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Remarkable Effect of Iridium Cyclometalation on the Nonlinear Absorption Properties of a Quadrupolar Imine Ligand

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Supporting Information

ABSTRACT: A new type of dinuclear iridium complex, based on a quadrupolar Schiff base ligand, is synthesized and its structure fully characterized. Its linear and nonlinear spectroscopic properties are investigated, evidencing a strong contribution of the metal-to-ligand transitions not only to the linear absorption but also to the two- and three-photon absorption properties.

Nonlinear-optical processes are among the most intriguing phenomena in physics, being of much interest as both a fundamental and applied research topic. The properties that arise from the nonlinear-optical processes can be advantageously used in a plethora of practical applications, in the fields of telecommunications, data storage, optical switches, optical power-limiting devices, and bioimaging.[1] Owing to the very active work of molecular engineering by various research groups worldwide, patterns have emerged in the last 3 decades that have allowed the design of molecules with constantly improving second- or third-order nonlinear-optical properties.[2]

A common feature of all molecules with high nonlinearities is the presence of low-lying electronic transitions of the charge-transfer type, which lead to an important redistribution of the electronic density of the molecule between its ground and excited states. Thus, a general molecular engineering strategy consists of using a large π-conjugated backbone, with strong electron-donor and/or -acceptor groups at their extremities, resulting in molecules with so-called intramolecular charge-transfer (ICT) excited states. Alternatively, it has also been proposed that the specific spectroscopic properties of transition-metal complexes and organometallics, with multiple low-lying electronic transitions of the metal-to-ligand (MLCT), ligand-to-metal (LMCT), or interligand (LLCT) charge-transfer type, could be advantageously used in the context of nonlinear optics.[3]

Surprisingly, apart from a few noticeable exceptions,[3f,4] cyclometalated complexes of heavy metals (iridium, ruthenium, and platinum) have been only very sparingly considered within this framework, although their exceptional potential has been increasingly acknowledged in recent years for related applications, such as electroluminescent materials.[5] Indeed, it has been shown in multiple examples that cyclometalation results in a strong mixing between the ligand and metal orbitals, resulting in particularly intense MLCT transitions, which can be tuned over a wide range of wavelengths depending on the nature of the metal and ligand.[6]

In this work, we describe the synthesis and spectroscopic study of a new type of cyclometalated iridium complexes with strongly enhanced multiphoton absorption properties. In order to do so, a classical quadrupolar molecule with an imine bridge (Schiff base), functionalized at both extremities with aniline donors,[7] is used as a scaffold, which complexes two iridium(III) cations by coordination to the nitrogen atoms of the imine bridge, and bis-cyclometalation to the central phenyl ring.

The quadrupolar ligand **1** (Figure 1, left) could be readily obtained in three steps from commercially available starting materials (see the experimental section in the Supporting Information). Briefly, nucleophilic aromatic substitution on 4-fluoronitrobenzene, using *N*,*N*-dioctylamine as a nucleophile, afforded the corresponding 4-nitro-*N*,*N*-dioctylaniline with good yield. The nitro function was then reduced to amino, and the resulting compound was involved in condensation with terephthaldehyde, leading to a mixture of mono- and bis-condensation products, from which the target compound could easily be recovered. The treatment of **1** with a dichloro(pentamethylcyclopentadienyl)iridium(III) dimer, in the presence of a base (potassium acetate), following reported procedures[8] afforded the target complex **1·Ir** (Figure 1, right). Crystals suitable for X-ray diffraction were obtained as dark-reddish needles by slow cooling of a boiling acetonitrile solution of **1·Ir**.

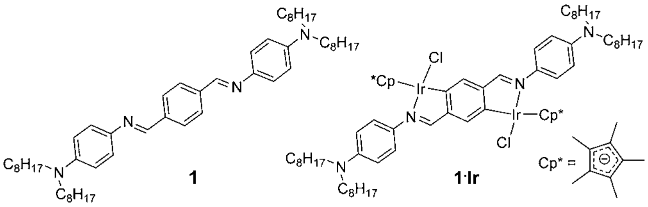

Figure 1. Structure of the ligand (**1**) and complex (**1·Ir**) involved in the study.

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The centrosymmetric crystal structure indicates that the consecutive cyclometalation reactions selectively take place in anti positions on the central phenyl ring, with the corresponding ancillary ligands (Cp* and Cl) locating opposite to one another with respect to this same ring (Figure 2). It also appears that the π-conjugated backbone of the quadrupolar ligand is significantly distorted from planarity with a $C_5{-}C_6{-}N_2{-}C_7$ dihedral angle of 51°. Upon examination of the crystal structure, it is clear that this distortion arises from steric hindrance between the Cp* ancillary ligand on each iridium cation and the terminal aniline rings, which lie parallel to one another.

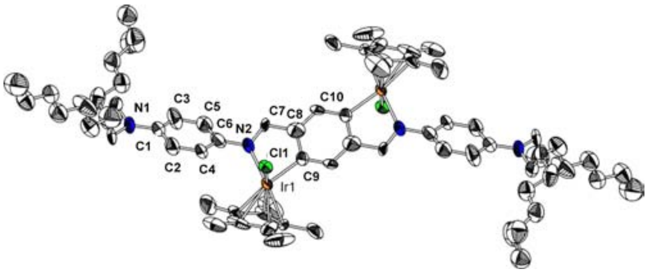

Figure 2. Perspective view of the iridium complex **1·Ir** with displacement ellipsoids plotted at the 30% probability level. Hydrogen atoms were omitted for clarity.

The effect of this distortion and of the consequent decreased conjugation along the molecule axis is clearly observed when the respective absorption spectra of **1** and **1·Ir** in dichloromethane (Figure 3) are compared. In the case of **1·Ir**, the ICT transition is significantly blue-shifted (λ_{max} = 430 nm), in comparison to that of **1** (λ_{max} = 452 nm), and its molar extinction coefficient ($\varepsilon_{ICT,1\cdot Ir}$= 2.2 × 10^4 $M^{-1}\cdot cm^{-1}$) is significantly reduced ($\varepsilon_{ICT,1}$ = 4.8 × 10^4 $M^{-1}\cdot cm^{-1}$). Moreover, while the ICT band is broad and almost structureless in the case of the ligand, a longer-wavelength shoulder (λ = 477 nm) is clearly observed in the case of the complex. By analogy with literature data on related phenyl-pyridine cyclometalated complexes,[9] this characteristic shape can be reasonably ascribed to a mixed ICT− ^{1}MLCT character of this electronic transition, which is a classical feature for coordination compounds and is particularly intense in cyclometalated complexes.[3f] Additionally, a less intense band is also observed at lower energies (λ_{max} = 598 nm), which we ascribe, by analogy with related compounds in the literature,[10] to a mixed ^{1}MLCT−^{3}MLCT transition with a unusually large molar extinction coefficient for that range of wavelengths (ε = 6900 $M^{-1}\cdot cm^{-1}$).

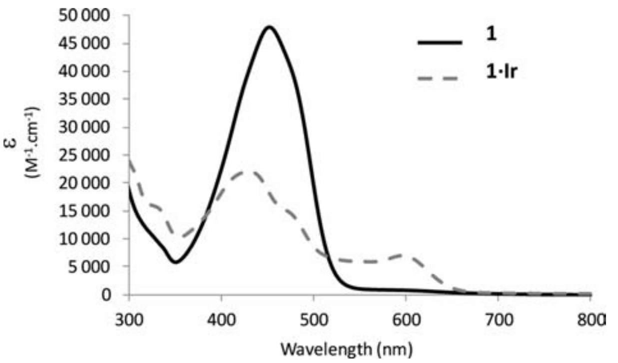

Figure 3. Absorption spectra of **1** and **1·Ir** in dichloromethane at 298 K.

In order to investigate the nonlinear absorption properties of **1** and **1·Ir**, *Z*-scan measurements of dichloromethane solutions of these compounds were performed in a range of wavelengths between 750 and 1600 nm, as described in ref 11 (see the experimental section in the Supporting Information).

Figure 4a shows the results of *Z*-scan measurements of absorptive nonlinearities of **1** in dichloromethane together with the one-photon absorption spectrum plotted against two and three times the wavelength. We identified the nonlinear absorption in the range 700−1100 nm as being dominated by a two-photon absorption process (2PA), whereas three-photon absorption (3PA) was seen to dominate for longer wavelengths (for details about the methodology and calculations, see refs 11b and 11c). The highest 2PA cross section, with a value ∼250 GM, is present at 825 nm, which is markedly shorter than twice the wavelength of the one-photon absorption peak. Simultaneously, 3PA is found to peak at 1300 nm, with a value of σ_3 of 1.0 × 10^{-79} $cm^6\cdot s^2$. The apparent blue shift of the two-photon absorption band can be expected, since in centrosymmetric molecules the selection rules for the one- and two-photon absorption are mutually exclusive. On the other hand, the three-photon absorption selection rule is the same as that for one photon. Here some shift between the positions of the peaks is observed, which may be due to different contributions of vibrational substates in the case of one- and three-photon transitions.

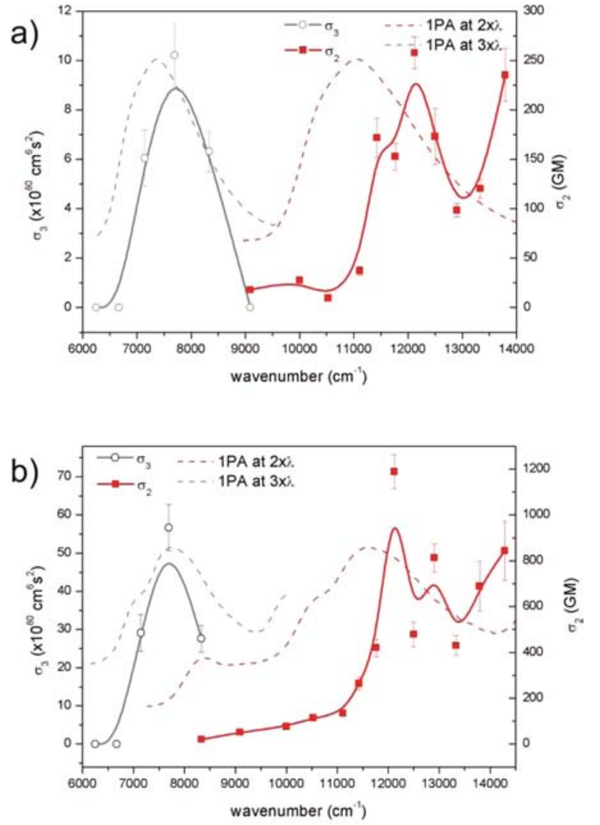

Figure 4. Plot of the two- and three-photon nonlinear-optical absorption spectra of (a) **1** and (b) **1·Ir**. The corresponding wavelength-doubled and -tripled linear absorption spectra (normalized, au) are displayed as red and gray dashed lines, respectively, for comparison.

The iridium complex **1·Ir** exhibits an intense 2PA band with a maximum value of the two-photon absorption cross section of

1180 GM at 825 nm (Figure 4b). The 2PA band is blue-shifted with respect to the absorption bands of the linear spectrum plotted at twice the wavelength, similar to the spectrum of a pure ligand. No feature is seen because of two-photon absorption in the range of the MLCT bands, but that may again be expected because of the mutual exclusion selection rule in a centrosymmetric complex. As for the ligand, we also observed a clear 3PA band at ~1300 nm, with the 3PA cross section equal to 5.8×10^{-79} $cm^6 \cdot s^2$ in the case of the complex. The highest values of the intrinsic 3PA cross sections are on the order of 150×10^{-79} $cm^6 \cdot s^2$, found in organometallic dendrimers.[11b] However, the σ_3 value of **1·Ir** is comparable with state-of-art literature values measured with femtosecond pulses for the most recently reported organic[12] or organometallic[11c] molecules of similar size.

Remarkably **1·Ir** shows a 4.7 times higher two-photon absorption cross section σ_2 and a 5.5 times higher three-photon absorption cross section σ_3 than **1**. This constitutes clear-cut evidence that the metal involving electronic transitions in **1·Ir** strongly participates in its nonlinear response, although the exact nature of this participation has yet to be confirmed by theoretical studies.

Therefore, we believe that this new class of quadrupolar, dinuclear cyclometalated Schiff bases constitutes a very promising approach toward material with enhanced multiphoton absorption properties in the near-IR, up to telecommunication wavelengths.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, material and methods, experimental details, synthetic procedures and characterization, ^1H and ^{13}C NMR spectra of all new compounds, IR spectra of **1** and **1·Ir**, and HR-mass spectrum of **1·Ir**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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