Review on the study of Nonlinear Optics of Iridium Metal Organic Complex

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Abstract

Nonlinear optical materials are one of the key research objects in the field of optics, which mainly research the nonlinear effects of the interaction between luminesce and matter. Compared with inorganic nonlinear optical materials, organic nonlinear materials have outstanding advantages: strong adaptability, high flexibility, low cost, easy modification and damage resistance. In this review, the electric field induced second harmonic generation (EFISH) experimental technology is used to measure and research the nonlinearity of iridium metal complexes. And because of its structural diversity, people can design molecules according to their needs to get the best nonlinear optical response. Organic molecules with large nonlinear coefficients should have the following characteristics: asymmetric charge distribution, the delocalized nature of π electrons, and easy polarization by external electric fields, and a large π conjugated system. In recent years, metal organic compounds have become a leader in the field of optics, mainly because of their very good nonlinear optical properties. In the future, people will do more investigation on the nonlinearity of metal organic complexes. Researchers have shown great interest in iridium metal organic complexes due in particular to their attractive stability and nonlinear activity. This review mainly studies the nonlinear principle, performance test and Measurement of nonlinearity of iridium metal complexes. The nonlinear properties of other metal-metal organic complexes will not be discussed.

Keywords

Nonlinear Optics, EFISH, Iridium Complexes

1. Introduction

The nonlinear optical effects of urea picric acid dinitroaniline and other organic compounds were discovered at the beginning of the study of nonlinear optical materials. Since organic molecules with large non-localized π-conjugated elec-

tron systems exhibit strong photoelectric coupling characteristics, they can obtain high response values and relatively large optical coefficients. After the 1980s, organic nonlinear optical materials developed rapidly. Compared with inorganic materials, organic materials have the advantages of high nonlinear optical coefficient, fast response, easy modification, damage resistance, easy processing, and strong molecular variability [1]. At present, the discovery or synthetic of organic nonlinear optical materials is a research hotspot, including various organic low-molecular nonlinear optical materials, high polymer nonlinear optical materials, metal organic complex nonlinear optical materials, etc. Metallocene complexes, metal carbonyl complexes, metal olefin organic complexes, metal polyacetylene polymers, metal porphyrin organic complexes, metal phthalocyanine organic complexes, metal iridium organic complexes and other complexes Type nonlinear optical materials, included. Iridium (III) complexes will undoubtedly become a hotspot in the research of second-order nonlinear optical materials because of their six-coordination, multiple valence states, diverse coordination forms and excellent performance [2]. In 1986, C. C. Frazier *et al.*, First reported the second harmonic effect of metal organic compounds. Since then, some non-linear effects of metal organic compounds had been discovered one after another. The molecular configuration has a direct effect on the nonlinear optical properties and color of the metal-organic complex. Due to the diversity of ligand metals, metal-organic compounds also have various structures, which have more advantages than nonlinear optical materials composed of simple organic molecules. Because metal atoms have different d or f electron numbers, different oxidation states and coordination numbers, they can form different three-dimensional structures, resulting in unique optoelectronic properties. For example, the redox change of the central metal may lead to a larger molecular hyperpolarizability; the central metal can also become a chiral center, and a non-centrosymmetric crystal can be obtained after splitting; the introduction of metal atoms can combine magnetic and electrical properties with optical properties to produce magneto-optical and electro-optical effects. In addition, metal-organic complexes have more absorption bands, and there are photons transition from metal to ligand and from ligand to metal, with larger ground state dipole moment and polarizability, and energy between ground state and excited state. The level difference is small, which is beneficial to improve the photoelectric response speed of the material. The design and synthesis of ligands with novel structures will be beneficial to the further development of complex research. Numerous reviews on non-linear review articles with rhodium, zinc and other metal organic complexes have been reported. Whereas, few reviews on iridium metal organic complexes are discussed [3]. This review mainly studies the nonlinear optical principle, performance test and application of iridium metal complexes.

2. Principles of Second-Order Nonlinear Optics

The electric polarization $P(r,t)$ is a prerequisite for the nonlinear optical ef-

fect. Under the laser high-intensity photoelectric field $E(r,t)$, the medium will produce a nonlinear electric polarization intensity $P^{NL}(r,t)$, which is a power relationship with the incident photoelectric field [4] describes the medium electric polarization intensity $P(r,t)$. The most important physical quantity of and optical field intensity $E(r,t)$ is the optical polarizability. Therefore, the study of nonlinear optical susceptibility is of great significance to the study of nonlinear optical effects [4]. Under the action of an electric field, the positive and negative charge centers of the atoms migrate, that is, polarization occurs, resulting in an induced dipole moment. Before the appearance of laser, the induced dipole moment was only related to the first order term of the applied electric field intensity *E*.

$$p = \alpha E \tag{1}$$

α is the linear polarizability of a molecule or atom.

Laser is a light source with high intensity, excellent monochromatism and coherence. The polarization intensity of the medium under such strong light is no longer a simple linear relation with the incident light intensity, but is related to the higher order term of the light field intensity.

At this point, the polarized pM of the molecule can be expressed as:

$$pM = \alpha E + \beta E^2 + \gamma E^3 + \cdots \tag{2}$$

β is the first-order molecular hyperpolarizability (second-order effect), and *γ* is the second-order molecular hyperpolarizability (third-order effect). The stronger of incident light intensity will lead to a stronger nonlinear effect. Molecules have non-central symmetry, which is one of the indispensable conditions for optical materials to have nonlinearity, so *β* must not be zero.

If the incident field is an alternating electric field, then:

$$E = E_0 \cos(\omega t) \tag{3}$$

Substituting Equation (3) into Equation (2), and taking into account the vector properties of electric field and polarization [5], Equation (2) can be written as:

$$P_M = \sum_j \alpha_{ij} E_j + \frac{1}{2} \sum_{jk} \beta_{ijk} E_j E_k + \frac{1}{6} \sum_{jkl} \gamma_{ijkl} E_j E_k E_l + \cdots \tag{4}$$

The optical susceptibility is only briefly introduced, and more details are in the literature [6]-[15].

Obtained from the classic two-level model theory: $\beta = \beta_1 + \beta_{CT}$, where β_1 reflects the interaction energy of each substituent with the π skeleton; And β_{CT} shows the contribution of charge transfer, that is, considering the interaction between the ground state and the excited state, its expression:

$$\beta_{CT} = \frac{e^2}{m\hbar^3} \frac{\omega_{ng} f_{ng} \Delta\mu_{ng}}{\left(\omega_{ng}^2 - 4\omega^2\right)\left(\omega_{ng}^2 - \omega^2\right)} \tag{5}$$

where f_{ng} is the oscillator strength of the transition between the ground state and the excited state, and $\Delta\mu_{ng}$ is the difference between the electric dipole

moments of the ground state and the excited state. The comparison between experimental test results and calculations shows that the β_{CT} term can explain the nonlinear response of disubstituted polyolefins and isomers of nitroaniline. From this equation, Equation (5) shows that in order to have a high β_{CT} value, a compound must have charge-transfer transitions at low energy and huge $\Delta\mu_{ng}$ and f_{ng} values. The oscillator strength of the transition should be increased as much as possible and the difference between the excited state and the ground state dipole moment should be increased. Therefore, the most effective method is to increase the electron activity of the donor and acceptor substituents.

By calculating the nonlinear optical susceptibility, the nonlinear optical properties of a series of organic molecules synthesized in the laboratory are theoretically calculated and predicted. The relationship between molecular structure and optical properties is discussed. A large number of studies have verified that the value β of the molecular system is extremely sensitive to the geometric structure characteristics of the molecule, so it is necessary to determine the geometric structure of the molecule in order to calculate the nonlinear response of the molecular system.
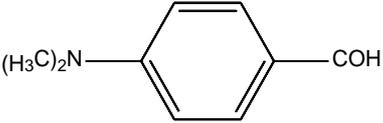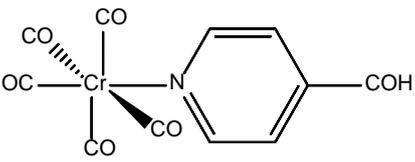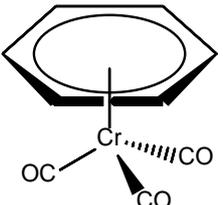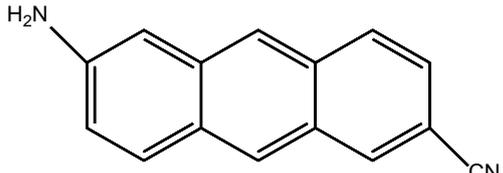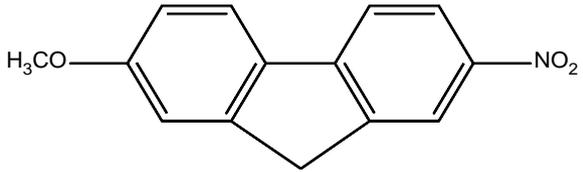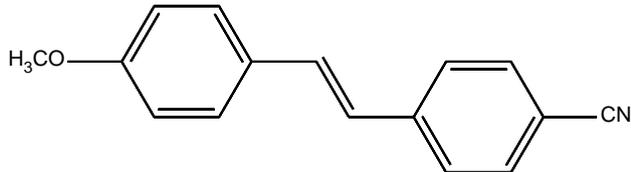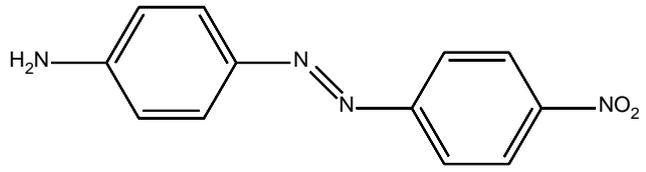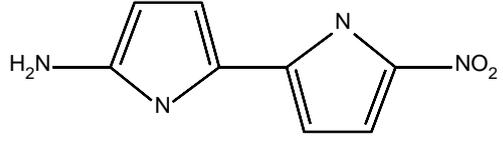
The results from Table 1 show that for most organic compounds and organic metal molecular materials, the contribution of the three-level term is approximately proportional to that of the two-level term. Herein, it is not necessary to consider the contribution of the three-level term everywhere, and the contribution of the charge transfer state to the two-level term can be used to qualitatively understand the nonlinear optical properties of the material. In the theory of quantum chemistry, another relatively important method is the molecular orbital image, that is, a molecule with many atoms or groups can be described by molecular orbital composed of atomic orbital and so on. The transition between orbitals is usually described by the mixing coefficient of the configuration interaction. The typical chromophore structure coefficient is listed in the above table. A transition between the orbital configurations describes the state-state transition of the molecule quite accurately. For some molecules, the primary excitation occurs between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LOMO). Table 1 can be used as an example to illustrate this transition.

3. Measurement of Nonlinearity of Iridium Metal Complexes

Optical susceptibility is one of the important indicators for studying the quality of nonlinear optical materials. The simplest and most direct method to measure the optical susceptibility of materials is the electric field-induced second harmonic generation (EFISH) experimental technique [1] [5] [16]-[22], this technology illustrates the relationship between structure and performance.

Figure 1 is a diagram of the EFISH experimental setup. The beam is polarized by the Glan prism and enters the sample cell after passing through the diaphragm and 1.06 μm color filter. The diameter of the light spot is about 0.5 mm.

Table 1. The relative contribution of the two-level term ($\beta_{vec,2}$) and the three-level term ($\beta_{vec,3}$) of some representative chromophores to the hyperpolarizability [23].

chromophore	β_{vec}	$\beta_{vec,2}$	$\beta_{vec,3}$	$\beta_{vec,2}/\beta_{vec,3}$	$M\%$	C_{CI}
$(H_3C)_2N$—⬡—COH	6.7	9.6	−2.9	−3.3	100	0.96
OC—Cr(CO)...—N⬡—COH	−11.4	−24	12.6	−1.9	73	0.97
Cr(CO)₃ benzene complex	−1.3	−2.4	1.1	−2.2	60	0.77
H_2N—anthracene—CN	11.8	31.6	−19.8	−1.6	86	0.90
H_3CO—fluorene—NO_2	14.6	34.6	−20.0	−1.7	81	0.92
H_3CO—stilbene—CN	8.8	19.4	−10.6	−1.8	84	0.98
H_2N—azobenzene—NO_2	31.4	67.7	−36.3	−1.9	88	0.87
H_2N—bipyrrole—NO_2	40.3	69.0	−28.7	−2.4	93	0.95

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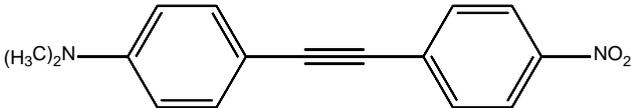
Structure						
$(H_3C)_2N$—⟨⟩—C≡C—⟨⟩—NO_2	30.4	77.9	−47.5	−1.6	80	0.80
ferrocenyl—CH=CH—⟨⟩—NO_2 (Fe)	30.8	71.8	−41.0	−1.8	76	0.77
Ru complex (Cl, Py, OC, CO, N)—CH=CH—⟨⟩—NO_2	−12.4	−24	11.6	−2.1	65	0.85
H_2N—C≡C—⟨⟩—C≡C—Ni(PH_3)(PH_3)—C≡C—⟨⟩—C≡C—NO_2	26.2	128	−102	−1.3	75	0.74
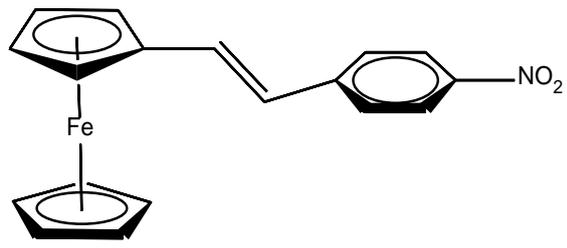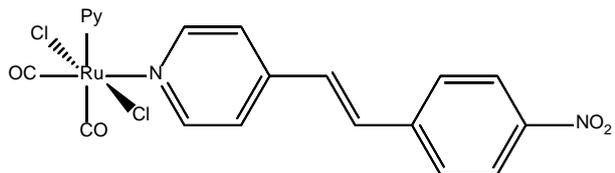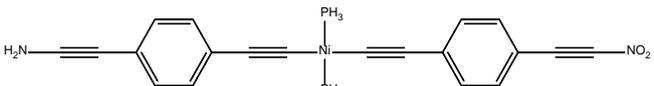
- the unit of β: 4.2×10^{-40} m⁴/V, M: the percentage of a major excitation contributed. C_{cI} : the mixing coefficient of interaction.
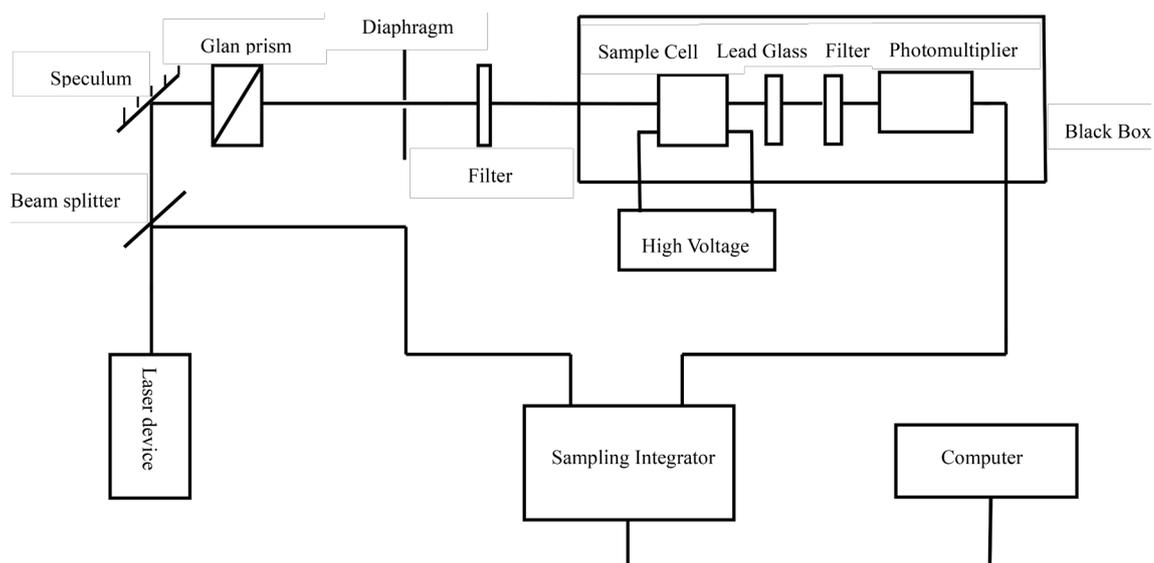
Figure 1. Experimental setup for the EFISH technique.

Using heat-insulating lead glass and interference filter to filter out the fundamental frequency light passing through the sample cell, and the frequency-doubled signal is received by a low-noise, high-sensitivity photomultiplier tube. When measuring quartz samples, a central attenuator must be added to prevent the signal from being too strong to reduce the sensitivity of the photomultiplier tube. The signal is averaged by the sampling integrator and recorded

by the computer. In order to ensure the reliability of the relative ratio of light intensity, the quartz sample is retested at fixed intervals (about half an hour). It summarizes the whole process of EFISH experimental data processing (**Figure 2**), which is mainly used to determine the nonlinear polarizability in the direction of the molecular dipole moment. The basic idea is that the molecules are randomly arranged in a disorderly manner in a liquid or solution state. Even if the molecules themselves have a non-centrosymmetric structure, their even sub-polarization affects cancel each other out, and the average value of the system is still zero. If a high voltage electrostatic field is added to the system, the inherent dipole moment of the molecules will cause the molecules to be aligned under the action of an applied electric field, thus generating the macroscopic frequency doubling effect that can be measured. According to the magnitude of the frequency doubling signal, the second-order nonlinear polarimetry of a single molecule is calculated. This method has become the most accurate and effective method to measure the second order nonlinear polarizability of molecules. The experimental technique can be used to study the second order nonlinear response by means of equations:

$$\gamma_{EFISH} = \left(\mu\beta_{\lambda}/5\kappa T\right) + \gamma\left(-2\omega;\omega,\omega,0\right) \tag{6}$$

$\mu\beta_{\lambda}/5\kappa T$: dipolar orientational contribution $\gamma\left(-2\omega;\omega,\omega,0\right)$: the electronic contribution to EFISH which is negligible for dipolar molecules is the projection along the dipole moment axis of the vectorial component of the tensor of the quadratic hyperpolarizability, working with an incident wavelength. μ is the ground state dipole moment. Extrapolation to zero frequency ($\vee_{\Lambda} = 0.0\text{eV}; \lambda = \infty$) obtains the determination of $\mu\beta_0$ where β_0 is the static quadratic hyperpolarizability, it is a key point for comparing the second-order NLO properties of molecules. The $\mu\beta_0$ value can be obtained by the following equation:

$$\mu\beta_0 = \mu\beta_{\lambda}\left[1 - \left(2\lambda_{max}/\lambda\right)^2\right]\left[1 - \left(\lambda_{max}/\lambda\right)^2\right] \tag{7}$$

λ and λ_{max} is the absorption wavelength. A molecule having a $\mu\beta_0$ higher than that of Disperse Red One (450×10^{-48} esu), which can prepare stable NLO-active hybrid polymeric films [24]. When determining the quadratic hyperpolarizability, it is necessary to ensure that an incident wavelength is far from the absorption wavelengths of the investigated compound.

1) quadratic hyperpolarizability of donor-acceptor molecules

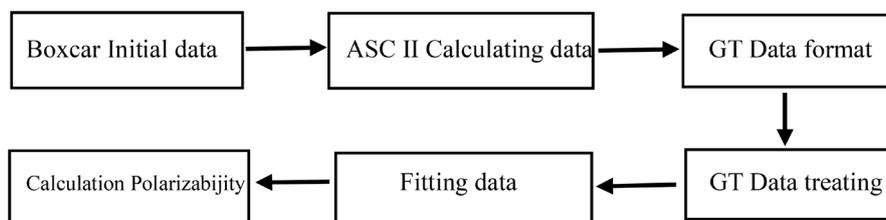The main feature of push-pull molecules is that they are conjugated by the

Figure 2. Data processing of the EFISH experiment.

principal end group, which makes the molecules have attractive optical nonlinearity. The strong absorption of these molecules in the ultraviolet region and the large ground state molecular dipole moment are mainly due to the influence of intramolecular charge transfer (ICT). The significant dipole moment variation is caused by the transition from the ground state to the excited state, and the static secondary polarizability is obtained between the ground state and the excited state. Secondary hyperpolarizability plays an important role in intramolecular charge transfer [25]. In brief, as shown in **Figure 3**, push-pull polyolefin can be seen as a mixture of the two forms of ultimate resonance. For most polyolefins, There is little correlation between hyperpolarizability and geometric parameters. Nonetheless, for push-pull polyolefin, Maker and coworkers reported that in the molecular structure the band length alternation (BLA) and π-electron bond order alternation make a huge positive effect on the hyperpolarizability [26]. In the analysis we used, the ground state and the first excited state (ICT) were described as a linear combination of the neutral (N) and amphoteric (Z) wave functions corresponding to the two resonant forms. In a quadratic approximation, the function of V and T can be represented as a dependent parameter. V is the band between Z and N. T the non diagonal coupling element. Herein, we can define a MIX parameter that determines the resonance shape. This paraeter is only a function of V and T. We analyze the relationship between secondary hyperpolarimetry and MIX. The necessary condition for producing the maximum secondary hyperpolarizability is the existence of an optimal mixture between the finite resonance forms (MIX = ±0.45) [27].

As shown in **Figure 4**, it is the most representative push-pull polyolefin studied so far. The experimental values $\mu\beta$ (0) measured by EFISH technology are listed in **Table 2**. We calculated the mixed values as well as the β_{CT} (0) and β_{max} (0) values using data from both absorption and electro-optical absorption measurements (EOAM) via a two-state bimorphological model [28]. The experimental value (0) and the calculated value CT (0) increased as the molecules grew,
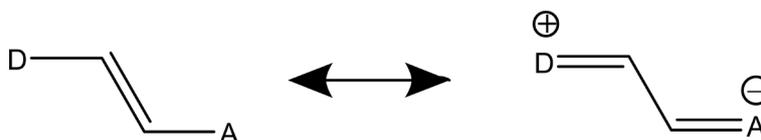

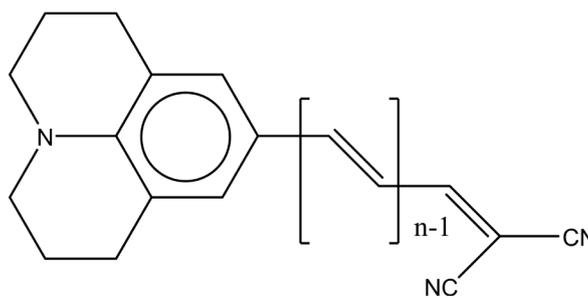**Figure 3.** Neutral and zwitterionic resonance forms of push-pull polyenes.

Figure 4. Structural formula of the series of molecules investigated.

Table 2. The β hyperpoiarizabilities are given in 10^{-30} esu [28].

n	MIX	β_μ (0)	β_{CT} (0)	β_{CT} (0)
1	−0.49	32	35	36
2	−0.65	97	96	129
3	−0.73	210	200	368
4	−0.76	405	288	600

The accuracy of the experimental values β_μ (0) is about 10%. The MIX and β_{max} (0) computed values obtained with the two-state two-form model. β_{CT} (0) from ref. [29].

but remained essentially the same except for long chains of n = 4, indicating that the quadratic approximation was suitable for push-pull polyolefins (**Table 2**). At the same time for short-chain compounds, the mixing value is almost optimized. But as the chain grows, the MIX value deviates more and more from the optimized value. Whereas, β_{max} (0) increased significantly, resulting in a significant increase in the second-order nonlinearity. This indicates that the growth of chain has a direct effect on the secondary hyperpolarimetry of these compounds.

2) Cyclometalated Ir (III) Complexes with Curcuminoid Ligands

It is well known that for pyridine-based iridium metal organic complexes, the free 2-phenylpyridine NLO response is very weak. Therefore, the metal iridium and the cyclometalization reaction play a decisive role in improving the nonlinear activity of such metal complexes. After studying a family of iridium (III) acetylacetonate compounds with various cyclometalated 4-styryl-2-phenylpyridines substituents (NEt_2, OMe, NO_2), In order to undestand that whether appropriate functionalization of 2-phenylpyridine ligands is beneficial to the improvement of secondary NLO activity [30]. The results indicate that the $\mu\beta_{1.907}$ value of the 4-styryl-2-phenylpyridine bearing the nitro group, is comparable to 2-phenylpyridine [34]. Undoubtedly, Iridium phosphorescent (III) complexes, two epoxided 2-phenylpyridine ligands and acetylacetone as auxiliary ligands have become the leading ones in the field of NLO research. But, this kind of hybrid polymer film was declared a failure by reason of its unstable nonlinear activity. As shown in **Figure 5**, As a consequence that researching two iridium (III) complexes with two cyclometalated 2-phenylpyridines and curcumin (complex 1) or tetrahydrocurcumin (complex 2) as an ancillary ligand. The complexes 1 and 2 were determined in chloroform solution (10^{-3} M) by The Electric Field Induced Second Harmonic generation (EFISH) method. For complexes Ir_1 and Ir_2, we choose a 1.907 μm as incident wavelength achieved by Raman-shifting the 1.064 μm wavelength obtained from a Q-switched, mode-locked Nd: YAG laser.

Obviously, the values of these two iridium metal complexes are negative. The $\mu\beta_{1.907}$ value of complex Ir_1 is -1050×10^{-48} esu, -930×10^{-48} esu for complex Ir_2 respectively. Some studies show that the $\mu\beta_{1.907}$ value of other cyclometalated iridium (III) complexes with β-diketonate is also negative [31] [32]. Hence it indicates that value of $\Delta\mu_{ng}$ (difference of the dipole moment in the excited state and in the ground state) is negative following the "two-level" model [33] [34].
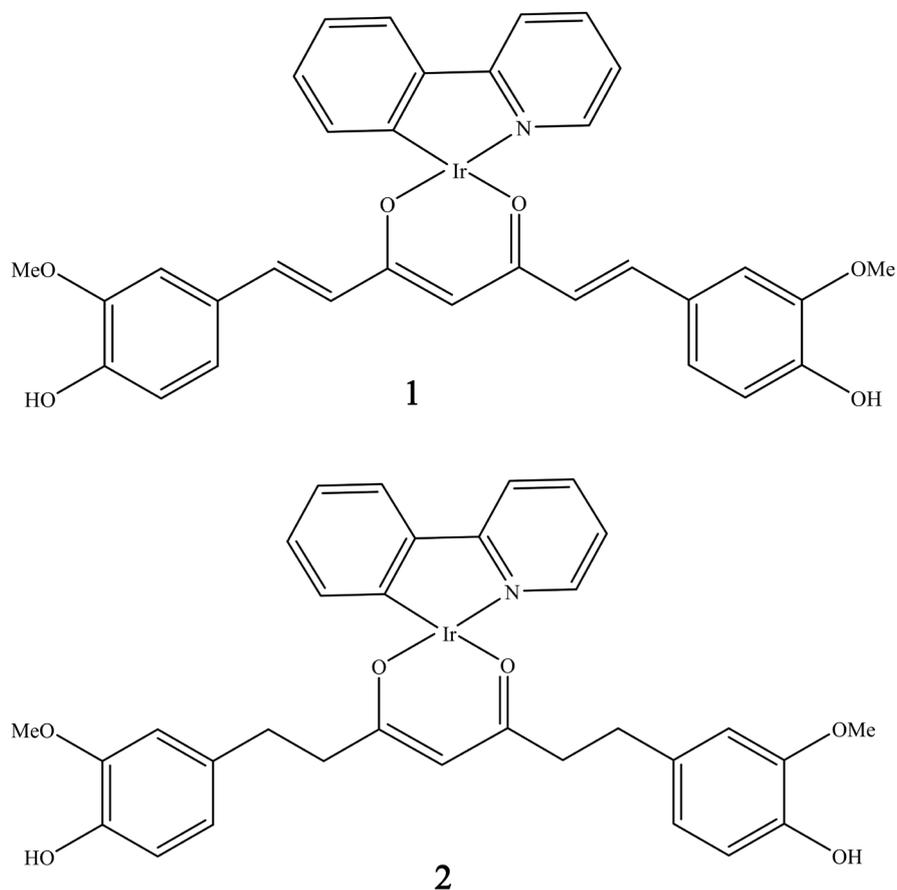
Figure 5. Investigated Iridium (III) complexes.

For complex Ir$_1$, the $\mu\beta_{1.907}$ experimental value (-1050×10^{-48} esu) is comparable to $\mu\beta_0$ calculated value (-747×10^{-48} esu) by Equation (7). The low energy charge transfer absorption band (470 nm [35]) much higher than that of Disperse Red One [24] and slightly larger than that of the related complex with acetylacetonate instead of the curcumin ligand. The complex Ir$_2$ with tetrahydrocurcumin as an ancillary ligand has a similar second-order NLO response ($\mu\beta_{1.907} = -930 \times 10^{-48}$ esu; $\mu\beta_0 = -661 \times 10^{-48}$ esu by Equation (7) and $\lambda_{max} = 470$ nm [36]. It is a tempting conclusion that because of their unique characteristics of luminescence and nonlinear optical properties, these compounds have become the focus of multifunctional molecular photoelectronic materials, attracting the attention of scientists and researchers today [37]-[46]. In Ir (III) complexes, the second-order NLO response mainly caused by various charge transfer transitions. And the observed negative value of $\beta_{1.907}$ EFISH is the result of positive and negative contributions to the quadratic hyperpolarizability [4] [32].

3) Iridium complexes with anellated hemicyanine ligands

The second-order NLO activity of anellated hemicyanine ligands [N,N-dimetyl-4-(pyridin-4-yl)aniline, L$_1$ and N-methyl-N-hexadecylaminostilbazole, L$_2$,7-N,N-dibutylamino-2-azaphenanthrene, L$_3$, and 8-N,N-dibutylamino-2-azachrysene, L$_4$. systems containing an electron-withdrawing substituent (-CN),

L_5], and iridium(III) compounds with anellated hemicyanine ligands {cis-[Ir(CO)$_2$ClL$_3$], IrL^3, and cis-[Ir(CO)$_2$ClL$_4$], IrL^4} have been investigated (**Figure 6**) [47]. Their second-order NLO activity was studied by EFISH techniques and the values $\mu\beta_{1.907}$ (EFISH) of iridium(III) compounds with anellated hemicyanine ligands are reported in **Table 2**, **Table 3**. With study of these iridium (III) compounds, we obtained that the selected compound L^1 in trichloromethane solution present a low absolute value of $\mu\beta_{1.907}$ (EFISH) (48×10^{-48} esu), which can be attributed to the absence of a complete π-conjugation between the two aromatic rings. However the absolute value of $\mu\beta_{1.907}$ (EFISH) (L^3: 430×10^{-48} esu) is 8.9 times as much as L^1, which is due to include the single bond into the polyaromatic scaffold of L^3. It is quite clear that a continuous enhancement of the π-conjugation for the free ligand gives rise to a huge positive effect on the second order NLO response. Hence, the absolute value of $\mu\beta_{1.907}$ (EFISH) of the free ligands: L^3 and L^4 is much lagerer (430×10^{-48} esu, 1800×10^{-48} esu) than that of L^2 (223×10^{-48} esu). Strangely enough, there is different to what was observed in the case of stilbazolium salts [48] [49], the effect of methylation of the pyridine ring of L^4 to the second order NLO is weak, although generating a bathochromic shift of the ILCT transition. That is usually originated from the difference in the direction of the dipole moment，which governs the overall EFISH response. More surprisingly, the β values of L^3 and L^4 ligands are large and positive, which become decrease and even negative. When coordinated (**Table 3**).
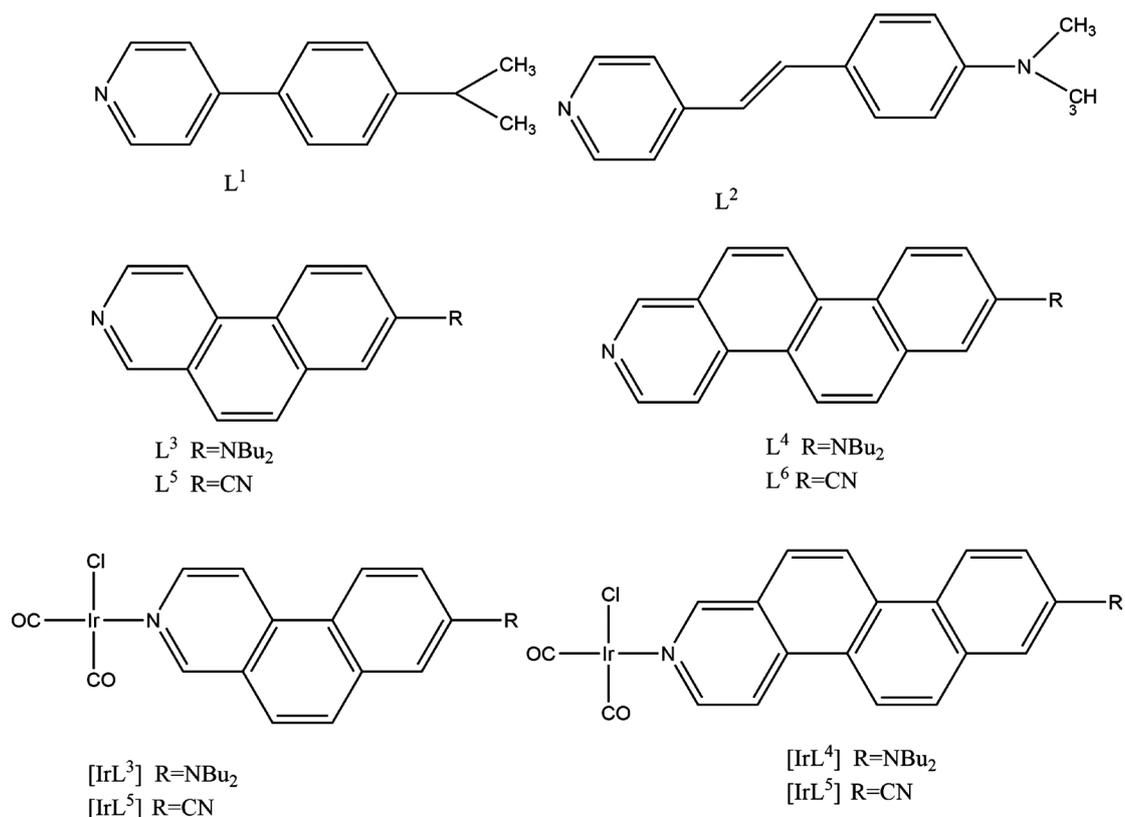

Figure 6. Schematic structure of anellated hemicyanine ligand and their related iridium complexes.

Table 3. EFISH $\mu\beta_{1.907}$ and μ values of ligands L$_3$ and L$_4$ and related iridium complexes [50].

	$\mu\beta_{1.907}$[a,b] ($\times10^{-48}$ esu)	μ[c] (μ_{theor}) [D]	$\beta_{1.907}$ ($\times10^{-30}$ esu)
L^1	48	2.4	20[d]
L^2	223[e]	3.7[e]	60[e]
L^3	430	3.5(7.6)	123[d](56)[e]
[IrL^3]	620	(16.2)	(38)[e]
L^4	1800	4.2(8.0)	429[d](224)[e]
[IrL^4]	−2310	(16.9)	(−137)[e]

[a]EFISH values determined in CHCl$_3$ with an incident wavelength of 1.907 mm. [b]The error on EFISH measurements is ±10%. [c]Values measured in CHCl$_3$ by the Guggenheim method. [d]By using experimental μ. [e]Data from ref.[47].

Table 4. NLO response of CN substituted ligands, L^5 and L^6 and related iridium complexes [50].

Ligands	$\mu\beta_{1.907}$ ($\times10^{-48}$esu)[a]	Complexes	$\mu\beta_{1.907}$ ($\times10^{-48}$ esu)[a]
L^3	587	[IrL^3]	819
L^5	−1030	[IrL^5]	−2350
L^6	−1830	[IrL^6]	−1990

[a]In DMF at 10^{-4} M with an incident radiation of 1.907 μm. The error on EFISH measurements is ±10%.

With this fundamental concern, it is easy to find that the μ of the ground state is lower than that of the excited state. This can be explained by two factors: ILCT transition ($\beta > 0$) and MLCT transition ($\beta < 0$). As shown in Table 3, This behaviour is compared to the observed upon coordination of L^2 to the same Ir(I) moiety where $\mu\beta_{1.907}$ is enhanced but remains positive, being dominated by an ILCT Transition [47]. The increasing NLO response when an annine substituted with a withdrawing group, CN L^5, is coordinated to the iridium fragment would be in agreement with the importance of the MLCT transition (Table 4).

4) Cationic cyclometallated iridium (III) complexes with substituted 1,10-phenanthrolines

A family of Ir(III) complexes of [Ir(ppy)2(5-R-1,10-phen)] [PF6] (ppy = cyclometallated 2-phenylpyridine), (1a-b), [Ir(ttpy)$_2$(5-R-1,10-phen)] [PF$_6$] (ttpy = cyclometallated 3'-(2-pyridil)-2,2':5',2''-terthiophene, phen = phenanthroline; 2a-b, R = Me, NO$_2$) and [Ir(pq)$_2$(5-R-1,10-phen)] [PF$_6$] (pq = cyclometallated 2-phenylquinoline, 3a-b) was investigated (Figure 7). The $\mu\beta$ values of these six complexes were determined by the EFISH method working in CH$_2$Cl$_2$. All compounds show a negative $\mu\beta_{1.907}$ (EFISH) (Table 5), ranging from -1320×10^{-48} esu to -2230×10^{-48} esu. Complex [Ir(ppy)2(5-R-1,10-phen)] [PF6] (ppy= cyclometallated 2-phenylpyridine) shows a large absolute value of $\mu\beta_{1.907}$ (EFISH), which presents a strong second order NLO response [51] and luminescence properties [52], A slightly higher value is observed for [Ir(pq)$_2$(5-R-1,10-phen)] [PF$_6$] (pq = cyclometallated 2-phenylquinoline). Substitution of ppy with the
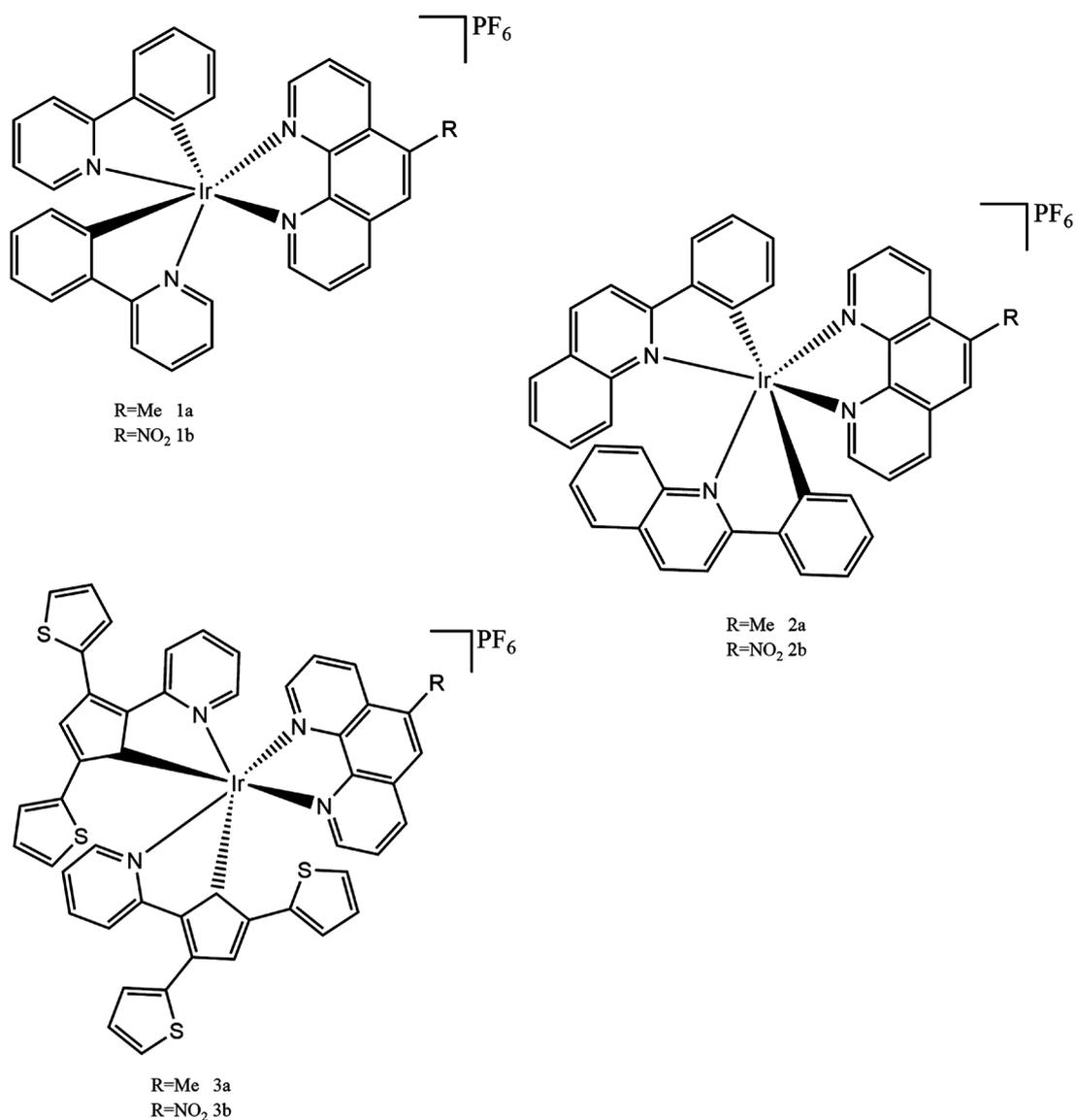
Figure 7. Bis-cyclometalated phenylpyridine iridium (III) complexes with phenanthroline ligands.

Table 5. Absorption and emission maxima, Φ and EFISH $\mu\beta_{1907}$ values in CH_2Cl_2 of 1 - 3 complexes [53].

	Absorption max (nm)	Emission max (nm)	Quantum yield Φ (%)	EFISH $\mu\beta_{1907}$[a,b] (10^{-30} Dcm^{5}esu^{-1})
1a	255(sh), 268, 333(sh), 377[c,d]	559[c]	38[c]	−1565[e]
1b	254(sh), 264, 378[c,d]	-	<0.1[c]	−2230[e]
2a	273, 329, 347(sh), 431[c,d]	556[c]	34	−2090
2b	268, 324, 430[c,d]	-	<0.1[c]	−1720
3a	260, 319(sh), 396[d]	563	1.3	−1320
3b	250(sh), 264, 360(sh), 377, 407(sh)[d]	-	<0.1	−1640

[a]EFISH measurements are carried out in CH_2Cl_2 at 10^{-3} M; [b]The error of EFISH measurements is ±10%; [c]Ref. [51]; [d]There is a band tail above 400 nm up to about 500 - 550 nm; [e]Ref. [51].

more π-delocalized pq does not affect significantly the luminescence and NLO properties. A slightly lower NLO response and a much poorer luminescence is observed for the related complexes with ttpy. It is worthwhile mentioning that these complexes have unique characteristics in good transparency towards the second harmonic emission renders appealing as building blocks for composite second order NLO materials [51]. The quadratic hyperpolarizability β of 2a-b and 3a-b was measured by the EFISH technique [53] at 1907 nm incident wavelength in CH_2Cl_2. Comparison of the properties of 2a-b with that of 1a-b puts in evidence that substitution of ppy with the more π-delocalized pq does not affect significantly the luminescence and NLO properties(Table 5).

4. Concluding Remarks

In this review, the nonlinear optical properties of iridium complexes were investigated, the relationship between their NLO activity and molecular structure was elucidated, and the great potential of iridium complexes in NLO optical materials was demonstrated. Nonlinear polarimetry is one of the main indexes to measure the quality of nonlinear optical materials, and its size is directly related to the molecular structure. Therefore, studying the molecular nonlinear polarimetry at the molecular level is of great help to design new and efficient nonlinear optical devices. There are several methods to determine the second-order nonlinear polarizability of molecules. At present, the most accurate and effective method is EFISH experimental method, namely EFISH(electric-field-induced second harmonic wave) method, which is used to determine the nonlinear polarizability in the direction of the molecular dipole moment. Which provides a bridge between micromolecules and molecular engineering, and points the way for synthetic chemists and materials scientists to find new nonlinear optical materials. In this paper, the working principle, experimental steps and calculation results of EFISH method are introduced in detail, and the results are discussed preliminarily. In this paper, the working principle, experimental steps and calculation of EFISH method are introduced in detail, and the results are discussed preliminarily. For most polyolefins, there is little correlation between hyperpolarization and geometric parameters. Nonetheless, for push-pull polyolefin, Maker and coworkers have been proved that in the molecular structure the band length alternation (BLA) and π-electron bond order alternation make a hugely positive effect on the hyperpolarizability [26]. For pyridine iridium metal organic complexes, free 2-phenylpyridine NLO response is very weak. Herein, the metal iridium and the cyclometalization reaction play a decisive role in improving the nonlinear activity of such metal complexes. It is no doubt that iridium (III) complex with tetrahydrocurcumin ligands are distinguished from NLO research. Additionally, due to the large nonlinear optical coefficient of organic molecular nonlinear optical materials, wide response band, good flexibility, high light damage threshold and low cost, as well as easy synthesis and can be cut and modified, the organic molecular nonlinear optical materials have attracted much

attention. Looking forward, the experimental work will be devoted to achieving the efficient conversion into light or redox of the second order NLO activity. The iridium complex has the properties of second order NLO and has the potential to combine second order NLO, two-photon absorption and luminescence and other functional materials.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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