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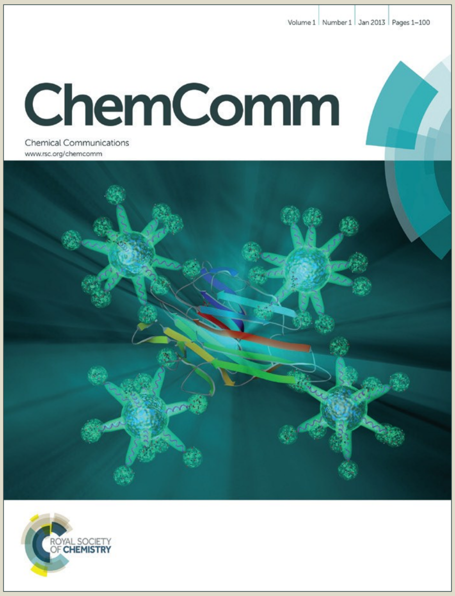

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COMMUNICATION

Two- & three-photon absorption and excitation phosphorescence of oligofluorene-substituted Ir(ppy)$_3$

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A series of triscyclometalated iridium complexes with oligofluorene-substituted ppy ligands manifest impressive two- and three-photon absorption properties. Particularly, a star-shaped complex bearing three carbazole-terminated trifluorenyl ppy demonstrates a large three-photon absorption cross section up to 81×10^{-78} cm^6·s^2·photon^{-2}. In combination with optimal phosphorescence quantum yields (0.5~0.8), such iridium complexes are effective two- and three-photon excited phosphorescence emitters.

Multiphoton absorption (MPA) and excitation (MPE) materials are of great theoretical and practical interests.[1-3] Boasting the appealing merits of low-energy photon excitation, nonlinear dependence on the excitation power, and photon frequency upconversion, MPA materials enable innovative applications in a range of scientific and technical fields including photochemistry,[4] drug delivery,[5] bio-imaging,[6] photodynamic therapy (PDT),[7] chemosensing,[8] frequency upconverted lasing,[9] optical light limiting,[10,11] data storage,[12,13] three-dimensional micro-fabrication,[14,15] etc. Among various MPA molecules, transition-metal complexes are uniquely useful for applications obligating triplet excited states. For example, the PDT technique relies on the *in vivo* generation of reactive oxygen species (e.g., singlet oxygen) through photo-sensitization. It is evidently desirable to realize this process with multiphoton excitable triplet sensitizers. In that case, less damaging but more tissue-penetrating near-infrared (NIR) light can be used for excitation. More importantly, higher targeting precision can also be achieved with the nonlinear optical effect-entailed spatial resolution. MPA materials with long excited-state lifetimes may as well make possible of additional new technologies such as tandem photon upconversion[16,17] solar cells operated with photon-energy upconversion mechanism, and so on.

To realize relevant applications, it is crucial to obtain optimal MPA materials with long triplet excited states. Among various metal complexes,[18-27] we deem triscyclometalated iridium complexes to be particularly suitable for developing relevant functions, as they exhibit attractively small nonradiative energy loss during triplet-state relaxation,[28-30] as well as very rapid and efficient intersystem crossing. Nonetheless, organoiridium molecules with detectable MPA properties were only reported intermittently.[20-24] Further improving the MPA cross sections (σ) are undoubtedly warranted.

Here, we report a series of triscyclometalated Ir(III) complexes comprising oligofluorene-substituted 2-phenylpyridine (ppy) ligands (Chart 1), which exhibit prominent two- and three-photon absorption (2PA & 3PA) properties. On the basis of our previous study, the triscyclometalated iridium core is quite powerful at enabling intersystem crossing in large π-conjugated organic scaffolds, while maintaining optimal phosphorescence efficiencies.[28] The oligofluorene groups are installed to extend the π-conjugation length of the ligands and thus promote the nonlinear optical attributes of the molecules. Combining the two aspects of properties, herein designed organoiridium complexes manifest pronounced 2PA and 3PA abilities, as well as MPE-enabled triplet states with potent phosphorescing properties.

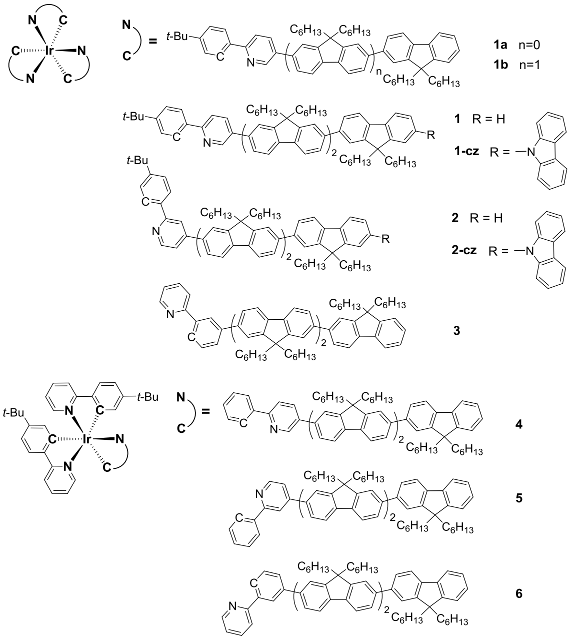

Chart 1. Studied MPA iridium complexes

To unveil the structure-property relationship, complexes containing different numbers of oligofluorene groups (**1-3** vs. **4-6**) and varied oligofluorene lengths (**1a** and **1b**) are prepared, and their properties are systematically compared. The results show that longer and greater numbers of the oligomer ligands are favorable for MPA capability. Moreover, the influence of altering the substitution position of oligofluorene on ppy is also important. We then install carbazole groups at the end of trifluorene moieties, which further improve the MPA cross sections by conferring D-π-A electronic effects. Among all synthesized complexes, **2-cz** exhibits the largest 2PA σ of 1180 GM (1 GM = 10^{-50}

$cm^4 \cdot s \cdot photon^{-1}$. More impressively, a 3PA σ of 81×10^{-78} $cm^6 \cdot s^2 \cdot photon^{-2}$ is determined for this molecule. To the best of our knowledge, such a value is the largest among so far reported iridium complexes.[20-24] Furthermore, with desirable emission quantum yields, relevant complexes display strong MPE phosphorescence upon excitation with far-red and NIR lasers.

Table S1. Photophysical data of studied iridium complexes

compd	1PA				2PA		3PA		
	λ_{abs}/nm[a] ($\varepsilon/10^5$ $mol^{-1} \cdot L \cdot cm^{-1}$)	λ_{em}/nm[b]	Φ_p[c]	$\tau/\mu s$[d]	λ_{max}/nm[f]	σ_{2PA}/GM[f]	σ_{3PA} (1064 nm)[g] /10^{-78} $cm^6 \cdot s^2 \cdot photon^{-2}$	λ_{max}/nm[h]	σ_{3PA}[i] /10^{-78} $cm^6 \cdot s^2 \cdot photon^{-2}$
1a	331 (1.3)	564	0.78	2.8	660	2.1×10^2	6.8	980	13
1b	352 (2.1)	571	0.74	3.9	670	4.5×10^2	17.5	980	23
1	363 (2.7)	572	0.74	4.5	670	6.9×10^2	38.0	1040	48
1-cz	368 (2.9)	573	0.69	4.2	680	1.1×10^3	53.2	1080	57
2	364 (2.8)	597	0.51	2.1	670	7.3×10^2	49.3	1040	60
2-cz	367 (2.9)	599	0.48	2.0	670	1.2×10^3	75.1	1080	81
3	372 (2.6)	523	0.47	320[e]	680	6.2×10^2	32.9	1060	33
4	363 (1.3)	568	0.72	4.0	660	1.4×10^2	7.6	1040	8.3
5	367 (1.3)	599	0.62	2.0	670	1.3×10^2	8.0	980	10
6	369 (1.1)	523	0.49	102[e]	680	1.2×10^2	6.2	1040	6.8

[a] Absorption maxima in THF with molar extinction coefficients in parentheses; [b] emission maxima in THF; [c] phosphorescence quantum yields in THF determined using $Ir(ppy)_3$ (Φ_p=0.97 in toluene) as the reference; [d] lifetimes (<10 μs) measured by time-correlated single-photon counting, excited with NanoLED of 370 nm; [e] long lifetimes determined from emission decays excited by a pulsed Xe lamp; [f] 2PA maxima and cross sections (1 GM = 10^{-50} $cm^4 \cdot s \cdot photon^{-1}$) measured with the comparative method based on the emission intensity, using Rhodamine B as the reference; [g] 3PA cross sections measured with the Z-scan method using 1064 nm ps laser; [h] 3PA maximum wavelengths; [i] 3PA maximum cross sections estimated using the relative method by comparing the emission intensity from excitation at varied wavelengths and using the σ_{3PA} data from Z-scan experiments as the standard values.

All studied complexes (Chart 1) are synthesized by cross coupling various bromine-substituted $Ir(ppy)_3$ derivatives with corresponding oligofluorenyl boronic acids or boronates under Pd-catalyzed conditions (Scheme S3). The preparation procedures of **1**, **4** and **6** were reported previously,[28] while the rest complexes are newly designed. The carbazole-terminated trifluorenyl boronates used for acquiring **1-cz** and **2-cz** are obtained via Buchwald amination of dibromotrifluorene, followed by Miyaura borylation. The *fac*-configurations of **2** and **2-cz** are determined on the basis of their synthetic precursor, a tribromo-substituted $Ir(ppy)_3$ derivative (**2-Br**), the stereochemistry of which is evident from its ^1H NMR spectrum. The chemical structures of all new complexes are confirmed by ^1H and ^{13}C NMR spectra along with mass spectroscopy. All oligofluorene-substituted complexes show good solubility in common organic solvents.

The linear photophysical properties of the complexes are first examined (Table 1), which show major absorption peaks around 330~400 nm in THF solution, attributable to oligofluorenyl ppy ligand-centered (LC) $^1\pi$-π* transitions (Fig. 1 and S1). The shoulder absorption bands appearing between 420 and 550 nm are assigned to MLCT processes.[28] As the length and number of oligofluorene groups increase, the extinction coefficients of the main LC absorption peaks rise accordingly (Fig. S1), but their influences over the CT bands are limited. Under deoxygenated conditions, all complexes show strong phosphorescence of green to orange color, with the quantum yields (Φ_p) ranging from 0.47 to 0.78 at room temperature. Such optimal phosphorescing abilities promise the molecules with desirable MPE phosphorescing and photon-frequency upconverting properties.

Having trifluorene groups attached to the 3-position of ppy units, complex **2** is a new structure with unknown photophysical properties. The absorption spectrum of **2** is nearly identical to that of its regio-isomer **1**, except that the MLCT band is noticeably red shifted (Fig. 1). Pronounced disparity is however displayed with emission behaviors. Compared to the phosphorescence spectrum of **1**, depicting evident vibronic structures, the emission band of **2** is red shifted and shows no vibronic feature. Moreover, the much shortened emission lifetime disclose accelerated decay rates of **2** relative to **1** (Table 1). All these property differences suggest that in contrast to the ^{3}MLCT-featured but ^{3}LC-disturbed T_1 of **1**,[28,29] the T_1 state of **2** is more completely dominated by ^{3}MLCT transition, with much less admixing of LC processes. This is a reasonable result considering that in complex **2** the trifluorene groups installed on pyridine units *para*- to iridium (compared to *meta*- in **1**) better promote the charge accepting ability of the ligand, and thus more effectively lower the energy level of ^{3}MLCT in **2** through electron delocalization. In contrast to **1** and **2**, complex **3** shows a T_1 state with dominant ^{3}LC characteristics, evidenced by its significantly prolonged phosphorescence lifetime. Similar to its structure analogue **6**,[28,29] such a behavior of **3** is related to the non-conjugated *meta*-phenylene linkage between trifluorene and pyridine unit, which facilitates the charge accepting ability of ppy ligands the least effectively. With such an exceptionally long triplet lifetime, complex **3** is an attractive candidate for (MPE) triplet sensitization applications.

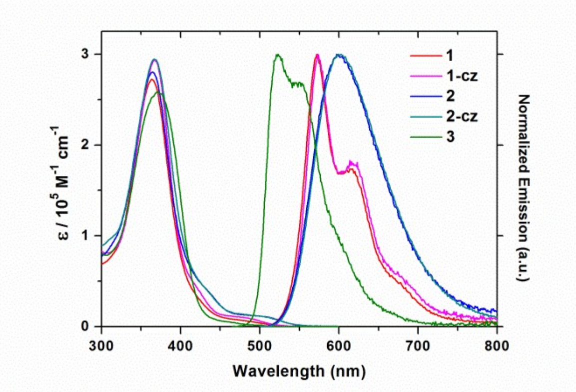

Fig. 1 UV-Vis absorption and photoluminescence spectra of selected iridium complexes in THF.

Similar regio-isomeric effects are also reflected in **4-6** with a single trifluorene group (Fig. S1). Upon attaching carbazole units to the end of trifluorene chains, little absorption and emission properties changes are detected with **1-cz** and **2-cz**, compared to **1** and **2** respectively (Table 1).

Subsequently, MPA properties of these molecules are investigated. Upon exciting with femtosecond (fs) laser at 780 nm, all examined complexes emit green to orange phosphorescence in deoxygenated THF solutions (Fig. S10). Since linear absorptions beyond 600 nm are absent for studied complexes, thus observed phosphorescence are plausibly attributed to originating from nonlinear absorption processes. The two-photon excitation (2PE) mechanism is further confirmed by quantifying the relationship between emission intensity and incident laser power. Namely, the phosphorescence of each complex manifests a linear dependence on the excitation power in the double-logarithmic coordinates, depicting a slope of ca. 2 (Fig. 2 and Table S2). Such results unambiguously support the 2PE nature of the emissions. Subsequently, by measuring the emission intensity at varied excitation wavelengths between 650 and 850 nm and compare to that from Rhodamine B with known 2PA cross section (σ_{2PA}),[32] the 2PA spectra of the complexes are obtained (Table 1). All studied complexes exhibit 2PA activities in a relatively broad range of wavelengths, with the 2PA maxima found between 670 and 680 nm (Fig. 3), well corresponding to double the energy of respective 1PA maxima or slightly higher.

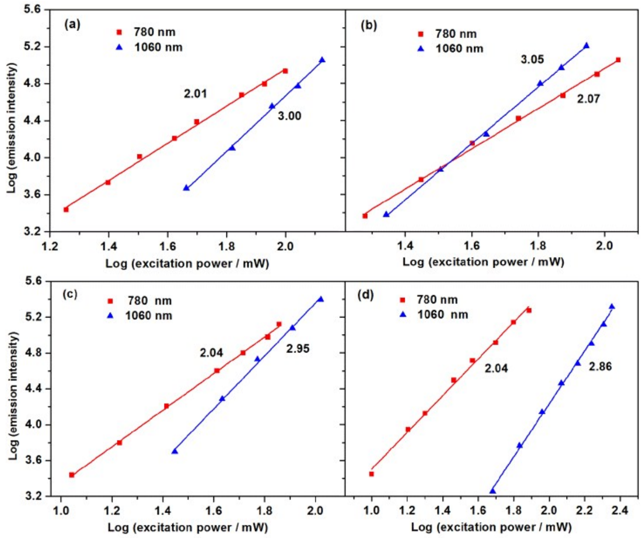

Fig. 2 Plots of emission intensity of **1** (a), **1-cz** (b), **2** (c) and **2-cz** (d) vs. excitation power (at 10^{-5} M in deoxygenated THF)

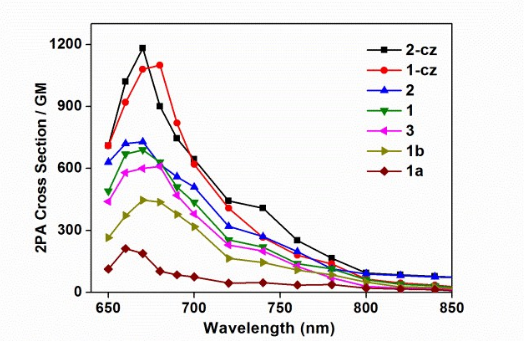

Fig. 3 Two-photon excitation spectra of studied complexes in deoxygenated THF solutions

In addition to 2PA, 3PA is an even more intriguing and attractive photophysical phenomenon, due to its unique features of higher-order nonlinearity, better spatial resolution, larger magnitude of photon frequency upconversion, etc. However, thus-far studied 3PA materials are mostly pure organic molecules.[33-37] Transition-metal complexes with 3PA attributes and three-photon excitation (3PE) triplet states are rarely reported.[38-40] Nonetheless, herein designed 3-dimensional organoiridium structures demonstrate prominent 3PA and 3PE phosphorescing abilities. Upon irradiation with 1060 nm laser, the complexes afford nearly identical emission spectra to those observed under one- and two-photon excitation conditions (Fig. S10). To verify the 3PA mechanism, open aperture Z-scan experiments are conducted using a picosecond (ps) laser at 1064 nm (Fig. 4 and S11-S13).[41] The obtained data are well consistent with the 3PA model,[42] and thereby the absolute 3PA cross sections (σ_{3PA}) are determined for each complex (Table 1).

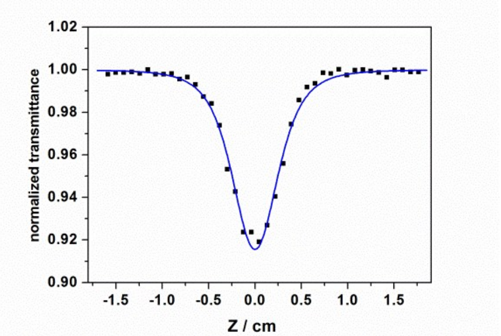

Fig. 4 Open aperture Z-scan data of **1** in THF solution at 1064 nm with the best fitting to 3PA model (pulse FHWM=25 ps; peak power density ≈10^{11} W/cm^2 at Z=0)

Next, taking advantage of the 3PE phosphorescing properties, we assess the overall 3PA spectra using the relative method, by measuring the emission intensity at varied excitation wavelengths.[36] First, the dependence of phosphorescence intensity on the laser power is studied to confirm the 3PE mechanism. When the emission intensity is plotted against the excitation power in the double-logarithmic coordinates, linear correlations with slopes of ca. 3 are observed for all studied complexes (Fig. 2 and S7-S9). Then phosphorescence intensities from excitation at varied wavelengths are recorded and calibrated relative to the intensity from excitation at 1064 nm under the same power density. Thereby, σ_{3PA} values at different wavelengths are estimated using the σ_{3PA} data at 1064 nm from the Z-scan experiments as the standard values (Fig. 5 and Table 1). The σ_{3PA} maxima are observed around 1000 to 1080 nm for different complexes, roughly matching three times the wavelengths of 1PA maxima of respective complexes.

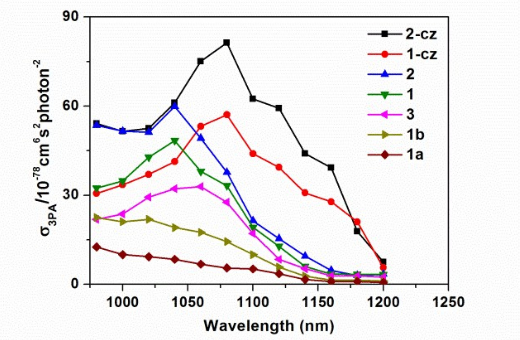

Fig. 5 Three-photon excitation spectra recorded in deoxygenated THF solutions

Finally, the structure-MPA relationship is analyzed by comparing the MPA behaviors of different complexes. As the chain length of conjugated ligand is extended from one to three fluorene units (**1a**, **1b** to **1**), the 2PA and 3PA cross section values increase nearly proportionally. When the number of trifluorene chain is changed from one to three (**4-6** vs. **1-3**), σ_{2PA} and σ_{3PA} data escalate by more than three times. All these results suggest that the 3-dimensional structures are particularly beneficial for MPA properties. Data are also compared between **1a** and **4**, which have the same number of fluorene units in their structures. Slightly greater σ_{2PA} and σ_{3PA} maximum values are determined for **1a**, which incorporates three fluorene units on separate ligands, while **4** has them inter-connected and tethered to one ppy. Furthermore, when a carbazole group is ligated to the end of trifluorene chains, **1-cz** and **2-cz** show further enhanced σ_{2PA} and σ_{3PA} values compared to **1** and **2**, which is an expected result in view of increased polarizablity conferred by D-π-A motifs.

In conclusion, we report a series of oligofluorene-substituted Ir(ppy)$_3$ derivatives exhibiting appealing 2PA and 3PA properties. Among all studied complexes, **2-cz** bearing three carbazole-terminated trifluorenyl ppy ligands exhibits the largest 2PA and 3PA cross sections. An impressive 3PA σ of 75×10^{-78} $cm^6\cdot s^2\cdot photon^{-2}$ at 1064 nm is determined by the Z-scan experiment, and a σ_{3PA} maximum of 81×10^{-78} $cm^6\cdot s^2\cdot photon^{-2}$ is estimated around 1080 nm. Such values are among the largest for so far reported transition metal complexes. Such optimal 3PA properties are believed to benefit from a number of structural features, including 3-dimensional scaffolds, large and multiple π-conjugated ligands, as well as the D-π-A electronic characteristics. Moreover, by virtue of highly efficient triplet-state emitting abilities, the designed complexes show strong two- and three-photon excited phosphorescence. These properties promise the molecules for desirable MPE phosphorescing materials and efficient photon-frequency upconverters. Additionally, MPA complexes with ultra-long triplet lifetimes are also developed in this work, which can be especially valuable MPE triplet sensitizers.

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Notes and references

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† Electronic Supplementary Information (ESI) available: syntheses, computational studies, two- and three-photon excited phosphorescence and Z-scan data. See DOI:10.1039/b000000x/

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