A novel multifunctional cyclometallated iridium(III) complex with interesting second-order nonlinear optical properties and two-photon absorption activity.

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Abstract

A novel cationic cyclometallated Ir(III) complex, namely [Ir(C^N-ppy-4-CH=CHC$_6$H$_4$NEt$_2$)$_2$(N^N-bpy-CH=CHC$_6$H$_4$NEt$_2$)] (ppy= 2-phenylpyridine; bpy= 2,2'-bipyridine), was prepared and well characterized. Its good second-order NLO response, as determined in solution by the EFISH technique, and its interesting two-photon absorption activity, as measured by the Z-scan technique in the femtosecond case, make it a good candidate for application in photonics and biomedicine.

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Introduction

Coordination compounds 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 often incorporated in Ir(III) complexes for various applications such as in organic light-emitting diodes (OLEDs) [3], light-emitting electrochemical cells (LEECs) [4], and 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 their second-order NLO properties [6, 7] or two-photon absorption (TPA) activity [8-11]. Yet, two-photon absorbing materials having large two-photon absorption cross-section (σ), especially in the near-infrared (NIR) region, are required for photodynamic therapy, bio-imaging, upconversion lasing and drug delivery [9] whereas the design of novel second-order NLO active compounds is crucial for many applications in the fields of optical communication and data processing [2]. Beeby and co-workers reported a series of iridium(III) acetylacetonate complexes, bearing two cyclometallated substituted 2-phenylpyridines, characterized by fair values of TPA cross sections (approximatively 20 GM) [10]. Another report concerning iridium complexes of a terpyridyl-stilbene system demonstrated TPA cross-sections in the range of 10-70 GM [11]. More recently, Das and co-workers reported the synthesis of cyclometallated iridium(III) complexes containing two cyclometallated unsubstituted 2-phenylpyridines and a 2,2'-bipyridine bearing highly π-delocalized substituents with TPA cross-sections in the range of 45-196 GM in the femtosecond case [8c]. Besides, some of us reported that iridium(III) acetylacetonate complexes bearing two substituted cyclometallated 4-styryl-2-phenylpyridines are characterized by a good second-order NLO response [7f], as determined by means of the Electric Field Induced Second Harmonic generation (EFISH) technique [12]. Remarkably, the simple luminescent cyclometallated Ir(III) complex [Ir(C^N-ppy-4-CH=CHC$_6$H$_4$NEt$_2$)$_2$(acetylacetonate)] (ppy = 2-phenylpyridine) [13] shows a $\mu\beta_{1.907}$ = -550 x 10^{-48} esu and is a useful tool for the preparation of NLO active polymeric films [7f]. These interesting results prompted us to investigate the effect of the substitution of the acetylacetonate ligand by a π-delocalized bipyridine incorporating electron-donor substituents on the second-order NLO response. Therefore, we prepared the novel cationic cyclometallated

Ir(III) complex [Ir(C^N-ppy-4-CH=CHC$_6$H$_4$NEt$_2$)$_2$(N^N-bpy-CH=CHC$_6$H$_4$NEt$_2$)] (**5**) (bpy=bipyridine; Figure 1) and studied its luminescent and NLO properties. Its second-order NLO response was measured in solution through the EFISH technique, working with an incident and non resonant wavelength of 1907 nm, whereas its two-photon absorption activity was evaluated by the Z-scan technique in the femtosecond case.
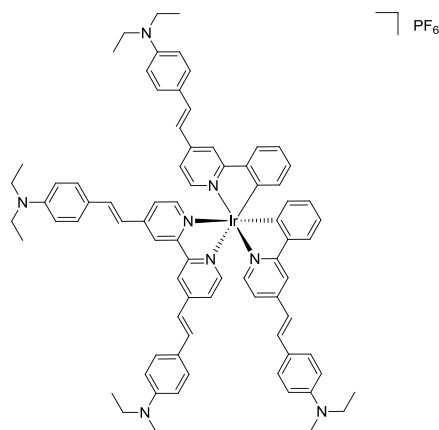

Figure 1. Investigated cyclometallated Ir(III) complex (**5**)

Material and methods

Synthesis

General comments

All reagents were purchased from Sigma-Aldrich and were used without further purification. Reactions requiring anhydrous conditions were performed under nitrogen. ^{1}H NMR spectra were recorded at 400 MHz on a Bruker AVANCE-400 instrument; chemical shifts (δ) are expressed in ppm relative to internal Me$_4$Si as standard; signals were abbreviated as s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The UV-Vis spectra of the samples solution in dichloromethane were recorded by a *Shimadzu UV-3150* spectrometer using 1 cm quartz cells.

4-methyl-2-phenylpyridine (1). An excess of lithium (1.82 g, 272 mmol) was suspended in 40 mL of Et$_2$O. The suspension was cooled down to 0°C and bromobenzene (21.34 g, 136 mmol) in 50 mL of Et$_2$O was added dropwise during 20 minutes. The reaction mixture was stirred overnight at room temperature. The freshly-prepared phenyllithium was added dropwise to a solution of 4-picoline (3.16 g, 34 mmol) in 90 mL toluene. The reaction was stirred at 30°C for 24 hours, distilled water was added dropwise, the residue was extracted with CH$_2$Cl$_2$, washed with water, dried over MgSO$_4$ and the solvent was removed under

reduced pressure. The product was purified by column chromatography (silica, n-heptane:AcOEt=9:1) to afford **1** as an orange/brown solid (2.44 g). Yield: 42%. ^{1}H-NMR (400 MHz, CDCl$_3$) δ (ppm): 8.58 (1H, d, J = 5.0 Hz), 8.00 (2H, d, J = 7.2 Hz), 7.57 (1H, s), 7.49 (2H, t, J = 7.4 Hz), 7.43 (1H, t, J = 7.2 Hz), 7.08 (1H, d, J = 4.9 Hz), 2.44 (3H, s).

4-*N*,*N*-diethylminostyryl-2-phenylpyridine (2). 4-Methyl-2-phenylpyridine (500 mg, 2.96 mmol), 4-*N*,*N*-diethylaminobenzaldehyde (620 mg, 3.5 mmol) and t-BuOK (700 mg, 6.2 mmol) were dissolved in DMF (20 mL). The reaction mixture was heated at reflux overnight, then CH$_2$Cl$_2$ (150 mL) was added. The organic phase was washed first with water and then with an aqueous solution of 1 M KOH, dried with MgSO$_4$ and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica, CH$_2$Cl$_2$:petroleum ether = 7:3) to obtain **2** as a yellow powder (546 mg). Yield: 56%. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.61 (1H, d, J = 5.2 Hz), 8.06 (2H, d, J = 7.2 Hz), 7.75 (1H, s) 7.51 (2H, t, J = 7.4 Hz), 7.45 (3H, d, J = 8.5 Hz), 7.30 (1H, d, J = 16.3 Hz), 7.26 (1H, m), 6.86 (1H, d, J = 16.2 Hz), 6.68 (2H, d, J = 8.8 Hz), 3.40 (4H, q, J = 7.1 Hz), 1.20 (6H, t, J = 7.0 Hz).

[Ir(C^N-ppy-4-CH=CHC$_6$H$_4$NEt$_2$)$_2$Cl]$_2$ (3). IrCl$_3$ • 3H$_2$O (165 mg, 0.55 mmol) and **2** (550 mg, 1.66 mmol) were suspended in a mixture of 2-ethoxyethanol:H$_2$O 3:1 (16 mL) in a Schlenk tube under inert atmosphere. The reaction mixture was heated at reflux for 24 h. The precipitate was decanted by centrifugation and the solid product was then washed successively with H$_2$O, EtOH and Et$_2$O. The solvent was removed with cannula to afford **3** as an orange powder (290 mg). Yield: 30%. ^{1}H-NMR (400 MHz, CD$_2$Cl$_2$) δ (ppm): 9.12 (4H, d, J = 5.9 Hz), 7.94 (4H, s), 7.63 (4H, d, J = 7.1 Hz), 7.41 (12H, m), 7.04 (4H, d, J = 16 Hz), 6.93 (4H, m), 6.83 (4H, t, J = 7.0 Hz), 6.64 (12H, m), 6.05 (4H, d, J = 8.0 Hz), 3.48 (16H, q, J = 6.8 Hz), 1.25 (24H, t, J = 6.8 Hz).

4,4'-*p*-[(*N*,*N*-diethyl)aminostyryl]-2,2'-bipyridine (4). Diisopropylamine (607.1 mg, 6 mmol) was dissolved in THF (2.5 mL) in a Schlenk tube and the mixture was cooled to 0°C. A n-BuLi solution (1.6 M in hexane, 3.75 mL, 6 mmol) was added slowly. After stirring one hour, the solution was cooled to -78°C and 4,4'-dimethyl-2,2'-bipyridine (501.1 mg, 2.72 mmol) in THF (13 mL) was added dropwise and the mixture stirred at low temperature for 2 hours. p-(N,N-diethyl)aminobenzaldehyde (957.1 mg, 5.4 mmol) was dissolved in 6 mL of THF (6 mL) and added slowly. The resulting mixture was stirred for one hour at low temperature and overnight at room temperature. After hydrolyzing with distilled water (12 mL), the phases were separated, the organic phase was dried over MgSO$_4$, filtered and the solvent was removed under reduced pressure. The dialcohol was dissolved in toluene (40 mL)

in a round-bottomed flask and pyridinium *p*-toluenesulfonate (PPTS, 67.6 mg, 0.27mmol) was added. The mixture was heated at reflux for 4 hours. After cooling to room temperature, the solvent was removed under reduced pressure and dichloromethane (16 mL) was added. The mixture was washed with a saturated solution of $NaHCO_3$. The precipitated bipyridine was filtered, abundantly washed first with H_2O and then with Et_2O to obtain **4** as an orange powder (970 mg). Yield: 71%. ^{1}H-NMR (400 MHz, CD_3Cl) δ (ppm): 8.63 (2H, d, *J* = 5.1 Hz), 8.48 (2H, s), 7.47 (4H, d, *J* = 8.9 Hz), 7.42 (2H, d, *J* = 16.2 Hz), 7.36 (2H, dd, *J* = 5.3, 1.8 Hz), 6.92 (2H, d, *J* = 16.2 Hz), 6.71 (4H, d, J = 8.9 Hz), 3.43 (8H, q, *J* = 7.1 Hz), 1.22 (12 H, t, *J* = 7.1 Hz).

[Ir(C^N-ppy-4-CH=CHC$_6$H$_4$NEt$_2$)$_2$(N^N-bpy-CH=CHC$_6$H$_4$NEt$_2$)][PF$_6$] (5). A suspension of **3** (250 mg, 0.14 mmol), **4** (178 mg, 0.35 mmol) and $AgPF_6$ (88 mg, 0.35 mmol) in 1,2-dichloroethane (20 mL) was kept at reflux for 2 hours and stirred at room temperature for 16 hours. The solvent was removed under reduced pressure leaving a residue which was washed with Et_2O (3 x 20 mL). The compound was precipitated from Et_2O/CH_2Cl_2 giving the desired complex (5) as a red solid after filtration (50 mg). Yield: 13%. ^{1}H NMR (500 MHz, CD_2Cl_2) δ (ppm): 8.32 (2H, s), 7.93 (2H, s), 7.84 (2H, d, *J* = 5.7 Hz), 7.80 (2H, d, *J* = 7.4 Hz), 7.42 (18H, m,), 7.08 (2H, t, *J* = 7.7 Hz), 7.02 (2H, d, *J* = 4.5 Hz), 6.95 (4H, m), 6.86 (2H, d, *J* = 16.0 Hz), 6.68 (8H, dd, *J* = 16, 8.9 Hz), 6.46 (2H, d, *J* = 7.9 Hz), 3.41 (16H, m), 1.20 (24H, m). Elem. Anal. Calcd for $C_{80}H_{84}F_6IrN_7P$: C,71.19; H, 6.27; N, 8.30. Found: C, 71.65; H, 6.28; N, 8.33.

EFISH measurements

EFISH measurements [12] were carried out at the Dipartimento di Chimica of the Università di Milano, in CH_2Cl_2 solutions at a concentration of 1 x 10^{-3} M, working with an incident non-resonant 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 reported μβ$_{EFISH}$ values are the mean values of 16 successive measurements performed on the same sample. The sign of μβ is determined by comparison with the reference solvent (CH_2Cl_2).

Two-photon absorption activity measurements

All open-aperture Z-scan measurements [13] were performed at AIST in Osaka, for the solution of the complex **5** held in a 2-mm quartz cuvette. The setup for the Z-scan

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measurements were reported elsewhere [14]. A femtosecond, wavelength-tunable laser (optical parametric amplifier, *SpectraPhysics TOPAS Prime*) was employed as light source to obtain the spectrum. Typical pulsewidth was 120 fs and the repetition rate was 1 kHz. First, the outline of the TPA spectrum was measured at a single excitation power (0.4 mW, corresponding to the on-axis optical intensity at the focal point of 99-150 GW/cm^2) by assuming that the observed open-aperture Z-scan signal originates from the TPA process (open dots in Fig. 4). Then the assumption was confirmed and the precise value of the TPA cross section ($\sigma^{(2)}$) were obtained by changing the excitation power (filled dots with experimental errors in Fig. 4). Finally, the relative TPA spectrum (open dots) were superimposed the absolute TPA spectrum (filled dots). For all measurements, in-house standard compounds (MPPBT [15] in DMSO) was measured at the same condition and used for the spectral correction of $\sigma^{(2)}$.

Results and Discussion

The complex $[Ir(C^\wedge N\text{-ppy-4-}CH=CHC_6H_4NEt_2)_2(N^\wedge N\text{-bpy-}CH=CHC_6H_4NEt_2)][PF_6]$ (**5**) was prepared as shown in Figure 2.
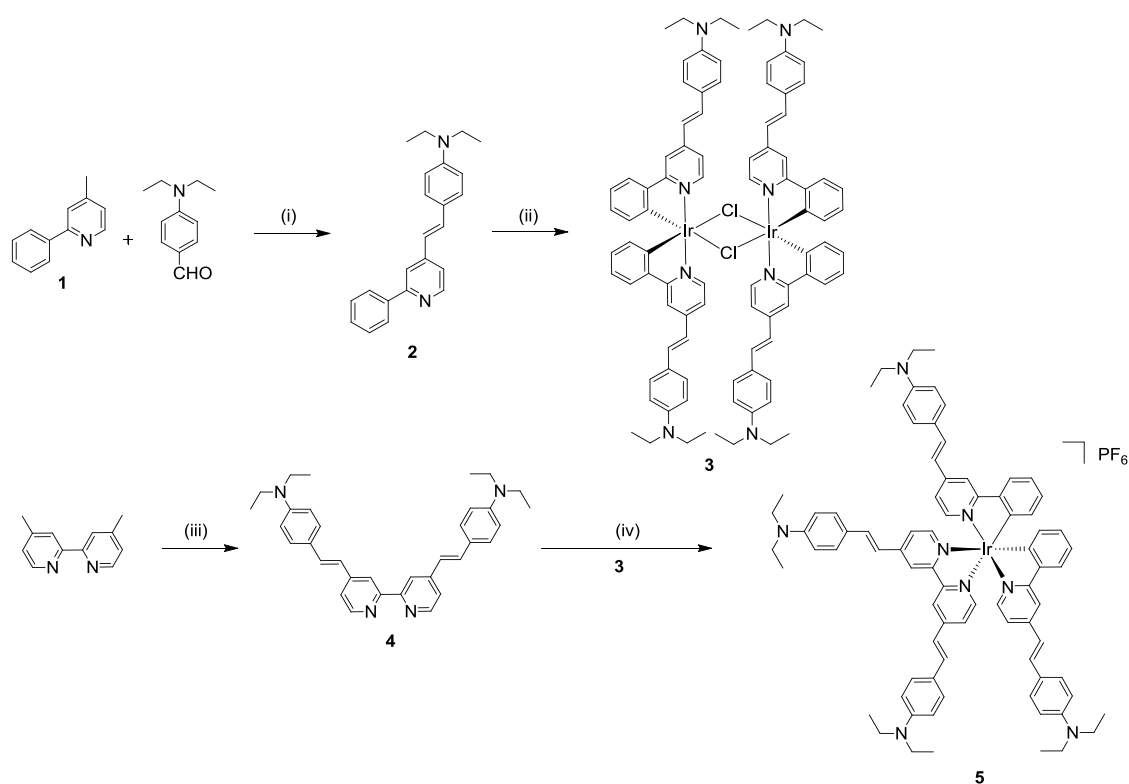
Figure 2. (i) t-BuOK, DMF, 155°C, 15 h; (ii) IrCl$_3$·3H$_2$O, 2-ethoxyethanol/H$_2$O, 100°C, 24 h; (iii) a) n-BuLi, iPr$_2$NH, p-(N,N-diethyl)aminobenzaldehyde, THF, 0°C → -78°C → rt, 15 h; b) PPTS, toluene, 110°C, 4 h; (iv) AgPF$_6$, 1,2-dichloroethane, 84°C, 2 h → rt, 15 h.

The pro-ligand 4-(*N,N*-diethyl)aminostyryl-2-phenylpyridine (**2**) was readily prepared upon deprotonation of the methyl group of 4-methyl-2-phenylpyridine, obtained by reaction of phenyllithium with 4-picoline, followed by condensation with *p*-(*N,N*-diethyl)aminobenzaldehyde, as previously reported [16]. Heating at reflux this pro-ligand with $IrCl_3 \cdot 3H_2O$ in a 2-ethoxyethanol:H_2O 3:1 mixture for 24 h afforded the related μ-dichloro-bridged cyclometallated iridium dimer intermediate (**3**) [16]. The ancillary ligand 4,4'-*p*-[(*N,N*-diethyl)aminostyryl]-2,2'-bipyridine (**4**) was prepared like **2** but starting from 4,4'-dimethyl-2,2'bipyridine [17]. The desired complex (**5**) was finally obtained by refluxing in 1,2-dichloroethane for 2 hours this π-delocalized substituted bipyridine with the μ-dichloro-bridged cyclometallated iridium dimer. It was obtained as a dark red powder and well characterized (see Material and methods).

The absorption spectrum of complex **5** was registered both in dichloromethane and dimethyl sulfoxide (DMSO, Figure 3a) whereas the photophysical data are listed in Table 1. By analogy with other cationic iridium(III) complexes bearing two cyclometallated phenylpyridines and a bipyridine [6e], the absorption bands under 350 nm can reasonably be assigned to $^1(\pi\text{-}\pi^*)$ transitions of the styrylphenylpyridine and styrylbipyridine ligands, the intense band between 350 and 550 nm can be assigned to an Intra-Ligand Charge Transfer (ILCT) transition in which the pyridyl moiety acts as a π*-acceptor group hiding the (d(Ir) → π*(ppy/bpy)) MLCT band, while the weak band centered at 620 nm may be due to direct population of triplet charge transfer states [6e]. A pronounced solvatochromic behavior is observed going from DMSO to CH_2Cl_2, typical of electronic transitions with an appreciable degree of charge-transfer character; the blue shift of the band with increasing solvent polarity suggests a lower dipole moment in the excited state than in the ground state [18].
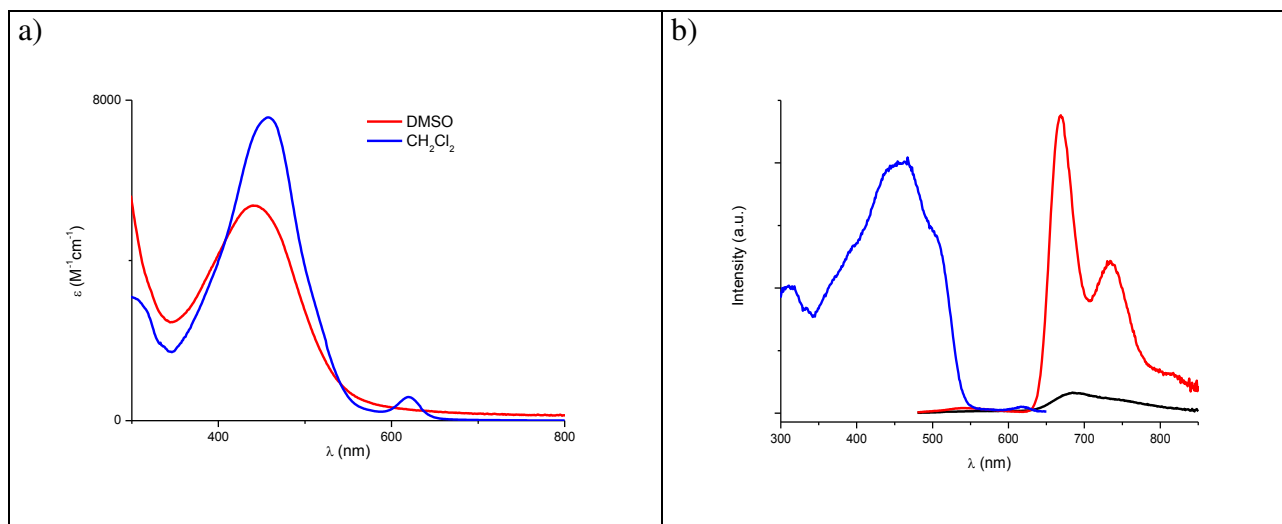
Figure 3. a) Superposition of absorption spectra of complex **5** in DMSO (red) and CH$_2$Cl$_2$ (blue)**; b)** Excitation spectrum at 77 K (blue line), emission spectrum at 298 K (black line) and emission spectrum at 77 K (red line), all in a degassed 5x10^{-5} M THF solution of **5** (λexc = 450 nm).

Tl   K

are shown in Figure 3b, and the data are summarized in Table 1. The novel complex is only very weakly emissive in fluid solution at room temperature (Figure 3b), because the radiative decay is quenched by the known competitive non-radiative *trans-cis* isomerization process of the C-C double bond, triggered by excitation with light before emission, of bipyridines linked to an Ir(III) center [6e, 19].

λ_{abs} / nm ($\varepsilon \times 10^3$ / M^{-1}cm^{-1})^a	λ_{em}/nm^b	τ/μs^b	$\mu\beta_{1.907}$ /x10^{-48} esu^c
454 (7.54), 621 (0.59)	669, 736	57	-960

Table 1. Photophysical data for complex **5**. [a] In CH$_2$Cl$_2$ solution at 298 K; in DMSO: λ_{abs} = 440 nm, $\varepsilon \times 10^3$ = 5.37 M^{-1}cm^{-1}. [b] In THF at 77 K (λ_{exc} = 460 nm). [c] In CH$_2$Cl$_2$ solution (10^{-3}M); uncertainty in EFISH measurements is ±10%

On the other hand, **5** is emissive at 77 K in THF, the luminescence spectrum is highly structured and the emission is located in the red region of the visible spectrum, as predicted upon incorporation of extended π-conjugated substituents in the ligands. With reference to previously reported Ir(III) complexes bearing two cyclometallated phenylpyridines and one bipyridine [6e], considering the highly structured spectrum and the long lifetime (57 μs), luminescence can be assigned to radiative decay from a triplet state predominantly localized on the styryl-substituted ligands, rather than from the MLCT state. In any case the

participation of the metal in the emission is necessary to promote the population of the formally forbidden triplet emissive state.

The quadratic hyperpolarizability of complex **5** was measured by the solution phase direct current EFISH generation method, which can provide direct information on the intrinsic molecular NLO properties through eq 1:

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

where $\mu\beta_\lambda/5kT$ is the dipolar orientational contribution and $\gamma(-2\omega; \omega, \omega, 0)$ is the third-order polarizability corresponding to the mixing of two optical fields at ω and the dc poling field at $\omega=0$. This latter term is often referred as the electronic cubic contribution to γ_{EFISH}, which is usually negligible. β_λ is the projection along the dipole moment (μ) axis of the vectorial component of the tensor of the quadratic hyperpolarizability at the incident wavelength λ. All EFISH measurements were carried out working in CH_2Cl_2 solutions at a concentration of 10^{-3} M, with a non resonant incident wavelength of 1.907 μm, obtained by Raman-shifting in a high pressure H_2 of the fundamental 1.064 μm wavelength produced by a Q-switched, mode-locked Nd^{3+}:YAG laser.

It turned out that complex **5** is characterized by a negative value of $\mu\beta_{1.907}$ (-960×10^{-48} esu, Table 1) in agreement with the observed solvatochromic behavior and with a negative value of $\Delta\mu_{eg}$ (difference of the dipole moment in the excited and ground state) upon excitation [2]. It is worth pointing out that the absolute $\mu\beta_{1.907}$ value of complex **5** is almost twice that reported for related $[Ir(C^\wedge N\text{-ppy-4-CH=CHC}_6H_4NEt_2)_2(\text{acetylacetonate})]$ (ppy = 2-phenylpyridine) [7e] suggesting that 4,4'-*p*-[(*N,N*-diethyl)aminostyryl]-2,2'-bipyridine is much better than acetylacetonate as ancillary ligand in this kind of cyclometallated Ir(III) complexes for second-order nonlinear optics.

Complex **5** was then investigated for its two-photon absorption activity. It was dissolved in DMSO (0.55 mM) and studied with the z-scan technique in the femtosecond case. The TPA spectrum is shown in Figure 4.

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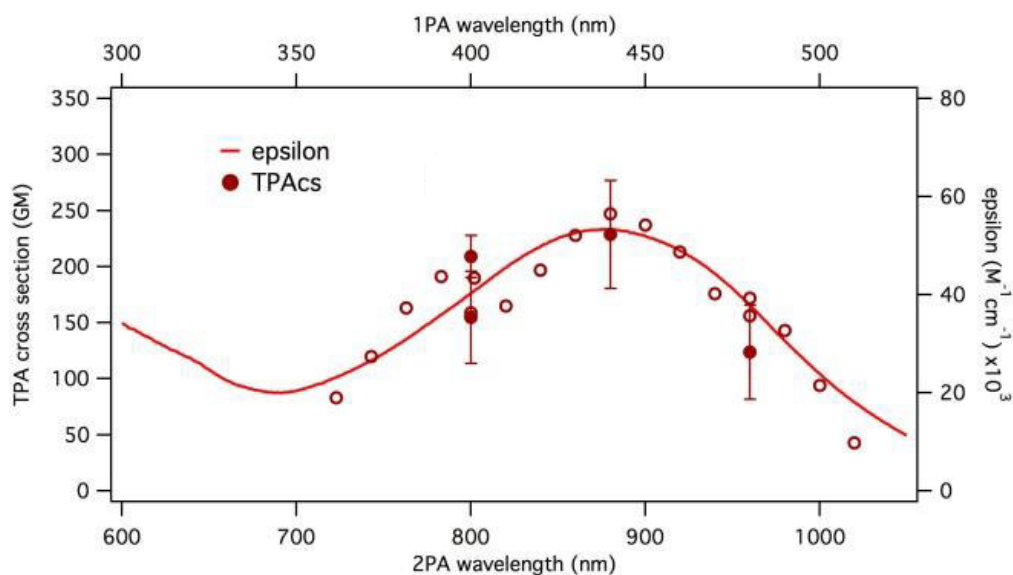
Figure 4. The OPA (line) and TPA (dots) spectra of complex **5**.

Remarkably, the two-photon absorption cross-sections are quite high, in the range 100-250 GM at 600-1000 nm. Contrarily to previously reported TPA active cationic iridium(III) complexes having two cyclometallated unsubstituted 2-phenylpyridines and a 2,2'-bipyridine bearing highly π-delocalized substituents [8c], the complex investigated here has less extended substituents on the bipyridine but it bears them also on the 2-phenylpyridine ligands. The excellent correspondence of the observed TPA peak with the wavelength-doubled one-photon absorption peak, as shown in Figure 4, suggests that the TPA peak mainly originates from the dipolar contribution [20] governed by asymmetric charge transfer, similar to the EFISH property. In this way, the charge-transfer property and the extended π-conjugation over the whole molecule results in good TPA properties of **5** compared to the previously reported complexes of similar structures. Besides, it is worth pointing out that some iridium(III) complexes bearing two cyclometallated unsubstituted 2-phenylpyridines and a 2-phenylimidazo[4,5-f][1,10]phenanthroline, characterized by two-photon absorption cross-sections in the range 48.8-65.5 GM at 750 nm, were utilized as efficient agents for mitochondrial imaging and tracking in living cells under two-photon (750 nm) excitation [21]. Similarly, complex **5** can find application in biomedical research.

Conclusion

In conclusion, our work put in evidence how a careful choice of the coordination sphere of cyclometallated iridium(III) complexes can lead to high second-order nonlinear optical properties and two-photon absorption activity, correlated through the charge-transfer character of the complex. Substitution of acetylacetonate by a 4,4'-*p*-[(*N,N*-diethyl)aminostyryl]-2,2'-bipyridine is a simple way to increase the second-order NLO response in this kind of cyclometallated Ir(III) complexes. In addition the use of simple π-delocalized donor substituents on both the cyclometallated 2-phenylpyridine and 2,2'-bipyridine allows to reach high two-photon absorption sections in a wide range of wavelengths. Clearly the novel complex reported here has a great potential for application in photonics and biomedicine.

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