



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

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ARTICLE INFO

Article history:

Received 8 March 2011

Received in revised form

8 June 2011

Accepted 10 June 2011

Available online 22 June 2011

Keywords:

Nonlinear optics

Octupolar tetrahedral complexes

Harmonic light scattering

Two-photon emission fluorescence

Z-scan

Bipyridine

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(diethylaminos-tyrilyl)-6,6'-diphenyl-bipyridine]copper(I) complex, which revealed a distorted pseudo-tetrahedral geometry. Molecular second-order nonlinear optical properties were determined for the complexes using the Harmonic Light Scattering 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.

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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 σ_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 (^1H , ^{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 ($\approx 10^{-5} \text{ mol L}^{-1}$) 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 (β) measurements which were performed in dichloromethane at a fundamental wavelength of $1.91 \mu\text{m}$. Using this wavelength ensures that any contribution to the

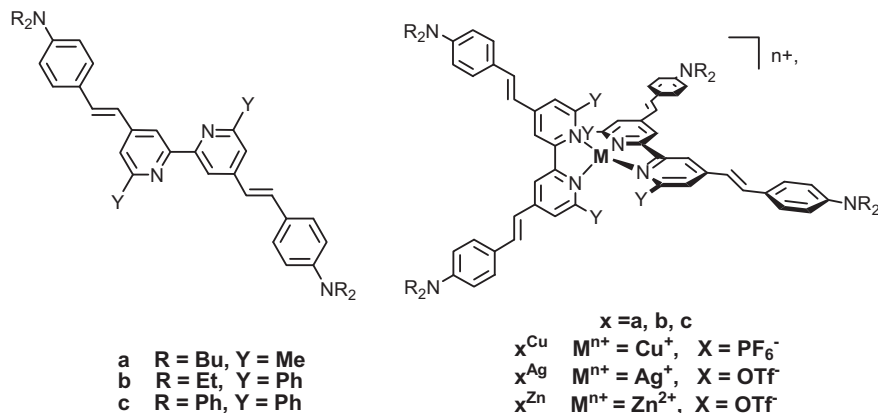
HLS signal from two-photon fluorescence becomes negligible, as its harmonic at 955 nm lies far from the fluorescence domain. The values of $\beta_{1,91}$ and the corresponding dispersion free hyperpolarizabilities β_0 for all the complexes are reported in Table 1. These “static” β_0 values are inferred 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 β values almost negligible. HLS measurements were carried out in concentrated dichloromethane solution ($1\text{--}5 \times 10^{-2} \text{ mol L}^{-1}$) with a concentrated solution of ethyl-violet as reference ($\beta_{1,91} = 170 \times 10^{-30} \text{ esu}$).

The TPA cross sections (δ) 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: $\sim 100 \text{ fs}$; repetition rate: 80 MHz ; wavelength range: $690\text{--}1020 \text{ nm}$). A 10^{-4} M solution of fluorescein [41] in water at $\text{pH} = 11$ ($\delta_r = 38 \pm 9.7 \text{ GM}$ at 782 nm) was used as the reference (r). The value of δ 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 Φ is the fluorescence quantum yield of the chromophores. η 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 $0.5\text{--}3 \times 10^{-4} \text{ M}$. The laser intensity was in the range of $0.2\text{--}2 \times \text{GW/cm}^2$. The experimental error on the reported cross section is $15\text{--}20\%$.

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 ($\times 4$), the laser beam is focused using an $f = 10 \text{ cm}$ 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 **b^{Cu}**.

Empirical formula	C93.50 H95 Cl3 Cu F6 N8 P	θ range (°)	2.60 to 27.00
Formula weight	1645.64	Index range	$-12 \leq h \leq 17$ $-21 \leq k \leq 20$ $-27 \leq l \leq 26$
Crystal system	Triclinic		
Space group	<i>P</i> -1		
<i>a</i> (Å)	13.8741(9)	Reflns collected	30,637
<i>b</i> (Å)	16.4820(10)	Unique reflns	18,285
<i>c</i> (Å)	21.2900(10)	Refinement method	Full-matrix
α (°)	70.931(7)	on <i>F</i> ²	Least-squares
β (°)	86.407(6)	Goodness-of-fit on <i>F</i> ²	0.919
γ (°)	84.681(6)	<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0970
<i>V</i> (Å ³), <i>Z</i>	4578.8(5)/2	<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.2470
<i>D</i> _{calc}	1.194 g/cm ⁻³	<i>R</i> ₁ (all data)	0.2175
μ (mm ⁻¹)	0.403	<i>wR</i> ₂ (all data)	0.2874
<i>F</i> (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 β (Note that there is some confusion over the term β 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):

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

where *z*₀ corresponds to the diffraction length of the incident beam, *l* the optical path length. The 2PA cross-section, δ , (in units of 1 GM: 10⁻⁵⁰ cm⁴ 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, ν 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 CH₂Cl₂ was in the range of 1–3 × 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 MgSO₄, 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 (CD₂Cl₂, 500 MHz): δ ppm 8.68 (s, 2H, H^{6,6'}), 8.31 (d, *J* = 8.3 Hz, 4H, C₆H₄–), 7.92 (s, 2H, H^{3,3'}), 7.58 (m, 12H, C₆H₅– + –CH=CH–), 7.10 (d, *J* = 16.3 Hz, 4H, –CH=CH–), 6.75 (d, *J* = 9.0 Hz, 4H, C₆H₅–), 3.46 (q, *J* = 7.1 Hz, 8H, CH₃CH₂–), 1.24 (t, *J* = 7.1 Hz, 12H, CH₃CH₂–). ¹³C NMR (CDCl₃, 400 MHz): δ 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. C₄₆H₄₆N₄·0.5H₂O Calc.: C, 83.22; H, 7.14; N, 8.44, *m/z* (Micro-TOF-Q II) 655.3793; ([M + H]⁺, C₄₆H₄₇N₄ 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 (CDCl₃, 500 MHz): δ ppm 8.68 (s, 2H, H^{6,6'}), 8.24 (d, *J* = 7.2 Hz, 4H, C₆H₄–), 7.87 (s, 2H, H^{3,3'}), 7.58 (t, *J* = 7.4 Hz, 4H, C₆H₅–), 7.49 (m, 6H, C₆H₅–), 7.32 (t, *J* = 7.3 Hz, 6H, C₆H₅–), 7.12 (m, 22H, C₆H₅–). ¹³C NMR (CDCl₃, 500 MHz): δ 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. C₆₂H₄₆N₄·0.75CH₂Cl₂ Calc.: C, 82.75; H, 5.26; N, 6.15; *m/z* (Micro-TOF-Q II) 847.3802, ([M + H]⁺, C₆₂H₄₇N₄ 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 CH₂Cl₂/pentane mixture (*v/v* = 1:10).

2.3.3.1. Complex [Cu(b)₂][PF₆] (b^{Cu}**). Dark-brown powder, 73% yield; ¹H NMR (CD₂Cl₂, 500 MHz): δ 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). ¹³C NMR (CD₂Cl₂, 500 MHz): δ 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. C₉₂H₉₂CuF₆N₈P·2C₅H₁₂ Calc.: C, 73.79; H, 7.03; N, 6.74; *m/z* (Zabspec-TOF) 1371.6741, ([M + H]⁺, C₉₂H₉₂N₈Cu requires 1371.67409).**

2.3.3.2. Complex [Ag(b)₂][OTf] (b^{Ag}**). Gold powder, 75% yield; ¹H NMR (CD₂Cl₂, 500 MHz): δ 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). ¹³C NMR (CD₂Cl₂, 500 MHz): δ 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. C₉₃H₉₂AgF₃N₈O₃S·3C₅H₁₂ Calc.: C, 72.75; H, 7.24; N, 6.28. *m/z* (Zabspec-TOF) 1415.6526, ([M + H]⁺, C₉₂H₉₂N₈Ag requires 1415.64959).**

2.3.3.3. Complex [Zn(b)₂][OTf]₂ (b^{Zn}**). Violet powder, 70% yield; ¹H NMR (CD₂Cl₂, 500 MHz): δ 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). ¹³C NMR (CD₂Cl₂, 500 MHz): δ 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^{Cu}). Dark-brown powder, 73% yield; 1H NMR (CD_2Cl_2 , 500 MHz): δ ppm 7.55 (d, 16H), 7.38 (m, 24H), 7.16 (m, 52H). ^{13}C NMR (CD_2Cl_2 , 500 MHz): δ 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. $C_{128}H_{98}AgF_3 \cdot N_8O_3S \cdot 1.5CH_2Cl_2$ 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^{Ag}). Gold powder, 75% yield; 1H NMR (CD_2Cl_2 , 500 MHz): δ 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): δ 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^{Zn}). Violet powder, 70% yield; 1H NMR (CD_2Cl_2 , 500 MHz): δ 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): δ 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^{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^{Cu} are listed in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

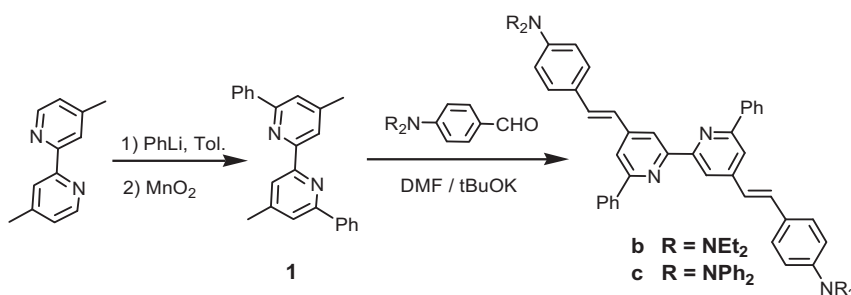
The 6,6'-diphenyl-4,4'-dimethyl-[2,2']-bipyridine **1** was synthesized according to previously reported procedures [46]. The target bipyridine derivatives **b** and **c** were readily prepared by means of a double Knoevenagel condensation between **1** and the corresponding aldehyde derivatives, respectively, 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 1H 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, 1H , ^{13}C NMR spectroscopy, UV–visible and fluorescence spectroscopy. The 1H 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^{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 π – π stacking (≈ 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 (dnpp = 2,9-dineopentyl-1,10-phenanthroline) reveals



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

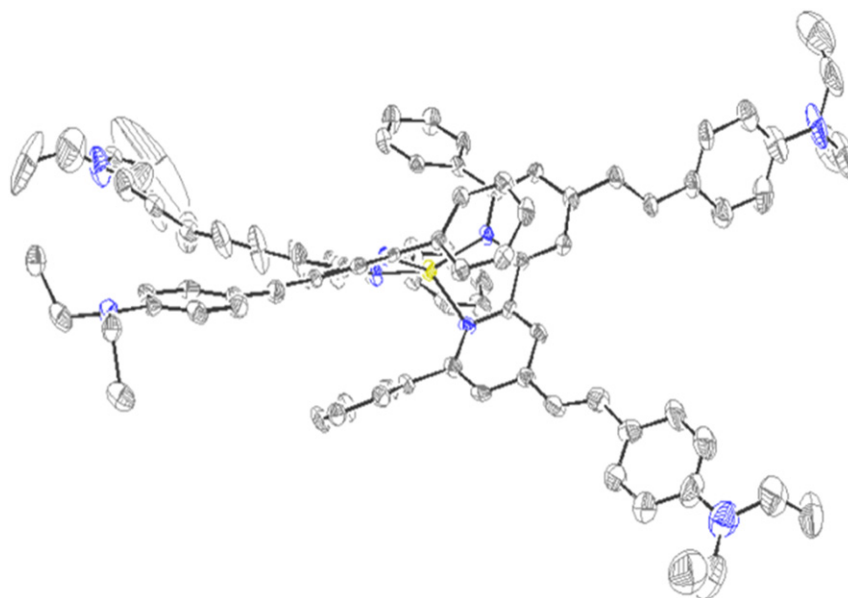


Fig. 1. ORTEP drawing of compound **b**^{Cu} (50% probability thermal ellipsoids); for clarity H atoms, solvents and counter-anions were omitted.

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 $\lambda_{\text{max}} \approx 400$ 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 ($\Delta\lambda_{\text{abs}}(\text{complex vs. ligand}) = 26\text{--}28$ nm) in the visible region assigned to intraligand charge transfer bands. In

addition a typical MLCT transition [$\text{Cu}^{\text{I}} \rightarrow \pi^*(\text{bpy})$] 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 Zn^{2+} complex within each series does show the largest λ_{ILCT} value, but those for the analogous Cu^+ and 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	$\lambda_{\text{abs}}/\text{nm}^{\text{a}}$ ($\epsilon_{\text{max}}^{\text{b}}$)	$\lambda_{\text{em}}/\text{nm}$	Stokes shift/ cm^{-1}	$\Phi_{\text{em}}^{\text{c}}$	$\beta_{1,91}^{\text{d}}/10^{-30}$ esu	$\beta_0^{\text{e}}/10^{-30}$ esu	$\lambda_{\text{TPA}}/\text{nm}$	$\delta_{\text{TPA}}/\text{GM}$	$\lambda^{\text{MAX}}(\delta^{\text{MAX}})$	Method
b	400 (71)	495	4798	0.15	—	—	780	160	810 (171)	TPEF
b ^{Cu}	426 (102) 438 (sh)	—	—	—	268	203	800/900	2080/712	—	Z-scan
b ^{Ag}	428 (122)	550	5182	0.10	241	182	780	355	850 (677)	TPEF
b ^{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
c ^{Cu}	428 (79) 445 (sh)	—	—	—	300	227	800/900	1931/988	—	Z-scan
c ^{Ag}	431 (84)	562	5408	0.33	283	214	780	210	800 (427)	TPEF
c ^{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 = $10^3 \text{ Mol}^{-1} \text{ cm}^{-1}$.

^c Fluorescence quantum yield with $\pm 10\%$ error.

^d Measured by HLS at $1.91 \mu\text{m}$ in CH_2Cl_2 (precision $\pm 10\%$) solution ($10^{-3} \text{ mol L}^{-1}$).

^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 **b**^{Ag} and **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** ($\Delta\lambda_{\text{em}}(\text{complex vs. ligand}) = 55\text{--}60\text{ nm}$). By contrast, copper(I) complexes **b**^{Cu} and **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 **b**^{Zn} and **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 β 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 β_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 β_0 values roughly follow those found for the relative energies of the ILCT transitions which dominate the second-order nonlinear response, i.e. $\text{Zn}^{2+} > \text{Cu}^+ \approx \text{Ag}^+$. All the complexes **b**^M and **c**^M (M = Cu, Ag, Zn) exhibit $\beta_{1,91}$ and β_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) (**a**^{Cu} $\beta_{1,91} = 113 \times 10^{-30}$ esu; **a**^{Ag} $\beta_{1,91} = 90 \times 10^{-30}$ esu; **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

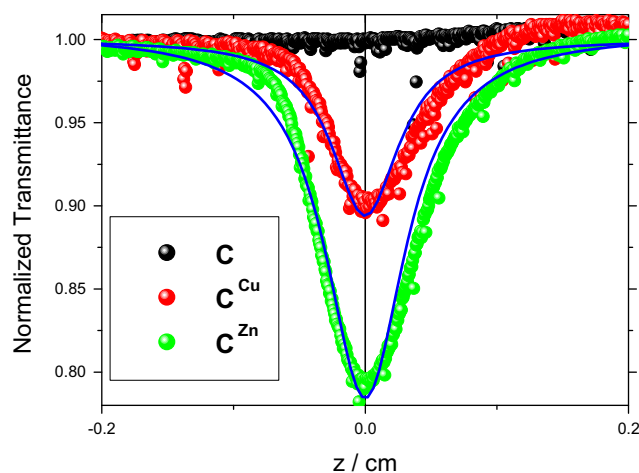


Fig. 3. Open aperture Z-scan traces for compounds **c** in dichloromethane at 900 nm. (**c**: 2.8×10^{-3} M, **c**^{Cu}: 1.1×10^{-3} M, **c**^{Zn}: 1.8×10^{-3} M). Theoretical fitting (full lines) using equation (1) (see text).

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).

Moreover, the maximum TPA cross-section is multiplied by factor 3.9 and 2.1 for **b**^{Ag} and **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 Zn²⁺ 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 β_0 values, in the range $182\text{--}258 \times 10^{-30}$ 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

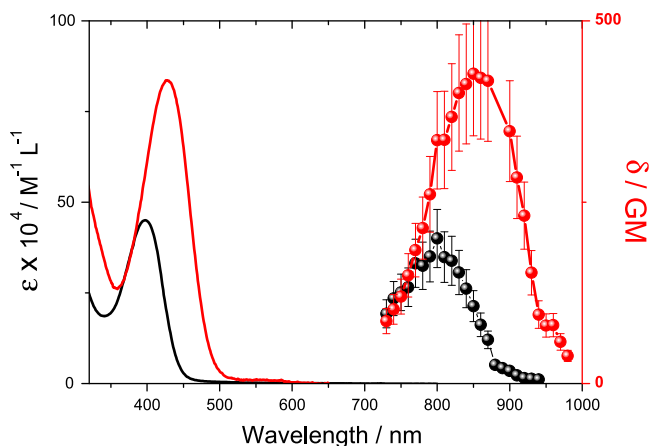


Fig. 2. One and two-photon absorption spectra of **c** (black) and **c**^{Ag} (gray) in dichloromethane.

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

This work is supported by COST D 035-0010-05. We also thank the CNRS (Centre National de la Recherche Scientifique) and the University of Rennes1 for financial support.

References

- [1] Chemla DS, Zyss J. Nonlinear optical properties of organic molecules and crystals. Orlando: Academic Press; 1987.
- [2] Nalwa HS, Miyata S. Nonlinear optics of organic molecules and polymers. Boca Raton: CRC Press; 1997.
- [3] Prasad NP, Williams DJ. Introduction to nonlinear optical effects in molecules and polymers. New York: Wiley; 1991.
- [4] Zyss J. Molecular nonlinear optics: materials, physics and devices. Boston: Academic Press; 1994.
- [5] Nalwa HS. Organometallic materials for nonlinear optics. Applied Organometallic Chemistry 1991;5:349–77.
- [6] Marder SR, Bruce DW, O'Hare D. Metal-containing materials for nonlinear optics. In: Inorganic materials. Chichester, UK: John Wiley and Sons; 1992.
- [7] Long NJ. Organometallic compounds for nonlinear optics—the search for en-light-enment! *Angewandte Chemie International Edition in English* 1995;34:21–38.
- [8] Heck J, Dabek S, Meyer-Friedrichsen T, Wong H. Mono- and dinuclear sesquifulvalene complexes, organometallic materials with large nonlinear optical properties. *Coordination Chemistry Reviews* 1999;190–192:1217–54.
- [9] Whittall JR, McDonagh AM, Humphrey MG, Samoc M. In: Stone FGA, Robert W, editors. *Advances in organometallic chemistry*, vol. 42. Academic Press; 1998. p. 291–362.
- [10] Andraud C, Maury O. Lanthanide complexes for nonlinear optics: from fundamental aspects to applications. *European Journal of Inorganic Chemistry*; 2009:4357–71.
- [11] Coe BJ, McCleverty JA, Meyer TJ. Nonlinear optical properties of metal complexes. In: *Comprehensive coordination chemistry II*. Oxford, UK: Elsevier Pergamon; 2004.
- [12] Di Bella S. Second-order nonlinear optical properties of transition metal complexes. *Chemical Society Reviews* 2001;30:355–66.
- [13] Renouard T, Le Bozec H, Brasselet S, Ledoux I, Zyss J. Tetrahedral bipyridyl copper(II) complexes: a new class of non-dipolar chromophore for nonlinear optics. *Chemical Communications*; 1999:871–2.
- [14] Cariati E, Pizzotti M, Roberto D, Tessoro F, Ugo R. Coordination and organometallic compounds and inorganic-organic hybrid crystalline materials for second-order non-linear optics. *Coordination Chemistry Reviews* 2006;250:1210–33.
- [15] Kanis DR, Lacroix PG, Ratner MA, Marks TJ. Electronic structure and quadratic hyperpolarizabilities in organotransition-metal chromophores having weakly Coupled pi-Networks. Unusual mechanisms for second-order response. *Journal of the American Chemical Society* 1994;116:10089–102.
- [16] Roberto D, Ugo R, Bruni S, Cariati E, Cariati F, Fantucci P, et al. Quadratic hyperpolarizability enhancement of para-substituted pyridines upon coordination to organometallic moieties: the ambivalent donor or acceptor role of the metal. *Organometallics* 2000;19:1775–88.
- [17] Roberto D, Ugo R, Tessoro F, Lucenti E, Quici S, Vezza S, et al. Effect of the coordination to M(II) metal centers (M = Zn, Cd, Pt) on the quadratic hyperpolarizability of various substituted 5-X-1,10-phenanthrolines (X = Donor Group) and of trans-4-(Dimethylamino)-4'-stilbazole. *Organometallics* 2002;21:161–70.
- [18] Tessoro F, Roberto D, Ugo R, Mussini P, Quici S, Ledoux-Rak I, et al. Large, concentration-dependent enhancement of the quadratic hyperpolarizability of [Zn(CH₃CO₂)₂(L)₂] in CHCl₃ on substitution of acetate by triflate. *Angewandte Chemie International Edition* 2003;42:456–9.
- [19] Bruce DW, Thornton A. Electronic hyperpolarisabilities of some mesogenic stilbazole complexes of Rh(I) and Ir(I), molecular crystals and liquid crystals science and technology. Section A. *Molecular Crystals and Liquid Crystals* 1993;231:253–6.
- [20] Bourgault M, Baum K, Le Bozec H, Pucetti G, Ledoux I, Zyss J. Synthesis and molecular hyperpolarisabilities of donor-acceptor bipyridyl metal complexes (M = Re, Zn, Hg). *New Journal of Chemistry* 1998;22:517–22.
- [21] Hilton A, Renouard T, Maury O, Le Bozec H, Ledoux I, Zyss J. New bipyridyl ligands bearing azo- and imino-linked chromophores. Synthesis and nonlinear optical studies of related dipolar zinc complexes[dagger]. *Chemical Communications*; 1999:2521–2.
- [22] Boucekkine A, Feuvrie C, Maury O, Ledoux I, Le Bozec H. Effects of the metal center and substituting groups on the linear and nonlinear optical properties of substituted styryl-bipyridine metal(II) dichloride complexes: DFT and TDDFT computational investigations and harmonic light scattering measurements. *The Journal of Physical Chemistry A* 2010;114:5429–38.
- [23] Sénéchal K, Maury O, Le Bozec H, Ledoux I, Zyss J. Zinc(II) as a versatile template for the design of dipolar and octupolar NLO-phores. *Journal of the American Chemical Society* 2002;124:4560–1.
- [24] Le Boudier T, Maury O, Bondon A, Costuas K, Amouyal E, Ledoux I, et al. Synthesis, photophysical and nonlinear optical properties of macromolecular architectures featuring octupolar tris(bipyridine) ruthenium(II) moieties: evidence for a supramolecular self-ordering in a dendritic structure. *Journal of the American Chemical Society* 2003;125:12284–99.
- [25] Maury O, Viau L, Sénéchal K, Corre B, Guégan J-P, Renouard T, et al. Synthesis, linear, and quadratic-nonlinear optical properties of octupolar D3 and D2d bipyridyl metal complexes. *Chemistry – A European Journal* 2004;10:4454–66.
- [26] Coe BJ, Samoc M, Samoc A, Zhu L, Yi Y, Shuai Z. Two-photon absorption properties of iron(II) and ruthenium(II) trischelate complexes of 2,2':4,4':4,4''-quaterpyridinium ligands. *The Journal of Physical Chemistry A* 2007;111:472–8.
- [27] Feuvrie C, Maury O, Le Bozec H, Ledoux I, Morral JP, Dalton GT, et al. Nonlinear optical and two-photon absorption properties of octupolar tris(bipyridyl)metal complexes. *The Journal of Physical Chemistry A* 2007;111:8980–5.
- [28] Coe BJ, Fielden J, Foxon SP, Brunschwig BS, Asselberghs I, Clays K, et al. Combining very large quadratic and cubic nonlinear optical responses in extended, tris-chelate metallochromophores with six π -conjugated pyridinium substituents. *Journal of the American Chemical Society* 2010;132:3496–513.
- [29] Dragonetti C, Balordi M, Colombo A, Roberto D, Ugo R, Fortunati I, et al. Two-photon absorption properties of Zn(II) complexes: Unexpected large TPA cross section of dipolar [ZnY₂(4,4'-bis(para-di-n-butylaminostyryl)-2,2'-bipyridine)] (Y = Cl, CF₃CO₂). *Chemical Physics Letters* 2009;475:245–9.
- [30] Mazzucato S, Fortunati I, Scolaro S, Zerbetto M, Ferrante C, Signorini R, et al. Two-photon absorption of Zn(II) octupolar molecules. *Physical Chemistry Chemical Physics* 2007;9:2999–3005.
- [31] Das S, Nag A, Goswami D, Bharadwaj PK. Zinc(II)- and copper(I)-mediated large two-photon absorption cross sections in a bis-cinnamaldimino Schiff Base. *Journal of the American Chemical Society* 2006;128:402–3.
- [32] Dietrich-Buchecker CO, Sauvage JP. Interlocking of molecular threads: from the statistical approach to the templated synthesis of catenands. *Chemical Reviews* 1987;87:795–810.
- [33] Moylan CR, Twieg RJ, Lee VY, Swanson SA, Betterton KM, Miller RD. Nonlinear optical chromophores with large hyperpolarizabilities and enhanced thermal stabilities. *Journal of the American Chemical Society* 1993;115:12599–600.
- [34] Whitaker CM, Patterson EV, Kott KL, McMahon RJ. Nitrogen and oxygen donors in nonlinear optical materials: effects of alkyl vs phenyl substitution on the molecular hyperpolarizability. *Journal of the American Chemical Society* 1996;118:9966–73.
- [35] Jen AKY, Cai Y, Bedworth PV, Marder SR. Synthesis and characterization of highly efficient and thermally stable diphenylamino-substituted thiophene stilbene chromophores for nonlinear optical applications. *Advanced Materials (Weinheim, Germany)* 1997;9:132–5.
- [36] Staub K, Levina GA, Barlow S, Kowalczyk TC, Lackritz HS, Barzoukas M, et al. Synthesis and stability studies of conformationally locked 4-(diarylamino) aryl- and 4-(dialkylamino)phenyl-substituted second-order nonlinear optical polyene chromophores. *Journal of Materials Chemistry* 2003;13:825–33.
- [37] Oudar JL. Optical nonlinearities of conjugated molecules. Stilbene derivatives and highly polar aromatic compounds. *The Journal of Chemical Physics* 1977;67:446–57.
- [38] Zyss J, Brasselet S. Multipolar symmetry patterns in molecular nonlinear optics. *Journal of Nonlinear Optical Physics and Materials* 1998;7:397–439.
- [39] Weibel JD, Yaron D, Zyss J. Quantum and tensorial modeling of multipolar nonlinear optical chromophores by a generalized equivalent internal potential. *The Journal of Chemical Physics* 2003;119:11847–63.
- [40] Rumi M, Ehrlich JE, Heikal AA, Perry JW, Barlow S, Hu Z, et al. Structure–property relationships for two-photon absorbing chromophores: bis-donor diphenylpolyene and bis(styryl)benzene derivatives. *Journal of the American Chemical Society* 2000;122:9500–10.
- [41] Webb WW, Xu C. Measurement of two-photon excitation cross sections of molecular fluorophores with data from 690 to 1050 nm. *Journal of the Optical Society of America B* 1996;13:10.
- [42] Sheik-Bahae M, Said AA, Wei TH, Hagan DJ, Stryland EWW. *IEEE Journal of Quantum Electronics* 1990;26:760.
- [43] Sheik-Bahae M, Said AA, Stryland EWW. High Sensitivity, single beam n₂ measurements. *Optical Letters* 1989;14:955–7.
- [44] Sengupta P, Balaji J, Banerjee S, Philip R, Kumar GR, Maiti S. Sensitive measurement of absolute two-photon absorption cross sections. *The Journal of Chemical Physics* 2000;112:9201–5.
- [45] Spek AL. PLATON, a multipurpose crystallographic tool. The Netherlands: Utrecht University; 1998.
- [46] Linnell R. Notes - 4,4',6,6'-tetramethyl-2,2'-bipyridine. *The Journal of Organic Chemistry* 1957;22:1691–2.
- [47] Munakata M, Kitagawa S, Asahara A, Masuda H. *Bulletin of Chemical Society of Japan* 1987;60:1927–9.
- [48] Klemens FK, Fanwick PE, Bibler JK, McMillin DR. Crystal and molecular structure of [Cu(bcp)₂]BF₄·CH₃OH (bcp = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline). *Inorganic Chemistry* 1989;28:3076–9.
- [49] Eggleston MK, Fanwick PE, Pallenberg AJ, McMillin DR. A twist on the copper center in the crystal structure of [Cu(dnpp)₂]PF₆ and the charge-transfer excited state? (dnpp = 2,9-Dineopentyl-1,10-phenanthroline). *Inorganic Chemistry* 1997;36:4007–10.

- [50] McMillin DR, McNett KM. Photoprocesses of copper complexes that bind to DNA. *Chemical Reviews* 1998;98:1201–20.
- [51] Parker WL, Crosby GA. Assignment of the charge-transfer excited states of bis(N-heterocyclic) complexes of copper(I). *The Journal of Physical Chemistry* 1989;93:5692–6.
- [52] Maury O, Guegan JP, Renouard T, Hilton A, Dupau P, Sardon N, et al. Design and synthesis of 4,4'-pi-conjugated 2,2'-bipyridines: a versatile class of tunable chromophores and fluorophores. *New Journal of Chemistry* 2001;25: 1553–66.
- [53] Cho BR, Son KH, Lee SH, Song Y-S, Lee Y-K, Jeon S-J, et al. Two photon absorption properties of 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives. *Journal of the American Chemical Society* 2001;123:10039–45.
- [54] Maury O, Le Bozec H. Molecular engineering of octupolar NLO molecules and materials based on bipyridyl metal complexes. *Accounts of Chemical Research* 2005;38:691–704.
- [55] Valore A, Balordi M, Colombo A, Dragonetti C, Righetto S, Roberto D, et al. Novel ruthenium(II) complexes with substituted 1,10-phenanthroline or 4,5-diazafluorene linked to a fullerene as highly active second order NLO chromophores. *Dalton Transactions* 2010;39:10314–8.
- [56] Valore A, Cariati E, Dragonetti C, Righetto S, Roberto D, Ugo R, et al. Cyclo-metalated Ir(III) complexes with substituted 1,10-phenanthrolines: a new class of efficient cationic organometallic second-order NLO chromophores. *Chemistry – A European Journal* 2010;16:4814–25.
- [57] Zhang X-B, Feng J-K, Ren A-M. Theoretical study of one- and two-photon absorption properties of octupolar D2d and D3 bipyridyl metal complexes. *The Journal of Physical Chemistry A* 2007;111:1328–38.
- [58] Beljonne D, Wenseleers W, Zojer E, Shuai Z, Vogel H, Pond SJK, et al. Role of dimensionality on the two-photon absorption response of conjugated molecules: the case of octupolar compounds. *Advanced Functional Materials* 2002; 12:631–41.