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Photoswitching of the second-order nonlinearity of a tetrahedral octupolar multi DTE-based copper(I) complex†

Hiroyuki Nitadori,[ab] Lucie Ordronneau,[a] Julien Boixel,[ac] Denis Jacquemin,*[d] Abdou Boucekkine,[a] Anu Singh,[c] Munetaka Akita,[b] Isabelle Ledoux,[c] Véronique Guerchais[a] and Hubert Le Bozec*[a]

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The modulation of the quadratic NLO response of an octupolar metal-based chromophore featuring four photochromic dithienylethene units is reported. Quantum mechanical simulations are consistent with a full switching of the DTE units and reproduce the strong enhancement of the NLO response.

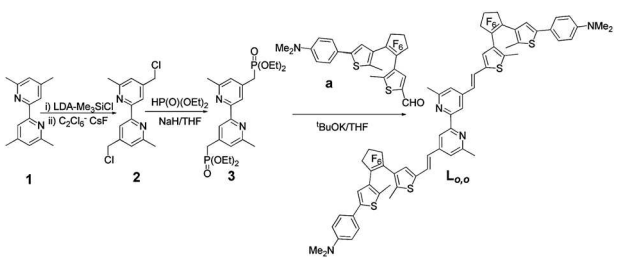
In the past years, much attention has been paid on the reversible switching or modulation of NLO properties.[1,2] As most of the NLO chromophores are based on push–pull (dipolar) systems, photochromic molecules incorporating dithienylethene (DTE) architectures are particularly suitable for the on/off modulation of the NLO response, due to reversible interconversion between a non-conjugated open form and a π-conjugated closed form by alternate irradiation with UV and visible light.[3] In this context, we have recently reported the first efficient phototriggered NLO enhancement of dipolar metal complexes featuring a bis-DTE bipyridine ligand.[4] Beyond the classical dipolar approach, non-dipolar (octupolar) molecules have emerged as an important and promising class of NLO chromophores, giving rise to two- and three-dimensional architectures.[5] Metal ions are versatile templates to build up tetrahedral (T_d, D_{2d}) and octahedral (D_3) octupolar arrangements.[6] For example, we have already shown that the association of d^{10} Cu(I), Ag(I) and Zn(II) ions with tetrasubstituted 4,4′,6,6′-bipyridyl ligands gives rise to pseudo-tetrahedral metal complexes with fairly large quadratic hyperpolarizabilities.[7]

To the best of our knowledge, the photoregulation of the NLO properties of octupolar chromophores has not been reported so far. Therefore, we have designed a new bis bipyridine copper(I) complex featuring four DTE units, and such systems are expected to display at strong contrast to the NLO response. It should be noted that only a very few number of single molecules containing four or more DTE have been synthesised up to now,[8] and in the majority of them, two vicinal DTE units cannot be entirely closed[8b–d] whereas the two reported cases with full switching[8a,e] use saturated or poorly conjugated bridging units to connect the different photochromic DTE fragments. In this communication, we demonstrate that the quadruple DTE copper complex is converted into its fully closed isomer upon UV irradiation, and we present for the first time the modulation of the quadratic NLO activity of an octupolar chromophore.

The synthesis of $\mathbf{L}_{o,o}$ was achieved by a controlled functionalization of the 4,4′ positions of 4,4′,6,6′-tetramethyl-2,2′-bipyridine **1**. Thus, dilithiation with LDA in THF at −78 °C, followed by reaction with chlorotrimethylsilane and subsequent chlorination with hexachloroethane afforded selectively the resulting bis-chloromethyl derivative **2** in good yields (Scheme 1). Finally, treatment of the diethylphosphonatomethyl-2,2′-bipyridine **3**, readily obtained from **2** through an Arbuzov reaction, with the DTE-aldehyde **a**[4] under normal Wadsworth–Emmons conditions[6b] afforded the target bipyridine ligand $\mathbf{L}_{o,o}$ in 70% yield after purification by recrystallization.

The corresponding copper complex $[Cu(\mathbf{L}_{o,o})_2]PF_6$ was formed almost quantitatively after mixing 2 equiv. of $\mathbf{L}_{o,o}$ with $[Cu(MeCN)_4]PF_6$ at room temperature in dichloromethane–acetonitrile solution (Fig. 1).

The ligand and complex were fully characterized by NMR and microanalysis (see ESI†). The copper(I) complex exhibits



Scheme 1 Synthesis of the photochromic bipyridine $\mathbf{L}_{o,o}$.

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† Electronic supplementary information (ESI) available: Synthesis and characterisations of ligands and complexes; details of theoretical calculations, extra TD-DFT analysis and NLO measurements. See DOI: 10.1039/c2cc34999j

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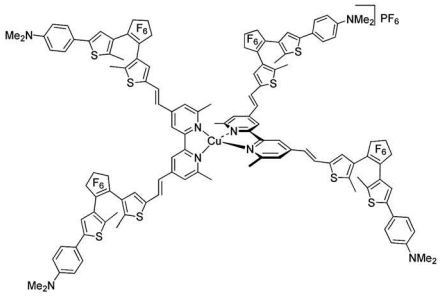

Fig. 1 Chemical structure of $[Cu(\mathbf{L}_{o,o})_2]PF_6$.

Table 1 Electronic absorption data in the open and closed (PSS) forms, HRS data before and after UV irradiation[a]

Compound	λ_{abs}[b] (ε[c]) open form	λ_{abs}[b] (ε[c]) closed form (PSS)	$\beta_{1.91}$[d] (β_{xyz}[d,e]) before UV irradiation	$\beta_{1.91}$[d] (β_{xyz}[d,e]) after UV irradiation[f]
L	340 (96 000)	340 (61 000) 395 (34 000) 431 (27 000 **668 (45 000)**		
$[Cu(\mathbf{L})_2]PF_6$	344 (166 000) 511 (24 000)	343 (119 000) 399 (sh) 450 (47 000) **701 (95 000)**	266 ± 52 (352 ± 70)	1672 ± 160 (2212 ± 220)

[a] At 298 K in CH_2Cl_2. [b] In nm. [c] In M^{-1} cm^{-1}. [d] In 10^{-30} esu. [e] $\langle\beta_{HLS}^2\rangle = 4/7\ \beta_{xyz}^2$. [f] 65% ring-closing determined by ^1H NMR spectroscopy.

only one set of signals as expected for D_{2d} complexes. The UV-visible spectrum of $[Cu(\mathbf{L}_{o,o})_2]PF_6$ (in CH_2Cl_2) shows like $\mathbf{L}_{o,o}$ an intense band at around 350 nm assigned to (IL) $\pi \rightarrow \pi^*$ transition of the bipyridyl moieties with some mixing of the DTE units (Table 1), and another band in the visible at 511 nm corresponding to the $d\pi(Cu) \rightarrow \pi^*(bipy)$ MLCT transition.[9] The photocyclization process for both ligand and complex was monitored by UV-vis and ^1H NMR spectroscopy in dichloromethane. Upon irradiation at 350 nm, the yellow solution of $\mathbf{L}_{o,o}$ and red solution of $[Cu(\mathbf{L}_{o,o})_2]PF_6$ turn green, due to the formation of the fully closed forms with a photostationary state (PSS) > 90% in both cases. A new broad band emerges in the visible at 668 and 701 nm, which is attributed to the intraligand (IL) $S_0 \rightarrow S_1$ transition of the closed DTE unit of the free and coordinated ligand, respectively (Fig. 2 and Fig. S1 (ESI†)). Upon irradiation at 650 nm, the quantitative regeneration of the fully open isomer was observed, indicating the fully reversible closed-to-open photoisomerization.

To further understand the photochromic behaviour of this multi-DTE compound, theoretical calculations have been performed using a methodology that has been successful for studying multi-DTE molecules.[10] We have focused our analysis on the different isomers using all possible closed–open combinations for the four photochromes, the fully open $[Cu(\mathbf{L}_{o,o})_2]^+$, the mono-closed $[Cu(\mathbf{L}_{o,o})(\mathbf{L}_{o,c})]^+$, the two doubly-open-doubly-closed $[Cu(\mathbf{L}_{o,c})_2]^+$ and $[Cu(\mathbf{L}_{o,o})(\mathbf{L}_{c,c})]^+$, the triply-closed $[Cu(\mathbf{L}_{c,c})(\mathbf{L}_{o,c})]^+$ and finally the fully closed $[Cu(\mathbf{L}_{c,c})_2]^+$ isomers. As shown in Fig. 3, $[Cu(\mathbf{L}_{o,o})_2]^+$ and $[Cu(\mathbf{L}_{c,c})_2]^+$ belong to the D_{2d} symmetry and the angles between the two ligands are nearly 90°, and our calculations also demonstrate that there is no steric hindrance (the distance between the two reactive carbon atoms

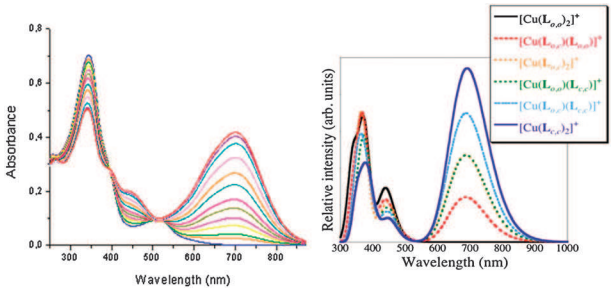

Fig. 2 (left) Experimental UV-vis absorption spectral change of $[Cu(\mathbf{L}_{o,o})_2]PF_6$ in dichloromethane upon excitation at 350 nm. (right) Simulated UV-vis spectra of $[Cu(\mathbf{L}_{o,o})_2]^+$, $[Cu(\mathbf{L}_{o,o})(\mathbf{L}_{o,c})]^+$, $[Cu(\mathbf{L}_{o,c})_2]^+$, $[Cu(\mathbf{L}_{o,o})(\mathbf{L}_{c,c})]^+$, $[Cu(\mathbf{L}_{c,c})(\mathbf{L}_{o,c})]^+$ and $[Cu(\mathbf{L}_{c,c})_2]^+$ isomers.

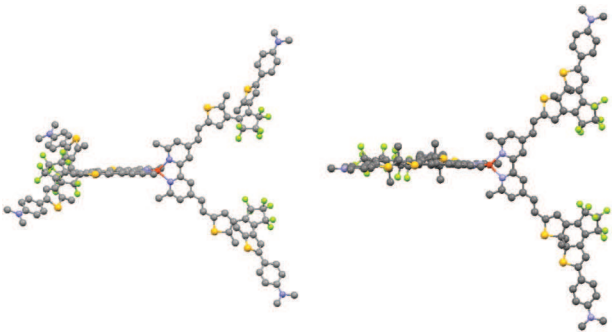

Fig. 3 Optimized geometry of $[Cu(\mathbf{L}_{o,o})_2]^+$ (left) and $[Cu(\mathbf{L}_{c,c})_2]^+$ (right) complexes.

is independent of the number of closed units), nor energetic problem (each closure of a DTE unit implies the same increase in the total energies) that would prevent the electrocyclisation of the four DTE units.

The simulated spectra of all different isomers can be found in Fig. 2, the numerical values for the dominant vertical transition wavelengths being listed in Table S1 (ESI†). It is striking that TD-DFT foresees that the successive cyclizations of the different DTE's imply: (i) the emergence of a strongly intense visible band at large wavelength; (ii) a decrease in the intensity of the stronger UV band when two DTE units are closed on the same ligand. These trends are in good qualitative agreement with experimental measurements. Quantitatively, theory is on the spot for the visible band (*ca.* 690 nm instead of 701 nm), and the position of the 450 nm band, but is less accurate for the position of the UV band, as well as for the 511 nm peak of the $[Cu(\mathbf{L}_{o,o})_2]^+$ structure, which theory foresees at 470 nm. An analysis of the orbital component of this hallmark band confirms that it corresponds to a MLCT transition from the copper(I) center to the complexed bipyridines. Nevertheless, TD-DFT provides a series of insights. First, there is no bathochromic shift accompanying the successive switching on, an outcome indicating nearly independent DTE units, which corroborates the ground-state energetic analysis above. Second, for the visible part, there is absolutely no difference between the $[Cu(\mathbf{L}_{o,c})_2]^+$ and $[Cu(\mathbf{L}_{o,o})(\mathbf{L}_{c,c})]^+$ isomers, which is consistent with a peak related to closed DTE rather than the central core of the molecule. Third, the virtual orbitals typical of the DTE core present the same energy for each open DTE

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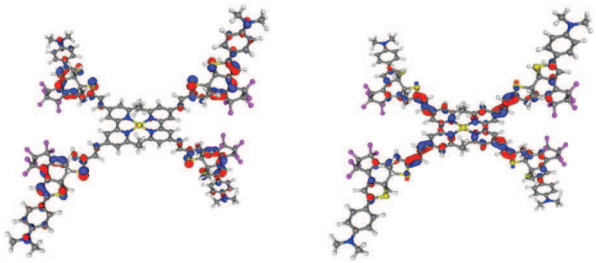

Fig. 4 HOMO (left) and LUMO (right) of $[Cu(\mathbf{L}_{c,c})_2]^+$.

irrespective of the status of other DTE's (see ESI†), which hints for a complete cyclisation of the compound. Fourth, the HOMO and LUMO levels (Fig. S2, ESI†) are, respectively, unstabilized and stabilized once a first DTE is switched on but remained unchanged afterwards, which also clearly corroborates a relatively weak coupling between the different DTE units. The HOMOs of Fig. 4 and Fig. S3 (ESI†) are clearly related to the DTE core, once they are closed, whereas the LUMOs are located on the central bipyridine and partly delocalized on the DTE.

The Harmonic Light Scattering (HLS) technique was used for the molecular first hyperpolarizability β measurements. They were performed in dichloromethane at a fundamental wavelength of 1.91 μm. The T_d (or D_{2d}) symmetry reduces the nonlinear microscopic coefficient to only one non-vanishing term, β_{xyz}, which can be easily deduced from the following relation: $\langle\beta_{HLS}^2\rangle = 4/7\ \beta_{xyz}^2$.[5b] The experimentally determined $\beta_{1.91}$ and the corresponding off-diagonal β_{xyz} coefficients for the Cu(I) complex before and after UV irradiation are given in Table 1. Before photocyclisation, $[Cu(\mathbf{L}_{o,o})_2]^+$ shows a fairly large β value which can be reasonably attributed to the low energy MLCT $d\pi(Cu) \rightarrow \pi^*(bipy)$ transition. A substantial enhancement of the second-order NLO activity is then observed after UV irradiation and subsequent accumulation of the ring-closed isomer, a result which is consistent with an NLO response mainly controlled by the red-shifted ILCT transition. The molecular first hyperpolarisability is increased almost six fold after only 65% of ring-closing, to reach an impressive β_{xyz} value of 2212×10^{-30} esu, which is to our knowledge the largest off-diagonal hyperpolarizability coefficient ever reported for octupolar chromophores having T_d or D_{2d} symmetry.[11] Theoretical calculations of the static β_{xyz} component using a range-separated hybrid DFT scheme (see ESI† for details) also predict a large enhancement of the nonlinear response by a factor of eight when switching all four DTE units.

In summary, we have described here a novel approach to the first molecular hyperpolarisability (β) modulation in an octupolar chromophore featuring four photochromic DTE units. Joint theory–experiment works are under way to design and construct other octupolar metal-based switches having an octahedral geometry and containing up to six DTE units.

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