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Cyclometalated Iridium(III) Complexes Containing 4,4'- π -Conjugated 2,2'-Bipyridine Derivatives as the Ancillary Ligands: Synthesis, Photophysics, and Computational Studies

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Supporting Information

ABSTRACT: This article demonstrates a series of cyclometalated Ir(III) complexes of the type $[Ir^{III}(C^{N})_2(N^{N})]$ -(PF₆), where C^N is 2-phenylpyridine, and N^N corresponds to the 4,4'- π -conjugated 2,2'-bipyridine ancillary ligands. All these compounds were synthesized through splitting of the binuclear dichloro-bridged complex precursor, $[Ir(C^{N})_2(\mu$ -Cl)]₂, with the appropriate bipyridine ligands followed by the anion exchange reaction. The linear and nonlinear absorption properties of the synthesized complexes were investigated. The



absorption spectra of all the title complexes exhibit a broad structureless feature in the spectral region of 350-700 nm with two bands being well-resolved in most of the cases. The structures of all the compounds were modeled in dichloromethane using the density functional theory (DFT) algorithm. The nature of electronic transitions was further comprehended on the basis of timedependent DFT analysis, which indicates that the origins of various bands are primarily due to intraligand charge transfer transitions along with mixed-metal and ligand-centered transitions. The synthesized compounds are found to be nonemissive at room temperature because of probable nonradiative deactivation pathways of the T₁ state that compete with the radiative (phosphorescence) decay modes. However, the frozen solutions of compounds Ir(MS 3) and Ir(MS 5) phosphoresce at the near-IR region, the other complexes remaining nonemissive up to 800 nm wavelength window. The two-photon absorption studies on the synthesized complexes reveal that values of the absorption cross-section are quite notable and lie in the range of 300-1000 GM in the picosecond case and 45-186 GM in the femtosecond case.

INTRODUCTION

The design of two photon absorbing materials has recently become an active topic of chemical research, which requires that the materials should have large two-photon absorption cross-section (σ_2) especially in the near-infrared (NIR) region, so as to be applicable in areas such as photodynamic therapy, upconversion lasing, drug delivery, etc.¹ There are various routes through which the two-photon absorption cross-section (σ_2) can be increased, that is, by increasing the conjugation in the π -backbone or increasing the charge transfer from donor to acceptor moiety.¹ Organic chromophores, based on such principles, yield large two-photon absorption cross-sections. Two-photon absorbing materials based on d-block transition metal complexes are found to be better candidates over organic molecules, especially due to their longer excitation wavelength, thereby reducing the phototoxicity and larger Stokes shift avoiding self-quenching because of reabsorption, etc. Even though these complexes possess attractive linear and nonlinear optical properties, only a handful of metal-based chromophores, with same design principles, have been investigated.¹ It has been observed that transition metal complexes of extended π conjugated ligands are excellent building blocks for studying the

nonlinear optical properties exhibited by relevant compounds. The metal ion, in such complexes, plays some pivotal roles, such as (i) acting as a powerful template to gather ligands in predetermined octupolar arrangements, (ii) inducing a low-energy metal-ligand charge-transfer transition (MLCT), and (iii) acting as a Lewis acid to induce a strong intraligand charge-transfer (ILCT) transition, thereby contributing to sizable nonlinear optical activity.^{1c}

Among various luminescent complexes having MLCT transitions, we opted for the iridium complexes because (i) their optical properties can be tuned very easily over the entire visible region even with slight variations in the coordinating ligands; (ii) they are photochemically as well as kinetically robust, and (iii) they can show unusual nonlinear optical properties.¹ Coordination complexes of iridium have received enormous interests since the past few decades, due to their potential applications in multidisciplinary areas such as organic light-emitting diodes (OLEDs), and light-emitting electrochemical cells (LECs),¹ biological imaging,² sensory materials,³

Received: December 30, 2015 Published: March 15, 2016 Chart 1. Molecular Structures of the Synthesized Cyclometalated Ir(III) Complexes



dye-sensitized solar cells,⁴ nonlinear optics,⁵ etc. Even though the coordination complexes of Ir^{III}, Ru^{II}, and Os^{II} exhibit almost similar type of photophysical properties, a majority of the previously reported studies involve mainly the complexes of Ru^{II} and Os^{II} and very few Ir^{III} complexes, probably due to the synthetic challenges associated with the kinetic inertness of Ir^{III} in the context of substitution.⁶ However, over the past decade, iridium complexes have also come to the limelight because of color tunability, high photoluminescent efficiency, etc.⁶ The strong spin-orbit coupling facilitated by the heavy metal ion, iridium, in the pertinent complexes results in efficient $S_1 \rightarrow T_1$ intersystem crossing upon photoexcitation, thereby making majority of the complexes to follow the phosphorescence deactivation pathway of the photoexcited state. Among the diverse classes of iridium complexes, the heteroleptic systems containing a combination of 2,2'-bipyridine (N^N) and cyclometalated-phenylpyridine (ppy, C^N) have gained special attention due to their synthetic ease compared to the trischelated homoleptic complexes. The photophysical properties of such complexes can easily be tuned by varying the nature of substituents on either the cyclometalating (C^N) ligand or ancillary (N^N) ligand, which in turn affects the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy gaps.⁷⁻⁵

Previous literature reports^{10,11} suggest that cyclometalated Ir(III) complexes have mostly been explored in the areas of OLEDs, LECs, second-order nonlinear optics, etc, whereas reports associated with such complexes being used as twophoton absorbers (third-order nonlinear process) are very scarce.^{1,11,12} Beeby and co-workers reported the NIR twophoton absorption (TPA) of a series of neutral cvclometalated iridium complexes using substituted phenylpyridines as the cyclometalated ligands and acetylacetonate as the ancillary ligand. These complexes, in fact, exhibit moderate values of TPA cross-section.¹² Another report concerning iridium complexes of a terpyridyl-stilbene system by Magennis and co-workers demonstrated two-photon cross sections in the range of 10-70 GM.^{1b} Recently, Zhao and co-workers reported a phosphorescent dinuclear cationic iridium(III) complex having a conjugated oligomer as N^N ligand and a triarylboron compound as C^N ligand, which exhibited a TPA cross-section near ca. 500 GM.^{1a} As such, there is an increasing necessity to improve the two-photon absorption cross sections of iridium complexes so as to make them promising candidates that can be applicable in this material world of science. Recently, we have shown that simple modification of the π -skeleton in a series of 4,4'- π -conjugated 2,2'-bipyridine dyads possessing a D- π -A-A- π -D architecture can effectively tune the linear optical

Scheme 1. Synthetic Pathway to Obtain the Complexes Ir(MS 3)-Ir(MS 8)



properties.¹³ We observed that the coexistence of two donor functionalities, namely, alkoxy and amino, in the same phenyl ring affect the emitting state of the molecules to a greater extent as compared to other reported chromophores having either alkoxy or amino donor groups.¹³ Also, changing the position of the alkoxy donors from one ring to the other alters the optical properties of the concerned chromophores. Therefore, we developed a keen interest to find out whether increasing the conjugation and varying the donor substituents on the ancillary (N^N) ligands could tune the optical properties of the resulting iridium complexes or not. Continuing our efforts to probe the structural factors that could improve the linear and nonlinear optical properties of π -conjugated bipyridyl metal complexes, we describe, in this Article, synthesis of a new series of cyclometalated Ir(III) complexes of the type [Ir(C^N)₂-(N^N)](PF₆), where C^N is 2-phenylpyridine, and N^N corresponds to the $4,4'-\pi$ -conjugated 2,2'-bipyridine ligands (see Chart S1, Supporting Information, for molecular structures of the ancillary N^N ligands and MS 3-8). The corresponding iridium complexes are pictorially presented in Chart 1. These complexes were easily synthesized, using proper metal precursor and the bipyridine derivatives, and isolated as their hexafluorophosphate salts. For an easy discussion in the text, the complexes are named as Ir(MS 3)-Ir(MS 8) based on the bipyridine ligand used. All these compounds were isolated as dark colored microcrystalline solids and characterized by NMR and mass (HRMS) spectroscopic techniques including elemental analysis. Photophysical properties of the synthesized compounds were investigated in a set of solvents with varying polarity. The geometric and electronic structures of the compounds were theoretically modeled in solvent medium. Finally, we performed the two-photon absorption studies of the synthesized complexes in dichloromethane (DCM) at room temperature.

RESULTS AND DISCUSSION

I. Synthesis. The synthetic pathway to obtain the desired iridium complexes (Chart 1) in the present study is shown in Scheme 1. The reaction between hydrated iridium trichloride and 2-phenylpyridine in 2-ethoxyethanol-water solvent mixture under refluxing condition leads to the formation of μ -chloro-bridged-dimer, which acts as the starting precursor. Subsequent splitting of the dimer, by the appropriate ancillary bipyridine ligand (MS 3-MS 8, Chart S1), and anionic

metathesis yielded the desired heteroleptic complexes, which were purified through column chromatography (see Experimental Section). All these synthesized compounds Ir(MS 3)–Ir(MS 8) were characterized through IR, NMR, and mass (HRMS) spectroscopic techniques including elemental analysis. The vinylic C=C bonds in the synthesized materials are found to have *E*- configuration, which is indicated by the splitting of each of the CH resonances by the neighboring protons with a ³J_{HH} coupling constant of ca. 16 Hz in their respective NMR spectra.

II. Computational Analysis. To comprehend the origins of various electronic transitions responsible for absorption of electromagnetic radiation by the Ir(III) complexes, quantum chemical calculations were performed on the molecular structures of the cationic counterpart of the synthesized complexes at the density functional theory (DFT) and time-dependent (TD) DFT level of theory using the Gaussian 09 program package.^{14,15} The energy-minimized structures of all the relevant metal complex cations are shown in Supporting Information (Figure S7).

The simulated structures of the title complexes exhibit some common features: (a) the calculated bond lengths, specifically, Ir-C(ppy), Ir-N(ppy), and Ir-N(bpy), are found to be ca. 2.02, 2.07, and 2.18 Å, respectively, in all the complexes, which match quite well with those in related cyclometalated complexes, reported previously (see Table 1);^{10,11} (b) the two pyridine rings of the bipyridine ligands in all the structures are twisted by ~4°, and (c) the two phenyl rings of the individual distyryl arms of the complexes comprising the oligophenylenevinylene (OPV) bipyridine ligands (except

Table 1. Selected F	Bond Lengths a	and Dihedra	l Angles of the
Energy-Minimized	Structures in t	the Iridium	Complexes

	bo	nd length (Å)	dihedral angle (deg)			
compound	Ir–C(ppy)	Ir–N(ppy)	Ir–N(bpy)	bpy- Ph(A) ^a	bpy- Ph(B) ^a	Ру- Ру	
Ir(MS 3)	2.02	2.07	2.18	8, 8		4	
Ir(MS 4)	2.02	2.07	2.18	9, 5	31, 23	4	
Ir(MS 5)	2.02	2.07	2.18	0, 8	12, 24	4	
Ir(MS 6)	2.02	2.07	2.18	11, 11	10, 10	4	
Ir(MS 7)	2.02	2.07	2.18	10, 11	41, 11	4	
Ir(MS 8)	2.02	2.07	2.18	10, 4	11, 25	4	

^aA and B refer to the two phenyl rings in the OPV bipyridine ligands.

Ir(MS 6)) are found to be out-of-plane displaced in differing degrees with respect to the pyridine plane (see Table 1).

The planarity of a molecule generally plays a crucial role in determining the charge-transfer character between the donor and acceptor moieties. Conjugation between the concerned functionalities becomes more facile with the increase in planarity of the molecules that directly affect the chargetransfer process. The order of planarity between the various functionalities of the 2,2'-bipyridine ligand cores in the optimized structure of the title complexes was analyzed on the basis of out-of-plane displacement of the phenyl rings from the bipyridine plane (see Table 1). It was found that the dibutylamino donors in the complexes, Ir(MS 4) and Ir(MS 7), are strongly rotated with respect to the phenyl rings they are attached with, whereas they are found to be almost planar in case of the complex Ir(MS 6). In contrast, the pyrrolidine donor systems in complexes Ir(MS 3), Ir(MS 5), and Ir(MS 8) are found to be almost in plane with the adjacent phenyl rings. It is thus evident that, based on the computed molecular geometries, differing degrees of conjugation or donor-acceptor interactions between the amino donor functionalities and pyridine acceptor core are present in the title complexes. Alternatively, it can be said that a greater degree of conjugation between the donor and acceptor functionalities makes the intramolecular charge transfer more feasible, and thus, the complexes, the geometry of which fulfills this criteria, would absorb at a lower energy region of the electromagnetic radiation compared to those with lesser extent of conjugation. This trend is indeed reflected in the absorption spectra of the title complexes as described in the next section (see Table 2).

 Table 2. Summary of the Linear Optical Data of the

 Synthesized Iridium Compounds

compd	$\lambda_{abs} (\varepsilon), nm$ (L mol ⁻¹ cm ⁻¹) ^{<i>a</i>}	transition	assignment	$\lambda_{\rm em}^{\prime}$ /nm ^b	τ, μs
Ir(MS 3)	503 (56 200)	$\begin{array}{c} \text{HOMO} \rightarrow \text{LUMO} \\ (65\%) \end{array}$	IL+LL'	725	86.7
	410 (33 100)	$HOMO-1 \rightarrow$ LUMO (67%)	+MLCT		
Ir(MS 4)	465 (58 600)	$\begin{array}{c} \text{HOMO} \rightarrow \text{LUMO} \\ (37\%) \end{array}$	IL+LL'		
	390 (57 100)	$HOMO-1 \rightarrow$ LUMO (38%)	+MLCT		
Ir(MS 5)	500 (52 400)	$\begin{array}{c} \text{HOMO} \rightarrow \text{LUMO} \\ (39\%) \end{array}$	IL+LL'	775	44.6
	395 (48 900)	HOMO−1 → LUMO (41%)	+MLCT		
Ir(MS 6)	515 (61 000)	$\begin{array}{c} \text{HOMO} \rightarrow \text{LUMO} \\ (44\%) \end{array}$	IL+LL'		
	415 (42 200)	HOMO−1 → LUMO (45%)	+MLCT		
		HOMO−1 → LUMO+1 (27%)			
Ir(MS 7)	500 (68 200)	$\begin{array}{c} \text{HOMO} \rightarrow \text{LUMO} \\ (34\%) \end{array}$	IL+LL'		
	415 (51 600)	HOMO−1 → LUMO (34%)	+MLCT		
		$\begin{array}{l} \text{HOMO-1} \rightarrow \\ \text{LUMO+1 (19\%)} \end{array}$			
Ir(MS 8)	524 (65 700)	$\begin{array}{c} \text{HOMO} \rightarrow \text{LUMO} \\ (32\%) \end{array}$	IL+LL'		
	423 (46 200)	HOMO−1 → LUMO (34%)	+MLCT		
		$\begin{array}{c} \text{HOMO-1} \rightarrow \\ \text{LUMO+1(18\%)} \end{array}$			

^aAt room temperature in DCM. ^bAt 77 K in frozen 2-Me-THF.

The examination of electronic structures of the title complexes reveals that the HOMO and HOMO-1 are almost degenerate and are predominantly localized on the donor-substituted phenyl rings and the vinylic C=C bonds of the 2,2'-bipyridine ligands, whereas the LUMO and LUMO+1 are the π^* molecular orbitals (MOs) of the bipyridine and phenylpyridine cores. The localization of the various MOs in the electronic structure of Ir(MS 3) is presented in Figure 1 as



Figure 1. Representation of various energy levels in Ir(MS 3).

an illustrative example. Note that our computation setup is based on linear-response TD-DFT without inclusion of the spin-orbit coupling scheme. It was observed that the calculated electronic excitation wavelengths are underestimated by $\sim 60-$ 70 nm as compared to the observed absorption maxima under the present theoretical level. This could be because we modeled only the cationic fragment in our quantum chemical setup. However, the calculated excitation energies could still be used to qualitatively assess the various absorption bands in the UVvisible absorption spectra of the relevant complexes. The variation of the estimated excitation wavelengths with alteration of the molecular structure follows a similar trend with the observed spectroscopic behavior of the pertinent complexes. As can be seen from Figure 1, the contribution due to the metal ion in HOMO or HOMO-1 is very small. In case of Ir(MS 3), it was found that the iridium metal center has a significant contribution in the HOMO-2. In fact, in most of the cases, the metal has some contribution typically in the HOMO-2.

III. Photophysical Properties. Absorption spectra of the title compounds were recorded in different solvents at room



Figure 2. (a) Absorption spectra of the title iridium complexes in DCM at room temperature. (b) 77 K phosphorescence spectra of Ir(MS 3) and Ir(MS 5) in 2-Me-THF, excited at the corresponding band maxima.

temperature (298 \pm 2 K). Figure 2a depicts spectra recorded in DCM, and the corresponding optical data are summarized in Table 2. As shown in Figure 2a, the absorption spectra of all the title complexes exhibit a broad structureless feature in the 350-700 nm spectral region. In most of the cases, the two bands are well-resolved in this region; however, in some cases, the shorter wavelength band appears as a shoulder. The main absorption bands are followed by "moderate to intense" bands at the higher energy region of the spectra (Figure 2a). The longest wavelength intense band is found to be sensitive to the structure of the 2,2'-bipyridine ligands and to the solvent polarity. The TD-DFT analysis predicts that these two bands are mainly due to HOMO \rightarrow LUMO and HOMO-1 \rightarrow LUMO excitations bearing ligand-centered character together with some MLCT character. The lowest-energy broad absorption band is largely bathochromically shifted with respect to the free ligand as the Lewis acidity of the metal ions enhances the electron-accepting propensity of the pyridine acceptor units by lowering the energy of its LUMO.⁷ The polarity sensitiveness of this band indicates a charge-transfer character. The lowest-energy absorption is also likely to be dominated by the bipyridine framework instead of interligand transition between the ancillary and cyclometalated ligands due to poorer orbital overlap between these ligands, which causes low oscillator strength. Though in the related iridium complexes,^{11a} a weak absorption due to the transition to the ³MLCT state is often observed in the visible region, we have not observed such absorption band in our compounds, probably because it can be masked by the highly intense transitions in the visible region. The higher-energy absorption bands are due to various $\pi \to \pi^*$ transitions within the ligand framework(s).

Absorption maxima of the complexes with cyclic pyrrolidine donors is bathochromically shifted by almost 25–35 nm as compared to their acyclic dibutylamino analogues irrespective of the solvent, that is, Ir(MS 4)/Ir(MS 5) and Ir(MS 7)/Ir(MS 8). The probable reason behind this observation can be explained on the basis of the energy-minimized structures of the concerned complex cations. The cyclic amino groups are found to be more conjugated with the π -framework as compared to the open-chain dialkylamines, thereby reducing the energy of the charge-transfer transition. Similarly, the absorption maxima of Ir(MS 4), Ir(MS 6), and Ir(MS 7) maintain a similar trend as noticed in case of the free ligands.¹³ However, the extent of spectral shifts in the complexes is found to be greater compared to that for the free ligands. The absorption maximum of $Ir(MS \ 6)$ is shifted to longer wavelength compared to $Ir(MS \ 4)$ and $Ir(MS \ 7)$ (see Table 2). This is again explained taking into account the quantum chemical calculation, which computes a more planar structure in case of $Ir(MS \ 6)$ compared to $Ir(MS \ 4)$ and $Ir(MS \ 7)$. The HOMO–LUMO energy gap for the three pertinent complexes vary in the order $Ir(MS \ 4) > Ir(MS \ 7) > Ir(MS \ 6)$, which justifies the shifts of the band maxima in the relevant absorption spectra (see Table 3).

Table 3. HOMO-LUMO Energy Gaps Obtained from Cyclic Voltammetry and Ultraviolet-Visible Data Recorded in Dichloromethane

compd	λ_{\max} (nm)	$E_{\rm oxt}$ V	HOMO/LUMO	$E_{\rm g}$ (expt), eV
Ir(MS 3)	503	1.34	-5.97/-3.92	2.05
Ir(MS 4)	465	1.32	-5.95/-3.77	2.18
Ir(MS 5)	500	1.34	-5.97/-3.91	2.06
Ir(MS 6)	515	1.33	-5.96/-3.92	2.04
Ir(MS 7)	500	1.32	-5.95/-3.89	2.06
Ir(MS 8)	524	1.34	-5.97/-3.90	2.02

Though iridium complexes are widely known as phosphorescent emitters, unfortunately, most of the title complexes are found to be dark up to the 800 nm wavelength window. Only weak phosphorescence could be observed for Ir(MS 3) and Ir(MS 5) in 2-methyl tetrahydrofuran (2-Me-THF) glass (Figure 2b). The phosphorescence state of such complexes is ³MLCT/³ILCT, which is populated from the corresponding singlet states through very effective spin-orbit coupling induced by the heavy iridium atom. The absence of phosphorescence could be either (a) due to inefficient spinorbit coupling or (b) due to competitive rate constants of the nonradiative decay modes with phosphorescence during the long lifetime of the triplet state. However, we exclude that the spin-orbit coupling is inefficient in our complexes. In that case, one would observe fluorescence emission, as the ancillary 2,2'bipyridine ligands (MS 3-8), used in the present study, are highly fluorescent in organic solvents at room temperature.¹³ The absence of room-temperature phosphorescence thus could be rationalized if the radiationless decay modes have

Table 4. Calculate	d Mulliken S	Spin-Density	Distribution	for th	e Title	Iridium	Complexes
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parameters	Ir(MS 3)	Ir(MS 4)	Ir(MS 5)	Ir(MS 6)	Ir(MS 7)	Ir(MS 8)
Ir	0.015	0.006	0.009	0.013	0.008	0.008
Вру	2.19	1.93	1.99	1.99	1.99	1.99
ppy1	~0	~0	~ 0	~0	~0	~0
ppy2	~0	~0	~0	~0	~0	~0

competitive rates. Because of the several orders of flexibility of the structures, the nonradiative intersystem crossing to the ground state could be facilitated by various bond rotations, vibrations, $E \leftrightarrow Z$ isomerization of the styryl groups, etc. during the elongated triplet lifetime.⁷ Interestingly, none of the free ligands are phosphorescent even in frozen matrix, though they do exhibit intense fluorescence under the same condition indicating very poor intersystem crossing efficiency in the free ligands. The emission maximum of Ir(MS 5) is found to be red-shifted (Figure 2b) compared to that of Ir(MS 3), probably due to the greater conjugation length in the OPV ligand MS 5 compared to that in MS 3 ligand.

To further probe the nonemissive nature of the present compounds, we simulated their T_1 state in open-shell selfconsistent field (SCF) approach on the ground-state energyminimized structures using the same functional/basis set combination as described in the experimental section. The Mulliken spin-density analysis^{14b} was then performed on the T_1 optimized structures to determine the spin-density localization^{14c,d} (Table 4). Thus, from the unpaired electron spin density, it is quite evident that the spin density is localized only on the bipyridine ligands and to some extent on the iridium center; that is, the metal contribution in these complexes is found to be very less, the highest being in **Ir**(**MS 3**).

The emission intensity for the compounds Ir(MS 3) and Ir(MS 5) was found to be very weak, which is quite common in red-emitting materials due to the energy gap law.¹⁶ Another reason for this lower emission intensity might be their apparently lower metal contribution in the excited states as shown by Mulliken spin density studies.^{14c,d} As evident from computational studies, the emission in the iridium complexes [Ir(MS 3) and Ir(MS 5)] might be assigned to mostly the intraligand charge transfer (³ILCT) in the bipyridine ligands and to some extent the metal-to-ligand charge transfer (³MLCT).

IV. Cyclic Voltammetry. The redox properties of the title complexes were measured versus ferrocene/ferrocenium (Fc/ Fc^+) couple in deoxygenated DCM solvent using the three electrode assembly consisting of the Pt electrode as the working electrode, Ag/AgCl as the reference electrode, and a Pt gauge as the auxiliary (counter) electrode with tetra(n-butylammonium) perchlorate (TBAP) as the supporting electrolyte. The HOMOs in these complexes are localized mainly on the donorsubstituted phenyl rings and the vinylic C=C bonds of the 2,2'-bipyridine and also partly on the d-orbitals of iridium. However, the LUMOs are π^* orbitals of the bipyridine ligand and the phenylpyridine cores. Thus, the well-resolved reversible oxidation peaks at ca. 1.3 V versus Fc/Fc⁺ (see Table 3) might be attributed to oxidation of the iridium(III) metal center to iridium(IV) with contribution from the ligands.^{16d} However, no significant reduction was observed under our experimental conditions. From the oxidation potentials and the absorption edge in UV-vis spectra, the HOMO and LUMO energy levels of the title iridium complexes were calculated (Table 3). Since the cyclic voltammograms look almost similar for all the

complexes, we have shown here the cyclic voltammograms (Figure 3) of only two complexes, that is, Ir (MS 4) and Ir(MS 5), one containing the acyclic bipyridine analogue, and the other containing the cyclic one as representative ones.



Figure 3. Cyclic voltammograms of the iridium complexes recorded in DCM at a scan rate of 100 mV s⁻¹ using *n*-Bu₄NClO₄ as a supporting electrolyte.

V. Two-Photon Absorption Spectroscopy. The thirdorder nonlinear optical (NLO) response of a variety of materials has been studied over the past decade, and a full portraval of this response can be obtained from the Z-scan or two-photon excited fluorescence techniques.^{17,18} Since the investigated complexes are nonemissive at room temperature, we used the Z-scan method (open and closed aperture with ~ 2 ps, 1 kHz pulses as well as ~70 fs, 1 kHz pulses) for recording the two-photon absorption properties of the synthesized complexes in DCM. The pulse energies during the closeaperture Z-scan were maintained low to circumvent contributions from any higher-order nonlinearities. The open-aperture Z-scan data provided the information that the relevant molecules exhibit moderately strong two-photon absorption (2PA) with the nonlinear absorption cross sections in the range of 300-1000 GM in the picosecond case and 45-186 GM in the femtosecond case. The 2PA cross-section, σ_2 (in units of cm⁴ s per photon or GM) were calculated using the formula:

$$h\nu\beta = \sigma_2 N_0 = h\nu\sigma_2 N_A d_0 \times 10^{-5}$$

where d_0 (in units of mol L⁻¹) denotes the concentration of the solution, β represents the TPA coefficient, $h\nu$ is the energy of the incident photon, and N_A is Avogadro's constant.

The sign and magnitude of the real part of third-order nonlinearity can, however, be obtained from the closed aperture data. The relevant open aperture plots obtained using ~2 ps pulses are displayed in Figure 4a-f (insets depict the closed aperture data), and the experimentally observed 2PA cross sections (σ_2) of the title complexes are tabulated in Table 5. In all the cases, except Ir(MS 7), a good fit was obtained between



Figure 4. Open aperture Z-scan data (recorded at peak intensity $I_{00} \approx 100 \text{ GW/cm}^2$) of the iridium complexes in DCM (a) **Ir(MS 3**), (b) **Ir(MS 4**), (c) **Ir(MS 5**), (d) **Ir(MS 6**), (e) **Ir(MS 7**), and (f) **Ir(MS 8**), obtained with ~2 ps pulses at 800 nm. (O) Experimental data for the solutions. Solid lines correspond to theoretical fits. (insets) The curves corresponding to closed aperture Z-scan data (recorded at peak intensity $I_{00} \approx 28 \text{ GW/cm}^2$). All compounds exhibit positive nonlinearity except the compound **Ir(MS 8**).

Table 5. Summary of Nonlinear Optical Coefficients of the Synthesized Iridium Complexes Obtained with \sim 2 ps Pulses at 800 nm

compound	$n_2 (cm^2/W) (1 \times 10^{-15})$	β (cm/W) (1 × 10 ⁻¹¹)	σ_2^a (GM)	${ m Re}\chi^{(3)}({ m e.s.u})\ (1 imes 10^{-14})$	$Im\chi^{(3)}(e.s.u) (1 \times 10^{-16})$	$\chi^{(3)}(e.s.u)$ (1 × 10 ⁻¹⁴)	$ \begin{array}{c} \gamma^{b} \text{ (e.s.u)} \\ (1 \times 10^{-31}) \end{array} $			
Ir(MS 3)	1.4	0.83	342	1.79	6.79	1.79	0.46			
Ir(MS 4)	6.2	2.4	990	7.94	19.00	7.95	2.03			
Ir(MS 5)	2.0	1.2	495	2.56	9.82	2.56	0.65			
Ir(MS 6)	1.6	1.1	454	2.05	9.00	2.05	0.52			
Ir(MS 7)	7.0	$1.4 \times 10^{-10} \text{ cm}^3/\text{W}^2$ (3PA)		8.97						
Ir(MS 8)	-5.0	1.2	511	-6.41	9.82	6.41	1.64			
${}^{a}\sigma_{2}$ is the two	${}^{a}\sigma_{2}$ is the two-photon absorption cross-section. ${}^{b}\gamma$ is the second hyperpolarizability.									

the predicted and experimentally obtained data, and the 2PA coefficient (β) for the samples was estimated to be ~1 × 10⁻¹¹ cm/W, while the same due to the solvent was found to be as low as 0.2 × 10⁻¹¹ cm/W at a peak intensity of ~100 GW/cm². Surprisingly, only the compound Ir(MS 7) shows three-photon absorption (3PA) as the dominant nonlinear absorption process, while the two-photon absorption (corresponding to the second lowest-energy absorption band near 400 nm, Figure 2a) is the chief nonlinear absorption phenomenon in all the other cases.

The three-photon absorption coefficient (see Table 5) for Ir(MS 7) was estimated to be ~1.4 × 10⁻²¹ cm³/W² (the solvent contribution again being negligible in this case). The three-photon absorption is expected to be similar to 2PA induced excited-state absorption (2 + 1 photons) as was reported earlier in dinaphthoporphycenes.^{18a,b} The closed aperture scans for all the complexes were recorded with a peak intensity of 28 GW/cm². The valley followed by the peak in the normalized transmittance data of all the complexes [except Ir(MS 8)] is clearly an indicative feature showing the presence of a positive type of nonlinearity. In all the cases, the

best fit between the theoretical¹⁹ and experimental data was obtained, and the value of the nonlinear refractive index n_2 was found to be in the order of $\sim 1 \times 10^{-15}$ cm²/W (n_2 for solvent was $\sim 1 \times 10^{-16}$ cm²/W). The closed aperture scans for all the complexes are shown in the insets of Figures 4a–f, respectively.

Figure 5a-f demonstrates both the open aperture and closed aperture Z-scan data obtained with \sim 70 fs pules at 680 nm for all the samples. The Z-scan experiments were performed with 680 nm pulses, since the energy output was relatively stable compared to other wavelengths in the visible spectral region (Figure 2a). It is evident from the data presented that all the samples demonstrate 2PA behavior, which is consistent with the observations of picosecond data. All the insets (a-f) depict the closed aperture Z-scan data. Except for Ir(MS 8), all the other compounds exhibit positive nonlinearity, and this observation is again consistent with that obtained using ~ 2 ps pulses (Figure 4). The NLO coefficients, retrieved from the fits to experimental data, are summarized in Table 6. The magnitudes of nonlinear absorption coefficients in the femtoseconds case (680 nm) are 2-4 times lower than those obtained with ~ 2 ps data at 800 nm. The n_2 values obtained are



Figure 5. Open aperture Z-scan data (recorded at peak intensity $I_{00} \approx 1 \text{ TW/cm}^2$) of the iridium complexes in DCM (a) Ir(MS 3), (b) Ir(MS 4), (c) Ir(MS 5), (d) Ir(MS 6), (e) Ir(MS 7), and (f) Ir(MS 8) obtained with ~70 fs pulses at 680 nm. (O) Experimental data for the solutions. Solid lines correspond to theoretical fits. (insets) The curves corresponding to closed aperture Z-scan data (recorded at peak intensity $I_{00} \approx 200 \text{ GW/cm}^2$). Except for compound Ir(MS 8), all other title compounds demonstrate positive nonlinearity.

Table 6. Summary of Nonlinear Coefficients of the Synthesized Iridium Complexes Obtained with ~ 10 fs I	s Pulses at 680 nm
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compound	$n_2 (cm^2/W) (1 \times 10^{-16})$	β (cm/W) (1 × 10 ⁻¹²)	σ_2^a (GM)	$ \begin{array}{c} \text{Re}\chi^{(3)}(\text{e.s.u}) \\ (1 \times 10^{-15}) \end{array} $	$Im\chi^{(3)}(e.s.u) (1 \times 10^{-16})$	$\chi^{(3)}(e.s.u)$ (1 × 10 ⁻¹⁵)	$\gamma^{b} \text{ (e.s.u)} \\ (1 \times 10^{-32})$
Ir(MS 3)	4.8	3.9	161	6.15	2.71	6.15	3.14
Ir(MS 4)	2.1	1.1	45	2.69	7.65	2.69	1.37
Ir(MS 5)	2.9	3.7	153	3.71	2.57	3.72	1.90
Ir(MS 6)	2.7	3.0	124	3.46	2.08	3.46	1.77
Ir(MS 7)	3.6	4.5	186	4.61	3.13	4.62	2.36
Ir(MS 8)	-1.5	3.5	145	-1.92	2.43	1.93	0.989
$a\sigma_{2}$ is the two	o-photon absorption	n cross-section. b_{γ} is	the second	hyperpolarizability.			

in the range of $(-1.5 \text{ to } 4.8) \times 10^{-16} \text{ cm}^2/\text{W}$. These values represent the pure electronic nonlinearity, since no other

processes (excited state absorption or thermal) are possible with such short pulse duration (\sim 70 fs) and repetition rate (1

kHz). The nonlinear absorption cross sections, obtained, are in the range of 45–186 GM. The solvent contribution to the open and closed aperture data (and overall nonlinearity) in the femtosecond case was negligible. To achieve concentrationindependent NLO coefficients, we also estimated the second hyperpolarizability¹⁹ of these molecules from the $\chi^{(3)}$ values, which in turn were obtained from the real (related to n_2) and imaginary parts (related to β). The γ -values evaluated for these molecules are $\sim 1 \times 10^{-31}$ e.s.u. in the picosecond case and ~ 1 $\times 10^{-32}$ e.s.u. in the femtosecond case. We estimated an error of $\pm 15\%$ in the measured NLO coefficients in both picosecond and femtosecond cases arising mainly from (a) estimation of spot size at focus (beam waist), (b) input laser energy fluctuations, (c) fitting errors, etc. The errors could be slightly higher in the femtosecond case, since the OPA output at 680 nm was relatively less stable compared to the picosecond output at 800 nm.

It has already been suggested in literature that similar design principles can be applied to inorganic materials akin to organic chromophores, for obtaining large TPA σ_2 values. These values can further be increased with increase in conjugation and/or by increasing the donor/acceptor strength.¹² It has also been suggested that, when the ancillary ligands bear weak electron donors, for example, alkyl oxy or alkyl thio groups, then upon metal coordination, an increase in the TPA cross-section was observed, while with ancillary ligands bearing strong electron donors such as dialkyl amino group, the TPA cross-section has been observed to decrease.²⁰

VI. Thermal Stability. The thermal durability of the benchtop synthesized iridium complexes Ir(MS 3)-Ir(MS 8) was examined by heating the samples in an analyzer under a flow of nitrogen. The relevant complexes show quite high stability in the range of 320–360 °C, except for the complexes Ir(MS 3)and Ir(MS 7) [the 10% weight loss temperature (Td₁₀) is ca. 200 °C; see Figure S9, Supporting Information].

SUMMARY AND CONCLUSION

In summary, we have demonstrated a new series of cyclometalated Ir(III) complexes of the type $[Ir(C^N)_2(N^N)]$ -(PF₆), which includes extended Ar-vinyl- π systems on the ancillary bipyridine core. The linear and NLO properties of the synthesized complexes were investigated, and their photophysical properties are found to be governed by ILCT, LL'CT, and MLCT transitions as depicted by the DFT and TD-DFT calculations. A systematic variation in the nature, position, and number of donor groups modulates their absorption behavior. Unfortunately most of the synthesized complexes are found to be dark up to the 800 nm wavelength window even in frozen matrix possibly due to competitive non-radiative decay modes. Only weak emission is observed from compounds Ir(MS 3)and Ir(MS 5) in the NIR region. Interestingly, the free ligands are also found to be non-phosphorescent, which we presume to be due to inefficient intersystem crossing. Furthermore, Mulliken spin-density analysis on the unrestricted triplet geometry predicts a low metal contribution, which might be a plausible reason for non-emissivity of the title complexes. Finally, the two-photon absorption studies on the synthesized complexes reveal that values of the absorption cross-section are quite notable and lie in the range of 300-1000 GM in the picosecond case and 45-186 GM in the femtosecond case. Such classes of cyclometalated iridium complexes can open new and exciting opportunities to have a better control over the

photophysical aspects intended to be used for a wide variety of applications.

EXPERIMENTAL SECTION

Materials and Methods. All the reactions were performed under ultrahigh pure nitrogen atmosphere unless mentioned elsewhere. All the deuterated NMR solvents were purchased from Acros Organics, and the other commercially procured chemicals were used as received. Column chromatography was performed with silica gel (100-200 mesh; SRL, India) unless mentioned. All the solvents used for the chromatographic purification were distilled prior to use. The NMR spectra were recorded by Bruker AV-400 400 MHz spectrometer using tetramethylsilane as internal standard in case of CDCl₃ solvent. Signal multiplicities are reported as follows: s = singlet, d = doublet, t =triplet, m = multiplet, br = broad. Elemental analysis was performed by FLASH EA series 1112 CHNS analyzer. HRMS spectra were recorded on Bruker Maxis spectrophotometer. Cary 100 Bio UV-visible spectrophotometer was used to record the electronic absorption spectra, while the emission (phosphorescence) spectra were recorded on a Fluorolog-3 (JobinYvon) spectrofluorimeter. A CH-Instruments Model 620A electrochemical analyzer was used for electrochemical experiments.

The ground-state geometry of the title complex cations were optimized by applying the CAM-B3LYP exchange correlation functional^{15a} together with LANL2DZ basis set^{15b} for iridium atom and 6-31g(d) basis set^{15c} for the rest of the atoms in DCM solvent reaction field. Effective core potential correction for the iridium heavy atom was included, and an identical computational setup was used throughout the simulation studies. In all the cases the local minima were asserted by absence of any imaginary frequency in the relevant frequency calculations. The triplet-state (T₁) geometry optimizations were performed on the ground-state model through unrestricted SCF and same functional/basis set combination as applied for the S₀ optimizations.

The NLO experiments¹⁸ were performed in DCM using 1 mm optical path length cuvette. For picosecond Z-scan measurements, a Ti-sapphire amplifier (Legend, Coherent) source was used that was operating at a repetition rate of 1 kHz with pulse duration of \sim 2 ps at 800 nm. The amplifier was seeded with \sim 15 fs pulses from the oscillator (Micra, Coherent). The input beam was spatially filtered to obtain a pure Gaussian profile in the far field. Z-scan studies were performed by focusing the 3 mm diameter input beam using a 200 mm focal length convex lens. The sample was placed on a high-resolution translation stage, and the detector (Si photodiode, SM1PD2A, Thorlabs) output was connected to a lock-in amplifier. Both the stage and lock-in were controlled by a computer program.

For femtosecond Z-scan experiments, the pulses were obtained from an optical parametric amplifier (OPA, TOPAS, Light Conversion) pumped by a Ti:sapphire amplifier (LIBRA, Coherent) delivering \sim 50 fs pulses at 800 nm with a maximum energy of \sim 4 mJ. Typically 2 mJ were used for pumping the OPA. The output pulses from the OPA were tunable from 260 to 2600 nm. The pulses (~2.5 mm input diameter) were focused using 75 mm lens providing an estimated spot size $(2\omega_0)$ of ~30 μ m at focus. The pulse duration at the sample after passing through various optical elements was estimated to be \sim 70 fs. The sample was translated manually, and the output transmittance was recorded using a sensitive power meter (Coherent). All the NLO studies were performed with solutions having the concentration of 0.5-1 mM providing 92-96% linear transmittance. Closed aperture scans were performed at peak intensities, where the contribution from the higher-order nonlinear effects was negligible (the value of $\Delta \phi$ estimated in all the cases was less than π).

Synthesis and Characterization Data. A mixture of the bridged dimer $[Ir(C^N)_2(\mu-Cl)]_2$ (0.075 mmol) and the corresponding bipyridine derivatives (**MS 3–MS 8**; 0.15 mmol), taken in 30 mL of DCM–MeOH (2:1) degassed solvent system, was heated under reflux in an inert atmosphere of N₂ in the dark for 4 h. The red-colored solution was then brought to room temperature, and a fivefold excess

of saturated KPF₆ in degassed MeOH was added to it with an additional stirring for 2 h. The solvent was then evaporated to dryness. The crude product was extracted with DCM, and the organic layer was washed several times with water. Evaporation of the solvent gave a dark red-colored compound, which was finally purified by column chromatography over silica using acetone/CHCl₃, 5:95 v/v, as the eluent.

Ir(MS 3). Red microcrystalline solid. Yield: 73%. ¹H NMR (400 MHz, CDCl₃): δ 8.66 (s, 2H), 7.91 (d, *J* = 8 Hz, 2H), 7.79–7.61 (m, 10H), 7.50 (d, *J* = 8 Hz, 2H), 7.35 (s, 2H), 7.28 (d, *J* = 8 Hz, 2H), 7.05–6.99 (m, 4H), 6.93–6.91 (m, 2H), 6.35 (d, *J* = 4 Hz, 2H), 6.16 (s, 2H), 3.95 (s, 6H), 3.82 (s, 6H), 3.46 (unresolved, 8H), 1.93 (unresolved, 8H). IR (KBr, cm⁻¹): 841 (P–F). HRMS: (*m*/*z*) calcd. 1119.415(M–PF₆)⁺. Found: 1119.426 (Figure S16, Supporting Information). Anal. Calcd for C₆₀H₅₈F₆IrN₆O₄P: C, 57.00; H, 4.62; N, 6.65. Found: C, 57.12; H, 4.56; N, 6.75%.

Ir(MS 4). Red microcrystalline solid. Yield: 71%. ¹H NMR (400 MHz, CDCl₃): *δ* 8.77 (s, 2H), 7.93 (d, J = 8 Hz, 2H), 7.79–7.74 (m, 4H), 7.69–7.65 (m, 4H), 7.61 (d, J = 8 Hz, 4H), 7.52–7.30 (m, 12H), 7.10–6.91 (m, 10H), 6.52 (s, 2H), 6.34 (d, J = 8 Hz, 2H), 3.88 (s, 6H), 3.86 (s, 6H), 3.17 (t, J = 8 Hz, 8H), 1.54–1.47 (m, 8H), 1.34–1.26 (m, 8H), 0.91 (t, J = 6 Hz, 12H). IR (KBr, cm⁻¹): 839 (P–F). HRMS: (*m*/*z*) calcd. 1439.665(M–PF₆)⁺. Found: 1439.660 (Figure S17, Supporting Information). Anal. Calcd for C₈₄H₉₀F₆IrN₆O₄P: C, 63.66; H, 5.72; N, 5.30. Found: C, 63.56; H, 5.64; N, 5.41%.

Ir(MS 5). Red microcrystalline solid. Yield: 77%. ¹H NMR (400 MHz, CDCl₃): δ 8.85 (s, 2H), 8.02 (s, 2H), 7.94 (d, *J* = 8 Hz, 2H), 7.79–7.34 (m, 22H), 7.25–6.89 (m, 10H), 6.34 (d, *J* = 8 Hz, 2H), 6.30 (s, 2H), 3.88 (s, 6H), 3.86 (s, 6H), 3.42 (unresolved, 8H), 2.36–2.33 (m, 8H). IR (KBr, cm⁻¹): 839 (P–F). HRMS: (*m*/*z*) calcd. 1323.508(M–PF₆)⁺. Found: 1323.507 (Figure S18, Supporting Information). Anal. Calcd for C₇₆H₇₀F₆IrN₆O₄P: C, 62.16; H, 4.80; N, 5.72. Found: C, 62.25; H, 4.87; N, 5.65%.

Ir(MS 6). Red microcrystalline solid. Yield: 80%. ¹H NMR (400 MHz, CDCl₃): δ 8.82 (s, 2H), 7.92−7.28 (m, 24H), 7.13−6.92 (m, 10H), 6.64 (d, *J* = 8 Hz, 4H), 6.35 (d, *J* = 8 Hz, 2H), 4.24 (m, 4H), 4.05 (t, *J* = 6 Hz, 4H), 3.30 (t, *J* = 7 Hz, 8H), 1.89−1.27 (m, 32H), 1.05−0.96 (m, 24H). IR (KBr, cm⁻¹): 839 (P−F). HRMS: (*m*/*z*) calcd. 1607.853 (M−PF₆)⁺. Found: 1607.831 (Figure S19, Supporting Information). Anal. Calcd for C₉₆H₁₁₄F₆IrN₆O₄P: C, 65.77; H, 6.55; N, 4.79. Found: C, 65.87; H, 6.51; N, 4.86%.

Ir(*MS* 7). Red microcrystalline solid. Yield: 75%. ¹H NMR (400 MHz, CDCl₃): δ 8.84 (s, 2H), 7.93 (d, *J* = 8 Hz, 2H), 7.87(d, *J* = 16 Hz, 2H), 7.79–7.75 (m, 4H), 7.71 (d, *J* = 8 Hz, 2H), 7.62–7.39 (m, 12H), 7.13 (d, *J* = 8 Hz, 4H), 7.07–7.01 (m, 4H), 6.96–6.92 (m, 2H), 6.52 (s, 2H), 6.35 (d, 8 Hz, 2H), 4.25 (t, *J* = 6 Hz, 4H), 4.05 (t, *J* = 6 Hz, 4H), 3.88 (s, 6H), 3.85 (s, 6H), 3.15 (t, *J* = 7 Hz, 8H), 1.90–1.26 (m, 32H), 1.05–0.98 (m, 12H), 0.91 (t, *J* = 8 Hz, 12H). IR (KBr, cm⁻¹): 839 (P–F). HRMS: (*m*/*z*) calcd.1727.895 (M–PF₆)⁺. Found: 1727.879 (Figure S20, Supporting Information). Anal. Calcd for C₁₀₀H₁₂₂F₆IrN₆O₈P: C, 64.12; H, 6.56; N, 4.49. Found: C, 64.25; H, 6.67; N, 4.41%.

Ir(MS 8). Red microcrystalline solid. Yield: 79%. ¹H NMR (400 MHz, CDCl₃): *δ* 8.81 (s, 2H), 7.92 (d, J = 8 Hz, 2H), 7.87 (d, J = 16 Hz, 2H), 7.78–7.69 (m, 6H), 7.61 (d, J = 8 Hz, 2H), 7.55–7.48 (m, 8H), 7.36 (d, J = 16 Hz, 2H), 7.13 (d, J = 8 Hz, 4H), 7.06–7.00 (m, 4H), 6.95–6.91 (m, 2H), 6.34 (d, J = 8 Hz, 2H), 6.31 (s, 2H), 4.25 (t, J = 6 Hz, 4H), 4.06 (t, J = 6 Hz, 4H), 3.86 (s, 6H),3.84 (s, 6H),3.4 (unresolved, 8H), 1.97–1.51 (m, 24H), 1.05–0.96 (m, 12H). IR (KBr, cm⁻¹): 839 (P–F). HRMS: (*m*/*z*) calcd. 1611.739 (M–PF₆)⁺. Found: 1611.719 (Figure S21, Supporting Information). Anal. Calcd for C₉₂H₁₀₂F₆IrN₆O₈P: C, 62.89; H, 5.85; N, 4.78. Found: C, 62.75; H, 5.81; N, 4.63%.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02999.

A chart for molecular structures for compounds MS3– MS8 ¹H and ¹³C NMR spectra, HRMS plots of all compounds, coordinates of all the optimized geometries, tables and figures related to the computational outputs. (PDF)

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Notes

The authors declare no competing financial interest.

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