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Functionalized styryl Iridium(III) complexes as active second-order NLO chromophores and building blocks for SHG polymeric films.

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Abstract

We studied the second-order NLO properties in solution of various Ir(III) acetylacetonate complexes bearing a substituted cyclometallated 4-styryl-2-phenylpyridine (ppy-4-styryl-R, with R = NEt₂, OMe, H, NO₂) with the EFISH technique. The dipole moments were evaluated by Density Functional Theory (DFT) calculations.

We have also investigated the Second Harmonic Generation (SHG) of composite films based on the various cyclometallated Ir(III) complexes dispersed and oriented in a polymethylmethacrylate (PMMA) matrix.

Keywords: Second-order nonlinear optics; EFISH; Second Harmonic Generation; cyclometallated Iridium(III) complexes.

1. Introduction

Organometallic complexes with both luminescent and second-order nonlinear optical (NLO) properties are of great interest as multifunctional materials, as they may offer additional flexibility, when compared to organic NLO chromophores, by introducing new NLO active electronic charge-transfer transitions between the metal and the ligand, tuneable by virtue of the nature, oxidation state and coordination sphere of the metal centre. [1,2]

Cyclometallating ligands are routinely incorporated in neutral Ir(III) complexes for organic light-emitting diodes (OLEDs), [3] and in cationic complexes for organic light-emitting electrochemical cells (OLECs). [4] More recently, cyclometallating ligands have also been used to give stability to Ir(III) complexes for dye-sensitized solar cells (DSSCs). [5] Whereas cyclometallated Ir(III) complexes have been intensively studied for their interesting luminescent properties, to our knowledge, only a few reports appeared in the literature on the NLO properties of cationic complexes [6] and of neutral complexes. [7] As concern neutral complexes, the second order nonlinear optical (NLO) response of various simple tris-cyclometallated Ir(III) complexes bearing 2-phenylpyridine ligands [7c, 7d] have been studied by means of the Electric Field Induced Second Harmonic generation (EFISH) technique, [8] evidencing how an appropriate substitution of the cyclometallated ligands may allow the tuning of the second-order NLO response of this unusual family of 3D chromophores. Some of us studied the interesting EFISH response of the simple luminescent Ir(III) complex [Ir(cyclometallated 2-phenylpyridine)₂(acetylacetonate)] [7a] that shows an unexpected large second order nonlinear optical response ($\mu\beta_{1,907} = -910 \times 10^{-48}$ esu), attributed by an SOS-TDDFT investigation mainly to intraligand charge transfer transitions involving the cyclometallated ligand. [7a] These results prompted us to investigate the effect of an increase of the π -delocalization of the phenylpyridine and of the addition of electron-withdrawing or electron-donor groups on the quadratic hyperpolarizability of this kind of complexes.

Therefore, we prepared various Ir(III) acetylacetonate complexes bearing a substituted cyclometallated 4-styryl-2-phenylpyridine (ppy-4-styryl-R, with R = NEt₂, OMe, H, NO₂, see Figure 1), recently studied for their interesting luminescent properties. [9] Their second order NLO properties were measured in solution through the EFISH technique, working with an incident and non resonant wavelength of 1907 nm. The dipole moments were evaluated by Density Functional Theory (DFT) calculations.

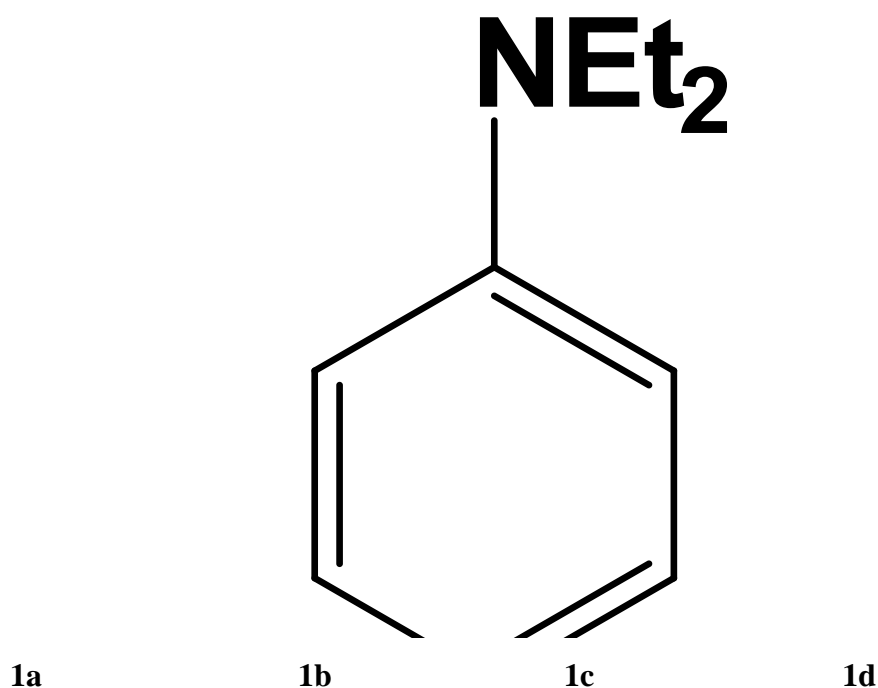


Figure 1. Various Ir(III) complexes investigated in the present work.

We have also investigated the Second Harmonic Generation (SHG) of composite films based on the various cyclometallated Ir(III) complexes dispersed and oriented in a polymethylmethacrylate (PMMA) matrix.

2. Experimental section

2.1 General Information

All 2-phenylpyridine ligands and related cyclometallated Ir(III) complexes $[\text{Ir}(\text{C}^{\wedge}\text{N-ppy-4-CH=CHC}_6\text{H}_4\text{R})_2(\text{acac})]$ (acac = acetylacetonate; R = OMe, NEt₂, H, NO₂) were prepared as previously described. [9]

2.4 DFT computations

DFT computations have been carried out in order to determine the geometrical and electronic structures of the complexes under consideration. The PBE0 hybrid functional [10] has been chosen with the LanL2DZ basis set [11] augmented with polarization functions on all atoms, except hydrogen ones. The optimizations of the geometries were first carried out; the optimized geometries of all species were characterized as true minima on the potential energy surfaces using vibration

frequency calculations. The used program for the DFT is Gaussian 09. [12] Representations of molecular structures and dipole moment were done using the Molekel program. [13] Solvent (CH_2Cl_2) effects have been taken into account using the PCM model. [14] (Optimized coordinates in Supporting Information).

2.2 EFISH measurements

All EFISH measurements [8] were carried out at the Dipartimento di Chimica of the Università degli Studi di Milano, in CH_2Cl_2 solutions at a concentration of 1×10^{-3} M, working with a non-resonant incident wavelength of 1.907 μm , obtained by Raman-shifting the fundamental 1.064 μm wavelength produced by a Q-switched, mode-locked Nd^{3+} :YAG laser manufactured by Atalaser. 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 (CH_2Cl_2).

2.3 Preparation of films of Ir(III) complexes in PMMA and related SHG measurements

Composite films were produced by spin coating on ordinary non-pretreated glass substrates (thickness 1 mm) previously cleaned with water/acetone. The solution was obtained from 400 mg of polymethylmethacrylate (PMMA) and 24 mg of the complex dissolved in dichloromethane (3.5 mL).

Parameters of spinning (RPM = revolutions per minute) RPM 1 : 700; Ramp 1 : 1 s, Time 1 : 5 s; RPM 2 : 1000; Ramp 2 : 5 s, Time 2 : 10 s; RPM 3 : 1000; Ramp 3 : 1 s, Time 3 : 10 s.

The film thickness of composite PMMA/complexes was measured by the profilometry 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 1.064 μm 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 dry box, in N_2 atmosphere. The fundamental beam was polarized in the plane of incidence (p-polarized) with an angle of about 55° with respect to the sample in order to optimize the SHG signal. The hot stage temperature was controlled by a GEFTRAN 800 controller, while the coronawire voltage (up to 9.0 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 cut-off filter, the p-polarized SHG signal at 532 nm was detected with

a UV-Vis photomultiplier (PT) Hamamatsu C3830. The setup for Maker fringe measurements was similar to the previous except that the fundamental beam was attenuated to 1 mJ and the sample was placed over a rotation stage. [2h, 15]

3. Results and discussion

3.1 Investigation of the second order nonlinear optical (NLO) properties in solution

All 2-phenylpyridine ligands and related cyclometallated Ir(III) complexes $[\text{Ir}(\text{C}^{\wedge}\text{N}\text{-ppy-4-CH=CHC}_6\text{H}_4\text{R})_2(\text{acac})]$ (acac = acetylacetonate; R = OMe, NEt₂, H, NO₂, see Figure 1) were prepared as previously reported. [9]

The known absorption spectra [9] of the complexes are reported in Table 1, together with the data of the reference complex $[\text{Ir}(\text{ppy})_2(\text{acac})]$. [7a] The absorption features originate mainly from $\text{Ir}(\text{C}^{\wedge}\text{N})_2$ moieties. [7a, 9]

The molecular quadratic hyperpolarizabilities of all $[\text{Ir}(\text{C}^{\wedge}\text{N}\text{-ppy-4-CH=CHC}_6\text{H}_4\text{R})_2(\text{acac})]$ complexes were measured by the solution-phase dc Electric Field Induced Second Harmonic (EFISH) generation method [8] which can provide direct information on the intrinsic molecular NLO properties through equation (1):

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

where $\mu\beta_{\lambda}/5\kappa T$ represents the dipolar orientational contribution and $\gamma(-2\omega; \omega, \omega, 0)$, a third order term at frequency ω of the incident light, is the electronic contribution to γ_{EFISH} which is negligible for the kind of molecules here investigated. [2] β_{λ} is the projection along the dipole moment axis of the vectorial component of the tensor of the quadratic hyperpolarizability, working with an incident wavelength λ . All EFISH data are reported in Table I.

Table I. Electronic spectra, $\mu\beta_{1.907 \text{ EFISH}}$, μ and $\beta_{1.907 \text{ EFISH}}$ of the investigated Ir(III) complexes in CH_2Cl_2 solution.

Complex	λ_{max} (nm) ^a ($\epsilon/M^{-1} \text{ cm}^{-1}$)	$\mu\beta_{1.907 \text{ EFISH}}$ ^b ($\times 10^{-48}$) esu	$\mu^{\text{b,c}}$ ($\times 10^{-18}$) esu	$\beta_{1.907 \text{ EFISH}}$ ($\times 10^{-30}$) esu
[Ir(ppy)₂(acac)]^d	260 (45000), 345 (38000), 412 (34000), 460 (33000), 497 (30000) ^d	-910 ^d	4.00 ^d	-228 ^d
1a	265 (62000), 410 (23000), 433 (26000), 480 sh (5500)	-550	3.73	-147
1b	270 (40000), 330 (45000), 373 (39000), 415 sh (21000), 475 (5300)	-570	5.90	-97
1c	268 (44000), 306 (45000), 370 (25000), 410 sh (12000), 468 (4700)	-408	3.55	-115
1d	263 (38000), 282 (36000), 332 (48000), 400 (33000), 442 sh (18000), 518 (5200)	-895	3.77 ^e	-237

^a From Reference 9, in CH_2Cl_2 . ^b Data from present work; estimated uncertainty in EFISH measurements is $\pm 10\%$. ^c Computed dipole moments. ^d From Reference 7a in CHCl_3 . ^e The experimental dipole moment μ in CHCl_3 solution is 3.6 D (+/- 1 D), measured with the Guggenheim method [16].

Similarly to the parent complex $[\text{Ir}(\text{ppy})_2(\text{acac})]$, [7a] all the four complexes investigated (**1a-1d**) are characterized by a negative value of $\mu\beta_{1.907 \text{ EFISH}}$, in agreement with a negative value of $\Delta\mu_{\text{eg}}$ (difference of the dipole moment in the excited and ground state) upon excitation. [2] The direction of ground state dipole moments are reported in Figure 2.

As expected, the dipole moments are directed along the pseudo C_2 axis exhibited by all molecules. As shown in Table I, the values of the dipole moments for all complexes are rather small and of the same order of magnitude. [17] They are quite similar except that of **1b** which is a bit higher.

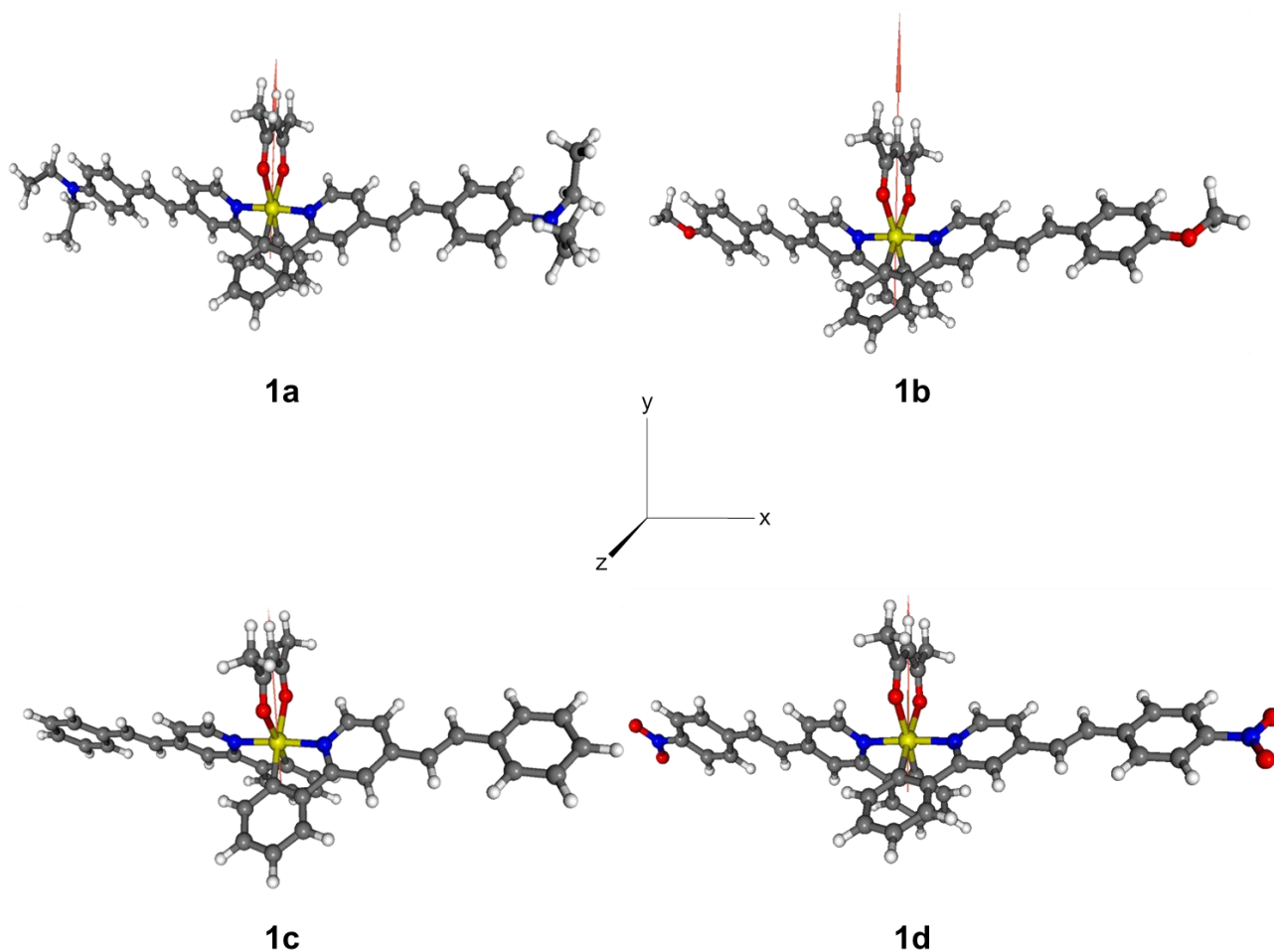


Figure 2. Graphical orientation of the computed dipole moments (red arrow).

The $\mu\beta_{1.907 \text{ EFISH}}$ values of complexes **1a**, **1b** and **1c** are quite similar, whereas the absolute value of **1d** is higher and similar to that previously reported [7a] for $[\text{Ir}(\text{ppy})_2(\text{acac})]$. The same trend is found for $\beta_{1.907 \text{ EFISH}}$. In these Ir(III) complexes the second-order NLO response is originated from various charge transfer transitions and the observed negative value of $\beta_{1.907 \text{ EFISH}}$ is the result of positive and negative contributions to the quadratic hyperpolarizability, as evidenced for similar complexes. [7a]

3.2 Investigation of the second order nonlinear optical (NLO) properties of composite films

The corona wire poling dynamic of the SHG behaviour of PMMA composite films were performed using the following parameters: poling temperature: 50°C with an electric field of 9 kV hold for 1 hour.

First of all, we have performed poling measurements on composite films of $[\text{Ir}(\text{ppy})_2(\text{acac})]$ in PMMA matrix. Unfortunately, the second harmonic signal, already low at the beginning in arbitrary units, rapidly (about two hours) fell down upon turning off the electric field.

A similar behaviour, with a low and unstable SHG, was observed for the film based on complex **1d** although it presents one of the highest $\mu\beta_{1.907}^{\text{EFISH}}$ value of the complexes investigated.

On the contrary interesting results were obtained with complex **1a**. The corona wire poling dynamic of the SHG behaviour of a PMMA film containing this complex is reported in Figure 3. The thickness of the film was 800 nm, as measured with a profilometer.

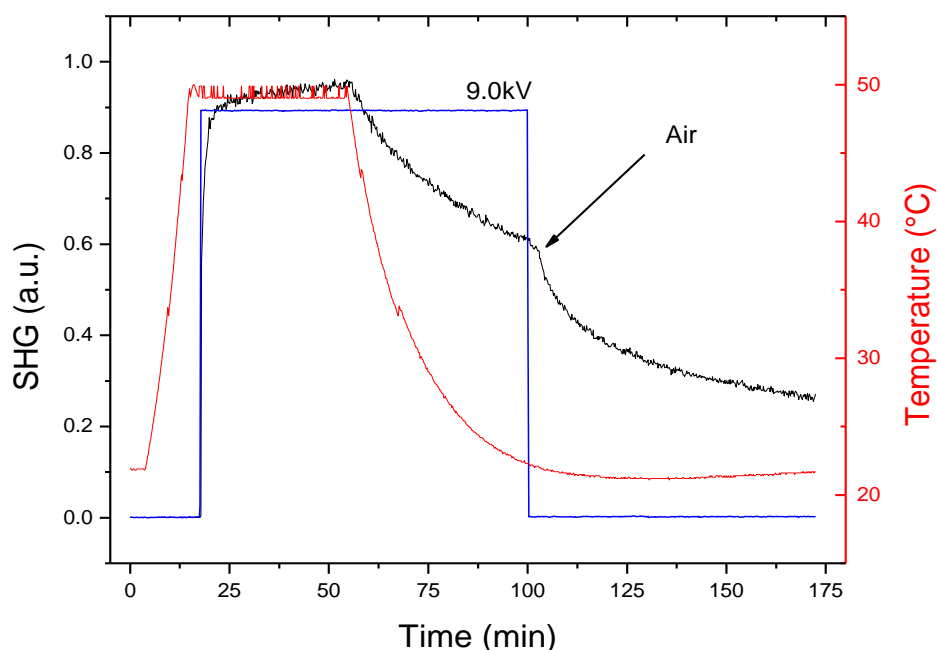


Figure 3. In situ corona wire poling dynamic of PMMA film containing complex **1a**.

The SHG was negligible at room temperature, but it quickly increased after application of the electric field (9 kV) at 50°C, as expected for the 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 dry box opened when room temperature was reached.

The final switch off of the electric field caused a drop of the SHG, in fact after about 1 hour the SHG signal was decreased of 56 %. Differently from what happened for $[\text{Ir}(\text{ppy})_2(\text{acac})]$ and complex **1d**, the signal didn't fall to zero, thus allowing to perform the Maker Fringe measurements.

Figure 4 shows the electronic absorption spectra of a PMMA film containing complex **1a** 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, [18] since no significant sublimation of the chromophore was observed during the poling experiments.

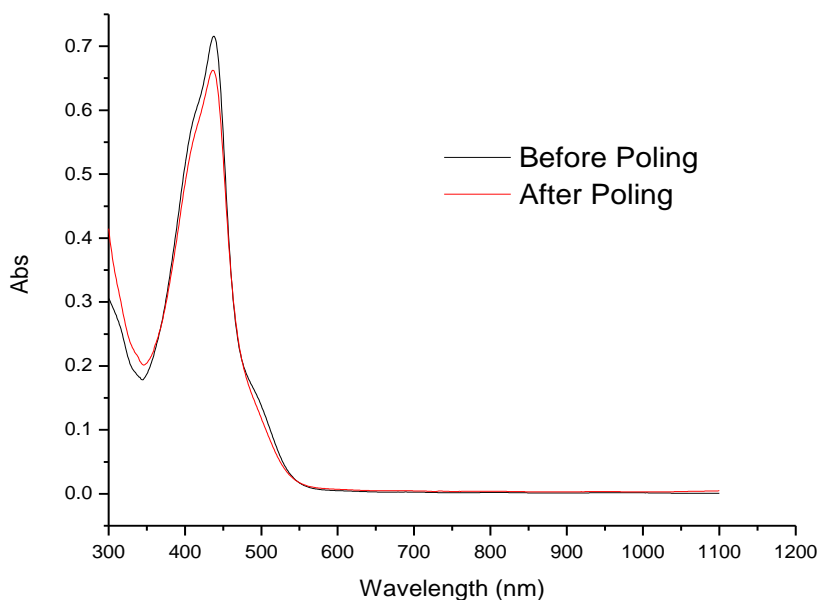


Figure 4. Absorption spectra of a PMMA film containing complex **1a** before and after poling.

The second order NLO coefficient matrix values d_{ij} for poled films ($C_{\infty v}$ symmetry) were obtained, after poling, by following the standard Maker fringe technique. [15] The SHG signal was normalized with respect to that of a calibrated quartz crystal wafer (X-cut) 1 mm thick whose d_{11} is 0.46 pm/V. The d_{ij} values were calculated by fitting the Maker fringe measurements of the different polarizations: $p \rightarrow p$, $s \rightarrow p$, and $45 \rightarrow s$, [15a] the error in these data being estimated as <20%. Since there is no absorption at 532 nm for the composite film of complex **1a**, the Kleinman's symmetry₁₀ ($d_{31} \approx d_{15}$) is satisfied.

The values obtained for the composite PMMA film containing complex **1a** are: $d_{31} = 0.31$ pm/V, $d_{15} = 0.31$ pm/V and $d_{33} = 1.52$ pm/V. The latter value is remarkably high for such a simple complex.

Conclusion

In summary, cyclometallated Ir(III) complexes bearing a variously substituted 2-phenylpyridine (ppy-4-styryl-R, with R = NEt₂, OMe, H, NO₂) are interesting second-order NLO chromophores.

Our work puts in evidence the important role and the influence of the nature of the 2-phenylpyridines' substituent on the SHG performance of the related composite film in PMMA. Interestingly, the best SHG efficiency is reached with the complex having a styryl group bearing a NEt_2 group although its quadratic hyperpolarizability in solution is lower than that of the related complex with a styryl group having a nitro group or that of $[\text{Ir}(\text{ppy})_2(\text{acac})]$. Clearly these organometallic complexes are excellent candidates for the preparation of convenient NLO active polymeric films.

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