# Second Order Optical Nonlinearities of Copper(II) and Palladium(II) Complexes with *N*-Salicylidene-*N*′-aroylhydrazine Tridentate Ligands

Fabio Borbone,[a] Ugo Caruso,[a] Roberto Centore,*[a] Antonella De Maria,[a] Alain Fort,[b] Michela Fusco,[a] Barbara Panunzi,[c] Antonio Roviello,*[a] and Angela Tuzi[a]

*Dedicated to Prof. A. Sirigu on the occasion of his 65th birthday*

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

Three new *N*-salicylidene-*N*′-aroylhydrazines tridentate ligands have been prepared: *N*-4-diethylaminosalicylidene-*N*′-(4-nitrocinnamoylhydrazine (L$^1$), *N*-4-diethylaminosalicylidene-*N*′-4-(2,4-dinitrophenylethylidene)benzoylhydrazine (L$^2$), *N*-4-diethylaminosalicylidene-*N*′-4-(6-nitro-2-benzoxazolyl)benzoylhydrazine (L$^3$). From these ligands, mononuclear acentric complexes of Copper(II) and Palladium(II), with pyridine as further ligand, have been prepared and characterized, also by single-crystal X-ray analysis. These complexes show high second order nonlinear optical activity (EFISH, $|\mu\beta|$ up to $3000 \cdot 10^{-48}$ esu, incident wavelength 1.907 μm). The properties of metallorganic polymers obtained by grafting commercial poly(4-vinylpyridine) with ML$^1$ fragment (M = Cu$^{II}$ or Pd$^{II}$) are also reported.

## Introduction

The design of dipolar metallorganic chromophores with second order optical nonlinearities has been carried out till now according to two chemical architectures: organometallic fragments as electron donor-acceptor groups at the end of a π conjugated system[1] or metals as constituents of the conjugation bridge between the donor and acceptor groups.[1c,2]

A nonlinear optically (NLO) active polymer material is obtained from the chromophore following two approaches widely used in the case of purely organic compounds:[3] noncovalent incorporation of active molecules (guest) in an organic polymeric matrix (host) or covalent incorporation of chromophores into a polymer chain or in a three dimensional network. In both cases a noncentrosymmetric polar alignment of the NLO active fragments ("poling") must be achieved (generally by applying a strong electric field while the polymer is kept above its glass transition temperature) which is a necessary condition for bulk second order NLO activity. Drawbacks of the first approach are in the low time stability of the noncentrosymmetric polar order and in the low solubility of the chromophore in the polymer matrix (the latter effect is probably enhanced in the case of metallorganic NLO-phores); in the second approach, on the other hand, the chemical synthesis of the organometallic chromophore must include steps for its functionalization as monomer for polymerization reactions (e.g. as diol or methacrylate ester).

We have recently proposed a new approach to metal-coordinated second order NLO active polymer materials, based on the use of tridentate ligands of the *N*-salicylidene-*N*′-aroylhydrazine type.[4] The use of such ligands, properly functionalized with strong electron donor-acceptor groups, is based on two factors (see Scheme 1). First, upon coordination, the ligand changes from the cheto (amide) to the enolic form with extension of π conjugation along the whole structure; second, the formed complex is electrically neutral but the metal (Cu$^{II}$, Pd$^{II}$) is coordinatively unsaturated.

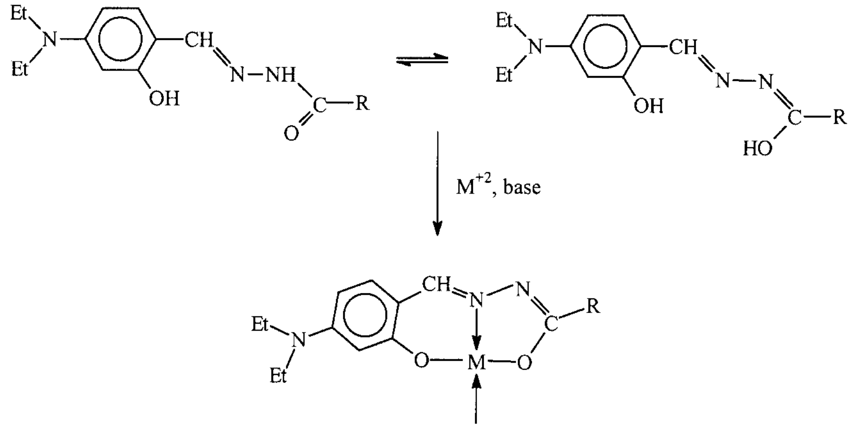
In the absence of other ligands the coordination sphere of the metal is completed by centrosymmetric coupling and dimers are formed (see Scheme 2); however, if other ligands are present, acentric monomeric complexes may be formed, as witnessed by the strong tendency of dimers to form monomeric adducts by reaction with neutral molecules containing N donor atoms (e.g. pyridine, imidazole, etc.).[4,5]

This feature is of relevant interest inasmuch as it allows the anchorage of NLO active metallorganic fragments to a suitable preformed polymer chain [e.g. poly(4-vinylpyri-

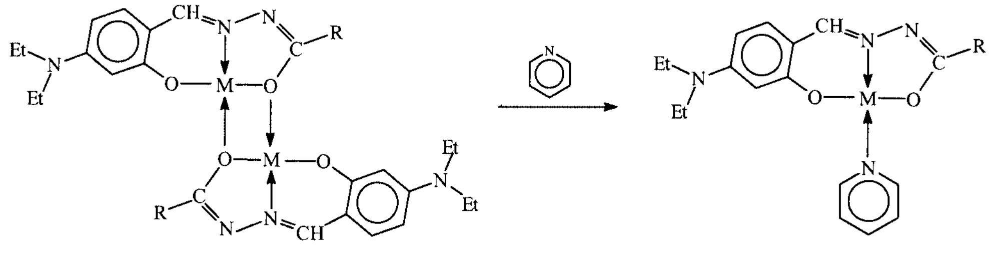
---

[a] Dipartimento di Chimica, Università di Napoli "Federico II",
Via Cinthia, 80126 Napoli, Italy
E-mail: centore@chemistry.unina.it
roviello@chemistry.unina.it
[b] IPCMS-CNRS, Groupe d'Optique Nonlinéaire et d'Optoelélectronique,
23 Rue du Loess, 67037 Strasbourg Cedex, France
[c] Dipartimento di Scienza degli Alimenti, Università degli Studi di Napoli "Federico II",
Via Università 100, 80055 Napoli, Italy

DOI: 10.1002/ejic.200300735



Scheme 1



Scheme 2

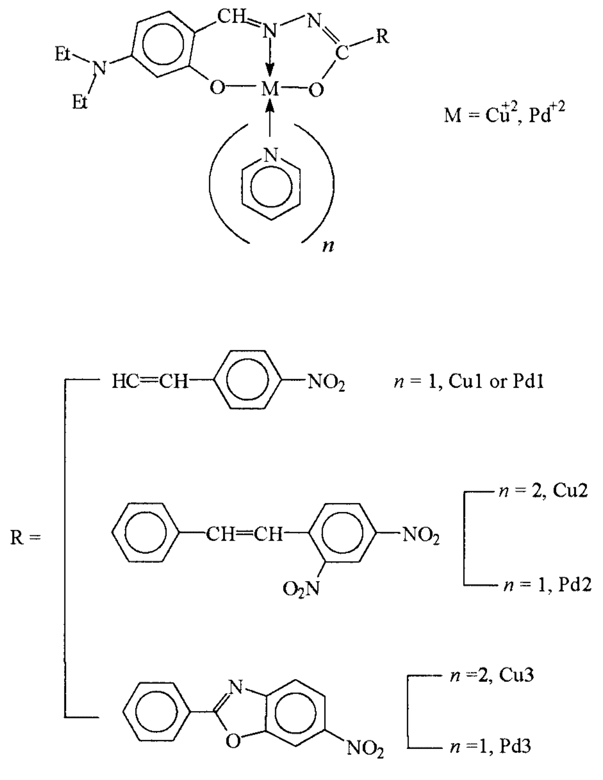
dine)] through a coordination bond.[4b] The advantages of this approach are evident. Among others, we stress that the chemical synthesis of the chromophore and of the polymer can be worked out in a substantially independent way, no functionalization of the organic ligand is required and commercially available polymers can be used.

In this paper we report the synthesis and characterization of new monomeric complexes of this type exhibiting high NLO activity, whose formulae are shown in Scheme 3.

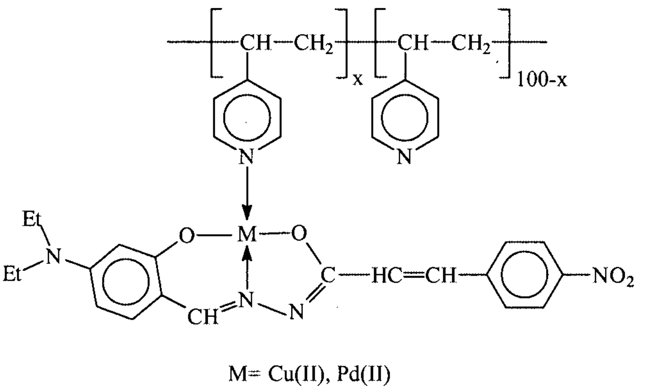
In addition we will also demonstrate the anchorage of one NLO active metallorganic fragment to commercial poly(4-vinylpyridine), according to Scheme 4, so that our complexes can be considered as rare examples of highly NLO active metallorganic chromophores from which polymers are successfully obtained. A full account of the properties of various commercial polymers grafted with all the above reported organometallic fragments will be given in a forthcoming publication from our laboratory.

## Results and Discussion

Drawings of the crystallographic independent units of Cu1, Cu2, Pd2, and Cu3 are reported in Figures 1, 2, 3, and 4; selected bond lengths, bond angles, and torsion angles are reported in Table 1.



Scheme 3



Scheme 4

In all the reported structures the tridentate ligand is in the enolic form. In fact, bond lengths C12−O2 [ranging from 1.286(5) to 1.306(5) Å] and C12−N3 [ranging from 1.298(7) to 1.320(5) Å] are respectively longer and shorter as compared with the values expected for an amide group.[6] On the other hand, IR spectra of free ligands in the solid state clearly show bands typical of the amide group. The structural change of the ligands upon coordination is also confirmed by the UV/Vis absorption patterns. In fact, as it is shown for $L^1$ in Figure 5, a significant red-shift of $\lambda_{max}$ is observed upon coordination, with the $\lambda_{max}$ of the coordinated ligand being substantially unchanged in the dimer, monomer, and grafted polymer.

The conformation of the ligands is close to be planar in all cases. In the complexes containing the ligand $L^2$ the nitro group in *para* position to the vinylene group is substantially coplanar with the phenyl, while the *ortho* nitro group is significantly twisted by torsion around the bond C26−N5 (Table 1). This is probably due to the close intramolecular contact between O6 and H atom bonded to C20 (the distance O6···C20 is 2.83 Å in Cu2 and 2.86 Å in Pd2). This contact could be relaxed also by torsion around the

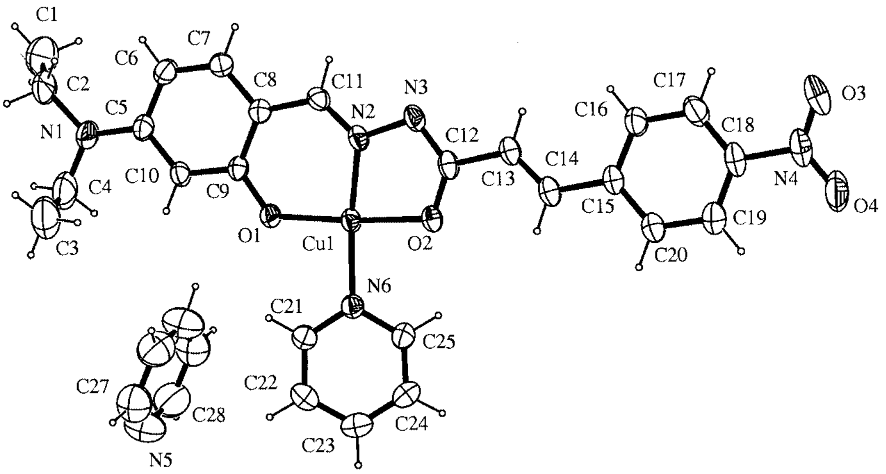


Figure 1. ORTEP view of Cu1; thermal ellipsoids are at 30% probability level; only one position of the non-coordinated pyridine molecule is shown

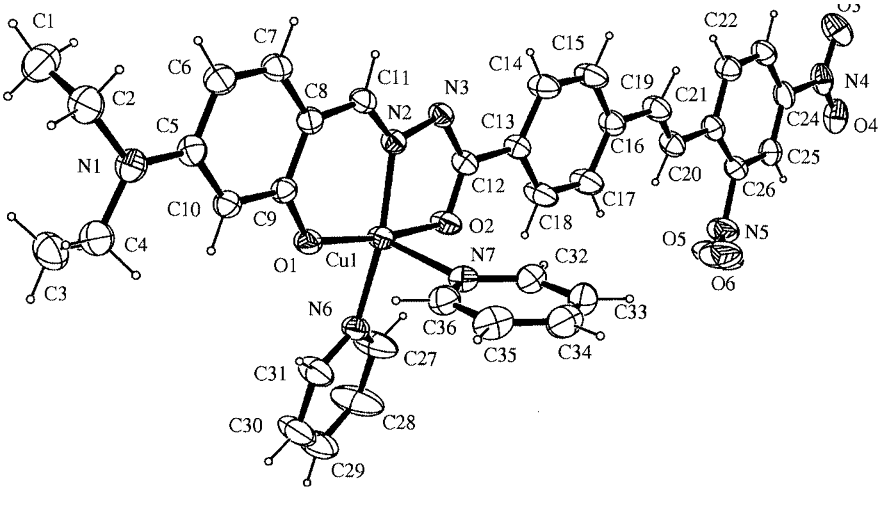


Figure 2. ORTEP view of Cu2; thermal ellipsoids are at 30% probability level

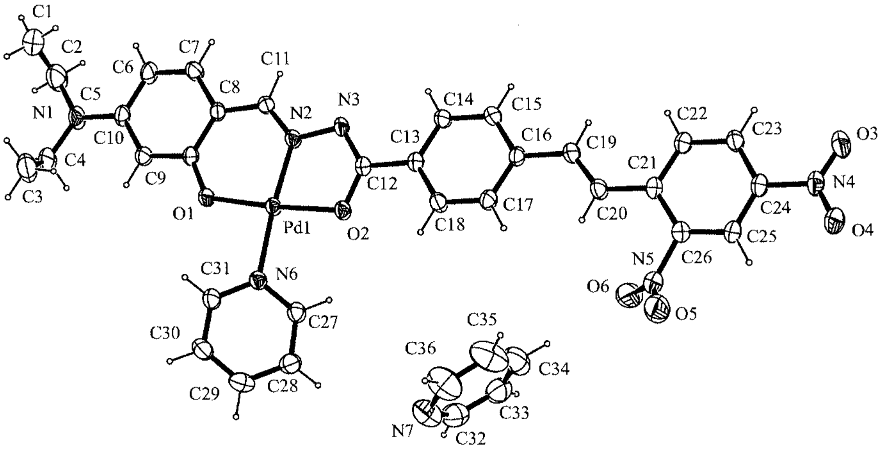


Figure 3. ORTEP view of Pd2; thermal ellipsoids are at 30% probability level

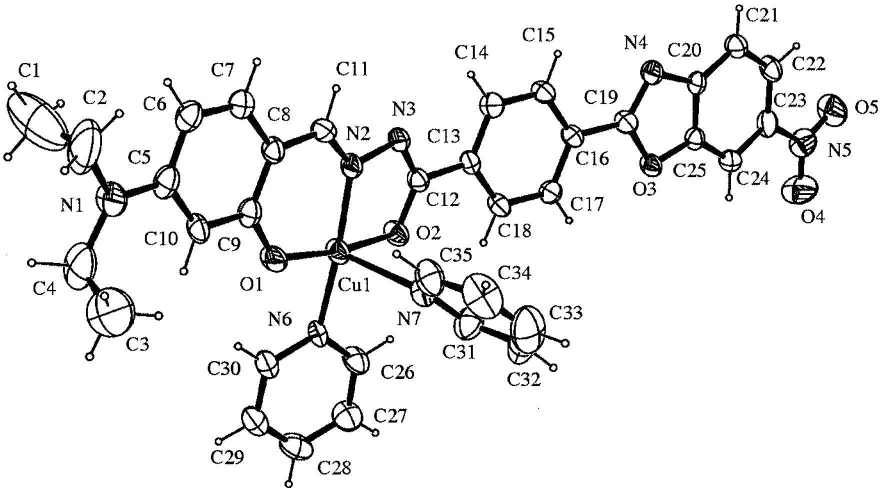


Figure 4. ORTEP view of Cu3; thermal ellipsoids are at 30% probability level

bond C20−C21, i.e. at cost of planarity of the ligand. The fact that this possibility is not adopted (it occurs instead in *trans*-stilbene which is twisted in the gas phase essentially for a similar reason[7]) seems to indicate a higher torsional potential around the bond C20−C21, probably resulting from charge transfer (CT) contributions to the ground state.

A coordination variability has been observed in the complexes of $Cu^{II}$. In fact, Cu1 is tetracoordinate (square planar) while Cu2 and Cu3 are pentacoordinate (square pyramidal with the metal atom lying substantially in the basal plane) and an additional pyridine molecule is bonded to the metal. For $Pd^{II}$, on the other hand, we have observed square-planar coordination with the same ligand giving a pentacoordinate copper complex; furthermore, the additional pyridine molecule present in the independent unit of crystals of Pd2 is not coordinated to the metal (Figure 3). This difference between $Cu^{II}$ and $Pd^{II}$ complexes is consistent with our previous results[4a] and is an evidence of the general tendency of $Pd^{II}$ to give preferentially 16-electron complexes.

In the complexes reported here and in the similar complexes already reported by us[4a] the tendency of $Cu^{II}$ to the pentacoordination appears to be favored by longer ligands. Since pentacoordination implies deviations from a flat molecular shape, may be that packing forces have a role in driving this behavior.

Both in tetracoordinate and in pentacoordinate complexes the ligand pyridine molecule in the basal plane is not coplanar with this plane but torsions around the M−N6 bond are observed (up to ca. 20°).

In the pentacoordinate complexes Cu2 and Cu3 the two ligand pyridine molecules are bonded to the metal with different strength, as it may be inferred by the corresponding bond lengths (Table 1). The more weakly bonded pyridine (i.e. the one-coordinated in apical position) is more easily lost as it is shown for example in the thermogravimetric analysis of Figure 6, while the second pyridine is lost at a much higher temperature.

This behavior is fairly reproducible so that loss of the apical pyridine is accomplished in all complexes in a tem-

Table 1. Selected bond lengths (Å), bond angles (°), and torsion angles (°) for Cu1, Cu2, Pd2, Cu3

| | Cu1 | Cu2 | Pd2 | Cu3 |
|---|---|---|---|---|
| M−O1 | 1.906(7) | 1.908(2) | 1.966(3) | 1.912(4) |
| M−O2 | 1.946(8) | 1.953(2) | 1.994(3) | 1.954(4) |
| M−N2 | 1.910(4) | 1.931(2) | 1.927(4) | 1.910(5) |
| M−N6 | 1.992(4) | 2.035(2) | 2.051(4) | 2.014(5) |
| M−N7 | | 2.299(2) | | 2.409(6) |
| O2−C12 | 1.286(5) | 1.289(3) | 1.306(5) | 1.295(6) |
| N1−C5 | 1.370(7) | 1.379(3) | 1.376(5) | 1.379(8) |
| N2−C11 | 1.286(5) | 1.281(3) | 1.290(5) | 1.280(7) |
| N2−N3 | 1.395(7) | 1.396(2) | 1.406(5) | 1.402(6) |
| N3−C12 | 1.320(5) | 1.306(3) | 1.299(5) | 1.298(7) |
| O1−M−N2 | 93.8(2) | 93.63(8) | 95.3(1) | 93.0(2) |
| N2−M−O2 | 81.3(2) | 80.28(8) | 80.4(1) | 80.7(2) |
| O1−M−N6 | 92.4(2) | 91.72(8) | 89.5(1) | 92.2(2) |
| O2−M−N6 | 92.6(2) | 92.40(8) | 94.9(1) | 93.2(2) |
| N2−M−N6 | 173.8(1) | 161.84(8) | 175.2(1) | 168.0(2) |
| N2−M−N7 | | 100.64(8) | | 96.7(2) |
| N6−M−N7 | | 96.39(9) | | 93.6(2) |
| C11−N2−N3−C12 | 175.9(3) | 179.6(2) | −180.0(4) | −177.4(5) |
| C7−C8−C11−N2 | 179.7(4) | −178.2(2) | −179.6(4) | −175.9(6) |
| N3−C12−C13−C18 | | −179.2(3) | 172.7(4) | 167.1(5) |
| O6−N5−C26−C21 | | −37.7(4) | 48.0(7) | |
| C17−C16−C19−N4 | | | | −178.5(6) |
| C15−C16−C19−C20 | | −169.7(3) | −179.5(5) | |
| C19−C20−C21−C26 | | 167.3(3) | −175.1(5) | |
| O1−M−N6−C25 | 168.9(3) | | | |
| O1−M−N6−C26 | | | | −164.4(5) |
| O1−M−N6−C27 | | 161.1(3) | 159.7(3) | |

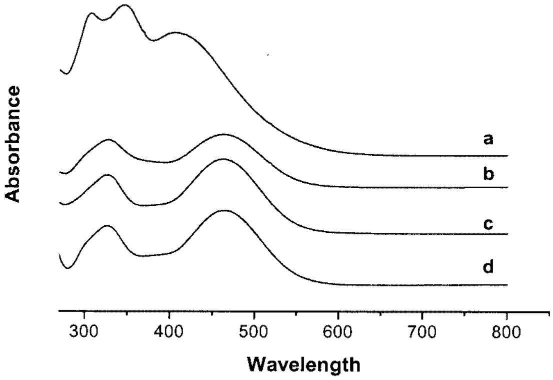


Figure 5. UV/Vis absorption spectra for: $L^1$ (curve a), $(PdL^1)_2$ (curve b), Pd1 (curve c), Pd35 (curve d)

perature interval ranging from 115 °C to 130 °C, while the basal pyridine is lost between 180 °C and 200 °C. The only relevant exception is given by Pd3 in which the pyridine ligand is lost around 276 °C (we have not succeeded in growing suitable single crystals of Pd3). In all cases, losing of all pyridine ligands restores $(ML^N)_2$ dimers as it is suggested by the decomposition temperatures which are identical.

Starting from commercial poly(4-vinylpyridine) we have prepared grafted polymers with a $(ML^1)_2$ content (by weight) of 35% and 60% both for Cu$^{II}$ and Pd$^{II}$. The resulting polymers have good solubility in NMP, tetrachloroethane and DMF. Some thermal and analytical data of the polymers are reported in Table 2. In Figure 7 are reported the DSC thermograms.

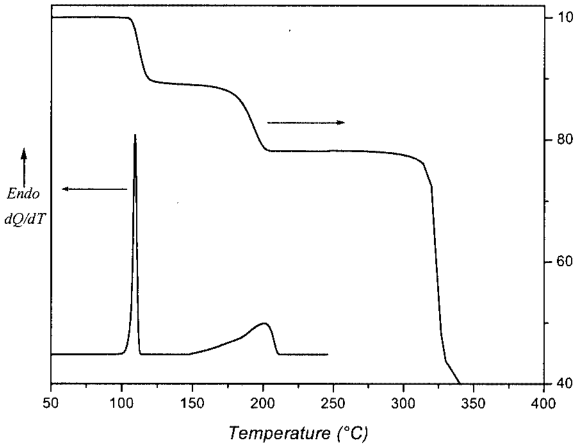


Figure 6. TGA/DTA curves of Cu2

Table 2. Relevant analytical data of grafted polymers MW

| W = % $(ML^1)_2$ grafted (by weight) | Cu | | | Pd | | |
|---|---|---|---|---|---|---|
| | $T_g$ (°C) | $\eta_{inh}$ (dL/g)[a] | $x$[b] | $T_g$ (°C) | $\eta_{inh}$ (dL/g)[a] | $x$[b] |
| 0 | 147 | 0.28 | 0 | 147 | 0.28 | 0 |
| 35 | 192 | 0.12 | 0.130 | 191 | 0.27 | 0.118 |
| 60 | 217 | 0.09 | 0.360 | 227 | 0.18 | 0.328 |

[a] Inherent viscosity measured in DMF at 25 °C in 0.05 g/dL solutions (for Cu60 the measurement was performed at 60 °C). [b] Molar ratio of coordinated and uncoordinated pyridine units in the polymer.

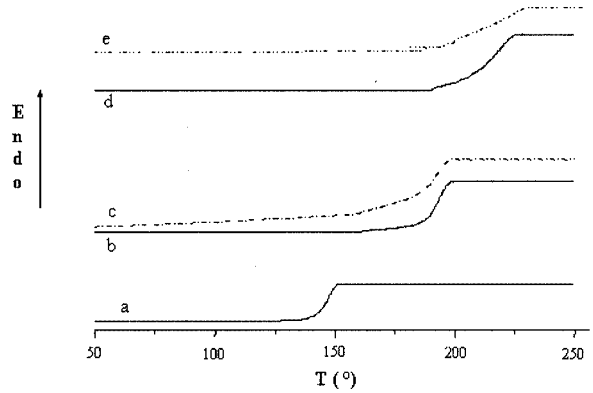


Figure 7. DSC thermograms, poly(2-vinylpyridine) (curve a); Pd35 (curve b); Cu35 (curve c); Pd60 (curve d); Cu60 (curve e)

The inflection corresponding to the glass transition is the only signal present in the curves. A regular increase of the glass transition temperature is observed upon grafting, with $T_g$'s almost independent from the nature of the metal (Pd$^{II}$ or Cu$^{II}$). The lack of any other inflection at temperatures lower than the $T_g$ of the ungrafted polymer is an evidence of the absence of uncoordinated complex acting as a plasticizing agent; a further evidence, at least in the case of Pd containing polymers, is given by $^1H$ NMR analysis. In fact, in the spectra of Pd polymers, recorded in [$D_2$]dichloromethane, only broad peaks of resonance are present, which are typical of polymer samples, and no sharp signal pertaining to free low molecular weight compounds is observed.[4b]

All polymers are amorphous, as confirmed by DSC and X-ray diffraction experiments. From concentrated solutions of polymers in NMP (ca. 0.10 g/mL) we have obtained clear, transparent films of optical quality by spin coating. The decomposition temperatures of the grafted polymers, which are around 300 °C, are well above the glass transition temperature, which, in any case, can be modulated by varying the extent of grafting, and this allows poling procedures to be safely done on the films. We think that these grafted polymers can show advantages as compared to all organic polymers tailored for second order NLO applications, particularly for what concerns the poling procedure. In fact, the peculiar nature of the bond between the NLO active fragment and the polymer chain (a coordinative bond) and the large molar excess of pyridine ligand groups, should allow some mobility of $ML^N$ fragment (through complexation-decomplexation equilibria) and, therefore, a high degree of orientation in the poling at high temperature ($> T_g$), with the mobility reduced (and the polar order frozen) at low temperature.

Second order optical nonlinearities of the complexes Cu*N* and Pd*N* are reported in Table 3. The discussion of their NLO properties can be usefully done at a comparative level with the similar complexes we have already studied.[4a]

Table 3. EFISH Results for the studied complexes

| Complex | $\lvert\mu_g\cdot\beta_{vec}\rvert$[a] |
|---|---|
| Cu1 | 1100 |
| Pd1 | 1500 |
| Cu2 | 1300 |
| Pd2 | 1100 |
| Pd3 | 3000 |

[a] Estimated errors are: ±10% for Cu1, Pd1, Cu2, Pd2 and ±20% for Pd3.

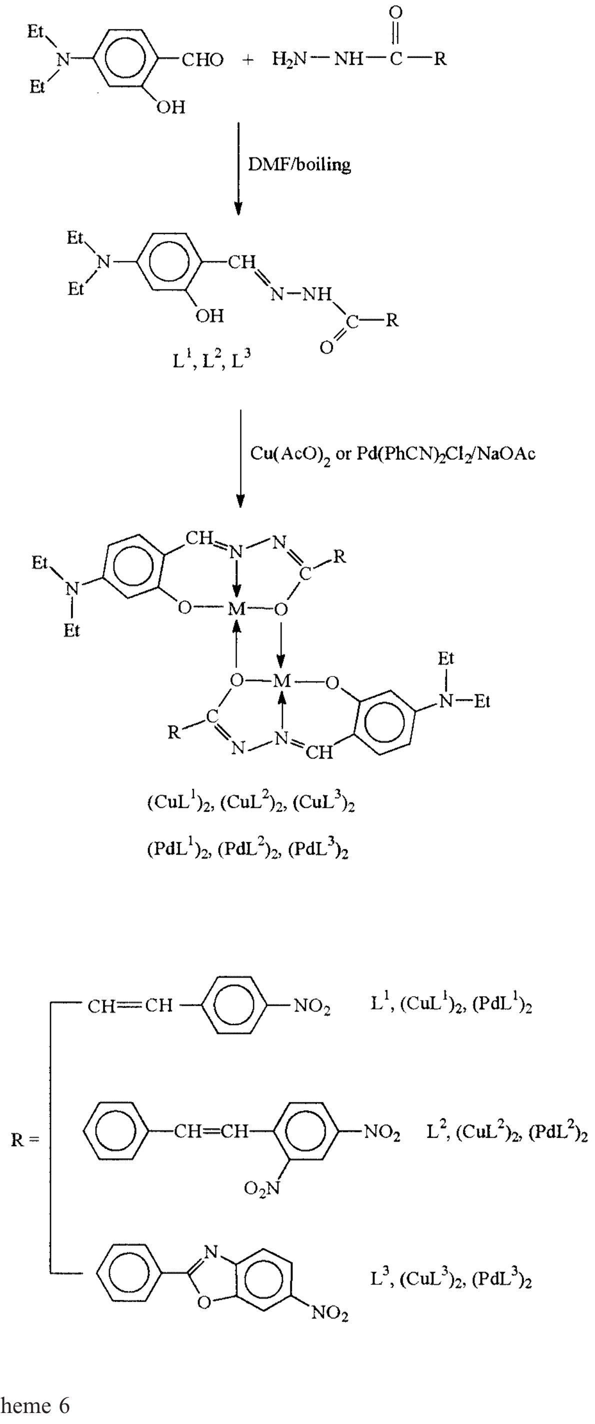
The NLO activity of Cu1 and Pd1 is considerably higher as compared with Cu1 and Pd1 complexes of ref.[4a] whose ligand only differs by lack of the vinylene group.[8] Actually, introduction of the vinylene group produces a fairly long polyene-like chain between the donor and acceptor groups (see Scheme 5) and it is well-known that push-pull polyenes are highly NLO active chromophores.[9]

$$-CH=N-N=\underset{|}{C}-CH=CH-$$

Scheme 5

The NLO activity of Cu2 and Pd2 is not significantly different as compared with Cu2 and Pd2 complexes of ref.[4a] whose ligand lacks the *ortho* nitro group. This finding may be explained on the basis of the crystallographic results; in fact, we have found that the *ortho* nitro group is significantly twisted with respect to the phenyl ring which is attached to (cf. Table 1) and so it gives a little contribution, if any, to the charge transfer.

The datum measured for Pd3 is consistent with the expected increase of nonlinear activity following the replacement of phenyl rings by low aromaticity heterocycles.[10] The high activity of this complex, which is among the highest reported to date for metallorganic chromophores,[1] coupled with the known features of high thermochemical and photochemical stability of the benzoxazole group,[11] make



Scheme 6

it a promising candidate for further developments of our research.

## Experimental Section

**Synthesis:** Complexes Cu*N* and Pd*N* (*N* = 1, 2, 3) were synthesized according to the general procedure outlined in the scheme below (Scheme 6) which starts with the synthesis of the organic ligands $L^N$ ($N$ = 1, 2, 3), followed by the synthesis of dinuclear complexes $(ML^N)_2$ and, from these, of the final mononuclear complexes M*N*, according to Scheme 2.

**4-Nitrocinnamohydrazide:** 4-Nitrocinnamoyl chloride (obtained from the acid refluxed in $SOCl_2$) is dissolved in boiling ethanol to obtain the ethyl ester. 4-Nitrocinnamic acid ethyl ester (5.00 g, 22.6 mmol) is dissolved in THF (50 mL). The solution is poured into a mixture of water (25 mL), ethanol (50 mL), hydrazine (18 mL) and it is stirred for 1.5 h at room temperature. Finally the mixture is poured into water (100 mL) and cooled in a freezer for 12 h. An orange solid is recovered by vacuum filtration. Yield 30%. M.p. 214 °C. $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C): δ = 4.52 ppm (s, 2 H), 6.80 (d, *J* = 16.2 Hz, 1 H), 7.53 (d, *J* = 16.2 Hz, 1 H), 7.77 (d, *J* = 8.7 Hz, 2 H), 8.22 (d, *J* = 8.3 Hz, 2 H), 9.50 (s, 1 H).

***N*-4-Diethylaminosalicylidene-*N′*-(4-nitrocinnamoyl)hydrazine ($L^1$):** 4-Nitrocinnamohydrazide (4.50 g, 21.7 mmol) and 4-*N*,*N*-diethylamino-2-hydroxybenzaldehyde (4.60 g, 23.8 mmol) are dissolved in boiling DMF (80 mL). After 15 minutes the solution is cooled and then poured into water (400 mL) containing concentrated sulfuric acid (5 mL). The red solid obtained is recovered by filtration, washed several times with water, dried, and recrystallized from DMF. Yield 6.06 g (73%). M.p. 223 °C. $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C): δ = 1.08 ppm (t, *J* = 6.8 Hz, 6 H), 3.33 (m, 4 H), 6.10 (s, 1 H), 6.25 (d, *J* = 8.6 Hz, 1 H), 6.83 (d, *J* = 15.6 Hz, 1 H), 7.22 (d, *J* = 8.8 Hz, 1 H), 7.70 (d, *J* = 8.8 Hz, 1 H), 7.87 (d, *J* = 8.8 Hz, 2 H), 8.24 (s, 1 H), 8.26 (d, *J* = 8.8 Hz, 2 H), 11.23 (s, 1 H), 11.71 (s, 1 H). IR (KBr): $\tilde{\nu}$ = 3409 cm$^{-1}$ (m), 3206 (m, N−H str.), 2978 (m), 2933 (w), 1632 (vs, C=O str.), 1592 (vs, N−H bend), 1520 (vs), 1355 (s), 1339 (s), 1247 (m), 1134 (m). UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 406, 2.2·10$^4$.

**Synthesis of $(CuL^1)_2$:** $L^1$ (1.00 g, 2.61 mmol) and copper(II) acetate (0.521 g, 2.61 mmol) are dissolved in DMF (35 mL). The solution is heated to boiling and stirred for 15 minutes, then it is cooled and poured into water (100 mL) containing sodium acetate (0.700 g, 8.53 mmol). A red-brown solid is recovered by filtration, washed repeatedly with water, and recrystallized from DMF. Yield 91%. M.p. 312 °C dec. $C_{40}H_{40}N_8O_8Cu_2$: calcd. C 54.11, H 4.51, N 12.63, Cu 14.31; found C 54.22, H 4.64, N 12.57, Cu 13.91%. UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 469, 4.5·10$^4$.

**Synthesis of $(PdL^1)_2$:** $L^1$ (1.00 g, 2.61 mmol) is dissolved in boiling THF (20 mL). The solution is added with THF (20 mL) containing bis(benzonitrile) Pd$^{II}$ dichloride (1.00 g, 2.61 mmol). After 15 minutes of stirring, a solution of sodium acetate (1.00 g, 12.2 mmol) in water (20 mL) is added. The pH is raised to about 8−9 by adding a 10 wt.% solution of KOH. After some minutes, the addition of 100 mL of water affords the precipitation of a dark red solid, which is filtered off, washed repeatedly with water, dried and finally washed with boiling heptane. Yield 91%. M.p. 311 °C dec. $C_{40}H_{40}N_8O_8Pd_2$: calcd. C 49.34, H 4.11, N 11.51, Pd 21.90; found C 49.66, H 4.27, N 11.51, Pd 22.30%. $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C): δ = 1.09 ppm (m, 12 H), 3.45 (m,8 H), 6.16 (s, 2 H), 6.26 (d, 2 H), 7.08 (d, 2 H), 7.33 (d, 2 H), 7.46 (d, 2 H), 7.90 (d, 4 H), 8.19 (d, 6 H). UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 459, 6.6·10$^4$.

**4-(2,4-Dinitrophenylethylidene)benzoic Acid:** 4-Formylbenzoic acid (10.0 g, 66.6 mmol) is dissolved in pyridine (50 mL) and piperidine (2 mL) and refluxed. 2,4-Dinitrophenylacetic acid (15.0 g, 66.6 mmol) is added in fractions of 3 g every 15 minutes. After 3 h the solution is concentrated to 30 mL and cooled. A yellow crystalline solid precipitates, then it is filtered off and washed with ethanol. Yield 72%. M.p. 263 °C. $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C): δ = 7.61 ppm (s, 2 H), 7.75 (d, *J* = 8.2 Hz, 2 H), 7.96 (d, *J* = 8.2 Hz, 2 H), 8.23 (d, *J* = 8.8 Hz, 1 H), 8.50 (d, *J* = 8.8 Hz, 1 H), 8.72 (d, *J* = 2.2 Hz, 1 H).

**4-(2,4-Dinitrophenylethylidene)benzohydrazide:** 4-(2,4-Dinitrophenylethylidene)benzoyl chloride (0.941 g, 2.83 mmol, obtained from the corresponding acid by reaction with thionyl chloride according to standard methods) is dissolved in hot anhydrous dioxane (20 mL). The solution is cooled and poured into a mixture of hydrazine (2.8 mL), dioxane (10 mL) and water (5 mL) whilst stirring. The reaction is rapid and after some minutes the mixture is poured in water (50 mL), affording the precipitation of a yellow solid, recovered by filtration, and washed repeatedly with water. Yield 86%. M.p. 234 °C. $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C): δ = 4.53 ppm (s, 2 H), 7.59 (s, 2 H), 7.72 (d, *J* = 7.8 Hz, 2 H), 7.87 (d, *J* = 7.8 Hz, 2 H), 8.23 (d, *J* = 8.8 Hz, 1 H), 8.51 (d, *J* = 8.6 Hz, 1 H), 8.74 (s, 1 H).9.83 (s, 1 H).

***N*-4-Diethylaminosalicylidene-*N′*-4-(2,4-dinitrophenylethylidene)-benzoylhydrazine ($L^2$):** 4-(2,4-dinitrophenylethylidene)benzohydrazide (3.55 g, 10.8 mmol) and 4-*N*,*N*-diethylamino-2-hydroxyibenzaldehyde (2.20 g, 11.4 mmol) are dissolved in boiling DMF (50 mL). After 15 minutes the solution is cooled and then poured into water (100 mL) containing concentrated sulfuric acid (2 mL). The brown solid obtained is recovered by filtration, washed several times with water, dried and recrystallized from DMF/water. Yield 5.06 g (93%). M.p. 276 °C. $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C): δ = 1.09 ppm (t, *J* = 6.8 Hz, 6 H), 3.33 (m, 4 H), 6.10 (s, 1 H), 6.23 (d, *J* = 8.8 Hz, 1 H), 7.17 (d, *J* = 8.8 Hz, 1 H), 7.62 (s, 2 H), 7.79 (d, *J* = 7.6 Hz, 2 H), 7.95 (d, *J* = 7.6 Hz, 2 H), 8.23 (d, *J* = 8.8 Hz, 1 H), 8.41 (s, 1 H), 8.50 (d, *J* = 8.6 Hz, 1 H), 8.73 (s, 1 H), 11.43 (s, 1 H), 11.82 (s, 1 H). IR (KBr): $\tilde{\nu}$ = 3334 cm$^{-1}$ (m), 3208 (w, N−H str.), 2977 (m), 2933 (w), 1630 (vs, C=O str.), 1595 (vs, N−H bend), 1520 (vs), 1355 (s), 1334 (s), 1246 (m), 1133 (m). UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 370, 5.6·10$^4$.

**Synthesis of $(CuL^2)_2$:** $L^2$ (1.00 g, 1.99 mmol) and copper(II) acetate (0.397 g, 1.99 mmol) are dissolved in DMF (35 mL). The solution is heated to boiling and stirred for 15 minutes, then it is cooled and poured into water (100 mL) containing sodium acetate (0.700 g, 8.53 mmol). A dark brown solid is recovered by filtration, washed repeatedly with water, and recrystallized from DMF. Yield 90%. M.p. 308 °C dec. $C_{52}H_{46}N_{10}O_{12}Cu_2$: Cu 11.25, C 55.27, H 4.10, N 12.39; found Cu 10.92, C 54.98, H 4.02, N 12.11%. UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 400, 5.8·10$^4$.

**Synthesis of $(PdL^2)_2$:** $L^2$ (1.00 g, 1.99 mmol) is dissolved in boiling THF (15 mL). The solution is added with THF (10 mL) containing bis(benzonitrile)Pd$^{II}$ dichloride (0.763 g, 1.99 mmol). A solution of sodium acetate (1.00 g, 12.2 mmol) in water (20 mL) is added. The pH is raised to 8−9 by adding a solution of 0.300 g of KOH in 100 mL of water. On heating, a dark red-brown solid coagulates, then filtered off, washed repeatedly with water, dried, and washed with boiling heptane. Yield 85%. M.p. 291 °C dec.

$C_{52}H_{46}N_{10}O_{12}Pd_2$: Pd 17.50, C 51.37, H 3.81, N 11.52%; found Pd 17.21, C 51.08, H 3.65, N 11.24%. $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 1.09 ppm (t, 12 H), 3.33 (m, 8 H), 6.15 (s, 2 H), 6.25 (d, 2 H), 7.32 (d, 2 H), 7.59 (s, 4 H), 7.66 (d, 4 H), 7.97 (d, 4 H), 8.25 (d, 2 H), 8.41 (s, 2 H), 8.48 (d, 2 H), 8.72 (s, 2 H). UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 369, 5.2·10$^4$.

***N*-(4-Carboxybenzylidene)-2-hydroxy-4-nitroaniline:** 4-Formylbenzoic acid (5.00 g, 33.3 mmol) is suspended in boiling absolute ethanol (60 mL). Successively a solution of 2-hydroxy-4-nitroaniline (5.00 g, 32.4 mmol) in ethanol (60 mL) is added. After boiling 30 min the solution is cooled, obtaining a pure yellow solid, then filtered off. Yield 54%. M.p. 246 °C. $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 7.35 ppm (d, $J$ = 6.3 Hz, 1 H), 7.76 (d, $J$ = 1.8 Hz, 1 H), 7.78 (dd, $J_1$ = 1.8, $J_2$ = 6.3 Hz, 1 H), 8.05 (d, $J$ = 6.3 Hz, 2 H), 8.17 (d, $J$ = 6.3 Hz, 2 H), 8.80 (s, 1 H), 13.32 (s, 1 H).

**4-(6-Nitro-2-benzoxazolyl)benzoic Acid:** *N*-(4-Carboxybenzylidene)-2-hydroxy-4-nitroaniline (5.20 g, 18.2 mmol) is suspended in glacial acetic acid (100 mL). Lead(IV) acetate (9.68 g, 21.8 mmol) is added slowly under strong stirring. The reaction takes 2 h. The product is filtered off, washed with acetic acid, and recrystallized from DMF. Yield 31%. M.p. 319 °C. $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 7.90 ppm (d, $J$ = 5.8 Hz, 1 H), 8.25 (d, $J$ = 5.2 Hz, 2 H), 8.37 (d, $J$ = 5.8 Hz, 1 H), 8.39 (d, $J$ = 5.2 Hz, 2 H), 8.54 (s, 1 H).

**4-(6-Nitro-2-benzoxazolyl)benzohydrazide:** 4-(6-Nitro-2-benzoxazolyl)benzoyl chloride (3.00 g, 9.91 mmol, obtained from the corresponding acid by reaction with thionyl chloride according to standard methods) is dissolved in hot anhydrous dioxane (60 mL). The solution is cooled and poured into a mixture of ethanol (50 mL) and hydrazine monohydrate (5 mL) whilst stirring. The product is a yellow solid which is recrystallized from DMF. Yield 57%. M.p. 280 °C. $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 4.67 ppm (s, 2 H), 8.06 (d, $J$ = 8.4 Hz, 1 H), 8.18 (d, $J$ = 8.4 Hz, 1 H), 8.30 (d, $J$ = 8.6 Hz, 2 H), 8.39 (d, $J$ = 8.4 Hz, 2 H), 8.76 (s, 1 H), 10.02 (s, 1 H).

***N*-4-Diethylaminosalicylidene-*N′*-4-(6-nitro-2-benzoxazolyl)benzoylhydrazine (L$^3$):** 4-(6-Nitro-2-benzoxazolyl)benzohydrazide (1.67 g, 5.60 mmol) and 4-*N*,*N*-diethylamino-2-hydroxyibenzaldehyde (1.14 g, 5.90 mmol) are dissolved in boiling DMF (30 mL). After 15 minutes the solution is cooled and then poured into water (100 mL) containing concentrated sulfuric acid (1 mL). The product is recovered by filtration, washed several times with water, dried, and recrystallized from DMF. Yield 2.39 g (90%). M.p. 257 °C. $^1$H NMR (200 MHz, [D$_6$]DMSO, 25 °C): $\delta$ = 1.13 ppm (t, $J$ = 6.6 Hz, 6 H), 3.37 (m, 4 H), 6.13 (s, 1 H), 6.27 (d, $J$ = 6.9 Hz, 1 H), 7.21 (d, $J$ = 8.7 Hz, 2 H), 8.05 (d, $J$ = 8.4 Hz, 2 H), 8.16 (d, $J$ = 8.4 Hz, 2 H), 8.23 (m, 2 H), 8.45 (s, 1 H), 8.73 (s, 1 H), 11.40 (s, 1 H), 11.99 (s, 1 H). IR (KBr): $\tilde{\nu}$ = 3474 cm$^{-1}$ (w), 3201 (m, N−H str.), 2979 (m), 1654 (vs), 1628 (vs, C=O str.), 1593 (vs, N−H bend), 1520 (vs), 1360 (s), 1342 (s), 1248 (m), 1135 (m). UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 343, 2.8·10$^4$.

**Synthesis of (CuL$^3$)$_2$:** L$^3$ (1.00 g, 2.11 mmol) and copper(II) acetate (0.422 g, 2.11 mmol) are solved in DMF (35 mL). The solution is heated to boiling and stirred for 15 minutes, then it is cooled and poured into water (100 mL) containing sodium acetate (0.700 g, 8.53 mmol). A dark orange solid is recovered by filtration, washed repeatedly with water, and recrystallized from DMF. Yield 89%. M.p. 327 °C dec. $C_{50}H_{42}N_{10}O_{10}Cu_2$: Cu 11.88, C 56.12, H 3.96, N 13.09 ; found Cu 12.30, C 55.96, H 3.77, N 12.86%. UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 435, 5.2·10$^4$.

**Synthesis of (PdL$^3$)$_2$:** L$^3$ (1.00 g, 2.11 mmol) is suspended in 20 mL of boiling THF. The solution is added with THF (10 mL) containing bis(benzonitrile)Pd$^{II}$ dichloride (0.809 g, 2.11 mmol), obtaining a yellow heterogeneous mixture which becomes a dark red solution by adding 20 mL of water containing sodium acetate (1.00 g, 12.2 mmol). The pH is raised to 8−9 with a solution of 0.300 g of KOH in 100 mL of water and a brown solid coagulates, which is filtered off, washed repeatedly with water, dried, and washed with boiling heptane. Yield 85%. M.p. 298 °C dec. $C_{50}H_{42}N_{10}O_{10}Pd_2$: Pd 18.41, C 51.96, H 3.66, N 12.12%; found Pd 18.35, C 51.85, H 3.55, N 12.01%. UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 446, 6.0·10$^4$.

**Synthesis of CuN and PdN:** The corresponding dinuclear precursor is dissolved in pyridine at room temperature, then the solvent is allowed to evaporate from the solution leaving crystals of the mononuclear complex.

**Cu1:** $C_{25}H_{25}N_5O_4Cu\cdot 1/2C_5H_5N$: calcd. C 58.71, H 4.93, N 13.69; found C 58.41, H 4.96, N 13.42. UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 471, 2.8·10$^4$.

**Pd1:** $C_{30}H_{30}N_6O_4Pd$: calcd. C 55.86, H 4.69, N 13.03; found C 55.33, H 4.68, N 12.86. UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 463, 3.3·10$^4$.

**Cu2:** $C_{36}H_{33}N_7O_6Cu$: calcd. C 59.79, H 4.60, N 13.56; found 59.51, H 4.70, N 13.36. UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 400, 2.9·10$^4$.

**Pd2:** $C_{36}H_{33}N_7O_6Pd$: calcd. C 56.44, H 4.34, N 12.80; found C 56.05, H 4.45, N 12.69. UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 361, 2.4·10$^4$.

**Cu3:** $C_{35}H_{31}N_7O_5Cu$: calcd. C 60.64, H 4.51, N 14.14; found C 59.21, H 4.40, N 13.80. UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 460, 2.8·10$^4$.

**Pd3:** $C_{30}H_{26}N_6O_5Pd$: calcd. C 54.85, H 3.99, N 12.18; found C 54.71, H 4.12, N 12.53. UV/Vis: $\lambda_{max}$ (nm), $\varepsilon_{max}$ (dm$^3$mol$^{-1}$cm$^{-1}$): 450, 2.9·10$^4$.

**Synthesis of Grafted Polymers:** Commercial poly(4-vinylpyridine) (Aldrich, $M_{av}$ ≈ 60000 D, $T_g$= 147 °C) was used as the starting material after drying at 120 °C in oven for 16 h. Grafted polymers were prepared according to a standard procedure. The polymer and the dinuclear complex (ML$^1$)$_2$ (total amount 1.0 g) in the proper weight ratio are solved in DMF (10 mL) at 90 °C. After stirring for 15′ at 90 °C, the mixture is poured in water (100 mL) containing 2% sodium acetate (by weight). The precipitated polymer is recovered by filtration (90% yield), washed repeatedly with water and dried in oven at 130 °C. Grafted polymers are indicated as MW, where M stands for Cu or Pd and W is the weight percent ratio of (ML$^1$)$_2$ to polymer. Grafted polymers Cu35, Pd35, Cu60, and Pd60 were prepared. Analytical data: Cu35: %Cu calcd. 5.01; found 5.08. Cu60: %Cu calcd. 8.59; found 8.47. Pd35: %Pd calcd. 7.67; found 7.67. Pd60: %Pd calcd. 13.13; found 13.21.

**Physical Measurements:** The thermal behavior of compounds was studied by differential scanning calorimetry (Perkin−Elmer Pyris, $N_2$ atmosphere, scanning rate 10 K/min), temperature controlled polarizing microscopy (Zeiss microscope, Mettler hot stage) and TGA-DTA analysis (TA Instruments SDT 2960, air atmosphere, scanning rate 10 K/min). Proton NMR spectra were recorded on a Varian XL 200 spectrometer. UV/Vis (DMF solution) and FT-IR (KBr) spectra were recorded with JASCO spectrometers. Films of the grafted polymers were obtained by the spin coating technique

Table 4. Crystal, collection and refinement data for Cu1, Cu2, Pd2, Cu3

| | Cu1 | Cu2 | Pd2 | Cu3 |
|---|---|---|---|---|
| Chemical formula | $2(C_{25}H_{25}N_5O_4Cu)\cdot C_5H_5N$ | $C_{36}H_{33}N_7O_6Cu$ | $C_{31}H_{28}N_6O_6Pd\cdot C_5H_5N$ | $C_{35}H_{31}N_7O_5Cu$ |
| Molecular mass | 1125.20 | 723.23 | 766.09 | 693.21 |
| $T$ [K] | 293 | 293 | 293 | 293 |
| Crystal system | monoclinic | triclinic | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $C2/c$ | $P2_1/c$ |
| $a$ [Å] | 15.85(5) | 9.224(4) | 36.84(1) | 16.029(7) |
| $b$ [Å] | 19.10(1) | 10.793(2) | 8.605(2) | 12.924(9) |
| $c$ [Å] | 16.12(4) | 18.132(7) | 27.73(1) | 16.59(1) |
| $\alpha$ [°] | 90 | 101.71(3) | 90 | 90 |
| $\beta$ [°] | 146.9(1) | 100.74(5) | 129.9(1) | 109.03(6) |
| $\gamma$ [°] | 90 | 98.69(2) | 90 | 90 |
| $V$ [Å$^3$] | 2660(10) | 1703(1) | 6744(3) | 3249(3) |
| $Z$, $D_x$ [g/cm$^3$] | 2, 1.402 | 2, 1.411 | 8, 1.509 | 4, 1.417 |
| $\mu$ [mm$^{-1}$] | 0.863 | 0.698 | 0.608 | 0.727 |
| Theta range | 1.71°−27.97° | 1.18°−27.97° | 1.44°−27.97° | 1.35°−27.97° |
| Data/parameters | 6284/343 | 8198/451 | 8084/451 | 7759/433 |
| $R1$, $wR2$ [$I > 2\sigma(I)$] | 0.0515, 0.1281 | 0.0419, 0.1090 | 0.0507, 0.1095 | 0.0662, 0.1307 |
| $R1$, $wR2$ (all data) | 0.1416, 0.1562 | 0.0792, 0.1231 | 0.1285, 0.1319 | 0.3336, 0.1924 |

$$R1 = \frac{\sum \left\| F_0 \right| - \left| F_c \right\|}{\sum \left| F_0 \right|} \; ; \quad wR2 = \left\{ \frac{\sum \left[ w\left(F_o^2 - F_c^2\right)^2 \right]}{\sum \left[ w\left(F_o^2\right)^2 \right]} \right\}^{1/2}$$

(NMP solutions, SCS P6700 spincoater operating at 800−1000 rounds/min). Residual solvent was removed by keeping the films in oven at 120 C for 12 h.

**X-ray Analysis:** Single crystals of Cu1, Cu2, Pd2, and Cu3 suitable for X-ray analysis were obtained by slow evaporation of pyridine solutions at ambient temperature. Cell parameters were obtained through a least-squares fit[12] to the θ angles of 25 accurately centered strong reflections in the ranges 12.173°≤ θ ≤ 13.480° for Cu1, 15.907°≤ θ ≤ 17.512° for Cu2, 12.009°≤ θ ≤ 13.551° for Pd2 and 9.140°≤ θ ≤ 12.147° for Cu3 on an Enraf−Nonius MACH 3 automated single crystal diffractometer, using graphite monochromated Mo-$K_\alpha$ radiation ($\lambda$= 0.71069 Å). Data collection was performed on the same apparatus. Semiempirical absorption correction (ψ scans) was applied in all cases. The structures were solved by direct methods (SIR92 program[13]), completed by difference Fourier methods and refined by the full-matrix least-squares method (SHELXL program of SHELX 97 package[14]). Refinement was on $F^2$ against all independent measured reflections; sigma weights were introduced in the last refinement cycles. The largest peaks and holes in the last Fourier difference were (e·Å$^{-3}$): 0.689 and −0.514 for Cu1, 0.379 and −0.235 for Cu2, 0.691 and −0.498 for Pd2, and 0.448 and −0.498 for Cu3. In all structures C, N, O and metal atoms were given anisotropic displacement parameters. H atoms were placed in calculated positions and refined by the riding model with $U_{iso}$ equal to $U_{eq}$ of the carrier atoms. In the crystals of Cu1 the pyridine molecule not coordinated to the metal is located on a crystallographic inversion center and therefore is statistically disordered (two centrosymmetrically related sites with 0.5 occupation factor). Some crystal, collection and refinement data are reported in Table 4. CCDC-221599 (for Cu1), -221600 (for Cu2), -221601 (for Pd2), and -221602 (for Cu3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

**NLO Measurements:** Second order optical nonlinearities of chromophores, in the form of $\mu_g\beta$ products ($\mu_g$ is the ground state permanent dipole moment and β the quadratic hyperpolarizability of the molecules), were measured by the EFISH (Electric Field Induced Second Harmonic generation) technique.[15] Measurements were carried out in DMSO solutions at a fundamental wavelength of 1.907 μm, using a Q-switched, mode locked Nd3:YAG laser, whose 1.064 μm initial wavelength was shifted by stimulated Raman scattering in a high-pressure hydrogen cell.

## Acknowledgments

We thank the CIMCF of the Università di Napoli "Federico II" for permission to use the Nonius MACH3 diffractometer and NMR spectrometers. Financial support of MIUR of Italy (PRIN 2002) is also acknowledged.

---

[1] [1a] N. J. Long, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 21−38; *Angew. Chem.* **1995**, *107*, 37. [1b] I. R. Whittall, A. M. McDonagh, M. G. Humphrey, M. Samoc, *Adv. Organomet. Chem.* **1998**, *42*, 291−361. [1c] S. Di Bella, *Chem. Soc. Rev.* **2001**, *30*, 355−366.

[2] [2a] B. J. Coe, J. A. Harris, L. J. Harrington, J. C. Jeffery, L. H. Rees, S. Houbrechts, A. Persoons, *Inorg. Chem.* **1998**, *37*, 3391−3399. [2b] J. Buey, S. Coco, L. Diez, P. Espinet, L. M. Martin-Alvarez, J. A. Miguel, S. Garcia-Granda, A. Tesouro, I. Ledoux, J. Zyss, *Organometallics* **1998**, *17*, 1750−1755. [2c] R. Centore, B. Panunzi, A. Roviello, A. Tuzi, *Acta Crystallogr., Sect. C* **2002**, *58*, m26−m28. [2d] C. Fave, M. Hissler, K. Senechal, I. Ledoux, J. Zyss, R. Reau, *Chem. Commun.* **2002**, 1674−1675.

[3] L. Dalton, *Adv. Polymer Sci.* **2002**, *158*, 1−86.

[4] [4a] F. Cariati, U. Caruso, R. Centore, W. Marcolli, A. De Maria, B. Panunzi, A. Roviello, A. Tuzi, *Inorg. Chem.* **2002**, *41*, 6597−6603. [4b] U. Caruso, A. De Maria, B. Panunzi, A. Roviello, *J. Polymer Sci., Part A: Polym. Chem.* **2002**, *40*, 2987−2992.

[5] [5a] M. F. Iskander, A. M. El-Aggan, L. S. Refaat, L. El Sayed, *Inorg. Chim. Acta* **1975**, *14*, 167−172. [5b] J. Jezierska, A. Jezierski, B. Jezowska-Trzebiatowska, A. Ozarowsky, *Inorg. Chim. Acta* **1983**, *68*, 7−13.

[6] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. Guy Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

[7] M. Traetteberg, E. B. Frantsen, F. C. Mijlhoff, A. Hoekstra, *J. Mol. Struc.* **1975**, *26*, 57−68.

[8] From preliminary results of dipole moment measurement with the Guggenheim method, a $\mu$ value of 5 D may be estimated for Pd1, from which $\beta \approx 300 \cdot 10^{-30}$ esu is deduced.

[9] [9a] S. R. Marder, J. W. Perry, B. G. Tiemann, C. B. Gorman, S. Gilmour, S. L. Biddle, G. Bourhill, *J. Am. Chem. Soc.* **1993**, *115*, 2524−2526. [9b] S. R. Marder, C. B. Gorman, B. G. Tiemann, L.-T. Cheng, *J. Am. Chem. Soc.* **1993**, *115*, 3006−3007.

[10] [10a] V. P. Rao, A. K.-Y. Jen, J. Chandrasekhar, I. N. N. Namboothiri, A. Rathna, *J. Am. Chem. Soc.* **1996**, *118*, 12443−12448. [10b] I. D. L. Albert, T. J. Marks, M. A. Ratner, *J. Am. Chem. Soc.* **1997**, *119*, 6575−6582. [10c] A. Abbotto, S. Bradamante, A. Facchetti, G. A. Pagani, *J. Org. Chem.* **1997**, *62(17)*, 5755−5765. [10d] M. He, T. M. Leslie, J. A. Sinicropi, *Chem. Mater.* **2002**, *14*, 4662−4668.

[11] [11a] C. Arnold, *J. Polymer Sci., Macromol. Rev.* **1979**, *14*, 265. [11b] L. J. Mathias, S. U. Ahmed, P. D. Livant, *Macromolecules* **1985**, *18*, 616. [11c] P. M. Hergenrother, J. W. Connell, J. W. Labadie, J. L. Hedrick, *Adv. Polymer Sci.* **1994**, *117*, 67−110.

[12] R. Centore, *CELLFIT*; Università di Napoli "Federico II": Naples, Italy, **2002**.

[13] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343−350.

[14] G. M. Sheldrick, *SHELX-97*; University of Göttingen: Göttingen, Germany, **1997**.

[15] T. Thami, P. Bassoul, M. A. Petit, J. Simon, A. Fort, M. Barzoukas, A. Villaeys, *J. Am. Chem. Soc.* **1992**, *114*, 915−921.

Received October 15, 2003