Tuning the dipolar second-order nonlinear optical properties of 5-π-delocalized-donor-1,3-di(2-pyridyl)benzenes, related cyclometallated platinum(II) complexes and methylated salts

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The synthesis and characterization of three 5-π-delocalized-donor-1,3-di(2-pyridyl)benzenes is reported along with that of their related cyclometallated platinum(II) complexes and N,N-dimethylated iodide salts. The second-order nonlinear optical (NLO) properties of all the compounds have been determined by the Electric Field Induced Second Harmonic generation technique, showing how the NLO response of 1,3-di(2-pyridyl)benzenes can be tuned by the nature of the substituent on position 5 of the central benzene ring, and greatly increased by cyclometallation to Pt or by N-methylation.

Introduction

Compounds with second-order nonlinear optical (NLO) properties are of great interest as molecular building blocks for the preparation of materials with potential applications in optical communications, optical data processing and storage, or electro-optical devices. Among them, metal complexes are fascinating because they give additional flexibility, when compared to organic compounds, due to the presence of NLO-active charge-transfer transitions between the metal and the ligands, usually at relatively low energy and of high intensity, and tunable by virtue of the nature, oxidation state and coordination sphere of the metal center.

In particular, it appeared that the second-order NLO response of variously substituted phenylypyridines increases significantly upon cyclometallation, an effect that has given rise to cyclometallated Ru(II), Ir(III) and Pt(II)

complexes characterized by interesting NLO properties. Platinum(II) complexes bearing an N^N^C-cyclometallated 6-phenyl-2,2′-bipyridine constitutes another interesting NLO-active family. Meanwhile, it was reported that Pt(II) complexes with tridentate ligands based on a cyclometallated 1,3-di(2-pyridyl)benzene bearing an electron-withdrawing substitutent, which offer the metal ion an N^C^N coordination environment, are characterized by an enhanced NLO efficiency with respect to the corresponding N^N^N-coordinated terpyridine complexes, as measured by the Hyper-Rayleigh Scattering technique. The good second-order nonlinear optical properties of Pt(Medpyb)Cl (MedpybH = 5-methyl-1,3-di(2-pyridyl)benzene; Chart 1) have also been evidenced by the electric-field induced second harmonic generation (EFISH) technique.

However, the effect of a π-delocalized electron-donating substituent on the cyclometallated 1,3-di(2-pyridyl)benzene ligand of such Pt(II) complexes has not been investigated from an NLO point of view. Such an investigation is appealing, because the absorption bands of this kind of complex are red shifted by increasing the donor ability of the substituent at the central 5-position of the cyclometallating ring, through stabilisation of charge transfer states, and it is known that the presence of charge-transfer transitions at low energy can lead to a high quadratic hyperpolarizability. In addition a recent EFISH study showed that trans-5-(p-(N,N-diphenylamino)styreryl)-1,3-di(2-pyridyl)benzene...
characterized by a fair second-order NLO response that is substantially increased upon methylation. The NLO response of the related methylpyridinium iodide salt of 5-(p-(N,N-diphenylamino)phenylethynyl)-1,3-di(2-pyridyl) benzene is much lower, showing the superiority of the double bond over the triple bond for conferring better NLO properties, in agreement with previous observations.

These results prompted us to investigate the second-order NLO properties of the cyclometallated Pt(II) chloro complex of trans-5-(p-(N,N-diphenylamino)styryl)-1,3-di(2-pyridyl)benzene, along with that of two new 5-π-delocalized-donor-1,3-di(2-pyridyl)benzenes, their corresponding cyclometallated platinum(II) complexes, and their methylated salts. The compounds studied are shown in Chart 1. Their NLO response was determined by the EPISH technique, working with a non-resonant incident wavelength of 1907 nm, whose second harmonic lies at 953 nm in a transparent region of the absorption spectra of all the compounds investigated.

### Experimental

**General comments.**

All solvents were dried by standard procedures: THF was freshly distilled from Na/benzophenone under nitrogen atmosphere; N,N-dimethylformamide (DMF) was dried over activated molecular sieves; triethylamine (Et3N) was freshly distilled over KOH. All reagents were purchased from Sigma-Aldrich and were used without further purification. Reactions requiring anhydrous or oxygen-free conditions were performed under nitrogen. Thin layer chromatography (TLC) was carried out with pre-coated Merck F254 silica gel plates. Flash chromatography (FC) was carried out with Macherey-Nagel silica gel 60 (230-400 mesh).

1H and 13C spectra were recorded at 400 MHz on a Bruker AVANCE-400 instrument. Chemical shifts (δ) are expressed in ppm relative to internal MeSi as standard. Signals are abbreviated as s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were obtained with a FT-ICR Mass Spectrometer APEX II & Xmass software (Bruker Daltonics) - 4.7 Magnet and Autospec Fission Spectrometer (FAB ionization). Elemental analyses were performed using an Exeter Analytical E-440 analyser. UV-visible spectra were recorded for solutions of the compounds in dichloromethane, in 1 cm pathlength quartz cuvettes using a Biotek Instruments XS spectrometer.

**Synthesis of the various compounds**

Trans-5-(p-(N,N-diphenylamino)styryl)-1,3-di(2-pyridyl)benzene (1), its methylpyridinium salt (1S), and the related Pt(II) complex (1Pt) were prepared as previously reported. The new compounds 2, 2Pt and 2S, and 3, 3Pt and 3S, were synthesized as described below, starting from the corresponding (E)-1-(3,5-dibromostyryl)-derivative (2b, 3b).

**General Procedure for the synthesis of (E)-1-(3,5-dibromostyryl)-derivatives (2b, 3b):**

A solution of 1,3-dibromo-5-diethoxyphosphorylmethylbenzene (184 mg, 0.47 mmol), commercially available pyrene-1-carbaldehyde (2a) (100 mg, 0.43 mmol) and potassium tert-butoxide (126.3 mg, 1.12 mmol) in THF (4.3 mL, 0.1 M). The pure compound was obtained as yellow solid in 92% yield (eluent for flash chromatography: hexane/dichloromethane 6/4) 1H-NMR (400 MHz, CDCl3); δ 8.47 (1H, d, J = 9.2 Hz), 8.27 (1H, d, J = 8 Hz), 8.23-8.15 (5H, m), 8.10-8.00 (3H, m), 7.48 (2H, d, J = 1.6 Hz), 7.60 (2H, t, J = 1.6 Hz), 7.18 (1H, d, J = 16 Hz). 13C-NMR (100 MHz, CDCl3); δ 141.5, 132.9, 131.6, 130.9, 130.7, 128.7, 128.4, 128.1, 127.9, 127.5, 126.3, 125.7, 125.5, 125.3, 125.1, 124.9, 123.8, 123.5, 122.9.

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*Chart 1* Compounds investigated for their nonlinear optical properties.
**General Procedure for the synthesis of Pt(NC^3@NCl) complexes (2Pt, 3Pt):**

Under a nitrogen atmosphere, a solution of K2PdCl4 (1.1 equiv.) and the appropriate preponderate pro-ligand 2 or 3 (1 equiv.) in an AcOH/H2O 1:1 mixture (0.3 M) was stirred for 18 h at 100°C. After cooling to room temperature, the reaction mixture was filtered. The precipitate was washed with methanol, water, ethanol and diethyl ether.

2Pt was prepared from pro-ligand 2 (170 mg, 0.36 mmol) and K2PdCl4 (165 mg, 0.40 mmol) in 10 mL of AcOH/H2O.

The desired product was obtained as a yellow solid (32% yield). ^1H-NMR (400 MHz, CDCl3): δ 9.36 (2H, d, δ = 5.7 Hz), 8.65 (2H, d, δ = 9.4 Hz), 8.46 (2H, d, δ = 8.2 Hz), 7.89 (1H, d, δ = 15.8 Hz), 7.82-8.24 (2H, m), 6.36-6.06 (4H, m), 5.93 (2H, d, δ = 8.2 Hz), 5.70 (2H, s), 4.92 (1H, d, δ = 15.8 Hz), 7.42 (2H, t, δ = 8.2 Hz). Anal. Calcd. (%) for C4H2N2Cl2PtC2: C 59.35, H 3.08, N 4.07. Found: C 59.64, H 3.10, N 4.05.

3Pt was prepared from pro-ligand 3 (180 mg, 0.24 mmol), K2PdCl4 (110 mg, 0.26 mmol) in 7 mL of AcOH/H2O.

The desired product was obtained as a red solid (30% yield). ^1H-NMR (400 MHz, CDCl3): 9.32 (2H, d, J = 7.8 Hz), 7.83 (2H, t, J = 7.8 Hz), 7.68 (2H, s), 4.71-7.37 (3H, m), 3.71 (1H, d, J = 5.2 Hz), 7.26 (1H, d, J = 3.2 Hz), 7.17-7.16 (3H, m), 7.11-7.08 (2H, m), 6.99 (1H, d, J = 15.9 Hz). Anal. Calcd. (%) for C10H8N2Cl2Pt3: C 49.08, H 2.61, N 3.82. Found: C 48.90, H 2.63, N 3.84.

**General Procedure for the synthesis of methylpyridinium salts (2S, 3S):**

Under a nitrogen atmosphere, a solution of the corresponding dipryridylbenzene derivative (2 or 3, 0.04 mmol) in methyl iodide (0.5 mL) was heated at 50°C for stirring for 24 h. After cooling to room temperature, the reaction mixture was filtered and the precipitated salt (2S, 3S) was washed three times with diethyl ether.

(E)-1-(3,5-dip(2-pyridin-2-yl)styryl)-2,2'-5',2''-terthiophene (2S, 3S): Obtained from a mixture of (E)-1-(3,5-dip(2-pyridin-2-yl)styryl)-2,2'-5',2''-terthiophene (2S, 127.2 mg, 0.25 mmol), 2-(tri-n-butylstannyl)pyridine (230 mg, 0.62 mmol), [PdCl2(PPh3)2] (105 mg, 0.015 mmol), LiCl (189 mg, 4.5 mmol) in toluene (3.12 mL). The product was obtained as a dark yellow solid in 92% yield (elegant for flash chromatography: hexane/ethyl acetate 7/3). ^1H-NMR (400 MHz, CDCl3): δ 8.75 (2H, d, J = 4 Hz), 8.47 (1H, s), 8.20 (2H, d, J = 0.8 Hz), 7.89 (2H, d, J = 8 Hz), 7.80 (1H, dt, J = 1.6 Hz, J = 7.6 Hz), 7.41 (1H, d, J = 16 Hz), 7.29 (2H, dd, J = 4.8 Hz, J = 5.6 Hz), 7.21 (2H, dd, J = 4.8 Hz, J = 2.8 Hz), 7.11-7.08 (4H, m), 7.06-7.01 (3H, m). ^13C-NMR (100 MHz, CDCl3): δ 157.2, 149.9, 142.1, 140.5, 138.1, 136.9, 136.2, 132.8, 128.1, 127.7, 125.6, 124.7, 124.6, 124.3, 123.9, 122.7, 122.6, 121. MS(FAB+): m/z 504. Anal. Calcd. (%) for C6H9N2S3: C 71.39, H 3.99, N 5.55. Found: C 71.43, H 3.94, N 5.49.

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18 equiv.) in dry toluene was stirred for 18 h at 130°C. After cooling to room temperature, NaOH (8 mL, 1 M) was added and the mixture was stirred for 1 h, then diluted with ethyl acetate and washed with water; the organic layer was dried over Na2SO4 and concentrated. The obtained crude product was purified by flash chromatography.

(E)-1-(3,5-dip(2-pyridin-2-yl)styryl)-2,2'-5',2''-terthiophene (3S): Obtained from a mixture of (E)-1-(3,5-dip(2-pyridin-2-yl)styryl)-2,2'-5',2''-terthiophene (3S, 127.2 mg, 0.25 mmol), 2-(tri-n-butylstannyl)pyridine (230 mg, 0.62 mmol), [PdCl2(PPh3)2] (105 mg, 0.015 mmol), LiCl (189 mg, 4.5 mmol) in toluene (3.12 mL). The product was obtained as a dark yellow solid in 92% yield (elegant for flash chromatography: hexane/ethyl acetate 7/3).

Under a nitrogen atmosphere, a solution of K2PdCl4 (1.1 equiv.) and the appropriate preponderate pro-ligand 2 or 3 (1 equiv.) in an AcOH/H2O 1:1 mixture (0.3 M) was stirred for 18 h at 100°C. After cooling to room temperature, the reaction mixture was filtered. The precipitate was washed with methanol, water, ethanol and diethyl ether.

2Pt was prepared from pro-ligand 2 (170 mg, 0.36 mmol) and K2PdCl4 (165 mg, 0.40 mmol) in 10 mL of AcOH/H2O.

The desired product was obtained as a yellow solid (32% yield). ^1H-NMR (400 MHz, CDCl3): δ 9.36 (2H, d, J = 5.3 Hz), 8.65 (2H, d, J = 9.4 Hz), 8.46 (2H, d, J = 8.2 Hz), 8.39 (1H, d, J = 15.8 Hz), 8.32-8.24 (2H, m), 8.12-9.06 (4H, m), 7.93 (2H, d, J = 8.2 Hz), 7.90 (2H, s), 7.49 (1H, d, J = 15.8 Hz), 7.43 (2H, t, J = 8.2 Hz). Anal. Calcd. (%) for C10H8N2Cl2Pt3: C 59.35, H 3.08, N 4.07. Found: C 59.64, H 3.10, N 4.05.

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EFISH measurements

EFISH measurements were carried out in CHCl₃ or DMF solutions at a concentration of 10⁻³ M, 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 Nd³⁺:YAG laser manufactured by Atalaser. The μ⁵EFISH values reported are the mean values of 16 measurements performed on the same sample.

Computational details.

The molecular geometry of all compounds has been optimized in vacuo, by a Density Functional theory (DFT) approach using the B3LYP³⁸ exchange-correlation functional and a 6-31G* basis set³⁸ for all atoms except for Pt which has been described with LANL2DZ basis set³⁸ along with the corresponding pseudopotentials. All the calculations were performed with Gaussian09 (G09),³⁹ without any symmetry constraints. We optimized the geometries in CHCl₃ (1S-3S) or DMF (1-3 and 1Pt-3Pt) solution including solvation effects by means of the conductor-like polarizable continuum model (C-PCM)³⁵ as implemented in G09. Ground state dipole moments have been computed for compounds both in vacuo and in DMF (1-3, 1Pt-3Pt) or CHCl₃ (1S-3S) solution, finding an overall increase of dipole moment going from vacuo to solution. In the evaluation of μ⁵EFISH from μ⁵EFISH, the value of μ computed in solution (Table 1) was always used.

Results and discussion

\textit{trans}-5-[(N,N-Diphenylamino)styryl]-1,3-dii[2-pyridyl]benzene (1),³⁰ related methylpyridinium iodide salt (1S)³³ and Pt(II) complex (1Pt)³⁰ were prepared as previously reported. The new compounds 2-3 were synthesized from the related (E)-1-(3,5-dibromostyryl)-derivative (2b,3b) as shown in Scheme 1. Complexes 2Pt and 3Pt were prepared by reaction of K₃PtCl₆ with the appropriate terdentate pro-ligand (2 or 3) in an AcOH/H₂O 1:1 mixture at 100°C for 18 h. The methylpyridinium salts (2S,3S) were readily formed by reaction of the corresponding 1,3-di(2-pyridyl)benzene derivative (2 or 3) with methyl iodide. All compounds were fully characterized by elemental analysis, mass spectrometry and NMR spectroscopy (see Experimental).

<table>
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<tr>
<th>Compound</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; / nm</th>
<th>μ&lt;sub&gt;EFISH&lt;/sub&gt; × 10⁻⁹ esu</th>
<th>μ&lt;sub&gt;v&lt;/sub&gt; [μ] in vacuo</th>
<th>β&lt;sub&gt;EFISH&lt;/sub&gt; × 10⁻⁹ esu</th>
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<tr>
<td>1</td>
<td>260 (32800), 286 (40200), 375 (33300)</td>
<td>230⁴</td>
<td>3.6⁴ [2.2]</td>
<td>64</td>
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<tr>
<td>1Pt</td>
<td>295 (21000), 378 (15700), 430 (4900)</td>
<td>-880⁵</td>
<td>10.7⁷ [7.4]</td>
<td>-82</td>
</tr>
<tr>
<td>1S</td>
<td>237 (24834), 290 (29280), 388 (24008)</td>
<td>1280⁶</td>
<td>27.0⁹ [10.0]</td>
<td>47</td>
</tr>
<tr>
<td>2</td>
<td>238 (41900), 295 (36400), 380 (34400)</td>
<td>400⁵</td>
<td>2.2⁵ [1.1]</td>
<td>182</td>
</tr>
<tr>
<td>2Pt</td>
<td>244 (65900), 281 (46900), 382 (41200)</td>
<td>-820⁷</td>
<td>9.4⁷ [6.3]</td>
<td>-87</td>
</tr>
<tr>
<td>2S</td>
<td>235 (32433), 285 (16378), 383 (16263)</td>
<td>1390⁷</td>
<td>29.6⁶ [11.8]</td>
<td>47</td>
</tr>
<tr>
<td>3</td>
<td>253 (37300), 279 (27700), 414 (44700)</td>
<td>303⁷</td>
<td>2.6⁷ [1.4]</td>
<td>116</td>
</tr>
<tr>
<td>3Pt</td>
<td>257 (22200), 325 (10400), 417 (26800)</td>
<td>-1260⁷</td>
<td>9.5⁷ [6.3]</td>
<td>-133</td>
</tr>
<tr>
<td>3S</td>
<td>238 (40285), 269 (26746), 423 (41106)</td>
<td>1250⁷</td>
<td>29.2² [10.9]</td>
<td>43</td>
</tr>
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</table>

(a) In CHCl₃. (b) at 1.907 μm; estimated uncertainty in EFISH measurements is ±10%. (c) computed dipole moments using B3LYP/6-31G* /LANL2DZ/C-PCM level of theory (see Experimental Section). (d) α<sub>EFISH</sub> was calculated using the μ value computed in solution. (e) from reference 30. (f) in DMF. (g) μ<sub>EFISH</sub> = 102 × 10⁻⁹ esu in CHCl₃. (h) in CHCl₃ (i) from reference 33.
The absorption band maxima and corresponding extinction coefficients of compounds 1–3, 1Pt-3Pt and 15–35, in CHCl₃ solution at room temperature, are presented in Table 1. Like related trans-S-(p-(N,N-diphenylylamino)styryl)-1,3-di(2-pyridyl)-benzene,³⁰,⁴⁶ the absorption spectra of the two new trans-S-R-vinyl-1,3-di(2-pyridyl)benzenes (2,3) show very intense bands in the UV region (λ < 400 nm), due to spin-allowed n–n⁰ transitions. The UV-visible absorption spectra of the new complexes 2Pt and 3Pt in dichloromethane solution at room temperature show intense bands at λ < 300 nm but also another set of intense bands at lower energy, around 400 nm and extending into the visible region. Though fairly similar to those of the corresponding proligands, they differ from those normally displayed by simple cyclometallated Pt(II) complexes with arylpyridine ligands, such as Pt(dpbb)Cl (dpbbH = 1,3-di(2-pyridyl)benzene), in that the lower-energy bands are so intense. Typically in complexes such as Pt(dpbb)Cl, the bands in the 350–400 nm region have ε values of around 7000 M⁻¹ cm⁻¹, with no counterparts in the proligands, and are due to metal-to-ligand and intra-ligand charge-transfer transitions that are introduced upon cyclometallation.³⁰,⁴⁷,⁴⁸ Such transitions will necessarily be present in the current complexes, but they are evidently superimposed by intense ligand-centred transitions. This leads to unusually high ε values in this region. A similar observation is made in the case of 1Pt.³⁰ The UV-visible absorption spectra of the methylpyridinium iodides (25 and 35) are quite similar to that of previously reported 1S.³³

The dipole moments, calculated both in vacuo and in solution, are reported in Table 1. We computed that substitution of the p-diphenylnaphthalene moiety by a pyrene group (2) or a terthiophene (3) leads to a slight decrease of the dipole moment. Higher dipole moments are computed in DMF with respect to vacuo but the trend is similar. The dipole moment of the three metal complexes show similar values of ca. 10 D. As expected from previous reports on the alkylation or protonation of other pyridine systems,³⁵-⁵⁰ the three methylated pyridinium salts are characterized by a huge dipole moment in CHCl₃, (a solvent that favours strong ion pairs),⁵¹ the computed values of the salts’ dipole moments are again similar within the investigated series.

Experimentally, we applied the EFISH method to study the NLO response in solution of compounds 1-3, 1Pt-3Pt and 15-35. This technique⁵²-⁵⁷ can provide direct information on the intrinsic molecular NLO properties, through

\[ \gamma_{\text{EFISH}} = (\mu_{\text{EFISH}}/5kT) + \gamma(-2\omega; \omega, \omega, 0) \]  

where \( \mu_{\text{EFISH}}/5kT \) is the dipolar orientational contribution to the molecular nonlinearity, and \( \gamma(-2\omega; \omega, \omega, 0) \), the third order polarizability, is a purely electronic cubic contribution to \( \gamma_{\text{EFISH}} \) which can usually be neglected when studying the second-order NLO properties of dipolar molecules. Although it has traditionally been used to study charge-neutral molecules, the EFISH technique can be applied to the determination of the second-order NLO response of ionic species by working in a solvent of low dielectric constant like CHCl₃, which favours ion-pairing.⁵¹ Therefore whereas the NLO responses of compounds 1–3 and 1Pt-3Pt were studied in DMF, those of 15-35 were investigated in CHCl₃, working with a non-resonant incident wavelength of 1.907 μm. To obtain \( \beta_{\text{EFISH}} \), the projection along the dipole moment axis of the vectorial component of the quadratic hyperpolarizability tensor, it is necessary to know the dipole moment, \( \mu \). In the present study we used the theoretical dipole moments calculated in the appropriate solvent (DMF or CHCl₃) as described in the Experimental section. We found that 1 is characterized by a good value of \( \mu_{\text{EFISH}} \) in DMF solution (230 x 10⁻⁴⁸ esu, see Table 1) which increases upon substitution of the p-diphenylnaphthalene moiety by a terthiophene (303 x 10⁻⁴⁸ esu) due essentially to an increase of the quadratic hyperpolarizability, \( \beta_{\text{EFISH}} \). Substitution by the pyrene moiety causes a further increase of \( \mu_{\text{EFISH}} \) (400 x 10⁻⁴⁸ esu), although there is a further diminution of the dipole moment, due to a much higher quadratic hyperpolarizability (\( \beta_{\text{EFISH}} = 182 x 10^{-48} \) esu, Table 1). The large \( \beta_{\text{EFISH}} \) value obtained for 2 and 3, with respect to 1 can reasonably be attributed to the higher electron π-delocalization due to the ligand planarity of terthiophene and to the high conjugation of the pyrene system. The higher charge delocalization reflects into the significant stabilization of the LUMO of 2 and 3 with respect to 1 (by 0.5–0.6 eV, see Figure 1). For these trans-S-R-vinyl-1,3-di(2-pyridyl)benzenes, the positive sign of \( \beta_{\text{EFISH}} \) is in agreement with an increase of the excited state dipole moment with respect to the ground state.⁵²

![Figure 1](image-url) Frontier molecular orbitals of all compounds. Isodensity plots of HOMO and LUMO are reported (isodensity contour plot=0.025). As expected from the positive effect of methylation on the second-order NLO properties of trans-S-(p-(N,N-diphenylylamino)styryl)-1,3-di(2-pyridyl)benzene (1),³³ the methylpyridinium iodide salts 2S and 3S are characterized by similar large \( \mu_{\text{EFISH}} \) values (1390 x 10⁻⁴⁸ and 1250 x 10⁻⁴⁸ esu, respectively). This increase can be fully attributed to the
intensification of the dipole moment upon methylation (Table 1). It is worth pointing out that the quadratic hyperpolarizability of the pyrene salt derivative 2S (\(\beta_{EFISH} = 47 \times 10^{-30}\) esu) is similar to that of 1S and 3S, and lower than that of the parents 1-3 probably because methylation leads to a loss of the planarity of the molecule (see Figure 1 and optimized structures in ESI) which appears an important factor in these systems to improve the NLO response. It is known that the second-order NLO response of variously substituted phenylpyridines increases significantly upon cyclometallation to platinum.\(^{23,24}\) In particular, the methyl derivative Pt(Medpyb)Cl is characterized by a good \(\mu\beta_{EFISH}\) value (\(-480 \times 10^{-30}\) esu), as evidenced by the EFISH technique, working in DMF solution with an incident radiation wavelength of 1.907 \(\mu\)m, due to a high dipole moment (10.2 D) and a good \(\beta_{EFISH}\) value (\(-47 \times 10^{-30}\) esu).\(^{28}\) The negative sign of the quadratic hyperpolarizability of this complex is in agreement with a decrease of the excited state dipole moment with respect to the ground state,\(^2\) suggesting that the second-order dipolar NLO response is dominated by the charge transfer from platinum to the cyclometallated ligand.\(^{28}\) The HOMO/LUMO plots reported in Figure 1 for 1Pt-3Pt are consistent with this picture: the HOMO of the metal complexes all show a Pt \(_n\) contribution and a charge delocalization on the central substituted phenyl systems, while the LUMO and LUMO+1 show an involvement of the cyclometallating pyridyl units. As shown in Table 1, substitution of the methyl group Pt(\(\text{Medpyb}\))Cl (Chart 1) by a \(\pi\)-delocalized vinyl donor group, in position 5 of the phenyl ring of the cyclometallated 1,3-di(2-pyridyl)benzene moiety, causes a significant enhancement of the absolute value of \(\mu\beta_{EFISH}\) (factor of 1.8, 1.7 and 2.6 for 1Pt, 2Pt and 3Pt, respectively). This enhancement is clearly due to a much higher quadratic hyperpolarizability, as expected for the substitution of a methyl group by a \(\pi\)-delocalised donor moiety.

Conclusions

In summary, this work has shown the good second-order nonlinear optical properties of novel \(\sigma\)-\(\pi\)-delocalized donor-1,3-di(2-pyridyl)benzenes that can be enhanced upon methylation of the pyridine moieties due to a large increase of the dipole moment. Cyclometallation of these pro-ligands to Pt(II) also leads to an enhancement of the \(\mu\beta_{EFISH}\) values with a change of sign from positive to negative, suggesting that the second-order dipolar NLO response is dominated by the charge transfer from platinum to the cyclometallated ligand, as previously observed in the case of the simpler Pt(\(\text{Medpyb}\))Cl complex. Both the methylated salts and the Pt(II) complexes prepared in the present work are characterized by large \(\mu\beta_{EFISH}\) values that make them appealing as building blocks for NLO materials and photonic applications.

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Notes and references

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