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Minding our L and X: Appropriate functionalization of the cyclometalated 1,3-di(2-pyridyl)benzene ligand, L, and the choice of the ancillary X ligand allow the dipolar second-order nonlinear optical response of [PtLX] complexes to be controlled (see figure).



Nonlinear Optics -

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Tuning the Dipolar Second-Order Nonlinear Optical Properties of Cyclometalated Platinum(II) Complexes with Tridentate N^C^N Binding Ligands



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Tuning the Dipolar Second-Order Nonlinear Optical Properties of Cyclometalated Platinum(II) Complexes with Tridentate N^CN Binding Ligands

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Dedicated to Dr. Rinaldo Psaro for his 60th birthday

Abstract: Appropriate functionalization of the cyclometalated ligand, L, and the choice of the ancillary ligand, X, allows the dipolar second-order nonlinear optical response of luminescent [PtLX] complexes—in which L is an N^C^N-coordinated 1,3-di(2-pyridyl)benzene ligand and X is a monodentate halide or acetylide ligand—to be controlled. The complementary use of electric-field-induced second-harmonic (EFISH) generation and harmonic light scattering (HLS) measure-

Keywords: chromophores • density functional calculations • ligand effects • nonlinear optics • platinum ments demonstrates how the quadratic hyperpolarizability of this appealing family of multifunctional chromophores, characterized by a good transparency throughout much of the visible region, is dominated by an octupolar contribution.

Introduction

Organometallic and coordination complexes that show both luminescent and second-order nonlinear optical (NLO) properties are new molecular multifunctional materials that might offer additional flexibility relative to organic molecular materials. Their luminescent and NLO properties can be tuned by introducing charge-transfer transitions between the metal and the ligands, the influence of which can be controlled according to the nature, oxidation state, and coordination sphere of the metal center.^[1,2]

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Recently we reported that various luminescent, cationic cyclometalated Ir^{III} complexes that contain a substituted 1,10-phenanthroline^[3] or 2,2'-bipyridine^[4] ligand are characterized by interesting second-order NLO properties. The use of the electric-field-induced second-harmonic (EFISH) generation method,^[5] supported by a sum-over-states time-dependent density functional theory (SOS-TD-DFT) investigation, revealed that the NLO properties are determined mainly by MLCT (metal-to-ligand charge-transfer) processes from the orbitals of the cyclometalated Ir-containing moiety, which acts as a donor system to π^* orbitals of the N^N bidentate ligand, which acts as an acceptor system.^[3] Also, some luminescent β-diketonate Ir^{III} and Pt^{II} complexes with a cyclometalated 2-phenylpyridine ligand show a significant second-order NLO response, as determined by the EFISH technique, attributed through a SOS-TD-DFT investigation to mainly intraligand charge-transfer transitions that involve the cyclometalated ligand.^[6] Tris-cyclometalated Ir^{III} complexes are also characterized by interesting secondorder NLO properties that can be tuned by the nature of the cyclometalated 2-phenylpyridine substituents.^[7]

It was recently reported^[8] that a series of unconventional terpyridine and cyclometalated dipyridylbenzene platinum(II) complexes, with the tridentate ligand carrying a strong electron-acceptor group, display large quadratic hyperpolarizabilities, as measured by the hyper-Rayleigh scattering technique (HRS). The N^C^N-coordinated cyclometalated dipyridylbenzene platinum complexes are characterized by an enhanced NLO efficiency with respect to the correspond-

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ing structurally related N^N^N-coordinated terpyridine complexes.^[8] Indeed, various luminescent 4,4'-stilbenoid-substituted N^C^N platinum(II) complexes show significant quadratic hyperpolarizabilities, as determined by the HRS technique, which are higher than those typical of purely organic 4,4'-disubstituted stilbenes, probably due to the polarization along the C–Pt bond.^[9]

These results prompted us to carry out an in-depth investigation of the electronic origin and the tuning of the second-order NLO properties of cyclometalated 1,3-di(2pyridyl)benzene platinum(II) complexes. This class of materials is of particular interest for study because of their remarkable luminescent properties.^[10] The effect of the nature of the substituents on the cyclometalated 1,3-di(2-pyridyl)benzene ligand and of the monodentate ancillary ligand (chloride or various substituted phenylacetylides) on the quadratic hyperpolarizability has been investigated by using complexes **1–10**. The interpretation of their electronic struc-



tures and optical properties has been facilitated by DFT and TD-DFT calculations. Meanwhile, the dipolar and octupolar contributions to the quadratic hyperpolarizability^[11,12] of these platinum(II) complexes have been determined experimentally by a combination of EFISH and harmonic light scattering (HLS)^[13] techniques, working with a nonresonant incident wavelength of 1907 nm, the second (2ω) and third harmonic (3ω) of which lie at 953 and 636 nm, respectively,

in a transparent region of the absorption spectra of all the Pt^{II} complexes investigated.

Experimental Section

General comments: Reagents were purchased from Sigma–Aldrich or Fluorochem. Complexes **1–5** were prepared as previously reported,^[14-18] whereas new complexes **6–10** were prepared as described below. Products were characterized by ¹H NMR (Bruker DRX-300 spectrometer) and UV-visible (Jasco V-530 spectrophotometer) spectroscopy, and by elemental analysis.

EFISH measurements: All EFISH measurements^[Sc] were carried out at the Dipartimento di Chimica of the Università degli Studi di Milano, on solutions of samples in DMF at a concentration of 1×10^{-4} M, with a nonresonant incident wavelength of 1.907 µm, which was obtained by Raman shifting the fundamental 1.064 µm wavelength produced by a Q-switched, mode-locked Nd³⁺:YAG laser manufactured by Atalaser. The apparatus used for EFISH and THG 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 $\mu\beta$ was determined by comparison with the reference solvent (DMF).

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HLS measurements: The HLS technique^[11-13] involves the detection of the incoherently scattered second-harmonic light generated by a solution of the molecule under irradiation with a laser of wavelength λ, thus leading to the measurement of the mean value of the $\beta \times \beta$ tensor product, $\langle \beta_{HLS} \rangle$. All HLS measurements were carried out at the École Normale Supérieure de Cachan in [D₇]DMF at a concentration of 1×10^{-3} M by working with a low-energy nonresonant incident radiation of 1.907 μm.

Preparation of platinum complexes: For the numbering used to assign the ¹H NMR spectroscopic signals, see Scheme 1.

N^C^N-5-Methyl-1,3-di(2-pyridyl)-

benzene platinum(II) pentafluorophenylacetylide (6): A mixture of pentafluorophenylacetylene (40.3 mg, 0.210 mmol) and 0.5 M sodium methoxide (0.4 mL, 0.210 mmol) in methanol (1 mL) was stirred for 30 min at room temperature. Then complex 1^[11] (101.0 mg, 0.210 mmol) dissolved in MeOH/ CH_2Cl_2 (4:1 v/v) was added, and the mixture was left for one day at room temperature. The solution changed color by passing from yellow to dark green. Then the solvents were removed, and the crude product was washed with water, methanol, and n-

hexane. Further purification by precipitation with dry pentane from CH₂Cl₂ gave the desired product as a green solid in almost quantitative yield (128.0 mg, 97%). ¹H NMR (300 MHz, CDCl₃): δ =9.46 (d, *J*= 5.6 Hz, *J*(¹⁹⁵Pt)=48.0 Hz, 2H; H⁶), 7.93 (t, *J*=8.0 Hz, 2H; H⁴), 7.67 (d, *J*=8.0 Hz, 2H; H⁵), 7.35 (s, 2H; H⁶), 7.23 (t, *J*=6.0 Hz, 2H; H⁵), 2.40 ppm (3H; -CH₃); ¹⁹F NMR (300 MHz, CDCl₃): δ =-136.7 (d, 2F), -157.7 (t, 1F), -159.9 ppm (t, 2F); IR (CH₂Cl₂): $\tilde{\nu}$ =2081 cm⁻¹ (C=C); elemental analysis calcd (%) for C₂₅H₁₃F₅N₂Pt: C 47.55, H 2.08, N 4.44; found: C 47.67, H 2.10, N 4.32.

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Scheme 1. ¹H NMR spectra numbering scheme.

N^C^N-5-Methyl-1,3-di(2-pyridyl)benzene platinum(II) p-nitrophenylacetylide (7): A mixture of 1-ethynyl-4-nitrobenzene (22.3 mg, 0.152 mmol) and 0.5 M sodium methoxide (0.3 mL, 0.152 mmol) in methanol (1 mL) was stirred for 30 min at room temperature. Then complex $\mathbf{1}^{[14]}$ (75.6 mg, 0.152 mmol) dissolved in MeOH/CH_2Cl_2 (4:1 v/v) was added, and the mixture was left for one day at room temperature. The solution changed color by passing from yellow to red. Then the solvents were removed, and the crude product was washed with water, methanol, and *n*-hexane. Further purification by precipitation with dry pentane from CH₂Cl₂ gave the desired product as a red solid in quantitative yield (89.0 mg, 100 %). ¹H NMR (400 MHz, CDCl₃): $\delta = 9.38$ (d, J = 5.6 Hz, J- $(^{195}\text{Pt}) = 40.8 \text{ Hz}, 2\text{H}; \text{H}^6), 8.16 \text{ (d, } J = 8.9 \text{ Hz}, 2\text{H}; \text{H}^{3''}), 7.95 \text{ (td, } J = 1.4,$ 7.8 Hz, 2H; H⁴), 7.67 (m, 4H; H^{5-2"}), 7.23 (td, J=1.4 Hz, 2H; H³), 2.62 ppm (s, 3H; –(CH₃)); IR (CH₂Cl₂): $\tilde{\nu}$ = 2083 cm⁻¹ (C=C); elemental analysis calcd (%) for C₂₅H₁₇N₃O₂Pt: C 51.20, H 2.92, N 7.16; found: C 50.97, H 2.77, N 7.03.

N^C^N-1,3-Di(2-pyridyl)-4,6-difluorobenzene platinum(II) phenylacetylide (8): A solution of 1-ethynylbenzene (15.8 mg, 0.155 mmol) and 0.5 M sodium methoxide (0.3 mL, 0.155 mmol) in methanol (1 mL) was stirred for 30 min at room temperature. Then the mixture was added to a solution of complex $\boldsymbol{3}^{[16]}$ (77.5 mg, 0.155 mmol) in MeOH/CH_2Cl_2 (5:1) that had been previously cooled to -20 °C. The mixture was left stirring at -20 °C for 4 h and then left at room temperature overnight. The solvents were removed, and the crude product was washed with water, methanol, and *n*-hexane. Further purification by precipitation with dry pentane from CH₂Cl₂ gave the desired product as a yellow solid (70.3 mg, 80%). ¹H NMR (400 MHz, $[D_8]$ THF): $\delta = 9.58$ (d, J = 5.5 Hz, $J(^{195}$ Pt) = 41.0 Hz, 2H; H⁶), 8.17 (d, J=7.8 Hz, 2H; H⁴), 8.00 (td, J=7.8 Hz, 2H; H³), 7.44 (m, 4H; H^{5-2"}), 7.27 (m, 2H; H^{3"}), 7.15 (m, 1H; H^{4"}), 6.85 ppm (t, J- $(^{19}\text{F}) = 11.4 \text{ Hz}, 1 \text{H}; \text{H}^{5}); \text{ IR (CH}_2\text{Cl}_2): \tilde{\nu} = 2091 \text{ cm}^{-1} \text{ (C=C)}; \text{ elemental}$ analysis calcd (%) for C₂₄H₁₄F₂N₂Pt: C 51.16, H 2.50, N 4.97; found: C 50.95, H 2.36, N 4.88,

N[°]*C*[°]*N*-**1,3**-**Bis**[5-(trifluoromethyl)pyridin-2-yl]-4,6-difluorobenzene platinum(II) phenylacetylide (9): A solution of phenylacetylene (24.0 mg, 0.234 mmol) and 0.5 M sodium methoxide (0.4 mL, 0.212 mmol) in methanol (1 mL) was stirred for 30 min at room temperature. Then the mixture was added to a solution of complex 4^[16] (134.7 mg, 0.212 mmol) in MeOH/CH₂Cl₂ (5:1) that had been previously cooled to -20 °C. The mixture was left stirring at -20 °C for 4 h and then left at room temperature overnight; the color changed from yellow to dark red. The solvents were removed, and the crude product was washed with water, methanol, and *n*-hexane. Further purification by precipitation with dry pentane gave the desired product as a green solid in almost quantitative yield (145.3 mg, 98%). ¹H NMR (400 MHz, THF): δ = 9.87 (s, $J_{1}^{195}Pt$) = 48.0 Hz, 2H; H⁶), 8.48 (d, J = 8.8 Hz, 2H; H⁴), 8.14 (d, J = 8.8 Hz, 2H; H³), 7.43 (d, J = 7.7 Hz, 2H; H^{2°}), 7.27 (t, J = 7.6 Hz, 2H; H^{3°}), 7.16 (t, J = 7.6 Hz, 1H; H^{4°}), 6.96 pm (t, $J_{1}^{(9}F)$ = 11.0 Hz, 2H; H^{4°}); IR (CH₂Cl₂): $\tilde{\nu}$ = 2091 cm⁻¹ (C=C); elemental analysis calcd (%) for C₂₆H₁₂F₈N₂Pt: C 44.65, H 1.73, N 4.01; found: C 44.72, H 1.72, N 4.06.

N^C^N-1,3-Bis[5-(trifluoromethyl)pyridin-2-yl]-4,6-difluorobenzene platinum(II) *p*-dimethylaminophenylacetylide (10): A solution of (4-ethynylphenyl)dimethylamine (30.8 mg, 0.213 mmol) and 0.5 M sodium methoxide (0.4 mL, 0.213 mmol) in methanol (1 mL) was stirred for 30 min at room temperature. Then the mixture was added to a solution of complex 4^[16] (134.7 mg, 0.212 mmol) in MeOH/CH₂Cl₂ (5:1) that had been previously cooled to -20°C. The mixture was left stirring at -20°C for 4 h and then left at room temperature overnight; its color changed from yellow to dark red. The solvents were removed, and the crude product was washed with water, methanol, and n-hexane. Further purification by precipitation with dry pentane from CH₂Cl₂ gave the desired product as a red solid (63.2 mg, 40 %). ¹H NMR (400 MHz, THF): $\delta = 9.58$ (s, J- $(^{195}Pt) = 48.0 \text{ Hz}, 2\text{ H}; \text{H}^{6}), 8.21 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; \text{H}^{4}), 7.86 \text{ (d, } J = 8.5 \text{ Hz}, 2\text{ H}; 100 \text{ Hz}, 2\text{ H}; 100 \text{ Hz}, 2\text{ Hz},$ 8.5 Hz, 2H; H³), 7.15 (d, J=8.8 Hz, 2H; H^{3"}), 6.68 (d, J=8.8 Hz, 2H; H^{2"}), 6.58 (d, $J({}^{19}\text{F}) = 11.0 \text{ Hz}$, 1H; H⁴), 2.37 ppm (6H; $-(CH_3)_2$); IR (CH₂Cl₂): $\tilde{\nu} = 2085 \text{ cm}^{-1}$ (C=C); elemental analysis calcd (%) for C₂₈H₁₇F₈N₃Pt: C 45.29, H 2.31, N 5.66; found: C 44.87, H 2.72, N 5.42.

Computational methods: The molecular geometry of all the Pt^{II} complexes was optimized in vacuo by means of a DFT approach using the B3LYP^[19] exchange-correlation functional and a LANL2DZ basis set^[20] for all atoms along with the corresponding pseudopotentials for Pt. We also reoptimized the geometries in DMF solution, finding a small difference of dipole moment compared to geometries in vacuo, which are therefore used throughout the manuscript. All the calculations were performed with Gaussian 03^[21] without any symmetry constraints. Singlepoint calculations were performed in DMF solution on the optimized geometry in vacuo using a LANL2DZ basis set. Solvation effects were included by means of the conductor-like polarizable continuum model (C-PCM)^[22] as implemented in Gaussian 03. Since in Gaussian 03 the DMF solvent was not parameterized, we employed the cavity parameters of the similar acetonitrile solvent and the ϵ and ϵ_{INF} values for DMF from Gaussian 09. Ground-state dipole moments have been computed for complexes 1-10 both in vacuo and in DMF solution. In the evaluation of β_{EFISH} from $\mu\beta_{\text{EFISH}}$, the value of μ_{tot} calculated in DMF solution (Table 1) was always used. Analysis of the electronic structure in terms of energy and character of the frontier molecular orbitals has been carried out for complexes 1-10 in DMF solution. TD-DFT calculations have been performed in DMF solution for complex 4 using the B3LYP functional, the SDD basis set for Pt, and the 6-31G** basis set for all the other atoms. Fifty singlet-singlet transitions have been computed and interpolated by Gaussian functions with σ =0.15 eV, which roughly corresponds to a full width at half-maximum (FWHM) value of approximately 0.36 eV. To qualitatively understand the electronic factors that govern the secondorder NLO response of complex 4, the lowest 50 singlet-singlet excitation energies, transition dipole moments, oscillator strengths, and excitedstate dipole moments of complex 4 were calculated by TD-DFT to evaluate the quadratic hyperpolarizability by means of the sum-over-states (SOS) approach. The excited-state dipole moments were calculated by using the RhoCI density for each calculated excited state, as implemented in Gaussian 03. The SOS approach requires in principle the calculation of dipole matrix elements between all possible couples of excited states (three level terms) in addition to the ground-to-excited-state transition dipole moments (two level terms).^[23] It turns out, however, that three-level terms show approximately the same scaling with the number of excited states as two-level terms, so that the latter can be used for a qualitative assessment of the contributions to the quadratic hyperpolarizability.[23]

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Table 1. Experimental electronic spectra and $\mu\beta_{\text{EFISH}}$, calculated total μ , and related β_{EFISH} of the investigated Pt^{II} complexes.

	Absorbance ^[a] $\lambda_{\max} \text{ [nm] } (\varepsilon \text{ [} M^{-1} \text{ cm}^{-1} \text{])}$	$\frac{\mu\beta_{\rm EFISH}{}^{\rm [b]}}{[\times 10^{-48}~{\rm esu}]}$	$\mu_{ m tot}^{[c]}$ [D]	$egin{aligned} η_{ ext{EFISH}}^{[b]}\ &[imes 10^{-30} ext{ esu}] \end{aligned}$
1	334 (8000), 382 (9600), 412 (9000)	-480	10.2	-47
2	325 sh (7100), 377 (8900), 420 (9500), 489 (400)	-1060	6.0	-177
3	321 (11300), 334 (14100), 366 (13000), 375 (15300), 438 (100), 467 (100)	-720	5.4	-144
4	331 (10000), 342 (10700), 387 (11300), 474 (300)	-2470	13.1	-188
5	335 (8500), 388 (8400), 410 (7300)	-2190	7.4	-296
6	340 (6600), 368 (4000), 384 (3200), 410 br (2300)	-2290	12.7	-180
7	329 (13 300), 361 (10 100), 394 br (7800), 465 (700)	-1860	17.9	-104
8	328 (9700), 334 (8900), 374 (8000), 410 (3200), 469(200)	-1060	2.4	-442
9	346 (7200), 399 (7200), 449 (3700)	-1980	9.2	-215
10	341 (14600), 384 (9200), 493 (4100)	-2020	4.3	-470

[[]a] From 320 nm in DMF. [b] Working in DMF with an incident radiation wavelength of 1.907 μ m; estimated uncertainty in EFISH measurements is $\pm 10\%$. [c] Calculated at the B3LYP level in DMF; values computed under vacuum were 7.2, 3.8, 3.6, 9.3, 5.7, 10.7, 14.3, 1.7, 6.3, and 1.8 Debye for complexes **1–10**, respectively. The error on μ is ± 1 D.

Results and Discussion

Synthesis and spectroscopic characterization: The known complexes (1-5) were prepared as previously reported,^[14-18] whereas the new complexes (6-10) were readily obtained in good to excellent yield by reaction of the cyclometalated platinum(II) chloride precursors with the suitable phenylacetylide anion, prepared by the deprotonation of HC \equiv CC₆F₅ or HC \equiv CC₆H₄-4-R (R = H, NO₂, NMe₂) with sodium methoxide (see the Experimental Section). All platinum(II) complexes were fully characterized by elemental analyses and by IR, NMR (see the Experimental Section), and UV-visible (see Table 1) spectroscopies. The electronic absorption spectra obey Lambert-Beer's law when the concentration is lower than 1.0×10^{-4} M, which suggests in this range of concentrations a lack of significant aggregation such as through π - π stacking or Pt-Pt interactions.^[24] The absorption band maxima at wavelengths greater than 330 nm and their extinction coefficients are presented in Table 1.

All complexes show intense bands in the 260-320 nm region, which can be assigned to intraligand ${}^{1}\pi$ - π * transitions of the cyclometalated 1,3-di(2-pyridyl)benzene^[25] and of the ancillary acetylide^[26] ligands. The less-intense absorption bands at 330-450 nm were reported to correspond to transitions of mixed charge-transfer/ligand-centered character.^[27] In accordance, they exhibit a pronounced negative solvatochromic behavior (for example, complex 4 in Figure 1), typical of electronic transitions with an appreciable degree of charge-transfer character; the blueshift of the peaks with increasing solvent polarity suggests a lower dipole moment in the excited state than in the ground state.^[25] Although the substitution of the chloride ligand by various phenylacetylide ligands does not change the spectral profile substantially, the individual bands in the region 330-450 nm become rather less well resolved, with evidence of a tail to longer wavelengths. This tail might tentatively be attributed to a $\pi_{C=C} \rightarrow \pi^*_{N^{\wedge}C^{\wedge}N}$ ligand-to-ligand charge-transfer (LLCT) transition, by analogy with other platinum(II) acetylide complexes.[26,28]



Figure 1. Absorption spectra of complex 4 in various solvents.

Dipole moments, electronic structure, and absorption spectra: The molecular geometries of complexes 1-10 were optimized by DFT calculations (see the Experimental Section). The structures were oriented in all cases with the 1,3-di(2pyridyl)benzene moiety in the xy plane and with the y axis crossing the Pt^{II} center (see Figure 2). The optimized geometries of the structure of complexes 1-10 are reported in Figure 2 along with the corresponding y component of the dipole moments (μ_{ν}) calculated in DMF solution, whereas the total dipole moments (μ_{tot}) calculated both in vacuo and in DMF solution are reported in Table 1. It appears that the dipole moment is located mainly along the y axis, which is in agreement with a $C_{2\nu}$ symmetry of the molecular architecture. Moreover, the calculated dipole moments in DMF solution are higher than those calculated in vacuo (there is an increase of about 1.2-1.6 times for complexes 1-9, with the largest increase of a factor of 2.4 for complex 10). For complexes 1-10, the energies of the frontier HOMO-LUMO molecular orbitals computed in solution are schematized in Figure 3, and the corresponding HOMO and LUMO isodensity plots are reported in Figure 4.

Comparison between the computed (TD-DFT calculations) and experimental absorption spectra of complex **4** (Figure 5) confirms that the simulated spectrum nicely re-

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Figure 2. The optimized geometry of complexes **1–10** and the dipole moment, calculated in DMF and expressed in Debye, along the *y* axis.



Figure 3. Schematic representation of the energy levels of complexes 1–10 calculated in DMF.

produces the main experimental features, with the calculated low-energy absorption band redshifted only by 0.05 eV with respect to the experimental one. Moreover, in correspondence with the experimental shoulder, we confirmed that we have a transition computed at 365 nm that is characterized by a very low oscillator strength.

The lowest-energy absorption band of complex 4 is characterized by a HOMO \rightarrow LUMO+1 transition in which the HOMO level is delocalized along the yz plane on the metal center, the ancillary Cl ligand, and the cyclometalated benzene ring, whereas the LUMO+1 level is delocalized on the pyridyl rings and on the central phenyl carbon bound to the metal center of the 1,3-di(2-pyridyl)benzene ligand, with



Figure 4. Isodensity plot (isodensity value = 0.035) of the HOMO and LUMO levels of complexes 1–10 calculated in DMF solution.

small participation of the Pt d_{yz} orbital (see Figure 5). The LUMO+1 of complex 4 has an electronic distribution similar to that of the LUMO+1 of complexes 2, 7, and 10, and to the LUMO of complexes 1, 3, 5, 6, and 8. The experimental shoulder at 365 nm originates from a HOMO-2 \rightarrow LUMO transition, in which HOMO-2 is a nonbonding combination of the Pt d_{xz} orbital and the π orbital on the pyridyl and benzene rings, whereas the LUMO is a π^* orbital completely delocalized on the 1,3-bis(5-(trifluoromethyl)-pyridin-2-yl)-4,6-difluorobenzene ligand with a small metal contribution. Both these transitions have MLCT character with partial intraligand π - π^* nature. Other experimental absorption bands at 342 and 330 nm are also of MLCT character character on the 1,3-di(2-pyridyl)benzene ligand.

Second-order NLO properties: The second-order NLO properties of the various platinum(II) complexes were first investigated by the EFISH^[5] technique (see Table 1). It is known that this technique can provide direct information on the intrinsic dipolar molecular second-order NLO properties through Equation (1):

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

in which $\mu\beta_{\text{EFISH}}/5kT$ is the dipolar orientational contribution, and $\gamma(-2\omega; \omega, \omega, 0)$, a third-order term at frequency ω



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Figure 5. Top: Comparison between the TD-DFT simulated spectrum (continuous line) and the experimental spectrum (dotted line) of complex 4 in DMF. Vertical lines correspond to calculated excitation energies and oscillator strengths. Inset: Isodensity surface plots (isodensity counter = 0.035) of molecular orbitals involved in the lowest intense transition that gives rise to the absorption band at 396 nm. Bottom: Calculated contributions to the quadratic hyperpolarizability β for complex 4 as a function of the excited-state wavelength.

of incident light, is a purely electronic cubic contribution that can usually be neglected when studying the second-order NLO properties of strongly dipolar molecules.^[2]

The experimental $\mu\beta_{\text{EFISH}}$ values of all the investigated Pt^{II} complexes, measured as solutions in DMF and working with a nonresonant incident wavelength of 1.907 µm, are reported in Table 1. The values of β_{EFISH} , the projection along the dipole moment axis of the vectorial component of the tensor of the quadratic hyperpolarizability, were obtained by using the values of the dipole moments calculated by DFT.

All complexes are characterized by a negative value of $\mu\beta_{\text{EFISH}}$ owing to the negative value of $\Delta\mu_{eg}$ upon excitation,^[2] which reflects a decrease in the dipole moment upon excitation as suggested by the negative solvatochromic behavior^[25] of the low-energy MLCT transitions reported above. It follows that the second-order dipolar NLO response is probably dominated by the charge transfer from platinum to the cyclometalated ligand. In accordance, when taking the Pt^{II}-chloride complexes (1–4; Table 1) into consideration, the substitution of a methyl group (complex 1)

by a fluorine atom (complex 2) on the metalated benzene ring causes an increase in the absolute value of $\mu\beta_{\rm EFISH}$ and a decrease in the dipole moment, therefore leading to a large increase (by a factor of 3.8) of $\beta_{\rm EFISH}$, as expected for a stronger charge-transfer process. The absolute value of $\mu\beta_{\rm EFISH}$ for complex 3, with two fluorine atoms on the 4- and 6-positions of the metalated benzene ring, is lower than that of complex 2 in part due to a decrease of the dipole moment, whereas the absolute value of $\beta_{\rm EFISH}$ is only slightly lower. A slightly higher value of $\beta_{\rm EFISH}$ is shown by complex 4, which has a structure that shows two additional CF₃ groups on the pyridine rings. Since the dipole moment is enhanced by a factor of 2.4, a large value of $\mu\beta_{\rm EFISH}$ (-2470× 10⁻⁴⁸ esu) is obtained.

A large $\mu\beta_{\text{EFISH}}$ value (-2190×10⁻⁴⁸ esu) is also reached upon substitution of the chloride ancillary ligand of complex 1 by a phenylacetylide ligand (complex 5) due to a strong increase in the absolute value of β_{EFISH} (by a factor of 6.3), probably caused by an increased charge transfer from the Pt–phenylacetylide moiety. Interestingly, the value of $\mu\beta_{\text{EFISH}}$ is not strongly affected by increasing the electron-withdrawing properties of the acetylide ligand, as observed upon going from the phenylacetylide 5 to the pentafluorophenylacetylide 6, due to the expected large decrease of the absolute value of β_{EFISH} buffered by an accompanying increase of the dipole moment. Substitution of the chloride ancillary ligand of complexes 3 and 4 by the phenylacetylide ligand to give complexes 8 and 9, respectively, also leads, as in the case of complexes 1 and 5, to an increase in the absolute value of β_{EFISH} with a parallel significant decrease in the dipole moment.

The addition of electron-withdrawing substituents on the 1,3-di(2-pyridyl)benzene cyclometalated ligand of Pt^{II}-chloride complexes thus leads to an enhancement of its acceptor properties, as confirmed by a decrease in the energy of the LUMO orbitals (Figure 3), and therefore to a more facile MLCT from the Pt atom, which corresponds to an increase in the absolute value of β_{EFISH} . Substitution of chloride with phenylacetylide as ancillary ligand (complexes 1, 3, 4 and 5, **8**, **9**, respectively) leads to an increase in β_{EFISH} in agreement with the calculated decrease in the HOMO-LUMO gap (by 0.40, 0.59, and 0.68 eV, respectively) that is caused by a shift of the HOMO orbitals, which are located mainly on the phenylacetylide ligand, at higher energy (see Figure 3). As shown in the isodensity plots reported in Figure 4, the HOMO-LUMO transition corresponds, with the exception of complex 7, to a charge transfer from the phenylacetylide ligand to the acceptor 1,3-di(2-pyridyl)benzene cyclometalated ligand. In accordance, for complex 6 (with the pentafluorophenylacetylide ligand) such charge transfer is less important (Figure 4). This lower charge transfer from the pentafluorophenylacetylide ligand relative to that of complex 5 (with phenylacetylide) and the increase in the HOMO-LUMO gap due to a strong stabilization of the HOMO with respect to the LUMO (Figure 3) are the origin of the decrease of the absolute value of $\beta_{1.907 \text{ EFISH}}$ upon going from 5 to 6.

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To qualitatively gauge the electronic factors that govern the second-order NLO properties for the prototype complex 4, we determined the contribution of each excited state to the static quadratic hyperpolarizability by means of the SOS method.^[23] In the bottom panel of Figure 5 the contribution to the quadratic hyperpolarizability as a function of the excited-state wavelength for complex 4 is reported. The overall quadratic hyperpolarizability has a negative value, as experimentally found, because the negative contributions dominate the small positive contributions. We found that three main transitions determine the negative sign of the hyperpolarizability, which are associated to the S₃, S₇, and S₃₆ excited states. These excited states are characterized by (relatively) strong transition dipole moments (absolute values of 0.30, 0.97, and 1.49 a.u., for the S₃, S₇, and S₃₆ excited states, respectively, along the y axis) and by a sizable decrease in the dipole moment with respect to the ground state ($\Delta \mu_{eg}$ 3.6, 4.9, and 4.7 D for the $S_3,\,S_7,$ and S_{36} excited states, respectively). Thus, even the high-lying S_{36} excited state partly contributes to the second-order NLO response by virtue of the very strong transition dipole moment. S_2 and S_7 have a strong MLCT character that involves as starting state the Pt-based orbitals (HOMO and HOMO-2, respectively) and the LUMO+1 as the arriving state (see Figure 5).

In addition to the transitions responsible for the dipolar NLO response, our SOS analysis for complex **4** has also highlighted the presence of several excitations endowed with high oscillator strength but that also give rise to a small variation in the excited-state dipole moments (e.g., S_9 and S_{10} , with f=0.18 and 0.17, and $\Delta \mu_{eg} \approx 1$ D), which could be associated with an octupolar NLO response.

Interestingly, complex **7**, with a phenylacetylide ancillary ligand carrying a nitro group in the *para* position of the phenyl ring, shows a completely different electronic structure. In fact, the HOMO level is not really localized on the nitrophenylacetylide ligand, whereas the LUMO level is, particularly on the strong acceptor nitro group (Figure 4), and not on the two pyridinic rings of cyclometalated 1,3-di(2-pyridyl)benzene, which is different to the other Pt^{II} complexes investigated. For complex **7**, the lowest unoccupied orbitals delocalized on the pyridyl rings of the cyclometalated ligand are the LUMO+1 and LUMO+2, with the LUMO+1 being 1.16 eV above the LUMO and the LUMO+2 still 0.10 eV above.

Calculation of the lowest SOS contributions to the hyperpolarizability for complex **7** shows that the HOMO–LUMO charge transfer along the *y* axis from the metalated benzene part of the chelated ligand to the nitrophenylacetylide ligand gives rise to a dominant positive contribution to β_{EFISH} , opposite in direction to the HOMO–LUMO charge transfer of all the other Pt^{II} complexes investigated.

The decrease in the β_{EFISH} value of complex 7, which maintains its negative sign, is due to the counteracting HOMO–LUMO positive contribution, which partly cancels the important negative contribution of the HOMO–LUMO+1/HOMO–LUMO+2 excitations to the NLO response. These excited states, characterized by a negative

 $\Delta \mu_{\rm eg}$ upon excitation, prevail over the overall $\beta_{\rm EFISH}$ sign, thus leading to an overall negative (albeit reduced) value of $\beta_{\rm EFISH}$.

On the contrary, in the case of complex **10**, which has a phenylacetylide ligand with a strong donor dimethylamino in the *para* position of the phenyl ring, the LUMO level is completely centered on the cyclometalated 1,3-di(2-pyridyl)-benzene chelated ligand and the HOMO on the phenylacetylide ligand. It follows a strong HOMO–LUMO electron transfer completely opposite to that of **7**, thereby producing one of the largest values of β_{EFISH} (-470×10⁻³⁰ esu) among the Pt^{II} complexes investigated (Table 1).

It turns out that in all cases, even if the direction of the HOMO-LUMO charge transfer is strongly opposite (complex 7 and 10), the platinum atom might act as an efficient bridge. Clearly the nature of the substituents on the phenylacetylide ligand can tune the second-order NLO response and the value of the dipole moment. Also, the substitution on the cyclometalated 1,3-di(2-pyridyl)benzene ligand might tune the second-order NLO response, since in the majority of complexes the LUMO level is delocalized on this chelated ligand, which is thus involved in the charge-transfer process. For instance, the introduction of a CF₃ group on the pyridinic rings upon going from 3 to 4 causes an increase in both β_{EFISH} and the dipole moment (Table 1) to afford a high value of $\mu\beta_{\text{EFISH}}$. Similarly, upon going from 8 to 9, there is an increase in the dipole moment and of $\mu\beta_{\text{EFISH}}$, but the β_{EFISH} value decreases, probably because the LUMO of complex 9 is not on both pyridinic rings (Figure 4).

To have a complete understanding of the various components of the second-order NLO properties of these platinum(II) complexes, and in particular to evaluate not only the dipolar but also the octupolar contribution to the quadratic hyperpolarizability, we carried out an HLS investigation of some representative complexes (1, 2, 6, and 10) by working at an incident wavelength of 1.907 μ m (Table 2). The dipolar

Table 2. HLS experimental values of $\langle \beta_{\rm HLS} \rangle$ and related dipolar and octupolar contributions and modulus of the quadratic hyperpolarizability of some of the investigated Pt^{II} complexes, working in DMF with an incident radiation wavelength of 1.907 μ m.^[a]

Complex	$\langle eta_{ m HLS} angle$	$\left\ \overline{\beta}^{J=1}\right\ $	$\left\ \overline{\beta}^{I=3}\right\ $	$\ \overline{\beta}\ $
	$[\times 10^{-30} \text{ esu}]$	$[\times 10^{-30} \text{esu}]$	[×10 ⁻³⁰ esu]	$[\times 10^{-30} \text{ esu}]$
1	285	36	922	923
2	432	136	1384	1391
6	345	140	1097	1105
10	278	364	709	797

[a] Estimated uncertainty in HLS measurements is $\pm 10\%$.

(J=1) and octupolar (J=3) contributions and the modulus of the quadratic hyperpolarizability $(||\overline{\beta}||)$ have been calculated by Equations (2), (3), and (4)^[11,12,29] since all compounds have a $C_{2\nu}$ symmetry:

$$\left|\overline{\beta}\right|^{2} = \left\|\overline{\beta}^{\prime-1}\right\|^{2} + \left\|\overline{\beta}^{\prime-3}\right\|^{2} \tag{2}$$

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$$\|\beta^{I=1}\| = \sqrt{\frac{3}{5}}\beta_{\text{EFISH}} \tag{3}$$

$$\left\langle \beta_{\text{HLS}}^2 \right\rangle = \left\langle |\beta_{XXX}|^2 \right\rangle + \left\langle |\beta_{ZXX}|^2 \right\rangle = \frac{2}{9} \left\| \overline{\beta}^{I=1} \right\|^2 + \frac{2}{21} \left\| \overline{\beta}^{I=3} \right\|^2 \tag{4}$$

The resulting values of $\|\overline{\beta}^{J=3}\|$ reported in Table 2 show that the dipolar contribution" is much lower than the octupolar one, as previously observed for various β -diketonates Ln^{III},^[29] Ir^{III},^[6b] and Pt^{II[6b]} complexes, [Ru(substituted 1,10phenanthroline)(PPh₃)₂Cl₂],^[6b] [Ru(substituted terpyridine)₂] [4-EtPhCO₂]₂^[6c] and cationic bipyridyl iridium(III)^[4] complexes. In particular, complexes 1, 2, and 6 are characterized by a remarkably high value of the quadratic hyperpolarizability $\|\overline{\beta}\|$ owing to an important contribution of the octupolar component, with the dipolar component being less than 13% of the octupolar one. As expected, the dipolar contribution to the quadratic hyperpolarizability $\|\overline{\beta}^{\prime = 1}\|$ of complex **10** is relatively high (51%) due to a particularly strong charge transfer from the ancillary NMe₂-phenylacetylide to the cyclometalated 1,3-di(2-pyridyl)benzene ligand. In agreement with this suggestion, by enhancing the acceptor properties of the cyclometalated chelated ligand, the increase in the quadratic hyperpolarizability is more relevant for the dipolar contribution than for the octupolar one (enhancement factor of 3.8 and 1.5, respectively, upon going from 1 to 2; Table 2).

Conclusion

This investigation on various cyclometalated 1,3-di(2-pyridyl)benzene platinum(II) complexes demonstrates the facile tuning of their significant dipolar second-order nonlinear optical properties measured by the EFISH technique. An appropriate substitution of the cyclometalated or phenylacetylide ligands might allow the tuning of the second-order NLO response $\beta_{1.907 \text{ EFISH}}$ of this family of chromophores that is characterized by a good transparency and also by multifunctional properties since they are intense emitters with high quantum yields when excited at shorter wavelengths than those used here for the NLO studies.^[10] The addition of electron-withdrawing substituents on the cyclometalated ligand leads to an increase in its acceptor properties and therefore to an enhancement not only of the dipolar contribution to the quadratic hyperpolarizability measured by the HLS technique but also of the octupolar one. A further enhancement is achieved by substitution of the chloride ancillary ligand with the phenylacetylide ligand, particularly when the latter bears a strong donor group. In this ligand, the dipolar second-order NLO response is controlled by a charge-transfer process from the acetylide ligand to the cyclometalated chelated ligand with very little involvement of the Pt metal, which acts mainly as a linker. This is a rather unusual process for metal complexes that act as secondorder NLO chromophores. In fact, in this kind of chromophores, the second-order NLO properties are usually dictat-

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ed by MLCT or LMCT transitions with a direct involvement of the metal; however, examples of ligand-to-ligand chargetransfer processes mediated by the metal have been reported for Ir^{III},^[3a] and for d⁸-metal complexes coordinated to two dithiolate ligands^[30] and to mixed diimine and dithiolate ligands.^[31] Finally, the presence of CF₃ groups on the 5-position of the pyridine ring of the cyclometalated chelated ligand is a tool to increase the dipole moment and lead to large $\mu\beta_{\text{EFISH}}$ values.

In conclusion, the Pt^{II} complexes investigated are a new family of organometallic second-order NLO chromophores with a response that is easily tunable by a rational approach, whereby in specific cases the Pt atom plays the role of a central bridge of the transfer process from the donor to the acceptor moieties of the molecular structure.

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