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Novel cyclometallated 5-π-delocalized donor-1,3-di(2-pyridyl)benzene platinum(II) complexes with good second-order nonlinear optical properties†

Mattia Fontani,[a] Eleonora Garoni,[a] Alessia Colombo, *[a] Claudia Dragonetti, [a,b] Simona Fantacci,*[c] Henri Doucet, [d] Jean-François Soulé, [d] Julien Boixel,[d] Véronique Guerchais [d] and Dominique Roberto [a,b]

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Five new platinum(II) complexes bearing a cyclometallated 5-π-delocalized donor-1,3-di(2-pyridyl)benzene were prepared and fully characterized. Their second-order nonlinear optical (NLO) properties were determined by the Electric-Field Induced Second Harmonic generation (EFISH) technique, working in DMF solution with an incident wavelength of 1907 nm, whereas the dipole moments were determined by Density Functional Theory (DFT) calculations. Remarkably, the platinum(II) complex with a cyclometallated 5-guaiazulene-CH=CH-1,3-di(2-pyridyl)benzene appears as a very good candidate for application in photonics, being characterized by the largest second-order NLO response. Besides, it appeared that the nature of substituents on thiophene, chosen as π-delocalized moiety in position 5 of the 1,3-di(2-pyridyl)benzene, strongly affects the NLO properties.

Introduction

Compounds with second-order nonlinear optical (NLO) properties are of great interest as building blocks to prepare materials suitable for optical communications, optical data processing and storage, or electrooptical devices.[1,2] Typically, in order to show a significant second-order NLO response, a molecule must be non-centrosymmetric, with charge-transfer transitions at relatively low energy and characterized by a large transition dipole moment and a large difference between the excited state and the ground state molecular dipole moment ($\Delta\mu_{eg}$). This can be achieved in linear organic molecules by connecting an electron-donor and an electron-acceptor group through a π-conjugated polarizable spacer, as it occurs in classical organic dipolar push–pull systems.[1–3] Organometallic complexes represent a fascinating and growing class of second-order NLO compounds that can offer additional flexibility, when compared to organic molecules, due to the presence of metal–ligand charge-transfer transitions usually at low energy and of high intensity. These transitions are tunable by virtue of the nature, oxidation state and coordination sphere of the metal center which may act as electron-donor or electron-acceptor.[4–11]

In particular, the second-order NLO response of phenylpyridines increases upon cyclometallation, an effect at the origin of cyclometallated Ru(II),[12] Ir(III)[13–24] and Pt(II)[24,25] complexes characterized by good NLO properties. Platinum(II) compounds incorporating an N^N^C-cyclometallated 6-phenyl-2,2′-bipyridine constitute another NLO-active family.[26,27] Besides, it was reported that Pt(II) complexes with tridentate ligands based on a cyclometallated 1,3-di(2-pyridyl)benzene, which offers the metal center 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.[28] The good second-order nonlinear optical properties of various platinum(II) complexes with a cyclometallated 1,3-di(2-pyridyl)benzene, well-known for their emissive properties,[29] have also been evidenced by the Electric-Field Induced Second Harmonic generation (EFISH) technique.[30–32] In particular, the cyclometallated Pt(II) chloro complex of *trans*-5-(*p*-(*N*,*N*-diphenylamino)styryl)-1,3-di(2-pyridyl)benzene is characterized by a high dipole moment in the ground state (μ = 10.7 D) and a good second-order NLO response ($\mu\beta_{\text{EFISH}} = -880 \times 10^{-48}$ esu) mainly determined by a charge transfer transition from

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[a] *Dipartimento di Chimica dell'Università degli Studi di Milano, UdR-INSTM, via Golgi 19, I-20133 Milano, Italy. E-mail: alessia.colombo@unimi.it*

[b] *ISTM-CNR and SmartMatLab dell'Università degli Studi di Milano, via Golgi 19, I-20133 Milano, Italy*

[c] *Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), CNR-ISTM, Via Elce di Sotto 8, I-06213 Perugia, Italy. E-mail: simona@thch.unipg.it*

[d] *UMR 6226 CNRS-Université de Rennes 1, Institut des Sciences Chimiques de Rennes, Campus de Beaulieu, 35042 Rennes, France. E-mail: julien.boixel@univ-rennes1.fr*

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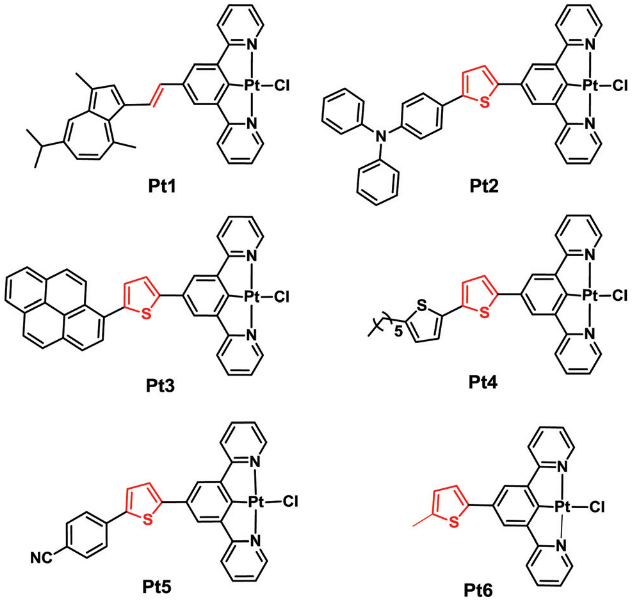


Chart 1 Compounds investigated for their second-order nonlinear optical properties.

platinum to the cyclometallated ligand.[31] Similar values (μ = 9.4 D; $\mu\beta_{EFISH}$ = −820 × 10^{-48} esu) were obtained by substitution of the *N*,*N*-diphenylamino group by a pyrene moiety.[31]

These results prompted us to prepare a Pt(II) chloro complex bearing a novel π-delocalized cyclometallated 5-guaiazulene-CH=CH-1,3-di(2-pyridyl)benzene (**Pt1**, Chart 1) in order to investigate its second-order NLO properties. Besides we prepared four novel complexes (**Pt2**, **Pt3**, **P4**, **Pt5**) bearing variously 5-substituted thiophene moieties in position 5 of the 1,3-di(2-pyridyl)benzene, in order to compare their NLO response with that of the known related complex with a methyl group on the thiophene (**Pt6**)[33] and thus to understand the effect of the nature of thiophene substituents. Their NLO response was determined by the EFISH technique[34–36] in DMF, 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. The dipole moments and the optical properties were evaluated by Density Functional Theory (DFT) calculations.

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. 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). ^{1}H and ^{13}C spectra were recorded at 400 MHz on a Bruker AVANCE-400 instrument. Chemical shifts (δ) are expressed in ppm relative to internal Me_4Si as standard. Signals are abbreviated as s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet. 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. The reference complex **Pt6** was prepared as previously reported.[33]

Synthesis of ligands L1–L5

General procedure for the synthesis of L1–L4. A mixture of the suitable 1,3 dibromophenyl derivative (0.14 mmol; prepared as described in the ESI†), 2-(tri-*n*-butylstannyl)pyridine (133 μL, 0.35 mmol), $PdCl_2(PPh_3)_2$ (29 mg, 0.04 mmol) and LiCl (53 mg, 1.26 mmol) was suspended in toluene (5 mL) and heated at reflux under argon atmosphere for 48 h. After cooling to room temperature, an aqueous solution of NaOH 1 M was added. The resulting solution was extracted with AcOEt and the organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel.

L1: Flash chromatography (hexane : AcOEt, from 7 : 3 to 2 : 8). The desired product was obtained as a green laque (64 mg). Yield: 56%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.70 (2H, m), 8.41 (2H, m), 8.21 (2H, m), 8.03 (1H, m), 7.97 (3H, m), 7.80 (3H, m), 7.28 (2H, m), 7.11 (1H, d, J = 15.8 Hz), 6.88 (1H, d, J = 10.9 Hz), 3.10 (3H, s), 3.02 (1H, d, J = 6.8 Hz), 2.65 (3H, s), 1.36 (6H, d, J = 6.8 Hz). Elem. anal. calcd for $C_{33}H_{30}N_2$: C, 87.19; H, 6.65; N, 6.16. Found: C, 87.21; H, 6.64; N, 6.18.

L2: Flash chromatography (hexane : AcOEt, 7 : 3). The desired product was obtained as a yellow solid (138 mg). Yield: 82%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.77 (2H, d, J = 4.8 Hz), 8.51 (1H, s), 8.33 (2H, d, J = 1.5 Hz), 7.9 (2H, d, J = 7.9 Hz), 7.81 (2H, dt, J = 1.7 Hz, 7.9 Hz), 7.54 (2H, d, J = 8.6 Hz), 7.49 (1H, d, J = 3.8 Hz), 7.29 (7H, m), 7.14 (4H, d, J = 7.6 Hz), 7.10 (2H, d, J = 8.6 Hz), 7.06 (2H, d, J = 7.3 Hz). Elem. anal. calcd for $C_{38}H_{27}N_3S$: C, 81.84; H, 4.88; N, 7.53. Found: C, 81.82; H, 4.89; N, 7.55.

L3: Flash chromatography (AcOEt : CH_2Cl_2, 1 : 4). The desired product was obtained as a yellow laque (23 mg). Yield: 32%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.78 (2H, d, J = 4.7 Hz), 8.65 (1H, d, J = 9.3 Hz), 8.59 (1H, s), 8.45 (2H, d, J = 1.5 Hz), 8.22 (4H, m), 8.16 (2H, m), 8.12, (1H, d, J = 1.8 Hz), 8.05 (1H, t, J = 7.6 Hz), 7.95 (2H, d, J = 7.9 Hz), 7.83 (2H, dt, J = 1.7 Hz, 7.8 Hz), 7.70 (1H, d, J = 3.6 Hz), 7.43 (1H, d, J = 3.6 Hz), 7.31 (2H, m). Elem. anal. calcd for $C_{36}H_{22}N_2S$: C, 84.02; H, 4.31; N, 5.44. Found: C, 83.99; H, 4.34; N, 5.48.

L4: Flash chromatography (hexane : AcOEt, 9 : 1). The desired product was obtained as a yellowish oil (50 mg). Yield: 52%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.68 (1H, s), 8.50 (2H, d, J = 4.3 Hz), 8.23 (2H, s), 7.49 (2H, m) 7.25 (2H, d, J = 4.3 Hz), 7.14 (2H, m), 7.04 (4H, m), 2.84 (2H, m), 2.11 (2H, m), 1.57 (6H, m), 0.88 (t, 3H). Elem. anal. calcd for $C_{30}H_{28}N_2S_2$: C, 74.96; H, 5.87; N, 5.83. Found: C, 75.03; H, 5.85; N, 5.81.

Synthesis of L5. To a 25 mL oven dried Schlenk tube, 4-(thiophen-2-yl)benzonitrile (370 mg, 2.0 mmol; prepared as described in the ESI†), 1-bromo-3,5-dipyridylbenzene (311 mg, 1 mmol), KOAc (196 mg, 4.0 mmol), PdCl(C_3H_5)(dppb) (12 mg, 0.02 mmol) and DMA (4 mL) were successively added. The reaction mixture was evacuated by vacuum–argon cycles (5 times) and stirred at 150 °C (oil bath temperature) for 16 hours. After cooling the reaction at room temperature and concentration, the crude product was purified by flash chromatography on silica gel (pentane–EtOAc, 60–40) to afford the desired compound **L5** (253 mg). Yield: 61%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.79 (d, J = 4 Hz, 2H), 8.55 (s, 1H), 8.34 (s, 2H), 7.92 (d, J = 8 Hz, 2H), 7.84 (td, J = 2, 8 Hz, 2H), 7.75 (d, J = 8 Hz, 2H), 7.69 (d, J = 8 Hz, 2H), 7.56 (d, J = 4 Hz, 1H), 7.46 (d, J = 4 Hz, 1H), 7.33 (m, 2H).

General procedure for the synthesis of complexes Pt1–Pt5

The suitable ligand (**L1–L5**; 0.25 mmol) and K_2PtCl_4 (114 mg, 0.28 mmol) were dissolved in a degassed mixture of AcOH : H_2O 1 : 1 (8 mL). The solution was degassed through freeze–pump–thaw cycles. The mixture was heated at reflux under argon for 48 h. The precipitate was filtered, washed with H_2O, MeOH, EtOH and Et_2O and dried *in vacuo*.

Pt1: The desired product was obtained as a dark green solid (25 mg). Yield: 74%. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ (ppm): 9.83 (1H, d, J = 5.9 Hz), 9.30 (1H, d, J = 5.6 Hz), 8.22 (2H, t, J = 7.6 Hz), 8.02 (4H, m), 7.77 (2H, m), 7.69 (2H, t, J = 6.9 Hz), 7.41 (2H, s), 7.35 (2H, d, J = 5.5 Hz), 3.10 (3H, s), 3.02 (1H, d, J = 6.8 Hz), 2.65 (3H, s), 1.36 (6H, d, J = 6.8 Hz). UV-Vis absorption spectra (CH_2Cl_2, 298 K): λ_{max}/nm (ε/×10^3 M^{-1} cm^{-1}): 284 (16.8), 378 (2.9). Elem. anal. calcd for $C_{33}H_{29}ClN_2Pt$: C, 57.94; H, 4.27; N, 4.09. Found: C, 57.97; H, 4.28; N, 4.11.

Pt2: The desired product was obtained as an ochre solid (87 mg). Yield: 44%. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ (ppm): 9.82 (1H, d, J = 5.9 Hz), 9.34 (1H, d, J = 4.9 Hz), 8.22 (2H, t, J = 7.7 Hz), 8.06 (3H, m), 7.87 (2H, d, J = 7.7 Hz), 7.79 (1H, s), 7.76 (1H, t, J = 7.7 Hz), 7.58 (2H, d, J = 8.5 Hz), 7.43 (1H, d, J = 3.8 Hz), 7.40 (2H, m), 7.32 (4H, m), 7.17 (3H, d, J = 7.7 Hz), 7.12 (3H, m). UV-Vis absorption spectra (CH_2Cl_2, 298 K): λ_{max}/nm (ε/×10^3 M^{-1} cm^{-1}): 285 (12.6), 379 (9.8). Elem. anal. calcd for $C_{38}H_{26}ClN_3PtS$: C, 57.98; H, 3.33; N, 5.34. Found: C, 57.95; H, 3.32; N, 5.31.

Pt3: The desired product was obtained as a dark green solid (19 mg). Yield: 61%. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ (ppm): 9.38 (2H, d, J = 5.6 Hz), 8.70 (1H, d, J = 9.2 Hz), 8.28 (3H, t, J = 6.4 Hz), 8.23 (3H, m), 8.19 (2H, d, J = 2.7 Hz), 8.10 (3H, m), 7.92 (3H, s), 7.65 (1H, d, J = 3.7 Hz), 7.48 (1H, d, J = 3.7 Hz), 7.43 (2H, t, J = 6.47 Hz). UV-Vis absorption spectra (CH_2Cl_2, 298 K): λ_{max}/nm (ε/×10^3 M^{-1} cm^{-1}): 280 (9.7), 375 (7.3). Elem. anal. calcd for $C_{36}H_{21}ClN_2SPt$: C, 58.10; H, 2.84; N, 3.76. Found: C, 57.98; H, 2.86; N, 3.78.

Pt4: The desired product was obtained as a brownish solid (21 mg). Yield: 50%. ^{1}H-NMR (400 MHz, CD_2Cl_2) δ (ppm): δ 8.75 (2H, d, J = 4.1 Hz), 8.21 (2H, s), 7.84 (2H, m) 7.53 (2H, d, J = 4.3 Hz), 7.45 (2H, m), 7.13 (4H, m), 2.84 (2H, m), 2.11 (2H, m), 1.55 (6H, m), 0.94 (3H, t). UV-Vis absorption spectra (CH_2Cl_2, 298 K): λ_{max}/nm (ε/×10^3 M^{-1} cm^{-1}): 265 (4.6), 356 (6.0). Elem. anal. calcd for $C_{30}H_{27}ClN_2PtS_2$: C, 50.73; H, 3.83; N, 3.94. Found: C, 50.80; H, 3.86; N, 3.92.

Pt5: The desired product was obtained as a brownish solid after recrystallization from a $CHCl_3$/pentane mixture (90 mg). Yield: 56%. ^{1}H-NMR (400 MHz, $(CD_3)_2SO$ δ (ppm): δ 9.16 (2H, d, J = 5.0 Hz), 8.35 (2H, d, J = 8.0 Hz), 8.28 (2H, d, J = 8.0 Hz), 8.18 (2H, s), 7.92 (4H, m), 7.84 (1H, d, J = 5.0 Hz), 7.81 (1H, d, J = 5.0 Hz), 7.61 (2H, t, J = 8.0 Hz). UV-Vis absorption spectra (CH_2Cl_2, 298 K): λ_{max}/nm (ε/×10^3 M^{-1} cm^{-1}): 373 (15.8), 436sh (4.7). Elem. anal. calcd for $C_{27}H_{16}ClN_3PtS.3CHCl_3$: C, 35.92; H, 1.91; N, 4.19. Found: C, 36.44; H, 1.96; N, 4.25.

EFISH measurements

EFISH measurements were carried out in 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 Nd^{3+}:YAG laser manufactured by Atalaser. The $\mu\beta_{EFISH}$ values reported are the mean values of 16 measurements performed on the same sample.

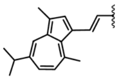
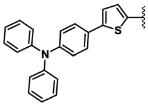
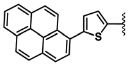
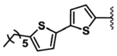
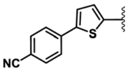
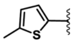
Computational details

The molecular geometry of all compounds has been optimized *in vacuo*, by a Density Functional theory (DFT) approach using the B3LYP[37] exchange–correlation functional and a 6-31G* basis set[38] for all atoms except for Pt which has been described with LANL2DZ basis set[39] along with the corresponding pseudopotentials. All the calculations were performed with Gaussian09 (G09),[40] without any symmetry constraints. We optimized the geometries in DMF solution including solvation effects by means of the conductor-like polarizable continuum model (C-PCM)[41] as implemented in G09. Ground state dipole moments have been computed for compounds in DMF solution. In the evaluation of β_{EFISH} from $\mu\beta_{EFISH}$, the value of computed μ (Table 1) was always used. This computational approach has been used by us to investigate a different class of 1,3-di(2-pyridyl)benzene cyclometallated Pt complexes.[31]

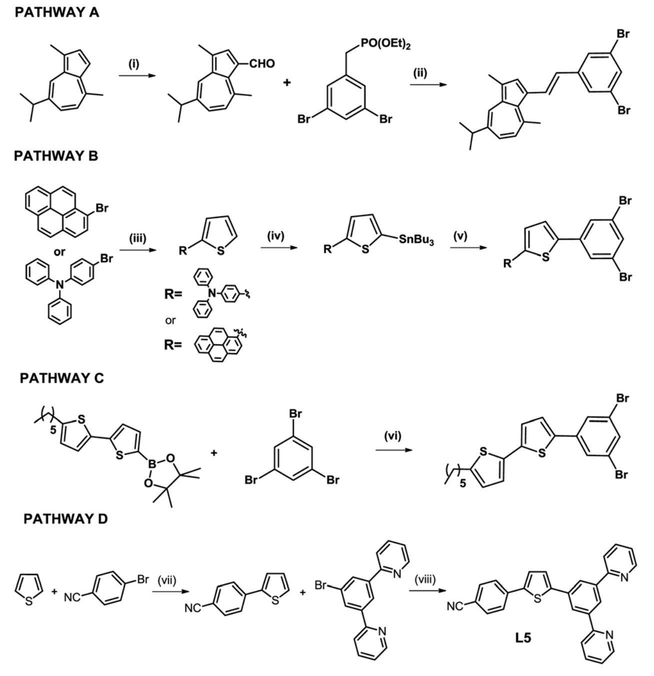
Results and discussion

The novel platinum(II) complexes (Chart 1) can be easily prepared following the pathways shown in Schemes 1 and 2. The related ligands **L1–L4** are synthesized by Pd-catalyzed Stille cross-coupling starting from the suitable 1,3-dibromo derivative and the commercially available 2-(tri-*n*-butylstannyl)pyridine. The 1,3-dibromophenyl derivatives can be prepared following one of the reported pathways A–C (Scheme 1), as fully described in the ESI.† Ligand **L5** is obtained by successive and regioselective pallado-catalysed C–H bond arylations.[42] From thiophene, selective C2-arylation with 4-bromobenzonitrile is achieved by using $Pd(OAc)_2$ associated to KOAc as base in DMA. Then, the less reactive C5-position is arylated with

Table 1 Dipole moments and second-order NLO response

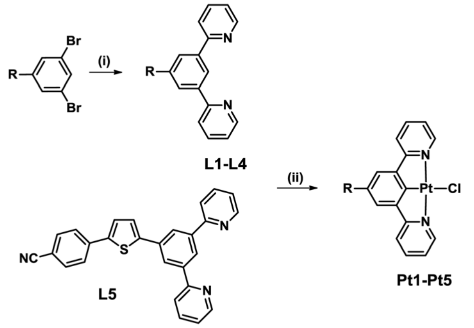
	R[a]	μ^b/D	$\mu\beta_{\mathrm{EFISH}}{}^c/\times10^{-48}$ esu	$\beta_{\mathrm{EFISH}}{}^d/\times10^{-30}$ esu
Pt1		13.4	−1540	−115
Pt2		10.8	−498	−46
Pt3		9.9	−1078	−109
Pt4		10.4	−945	−91
Pt5		4.9	−570	−116
Pt6		10.5	−520	−50

[a] R is the substituent on the position 5 of the cyclometallated 1,3-di(2-pyridyl)benzene. [b] Computed dipole moments in DMF (see Experimental). [c] At 1.907 μm in DMF; estimated uncertainty in EFISH measurements is ±10%. [d] β_{EFISH} was calculated using the computed μ value.



Scheme 1 A: (i) $POCl_3$, 1,2-dichloroethane, DMF, rt, then 80 °C, 20 min; (ii) *t*-BuOK, THF, Ar, 0 °C, then rt, 15 h; B: (iii) 2-(tri-*n*-butylstannyl)thiophene, $Pd(PPh_3)_4$, toluene, 110 °C, 24 h; (iv) *n*-BuLi, Bu_3SnCl, THF, Ar, −50 °C to rt, 15 h; (v) 1,3,5-tribromobenzene, $Pd(PPh_3)_4$, toluene, 110 °C, 48 h; C: (vi) $Pd(PPh_3)_4$, Na_2CO_3, THF/H_2O, 90 °C, 24 h; D: (vii) $Pd(OAc)_2$, KOAc, DMA, 150 °C, 16 h; (viii) $PdCl(C_3H_5)(dppb)$, KOAc, DMA, 150 °C, 16 h.

2,2′-(5-bromo-1,3-phenylene)dipyridine in the presence of air-stable diphosphine palladium catalyst (Scheme 1, pathway D). The desired platinum complexes **Pt1–Pt5** are then obtained in good yield by reaction of the ligands with K_2PtCl_4 in a mixture acetic acid/water (Scheme 2).



Scheme 2 (i) 2-(Tri-*n*-butylstannyl)pyridine, LiCl, $PdCl_2(PPh_3)_2$, toluene, 110 °C, 48 h; (ii) K_2PtCl_4, AcOH/H_2O, 118 °C, 48 h.

All complexes were fully characterized by elemental analysis, NMR and UV-Vis spectroscopy (see Experimental). They all show absorption bands in the 350–450 nm region due to metal-to-ligand and intraligand charge-transfer transitions as expected for this kind of Pt(II) complex with a cyclometallated 1,3-di(2-pyridyl)benzene.[43,44]

NLO study

We used the EFISH method in order to study the second-order NLO response in solution of the complexes. This technique[34–36] can provide direct information on the intrinsic molecular NLO properties, through eqn (1):

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

Where $\mu\beta_{\mathrm{EFISH}}/5kT$ is the dipolar orientational contribution to the molecular nonlinearity, and $\gamma(-2\omega;\ \omega,\ \omega,\ 0)$, the third order polarizability, is an electronic cubic contribution to γ_{EFISH}, which can usually be neglected when studying the second-order NLO properties of dipolar molecules. β_{EFISH} is the projection along the dipole moment axis of β_{vec}, the vectorial component of the tensor of the quadratic hyperpolarizability, working with an incident wavelength of a pulsed laser. To obtain the value of β_{EFISH}, it is necessary to know the ground state dipole moment μ of the molecule. Therefore, we used the theoretical dipole moments calculated in DMF as described in the Experimental section. Besides, to avoid overestimation of the quadratic hyperpolarizabilty value due to resonance enhancements, it is essential to choose an incident wavelength whose second harmonic is remote from any absorption of the molecule investigated. In the present study, EFISH measurements were carried out in DMF solutions, with a non-resonant incident wavelength of 1.907 μm.

All the investigated complexes (Chart 1) are characterized by a negative value of $\mu\beta_{\mathrm{EFISH}}$ (Table 1), in agreement with a negative value of $\Delta\mu_{\mathrm{eg}}$ (difference of the dipole moment in the excited and ground state) upon excitation,[45] as reported for other cyclometallated metal complexes,[8] because the second-order dipolar NLO response is dominated by the charge transfer from platinum to the cyclometallated ligand.

Remarkably, the Pt(II) chloro complex bearing a novel π-delocalized cyclometallated 5-guaiazulene-CH═CH-1,3-di(2-pyridyl)benzene (**Pt1**, Chart 1) is characterized by the best second-order NLO response ($\mu\beta_{\text{EFISH}} = -1540 \times 10^{-48}$ esu), almost twice that previously reported for the related complex with the cyclometallated *trans*-5-(*p*-(*N*,*N*-diphenylamino)styryl)-1,3-di(2-pyridyl)benzene,[31] due to both a higher β_{EFISH} value (enhancement factor of 1.4) and a higher dipole moment (enhancement factor of 1.3). The observed high $\mu\beta_{\text{EFISH}}$ value shows the good potential of the guaiazulene fragment in the design of NLO compounds. Besides, it appeared that substitution of the double bond with thiophene as bridge between the cyclometallated 1,3-di(2-pyridyl)benzene and the organic substituent can affect the second-order NLO response negatively (**Pt2**, β_{EFISH} is reduced by a half) or slightly positively (**Pt3**, β_{EFISH} increases by a factor of 1.2).[31]

We found that the $\mu\beta_{\text{EFISH}}$ of the known complex with a methyl group on the thiophene (**Pt6**) measured in DMF (-520×10^{-48} esu) is similar to that previously reported in CH_2Cl_2,[33] showing that the nature of the solvent doesn't affect the second-order NLO response of this kind of complexes. The EFISH study of the four novel related complexes (**Pt2**, **Pt3**, **P4**, **Pt5**; Table 1) puts in evidence the effect of the nature of the substituent on the position 5 of the thiophene moiety. Substitution of the methyl group (**Pt6**) with a triphenylamino group (**Pt2**) doesn't cause a significant effect neither on the dipole moment nor on the β_{EFISH} value. Similarly there isn't an effect on the dipole moment by using an hexylthiophene substituent (**Pt4**), however a much higher $\mu\beta_{\text{EFISH}}$ is obtained due to an increase of the quadratic hyperpolarizability. The use of a pyrene fragment (**Pt3**) instead of the methyl group leads to an even better second-order NLO response, although there is a slight decrease of the dipole moment, due to a large enhancement of β_{EFISH} (by a factor of 2.2). Besides, although a similar $\mu\beta_{\text{EFISH}}$ value is obtained for **Pt5** and **Pt6**, substitution of methyl with a cyanophenyl group halves the dipole moment and increases the β_{EFISH} value by a factor of 2.3.

To gain some insight into the reasons underlying the variations in the second-order NLO behavior of these complexes, the energies of their frontier HOMO–LUMO molecular orbitals were computed in DMF solution. They are schematized in Fig. 1, along with the corresponding HOMO and LUMO isodensity plots.

As expected for its particularly low HOMO–LUMO gap (Fig. 1) and in line with the Oudar two-level model,[2] **Pt1** shows the highest experimentally determined β_{EFISH} (Table 1). However, surprisingly, for the platinum complexes bearing a substituted cyclometallated 5-thiophene-1,3-di(2-pyridyl)benzene, **Pt2–Pt6**, β_{EFISH} doesn't increase systematically with a decrease of the HOMO–LUMO gap. For example, **Pt5** has the highest β value of this series although the difference between the energy of its highest occupied and lowest unoccupied molecular orbitals is relatively high. As shown in Table 1, β_{EFISH} increases in the order **Pt2** = **Pt6** < **Pt4** < **Pt3** < **Pt5**, a behavior that can be attributed to an increase of the polarizability of such molecules due to increased delocalization of the lowest unoccupied molecular orbitals (Fig. 1). In fact, the lowest β_{EFISH} values of the series are observed when the LUMO is essentially localized on the cyclometallated Pt core without involving the thiophene on the position 5 of the 1,3-di(2-pyridyl)benzene (**Pt2** and **Pt6**). This suggests that, in order to reach a high quadratic hyperpolarizability, the charge transfer should not be limited to the cyclometallated pyridines. In agreement with this observation, the LUMOs of complexes **Pt3** and **Pt5**, characterized by large β_{EFISH} values despite higher HOMO–LUMO gaps than **Pt1**, are much more delocalized than the others of the **Pt2–Pt6** series, Fig. 1. Also, in the case of *trans*-5-(*p*-(*N*,*N*-diphenylamino)styryl)-1,3-di(2-pyridyl)benzene,[31] the decrease of the quadratic hyperpolarizability upon substitution of the double bond[31] by a thiophene (**Pt2**) can be related to the less delocalized LUMO. Such a decrease in the case of the pyrene derivatives doesn't occur because the LUMOs are delocalized also on the pyrene fragment both with the double bond[31] or the thiophene (**Pt3**) bridge.

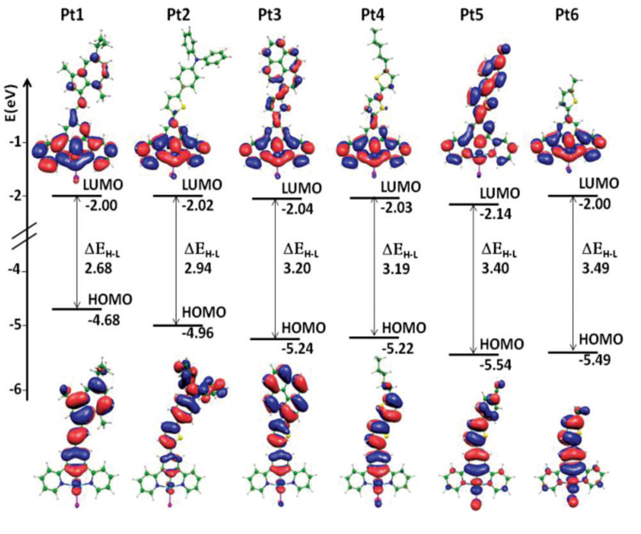


Fig. 1 Schematic representation of the energy levels of complexes **Pt1–Pt6**. Isodensity surface plots (isodensity contour: 0.020) of HOMO and LUMO molecular orbitals are also shown.

Conclusions

In summary, five novel Pt(II) complexes were prepared and well characterized. Our results suggest that a LUMO delocalized not only on the pyridine rings but also on the substituent on the position 5 of the cyclometallated 1,3-di(2-pyridyl)benzene is a key point to increase the quadratic hyperpolarizability of this kind of complexes. The best $\mu\beta_{\text{EFISH}}$ values are reached by using very π-delocalized organic substituents such as "5-guaiazulene-CH═CH" and "pyrene thiophene". The large second-order NLO activity of the related complexes makes them appealing as building blocks for NLO materials and photonic applications.

Conflicts of interest

There are no conflicts to declare.

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