Tetrahedral bipyridyl copper(I) complexes: a new class of non-dipolar chromophore for nonlinear optics

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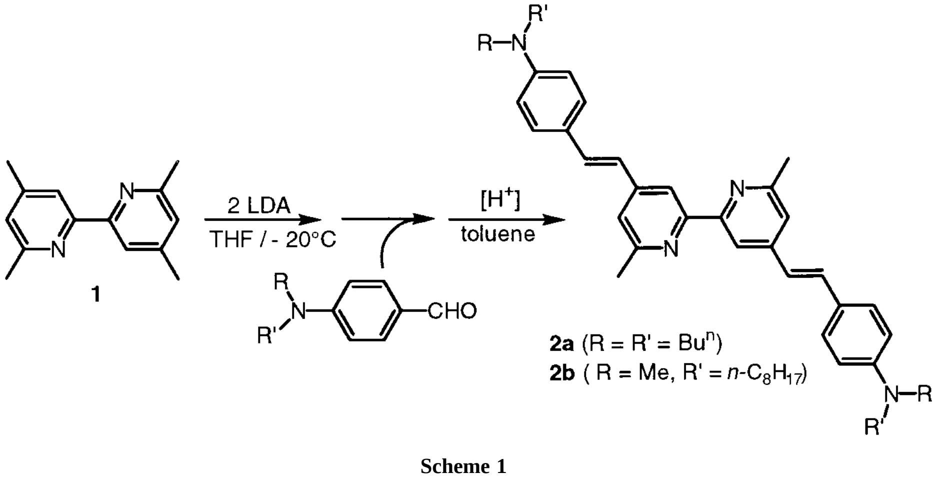
The synthesis of 4,4′-bis(dialkylaminostyryl)-6,6′-dimethyl-2,2′-bipyridine ligands is described; the corresponding tetrahedral bis(bipyridyl) copper(I) complexes have been prepared, and their second-order nonlinear optical properties determined by harmonic light scattering (HLS) at 1.34 µm; these new octupolar complexes exhibit large molecular hyperpolarisabilities β.

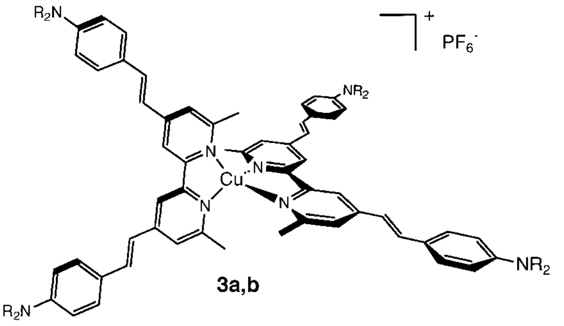
A new concept of octupolar non-linearities of two- and three-dimensional (2D and 3D) molecules has recently been proposed and has opened new perspectives in elaboration of efficient nonlinear optical materials.[1] Research on octupolar structures has mainly focused on organic chromophores with threefold symmetry such as 1,3,5-triamino-2,4,6-trinitrobenzene and related derivatives,[2] crystal violet,[3] trisubstituted amines[2,4] and cyanine salts.[2,5] The first examples of nondipolar tetrahedral organotin,[6] phosphonium[7] and biphenyl[8] chromophores have recently been investigated. Organotransition metal complexes also offer many possibilities for the design of 3D non-centrosymmetric octupolar molecules owing to the large diversity of metals, ligands and geometries. Thus, nonlinearities of tris(bipyridine) ruthenium(II) complexes has been demonstrated[9,10] and we have recently reported the enhanced molecular hyperpolarisability β of octahedral ruthenium(II) complexes possessing three bipyridine ligands substituted in 4,4′-positions by *p*-dialkylaminostyryl groups.[11] In the course of our study of nondipolar complexes for NLO, we have been interested in the generation of metal complexes displaying tetrahedral coordination geometries. Copper(I)–bipyridine or –phenanthroline complexes with substituents α to the nitrogen atoms are known to give stable tetrahedral molecules of D_{2d} symmetry[12] and such complexes have been widely used to prepare molecular architectures such as catenates and knots,[13] helicates[14] and polymers.[15] Using this approach, we sought to design 4,4′-dialkenyl-6,6′-dimethyl-2,2′-bipyridines in which the alkenyl fragments bear π-donor groups. Here we describe the synthesis of such ligands and we show that the corresponding copper(I) complexes represent a new class of nondipolar NLO organometallic chromophore combining good transparency and large nonlinearity.

The new ligands **2a** and **2b** were prepared by a controlled functionalisation of the 4,4′-positions of 4,4′,6,6′-tetramethyl-2,2′-bipyridine **1**: dilithiation of **1** with LDA at −20 °C followed by reaction with 2 equiv. of *p*-dibutylaminobenzaldehyde afforded the corresponding dialcohol, and subsequent dehydration with pyridinium toluene-*p*-sulfonate (PTPS) in boiling toluene yielded exclusively **2a** in 75% overall yield. Ligand **2b** was prepared analogously as described for **2a** (Scheme 1). The observation of a strong NOE (10%) between the methyl groups at $C^{6,6'}$ and the $H^{5,5'}$ protons clearly established the regioselectivity of the reaction. In their UV–VIS spectra, **2a**,**b** show typical bands at *ca.* 390 nm ($\varepsilon \approx 50\,000$ dm^3 mol^{-1} cm^{-1}) which are assigned to intramolecular charge-transfer transitions.[16]

Copper(I) complexes were obtained upon treatment of the ligands **2a**,**b** (2 equiv.) with $[Cu(MeCN)_4]PF_6$ (1 equiv.) in dichloromethane solution (Fig. 1). The red complexes **3a**,**b** were isolated in nearly quantitative yield and their structures were demonstrated by FAB-MS and ^{1}H NMR spectroscopy. In the ^{1}H NMR spectra, the methyl groups in the 6,6′ positions are characteristically shifted upfield by 0.45 ppm with respect to the free ligands, and according to the strong vicinal coupling constants of the olefinic protons ($J_{HH} \approx 16$ Hz) no detectable *E/Z* isomerization of the alkenyl fragments is observed. The UV–VIS spectra recorded in dichloromethane are dominated by intense intraligand charge-transfer bands ($\lambda_{ILCT} \approx 420$ nm, $\varepsilon \approx 80\,000$ dm^3 mol^{-1} cm^{-1}) which are 30–40 nm red-shifted upon complexation. It is noteworthy that the bis(bipyridyl)copper(I) derivatives **3a**,**b** have a considerably blue-shifted ILCT band when compared to the corresponding tris(bipyridyl)ruthenium(II) complexes ($\lambda_{ILCT} \approx 515$ nm),[11] which is of crucial importance for second-harmonic generation. The MLCT transi-



Scheme 1



3a,b

Fig. 1

tion [Cu^{I} $\longrightarrow$ π*(bpy)] is typically observed at *ca.* 480 nm with relatively smaller absorption coefficients and can be discerned in the spectra as a shoulder of the more intense ILCT band.

As EFISH experiment is precluded for nondipolar and/or ionic molecules like **3**, the molecular hyperpolarisability β was measured by means of the harmonic light scattering technique (HLS).[17] The experiments were performed in chloroform at a fundamental wavelength of 1.34 μm, generated by a Q-switched, mode-locked Nd:YAG laser providing subnanosecond pulse train at 10 Hz repetition rate. The T_d (or D_2) symmetry reduces the nonlinear microscopic coefficient to only one non-vanishing term, β_{xyz}, which can be easily deduced from the following relation: $<\beta^2_{\mathrm{HLS}}> = 4/7\ \beta^2_{xyz}$. The experimentally determined $<\beta^2>^{1/2}$, the static $<\beta_0>^{1/2}$, deduced from $<\beta^2>$ using a degenerate three-level dispersion model valid in the case of purely octupolar molecules,[18] and the corresponding β_{xyz} coefficients for **3a**,**b** are given in Table 1.

Table 1 Linear[a] and nonlinear[b] optical data

Complex	λ/nm (ε/dm^3 mol^{-1} cm^{-1})	10^{30} β_{HLS}/esu	10^{30} β_{HLS}^0/esu	10^{30} β_{xyz}/esu	10^{30} β_{xyz}^0/esu
3a	424(83300) 484(sh)	144	78	190	103
3b	420(73800) 475(sh)	128	70	169	93

[a] In CH_2Cl_2. [b] HLS measurements in $CHCl_3$ at 1.34 μm. The error in the measurements is estimated to be ±10%.

Results show that chromophores **3a** and **3b** exhibit microscopic optical nonlinearities which are larger than those of recently reported tetrahedral molecules such as the tetrakis(dibutylaminoazobenzenephosphonium)chromophore [$\lambda_{\max}$ = 511 nm; $\beta_{\mathrm{HLS}}^0 = 56.7 \times 10^{-30}$ esu].[7] Dibutylaminophenyl is slightly more efficient than the methyl(octyl)aminophenyl donor group, a trend that have already been observed for octahedral trisbipyridyl ruthenium(II) complexes bearing the same dialkylaminophenyl groups.[11] Compared to these latter complexes, the copper(I) derivatives **3** have lower β_{HLS} values. At first glance, this may be due to the presence of four *vs.* six donor groups and to the less efficient acceptor strength of Cu$^+$ *vs.* Ru^{2+} metallic ion. A more pronounced blue-shift of the absorption maximum is observed in the copper complexes, and the higher energy of the ILCT excited state also contributes to this observed decrease of β as compared to the octupolar ruthenium species.

To summarize, we have synthesized and investigated a new class of nondipolar NLO complexes showing good transparency/efficiency trade-off. Work towards the incorporation of such chromophores into macromolecular architectures are under progress.

Notes and references

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