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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 $\mu\beta_{\text{EFISH}}$ absolute value 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.¹⁻² 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.³⁻¹¹

In particular, it appeared that the second-order NLO response of variously substituted phenylpyridines increases significantly upon cyclometallation, an effect that has given rise to cyclometallated Ru(II),¹² Ir(III)¹³⁻²³ and Pt(II)²³⁻²⁴

complexes characterized by interesting NLO properties. Platinum(II) complexes bearing an $N^{\wedge}N^{\wedge}C$ -cyclometallated 6-phenyl-2,2'-bipyridine constitutes another interesting NLO-active family.²⁵⁻²⁶ 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 substituent, which offer the metal ion an $N^{\wedge}C^{\wedge}N$ coordination environment, are characterized by an enhanced NLO efficiency with respect to the corresponding $N^{\wedge}N^{\wedge}N$ -coordinated terpyridine complexes, as measured by the Hyper-Rayleigh Scattering technique.²⁷ 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.²⁸

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,^{29,30} and it is known that the presence of charge-transfer transitions at low energy can lead to a high quadratic hyperpolarizability.^{31,32} In addition a recent EFISH study showed that *trans*-5-(*p*-(*N,N*-diphenylamino)styryl)-1,3-di(2-pyridyl)benzene is

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characterized by a fair second-order NLO response that is substantially increased upon methylation.³³ 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.³⁴

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 EFISH technique,³⁵⁻³⁷ 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.

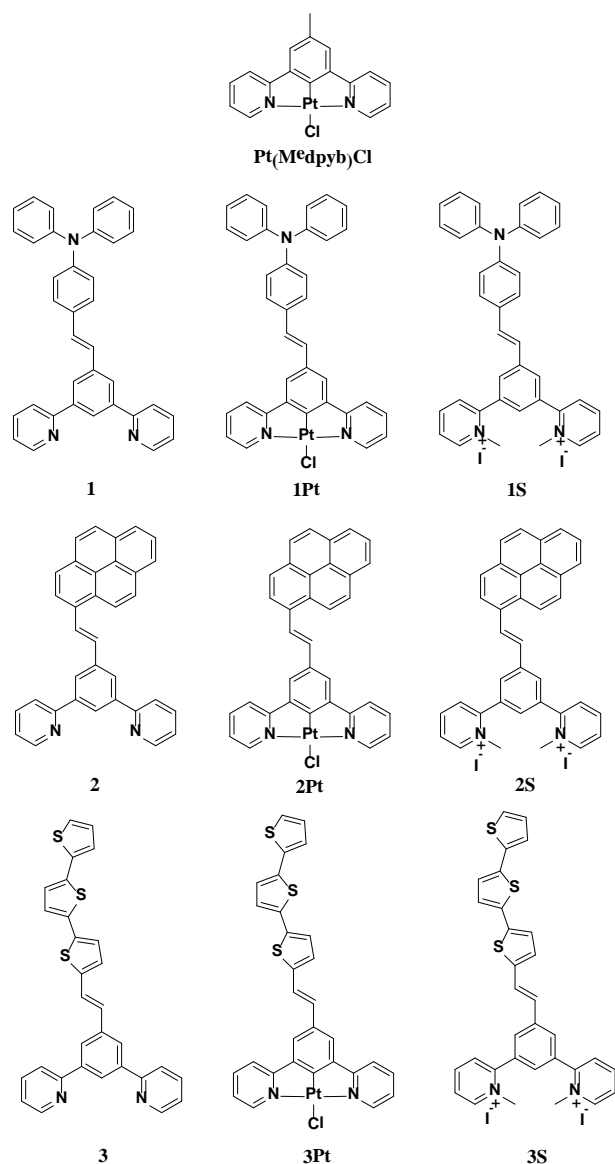


Chart 1 Compounds investigated for their nonlinear optical properties.

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 Me₄Si 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**),³⁰ its methylpyridinium salt (**1S**)³³ and the related Pt(II) complex (**1Pt**)³⁰ 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-diethoxyphosphorylmethylbenzene³⁸ (1.1 equiv.) and the appropriate aldehyde (**2a** or **3a**; 1 equiv.) in THF under nitrogen was cooled to 0 °C. Potassium *tert*-butoxide (2.6 equiv.) was added in small portions. The cool bath was then removed and the mixture stirred for 18h at room temperature. After hydrolysis with water, the mixture was stirred for further 30 min. The reaction mixture was diluted with ethyl acetate and washed with water: the organic layer was dried over Na₂SO₄ and concentrated. The crude product was purified by flash chromatography on silica gel.

(*E*)-1-(3,5-dibromostyryl)-pyrene (**2b**):

Obtained from 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), 7.74 (2H, d, *J* = 1.6 Hz), 7.60 (2H, t, *J* = 1.6 Hz), 7.18 (1H, d, *J*_{trans} = 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.

(E)-1-(3,5-dibromostyryl)-2,2':5',2''-terthiophene (3b):

Obtained following the above reported general procedure starting from 1,3-dibromo-5-diethoxyphosphorylmethylbenzene (182 mg, 0.47 mmol), the known 2,2':5',2''-terthiophene-1-carbaldehyde **3a**^{39,40} (117.8 mg, 0.43 mmol) and potassium *tert*-butoxide (126.3 mg, 1.12 mmol) in THF (4.3 mL). The pure product was obtained as yellow solid in 91% yield. (eluent for flash chromatography: hexane/dichloromethane 1/1).

¹H-NMR (400 MHz, CDCl₃): δ 7.51 (3H, s), 7.23 (1H, dd, *J* = 0.8 Hz, *J* = 1.2 Hz), 7.19 (1H, dd, *J* = 0.8 Hz), 7.14-7.07 (3H, m), 7.03 (1H, dd, *J* = 3.6 Hz, *J* = 3.6 Hz), 7.00 (1H, d, *J* = 4 Hz), 6.70 (1H, d, *J*_{trans} = 16 Hz). ¹³C-NMR (100 MHz, CDCl₃): δ 140.8, 140.7, 137.2, 137.1, 136.9, 135.9, 132.5, 128.8, 128.1, 127.9, 125.1, 124.8, 124.6, 124.4, 124.2, 124, 123.4. Anal. Calcd. (%) for C₂₀H₁₂Br₂S₃: C 47.26, H 2.38. Found: C 47.39, H 2.39.

General Procedure for the synthesis of (E)-1-(3,5-di(pyridin-2-yl)styryl)-derivatives (2, 3):

Under a nitrogen atmosphere, a mixture of the opportune (*E*)-1-(3,5-dibromostyryl) derivative (**2b** or **3b**, 1 equiv.), 2-(tri-*n*-butylstannyl)pyridine (2.5 equiv.), [PdCl₂(PPh₃)₂] (0.06 equiv.), LiCl (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 1h, 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-di(pyridin-2-yl)styryl)-pyrene (2b):

Obtained from a mixture of (*E*)-1-(3,5-dibromostyryl)-pyrene (**2b**, 122.2 mg, 0.26 mmol.), 2-(tri-*n*-butylstannyl)pyridine (243 mg, 0.66 mmol.), [PdCl₂(PPh₃)₂] (10.9 mg, 0.016 mmol.), LiCl (196.6 mg, 4.68 mmol.) in toluene (3.25 mL). The product was obtained as a yellow solid in 95% yield (eluent for flash chromatography: hexane/ethyl acetate 8/2). ¹H-NMR (400 MHz, CD₂Cl₂): δ 8.79-8.77 (2H, m), 8.63 (1H, d, *J* = 9.2 Hz), 8.56 (1H, t, *J* = 1.6 Hz), 8.45-8.41 (3H, m), 8.35 (1H, d, *J* = 8.4 Hz), 8.20-8.16 (4H, m), 8.07 (2H, s), 8.02-7.99 (3H, m), 7.86 (2H, dt, *J* = 7.6 Hz, *J* = 2 Hz), 7.51 (1H, d, *J*_{trans} = 16 Hz), 7.32 (1H, dd, *J* = 1.2 Hz, *J* = 4.8 Hz), 7.32 (1H, dd, *J* = 0.8 Hz, *J* = 4.8 Hz). ¹³C-NMR (100 MHz, CDCl₃): δ 156.7, 149.1, 139.7, 139.2, 137.8, 131.9, 131.6, 131.3, 131.1, 128.7, 127.8, 127.8, 127.6, 127.5, 127.1, 126.4, 126.1, 125.4, 125.3, 125.2, 123.9, 123.5, 122.8, 121.5. MS(FAB⁺): *m/z* 458. Anal. Calcd. (%) for C₃₄H₂₂N₂: C 89.06, H 4.84, N 6.11. Found: C 89.01, H 4.87, N 6.05.

(E)-1-(3,5-di(pyridin-2-yl)styryl)-2,2':5',2''-terthiophene (3):

Obtained from a mixture of (*E*)-1-(3,5-dibromostyryl)-2,2':5',2''-terthiophene (**3b**, 127.2 mg, 0.25 mmol.), 2-(tri-*n*-butylstannyl)pyridine (230 mg, 0.62 mmol.), [PdCl₂(PPh₃)₂] (10.5 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 (eluent 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*_{trans} = 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, 128.3, 128.1, 127.7, 125.6, 124.9, 124.7, 124.6, 124.3, 123.9, 122.7, 122.6, 121. MS(FAB⁺): *m/z* 504. Anal. Calcd. (%) for C₃₀H₂₀N₂S₃: C 71.39, H 3.99, N 5.55. Found: C 71.43, H 3.94, N 5.49.

General Procedure for the synthesis of Pt(N^{^C^A^N})Cl complexes (2Pt, 3Pt):

Under a nitrogen atmosphere, a solution of K₂PtCl₄ (1.1 equiv.) and the appropriate terdentate pro-ligand **2** or **3** (1 equiv.) in a 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 K₂PtCl₄ (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, CD₂Cl₂): δ (ppm) 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 (3H, 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 C₃₄H₂₁ClN₂Pt: 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), K₂PtCl₄ (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, CD₂Cl₂): 9.34 (2H, d), 8.05 (2H, 7, *J* = 7.8 Hz), 7.83 (2H, t, *J* = 7.8 Hz), 7.66 (2H, s), 7.41-7.37 (3H, m), 7.31 (1H, d, *J* = 5.2 Hz), 7.26 (1H, d, *J* = 3.2 Hz), 7.19-7.16 (3H, m), 7.11-7.08 (2H, m), 6.99 (1H, d, *J* = 15.9 Hz). Anal. Calcd. (%) for C₃₀H₁₉ClN₂PtS₃: 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 dipyrilidylbenzene derivative (**2** or **3**, 0.04 mmol) in methyl iodide (0.5 mL) was heated at 50°C with stirring for 24h. After cooling to room temperature, the reaction mixture was filtered and the precipitated salt (**2S**, **3S**) was washed three times with diethyl ether.

(E)-2,2'-(5-(2-(pyren-1-yl)vinyl)-1,3-phenylene)bis(1-methylpyridinium)iodide (2S)

Yield 87%. ¹H-NMR (400 MHz, CD₃OD): δ 9.13 (2H, d, *J* = 6.4 Hz), 8.72 (2H, t, *J* = 8 Hz), 8.67 (1H, d, *J* = 2 Hz), 8.64 (1H, t, *J* = 4.4 Hz), 8.47 (1H, d, *J* = 8.4 Hz), 8.39 (2H, d, *J* = 3.6 Hz), 8.29-8.20 (7H, m), 8.12 (2H, d, *J* = 3.6 Hz), 8.03 (2H, t, *J* = 7.6 Hz), 7.87 (1H, s), 7.65 (1H, d, *J*_{trans} = 16 Hz), 4.39 (6H, s). Anal. Calcd. (%) for C₃₆H₂₈I₂N₂: C 58.24, H 3.80, N 3.77. Found: C 58.32, H 3.82, N 3.76.

(E)-2,2'-(5-(2-(terthiophen-1-yl)vinyl)-1,3-phenylene)bis(1-methylpyridinium)iodide (3S)

Yield 87%. ¹H-NMR (400 MHz, CD₃OD): δ 9.12 (2H, d, *J* = 6 Hz), 8.71 (2H, t, *J* = 7.6 Hz, *J* = 8 Hz), 8.25 (2H, d, *J* = 8 Hz), 8.20 (2H, t, *J* = 7.2 Hz, *J* = 7.6 Hz), 8.16 (2H, s), 7.89 (1H, s), 7.69 (1H, d, *J*_{trans} = 16 Hz), 7.38 (1H, d, *J* = 5.2 Hz), 7.27 (1H, d, *J* = 3.6 Hz), 7.23-7.13 (5H, m), 7.08 (1H, dd, *J* = 4 Hz, *J* = 4.8 Hz), 4.37 (6H, s). ¹³C-NMR (100 MHz, CD₃OD): δ 154.4, 146.8, 145.7, 140.6, 139.9, 136.8, 133.2, 130.3, 129.4, 129.1, 127.8, 127.7, 127.3, 125.7, 124.7, 124.5, 124.1, 123.7, 47.8. Anal. Calcd. (%) for C₃₂H₂₆I₂N₂S₃: C 48.74, H 3.32, N 3.55. Found: C 48.78, H 3.31, N 3.57.

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

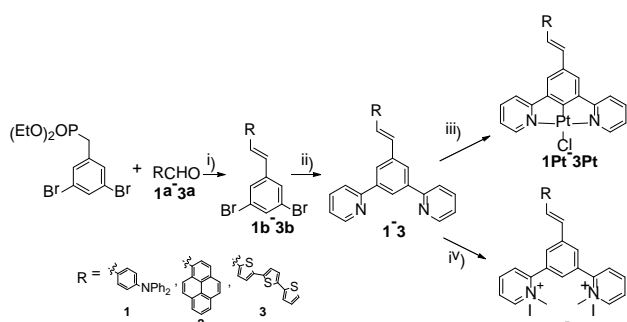
the fundamental 1.064 μm wavelength produced by a Q-switched, mode-locked Nd³⁺:YAG laser manufactured by Atalaser. The $\mu\beta_{\text{EFISH}}$ values reported are the mean values of 16 measurements performed on the same sample.

Computational details.

The molecular geometry of all compounds has been optimized in vacuo, by a Density Functional theory (DFT) approach using the B3LYP⁴¹ exchange-correlation functional and a 6-31G* basis set⁴² for all atoms except for Pt which has been described with LANL2DZ basis set⁴³ along with the corresponding pseudopotentials. All the calculations were performed with Gaussian09 (G09),⁴⁴ 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)⁴⁵ 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. In the evaluation of β_{EFISH} from $\mu\beta_{\text{EFISH}}$, the value of μ computed in solution (Table 1) was always used.

Results and discussion

trans-5-(*p*-(*N,N*-Diphenylamino)styryl)-1,3-di(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 K₂PtCl₄ with the appropriate terdentate pro-ligand (**2** or **3**) in a 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.



Scheme 1 i) tBuOK⁺, THF, RT, 16h, 92%; ii) 2⁻(*tert*-*n*-butylstanny)pyridine⁻, Pd(PPh₃)₂Cl₂, LiCl, Toluene, 130°C, 18h, 95%; iii) K₂PtCl₄, CH₃COOH/H₂O 24h; iv) CH₃I

Table 1. Main absorption bands in the UV-visible spectra, dipole moments and second-order NLO response.

	Absorption ^a $\lambda_{\text{max}} / \text{nm}$ ($\epsilon / \text{M}^{-1} \text{cm}^{-1}$)	$\mu\beta_{\text{EFISH}}^{\text{b}}$ ($\times 10^{-48}$ esu)	μ^{c} [μ in vacuo] (D)	$\beta_{\text{EFISH}}^{\text{d}}$ ($\times 10^{-30}$ esu)
1	260 (32800), 286 (40200), 375 (33300) ^e	230 ^{f,g}	3.6 ^f [2.2]	64
1Pt	295 (21000), 378 (15700), 430sh (4900) ^e	-880 ^f	10.7 ^f [7.4]	-82
1S	237 (24800), 290 (29300), 388 (24000)	1280 ^{h,i}	27.0 ^h [10.0]	47
2	238 (41900), 295 (36400), 380 (34400)	400 ^f	2.2 ^f [1.1]	182
2Pt	244 (65900), 281 (46900), 382 (41200)	-820 ^f	9.4 ^f [6.3]	-87
2S	235 (32400), 285 (16400), 383 (16300)	1390 ^h	29.6 ^h [11.8]	47
3	253 (37300), 279sh (27700), 414 (44700)	303 ^f	2.6 ^f [1.4]	116
3Pt	257 (22200), 325 (10400), 417 (26800)	-1260 ^f	9.5 ^f [6.3]	-133
3S	238 (40300), 269 (26700), 423 (41100)	1250 ^h	29.2 ^h [10.9]	43

(a) In CH₂Cl₂. (b) at 1.907 μm ; estimated uncertainty in EFISH measurements is $\pm 10\%$. (c) computed dipole moments using B3LYP//6-31g*/LANL2DZ//C-PCM level of theory (see Experimental Section). (d) β_{EFISH} was calculated using the μ value computed in solution. (e) from reference 30. (f) in DMF. (g) $\mu\beta_{\text{EFISH}} = 102 \times 10^{-48}$ 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 **1S-3S**, in CH₂Cl₂ solution at room temperature, are presented in Table 1. Like related *trans*-5-(*p*-(*N,N*-diphenylamino)styryl)-1,3-di(2-pyridyl)-benzene,^{30,46} the absorption spectra of the two new *trans*-5-R-vinyl-1,3-di(2-pyridyl)benzenes (**2,3**) show very intense bands in the UV region ($\lambda < 415$ nm), due to spin-allowed $^1\pi-\pi^*$ transitions. The UV-visible absorption spectra of the new complexes **2Pt** and **3Pt** in dichloromethane solution at room temperature show intense bands at $\lambda < 300$ 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(dpyb)Cl (dpybH = 1,3-di(2-pyridyl)benzene), in that the lower-energy bands are so intense. Typically in complexes such as Pt(dpyb)Cl, the bands in the 350 – 400 nm region have ϵ values of around $7000 \text{ M}^{-1}\text{cm}^{-1}$, 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 salts (**2S** and **3S**) 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. For compounds **1-3** and **1Pt-3Pt** the dipole moment is computed to increase by a factor ~ 2 and ~ 1.5 , respectively, on going from vacuo to DMF solution, while for the three pyridinium salts the dipole moment increases by a factor ~ 3 in CHCl_3 solution. We computed that substitution of the *p*-diphenylaminobenzene 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,⁴⁹⁻⁵⁰ the three methylated pyridinium salts are characterized by a huge dipole moment in CHCl_3 , (a solvent that favours strong ion pairs);⁵¹ the computed values of the salts' dipole moments are again similar within the investigated series. The larger dipole increase in a less polar solvent observed for the salts (compared to the neutral molecules) is related to a more pronounced charge localization on the positive/negative moieties of the pyridinium salts due to the solvent stabilization of the separated charges.

Experimentally, we applied the EFISH method to study the NLO response in solution of compounds **1-3**, **1Pt-3Pt** and **1S-3S**. This technique³⁵⁻³⁷ can provide direct information on the intrinsic molecular NLO properties, through

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

where $\mu\beta_{\text{EFISH}}/5kT$ 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 γ_{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 CHCl_3 , which favours ion-pairing.⁵¹ Therefore whereas the NLO responses of compounds **1-3** and **1Pt-3Pt** were studied in DMF, those of **1S-3S** were investigated in CHCl_3 , working with a non-resonant incident wavelength of $1.907 \mu\text{m}$. To obtain β_{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, μ . In the present study we used the theoretical dipole moments calculated in the appropriate solvent (DMF or CHCl_3) as described in the Experimental section. We found that **1** is characterized by a good value of $\mu\beta_{\text{EFISH}}$ in DMF solution (230×10^{-48} esu, see Table 1) which increases upon substitution of the *p*-diphenylaminobenzene moiety by a terthiophene (303×10^{-48} esu) due essentially to an increase of the quadratic hyperpolarizability, β_{EFISH} . Substitution by the pyrene moiety causes a further increase of $\mu\beta_{\text{EFISH}}$ (400×10^{-48} esu), although there is a further diminution of the dipole moment, due to a much higher quadratic hyperpolarizability ($\beta_{\text{EFISH}} = 182 \times 10^{-30}$ esu, Table 1). The large β_{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*-5-R-vinyl-1,3-di(2-pyridyl)benzenes, the positive sign of β_{EFISH} is in agreement with an increase of the excited state dipole moment with respect to the ground state.⁵²

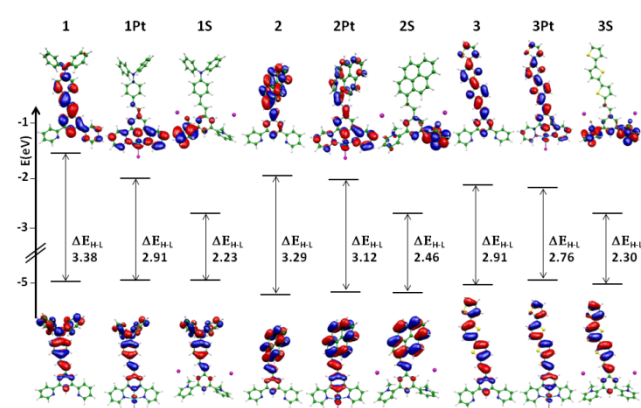


Figure 1 Frontier molecular orbitals of all compounds. Isodensity plots of HOMO and LUMO are reported (isodensity contour plot=0.025).

As expected from the positive effect of methylation on the $\mu\beta_{\text{EFISH}}$ value of *trans*-5-(*p*-(*N,N*-diphenylamino)styryl)-1,3-di(2-pyridyl)benzene (**1**),³³ the methylpyridinium iodide salts **2S** and **3S** are characterized by similar large $\mu\beta_{\text{EFISH}}$ values (1390×10^{-48} and 1250×10^{-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** ($\beta_{\text{EFISH}} = 47 \times 10^{-30}$ 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 $\mu\beta_{\text{EFISH}}$ value (-480×10^{-48} esu), as evidenced by the EFISH technique, working in DMF solution with an incident radiation wavelength of $1.907 \mu\text{m}$, due to a high dipole moment (10.2 D) and a good β_{EFISH} value (-47×10^{-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,⁵² suggesting that the second-order dipolar NLO response is determined by a charge transfer transition from platinum- to the cyclometallated ligand, partly screened by the intra-ligand charge transfer transition showing an opposite NLO response.²⁸ The HOMO/LUMO plots reported in Figure 1 for **1Pt-3Pt** are qualitatively consistent with this picture: the HOMO of the metal complexes all show a Pt d_{yz} 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. We can thus envisage two contributions to the NLO response of opposite sign, as previously found for analogous metallorganic compounds, with the prevalence of the negative contribution determining the final hyperpolarizability sign. Within this general electronic structure picture, a fine-tuning of the compounds properties is obtained by ligand modification. As shown in Table 1, substitution of the methyl group Pt(Medpyb)Cl (Chart 1) by a π -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 $\mu\beta_{\text{EFISH}}$ (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 π -delocalised donor moiety.

Conclusions

In summary, this work has shown that the good $\mu\beta_{\text{EFISH}}$ values of novel 5- π -delocalized-donor-1,3-di(2-pyridyl)benzenes 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 $\mu\beta_{\text{EFISH}}$ values with a change of sign from positive to negative, as previously observed in the case of the simpler Pt(Medpyb)Cl complex. Both the methylated salts and the Pt(II) complexes prepared in the present work are characterized by large $\mu\beta_{\text{EFISH}}$ values that make them appealing as building blocks for NLO materials and photonic applications.

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