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# Towards chiral 1,2-naphthalocyanines: 2. Synthesis of lutetium bismacrocyclic derivatives

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**ABSTRACT:** Starting from 1,2-naphthalocyanine lutetium acetate (1,2-NcLuOAc) the unsymmetrical lutetium phthalo(naphthalo)cyanine (1,2-NcLuPc) has been synthesized and characterized by optical absorption spectra and fast atom bombardment (FAB) mass spectrometry. 1,2-Naphthalocyanine shows several geometrical isomers, both the mixture (noted Nc<sup>S</sup>) and one of them (Nc<sup>Cs</sup>) have been used for forming the corresponding bismacrocycles. As a result the first racemic mixture of a chiral unsubstituted phthalo(naphthalo)cyanine complex has been synthesized and characterized. Copyright © 2001 John Wiley & Sons, Ltd.

**KEYWORDS:** naphthalocyanines; lutetium; bismacrocyclic compounds; chirality

## INTRODUCTION

Since their synthesis [1], the lanthanide bisphthalocyanines attracted the attention of many research groups as electrochroms [2, 3], molecular semiconductors [4, 5] and sensors [6, 7]. The properties of the molecular unit may be varied by introducing substituents on the phthalocyanine ring or by extending the conjugation of the macrocycle, as in naphthalocyanines [8–10]. In order to get a chiral molecular semiconductor, we chose to work on 1,2-naphthalocyanine derivatives. These molecules have been described [11] but only a few studies have been published due to the existence of several isomers leading to difficulty in obtaining a pure single one [12, 13].

1,2-Naphthalocyanines present four different isomers of symmetries C<sub>4h</sub>, C<sub>S</sub>, C<sub>2v</sub> and D<sub>2h</sub> [13]. The symmetry groups indicated are correct only when the macrocycle is considered to be planar. All of them present a plane of symmetry and are therefore not chiral. By synthesizing the unsymmetrical phthalo-naphthalocyanines this mirror plane is removed and the C<sub>S</sub> and C<sub>4h</sub> isomers can lead to chiral molecules. Calculations [14] show that the C<sub>S</sub> isomer cannot be planar because of steric hindrance between two out of the four naphthalene moieties. This will not be considered in subsequent sections. The synthesis of mixtures of different isomers of lutetium 1,2-naphthalocyanines complexes (1,2-Nc)<sub>2</sub>Lu and (1,2-Nc)<sub>3</sub>Lu<sub>2</sub> has been published [15, 16]. In a previous paper [13] we reported, for the first time, the separation of the four isomers of a magnesium 1,2-naphthalocyanine derivative (1,2-NcMg). We transformed the compounds assigned to the C<sub>4h</sub> and C<sub>S</sub> isomers into the

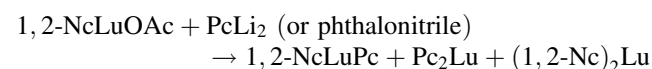
corresponding lutetium mononaphthalocyanines: 1,2-NcLuOAc. The separation of the optical isomers is difficult at this stage of the synthesis. We therefore proposed a synthetic pathway to chiral 1,2-naphthalocyanine complexes which involves the transformation of the previous mononaphthalocyanine complexes into the bisnaphthalocyanine derivatives [13].

In this paper we report the synthesis of bismacrocyclic naphthalo-phthalocyanine derivatives. One of them is shown in Fig. 1.

In order to simplify the notation of the different isomers only the symmetry group of the original magnesium complex will be written: 1,2-Nc<sup>C<sub>4h</sub></sup>Mg → 1,2-Nc<sup>C<sub>4h</sub></sup>H<sub>2</sub> → 1,2-Nc<sup>C<sub>4h</sub></sup>LuOAc. This notation therefore does not always indicate the symmetry group of the overall molecular unit. For mixtures of isomers the notation Nc<sup>S</sup> will be used.

## EXPERIMENTAL

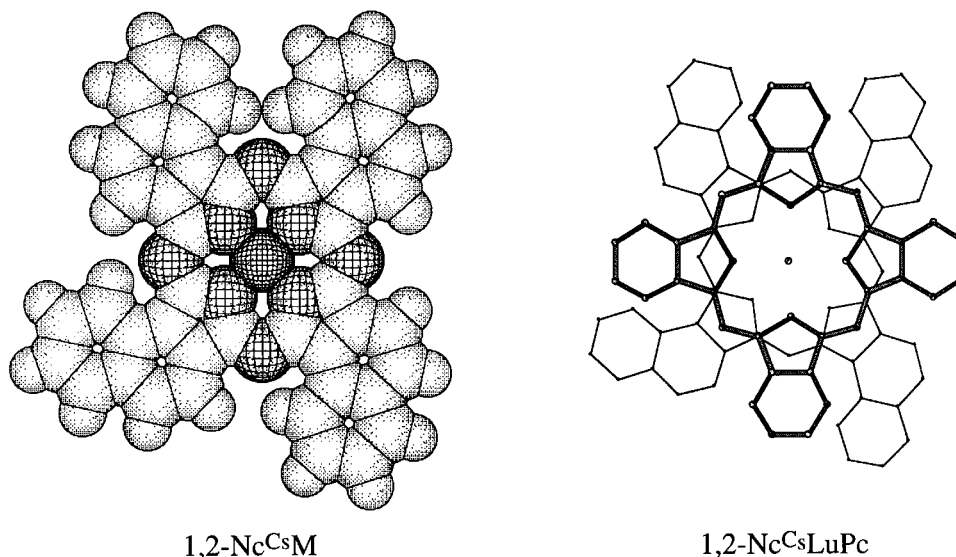
1,2-NcLuPc complexes have been synthesized in two ways starting from 1,2-NcLuOAc. The first one uses PcLi<sub>2</sub>, and the second one phthalonitrile. Both reactions lead not only to the unsymmetrical derivative but also to the symmetrical lutetium bismacrocyclic compounds, lutetium bisphthalocyanine Pc<sub>2</sub>Lu and lutetium bisnaphthalocyanine (1,2-Nc)<sub>2</sub>Lu.



This means that some chemical rearrangement occurs during the reaction process [17].

When a mixture of 1,2-Nc<sup>S</sup>LuOAc and PcLi<sub>2</sub> is heated in *n*-hexanol, under reflux for 20 h, three different products are separated by thin layer chromatography (SiO<sub>2</sub>, eluent: CHCl<sub>3</sub>). UV-vis absorption studies have been carried out on

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**Fig. 1.** Right: the unsymmetrical lutetium 1,2-naphthalo-phthalocyanine (1,2-Nc<sup>Cs</sup>LuPc) left: the C<sub>S</sub> isomer of a metal mononaphthalocyanine 1,2-Nc<sup>Cs</sup>M (80% of the van der Waals volume). The geometries have been optimized with Biosym, and the molecules represented with Moldraw (notation see text).

these three products and on the corresponding derivatives reduced with hydrazine. The three compounds correspond to different bismacrocycles, Pc<sub>2</sub>Lu (R<sub>f</sub> = 0.35), 1,2-NcLuPc (R<sub>f</sub> = 0.55) and (1,2-Nc)<sub>2</sub>Lu (R<sub>f</sub> = 0.70) in relative proportions 15% 20% and 65%, respectively. The UV-vis spectra in CHCl<sub>3</sub> of these three complexes are shown in Figs 2 and 3, in their neutral and reduced forms (Table 1). A slight red-shift of all the optical transitions is observed when bisphthalocyanine is changed to bisnaphthalocyanine. The absorption band of Pc<sub>2</sub>Lu at 460 nm has been assigned to a transition of a full level to the semi-occupied molecular orbital (SOMO) [18–20]. This band can therefore be considered as an indication of the radical nature of the molecule. This band exists for the three bismacrocyclic derivatives obtained, and disappears, as expected, when the complexes are reduced (Fig. 3).

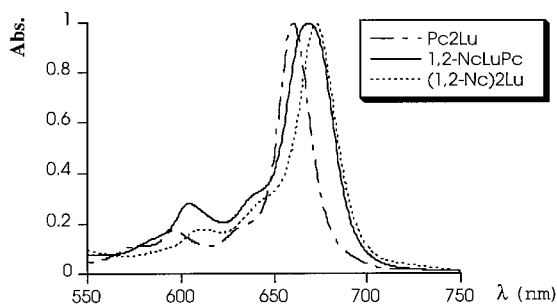
The ease of oxidation increases from Pc<sub>2</sub>Lu to (1,2-Nc)<sub>2</sub>Lu as evidenced by the rate of colour change when TLC plates are kept in open air: Pc<sub>2</sub>Lu turns from green to brown, 1,2-NcLuPc from bluish-green to greenish-brown, and (1,2-Nc)<sub>2</sub>Lu from greyish-blue to violet.

When the reaction is carried out with phthalonitrile instead of PcLi<sub>2</sub>, the three lutetium bismacrocyclic derivatives are obtained in different ratios. The proportions

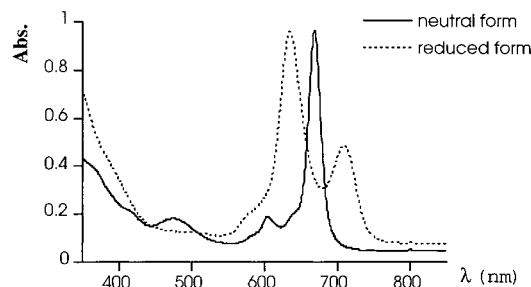
of Pc<sub>2</sub>Lu, 1,2-NcLuPc and (1,2-Nc)<sub>2</sub>Lu, estimated from UV-vis spectroscopy in CHCl<sub>3</sub> from the fractions separated by thin layer chromatography, are 8% 90% and 2%, respectively. This method is therefore appropriate to synthesize unsymmetrical 1,2-NcLuPc. The previous reaction has been carried out with 1,2-Nc<sup>Cs</sup>LuOAc and 1,2-Nc<sup>Σ</sup>LuOAc. The main product separated after three column chromatographies on silica (deposition and elution: chloroform) is the same in both cases, and is thought to be 1,2-Nc<sup>Cs</sup>LuPc, from <sup>1</sup>H NMR spectra (see Fig. 4). This surprising result is probably due to a lower solubility of the C<sub>4h</sub> derivative, compared to the C<sub>s</sub> one. Indeed, when 1,2-Nc<sup>C<sub>4h</sub></sup>LuOAc is used as starting material the solubility is too low in *n*-hexanol to allow the reaction to proceed. When 1,2-Nc<sup>Σ</sup>LuOAc is used the transformation of the C<sub>4h</sub> isomer is consequently disfavoured.

### Syntheses of 1,2-Nc<sup>Cs</sup>LuPc

**From 1,2-Nc<sup>Cs</sup>LuOAc.** A mixture of 1,2-Nc<sup>Cs</sup>LuOAc (100 mg, 0.106 mmol), phthalonitrile (80 mg, 0.625 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (32 μl) in *n*-hexanol (5 ml) was heated at 160 °C under nitrogen for 18 h. The solution was diluted with *n*-hexane, filtered and the



**Fig. 2.** Optical absorption spectra of solutions of the neutral forms of Pc<sub>2</sub>Lu (---), 1,2-Nc<sup>Σ</sup>LuPc (—) and (1,2-Nc<sup>Σ</sup>)<sub>2</sub>Lu (.....) in CHCl<sub>3</sub>.



**Fig. 3.** Optical absorption spectra of solutions (CHCl<sub>3</sub>) of the reduced form (.....) of 1,2-Nc<sup>Σ</sup>LuPc in comparison with the neutral form (—).

**Table 1.** UV-vis absorption data of the three lutetium bismacrocylic complexes in chloroform

	$\lambda_{\max}$ neutral forms (nm)			$\lambda_{\max}$ reduced forms (nm)	
	Soret band	Q band		Soret band	Other bands
Pc <sub>2</sub> Lu	316	458	660	350	622, 703
1,2-NcLuPc		475	669		635, 710
(1,2-Nc) <sub>2</sub> Lu	379	516	673	375	644, 716

solid was washed with *n*-hexane and dried. The solid was extracted with chloroform, and the solution was evaporated to dryness, the residue was solubilized in a small quantity of dimethylformamide (DMF) and purified by chromatography on silica (eluent: chloroform). After three successive chromatographies, 23 mg of 1,2-Nc<sup>Cs</sup>LuPc was separated. (Yield = 16%)

**From 1,2-Nc<sup>Σ</sup>LuOAc.** A mixture of 1,2-Nc<sup>Σ</sup>LuOAc (300 mg, 0.316 mmol), phthalonitrile (240 mg, 1.90 mmol) and DBU (90 μl) in *n*-hexanol (10 ml) was heated under reflux and nitrogen for 16 h. The following experimental procedure is identical to the previous one. After three chromatographies (chloroform), 4 mg of (1,2-Nc<sup>Σ</sup>)<sub>2</sub>Lu (0.8%) and 55 mg of 1,2-Nc<sup>Cs</sup>LuPc (yield = 12.5%) were obtained.

The products were characterized by fast atom bombardment (FAB) mass spectrometry (matrix: *meta*-nitrobenzyl alcohol; gas: xenon), <sup>1</sup>H NMR spectroscopy and UV-vis spectroscopy. The parent peaks ([MH]<sup>+</sup>) (M: molar mass), the peak (MH<sup>+</sup> + 16) corresponding to the addition of an oxygen atom from the matrix [21], and a peak (MH<sup>+</sup> + 151) where 151 corresponds to the matrix itself are observed by FAB mass spectrometry (Table 2).

As it has been already observed [22] the main fragments are those due to the departure of one macrocycle. The symmetrical derivative (1,2-Nc)<sub>2</sub>Lu leads to one peak at 887 (NcLu<sup>+</sup>) whereas 1,2-NcLuPc leads to two peaks, at 887 (NcLu<sup>+</sup>) and 687 (PcLu<sup>+</sup>).

On the basis of the assignments of <sup>1</sup>H NMR spectra of PcM, 1,2-NcM, Pc<sub>2</sub>Lu<sup>−</sup> and (2,3-Nc)<sub>2</sub>Lu<sup>−</sup> [15, 23, 24], the

**Table 2.** Results of mass spectrometry (FAB) obtained for lutetium bismacrocylic derivatives (matrix: *meta*-nitrobenzyl alcohol)

Molecules	Molar mass	Main peak ([MH] <sup>+</sup> )	Other peaks	Ref.
Pc <sub>2</sub> Lu	1199	1200	687 (PcLu <sup>+</sup> )	22
2,3-NcLuPc	1399	1400	687 (PcLu <sup>+</sup> ) (3.5*), 887 (NcLu <sup>+</sup> ) (1*)	17, 22
1,2-Nc <sup>Cs</sup> LuPc	1399	1400	687 (PcLu <sup>+</sup> ) (4*), 887 (NcLu <sup>+</sup> ) (3*)	This work
			1417 (MH <sup>+</sup> + 16), 1553 (MH <sup>+</sup> + matrix)	
(1,2-Nc <sup>Σ</sup> ) <sub>2</sub> Lu	1600	1601	887 (NcLu <sup>+</sup> )	This work
			1617 (MH <sup>+</sup> + 16), 1685 (MH <sup>+</sup> + matrix)	

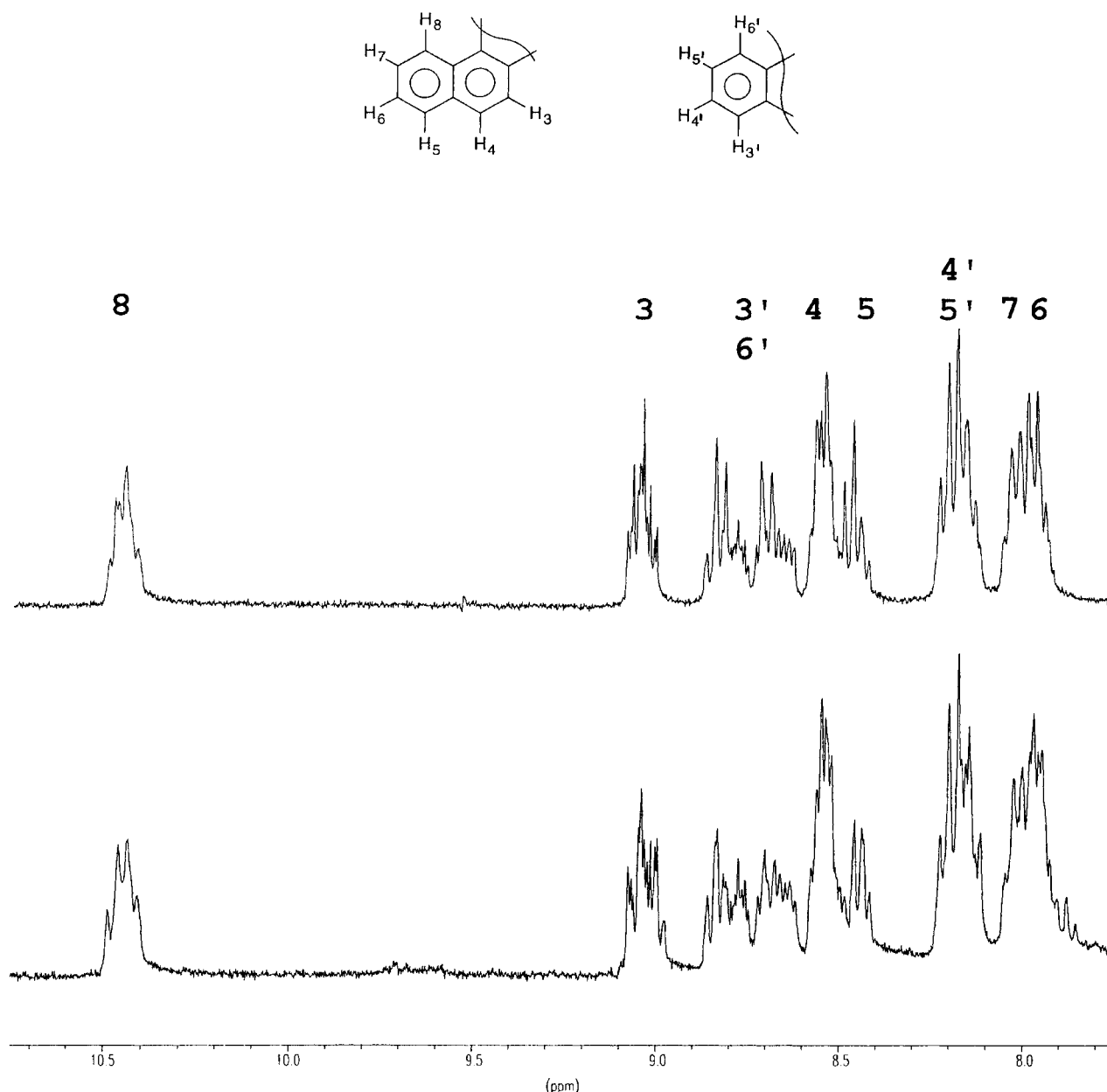
\* Relative intensities.

**Table 3.** <sup>1</sup>H NMR (300 MHz) spectroscopy results for phthalocyanine and naphthalocyanine derivatives (chemical shifts are given vs TMS) (for the numbering see Fig. 4)

Protons	PcLuOAc	Pc <sub>2</sub> Lu <sup>−</sup>		2,3-NcLuPc <sup>−</sup>	1,2-Nc <sup>Cs</sup> LuPc <sup>−</sup>	1,2-Nc <sup>Σ</sup> Li <sub>2</sub>	1,2-Nc <sup>C4h</sup> LuOAc	
H3', H6'	9.48	8.83	8.90	8.79	8.7, 8.8			
H4', H5'	8.11	8.13	8.17	8.15	8.15			
H3					9.04	9.7	9.74	9.36
H4					8.55	8.6	8.78	8.25
H5					8.45	8.4	8.54	8.03
H6					7.98	7.85	8.00	7.58
H7					8.18	8.25	8.37	7.90
H8					10.44	11.5	11.31	10.99
Solvent	CDCl <sub>3</sub>	CD <sub>3</sub> CN	DMF- <i>d</i> <sub>7</sub>	DMF- <i>d</i> <sub>7</sub>	DMSO- <i>d</i> <sub>6</sub>	Acetone- <i>d</i> <sub>6</sub>	DMSO- <i>d</i> <sub>6</sub>	CDCl <sub>3</sub> /CD <sub>3</sub> OD
		NBu <sub>4</sub> <sup>+a</sup>	N <sub>2</sub> D <sub>4</sub> <sup>b</sup>	N <sub>2</sub> D <sub>4</sub> <sup>b</sup>	N <sub>2</sub> D <sub>4</sub> <sup>b</sup>			(3/1)
Ref.		24	15	15	This work	15	This work	This work

<sup>a</sup> Counterion.

<sup>b</sup> Reducing agent.



**Fig. 4.**  $^1\text{H}$  NMR (300 MHz) spectra of  $1,2\text{-Nc}^{\text{C}}\text{LuPc}^-$  ( $\text{DMSO-}d_6$ ) synthesized from  $1,2\text{-Nc}^{\Sigma}\text{LuOAc}$  (upper spectrum) and from  $1,2\text{-Nc}^{\text{C}}\text{LuOAc}$  (lower spectrum). Reduction of the lutetium complexes was achieved by  $\text{N}_2\text{D}_4$ .

$^1\text{H}$  NMR peaks of  $1,2\text{-Nc}^{\text{C}}\text{LuPc}^-$  could be assigned (Table 3 and Fig. 4).

In the discussion, the numbering used is as shown in Fig. 4 for the phthalocyanine and 1,2-naphthalocyanine moieties. For the 2,3-naphthalocyanine, the protons are numbered in the same way as for the 1,2-derivative. Prime numbers are used for the phthalocyanine macrocycle.

In the case of  $\text{PcSi}(\text{OSiR}_3)_2$ , previous assignments [25] have shown that the  $\text{H}4'$ ,  $\text{H}5'$  protons lead to a multiplet around 8.3 ppm whereas the  $\text{H}3'$ ,  $\text{H}6'$  protons are associated with a multiplet around 9.7 ppm. Approximately the same chemical shifts are found in the case of  $\text{PcLuOAc}$ . A correlation may be attempted when the monophthalocyanine is transformed into the corresponding reduced bisphthalocyanine  $\text{Pc}_2\text{Lu}^-$ : the  $\text{H}4'$ ,  $\text{H}5'$  protons, which are the further from the inner conjugated ring, remain at the same chemical shift, whereas the protons close to the inner ring,  $\text{H}3'$ ,  $\text{H}6'$  are shifted downfield by approximately

0.6 ppm (Table 3). The couple of protons ( $\text{H}3'$ ,  $\text{H}6'$ ) and ( $\text{H}4'$ ,  $\text{H}5'$ ) are unshifted when going from  $\text{Pc}_2\text{Lu}^-$  to  $2,3\text{-NcLuPc}^-$  [15]. Consequently, it is possible to assign the corresponding protons in the case of  $1,2\text{-Nc}^{\text{C}}\text{LuPc}^-$  (the chemical shifts of  $2,3\text{-NcLuPc}^-$  are roughly the same in  $\text{DMF-}d_7$  and  $\text{DMSO-}d_6$ ). The assignment of the protons of  $1,2\text{-Nc}^{\Sigma}\text{Li}_2$  has been previously described [15] and is figured in Table 3. A one-to-one correspondence between the chemical shifts found for  $1,2\text{-Nc}^{\Sigma}\text{Li}_2$  and  $1,2\text{-Nc}^{\text{C}}\text{LuPc}^-$  may be easily found. The proton assignment has been made following this observation. The same procedure has been followed for  $1,2\text{-Nc}^{\text{C}}\text{LuOAc}$ . The protons ( $\text{H}3'$ ,  $\text{H}6'$ ) lead to two multiplets due to the symmetry of the  $1,2\text{-Nc}^{\text{C}}\text{LuPc}^-$  isomer.

Infrared spectroscopy measurements have also been carried out to characterize the products. The four main peaks of  $1,2\text{-Nc}^{\text{C}}\text{LuPc}$  appear at about the same energies as for  $\text{Pc}_2\text{Lu}$  and have been attributed to C–H wagging

vibration ( $732\text{ cm}^{-1}$ ), C–H bending vibration ( $1117\text{ cm}^{-1}$ ), and to two isoindole stretching vibrations ( $1321$  and  $1450\text{ cm}^{-1}$ ) [26].

## CONCLUSION

Two new lutetium bismacrocylic complexes, 1,2- $\text{Nc}^{\text{C}}\text{LuPc}$  and  $(1,2\text{-Nc}^{\Sigma})_2\text{Lu}$ , have been synthesized and characterized. The first one has no improper axis of rotation and is therefore chiral. The ease of oxidation and reduction of the lutetium complexes which permits the attainment of intrinsic molecular semiconductors can be allied with the chiral character, this represents a new approach to the field of semiconducting molecular materials. The separation of the optical isomers is under progress.

## Acknowledgements

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