

Large Second-Order NLO Activity in Poly(4-vinylpyridine) Grafted with Pd^{II} and Cu^{II} Chromophoric Complexes with Tridentate Bent Ligands Containing Heterocycles

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Keywords: Nonlinear optics / Polymers / Tridentate ligands / Copper / Palladium

Two *N*-salicylidene-*N'*-acylhydrazines tridentate ligands containing heterocycles were prepared and utilized for the synthesis of mononuclear acentric complexes of Cu^{II} and Pd^{II} and pyridine serves as an additional ligand (ML^xPy, M = metal, L^x = ligand). Characterization also includes single-crystal X-ray diffraction analysis. These complexes show high second-order nonlinear optical activity ($\mu\beta = 620 \times 10^{-48}$ esu for both CuL^{II}Py and PdL^{II}Py and $\mu\beta = 1600 \times 10^{-48}$ and 1400×10^{-48} esu for CuL^IPy and PdL^IPy, respectively, at incident wavelength of 1907 nm). The properties of polymers (PML^x) obtained by grafting poly(4-vinylpyridine) with fragments of the complexes are also reported.

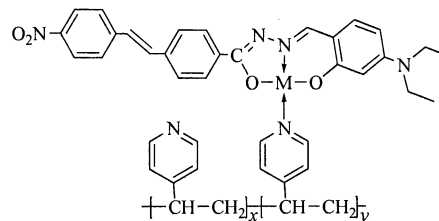
The polymers exhibit good thermal stability, high glass-transition temperatures and the absence of crystallinity. The second-order nonlinear optical (NLO) properties of thin, transparent poled films, prepared by spin coating and thermal corona poling, were investigated for some of the polymers. The value of the d_{33} parameter was measured at 1064 and 1500 nm (i.e., with and without resonance contribute). In the latter case, the d_{33} values are 21 and 12 pm/V for PCuL^{II} and PPdL^{II}, respectively. A high time stability of the NLO properties of these materials was found.

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Introduction

Nonlinear optically active polymers are widely studied for their great applicative potential in electrooptical devices with broad bandwidth and low drive voltage.^[1,2] The main problem with these materials is related to the low time stability of the dipole orientation, and several approaches are being investigated to obtain highly active materials with long-term stability of the NLO properties. As far as side-chain systems are concerned, we have recently proposed a simple way of grafting chromophoric metal complexes onto polymeric matrices by means of a coordination bond between a side-chain donor group and a transition-metal ion.^[3,4] It was observed that these polymers show some interesting properties, such as a rather high glass-transition temperature related to the free polymeric backbone, high thermal stability and good solubility. Furthermore, the possibility of reversible thermal cleavage of the polymer–metal bond may promote enhanced chromophore orientation

during the poling procedure. In particular, Cu^{II}, Pd^{II} and Ni^{II} complexes of some *N*-salicylidene-*N'*-aroylhydrazines are easily coordinated by the nitrogen atom of the pyridine group of poly(4-vinylpyridine), and they were found to give amorphous, simple-to-formulate, soluble and stable NLO polymers (Scheme 1).^[5]



Scheme 1.

In this paper, we report on the synthesis and the characterization, including single-crystal X-ray diffraction analysis and EFISH measurements of $\mu\beta$, of some Cu^{II} and Pd^{II} chromophoric complexes (ML^xPy; M = Cu, Pd; x = I, II) containing a thiophene or a furan ring in their conjugated path (Scheme 2).

Owing to the presence of heterocycles and to their bent molecular shape, it is expected that they would possess good NLO activity. In fact, as demonstrated by theoretical^[6] and experimental^[7] reports, the presence of heterocycles contributes to a general increase in NLO activity relative to a fully aromatic system and, according to Dalton

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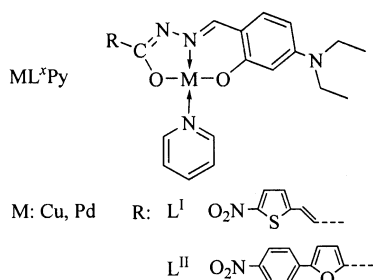
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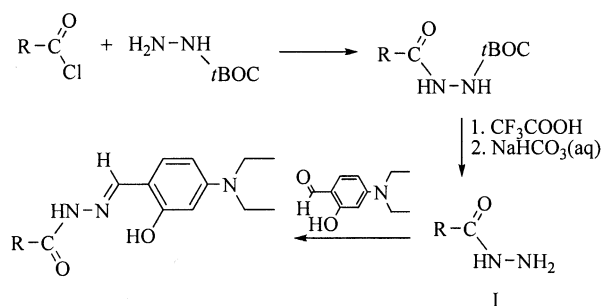
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Scheme 2.

et al.,^[1] a bent molecular shape seems to favour efficient chromophore orientation and therefore high NLO activity.

A notable problem in the synthesis of these ligands lies in the low yield of the hydrazide synthesis (Scheme 3, Compound I) reported in the literature.^[4] This problem is due to the low chemical stability of the thiophene ring in basic solutions. For this reason, the adopted ligand synthesis excludes the presence of a large excess of hydrazine, which is needed in the literature procedure, and it is performed following a procedure suggested by Gordon.^[8] In this way, the synthesis of organic ligands requires only a few simple steps (Scheme 3) and great improvements in purity and yield of the ligands are obtained, as described in the Experimental Section. The successive grafting of the complexes with commercial poly(4-vinylpyridine) is a fast and simple operation. Grafting is easily performed in one step by adding the appropriate suspension of the complex to the polymer solution and recovering the grafted polymer from the reaction mixture by precipitation. Alternatively, the former grafted polymer solution may be utilized directly for the preparation of films by means of spin-coating techniques.



Scheme 3.

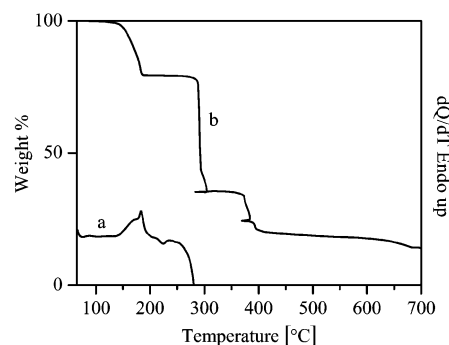
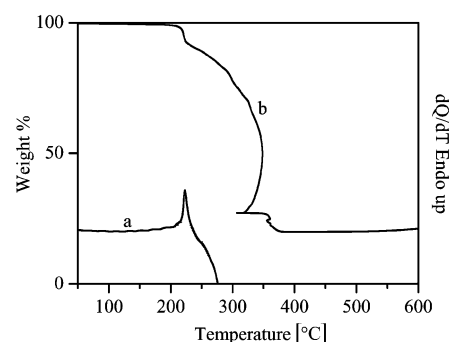
Grafted polymers (PML^x, M = Cu, Pd; x = I, II) containing 35 wt.-% of the chromophoric complexes on poly(4-vinylpyridine) were synthesized and characterized, including *d*₃₃ calculations from SHG measurements and temperature/time stability analysis.

Results and Discussion

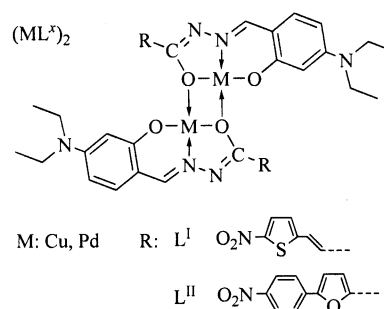
Complexes (ML^xPy; M = Cu, Pd; x = I, II)

The mononuclear complexes were prepared from the appropriate ligand following the procedure reported in the Ex-

perimental Section. Both thermogravimetric and calorimetric analysis showed the loss of pyridine molecules upon heating. For CuL^IPy (Figure 1) the thermogravimetric curve is characterized by the presence of two steps. The first one, starting at 150 °C, is related to the loss of pyridine; the second one, starting at 300 °C, is due to thermal decomposition. The PdL^IPy complex (Figure 2) shows different thermogravimetric behaviour: the curve is characterized by only one step at 230 °C. In this case, the loss of pyridine and thermal decomposition are superimposed.

Figure 1. (a) Calorimetric and (b) thermogravimetric curves for the CuL^IPy complex.Figure 2. (a) Calorimetric and (b) thermogravimetric curves for the PdL^IPy complex.

A similar behaviour is observed for analogous ML^{II}Py, and the thermogravimetric curve shows two steps for the Cu complex and only one for the Pd complex. In this case, the thermal stability is lower than that observed for ML^IPy. From the thermogravimetric data, it is possible to determine that the loss of pyridine produces the formation of dimeric species (ML^I)₂ (Scheme 4), as already described^[4] for analogous complexes.



Scheme 4.

These observations are coherent with X-ray analysis data showing that one pyridine molecule is coordinated to the metal in both $ML^I Py$ complexes, and for $CuL^I Py$, one more pyridine molecule is present as a crystallization solvent per two molecules of complex.

The molecular structures of $CuL^I Py$, $PdL^I Py$ and $PdL^{II} Py$ are sketched in Figures 3, 4 and 5, respectively, and selected bond lengths and angles are reported in Table 1.

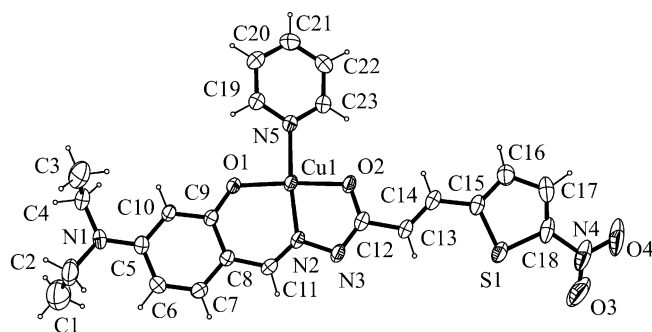


Figure 3. X-ray molecular structure of $CuL^I Py$. Thermal ellipsoids are shown at the 30% probability level. Pyridine solvent molecule is not shown.

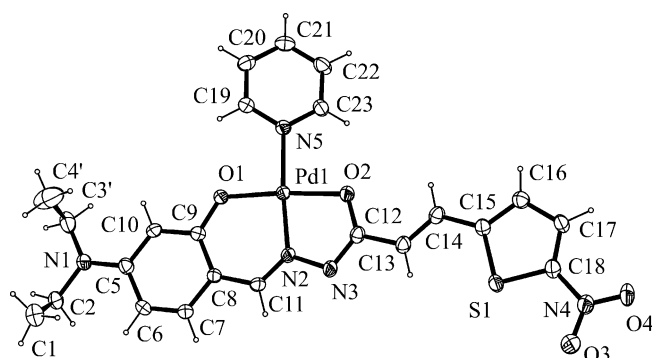


Figure 4. X-ray molecular structure of $PdL^I Py$. Thermal ellipsoids are shown at the 30% probability level. Only one statistical position for the disordered ethyl group is shown.

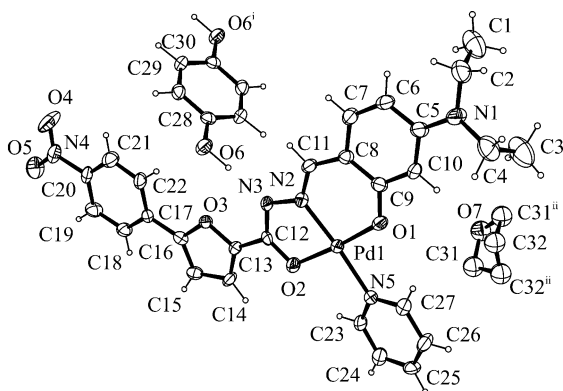


Figure 5. X-ray molecular structure of $PdL^{II} Py$. Thermal ellipsoids are shown at the 30% probability level. Only one statistical position for the disordered ethyl group is shown. Solvent molecules are shown, symmetry operations: $i = -x + 1, -y, -z + 2$; $ii = -x + 1/2, -y + 1/2, z$.

Table 1. Selected bond lengths [Å], bond angles [°] and torsion angles [°] for $CuL^I Py$, $PdL^I Py$ and $PdL^{II} Py$ with ESDs in parentheses.

$CuL^I Py$			
Cu1–O1	1.894(2)	N2–C11	1.294(4)
Cu1–O2	1.940(2)	N2–N3	1.394(3)
Cu1–N2	1.914(3)	N3–C12	1.319(4)
Cu1–N5	2.001(3)	O2–C12	1.301(4)
N1–C5	1.378(4)		
O1–Cu1–N2	93.9(1)	O2–Cu1–N5	92.5(1)
O1–Cu1–N5	92.2(1)	N2–Cu1–N5	173.7(1)
O2–Cu1–N2	81.2(1)	C15–S1–C18	90.0(2)
O1–Cu1–N5–C23	–168.1(3)	C7–C8–C11–N2	179.4(3)
C2–N1–C5–C10	–161.8(4)	C13–C14–C15–S1	–0.3(5)
C11–N2–N3–C12	–176.0(3)	S1–C18–N4–O3	178.9(4)
$PdL^I Py$			
Pd1–O1	1.980(1)	N2–C11	1.289(4)
Pd1–O2	2.006(2)	N2–N3	1.395(3)
Pd1–N2	1.933(2)	N3–C12	1.309(4)
Pd1–N5	2.056(2)	O2–C12	1.309(3)
N1–C5	1.381(4)		
O1–Pd1–N2	94.69(9)	O2–Pd1–N5	94.68(9)
O1–Pd1–N5	89.89(8)	N2–Pd1–N5	175.39(9)
O2–Pd1–N2	80.75(9)	C15–S1–C18	90.21(1)
O1–Pd1–N5–C23	–160.0(2)	C7–C8–C11–N2	–178.3(3)
C2–N1–C5–C10	–177.9(3)	C13–C14–C15–S1	2.3(4)
C11–N2–N3–C12	0.1(3)	S1–C18–N4–O3	–1.8(4)
$PdL^{II} Py$			
Pd1–O1	1.978(4)	N2–N3	1.405(6)
Pd1–O2	2.005(4)	N3–C12	1.320(7)
Pd1–N2	1.947(4)	O2–C12	1.294(6)
Pd1–N5	2.058(5)	O3–C13	1.376(6)
N1–C5	1.357(7)	O3–C16	1.375(6)
N2–C11	1.303(7)		
O1–Pd1–N2	95.4(2)	O2–Pd1–N5	94.1(2)
O1–Pd1–N5	90.1(2)	N2–Pd1–N5	174.5(2)
O2–Pd1–N2	80.5(2)	C13–O3–C16	106.0(4)
O1–Pd1–N5–C23	–168.2(4)	N3–C12–C13–O3	–0.4(8)
C2–N1–C5–C10	–178.8(6)	O3–C16–C17–C22	–2.0(9)
C11–N2–N3–C12	177.3(5)	C19–C20–N4–O5	0.5(8)
C7–C8–C11–N2	176.3(5)		

Some similar features may be observed in the three complexes. The tridentate ligand is always in the enolic form, as it is usually found in similar complexes.^[4] The coordination geometry of the metal is always square planar, and the mean plane of the coordinated pyridine molecule is slightly tilted with respect to the mean coordination plane [angles between mean planes are in the range from 12.7(3)° to 18.63(7)°]. The heteroatom of the heterocyclic group is always on the opposite side of the coordinated pyridine molecule. The amino group is always planar, which thus indicates a degree of conjugation between the N atom and the bonded phenyl ring; moreover, the overall planarity of the molecule in the three complexes suggests the possibility of extension of conjugation to the whole molecule through the metal.

The square-planar coordination geometry found around the metal in $PdL^I Py$ and $PdL^{II} Py$ is typical of Pd^{II} complexes. Cu^{II} complexes with similar *N*-salicylidene-*N'*-aroylhydrazine ligands may exhibit different geometrical environments driven by packing forces.^[4] In $CuL^I Py$, the ob-

served square-planar geometry could also be favoured by packing forces, as the almost complete planarity of the molecule allows parallel facing of the entire molecule at a strict van der Waals distance (shorter distance is $\text{Cu}\cdots\text{N3}^{\text{i}} = 3.04 \text{ \AA}$; $i = -x, -y, -z$).

The overall molecular geometries of $\text{CuL}^{\text{I}}\text{Py}$ and $\text{PdL}^{\text{I}}\text{Py}$ are very similar, and the only difference is the mutual arrangement of the ethylic groups bonded to the amminic N atom. A different and more bent molecular shape is instead observed in $\text{PdL}^{\text{II}}\text{Py}$ as a consequence of the presence of a longer nitrophenyl group attached to the furan ring (Figure 6).

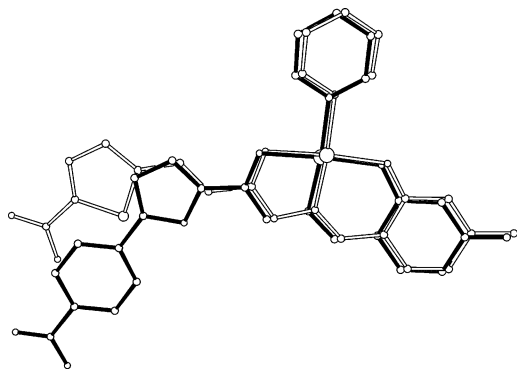


Figure 6. Superimposition of the molecular structures of $\text{PdL}^{\text{I}}\text{Py}$ (open line) and $\text{PdL}^{\text{II}}\text{Py}$ (bold line) in a view perpendicular to the coordination plane. Atoms are drawn as spheres of arbitrary radius. H atoms and ethylic groups are not shown.

Complexes containing L^{II} are not easily crystallizable, and this is probably because of their strongly bent shape. Voids may be formed during the crystallization process, so the presence of a suitable crystallization solvent seems to be a necessary condition to form a stable crystalline phase. In particular, single crystals of $\text{PdL}^{\text{II}}\text{Py}$ suitable for X-ray analysis were only obtained from THF containing hydroquinone as a stabilizing agent, and resolution of the structure revealed the presence of both substances as crystallization solvents (Figure 5). The THF molecule is statistically disordered on the binary axis along the c axis, the hydroquinone molecule sits on an inversion centre and is hydrogen bonded to the imminic N atom of an adjacent molecule [$\text{O6}\cdots\text{N3} \ 2.011(7) \text{ \AA}$, 173.57°].

UV/Vis spectra of mononuclear complexes show two optical transitions (see Experimental Section) localized at 330–380 and 450–510 nm. Similar compounds reported in the literature^[9] show analogous optical behaviour, and the higher-energy transition was assigned to an intraligand π – π^* charge transfer and the second one to a charge transfer involving the metal as a bridge between the strong donor and acceptor groups.

Second-order NLO activity of mononuclear complexes was measured by the electric field-induced second-harmonic (EFISH) technique in chloroform solution. The $\mu\beta$ coefficient of $\text{CuL}^{\text{I}}\text{Py}$ is higher ($1600 \times 10^{-48} \text{ esu}$) than that of $\text{PdL}^{\text{I}}\text{Py}$ ($1400 \times 10^{-48} \text{ esu}$) and both fall into line with the expected values for this class of chromophores. The role played by the heterocycle in determining the molecular non-

linear properties can be inferred by comparison of these values with those of similar chromophores previously reported,^[4] where the thiophene ring is replaced by a full aromatic system. This contribution is relevant for the copper complex ($1100 \times 10^{-48} \text{ esu}$), whereas no enhancement is observed for the palladium complex whose coefficient remains nearly constant within the experimental error ($1500 \times 10^{-48} \text{ esu}$). $\text{CuL}^{\text{II}}\text{Py}$ and $\text{PdL}^{\text{II}}\text{Py}$ show lower $\mu\beta$ coefficients (both $620 \times 10^{-48} \text{ esu}$), probably due to the shorter central sequence of consecutive double bonds (two instead of three) with respect to the L^{I} complexes.

Polymers

Polymers (PML^x , $x = \text{I,II}$) are obtained by grafting (ML^x)₂ onto commercial poly(4-vinylpyridine) (Aldrich, $M_w = 60000$). The dimeric species is split in solution and a single complex fragment is anchored onto the pyridine groups of the polymer backbone, as previously observed.^[4] According to this observation, the composition of 35 wt.-% of the chromophore appears to be a good balance between chromophore content and solubility of the final polymer. The main thermodynamic and spectroscopic data are reported in Table 2 together with the metal content.

Table 2. Some relevant data for polymers.

	T_g [a][°C]	T_d [b][°C]	η_{inh} [c][dL/g]	λ_{max} [d][nm]	%calcd. [e]	%exp. [f]
PCuL ^I	188	220	0.18	516	6.19	6.15
PCuL ^{II}	192	290	0.22	462	5.75	5.73
PPdL ^{II}	199	340	0.23	454	7.07	7.11

[a] Glass-transition temperature. [b] Decomposition temperature (measured at 5% weight loss). [c] Inherent viscosity. [d] UV absorption maximum. [e] Calculated metal content as Pd or CuO. [f] Experimental metal content as Pd or CuO.

The DSC and TGA curves of both PCuL^{II} and PPdL^{II} polymers show the expected thermal stability with decomposition temperatures near 290 and 340 °C, respectively. For PCuL^I, polymer decomposition starts at 220 °C, which is 30 °C higher than T_g . This behaviour is not in agreement with that observed for analogous polymers previously reported,^[4] whose decomposition temperatures lie beyond 300 °C. The thermogravimetric analysis of complex $\text{CuL}^{\text{I}}\text{Py}$ (Figure 1) shows a plateau between 400 and 600 °C, which corresponds to CuS residue. Sulfide formation is confirmed by subsequent treatment at higher temperatures in air, which produces a residue corresponding to CuO. The lower stability observed for the $\text{CuL}^{\text{I}}\text{Py}$ complex when grafted onto a polymeric backbone may be related to the formation of the stable compound CuS, which induces breaking of the thiophene ring and the beginning of decomposition.

Preparation of Poled Films and SHG Measurements

NLO characterization was carried out by measuring the d_{33} component of nonlinear second-order optical susceptibility $\chi^{(2)}$ on poled thick films deposited by spin-coating on soda–lime glass slides. In order to prepare the poled

films, appropriate amounts of polymers (about 50 mg/mL) were dissolved in 1,1,2,2-tetrachloroethane, and the solutions were filtered through 0.2- μm Teflon filters. A spin coater SCS P6700 was utilized for the formation of the polymer film, and the instrument was operated at a rate of 1000 rpm for 60 seconds at room temperature, whereas the solution was deposited at about 120 °C. Residual solvent was removed by keeping the films at 120 °C under vacuum. The film thickness was measured with an Alphastep 200 profilometer. The poling treatment was performed under an argon atmosphere by use of a vertical golden wire as a corona electrode. The wire tip was at a distance of 1 cm from the film surface. The samples were both heated to the poling temperature (205 °C for PPdL^{II} and 190 °C for PCuL^{II}) under applied voltage of 10 and 9 kV for PPdL^{II} and PCuL^{II}, respectively, and held for 30 min and then cooled down to room temperature at about 3 °C/min. Finally, the electric field was removed (Figure 7).

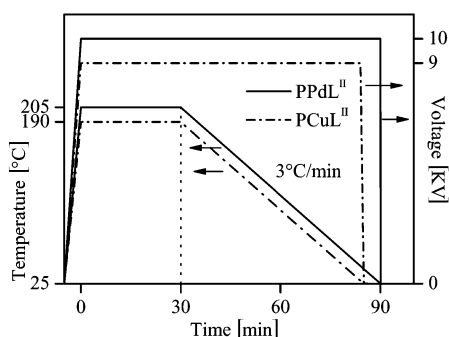


Figure 7. Best poling conditions for polymers PCuL^{II} and PPdL^{II}.

The Maker fringes technique allows the NLO coefficients to be determined by measuring the second harmonic signal generated by the sample as a function of the angle of incidence. Absolute values of the d_{33} coefficient of an isotropic nonlinear film can be determined once the experimental setup is calibrated by performing measurements on a sample whose second-order nonlinear optical susceptibility is known. Here we employed a 1-mm thick X-cut quartz plate for calibration. The Maker fringes pattern of X-cut quartz is shown in Figure 8, where the full line corresponds to the best-fit curve obtained by using the expression for the transmitted SH power.^[10]

The nonlinear second-order optical susceptibility (d_{33} component) of the polymer film is determined at wavelength $\lambda = 1064$ nm and $\lambda = 1500$ nm by comparing the results of the numerical fit obtained for investigated samples and the reference quartz plate, once their thickness and refractive index at the fundamental and at the SH wavelength are given and once the Kleinmann symmetry condition ($d_{15} = d_{31}$) is assumed for the polymeric poled film. Figure 8 shows also the Maker fringes pattern of transmitted SH signal for PCuL^{II} poled film measured at 1500 nm. The closed circles and the full-line curve represent the experimental data and the best-fit curve, respectively. The high NLO activity of these materials is shown from the d_{33} determinations; values of 167 pm/V for PCuL^{II} and

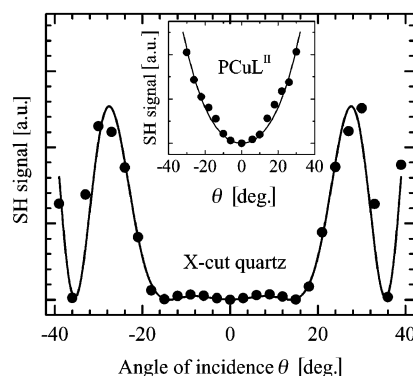


Figure 8. Maker fringes pattern of transmitted SH signal for the reference X-cut quartz plate and (inset) PCuL^{II} poled film. The closed circles and the full-line curves represent the experimental data and the best-fit curve, respectively.

93 pm/V for PPdL^{II} were measured for the d_{33} coefficient at 1064 nm, whereas values of 21 pm/V for PCuL^{II} and 12 pm/V for PPdL^{II} were measured at 1500 nm. The highest NLO activity observed for PCuL^{II} is unexpected if compared with the intrinsic activity of the chromophores (620×10^{-48} esu for both). This behaviour could be related to the high mobility of the chromophoric fragments grafted onto the polymer that favoured a higher polar order obtained in the poling process. Both the high degree of empty spaces due to the bent shape of the molecule and the visco-elastic phase of the polymer system above T_g favour this high mobility. This difference in polar order is quite evident also by UV/Vis analysis, where the order parameter for PCuL^{II} (0.23) results sensibly higher with respect to PPdL^{II} (0.17). One more facet to point out is the one order of magnitude difference between the d_{33} values at 1064 and 1500 nm. This behaviour could be reasonably ascribed to the resonance contribution that affects the measurement at 1064 nm due to absorption at the second harmonic (532 nm) in the visible spectrum (Figure 9).^[11,12]

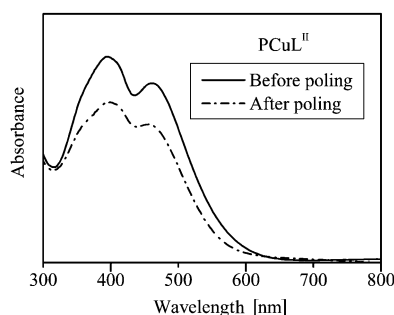


Figure 9. UV/Vis spectra for the PCuL^{II} polymer.

Finally, in Figure 10 the trend of nonlinear response in time at a temperature of 80 °C is shown.

It can be seen that, after an initial loss of 30% in the beginning 300 h, the NLO activity remains constant for a period as long as 750 h. This very large time stability is a very important feature in view of a possible use of the reported polymers for applications.

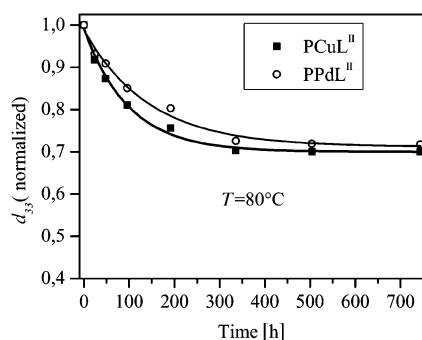


Figure 10. Time stability of NLO activity at 80 °C for the PCuL^{II} and PPdL^{II} polymers.

Conclusions

An easy and inexpensive synthetic path was successfully applied in the preparation of new Cu^{II} and Pd^{II} chromophoric complexes containing heterocycles, and the NLO properties of the grafted polymers were investigated. The molecular structures of the complexes with pyridine exhibit similar geometric features. All the ligands are in the enolic form and then act as tridentate ligands; the metal coordination geometry is square-planar; the heteroatom of the heterocyclic group is always in the opposite side of the coordinated pyridine; the whole molecular geometry is planar with a more bent shape when the L^{II} substituent is present in the complexes. All synthesized polymers show good solubility, thermal stability and a suitable glass-transition temperature. The better thermal stability was found for grafted polymers containing an L^{II} substituent. The high NLO activity of these materials is shown by the d_{33} determinations; values of 21 pm/V for PCuL^{II} and 12 pm/V for PPdL^{II} were calculated for d_{33} coefficients in nonresonant conditions (1500 nm). The d_{33} values were also calculated in resonant conditions (1064 nm) and were recorded as 167 and 93 pm/V for PCuL^{II} and PPdL^{II}, respectively. To the best of our knowledge this is one of the few examples in which the d_{33} values in both resonant and nonresonant conditions are compared. Finally, measurements of SHG decay at 80 °C evidence a good stability of the polar order with time. Owing to their excellent properties, the ease and versatility of their synthetic path, the possibility to modulate T_g and their solubility as a function of complex content, these materials are good candidates to be employed in the production of electrooptic devices as wave guides or Mach-Zehnder modulators.

Experimental Section

The differential scanning calorimetry (DSC) technique was employed for the characterization of the phase behaviour, transition temperature and enthalpies. For the DSC analysis, an indium-calibrated Perkin–Elmer Pyris apparatus was utilized. Samples were examined under a dry nitrogen atmosphere with a temperature-scanning rate of 10 °C/min. The phase-transition temperatures were measured at the maximum of the transition endotherm for polymers, whereas for low molecular weight compounds the onset val-

ues are reported. Thermogravimetric measurements were performed by utilizing a Mettler TG50 apparatus. Optical observations were performed with a Zeiss Axioscop polarizing microscope equipped with an FP90 Mettler hot stage. Intrinsic viscosities of polymer solutions with a concentration of 0.500 g/L in *N,N*-dimethylformamide (DMF) were measured at 25.0 °C by utilizing an Ubbelohde viscosimeter. ¹H NMR spectra were recorded with a Varian XL 200 or 300 MHz instrument. UV/Vis absorption spectra were recorded with a Jasco V560 spectrophotometer; sample solutions were examined in the 190–900 nm range at a scanning rate of 120 nm/min.

(*E*)-3-(5-Nitrothiophen-2-yl)acryloyl Hydrazide: (*E*)-3-(5-Nitrothiophen-2-yl)acrylic acid was prepared as described by Taniguchi and Kato.^[13] The hydrazide was synthesized by following the procedure described by Gordon et al.^[14] (*E*)-3-(5-nitrothiophen-2-yl)acrylic acid (2.00 g, 10.0 mmol) was heated at reflux in SOCl₂ to obtain the corresponding chloride. This was dissolved in dry THF (20 mL) and slowly dropped into a solution of *tert*-butyl carbazate (2.65 g, 20.0 mmol) in dry THF (20 mL) whilst stirring. After 1 h, the solvent was distilled to isolate a yellow solid corresponding to a mixture of *t*BOC-protected (*E*)-3-(5-nitrothiophen-2-yl)acryloyl hydrazide and exceeding *tert*-butyl carbazate. To this mixture was added trifluoroacetic acid (20 mL) at room temperature, and the solution was stirred for 2 h. The acid was removed in vacuo, and the residue was triturated with 10% aqueous sodium hydrogen carbonate to obtain a yellow solid that was isolated by vacuum filtration and washed with water. Crystallization (acetone/heptane) yielded the pure product (1.16 g, 54.3%). M.p. 202 °C (dec.). ¹H NMR (200 MHz, [D₆]DMSO, 25 °C): δ = 4.56 (s, 2 H, NH₂), 6.56 (d, J = 15.6 Hz, 1 H, CH=), 7.46 (d, J = 4.3 Hz, 1 H, CH th.), 7.59 (d, J = 15.6 Hz, 1 H, CH=), 8.08 (d, J = 4.3 Hz, 1 H, CH th.), 9.52 (s, 1 H, NH) ppm.

Ligand L^I: (*E*)-3-(5-Nitrothiophen-2-yl)acryloyl hydrazide (3.00 g, 14.1 mmol) and 4-(*N,N*-diethylamino)-2-hydroxybenzaldehyde (2.85 g, 14.8 mmol) were dissolved in boiling DMF (50 mL). After 10 min, the solution was poured into water (300 mL) containing concentrated sulfuric acid (8 mL). The dark-red solid obtained was isolated by vacuum filtration and recrystallized from boiling DMF (80 mL). Yield: 3.52 g (64.4%). M.p. 216 °C. ¹H NMR (200 MHz, [D₆]DMSO, 25 °C): δ = 1.02 (t, J = 6.9 Hz, 6 H, CH₃), 3.29 (q, J = 6.9 Hz, 4 H, CH₂), 6.02 (s, 1 H, CH ar.), 6.19 (d, J = 9.0 Hz, 1 H, CH ar.), 6.60 (d, J = 15.6 Hz, 1 H, CH=), 7.15 (d, J = 9.0 Hz, 1 H, CH ar.), 7.47 (d, J = 4.3 Hz, 1 H, CH th.), 7.67 (d, J = 15.6 Hz, 1 H, CH=), 8.04 (d, J = 4.3 Hz, 1 H, CH th.), 8.14 (s, 1 H, CH=N), 11.10 (s, 1 H, NH), 11.66 (s, 1 H, OH) ppm. C₁₈H₂₀N₄O₄S (388.12): calcd. C 55.66, H 5.19, N 14.42; found C 55.48, H 5.20, N 14.38.

(CuL^I)₂: Water (40 mL) containing copper(II) acetate monohydrate (0.467 g, 2.57 mmol) was poured into a stirred boiling solution of L₁ (1.00 g, 2.57 mmol) in DMF (100 mL). A dark solid precipitated that was filtered after cooling and washed repeatedly with water. Yield: 97%. C₃₆H₃₆Cu₂N₈O₈S₂ (898.07): calcd. C 48.05, H 4.03, N 12.45; found C 48.11, H 4.07, N 12.41.

CuL^IPy: L^I (1.00 g, 2.57 mmol) was dissolved in pyridine (20 mL) whilst stirring. Copper(II) acetate monohydrate (0.467 g, 2.57 mmol) was added to the boiling L^I solution. Then, water (20 mL) was slowly poured into the solution, and after few minutes the mixture was left to cool to room temperature. The dark crystalline solid obtained was isolated by vacuum filtration and washed with water. Yield: 86%. UV/Vis: λ (ε, dm³/mol cm): 380 (2.5 × 10⁴), 510 (2.5 × 10⁴) nm. C₂₃H₂₃CuN₅O₄S·1/2C₅H₅N (567.60): calcd. C

53.86, H 4.52, N 13.55, S 5.64; found C 53.80, H 4.52, N 13.50, S 5.66.

(PdL)₂: A solution of L^I (1.00 g, 2.57 mmol) and Pd^{II} bisbenzonitrile dichloride (0.987 g, 2.57 mmol) in DMF (20 mL) was heated to 80–100 °C. After 5 min, water (60 mL) containing sodium acetate (2.00 g) was poured in order to precipitate a dark solid that was filtered and washed with water. Yield: 96%. C₃₆H₃₆N₈O₈Pd₂S₂ (984.02): calcd. C 43.87, H 3.68, N 11.37; found C 43.86, H 3.68, N 11.35.

PdL^IPy: L^I (1.00 g, 2.57 mmol) and Pd^{II} bisbenzonitrile dichloride (0.987 g, 2.57 mmol) were dissolved in pyridine (35 mL). The solution was kept boiling and water (30 mL) was added. After cooling to room temperature dark crystals of the PdL^IPy complex were obtained, filtered and washed with water. Yield: 84%. ¹H NMR (200 MHz, [D]CHCl₃, 25 °C): δ = 1.21 (t, *J* = 6.8 Hz, 6 H, CH₃), 3.39 (q, *J* = 6.8 Hz, 4 H, CH₂), 6.24 (dd, *J*₁ = 8.8 Hz, *J*₂ = 2.4 Hz, 1 H, CH ar.), 6.35 (d, *J* = 2.4 Hz, 1 H, CH ar.), 6.88 (d, *J* = 15.6 Hz, 1 H, CH=), 7.05 (d, *J* = 4.4 Hz, 1 H, CH th.), 7.19 (d, *J* = 8.8 Hz, 1 H, CH ar.), 7.45 (d, *J* = 15.6 Hz, 1 H, CH=), 7.53 (t, *J* = 6.8 Hz, 2 H, Py), 7.65 (s, 1 H, CH=N), 7.80 (d, *J* = 4.4 Hz, 1 H, CH th.), 7.93 (t, *J* = 7.6 Hz, 1 H, Py), 8.93 (d, *J* = 5.4 Hz, 2 H, Py) ppm. UV/Vis: λ (ε, dm³/molcm): 330 (2.6 × 10⁴), 494 (2.4 × 10⁴) nm. C₂₃H₂₃N₅O₄PdS (571.05): calcd. C 48.30, H 4.05, N 12.24, S 5.61; found C 48.38, H 4.05, N 12.20, S 5.63.

5-(4-Nitrophenyl)furan-2-carboxylic Acid: The acid was synthesized according to Holla et al.^[15] 4-Nitroaniline (1.38 g, 10.0 mmol) were suspended in water (125 mL) containing HCl (37 wt.-%, 25 mL) at 0–5 °C. NaNO₂ (0.720 g, 10.4 mmol) in water (25 mL) was slowly added whilst stirring. After 15 min, water (50 mL) containing 2-furoic acid (1.12 g, 10.0 mmol) was poured into the solution. Ammonium cerium(IV) nitrate (4.00 g) dissolved in water (10 mL) was added dropwise, and the solution was stirred for 2 h at room temperature. By cooling the solution an orange solid precipitated. This was purified by dissolving in excess KOH solution, filtering and precipitating at low pH. Finally the yellow solid was recrystallized from acetone/heptane. Yield: 70%. M.p. 256 °C. ¹H NMR (200 MHz, [D₆]DMSO, 25 °C): δ = 7.35 (d, *J* = 4.0 Hz, 1 H, CH fur.), 7.43 (d, *J* = 4.0 Hz, 1 H, CH fur.), 8.03 (d, *J* = 8.8 Hz, 2 H, CH ar.), 8.30 (d, *J* = 8.8 Hz, 2 H, CH ar.) ppm.

5-(4-Nitrophenyl)furan-2-carbohydrazide: The hydrazide was synthesized as described above for *trans*-3-(5-nitro-2-thienyl)acryloyl hydrazide. This gave a yellow solid that was recrystallized from acetone/heptane. Yield: 85%. ¹H NMR (200 MHz, [D₆]DMSO, 25 °C): δ = 7.32 (d, *J* = 2.4 Hz, 1 H, CH fur.), 7.39 (d, *J* = 2.4 Hz, 1 H, CH fur.), 8.13 (d, *J* = 8.8 Hz, 2 H, CH ar.), 8.31 (d, *J* = 8.8 Hz, 2 H, CH ar.), 9.90 (s, 1 H, NH) ppm.

Ligand L^{II}: Ligand L^{II} was synthesized as described above for ligand L^I. An orange solid was obtained by recrystallization from DMF. Yield: 75%. M.p. 222 °C. ¹H NMR (200 MHz, [D₆]DMSO, 25 °C): δ = 0.97 (t, *J* = 6.9 Hz, 6 H, CH₃), 3.21 (q, *J* = 6.9 Hz, 4 H, CH₂), 5.99 (d, *J* = 2.1 Hz, 1 H, CH ar.), 6.17 (dd, *J*₁ = 9.0 Hz, *J*₂ = 2.1 Hz, 1 H, CH ar.), 7.11 (d, *J* = 9.0 Hz, 1 H, CH ar.), 7.26 (d, *J* = 3.6 Hz, 1 H, CH fur.), 7.36 (d, *J* = 3.6 Hz, 1 H, CH fur.), 8.06 (d, *J* = 8.7 Hz, 2 H, CH ar.), 8.21 (d, *J* = 8.7 Hz, 2 H, CH ar.), 8.37 (s, 1 H, CH=N), 11.06 (s, 1 H, NH), 11.75 (s, 1 H, OH) ppm. C₂₂H₂₂N₄O₅·H₂O (440.17): calcd. C 59.99, H 5.49, N 12.72; found C 60.09, H 5.48, N 12.75.

(CuL^{II})₂: L^{II} (1.00 g, 2.37 mmol) was dissolved in boiling DMF (40 mL). Copper(II) acetate monohydrate (0.520 g, 2.60 mmol) was added and after 10 min the complex was precipitated by adding water (5 mL). The brown solid was filtered and washed with water.

Yield: 98%. C₄₄H₄₀Cu₂N₈O₁₀ (966.15): calcd. C 54.60, H 4.17, N 11.58; found C 54.65, H 4.17, N 11.54.

CuL^{II}Py: The (CuL^{II})₂ complex (1.00 g) was dissolved in boiling pyridine (15 mL). After 5 min, water (10 mL) was slowly added to precipitate a brown, crystalline solid. Yield: 97%. UV/Vis: λ (ε, dm³/molcm): 400 (2.4 × 10⁴), 456 (2.6 × 10⁴) nm. C₂₇H₂₅CuN₅O₅·2H₂O (598.14): calcd. C 54.13, H 4.88, N 11.69; found C 54.02, H 4.90, N 11.71.

(PdL^{II})₂: L^{II} (1.00 g, 2.37 mmol) was dissolved in boiling THF (30 mL). Pd^{II} bisbenzonitrile dichloride (0.920 g, 2.40 mmol) in THF (10 mL) and sodium acetate (1.00 g) in water (20 mL) were added. The pH was raised to 9 and a dark-red solid precipitated, which was then filtered and washed with water and ethyl acetate. Yield: 97%. C₄₄H₄₀N₈O₁₀Pd₂ (1052.09): calcd. C 50.15, H 3.83, N 10.63; found C 50.15, H 3.83, N 11.64.

PdL^{II}Py: The (PdL^{II})₂ complex (1.00 g) was dissolved in boiling pyridine (15 mL). After 5 min, water (10 mL) was slowly added to precipitate an orange, crystalline solid. Yield: 95%. ¹H NMR (200 MHz, [D]CHCl₃, 25 °C): δ = 1.21 (t, *J* = 10.2 Hz, 6 H, CH₃), 3.40 (q, *J* = 10.2 Hz, 4 H, CH₂), 6.24 (dd, *J*₁ = 14.1 Hz, *J*₂ = 3.6 Hz, 1 H, CH ar.), 6.37 (d, *J* = 3.6 Hz, 1 H, CH ar.), 6.93 (d, *J* = 5.1 Hz, 1 H, CH fur.), 7.12 (d, *J* = 5.1 Hz, 1 H, CH fur.), 7.22 (d, *J* = 14.1 Hz, 1 H, CH ar.), 7.54 (t, *J* = 10.2 Hz, 2 H, Py), 7.79 (s, 1 H, CH=N), 7.90 (d, *J* = 13.2 Hz, 2 H, CH ar.), 7.92 (t, *J* = 11.0 Hz, 1 H, Py), 8.24 (d, *J* = 13.2 Hz, 2 H, CH ar.), 8.95 (d, *J* = 8.1 Hz, 2 H, Py) ppm. UV/Vis: λ (ε, dm³/molcm): 352 (2.4 × 10⁴), 450 (3.3 × 10⁴) nm. C₂₇H₂₅N₅O₅Pd·2H₂O (641.11): calcd. C 50.51, H 4.55, N 10.91; found C 50.60, H 4.54, N 10.91.

Polymers (PML^x): All polymers were synthesized by dissolving poly(4-vinylpyridine) (0.650 g) and the (ML^x)₂ complex (0.350 g) in boiling DMF and precipitating in water (100 mL). The product was washed repeatedly with water. Yield: 98%.

The synthesis of PPdL^I gave an insoluble and crosslinked-like product probably due to further polymerization of the ethylene bridges contained in the chromophore structure so that no characterization was possible for this polymer.

SHG Measurements: Measurements of nonlinear coefficient *d*₃₃ were performed by means of the Maker fringes technique.^[16] The laser beam at fundamental frequency was provided by an optical parametric oscillator (OPO), whose wavelength can be tuned in the near-infrared range (800–1600 nm). The OPO was pumped by a Q-switched Nd:YAG laser having 10 ns pulse duration and 10 Hz repetition rate. The laser beam impinged on a variable attenuator made by a half-wave retardation plate and a polarizing beam splitter cube, which allowed continuous variation of optical power impinging on the sample. The fundamental beam reflected by the polarizing beam splitter cube impinged on a potassium dideuteriophosphate (KDP) crystal, whose second harmonic signal, detected by a photodiode, was employed as a reference signal in order to take into account the power fluctuations of the fundamental laser beam. A double Fresnel rhomb selected the proper polarization direction for the fundamental beam impinging on the sample, which was placed on a goniometric stage to allow variation of the angle of incidence. A coloured filter absorbed the unwanted signal at fundamental wavelength transmitted through the sample, whereas the second harmonic signal was detected by a high sensitivity amplified photodiode. Both the electric signals coming from photodiodes are acquired by a computer interfaced Tektronix TDS540 500 MHz bandwidth digitizing oscilloscope.

X-ray Analysis: Single crystals of CuL^IPy, PdL^IPy and PdL^{II}Py suitable for X-ray analysis were obtained at room temperature by

Table 3. Crystal data and structure refinement details.^[a]

	CuL ^I Py	PdL ^I Py	PdL ^{II} Py
Chemical formula	2(C ₂₃ H ₂₃ N ₅ O ₄ SCu)·C ₅ H ₅ N	C ₂₃ H ₂₃ N ₅ O ₄ SPd	8(C ₂₇ H ₂₅ N ₅ O ₅ Pd)·4(C ₆ H ₆ O ₂)·C ₄ H ₈ O
Formula weight	1137.27	571.92	5360.06
Temperature [K]	293	293	173
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Pccn</i>
<i>a</i> [Å]	9.051(2)	11.665(2)	19.577(2)
<i>b</i> [Å]	18.837(4)	12.098(2)	35.358(4)
<i>c</i> [Å]	16.5670(4)	19.179(4)	8.43(1)
α [°]	90.	90.	90.
β [°]	109.89(2)	118.50(1)	90.
γ [°]	90.	90.	90.
<i>V</i> [Å ³]	2656.1(9)	2378.6(8)	5835(7)
<i>Z</i> , <i>D</i> _{calcd.} [g/cm ³]	2, 1.422	4, 1.597	1, 1.525
μ [1/mm]	0.943	0.908	0.689
θ range [°]	3.08, 27.50	3.25, 27.51	3.06, 25.00
Reflections collected/unique	25944/5985 (<i>R</i> _{int} = 0.0507)	15073/5397 (<i>R</i> _{int} = 0.0428)	19158/5067 (<i>R</i> _{int} = 0.0924)
Parameters, restraints	336, 0	327, 6	384, 1
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ (<i>I</i>)] ^[b]	0.0436, 0.1013	0.0332, 0.0733	0.0601, 0.1486
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0989, 0.1299	0.0598, 0.0833	0.1005, 0.1647
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ [e/Å ³]	0.640, −0.383	0.393, −0.623	1.363, −1.242

[a] Common wavelength (Mo-*K*_α) = 0.71073 Å. [b] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

slow evaporation of a pyridine solution for CuL^IPy and PdL^IPy and of a THF solution for PdL^{II}Py. Data were collected with a Bruker-Nonius KappaCCD diffractometer (Mo-*K*_α radiation, thick slices, ϕ scans plus ω scans to fill the asymmetric unit) at room temperature for CuL^IPy and PdL^IPy and at 173 K in flowing N₂ for PdL^{II}Py. Semiempirical absorption corrections (multiscan SADABS) were applied. All structures were solved by using the direct methods (SIR97) program^[17] and anisotropically refined by the full-matrix least-squares method on *F*² against all independent measured reflections (SHELXL-97 program of SHELX-97 package^[18]). H atoms in all structures were placed in calculated positions with *U*_{eq} equal to those of carrier atom and refined by the riding method. In the asymmetric unit of CuL^IPy the pyridine molecule present as crystallization solvent is located on an inversion centre so that it is statistically disordered on two sites with occupancy factor 0.5. In PdL^IPy, one of the ethylic groups is disordered on two different positions with refined occupancy factors 0.55 and 0.45. In the crystals of PdL^{II}Py, both THF and hydroquinone solvent molecules are found. The molecule of THF is located on a binary axis along *c* with statistical positional disorder, the molecule of hydroquinone is located on an inversion centre. Some crystal, collection and refinement data are reported in Table 3.

CCDC-644411, -644412 and -644413 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

Research supported by Fondo per gli Investimenti della Ricerca di Base (FIRB) 2001 grant from Ministero dell'Università e della Ricerca (MIUR, n. RBNEOI P4JF). Thanks are also due to Centro Interdipartimentale di Metodologie Chimico Fisiche (CIMCF) of University "Federico II" of Naples for NMR spectroscopic and X-ray facilities.

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Received: October 30, 2007

Published Online: February 28, 2008