



# SYNTHESIS OF PRECURSORS OF SEMICONDUCTOR QDs: TECHNOLOGY REVIEW

**Grant Agreement number:** 247928

**Project acronym:** LAMP

**Project title:** **L**ASER INDUCED SYNTHESIS OF POLYMERIC NANOCOMPOSITE MATERIALS AND DEVELOPMENT OF **M**ICRO-**P**ATTERNED HYBRID LIGHT EMITTING DIODES (LED) AND TRANSISTORS (LET)

**Funding Scheme:** STREP

**Date of latest version of Annex I against which the assessment will be made:**

**Periodic report:** D2.1 – Precursors Synthesis

**Period covered:** from M1 to M15

**Name, title and organisation of the scientific representative of the project's coordinator<sup>1</sup>:** Dr. Francesco Antolini ENEA

**Tel:** +39 0546 678535 **Fax:** +39 0546 678575

**E-mail:** francesco.antolini@enea.it

**Name, title and organisation of the scientific representative of the deliverable responsible:** Dr. Francesco Antolini

**Tel:** +39 0546 678535

**Fax:** +39 0546 678575

**E-mail:** francesco.antolini@enea.it

**Project website address:** [www.lamp-project.eu](http://www.lamp-project.eu)

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<sup>1</sup> Usually the contact person of the coordinator as specified in Art. 8.1. of the grant agreement

## 1. Section

Company: **ENEA**

Expected contribution

*In this report the progress in the synthesis of QDs precursors between month 1 (June 2010) and month 15 (August 2011) is illustrated. Four different CdS precursors of CdS and one of CdSe have been synthesized and characterized. The synthesis of CdSe and solid state NMR spectrum of one precursor were carried out in collaboration with BUW.*

The main objective of this task is the preparation and characterisation of organometallic precursors for the preparation of QDs both in solution and "in situ". Recently single source precursors have been studied as good candidate to produce QDs directly in the polymeric matrix also with laser sources [1-3] and represent one of the main goals of the project.

The work was focused on the synthesis of four different CdS precursors belonging to three different classes of metallorganic molecules: the metal-thiolates, metal-carbamates and metal xanthates and one cadmium selenide precursor. The synthesis of this compound and the solid state NMR spectrum of the PR02 precursor was carried out by BUW.

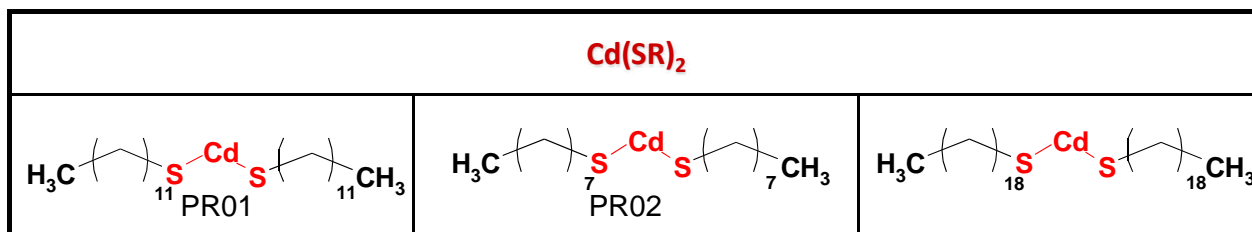
The synthesis and characterisations reported here do not take into account several other molecules synthesised in the laboratory, that were not described here because they didn't fit some of the criteria established for the precursor molecules (too high decomposition temperature or PL emission).

1. J of Nanomaterials (in press) "Time and temperature dependence of CdS nanoparticles growth in a polystyrene matrix", F. Antolini, E. Burresi, L. Stroea, V. Morandi, L. Ortolani, G. Accorsi and M. Blosi.
2. J. Nanosci. Nanotechnol. Vol 10, 1-6, 2010 "The effect of polymer matrices in the in situ CdS formation under UV irradiation of precursor polymer films" D. Fragouli, A.M. Laera, G. Caputo, V. Resta, P.P. Pompa, L. Tapfer, R. Cingolani, A. Athanassiou
3. Physica (B) Vol. 244(8), 2768-2781, 2007 "Direct synthesis of II-VI compound nanocrystals in polymer matrix" F.Antolini, T. Di Luccio, A.M. Laera, L. Mirengi, E. Piscopiello, M. Re, L. Tapfer;
4. Materials Letters (B) Vol. 60, 2657-2661, 2006 "A solid state nuclear magnetic resonance study on the thermolytic synthesis of the CdS nanoparticles in a polystyrene matrix" M. Pentimalli, F.Antolini, E. M. Bauer, Capitani D., T. Di Luccio, S. Viel;

## 1.1 Synthesis of Cadmium bis-thiolates.

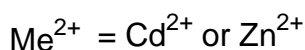
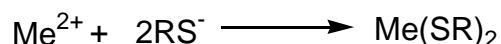
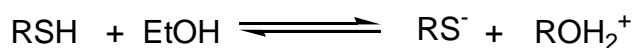
The first class of precursors studied is the Cadmium-bis thiolated precursors. We started with this class because their synthesis is fast (one pot) and the relatively simple. This is a great advantage for a possible industrial application of these molecules.

Three different molecules differing for the length of their chain length were synthesised. The molecular structure of these molecules are reported in figure 1.



**Figure 1:** molecular structures of the cadmium bis-thiolates

The synthesis of these compounds follow the same procedure (scheme 1) as reported in Antolini et al. [1, 3].



**Scheme 1:** the two steps synthesis of metal bis thiolates

The details of the synthesis are described below:

an amount of  $\text{Cd}[(\text{NO})_3]_2$  and dodecanethiol (or octanethiol, or octadecanol) were solubilized separately in absolute ethanol at a final concentration of 0.1 M and 0.2 M respectively. Two aliquots of 50 ml of both solutions were mixed and a white precipitate immediately appears. The suspension was mixed for one hour, the precipitate was centrifuged at 4000 rpm for 5 minutes and washed three times in ethanol, then the powder was dried over night at RT.

The yield of the synthesis range between the 50% - 65%. All the molecules are not solubles in the common organic solvents. The compound  $\text{Cd}[\text{S}(\text{CH}_2)_{17}\text{CH}_3]_2$ . was not fully characterised because is insoluble and shows a high decomposition temperature. In the following only the compounds with 8 or 12 carbon atoms will be taken into account as precursors.

The  $\text{Cd}[\text{S}(\text{CH}_2)_{11}\text{CH}_3]_2$ . will be named precursor 1 (PR01) and the compound  $\text{Cd}[\text{S}(\text{CH}_2)_7\text{CH}_3]_2$ . will be named precursor 2 (PR02).

## 1.2 Structural characterisation of the PR01 ( $\text{Cd}[\text{S}(\text{CH}_2)_{11}]_2$ ) and PR02 ( $\text{Cd}[\text{S}(\text{CH}_2)_7\text{CH}_3]_2$ )

The elemental analysis of the two molecules indicates that the expected compounds are successfully synthesised.

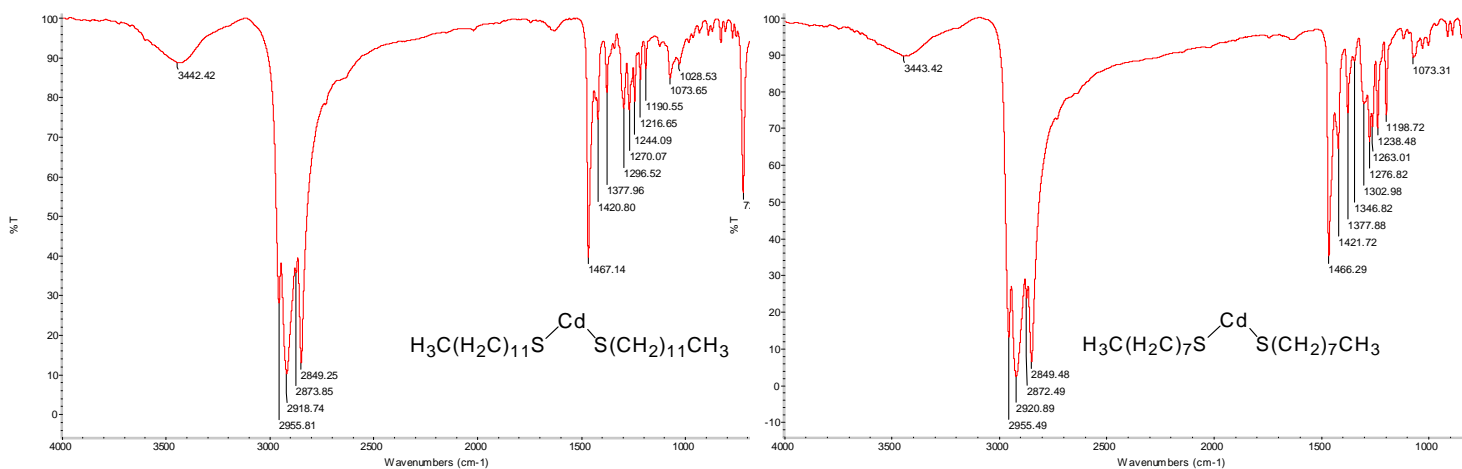
Formula PR01	Cd	C	H	S	Mw
$\text{Cd}[\text{S}(\text{CH}_2)_{11}\text{CH}_3]_2$	112,41	12	1	32	
	1	24	50	2	514,41
Teor. (%)	21,85	55,99	9,72	12,44	100
Measur. (%)	19.51	51.36	9.86	12.73	

Formula PR02	Cd	C	H	S	Mw
$\text{Cd}[\text{S}(\text{CH}_2)_7\text{CH}_3]_2$	112,41	12	1	32	
	1	16	34	2	402,41
Teor (%)	27.93	47.71	8.45	15.90	100
Measur (%)	24.92	47.95	8.76	15.98	

The molecular structure of the molecules was investigated by means of FTIR and NMR.

The FTIR spectra of the are reported in figure 2 and agree to the expected structure.



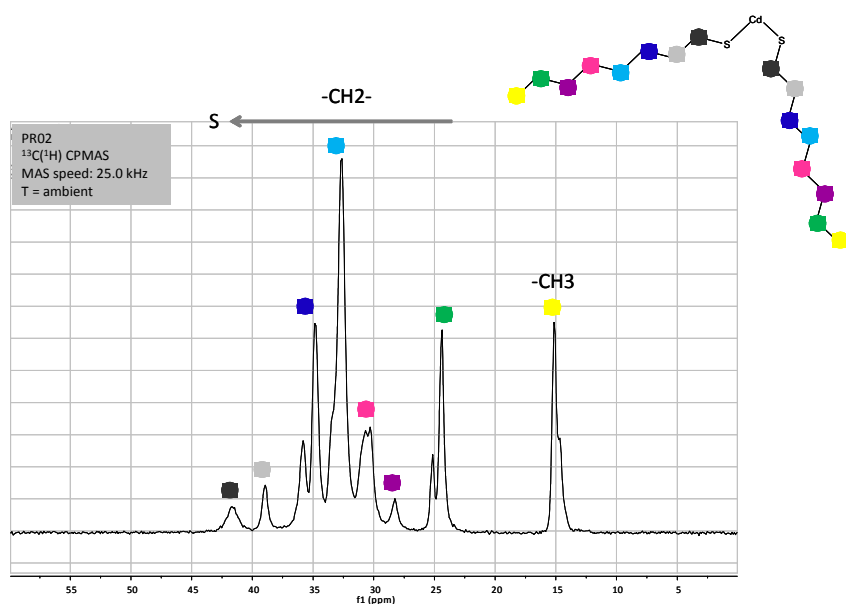
**Figure 2:** FTIR spectra of PR01 and PR02

The assignments of the FTIR spectra are reported below:

**PR01:** 2956 (antisymmetric stretching -CH<sub>3</sub>); 2919 (antisymmetric str. -CH<sub>2</sub>-); 2874 (symmetric str. -CH<sub>3</sub>); 2849 (symmetric str. -CH<sub>2</sub>-); 1467 (-CH<sub>2</sub>- deformation); 1377 (-CH<sub>3</sub> deformation); 722 (-CH<sub>2</sub>- rocking); 647 (C-H deformation).

**PR02:** 2955 (antisymmetric stretching -CH<sub>3</sub>); 2921 (antisymmetric str. -CH<sub>2</sub>-); 2872 (symmetric str. -CH<sub>3</sub>); 2849 (symmetric str. -CH<sub>2</sub>-); 1466 (-CH<sub>2</sub>- deformation); 1378 (-CH<sub>3</sub> deformation); 722 (-CH<sub>2</sub>- rocking); 647 (C-H deformation).

The two precursors are insoluble and therefore the NMR spectra are not possible with the standard NMR techniques. The synthesis of PR01 is well established and its spectrum is reported in the work [4]. The compound PR02 is new and its spectrum was carried out within the collaboration with BUW (figure 3).



The colour code of the peaks in figure 3 represents the assignment of the carbon of the molecule.

The expected resonances are 8 but the signals seem to be the double. This phenomenon could be ascribed to the presence of two different phases (crystalline and amorphous) on the powder.

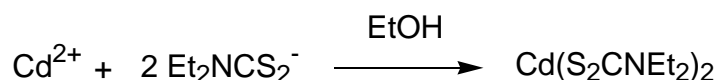
$^{13}\text{C}$  ( $^1\text{H}$ ) CPMAS solid state spectrum of PR02.

MAS speed 25 KHz, T = ambient

**Figure 3:** solid state spectrum of PR02

## 2.1 Synthesis of Cadmium diethyl-thiocarbamate (Cd(DDC)<sub>2</sub>)

The synthesis of the cadmium diethyldithiocarbamate (scheme 2) followed the same requests of the single-source precursor approach, in which the final product have to contain all the elements in an individual molecule.



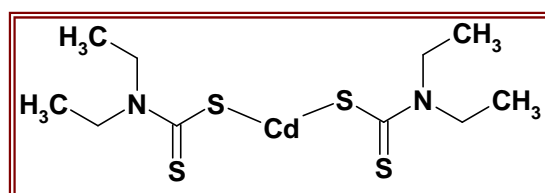
**Scheme 2:** the one step synthesis of cadmium diethyldithiocarbamate

Accordingly to the scheme 2, a cadmium diethyldithiocarbamate complex was prepared starting from a 0.1 M of Cd(NO<sub>3</sub>)<sub>2</sub> and 0.2 M of (Et)<sub>2</sub>NCS<sub>2</sub>Na solutions in ethanol. Then, two aliquots were mixed and stirred with the formation of a abundant precipitate. The white powder was washed several times with ethanol and dried in air at 60 °C.

The molecule is slightly soluble in chloroform and other organic solvents.

## 2.2 Structural characterisation of the Cadmium diethyl-dithiocarbamate (Cd(DDC)<sub>2</sub>).

The predicted structure of the cadmium diethyldithiocarbamate is presented in figure 4:

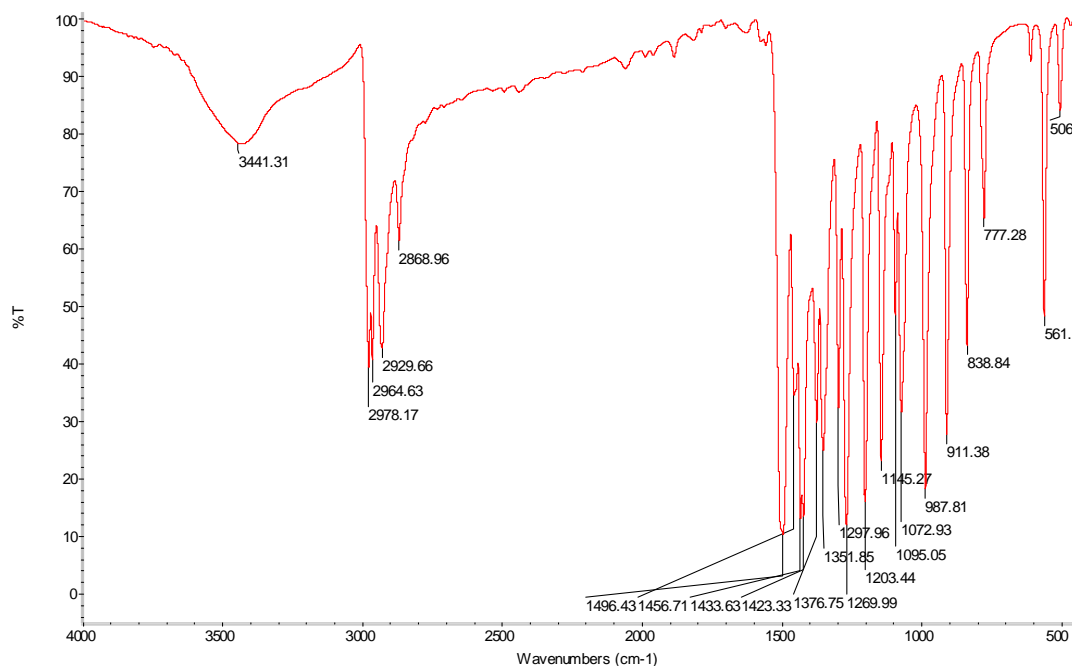


**Figure 4:** molecular structure of the Cd(DDC)<sub>2</sub>.

The elemental analysis shows that the content of the atoms is in good agreement with the expected values.

Formula PR03	Cd	C	H	S	N	Mw
Cd[S <sub>2</sub> NEt <sub>2</sub> ] <sub>2</sub>	112	12	1	32	14	
	1	10	20	4	2	408
Teor (%)	27.45	29.41	4.90	31.37	6.86	100.00
Measur (%)	22.27	28.54	4.97	30.60	7.50	

The molecular structure of the molecule was investigated by means of FTIR and NMR.



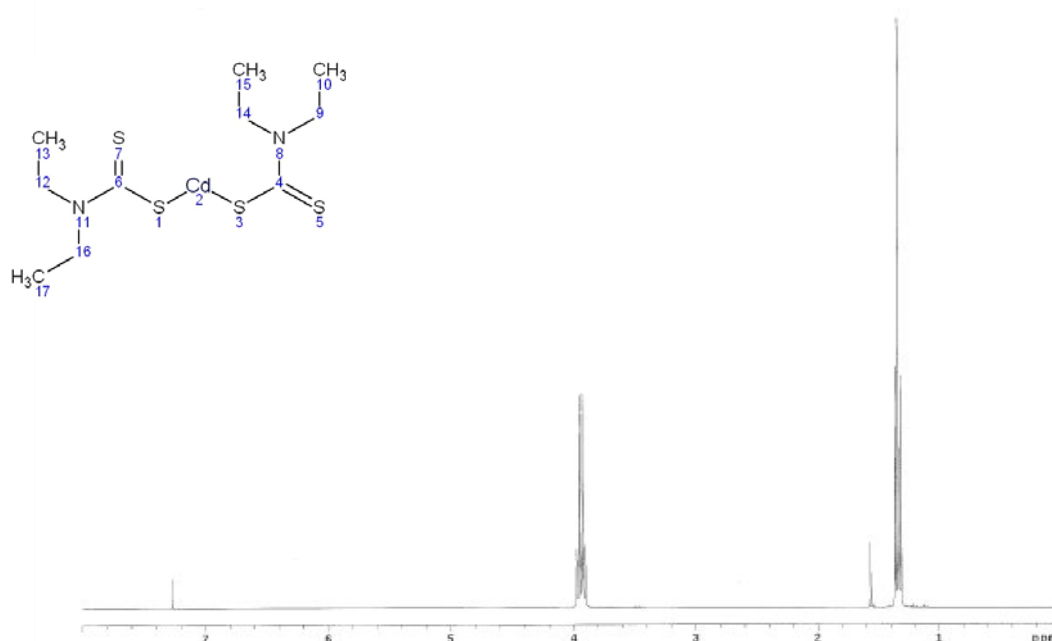
**Figure 5:** FTIR spectrum of the PR03 precursor

The FTIR peaks assignments of the PR03 (figure 5) are the following and fit with the expected product:

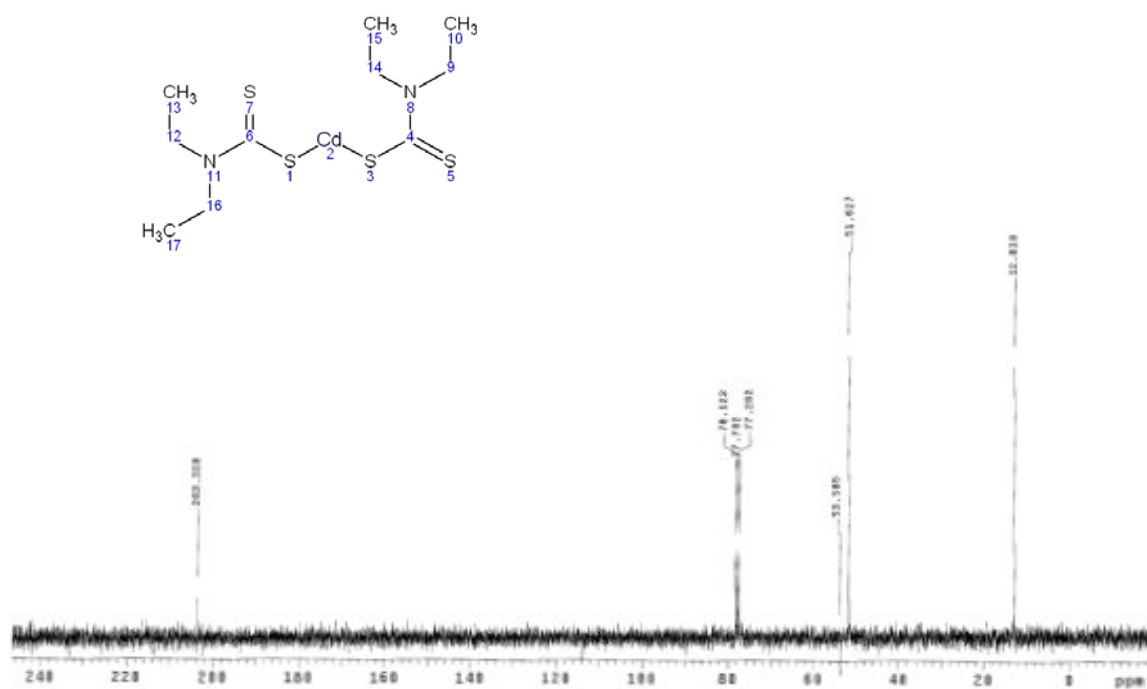
2978 (antisymmetric stretching -CH<sub>3</sub>); 2965 (antisymmetric str. -CH<sub>2</sub>-); 2930 (symmetric str. -CH<sub>3</sub>); 2869 (symmetric str. -CH<sub>2</sub>-); 1496 (-CH<sub>2</sub>- deformation); 1377 (-CH<sub>3</sub> deformation); 1269 (C-N stretching); 1203 (C=S stretching); 777 (-CH<sub>2</sub>- rocking).

The <sup>1</sup>H NMR (figure 6) and <sup>13</sup>C NMR (figure 7) spectra of the Cd(DDC)<sub>2</sub> were carried out in chloroform. The chemical shifts reported for both spectra confirm the structure of the compound:

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): 3.92 (8H, q, H<sub>16</sub>+H<sub>12</sub>+H<sub>14</sub>+H<sub>9</sub>); 1.32 (12H, t, H<sub>17</sub>+H<sub>13</sub>+H<sub>15</sub>+H<sub>10</sub>) ppm.



**Figure 6:** <sup>1</sup>H NMR spectrum of the PR03



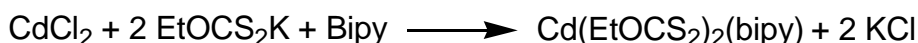
**Figure 7:** <sup>13</sup>C NMR spectrum of the PR03

The assignments of the <sup>13</sup>C-NMR (CDCl<sub>3</sub>) spectrum are the following: 203.3 (C4+C6); 51.6 (C12+C16+C9+C14); 12.8 (C13+C17+C15+C10) ppm.



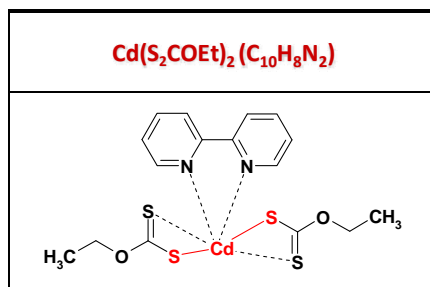
### 3.1 Synthesis of Cadmium Xanthates

The PR04 belong the Xanthate family and its formation is illustrated in the scheme below:



A cadmium diethyloxanthate complex was prepared starting from a 0.1 M of  $\text{CdCl}_2$  and 0.2 M of  $\text{EtOCS}_2\text{K}$  solution in water. The 2,2' bipyridil (Bipy) was added to the cadmium solution and was leaved to stir for one hour. Then the Xanthate solution was added after filtration with paper filter and the mixture was stirred for one hour. The precipitate was filtered, washed with water and dried in air O.N. The powder was then resuspended in 20 ml of  $\text{CH}_2\text{Cl}_2$  and the cadmium xanthahte precipitated in 80 ml of hexane. The product was centrifuged at 4000 rpm for 10 minutes and leaved to dry in air at R.T. The yield is about 40% and the final powder is soluble in the common organic solvents.

The chemical structure of the compound is reported in figure 8



**Figure 8:** chemical structure of the Cadmium ethyl Xanthate (PR04)

### 3.2 Structural characterisation of the Cadmium Xanthate

The structural characterisation of the PR04, obtained by means of FTIR and NMR spectra, indicates that the expected compound is obtained.

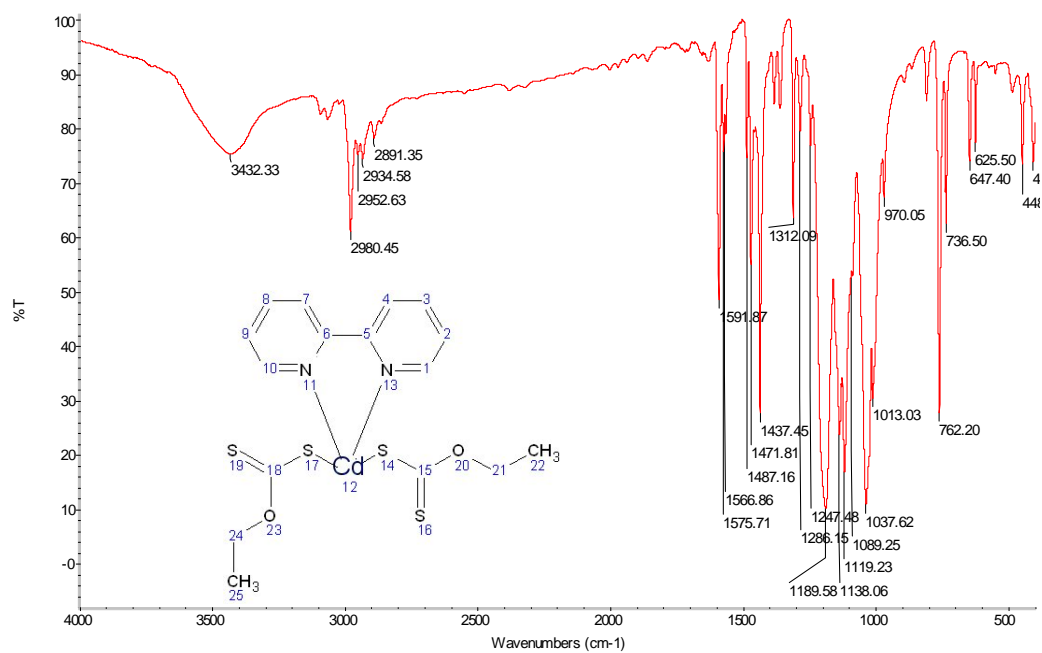
The peak assignments of the FTIR spectrum of PR04 (figure 9) are reported below:

3061 (antisymmetric str. C-H aromatic ring); 3040 (symmetric str. C-H aromatic ring); 2980 (antisymmetric stretching -CH<sub>3</sub>); 2953 (antisymmetric str. -CH<sub>2</sub>-); 2934 (symmetric str. -CH<sub>3</sub>); 2891 (symmetric str. -CH<sub>2</sub>-); 1591,1437 (aromatic ring deformation); 1487 (-CH<sub>2</sub>- deformation); 1312 (-CH<sub>3</sub> deformation); 1189 (C=S stretching); 1037 (C-O-C stretching); 762 (-CH<sub>2</sub>- rocking).

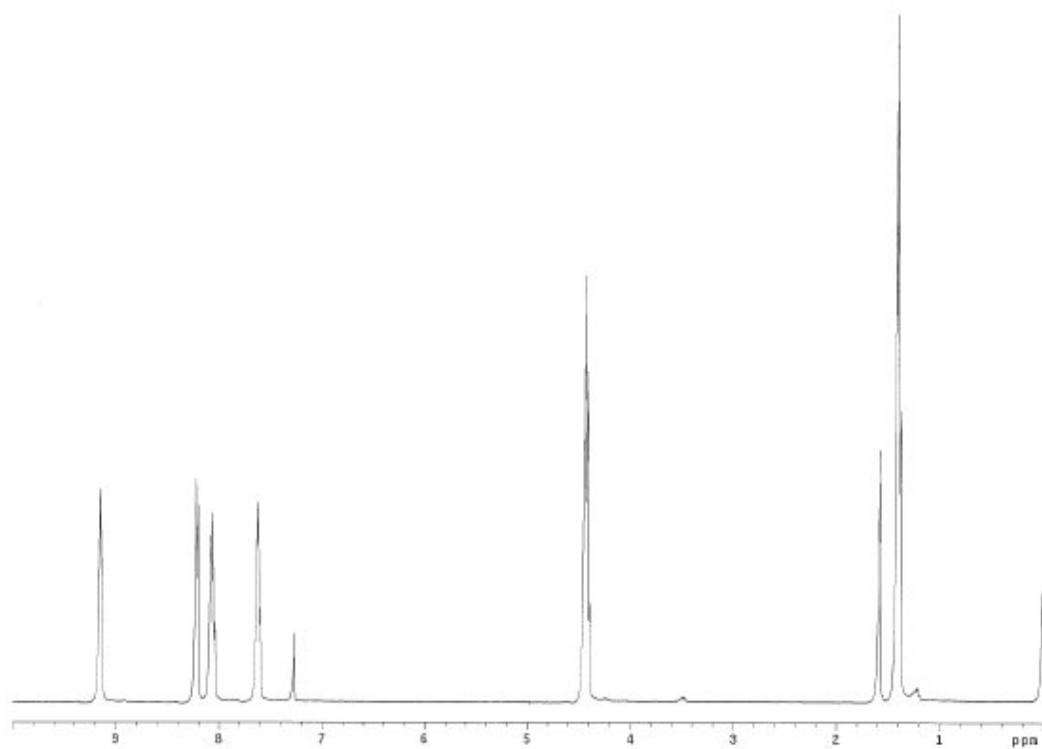
The <sup>1</sup>H NMR (figure 10) and the <sup>13</sup>C NMR (figure 11) spectra of PR04 confirm the expected chemical structure.

The <sup>1</sup>H-NMR ( $\text{CDCl}_3$ ) assignments are: 9.18 (2H, m, H1+H10); 8.20 (2H, m, H7+H4); 8.05 (2H, m, H8+H3); 7.61 (2H, m, H9+H2); 4.42 (4H, q, H24+H21); 1.39 (6H, t, H25+H22) ppm.

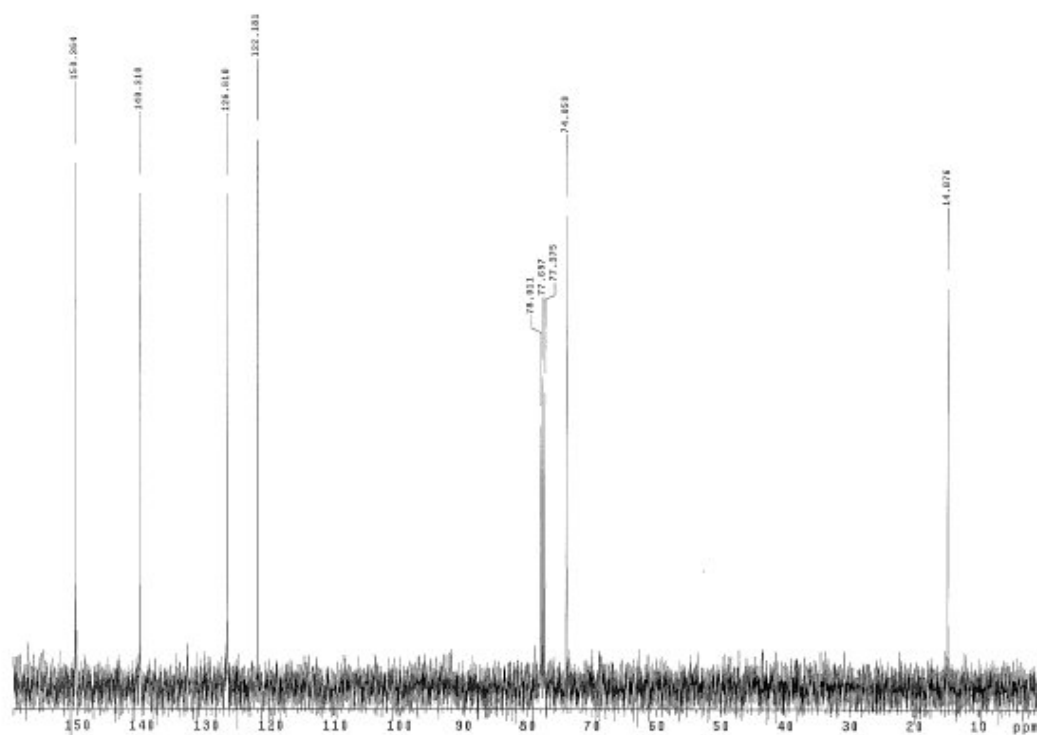
The <sup>13</sup>C-NMR ( $\text{CDCl}_3$ ) chemical shifts are the following: 150.4 (C1+C5+C6+C10); 140.3 (C3+C8); 126.8 (C2+C9); 122.2 (C4+C7); 74.1 (C24+C21); 14.9 (C25+C22) ppm.



**Figure 9:** FTIR spectrum of the PR04



**Figure 10:** <sup>1</sup>H-NMR spectrum of PR04



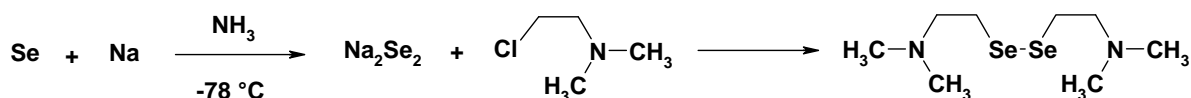
**Figure 11:**  $^{13}\text{C}$ -NMR spectrum of PR04

#### 4.1 Synthesis of cadmium selenide precursor

Within the ENEA and BUW teams the synthesis of CdSe single source precursors with aliphatic moiety was investigated. The synthetic procedure is more complex with respect to the previous ones and the synthesis was carried out in the BUW laboratories.

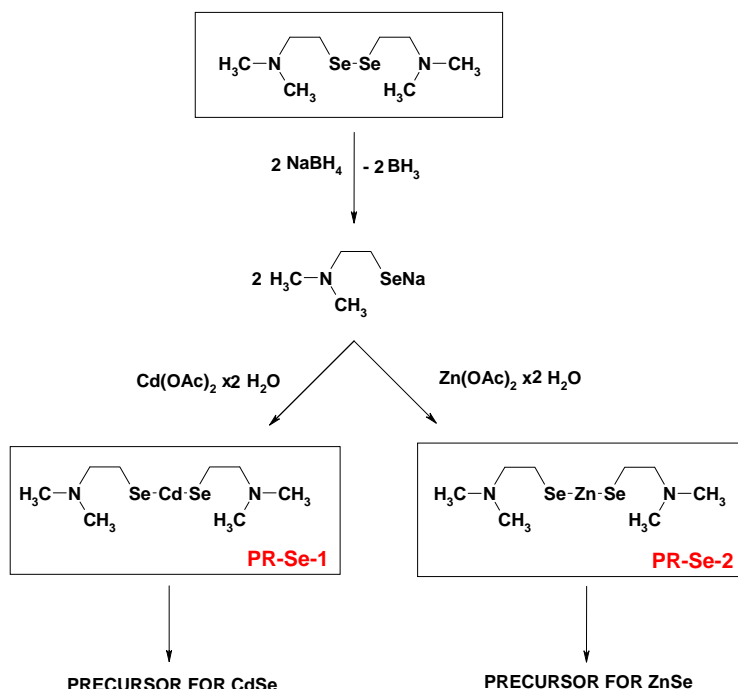
The selected procedure [5, 6] involved the formation of an aliphatic derivative of a diselenide molecules (step 1) and its reaction with a metal salt of Cd (or Zn) (step 2) forming of the selenide metallorganic precursor. The advantage of the proposed methodology is the preparation of CdSe single-source precursor binding two  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{Se}$  fragments allowing better results over the thermal decomposition process and the precursor solubility.

In the scheme 3 are reported the reactions involved in the synthesis of bis-(2-dimethylaminoethyl diselenide). The diselenide was prepared following standard methods reported in the literature.



**Scheme 3.** The reaction steps for the preparation of bis (2-dimethylaminoethyl diselenide) intermediary

The second step of the reaction is the formation of the precursor (Scheme 4). Here the diselenide intermediate in presence of reducing ambient reacts with a Cd (or Zn) atom forming the desired precursor.



**Scheme 4.** Reaction steps for the synthesis of Cd(Zn) selenolate single-source precursors

- J. Chem. Soc. Dalton Trans, 2001, 723-728, "2-(dimethylamino)ethaneselenolates of palladium II: synthesis, structure, spectroscopy and transformation into palladium selenide", S. Dey, V.K. Jain, S. Chaudhury, A. Knoedler, F. Lissner, W. Kaim;
- Polyhedron, 2006, 25, 2383-2391, 2-(N,N-dimethylamino)ethylselenolates of cadmium II: synthesis, structure of  $[\text{Cd}_3(\text{OAc})_2(\text{SeCH}_2\text{CH}_2\text{NMe}_2)_4]$  and their use as single source precursors for the preparation of the CdSe nanoparticles" G. Kedarnath, S. Dey, V.K.Jain, G.K. Dey, B. Varghese

## 4.2 Structural characterisation of the cadmium selenide precursor

The synthesis was tried once and unfortunately the final product does not correspond to the expected one, because even if the elemental analysis seems fit the expected formula, the NMR spectra (figure 12 and 13) didn't show the expected peaks.

Formula CdSe	Cd	C	H	Se	N	Mw
$\text{Cd}[\text{Se}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2]_2$	112	12	1	79	14	
	1	8	20	2	2	414
Teor (%)	27,05	23,19	4,83	38,16	6,76	100.00
Measur (%)	26,55	20,34	4,33	41,22	5,91	

In fact the proton spectrum (figure 12) should show three distinct signals: 2.28 (12H, -NCH<sub>3</sub>); 2.56 (4H, -SeCH<sub>2</sub>-); 2.74 (4H, -N-CH<sub>2</sub>-) but on the contrary it is possible to observe only two peaks at about 1 and 6 ppm. The same conclusion could be reached for the <sup>13</sup>C spectrum showing only a signal at 77 ppm (solvent) instead of three expected peaks at 15.5 (SeCH<sub>2</sub>), 45.8 (NMe<sub>2</sub>) e 62.9 (NCH<sub>2</sub>).

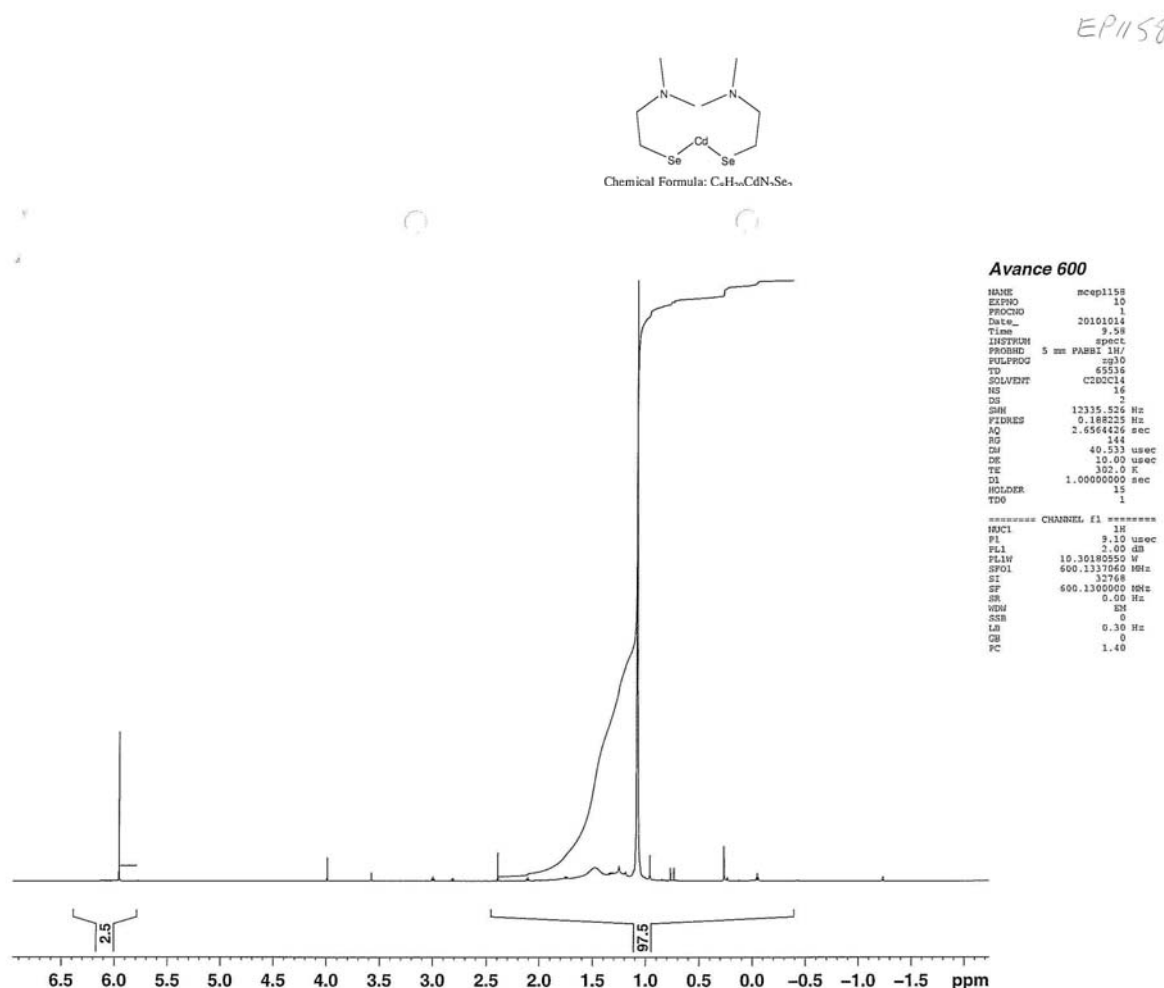
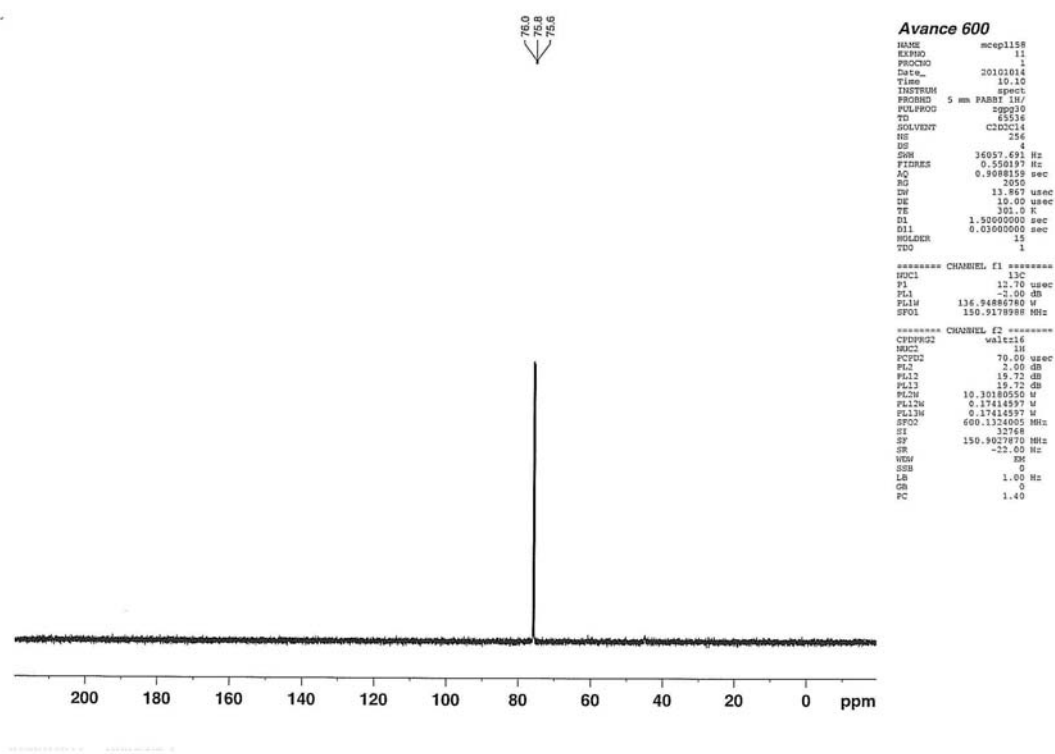


Figure 12: <sup>1</sup>H NMR spectrum of the Cd[Se(CH<sub>2</sub>)<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>



**Figure 12:**  $^{13}\text{C}$  NMR spectrum of the  $\text{Cd}[\text{Se}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2]_2$