of magnitude (~170 GM at 780 nm). This suggests that both diethylamino and diphenylamino substituents have similar effects toward the TPA ability of the D-π-A chromophores. Such an equivalency has also been observed for a series of bis dialkylamino- or diarylamino-substituted bis(styryl)benzenes [40]. The pre-organization of the ligands around a metal-ion core leads to substantial changes of the TPA spectra. For instance, the coordination to $Ag^{+}$ induces a red shift of the TPA band as previously observed for linear absorption spectra (Fig. 2).

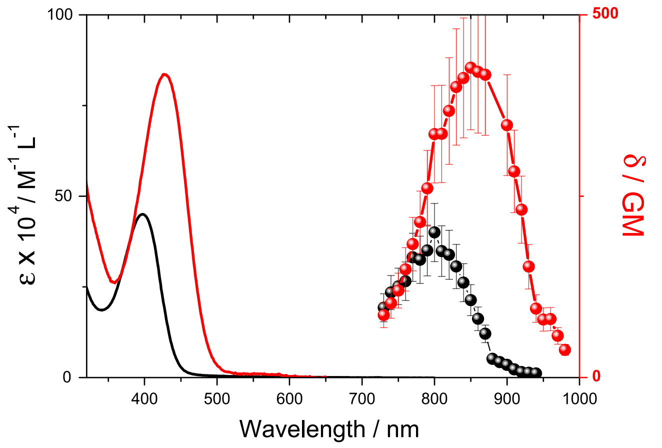


**Fig. 2.** One and two-photon absorption spectra of **c** (black) and $\mathbf{c^{Ag}}$ (gray) in dichloromethane.

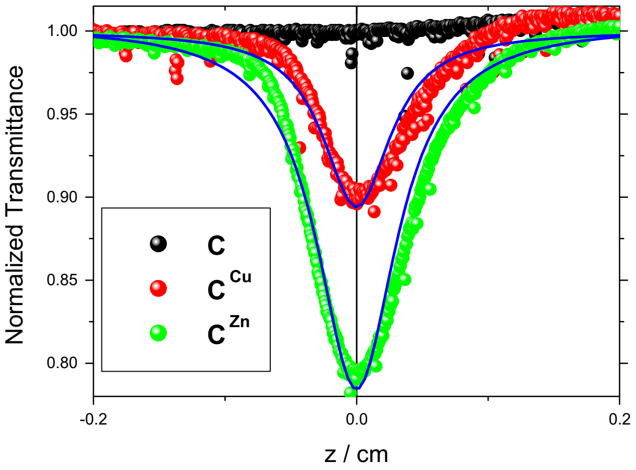


**Fig. 3.** Open aperture Z-scan traces for compounds in dichloromethane at 900 nm. ([**c**]: $2.8 \times 10^{-3}$ M, [$\mathbf{c^{Cu}}$]: $1.1 \times 10^{-3}$ M, [$\mathbf{c^{Zn}}$]: $1.8 \times 10^{-3}$ M). Theoretical fitting (full lines) using equation (1) (see text).

Moreover, the maximum TPA cross-section is multiplied by factor 3.9 and 2.1 for $\mathbf{b^{Ag}}$ and $\mathbf{c^{Ag}}$ respectively and as compared to their corresponding ligands. This effect is amplified with the increase of the Lewis acidity of the cation which promotes a stronger electron-withdrawing ability of bipyridyl and strengthens the charge transfer character of the ILCT transition. It is to be noted that free ligands show a weak nonlinear absorption behavior at 900 nm ($\delta < 20$ GM) whereas their corresponding $Zn^{2+}$ and $Cu^{+}$ complexes exhibit very large δ superior to 1000 GM (Fig. 3). Theoretical calculations relative to analogues of these octupolar tetrahedral complexes [57] predicted such very large TPA enhancements. We therefore demonstrate that metal ions can be used as a 3D template to generate highly two-photon active compounds with increased dimensionality [58].

## 4. Conclusion

In this study we have described the synthesis, linear properties and second and third-order nonlinearities of a series of $D_{2d}$ [Cu(I), Ag(I), Zn(II)] octupolar metal complexes featuring two new functionalized 4,4′-dialkenyl-6,6′-diphenyl-2,2′-bipyridine ligands. These compounds are found to display relatively large first hyperpolarizabilities $\beta_0$ values, in the range 182–258 $\times 10^{-30}$ esu, which follow the expected relationship with respect to the ILCT energies and the strength of the Lewis acidity of the metallic center. Remarkably, the presence of the phenyl substituents on the ortho positions of the bipyridine ligands produces stable pseudo-tetrahedral complexes with a strong enhancement of the second-order NLO responses, as compared to those of the related chromophores featuring methyl substituents. Finally, these complexes represent an interesting new family of two-photon absorption dyes which display red-shifted TPA bands compared to their metal ion-free chromophores and a large increase of the TPA cross sections.

## Acknowledgment

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