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# Cyclometalated 4-Styryl-2-phenylpyridine Platinum(II) Acetylacetonate Complexes as Second-Order NLO Building Blocks for SHG Active Polymeric Films

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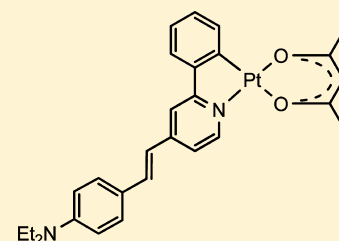
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## Supporting Information

**ABSTRACT:** The second-order nonlinear optical (NLO) properties of various Pt(II) acetylacetonate complexes bearing a substituted cyclometalated 4-styryl-2-phenylpyridine (ppy-4-styryl-R, with R = NEt<sub>2</sub>, OMe, H, NO<sub>2</sub>) were investigated in DMF solution on working with an incident wavelength of 1907 nm by the EFISH technique, whereas the dipole moments were determined by density functional theory (DFT) calculations. In addition, a Pt(II) complex with the ppy-4-styryl-NEt<sub>2</sub> ligand, which was the most NLO efficient chromophore due to a particularly high dipole moment, was dispersed in a polymethylmethacrylate matrix and then oriented by poling to give a composite film characterized by a good and quite stable second harmonic generation (SHG) signal.



## INTRODUCTION

Organometallic and coordination complexes with both luminescent and second-order nonlinear optical (NLO) properties are of growing interest as new molecular multifunctional materials, since they offer additional flexibility, in comparison to organic chromophores, by introducing NLO active electronic charge-transfer transitions between the metal and the ligands tunable by virtue of the nature, oxidation state, and coordination sphere of the metal center.<sup>1,2</sup>

Whereas square-planar cyclometalated Pt(II) complexes have been intensively studied for their luminescent properties, there have been only a few reports on their NLO properties,<sup>3</sup> and recently some of us reported that various simple luminescent Pt(II) complexes of the kind [Pt(cyclometalated 2-phenylpyridine)(RCOCHCOR)] (R = Me, Ph) complexes show an unexpectedly large second-order nonlinear optical response ( $\mu\beta_{1,907} = -535$  and  $-770 \times 10^{-48}$  esu for R = Me, Ph, respectively), as determined by the electric field induced second harmonic generation (EFISH) method, attributed by an SOS-TDDFT investigation mainly to intraligand charge transfer transitions involving the cyclometalated ligand.<sup>3c</sup>

These results prompted us to investigate the effect of an increase of the  $\pi$  delocalization of the phenylpyridine and of the addition of electron-withdrawing or electron-donating groups on the quadratic hyperpolarizability of these kinds of complexes. Since Pt(II) acetylacetonate complexes bearing a variously substituted cyclometalated 4-styryl-2-phenylpyridine

(ppy-4-styryl-R, with R = NEt<sub>2</sub>, OMe, H, NO<sub>2</sub>) were recently reported for their interesting luminescent properties,<sup>4</sup> we decided to prepare the various 4-styryl-2-phenylpyridines and related Pt(II) complexes again and study their second-order NLO properties in solution using the EFISH technique, working with an incident wavelength of 1907 nm. The dipole moments were evaluated by density functional theory (DFT) calculations. In addition, due to the importance of second-order NLO active polymeric films for NLO applications,<sup>2h</sup> the most NLO efficient Pt(II) chromophore bearing the ppy-4-styryl-NEt<sub>2</sub> ligand was dispersed and oriented by poling in a poly(methyl methacrylate) (PMMA) matrix, affording a composite film from which second harmonic generation (SHG) was investigated.

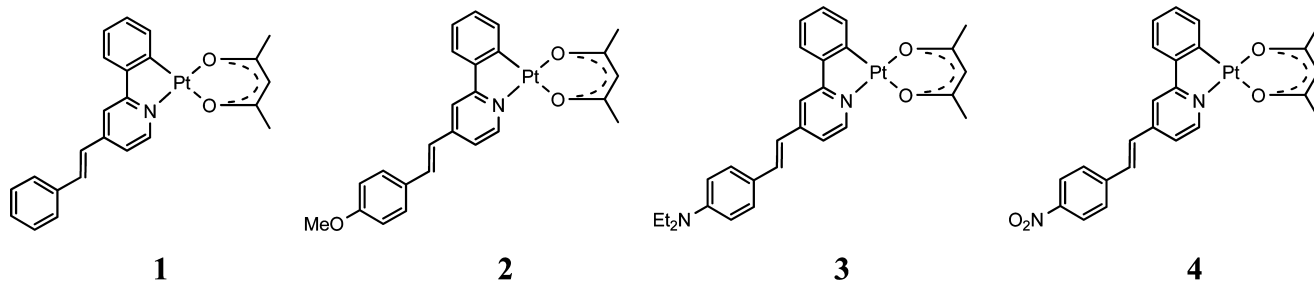
## EXPERIMENTAL SECTION

**General Comments.** Reagents were purchased from Sigma-Aldrich or Fluorochem. Ligands and complexes were prepared as previously reported.<sup>4</sup>

**EFISH Measurements.** All EFISH measurements<sup>5</sup> were carried out at the Dipartimento di Chimica of the Università degli Studi di Milano, in DMF solutions at a concentration of  $1 \times 10^{-3}$  M, working with a nonresonant incident wavelength of 1.907  $\mu$ m, obtained by Raman-shifting the fundamental 1.064  $\mu$ m wavelength produced by a Q-switched, mode-locked Nd<sup>3+</sup>:YAG laser manufactured by Atalaser.

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Chart 1. Structure of the Investigated Pt(II) Complexes



The apparatus for the EFISH measurements is a prototype made by SOPRA (France). The  $\mu\beta_{\text{EFISH}}$  values reported are the mean values of 16 successive measurements performed on the same sample. The sign of  $\mu\beta$  is determined by comparison with the reference solvent (DMF).

**Preparation of Composite Films of Complex 3 in PMMA and SHG Measurements.** Composite films were produced by spin coating on ordinary nonpretreated glass substrates (thickness 1 mm) previously cleaned with water/acetone. The solution was obtained from 200 mg of poly(methyl methacrylate) (PMMA) and 10 mg of complex 3 dissolved in dichloromethane (4 mL). Parameters of spinning (RPM = revolutions per minute): RPM 1 = 1000; ramp 1 = 3 s, time 1 = 3 s; RPM 2 = 2000; ramp 2 = 9 s, time 2 = 1 s; RPM 3 = 3000; ramp 3 = 2 s, time 3 = 12 s.

The film thickness of composite PMMA/complex 3 ( $1157 \pm 58$  nm) was measured by the ellipsometry technique. Electronic absorption spectra of the composite films were recorded with a JASCO UV-530 spectrophotometer.

Second harmonic generation (SHG) experiments were performed using a Q-switched Nd:YAG (Quanta System Giant G790–20) laser at 1064 nm wavelength with a pulse of 7 ns and 20 Hz repetition rate. For poling measurements the fundamental beam was attenuated to 0.57 mJ and was focused with a lens ( $f = 600$  mm) on the sample, placed over the hot stage. The corona poling process was carried out inside a specially built drybox, under an  $\text{N}_2$  atmosphere. The fundamental beam was polarized in the plane of incidence (p-polarized) with an angle of about  $55^\circ$  with respect to the sample in order to optimize the SHG signal. The hot stage temperature was controlled by a GEFRAN 800 controller, while the corona-wire voltage (up to 8.5 kV across a 10 mm gap) was applied by a TREK610E high-voltage supply. After rejection of the fundamental beam by an interference filter and a glass cutoff filter, the p-polarized SHG signal at 532 nm was detected with a Hamamatsu C3830 UV–vis photomultiplier (PT). The setup for Maker fringe measurements was similar to that used previously, except that the fundamental beam was attenuated to 1 mJ and the sample was placed over a rotation stage.

## RESULTS AND DISCUSSION

The various 4-styryl-2-phenylpyridines para-substituted by different R groups, from strongly withdrawing to strongly donating substituents ( $\text{R} = \text{NO}_2$ , H, OMe,  $\text{NEt}_2$ ), and related platinum(II) complexes (1–4; Chart 1) were prepared as previously reported.<sup>4</sup>

The known absorption spectra<sup>4</sup> of the four complexes are reported in Table 1. The spectrum of the unsubstituted styryl compound (1) displays a very strong band in the UV ( $\lambda_{\text{max}}$  316 nm) and a second band of about half the intensity tailing well into the visible region ( $\lambda_{\text{max}}$  392 nm). The spectra of the *p*-nitro- and *p*-methoxystyryl analogues (4 and 2) are very similar to that of 1 but with a red shift in the higher energy band (to  $\lambda_{\text{max}}$  333 and 336 nm, respectively). Meanwhile, the low-energy band is slightly red-shifted in 4 and blue-shifted in 2. The former was attributed to intraligand  $\pi$ – $\pi^*$  transitions, while the lower energy bands were assigned to MLCT ( $d\pi(\text{Pt}) \rightarrow \pi^*$ ) transitions. In contrast, the absorption spectrum of the amino-

Table 1. Electronic Spectra and  $\mu\beta_{1.907 \text{ EFISH}}$ ,  $\mu$ , and  $\beta_{1.907 \text{ EFISH}}$  Values of the Investigated Pt(II) Complexes

complex	absorbance <sup>a</sup> $\lambda_{\text{max}}$ (nm) ( $\epsilon$ ) ( $\text{M}^{-1} \text{cm}^{-1}$ )	$\mu\beta_{1.907 \text{ EFISH}}$ <sup>b</sup> ( $10^{-48}$ esu)	$\mu^c$ ( $10^{-18}$ esu)	$\beta_{1.907 \text{ EFISH}}$ ( $10^{-30}$ esu)
1	248 (21650), 316 (27750), 392 (12960)	1060	6.20	171
2	253 (35130), 289 sh (26680), 336 (19230), 386 (14120)	1330 <sup>d</sup>	7.25	183
3	432 (24360)	1790	13.0	138
4	333 (17330), 400 (8840)	620	4.52	137

<sup>a</sup>From ref 4, in  $\text{CH}_2\text{Cl}_2$ . <sup>b</sup>Working in  $10^{-3}$  M DMF with an incident radiation wavelength of 1.907  $\mu\text{m}$ . The error is 10%. <sup>c</sup>Calculated at the PBE0/LanL2DZ level in DMF (see the Supporting Information).

<sup>d</sup>The free 4-styryl-2-phenylpyridine ligand bearing a methoxy group has  $\mu\beta_{1.907 \text{ EFISH}} = 370 \times 10^{-48}$  esu.

substituted complex 3 is markedly different, displaying a very strong low-energy absorption band at 432 nm arising from the influence of the strongly electron-donating nature of the amino group favoring the formation of a charge-separated excited state (ILCT).<sup>4</sup> The orbital parentage of the transitions giving rise to the observed absorption bands was confirmed by theoretical calculations (see the Supporting Information).

In order to investigate their second-order NLO properties, the various platinum(II) complexes were investigated by the EFISH technique (see Table 1). It is known that this technique<sup>5</sup> can provide direct information on the intrinsic molecular NLO properties through eq 1, where  $\mu\beta_{\text{EFISH}}/5kT$  is

$$\gamma_{\text{EFISH}} = (\mu\beta_{\text{EFISH}}/5kT) + \gamma(-2\omega; \omega, \omega, 0) \quad (1)$$

the dipolar orientational contribution and  $\gamma(-2\omega; \omega, \omega, 0)$ , a third-order term at frequency  $\omega$  of the incident light, is a purely electronic cubic contribution to  $\gamma_{\text{EFISH}}$  which can usually be neglected when studying the second-order NLO properties of dipolar compounds.<sup>2</sup>

In Table 1 are reported the  $\mu\beta_{1.907 \text{ EFISH}}$  values of all the investigated complexes, measured in DMF solution with an incident wavelength of 1.907  $\mu\text{m}$ . To obtain  $\beta_{1.907 \text{ EFISH}}$ , the projection along the dipole moment axis of the vectorial component of the tensor of the quadratic hyperpolarizability, it is necessary to know the dipole moment,  $\mu$ . In the present study we used the theoretical dipole moments calculated as described in the Supporting Information.

In contrast to the parent cyclometalated phenylpyridine Pt(II) acetylacetonate complex,<sup>3c</sup> all the investigated complexes with a 4-styryl-2-phenylpyridine ligand (1–4; Table 1) are characterized by a positive value of  $\mu\beta_{1.907 \text{ EFISH}}$ , in agreement with a positive value of  $\Delta\mu_{\text{eg}}$  (difference of the dipole moments

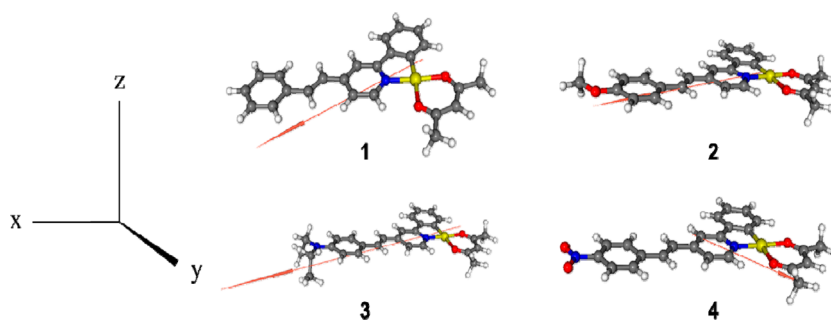


Figure 1. DFT computed ground state dipole moments.

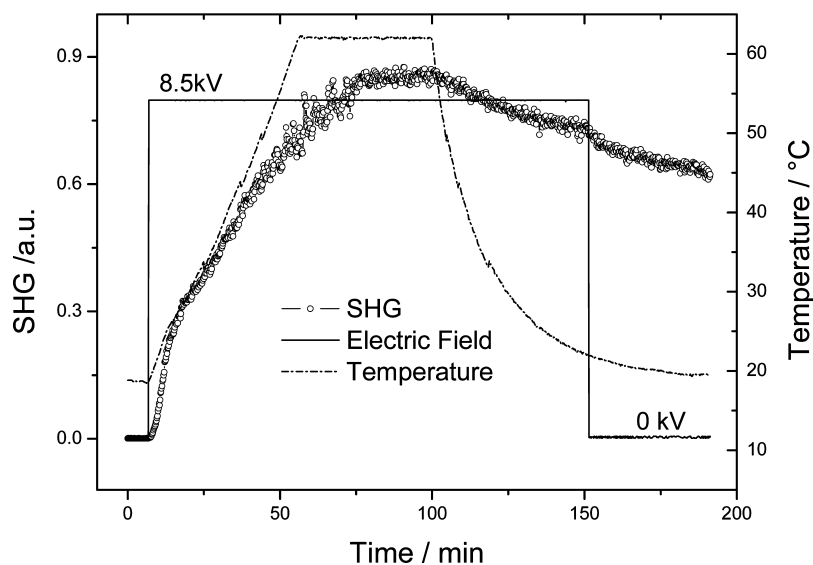


Figure 2. In situ corona-wire poling dynamic of a PMMA film containing complex 3.

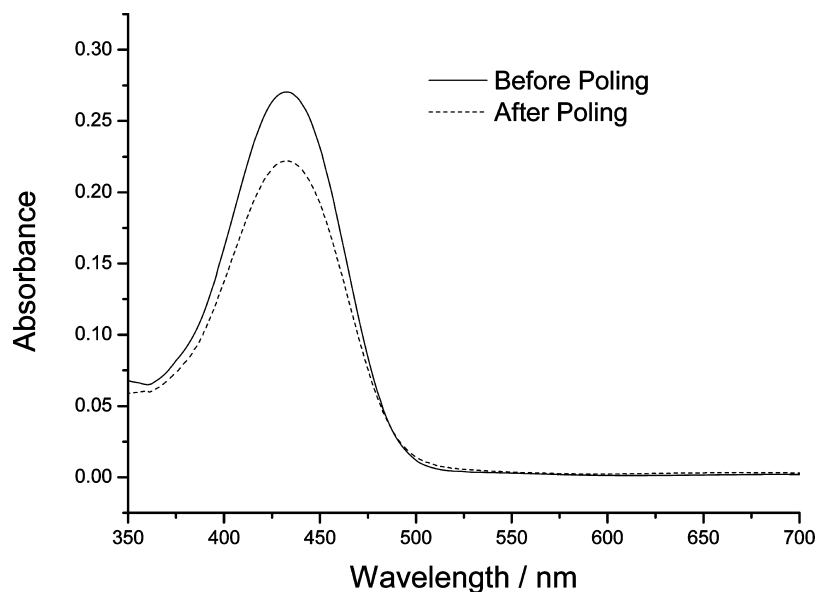


Figure 3. Absorption spectra of a PMMA film containing complex 3 before and after poling.

in the excited and ground states) upon excitation.<sup>2</sup> Therefore an increase of the  $\pi$  delocalization of the pyridine moiety of the cyclometalated phenylpyridine leads to an inversion of the sign of  $\mu\beta_{1,907}^{EFISH}$  whether it bears an electron-withdrawing or electron-donating group. This behavior can be reasonably

attributed to the direction of the ground-state dipole moment, since in the EFISH measurements only the components of the vectorial component of the quadratic hyperpolarizability along the dipole moment axis are relevant. Thus, in the case of the parent cyclometalated phenylpyridine Pt(II) complex with  $\beta$ -

acetylacetonate, the dipole moment has the major contribution along the direction connecting the pyridine and phenyl moieties of the phenylpyridine ligand and therefore the major contributions to EFISH  $\beta$  are those involving the mixed MLCT–ILCT transitions going from the phenyl to the pyridine in the phenylpyridine cyclometalated ligand.<sup>3c</sup> In marked contrast, in complexes 1–3, the calculated dipole moment has the major contribution along the styryl moiety as shown in Figure 1, and the EFISH  $\beta$  value is dominated by ILCT transitions of the styryl moiety. In complex 4 the calculated dipole moment is almost perpendicular to the styryl moiety and the NLO response can reasonably be attributed to MLCT transitions.

In addition, it appears that the value of  $\mu\beta_{1,907}^{\text{EFISH}}$  of the complexes increases ( $4 < 1 < 2 < 3$ ) on increases in the electron-donating properties of the substituent of the 4-styryl-2-phenylpyridine ligand ( $\text{NO}_2 < \text{H} < \text{OMe} < \text{NEt}_2$ ), a trend in agreement with previous reports,<sup>6</sup> but this is mainly due to an increase of the ground state dipole moment (Table 1). Finally it is interesting to point out that complex 2 has a  $\mu\beta_{1,907}^{\text{EFISH}}$  value almost 4 times higher than that of the related free 4-styryl-2-phenylpyridine ligand bearing a methoxy group ( $\mu\beta_{1,907}^{\text{EFISH}} = 370 \times 10^{-48}$  esu), showing how cyclometalation to a platinum(II) center is a way to increase the second-order NLO response.

From an NLO application point of view, complex 3 is of particular interest due to its high  $\mu\beta_{1,907}^{\text{EFISH}}$  value. Therefore, we produced a composite film of complex 3 in poly(methyl methacrylate) (PMMA) and studied the second harmonic generation (SHG) signal of the resulting poled host–guest system (see the Experimental Section).

The corona-wire poling dynamic of the SHG behavior of a PMMA film containing complex 3 is reported in Figure 2. The SHG was negligible at room temperature, but it quickly increased within 1–2 s after application of the electric field (8.5 kV). When the temperature was increased up to 62 °C, we observed a large increase of the SHG, as expected for a decrease of the polymeric matrix viscosity, which allows a more facile orientation of the dipolar NLO chromophores. Once the second harmonic signal had stabilized, the sample was cooled and the drybox opened when room temperature was reached. The final switching off of the electric field caused a small drop of the SHG.

Figure 3 shows the electronic absorption spectra of a PMMA film containing complex 3 recorded before and after the poling process. No appreciable Stark shift of the main absorption peak is observed after poling, whereas the decrease of its intensity is probably due to a dichroism effect, originated by the chromophore reorientation,<sup>7</sup> since no significant sublimation of the chromophore was observed during the poling experiments.

The second-order NLO coefficient matrix values  $d_{ij}$  for poled films ( $C_{\infty v}$  symmetry) were obtained by following the standard Maker fringe technique.<sup>8,9</sup> The SHG signal was normalized with respect to that of a calibrated quartz crystal wafer (X-cut) of 1 mm thickness whose  $d_{11}$  value is 0.46 pm/V. In Table 2 we present the  $d_{ij}$  values calculated by fitting the Maker fringe measurements of the different polarizations:  $p \rightarrow p$ ,  $s \rightarrow p$ , and  $45 \rightarrow s$ ;<sup>8</sup> the error in these data can be estimated as <20%.

Table 2 shows that the  $d_{33}$  value tends to stabilize after 1 week, while the decrease from 4.22 to 2.81 pm/V 1 day after the poling is probably due to the neutralization of the surface charges present on the film after the corona-wire poling

**Table 2.** Values of the NLO Coefficient Matrix  $d_{ij}$  for the Poled Composite Film of Complex 3 in PMMA

	$d_{15}$ (pm/V)	$d_{31}$ (pm/V)	$d_{33}$ (pm/V)
after poling	0.74	0.76	4.22
1 day after poling	0.51	0.56	2.81
1 week after poling	0.45	0.47	2.33 <sup>a</sup>

<sup>a</sup>After 3 months the  $d_{33}$  value was 1.40 pm/V.

process.<sup>10</sup> Moreover, since there is no absorption at 532 nm for the composite film of complex 3, we can observe that the Kleinman symmetry<sup>11</sup> ( $d_{31} \approx d_{15}$ ) is satisfied (from Table 2).

In many works<sup>12</sup> it was reported that the SHG signal of various chromophores in PMMA matrix progressively faded due to a loss of orientation of the NLO dyes, and this is not surprising if the  $\beta$  transition of PMMA, which has been attributed to rotation of the ester side group,<sup>13</sup> is considered. For example, recently some of us found that the SHG signal of diarylethene chromophores in PMMA matrix rapidly faded, becoming too low to be detectable after a few hours.<sup>14</sup> A much better SHG stability of host–guest PMMA films could be reached with NLO active organic chromophores linked on a cyclotetrasiloxane scaffold, due to the relatively large size of the macrocycle, but the  $d_{33}$  value was low.<sup>15</sup> Remarkably, the  $d_{33}$  value of the composite PMMA film containing the simple complex 3 is high and rather stable, the signal after 3 months being 60% of that of the signal after 1 week.

## CONCLUSION

In summary, Pt(II) acetylacetonate complexes bearing a variously substituted cyclometalated 4-styryl-2-phenylpyridine (ppy-4-styryl-R, with R =  $\text{NEt}_2$ , OMe, H,  $\text{NO}_2$ ) are interesting second-order NLO chromophores whose NLO response can be easily modulated by the nature of the styryl substituent. An increase of the donor strength of the styryl substituent leads to an increase of the dipole moment and therefore to large values of  $\mu\beta_{1,907}^{\text{EFISH}}$ , the best response being for the Pt(II) chromophore bearing the ppy-4-styryl- $\text{NEt}_2$  ligand. Remarkably, the latter complex can be easily dispersed and oriented by poling in a poly(methyl methacrylate) (PMMA) matrix, affording a host–guest composite film characterized by a good and surprisingly stable second harmonic generation (SHG) signal. Clearly, organometallic complexes are excellent candidates for the preparation of convenient host–guest SHG active polymeric films with a stable response.

## ASSOCIATED CONTENT

### Supporting Information

Text, figures, and tables giving computational details, MO diagrams of the investigated complexes, frontier MO energies, DFT computed ground state dipole moments, and CAM-B3LYP simulated absorption spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.



## ■ ACKNOWLEDGMENTS

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