



Preliminary communication / Communication

Supramolecular associations of anionic and cationic octupoles

Christophe Feuvrie ^a, Isabelle Ledoux ^b, Joseph Zyss ^b, Hubert Le Bozec ^a,
Olivier Maury ^{a,*}

^a « Organométalliques et catalyse : chimie et électrochimie moléculaires », UMR 6509 CNRS, université Rennes-1,
Institut de chimie de Rennes, campus de Beaulieu, 35042 Rennes cedex, France

^b « Laboratoire de physique quantique moléculaire », Institut d'Alembert, ENS Cachan, 61, avenue du Président-Wilson,
94235 Cachan, France

Received 29 July 2004; accepted after revision 9 November 2004

Available online 17 March 2005

Abstract

In this communication, we describe the first attempts for supramolecular associations between cationic and anionic octupolar derivatives. To this end, the synthesis and second-order non-linear optical (NLO) activity of new classes of anionic octupolar compounds will be reported and we will try to estimate the effect of the anion/cation association on the NLO activity of the resulting supramolecule. *To cite this article: C. Feuvrie et al., C. R. Chimie 8 (2005).*

© 2005 Académie des sciences. Published by Elsevier SAS. All rights reserved.

Résumé

Cette communication décrit nos premiers essais d'association supramoléculaire entre composés octupolaires anioniques et cationiques. Dans ce but, la synthèse et l'activité en optique non linéaire (ONL) du second ordre de nouvelles catégories de composés anioniques seront décrites et nous essaierons d'estimer l'impact de cette association anion/cation sur l'activité ONL de la supramolécule résultante. *Pour citer cet article : C. Feuvrie et al., C. R. Chimie 8 (2005).*

© 2005 Académie des sciences. Published by Elsevier SAS. All rights reserved.

Keywords: Non-linear optics; Octupole; Supramolecular chemistry

Mots clés : Optique non linéaire ; Octupôle ; Chimie supramoléculaire

1. Introduction

In the field of second-order non-linear optics (NLO), two complementary approaches are currently actively

studied. Beyond the 'classical' *dipolar* one, which has led to the elaboration of quasi-optimized electrooptic materials [1], the enlarged potential of the *octupolar* approach has been recognized since the early 1990s and have triggered the emergence of a new field of research [2]. In this latter case, the non-centrosymmetry can be obtained by a strict control of the molecular symmetry;

* Corresponding author.

E-mail address: olivier.maury@univ-rennes1.fr (O. Maury).

and for molecules belonging to purely octupolar space groups, like D_3 , D_{3h} , T_d , D_{2d} , the vectorial part of the hyperpolarizability tensor $\beta(J = 1)$, corresponding to the dipolar contribution, is cancelled out, and only the octupolar contribution $\beta(J = 3)$ remains [2]. Since the pioneering report on 1,3,5-triamino-2,4,6-trinitrobenzene, the concept of octupolar non-linearity has been widely demonstrated at the molecular level and numerous examples of octupolar molecules exhibiting large hyperpolarizability, in the same order of magnitude than that of the best dipoles, are reported in [3].

However, the extension of this concept at the macroscopic level still remains a challenge. For that purpose two different strategies can be envisaged for the elaboration of non-centrosymmetric materials, namely the *orientation* or the *organization*. The first one, of statistical nature, consists in the orientation of octupolar compounds possessing additional photoisomerization properties, dispersed or grafted in a polymeric matrix by means of the all-optical poling technique [4]. Here, we will focus on the second strategy that requires the non-centrosymmetric macroscopic organization of octupolar compounds by means of the control of the intermolecular interactions. Recently, Zyss [5] reported a general organization scheme study towards the optimization of 2D and 3D macroscopic arrangements of octupoles. The 2D organization, consisting in a non-centrosymmetric trigonal arrangement of trigonal octupoles (Fig. 1) [6], has been already illustrated by crystal engineering examples [7a] or by pre-organization of octupoles within a dendritic structure [7b]. The 3D generalization has been proposed in the form of a heli-

coidal hypercubic arrangement, by a stacking of the elementary cubic units along the threefold axis [5].

In this communication, we would like to report on our first attempts to design such supramolecular architectures by means of the electrostatic shape recognition between D_3 ruthenium(II) dication or D_{2d} copper(I) cation and anions featuring the same symmetry.

The starting point of this study was the discovery of the homochiral interaction between $(\text{DEASbpy})_3\text{Ru}^{2+}$ ($\text{DEASbpy} = 4,4'$ -bis(diethylaminostyryl)-2,2'-bipyridine) and tris(tetrachlorobenzendiolato)phosphat anion also called TRISPHAT (Fig. 2) [8]. It is worth noting that these two ionic derivatives are propeller-shaped with a helicoidal axis of chirality (isomer Λ and Δ) and exhibit the D_3 octupolar symmetry. A diastereoselective self-assembling process was evidenced at room temperature by ^1H NMR in a dichloromethane solution containing a racemic mixture of anion and cation, resulting in the formation of the homochiral ion pairs (preferred association of propeller featuring identical handedness). This supramolecular association consists in the 'stacking' of the octupolar anion and cation along their threefold axis and corresponds exactly to the optimized macroscopic octupolar arrangement (Fig. 1) [6].

This paper is devoted to the NLO study of such supramolecular assembly. To this end, we have synthesized mono and dianion based on P, Sn or B catecholate complexes presenting octupolar D_3 or D_{2d} symmetry and studied their interaction in solution with D_3 tris{4,4'-bis(dibutylaminostyryl)-2,2'-bipyridine}ruthenium(II) [**Ru**] or D_{2d} bis{4,4'-bis(dibutylaminostyryl)-6,6'-dimethyl-2,2'-bipyridine}copper(I) [**Cu**] (Fig. 2).

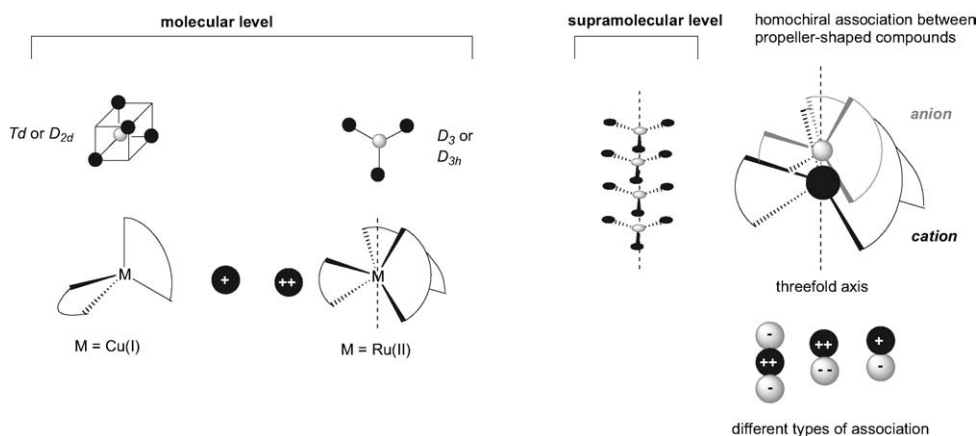


Fig. 1. Schematic representation of octupolar symmetries and of the optimized supramolecular association of octupole (right).

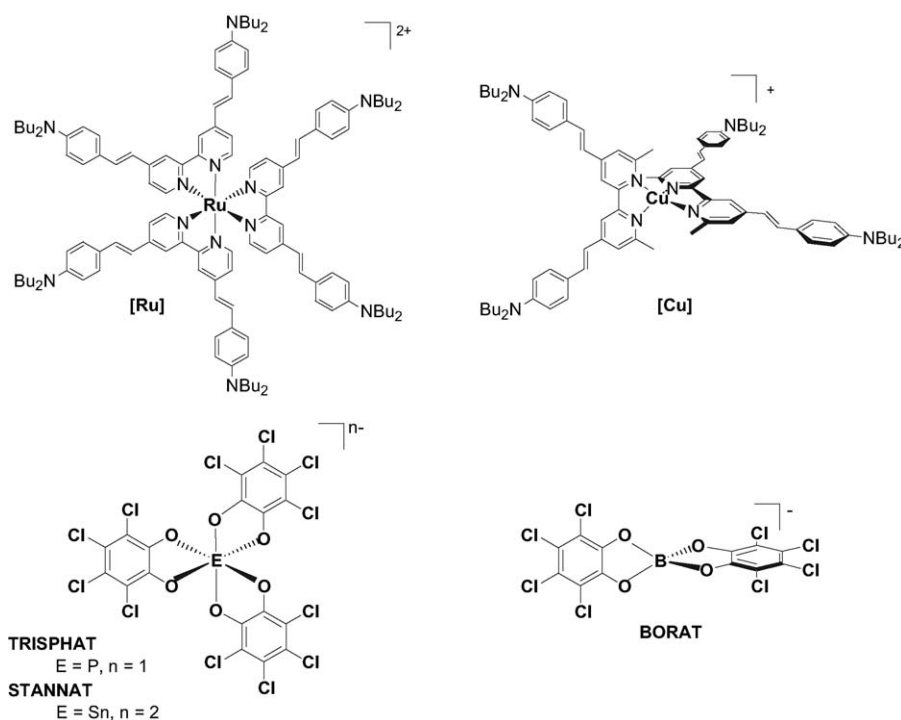


Fig. 2. Cationic (top) and anionic (bottom) octupolar compounds.

2. Synthesis

The preparation of $[\mathbf{Ru}](\text{PF}_6)_2$ and $[\mathbf{Cu}](\text{PF}_6)$ has already been described [3]. The synthesis of $[\text{HNBu}_3][\text{TRISPHAT}]$ and $[\text{HNBu}_3]_2[\text{STANNAT}]$ was achieved by mixing PCl_5 or SnCl_4 with three equivalents of tetrachlorocatechol in the presence of tributylamine according to procedures described by the groups of Lacour [9a] and Lambert et al. [9b] or Annan et al. [9c], respectively. The BORAT, $[\text{Na}][\text{B}(\text{O}_2\text{C}_6\text{Cl}_4)_2]$ was simply prepared by treatment of NaBH_4 with 2 equiv of catechol in tetrahydrofuran [10]. All these anions were characterized by heteronuclear NMR spectroscopy and exhibit a characteristic signal at -80.7 , -554.5 and 14.5 ppm for TRISPHAT (^{31}P NMR), STANNAT (^{119}Sn NMR)¹, and BORAT (^{11}B NMR), respectively.

¹ STANNAT exhibits a singlet signal in $^{119}\text{Sn}\{-\text{H}\}$ NMR (CD_2Cl_2 , 111.9 MHz, SnMe_4 as standard) $\delta = -554.5$ vs. 353 ppm described in [9b] in the same conditions. This latter signal was also detected and attributed to a cavity resonance.

3. Supramolecular association

The association of the D_3 symmetric anions and $[\mathbf{Ru}]$ dication was achieved by an anionic metathesis reaction. Since the STANNAT anion is not able to displace the PF_6^- , the $[\mathbf{Ru}]\text{STANNAT}$ complex can only be prepared from $[\mathbf{Ru}]\text{Cl}_2$ precursor. By contrast, the synthesis of $[\mathbf{Ru}](\text{TRISPHAT})_2$ can be carried out either from the chloro, the hexafluorophosphate or even the STANNAT ruthenium complex and no other anion, even in large excess is able to displace the TRISPHAT. Finally from this competitive experiments, the following order of affinity of the tris(bipyridyl)ruthenium complex for the different anions can be proposed: $\text{Cl}^- < \text{STANNAT}^{2-} < \text{PF}_6^- < \text{TRISPHAT}^-$. These three complexes were fully characterized by ^1H , ^{13}C NMR, UV–visible spectroscopy and microanalysis (see Section 6) and exhibit a completely different behavior in analytical thin layer chromatography (TLC) on silica plates with dichloromethane as eluent. Whereas the TRISPHAT salts are easily eluted ($R_f = 1$, Table 1), the hexafluorophosphate and STANNAT ruthenium salts does not migrate under the same conditions ($R_f < 0.1$). This dif-

ferent behavior indicates a strong difference of polarity dependent on the nature of the anion and is in agreement with the stronger ion pairing effect observed in the case of TRISPHAT. Indeed, TRISPHAT, as well as STANNAT is strongly lipophilic and a stronger anion/cation interaction will result in a decrease of the ion pair polarity.

In addition, ^1H NMR spectroscopy (Fig. 3) gives significant information concerning the nature of the anion/cation interaction. All the spectra were recorded with the same concentration in ruthenium species. As already observed for TRISPHAT, the racemic mixture of $[\text{Ru}]$ and STANNAT (isomer Λ and Δ) results only in the presence of a single set of signals for the bipyridyl ligand even at low temperature. This phenomenon is explained by the preferential co-threefold embrace of charged propeller-like derivatives [8]. In a non-dissociating solvent like dichloromethane, this strong ion pairing effect results in a modification of the ^1H NMR spectra. The major effect is the deshielding of H_6 proton in the case of TRISPHAT ($\Delta\delta_{\text{H}_6} = 0.46$ ppm vs. $[\text{Ru}](\text{PF}_6)_2$), whereas in the case of STANNAT, this deshielding effect occurs on the H_3 proton ($\Delta\delta_{\text{H}_3} = 0.26$ ppm vs. $[\text{Ru}](\text{PF}_6)_2$). On the contrary, in a strongly polar solvent like deuterated dimethylsulfoxide, the charged species are completely dissociated and only the spectra of the solvated $[\text{Ru}]$ species is observed (Fig. 3, bottom) [11]. It has to be pointed out that the shielding effect occurs on the proton closed to the metal (H_6) in the case of TRISPHAT, and in the periphery of the ligand (H_3) in the case of STANNAT. This should be explained by a more intimate interaction between $[\text{Ru}]$ and TRISPHAT in agreement with the smaller size of the phosphorus anion when compared to that of the tin derivative (average $d(\text{P}-\text{O}) = 1.71 \text{ \AA}$ [9a] vs. $d(\text{Sn}-\text{O}) = 2.06 \text{ \AA}$ [[9b,c]).

In the case of the pseudo-tetrahedral derivatives, the anionic metathesis between $[\text{Cu}]\text{Cl}$ and NaBORAT leads to the formation of $[\text{Cu}]\text{BORAT}$. This ion pair

Table 1
 ^1H NMR chemical shift (CD_2Cl_2 , RT) and TLC behavior (silica plate, CH_2Cl_2) of various anion/cation combination

Compound	H3–H5–H6	H7–H8	R_f
$[\text{Ru}](\text{PF}_6)_2$	8.36–7.33–7.52	6.92–7.43	0
$[\text{Ru}](\text{TRISPHAT})_2$	8.34–7.28– 7.98	6.57–7.22	1
$[\text{Ru}]\text{STANNAT}$	8.62 –7.28–7.63	6.84–7.53	0
$[\text{Cu}](\text{PF}_6)$	8.16–7.41	6.92–7.41	0
$[\text{Cu}](\text{BORAT})$	8.22–7.5	6.96–7.47	0.58

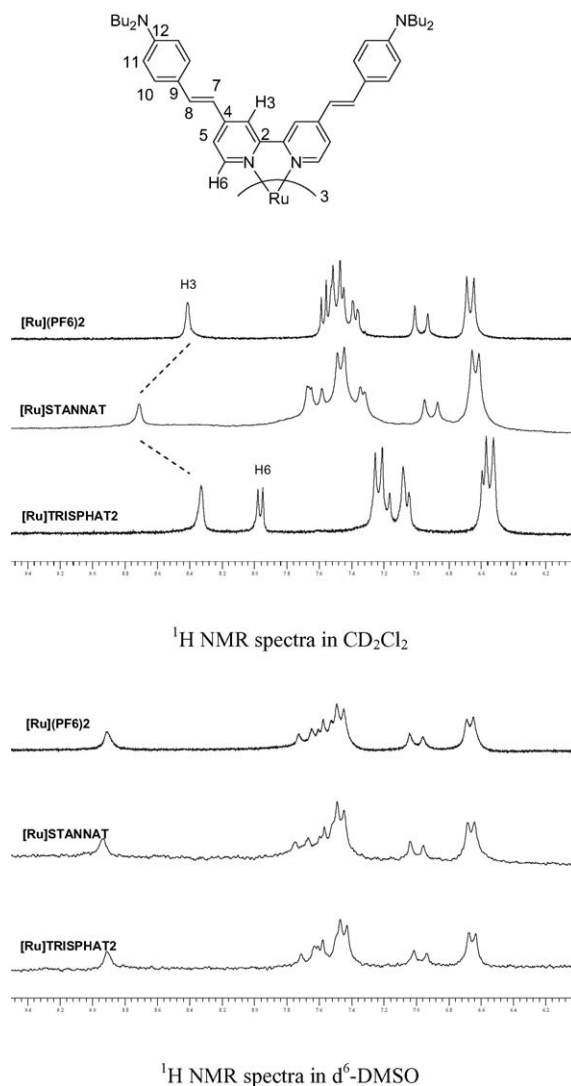


Fig. 3. Influence of the anion on the ^1H NMR spectra (conc. $10^{-2} \text{ mol l}^{-1}$, room temperature).

formation does not induced significant modification in the ^1H NMR spectra but results in a completely different behavior in TLC (Table 1). Whereas the hexafluorophosphate salt is strongly retained, the BORAT one can be easily eluted with dichloromethane with a R_f value of 0.58.

4. Linear and non-linear properties

BORAT, TRISPHAT or STANNAT anions are completely transparent in the visible and exhibit only

absorption in the UV (Table 2). Therefore, their association either with [Cu] or [Ru] does not modify the ILCT or MLCT transition located in the visible part of the spectrum (Table 2). The NLO activity of the D_3 octupolar anions was estimated by means of the harmonic light scattering (HLS) technique using 1.06 μm as fundamental laser wavelength. Their hyperpolarizabilities are low (Table 2) in the same order of magnitude than that of tris(isopropyl)aminotrinitrobenzene [12]. These low NLO activities are in marked contrast with the large β values of [Ru](PF₆)₂, $\beta = 340 \times 10^{-30}$ esu that must be measured at 1.91 μm , this fundamental wavelength precluding any perturbation of the experimental data by absorption effects at the second harmonic frequency or by two-photon induced fluorescence phenomena. Hence, changing the hexafluorophosphate by a TRISPHAT or a STANNAT anion does not induced any significant modification of the NLO activity (Table 2) and the observed variations remain within the experimental error of the measurement technique ($\pm 15\%$).

5. Concluding remarks

In this communication, we have described the supramolecular association between D_3 or D_{2d} symmetric octupolar cations and anions, evidenced by NMR

or TLC. The too large difference between the NLO activity of the anion and the cation does not allow to measure the effect of this association on the NLO activity. This preliminary work opens interesting perspectives for the design of supramolecular assemblies of octupoles. The P, B, Sn catecholate derivatives seem to be well suited for the supramolecular association with tris(bipyridyl)ruthenium(II) or bis(bipyridyl)copper(I) complexes. Further functionalization of this catecholate ligands should increase the NLO activity of the corresponding octupolar derivatives enabling to measure the effect of supramolecular associations of octupoles on the NLO activity.

6. Experimental section

6.1. [Ru]STANNAT

In a Schlenk vessel RuCl₂(DMSO)₄ (131.32 mg, 0.27 mmol, 1 equiv) and 4,4'-[(*N,N*-dibutyl)aminostyryl]-2,2'-bipyridine (500 mg, 0.81 mmol, 3 equiv) were dissolved in ethanol (30 ml). The red mixture was heated at reflux under nitrogen for 7 h. After the solution was cooled to room temperature, (HNBu₃)₂STANNAT (0.515 g, 0.54 mmol, 2 equiv), was added and the solution was stirred for 3 h. The desired complex was precipitated by addition of water (300 ml), filtered off and washed several times with pentane and diethylether. The crude product was dissolved in CH₂Cl₂, dried with MgSO₄; the solution was concentrated and the product was precipitated by addition of pentane (v/v = 1/10). Finally the red microcrystalline powder was dried under vacuum (400 mg, 55%). ¹H NMR (200.13 MHz, CD₂Cl₂) δ ppm: 8.62 (s, 6H, H₃); 7.63 (d, $J = 5.8$ Hz, 6H, H₆); 7.53 (d, $J = 16.0$ Hz, 6H, H₈); 7.40 (d, $J = 8.5$ Hz, 12H, H₁₀); 7.28 (d br., $J = 5.8$ Hz, 6H, H₅); 6.84 (d, $J = 16.0$ Hz, 6H, H₇); 6.58 (d, $J = 8.5$ Hz, 12H, H₁₁); 3.25 (t, $J = 5.9$ Hz, 24H, H₁₃); 1.60–1.50 (m, 24H, H₁₄); 1.40–1.22 (m, 24H, H₁₅); 0.94 (t, $J = 7.1$ Hz, 36H, H₁₆). ¹³C NMR (75.47 MHz, CD₂Cl₂) δ ppm: 157.0 (C₂); 150.3 (C₆); 149.4 (C₁₂); 149.3 (C_{stannat}); 147.4 (C₄); 137.0 (C₈); 129.4 (C₁₀); 123.0 (C₅); 122.5 (C₉); 120.2 (C₃); 117.8 (C₇); 117.5 (C_{stannat}); 116.1 (C_{stannat}); 111.5 (C₁₁); 50.7 (C₁₃); 29.4 (C₁₄); 20.3 (C₁₅); 13.7 (C₁₆). Elemental analysis calculated for C₁₄₄H₁₆₂N₁₂O₆Cl₁₂RuSn₃CH₂Cl₂: C 57.76; H 5.54; N 5.50. Found: C 57.51; H 6.01; N 6.14.

Table 2
Linear and NLO data

Compound	λ_{max} (ϵ) ^a (nm l mol ⁻¹ cm ⁻¹)	β^b (10 ⁻³⁰ esu)
[HNBu ₃](TRISPHAT)	300 (12,000)	10 \pm 2 ^c
[HNBu ₃] ₂ (STANNAT)	306 (6000)	30 \pm 5 ^c
[Ru](PF ₆) ₂	446 (142,000) 520 (150,000)	340 \pm 51 ^d
[Ru](TRISPHAT) ₂	449 (124,000) 524 (133,000)	320 \pm 48 ^d
[Ru]STANNAT	447 (130,000) 517 (133,000)	310 \pm 46 ^d
NaBORAT	301 (8000) ^e	–
[Cu](PF ₆)	436 (106,000) 480 sh	113 \pm 17 ^d
[Cu](BORAT)	437 (106,000) 480 sh	–

^a In CH₂Cl₂.

^b Precision $\pm 15\%$.

^c Measured by HLS in CH₂Cl₂ at 1.064 μm .

^d Measured by HLS in CH₂Cl₂ at 1.91 μm .

^e In THF.

6.2. [Ru](TRISPHAT)₂

Using similar procedure but with (HNBu₃)-TRISPHAT, the red complex was prepared in 65% yield. ¹H NMR (200.13 MHz, CD₂Cl₂) δ ppm: 8.34 (s, 6H, H₃); 7.98 (d, *J* = 6.2 Hz, 6H, H₆); 7.25 (d, *J* = 8.9 Hz, 12H, H₁₀); 7.22 (d, *J* = 16.3 Hz, 6H, H₈); 7.08 (d. br., *J* = 6.2 Hz, 6H, H₅); 6.57 (d, *J* = 16.3 Hz, 6H, H₇); 6.56 (d, *J* = 8.9 Hz, 12H, H₁₁); 3.26 (t, *J* = 6.4 Hz, 24H, H₁₃); 1.60–1.50 (m, 24H, H₁₄); 1.40–1.22 (m, 24H, H₁₅); 0.94 (t, *J* = 6.9 Hz, 36H, H₁₆). ¹³C NMR (75.47 MHz, CD₂Cl₂) δ ppm: 156.9 (C₂); 150.9 (C₆); 149.4 (C₁₂); 147.0 (C₄); 141.6 (d, ³*J*_(P-C) = 6.6 Hz, 2C, C_{2trispbat}); 136.3 (C₈); 129.3 (C₁₀); 122.6 (C₅); 122.4 (d, ⁴*J*_(P-C) = 2.2 Hz, 2C, C_{4trispbat}); 122.1 (C₉); 119.6 (C₃); 117.2 (C₇); 113.9 (d, ²*J*_(P-C) = 19.8 Hz, 2C, C_{1trispbat}); 111.4 (C₁₁); 50.7 (C₁₃); 29.4 (C₁₄); 20.3 (C₁₅); 13.7 (C₁₆). ³¹P NMR (121.47 MHz, CD₂Cl₂) δ ppm: –80.71. Elemental analysis calculated for C₁₆₂H₁₆₂N₁₂O₁₂Cl₂₄P₂Ru: C 55.86; H 4.69; N 4.83. Found: C 55.61; H 4.83; N 4.60.

6.3. [Cu]BORAT

In a Schlenk vessel, the (4,4'-[(*N,N*-dibutyl)aminostyryl]-6,6'-dimethyl-2,2'-bipyridine)CuCl complex (100 mg, 7.22 mmol, 1 equiv), and one equivalent of NaBORAT (37.96 mg, 7.22 mmol, 1 equiv), were dissolved in dichloromethane (20 ml). The orange mixture was stirred for 3 h at room temperature. The crude mixture was filtered to remove NaCl. The solution was then dried with MgSO₄; concentrated and the product was precipitated by addition of pentane (*v/v* = 1/10). Finally the brown microcrystalline powder was dried under vacuum (90 mg, 65%). ¹H NMR (200.13 MHz, CD₂Cl₂) δ ppm: 8.22 (s, 4H, H₃); 7.52 (d, *J* = 7.5 Hz, 8H, H₁₀); 7.50–7.46 (m, 12H, H₅, H₈); 6.96 (d, *J* = 14.6 Hz, 4H, H₇); 6.72 (d, *J* = 7.5 Hz, 8H, H₁₁); 3.38 (t, *J* = 7.0 Hz, 16H, H₁₃); 2.28 (s, 12H, H₁₇); 1.64

(m, 16H, H₁₄); 1.42 (m, 16H, H₁₅); 1.02 (t, *J* = 7.2 Hz, 24H, H₁₆). ¹³C NMR (75.47 MHz, CD₂Cl₂) δ ppm: 156.8 (C₆); 152.2 (C₄); 149.5 (C₁₂); 147.9 (C₂); 147.7 (C_{borat}); 135.2 (C₈); 128.9 (C₁₀); 122.5 (C₉); 121.4 (C₅); 122.5 (C₉); 121.4 (C₅); 120.3 (C₃); 119.9 (C_{borat}); 115.7 (C₇); 112.0 (C₁₁); 111.5 (C_{borat}), 50.7 (C₁₃); 29.4 (C₁₄); 24.8 (C₁₇); 20.3 (C₁₅); 13.8 (C₁₆); ¹¹B NMR (96.29 MHz, CD₂Cl₂) δ ppm: 14.4.

References

- [1] Y.Q. Shi, C. Zhang, H. Zang, J.H. Bechtel, L.R. Dalton, B.H. Robinson, W.H. Steier, *Science* 288 (2000) 119.
- [2] (a) J. Zyss, *J. Chem. Phys.* 98 (1993) 583–6599 (b) J. Zyss, I. Ledoux, *Chem. Rev.* 94 (1994) 77.
- [3] O. Maury, L. Viau, K. Sénéchal, B. Corre, J.-P. Guégan, T. Renouard, I. Ledoux, J. Zyss, H. Le Bozec, *Chem. Eur. J.* 10 (2004) 4454.
- [4] (a) S. Brasselet, J. Zyss, *J. Opt. Soc. Am. B*, 15 (1998) 257; (b) L. Viau, S. Bidault, O. Maury, S. Brasselet, I. Ledoux, J. Zyss, E. Ishow, K. Nakatani, H. Le Bozec, *J. Am. Chem. Soc.* 126 (2004) 8386.
- [5] (a) I. Ledoux, *J. Zyss C. R. Phys.* 3 (2002) 407; (b) J. Zyss, unpublished results.
- [6] I. Ledoux, J. Zyss, J.S. Siegel, J. Brienne, J.-M. Lehn, *Chem. Phys. Lett.* 172 (1990) 440.
- [7] (a) V.R. Thalladi, S. Brasselet, H.-C. Weiss, D. Bläser, A.K. Katz, H.L. Carrell, R. Boese, J. Zyss, A. Nangia, G.R. Desiraju, *J. Am. Chem. Soc.* 120 (1998) 2563; (b) T. Le Boudier, O. Maury, A. Bondon, K. Costuas, E. Amouyal, I. Ledoux, J. Zyss, H. Le Bozec, *J. Am. Chem. Soc.* 125 (2003) 12884.
- [8] O. Maury, J. Lacour, H. Le Bozec, *Eur. J. Inorg. Chem.* (2001) 201–204.
- [9] (a) J. Lacour, C. Glinglinger, C. Grivet, G. Bernardelli, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 608; (b) C. Lambert, J.C. Machell, D.M. Mingos, T.L. Stolberg, *J. Mater. Chem.* 1 (1991) 775; (c) T. Annan, R.K. Chadha, D.G. Tuck, K.D. Watson, *Can. J. Chem.* 65 (1987) 2670.
- [10] (a) For a review on borate and phosphate anion see: J. Lacour, V. Hebbe-Viton, *Chem. Soc. Rev.* 32 (2003) 373.
- [11] J.J. Jodry, R. Frantz, J. Lacour *Inorg. Chem.* 43 (2004) 3329.
- [12] T. Verbiest, K. Clays, C. Samyn, J. Wolff, D. Reinhoudt, A. Pearsons, *J. Am. Chem. Soc.* 116 (1994) 9320.