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Multifunctional Organometallic Compounds: An Interesting Luminescent NLO-Active Alkynylplatinum (II) Complex

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Reaction of 4-methylphenylacetylide with the known chlorido platinum(II) complex bearing the cyclometalated 1,3-bis(pyridin-2-yl)-4,6-difluoro-benzene ligand afforded a novel alkynyl platinum(II) complex, **1**, that was fully characterized by elemental analysis, NMR and UV-visible spectroscopies, by photoluminescence measurements, and by computational modelling. Its structure was determined by X-ray diffraction

studies on a single crystal whereas its second-order nonlinear optical (NLO) properties were determined in solution by the Electric-Field Induced Second Harmonic generation method. The novel multifunctional complex **1** is characterized by good luminescence properties, like the related chlorido Pt(II) complex, but by a much higher second-order NLO response.

Introduction

Organometallic and coordination complexes characterized by both luminescent and second-order nonlinear optical (NLO) properties are fascinating multifunctional molecular materials that might offer additional flexibility relative to organic molecules.^[1,2] 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 modulated by the nature, oxidation state, and coordination sphere of the metal center.^[3] The presence of a heavy metal center allows a strong spin-orbit coupling, favoring intersystem crossing and light emission from triplet excited states; an internal electro-luminescence quantum efficiency of unity can be reached in devices, because both the singlet and triplet excitons generated by electron-hole recombination (ratio is 1:3) can be induced to emit (triplet harvesting).^[4]

As a consequence, a lot of work has been dedicated to square planar Pt(II) compounds for answering requests from

various fields such as nonlinear optics (NLO),^[5,6] bio-imaging,^[7] Organic Light Emitting Diodes (OLEDs),^[8] and sensors.^[9] Among these Pt(II) compounds, those with a cyclometalated terdentate NCN 1,3-bis(pyridin-2-yl)benzene ligand (bpyb) constitute an interesting family of multifunctional molecular materials which can show remarkable luminescent^[10] and NLO^[5e,11] properties. Thus, the related platinum(II) chloride complexes emit efficiently even at 25 °C,^[12] the color of the emission being controlled by the nature of the substituents both on the cyclometalated phenyl ring and on the pyridines.^[13] One of the actual requests in the field of OLED color displays, is to find photostable and efficient blue emitters.^[14] It was reported that in this class of NCN bpyb platinum(II) complexes, the use of cyclometalated 1,3-bis(pyridin-2-yl)-4,6-difluoro-benzene as ligand causes a shift of the emission towards the blue region,^[15,16] an approach that recently showed its potential as a springboard for blue OLEDs.^[17] Remarkably, the fascinating luminescent properties of NCN platinum(II) complexes are usually preserved even upon substitution of the ancillary chloride ligand by other anionic species such as isothiocyanates,^[18] azides,^[19] acetylides,^[20] and thiolates.^[21]

Besides, it was reported that NCN platinum(II) complexes, functionalized with electron-acceptor groups on the cyclometalated bpyb ligand, display a large NLO response, as measured by the Hyper-Rayleigh Scattering technique (HRS).^[11b] These NCN-coordinated cyclometalated bpyb platinum complexes are characterized by an enhanced NLO efficiency with respect to the corresponding structurally related MNM-coordinated terpyridine complexes,^[11b] probably due to the polarization along the C–Pt bond.^[22] Suitable functionalization of the cyclometalated bpyb ligand and the choice of the ancillary ligand allow the control of the dipolar second-order nonlinear optical response, as put in evidence by Electric-Field Induced Second-Harmonic (EFISH) generation measurements.^[6] Thus, the addition of electron-withdrawing substituents on the cyclometalated ligand leads to an increase in its acceptor properties and therefore to an enhancement of the quadratic hyperpolarizability. A further enhancement is achieved by substitu-

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tion of the chloride ancillary ligand with a phenylacetylide ligand, the second-order NLO response being controlled by a charge-transfer process from the acetylide ligand to the cyclometalated chelated ligand with very little contribution of the Pt centre, which acts mainly as a linker.^[6] This greater NLO performance is in agreement with a lower HOMO-LUMO gap, calculated by means of a Density Functional Theory (DFT) approach, that is caused by a shift at higher energy of the HOMO orbitals, located mainly on the phenylacetylide ligand. Thus, the high second-order nonlinear optical response reached for the complex with a fluorinated cycloplatinated 1,3-bis(pyridin-2-yl)-4,6-difluoro-benzene ligand was enhanced upon substitution of the ancillary chloride ligand with phenylacetylide.^[6] The luminescence properties of this latter NLO-active complex were never reported. These observations prompted us to prepare and characterize well the related novel complex with a methyl group in *para* position of the phenylacetylide (1, Figure 1) in order to investigate both its second-order NLO and luminescence properties.

Results and Discussion

Synthesis and Characterization

Complex 1 was prepared by reaction of 4-methylphenylacetylide with the known chlorido Pt(II) complex [(dFdpyb)PtCl] bearing the cyclometalated ligand 1,3-bis(pyridin-2-yl)-4,6-difluoro-benzene^[16] (see Scheme 1, Experimental, and Supporting Information). The novel complex was fully characterized by elemental analysis, NMR and UV-visible spectroscopies, by photoluminescence measurements, and by computational modelling. Its second-order NLO properties were determined by the EFISH method whereas its structure was determined by X-ray diffraction studies on a single crystal.

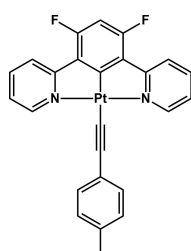


Figure 1. Investigated novel complex 1.



Scheme 1. Synthesis of complex 1.

Photophysical Properties in Solution

Complex 1 was investigated by registering at first UV-Visible spectra in CH₂Cl₂ solutions. The absorption spectra show intense bands in the 250–340 nm region ($\epsilon_{289} = 38.8 \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), which can be attributed to $^1\pi\text{-}\pi^*$ transitions centered on the NCN ligand, and a less intense band at 350–420 nm ($\epsilon_{377} = 8.0 \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) due to metal-to-ligand-charge-transfer transitions (Figure 2). The mentioned absorption bands are typical of compounds belonging to the family of 1,3-(2-pyridyl)benzene-Pt(II) complexes. When compared to the spectrum of the parent compound bearing an ancillary Cl,^[16] the band immediately below 400 nm appears to be less resolved, as previously reported for related complexes,^[20] due to the presence of a $\pi_{\text{alkyne}}\text{-}\pi^*_{\text{NCN}}$ ligand-centered transition.

Moreover, in the absorption spectrum of a more concentrated solution ($1.5 \cdot 10^{-4} \text{ M}$) it is possible to observe a peak at 472 nm which corresponds to the direct population of triplet states (inset in the graph of Figure S4, see SI).

A $1 \cdot 10^{-5} \text{ M}$ solution of 1 in CH₂Cl₂ was employed to study the luminescence properties of the Pt(II) complex. As reported in Figure 2, the emission occurs in the blue-green region, with a maximum at 501 nm somewhat red-shifted with respect to that of the chloride derivative [(dFdpyb)PtCl] (472 nm).^[16]

Spectra were registered after the Freeze-Pump-Thaw (FPT) procedure, required to remove dioxygen present in the cuvette and in solution; this procedure was needed since O₂ is a very efficient quencher of phosphorescence, as a consequence of its triplet fundamental state.

The effect of the removal of oxygen is particularly evident when considering the absolute Quantum Yields (QY), measured for the $1 \cdot 10^{-5} \text{ M}$ solution both before and after the FPT procedure: from a starting value of 4.8%, a remarkable 43.2% is reached. This QY value is however lower than that previously reported for the related chloride Pt(II) complex (80%).^[16]

Finally, the emission spectrum of complex 1 (Figure 2) shows a broad red-shifted band at around 700 nm, due to bimolecular species which can be easily formed in solutions by means of the square planar coordination around the Pt(II) centre.^[17]

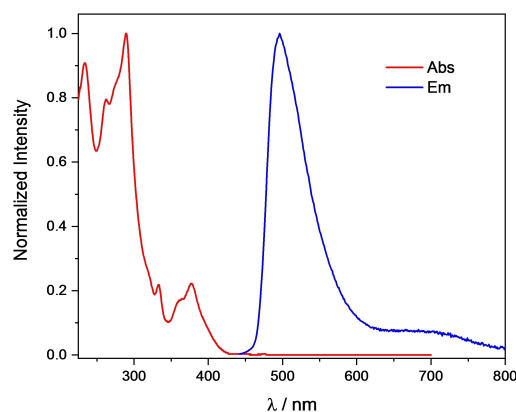


Figure 2. Normalized absorption (red) and emission (blue) spectra of 1 in CH₂Cl₂. Emission spectrum registered in deaerated solution, with $\lambda_{\text{ex}} = 425 \text{ nm}$.

The luminescence lifetimes at the emission wavelength 496 nm, exciting to 427 nm, show two different decay profiles having τ values of 1.32 and 3.40 μs , which are attributed to the decay of excited monomeric and bimolecular species (see Figure S7 in the SI).

X-ray Structure

The X-ray structure of complex **1** was obtained from a single crystal formed after the slow evaporation of a CH_2Cl_2 solution. The compound crystallized in a monoclinic system with $P 2_1/n$ space group; as shown in Figure 3, there are two independent molecules in the asymmetric unit, differing from the torsion angle measured between the *NCN* plane and the phenyl rings of the ancillary alkyne ligand: it has a value of 73.53° for the former molecule, while 124.17° for the latter.

The distance between the Pt center and the cyclometalating carbon atom has a typical value of $\sim 1.95 \text{ \AA}$, while the terdentate ligand scaffolds lay parallel to each other, with a short Pt–Pt distance of $\sim 4.58 \text{ \AA}$, this being similar to the related compound bearing a 4-formylphenylacetylide (Pt–Pt distance of $\sim 4.90 \text{ \AA}$).^[20e]

Other views of the crystal structure of complex **1**, showing the pattern and orientation of the molecules, are present in Figure S8 in the SI, together with a Table with key data.

Second-order NLO Properties

The second-order NLO properties of complex **1** were investigated by the Electric Field Induced Second Harmonic generation (EFISH) technique,^[23] which can provide direct information on the intrinsic dipolar molecular second-order NLO properties through the following Equation:

$$g_{\text{EFISH}} = (mb_i/5kT) + g(-2\omega; \omega, \omega, 0)$$

in which $\mu\beta_i/5kT$ is the dipolar orientational impact on the molecular nonlinearity, and $\gamma(-2\omega; \omega, \omega, 0)$ describes the third order polarizability, which is an electronic cubic contribution to χ_{EFISH} . The latter can usually be neglected when investigating the second-order NLO properties of dipolar molecules.^[24] β_λ is the vector component of the quadratic hyperpolarizability

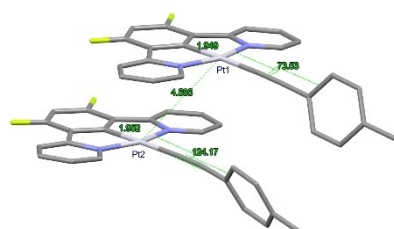


Figure 3. View of the two independent molecules of **1** in the asymmetric unit, together with Pt–Pt and C–Pt distances, and torsion angles of the phenyl rings with respect to the *NCN* plane. Hydrogens are omitted for clarity.

tensor (β_{ijk}) along the ground state dipole moment (μ) axis, when working with an incident wavelength λ . A molecule having a $\mu\beta_\lambda$ higher than that of Disperse Red One, ([*trans*-4,4'- $\text{O}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{NET}(\text{CH}_2\text{CH}_2\text{OH})$]), $\mu\beta_{1,907} = 440 \cdot 10^{-48}$ esu), which found application in electrooptic polymeric poled films,^[25] is commonly considered of interest for second-order NLO applications.^[5e,24]

When investigating the quadratic hyperpolarizability, it is imperative to avoid resonance enhancements that would lead to an overestimated value. Therefore, it is essential to choose an incident wavelength with a second harmonic far from the absorption wavelengths of the investigated compound. In order to study complex **1**, we operated with a 1.907 μm incident wavelength, achieved by Raman-shifting the 1.064 μm wavelength obtained from a Q-switched, mode-locked Nd:YAG laser.

The $\mu\beta_{1,907}$ value of complex **1**, measured as solutions in DMF, is $-1070 \cdot 10^{-48}$ esu, much higher than that of Disperse Red One and similar to that previously reported for the related complex without the methyl group in *para* of the phenylacetylide ligand ($-1060 \cdot 10^{-48}$ esu),^[6] as expected for the relatively weak electron-donor capacity of a methyl group. The $\mu\beta_{1,907}$ value of complex **1** is much higher than that of [(dFdp**py**)PtCl] ($-720 \cdot 10^{-48}$ esu),^[6] confirming the positive effect of the substitution of the chloride ligand by acetylide on the second-order NLO response. In contrast to Disperse Red One, this family of *NCN* platinum(II) complexes is characterized by a negative value of $\mu\beta_{1,907}$ owing to the negative value of $\Delta\mu_{\text{eg}}$ (difference of the dipole moment on going from the excited to the ground state) which reflects a decrease in the dipole moment upon excitation, according to the two-level model.^[26]

Dipole Moments, Electronic Structure, and Quadratic Hyperpolarizability

To give insight into the linear and nonlinear optical properties of the experimentally characterized Pt-complex, we performed quantum chemical calculations based on DFT methods (see Experimental section). The optimized molecular geometry of complex **1** in DMF is reported in Figure 4 with the 1,3-di(2-pyridyl)benzene moiety lying in the *xy* plane and the *y* axis

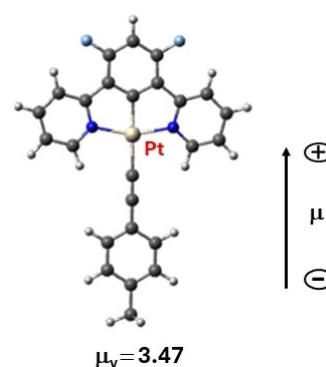


Figure 4. The optimized geometry of complex **1** and the dipole moment, calculated in DMF, and expressed in Debye, along the *y* axis.

crossing the Pt(II) center. In the optimized molecular structure in DMF solution (as well in CH_2Cl_2) the phenyl ring is co-planar with the alkyne ligand, differently to what observed in the X-ray structure, probably due to the different environments. In Figure 4 is reported the y component of the dipole moment (μ_y) computed in DMF solvent (3.47 D); the total dipole moment (μ) computed in DMF is 3.54 D and is located mainly along the y axis with a small component along the x axis (0.72 D), in agreement with a C_{2v} symmetry of the molecular architecture.

Knowing that the experimental EFISH $\mu\beta_{1,907}$ value of complex 1 is $-1070 \cdot 10^{-48}$ esu, (see Second-order NLO properties section), the use of the value of the total dipole moment calculated by DFT allows to determine the value of $\beta_{1,907}$. It is $-302 \cdot 10^{-30}$ esu, much larger than that of the related chlorido derivative ($\beta_{1,907} = -144 \cdot 10^{-30}$ esu),^[6] confirming the positive effect on the quadratic hyperpolarizability of the substitution of the chloride ligand by acetylide. This behaviour is in agreement with a lower HOMO-LUMO gap for complex 1, as described below.

Thus, Figure 5 shows the electronic structure of complex 1 in terms of energy levels and isodensity plots of the frontier molecular orbitals computed in DMF, (a) and (b) panels, respectively. We optimized the molecular geometry and analyzed the frontier molecular orbitals also in CH_2Cl_2 solvent finding minimal differences both in the optimized geometries and in the electronic structures with respect to the DMF computed data.

The HOMO-LUMO gap has been computed 3.35 eV, lower than that of the related chlorido complex (3.98 eV)^[6] caused by a shift of the HOMO orbitals, which are located mainly on the phenylacetylide ligand, at higher energy. Indeed, the HOMO shows a relevant contribution of the Pt d_{yz} along with bonding π combinations of p orbitals on the alkyne, on the phenyl ring and on the ancillary difluorinated phenyl. The electron density in the LUMO is distributed between pyridyl rings and Pt center. HOMO-1 is the combination of the Pt d_{xy} and the alkyne and pyridyl rings p orbitals, while HOMO-2 is delocalized on Pt d_{xz} orbital and π bonding combinations of C, N and F p on the cyclometallated ligand. The HOMO-3 is delocalized over the entire complex from the F atoms to the methyl ligand involving the Pt d_{yz} orbital. The HOMO-4 is essentially the Pt d_z^2 . The LUMO+1 and LUMO+2 are different combinations of the C

and N p orbitals almost entirely delocalized on the cyclometallated ligand with small contribution from Pt, while the LUMO+3 is the antibonding π combination of C and N p orbitals on the complex with any contribution from Pt. LUMO+4 is similar to LUMO+3 but with a larger contribution coming from the C p orbitals of the alkyne and of the phenyl ring.

The described frontier molecular orbitals should be the involved starting and arriving state of the lower energies charge transfer transitions from Pt (or Pt-alkyne-Ph) to the cyclometallated ligand, having therefore a metal-to-ligand charge transfer character. We expect that the second-order dipolar NLO response should be dominated by these MLCT transitions. For complex 1 we computed also the static quadratic hyperpolarizability tensor, finding that the main component contributing to the total β is the yyy component (β_{yyy}) which is the component along the dipole moment direction that can be essentially compared to our experimental EFISH $\beta_{1,907}$ value. The computed value for complex 1 is $-47 \cdot 10^{-30}$ esu, according to the "phenomenological" convention,^[28] Although it is a bit lower than the experimental value, as expected from other reports,^[35] it confirms the negative value of the quadratic hyperpolarizability due to a decrease in the dipole moment upon excitation.

Conclusions

In conclusion, an interesting alkynyl platinum(II) complex has been prepared and well characterized. It emits in the blue-green region of the visible spectrum with a good quantum yield (43%). Its second-order NLO response is more than twice that of Disperse Red One, which found application in electrooptic polymeric poled films and which is usually used as benchmark. Its good luminescence properties together with its excellent second-order NLO properties confirm the great potential of NCN platinum(II) complexes as multifunctional organometallic molecular materials.

Experimental

General Information

Solvents and all commercially available chemicals were used without further purification. Air- and water-sensitive reactions were performed in flame-dried glassware under argon atmosphere. NMR spectra were recorded on a Bruker AC 400 spectrometer. Chemical shifts are given in ppm and coupling constants in Hz. Multiplicities are presented as follows: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet.

Synthesis

4-methylphenylacetylene (28 mg, 0.240 mmol) and NaOH (10 mg, 0.240 mg) were dissolved in MeOH (3 mL) and the mixture was left under stirring at rt for 30 minutes; then, a solution of [dFdpb]PtCl₂ (40 mg, 0.080 mmol) in CH_2Cl_2 (3 mL) was added and the reaction was left under Ar atmosphere at rt. After 48 h MeOH was added to

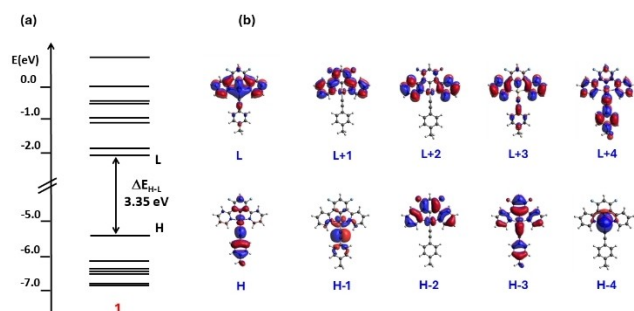


Figure 5. (a) The computed energy levels of the frontier molecular orbitals in DMF; (b) the isodensity plots of the frontier molecular orbitals computed in DMF (isodensity value = 0.025).

precipitate the product (yellow solid), which was filtered, washed with MeOH and Et₂O, and dried (36 mg, 77% yield).

¹H NMR (400 MHz, THF-*d*₆, δ): 9.51 (d, J = 5.7 Hz, J(¹⁹⁵Pt) = 47 Hz, 2H), 8.07 (dd, J₁ = 5.8 Hz, J₂ = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.34 (dd, J₁ = 5.7 Hz, J₂ = 5.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 7.01 (d, J = 7.8 Hz, 2H), 6.77 (t, J(¹⁹F) = 11.4 Hz, 1H), 2.29 (s, 3H).

¹⁹F NMR (376 MHz, CDCl₃, δ): -108.87 (s).

Anal. calcd. for C₂₅H₁₆F₂N₂Pt: C, 52.00; H, 2.79; N, 4.85; found: C, 53.18; H, 2.82; N, 4.81.

Photophysical Properties in Solution

Electronic absorption spectra were recorded at room temperature using a Shimadzu UV3600 spectrophotometer and quartz cuvettes with 1 cm optical path length.

The absolute photoluminescence quantum yield (Φ) was measured using a C11347 Quantaurus Hamamatsu Photonics K.K. spectrometer; steady state and time-resolved fluorescence data were obtained using a FLS980 spectrofluorimeter (Edinburgh Instrument Ltd). More details are provided in the SI.

X-ray Structure

The structure's parameters were determined performing the X-ray analysis using a D8 VENTURE Bruker AXS diffractometer, Mo-Kα radiation (λ = 0.71073 Å), T = 150 K.

The structural data are deposited with the Cambridge Crystallographic Data Centre with deposition number 2357874.^[27]

Second-Order NLO Properties

All EFISH measurements^[23c] were carried out at the Department of Chemistry of the Università degli Studi di Milano, on DMF solutions of samples 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 Nd:YAG laser manufactured by Atalaser. The apparatus used for EFISH measurements is a prototype made by SOPRA (France). The EFISH μβ values reported are the mean values of 16 successive measurements performed on the same sample. The sign of μβ was determined by comparison with the reference solvent (DMF).

Quantum Chemical Calculations

All the calculations discussed in this paper were performed with Gaussian 09^[29] without any symmetry constraints. The molecular geometry of the investigated complex was optimized in CH₂Cl₂ by means of Density Functional Theory (DFT) approach using the B3LYP^[30] exchange-correlation functional and a 6-31 g** basis set^[31] for all atoms except Pt for which sdd basis set has been employed along with the corresponding pseudopotentials.^[32] Solvation effects were included by means of the conductor-like polarizable continuum model (CPCM)^[33] as implemented in Gaussian 09 both for DMF and CH₂Cl₂ solutions. The ground-state dipole moment has been computed in DMF and CH₂Cl₂ solutions. By means of Gaussian09 we computed the static hyperpolarizability tensor consisting in the following 10 components: β_{xxx}, β_{xyx}, β_{xyy}, β_{yyx}, β_{xxz}, β_{xyz}, β_{yyz}, β_{zzx}, β_{yyz}, β_{zzz}.^[34]

Supporting Information Summary

Supporting Information containing NMR spectra, absorption spectra, lifetime decay and X-ray data are provided.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Cyclometalated platinum(II) complexes · Dipyritydylbenzene ligand · Second-order nonlinear optics · EFISH · Luminescence

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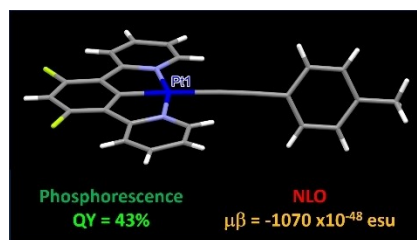
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RESEARCH ARTICLE

Great potential of *NCN* platinum(II) complexes as multifunctional organometallic molecular materials: a blue-green emitting *NCN* alkynyl platinum(II) complex, characterized by a good quantum yield and an excellent second-order nonlinear optical response.



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**Multifunctional Organometallic
Compounds: An Interesting Luminescent
NLO-Active Alkynylplatinum (II)
Complex**

