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PAPER

Two-photon spectroscopy of cyclometalated iridium complexes†

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The near-infrared two-photon absorption (TPA) spectra of a series of cyclometalated iridium complexes have been measured. These complexes exhibit moderately large TPA cross-sections of approximately 20 GM at the biological relevant wavelength of 800 nm. A new complex has been designed and synthesised, and found to have an increased cross-section of 44 GM at 800 nm. Full photophysical characterisation of this complex is presented.

Introduction

The design of materials for the application of two-photon absorption (TPA) to biological imaging,[1] photodynamic therapy[2] and optical power limiting at telecommunication wavelengths[3] continues to be a topic of active research. These applications demand materials with large two-photon absorption cross-sections (σ_2), especially in the near-infrared (NIR) region where biological tissue is most transparent and least susceptible to photodamage.[4]

A recent review by He *et al.*[5] summarised the TPA properties of a large number of chromophores, but was predominantly focused on organic compounds. This is not surprising because many organic species have been highly engineered to induce large two-photon cross-sections. However, lanthanide and transition metal complexes often exhibit other favourable properties, in addition to the potential for large cross-sections, that make them attractive TPA materials, for example, long phosphorescence lifetimes (τ_P), large Stokes' shifts and high quantum yields.

Previous studies of metal complexes exhibiting enhanced two-photon absorption include those of Pt(II)[6] and Ru(II)[7] acetylides, Ru(II) with modified 2,2′-bipyridyl (bipy) ligands,[8] lanthanide antennae systems in particular those of Eu(III)[9,10] and Tb(III),[11] as well as Zn(II) porphyrins.[12] In another example, a bipyridine-based ligand with a large TPA cross section was complexed to iridium to promote intersystem crossing (ISC) to the triplet excited state and resulted in a system which exhibits a mixed metal to ligand charge-transfer (MLCT) and ligand centred (LC) π–π* transition.[13] In this system a dual mechanism reverse saturable absorption and TPA process was observed when irradiated with 5 ns, 1064 nm pulses, although no value of σ_2 was reported. More recently there has been a report of TPA observed in iridium(III) terpyridine systems.[14] In these systems TPA cross-sections of up to 67 GM were reported for a styryl extended system which undergoes an intraligand charge transfer (ILCT) transition in the case of a methoxy substituted example or ligand-centred (LC) transition for the parent compound. There have also been two reports[15] of two-photon induced luminescence of cyclometalated Ir(III) species, but importantly these did not investigate the potential for excitation in the NIR region, instead exciting the sample at 438 nm. In these earlier studies the TPA induced luminescence can be attributed to ligand based emission rather than lower energy MLCT transitions, and was short-lived, with a lifetime of 3–4 ns as part of a complicated multi-exponential decay when doped at low concentration in a poly(methylmethacrylate) (PMMA) film. This is a crucial distinction since MLCT transitions may be expected to enhance σ_2 as charge transfer is usually regarded as a requisite for strongly two-photon absorbing chromophores.[16]

Over the past decade cyclometalated iridium complexes have been extensively studied for their tunable phosphorescence, high photoluminescence quantum yields (PLQY)[17] for use in organic light emitting devices (OLEDs).[18] To date, there have been no reports of NIR-TPA of neutral iridium complexes. These materials would possess several favourable properties for time-resolved two-photon imaging: namely their high quantum yields and relatively long-lived excited states (typically 1–5 μs)[17] compared to the autofluorescence encountered in biological systems. Additionally, they have a large quantum yield for the generation of cytotoxic singlet oxygen,[19] which if generated by TPA, could be used for high resolution photodynamic therapy with good tissue penetration.

In this paper we report the TPA spectra measured for a series of neutral cyclometalated Ir(III) compounds. The selected compounds are summarised in Fig. 1. These were chosen to include examples of various structural types and include the tris-cyclometalated homoleptic complex $Ir(ppy)_3$ (ppyH = 2-phenylpyridine) and the related $Ir(ppm)_3$ (ppmH = 2-phenylpyrimidine), allowing the influence of the heterocycle to be probed. A heteroleptic complex containing two different

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† Electronic supplementary information (ESI) available: Full experimental and CIF file of $Ir(4\text{-pe-2-ppy})_2(acac)$. CCDC reference numbers 831044. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11164g

‡ It is with great sadness that we report the death of Dr Andrés Goeta on 29th July 2011.

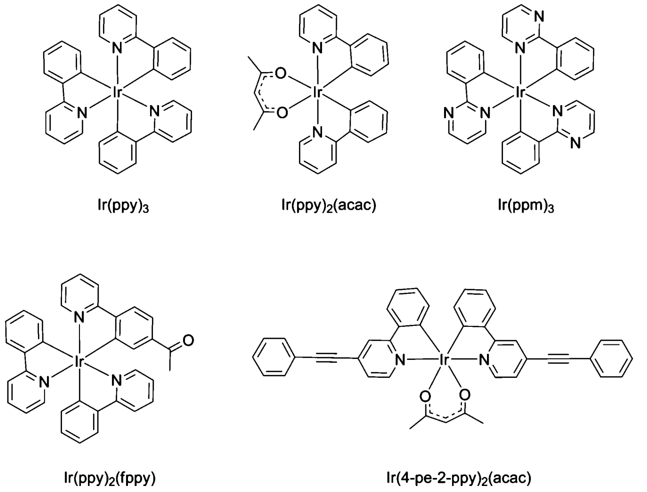


Fig. 1 Iridium cyclometalated compounds studied by two-photon absorption spectroscopy, including the newly designed Ir(4-pe-2-ppy)$_2$(acac).

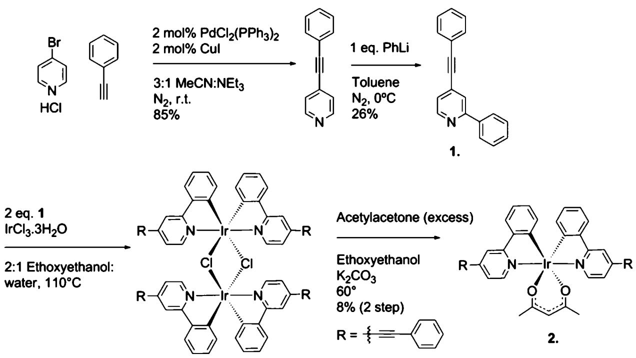
cyclometalated ligands Ir(ppy)$_2$(fppy) (where fppyH is 4-(2-pyridyl)-benzaldehye) was selected along with Ir(ppy)$_2$(acac), which includes the widely used ancillary ligand acacH (acetylacetone). The σ_2 values were measured using the two-photon luminescence method using the focussed output of a mode-locked Ti:sapphire laser ($\tau = 150$ fs fwhm). A compound with an increased cross-section was then designed based on the principles governing the magnitude of σ_2 in organic systems, that is an extended π-system with the capacity to act as a multipolar system. The synthesis, structure, photophysics and a computational study of this new complex, Ir(4-pe-2-ppy)$_2$(acac) (4-pe-2-ppyH is 4-phenylethynyl-2-phenylpyridine), are first presented, followed by the results of the TPA experiments.

Results and Discussion

Synthesis

Organic materials have been shown to have large TPA cross-sections when they have dipolar,[20] quadrupolar[21] or octapolar[22] ground state charge distributions and undergo a large charge redistribution in the excited state. Quadrupolar A-π-D-π-A (A, π and D are acceptor, pi-conjugated bridge and donor, respectively) for example have been especially well studied. In the MLCT transition of iridium ppy systems, the iridium can be considered a donor to the accepting pyridyl unit, whose π* orbitals have been shown by density functional theory (DFT) calculations to be the major contributor to the LUMO.[23] It therefore seemed reasonable to suggest that if the conjugation of the pyridyl fragment was increased, greater charge separation of the MLCT state could occur, resulting in larger TPA cross-sections. π-Conjugated substituents at the 4 position of the pyridine *trans* to the iridium in the complex, were considered for this purpose. Iridium complexes of simple derivatives of 2-phenyl-4-styrylpyridine have been reported,[24] and, although it has been shown that olefinic π-bridges give larger TPA cross sections than their acetylinic equivalents,[25] it was the acetylenes that were chosen for this study. This is because incorporation of olefins introduces the possibility of *cis-trans* photo-induced isomerism, which could complicate the interpretation of the photophysical measurements. Based on this, the potential ligand 2-phenyl-4-(phenylethynyl) pyridine, 4-pe-2-ppyH, was identified as a synthetic target. The complex Ir(4-pe-2-ppy)$_2$(acac) would be expected to have *trans* substituted pyridines giving the simplest A-π-D-π-A linear structure for these compounds.

The novel ligand 4-pe-2-ppyH was synthesised in a two step procedure as outlined in Scheme 1. Commercially available 4-bromopyridine hydrochloride was cross-coupled with phenylacetylene using standard Sonogashira methodology. The resultant pyridine was reacted with phenyllithium under anaerobic conditions to afford the ligand in moderate yield (26%). Complexation of the ligand was achieved using standard protocols; first formation of a di-μ-chloro bridged dimer by reaction with $IrCl_3 \cdot 3H_2O$ in aqueous 2-ethoxyethanol[26] and second, reacting the dimer material with acetylacetone in basic acetone/ethanol mixed solvent followed by purification by column chromatography.[27]



Scheme 1 Synthetic route to Ir(4-pe-2-ppy)$_2$(acac).

When the styryl analogues were synthesised, the authors reported that the double bonds were reduced under the experimental conditions if the reaction was carried out at high temperatures, catalysed by the intermediate dimer.[28] Under the conditions employed here for the synthesis of Ir(4-pe-2-ppy)$_2$(acac) we found no evidence for reduction of the acetylene bond. This was confirmed by the presence of characteristic bands associated with the acetylene in the Raman spectra at 2217 and 2234 cm^{-1} and the absence of styryl or alkyl resonances in the ^{1}H NMR spectrum.

X-ray crystallography

Crystallisation of Ir(4-pe-2-ppy)$_2$(acac) by slow diffusion between $CDCl_3$ and cyclohexane resulted in the formation of orange needles, allowing the molecular structure to be fully elucidated by single-crystal X-ray diffraction (Fig. 2).

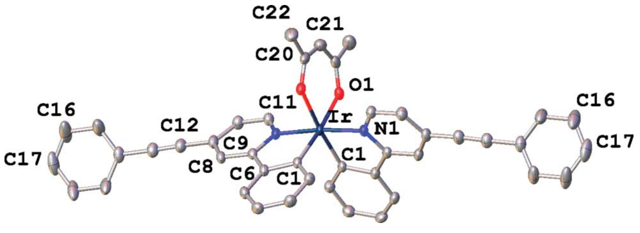


Fig. 2 The molecular structure of Ir(4-pe-2-ppy)$_2$(acac). Element (colour): iridium (green), carbon (grey), nitrogen (blue) and oxygen (red). Hydrogen atoms are omitted for clarity. Thermal ellipsoids drawn at 50% probability. Crystal data in footnote.[29] See ESI for full CIF.†

The two symmetry related chelating 4-pe-2-ppy ligands have *trans* Ir–N bonds as a consequence of the geometry of the intermediate dichloride-bridged dimer that does not rearrange under the conditions of the reaction with acetylacetone. This results in an extended structure centred on the iridium atom with an end to end length of 2.50 nm. The complex deviates from linearity with a C17–Ir–C17A angle of 169.22(5)° due to the constraint of the C1–Ir–N1 and O1–Ir–O1 angles to 80.90(10)° and 87.39(11)° respectively, resulting in a distorted octahedral environment about the iridium centre.

One-photon photophysics

The UV-visible absorption spectrum (Fig. 3) of Ir(4-pe-2-ppy)$_2$(acac) is typical of this type of material in both shape and position of features. In analogy with previous assignments,[30] these include a π–π* ^{1}LC band below 320 nm, ^{1}MLCT bands between 370 and 420 nm and spin-forbidden ^{3}MLCT transitions above 450 nm. These features are also reproduced in the excitation spectrum.

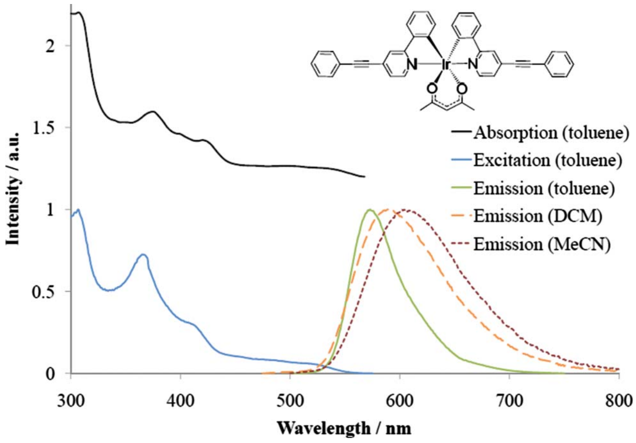


Fig. 3 Absorption, excitation and emission spectra of Ir(4-pe-2-ppy)$_2$-(acac). λ_{ex} = 400 nm, λ_{em} = 610 nm. All spectra are normalised and the absorption spectrum offset in intensity for clarity. All measurements were made in degassed solvent.

The presence of a MLCT contribution to the emissive state of Ir(4-pe-2-ppy)$_2$(acac) is supported by a positive solvatochromic emission shift on changing from toluene (λ_{em} = 570 nm) to acetonitrile (λ_{em} = 603 nm), a shift totalling some 960 cm^{-1}. Further, the broad and essentially structureless emission profile is indicative of an MLCT component. Compared to the parent complex Ir(ppy)$_2$(acac), the emission maximum is bathochromically shifted by approximately 1800 cm^{-1}.

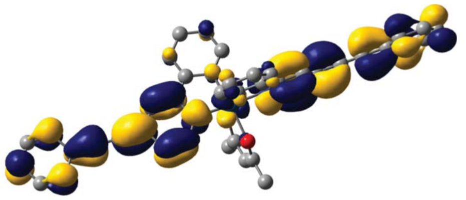
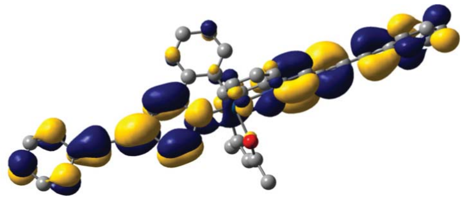
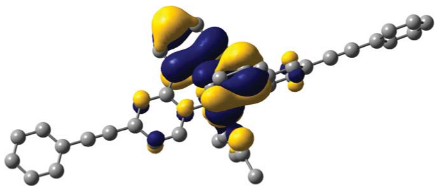
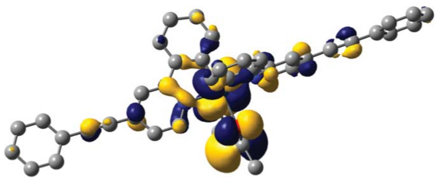
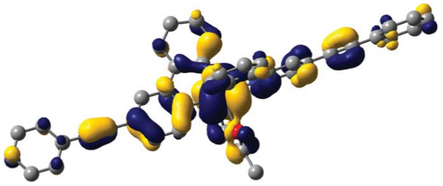
The luminescence lifetime of Ir(4-pe-2-ppy)$_2$(acac) in degassed and aerated toluene solution was measured as being 0.93 and 0.068 μs, respectively. The relatively short phosphorescence lifetime is also typical of a MLCT state and of a red emitter in which non-radiative decay is enhanced due to the energy gap law.

The value of Φ_P was measured in degassed toluene and found to be 0.28. For comparison, the parent compound Ir(ppy)$_2$(acac) in the same solvent has a longer lifetime and higher quantum yield of 1.6 μs and 0.46, respectively.

Computational study

The ground state optimised structure of Ir(4-pe-2-ppy)$_2$(acac) was calculated using DFT, employing the exchange–correlation functional B3LYP and a split basis set 6-31+G/LANL2DZ (see experimental for full details). The calculated Ir–O, Ir–C and Ir–N bond lengths agree with those determined experimentally from the X-ray structure to within ± 2%. A time-dependent DFT (TD-DFT) calculation was also carried out with the CAM-B3LYP functional, chosen because of its better description of charge transfer states compared to B3LYP,[31] and the same 6-31+G/LANL2DZ basis set. This calculation showed that the $T_1 \leftarrow S_0$ excitation is best described by a multi-component set of orbital transitions. The greatest contribution is LUMO+1 ← HOMO-2, which is a transition onto the phenylethynylpyridine moiety from an orbital based predominantly on the Ir atom with a small proportion on the 4-pe-2-ppy ligand (Table 1 for orbital plots). The second most important contribution comes from a transition from the HOMO-1 based on the Ir atom and acac ancillary ligand, to the LUMO distributed across the 4-(phenylethynyl)pyridine moiety.

Table 1 DFT 6-31+G/LANL2DZ calculated orbitals of Ir(4-pe-2-ppy)$_2$(acac). Hydrogen atoms have been removed for clarity

LUMO+1 *E* = -1.87eV	
LUMO *E* = -1.89 eV	
HOMO *E* = -4.75 eV	
HOMO-1 *E* = -5.21 eV	
HOMO-2 *E* = -5.58 eV	

The lowest energy excitation is therefore best described as an admixture of MLCT, ligand to ligand charge transfer (LLCT) and ligand-centred (LC) transitions, with MLCT being the principle constituent. This is in agreement with the observed photophysics which indicate some degree of charge transfer. Importantly, it shows a large spatial extent of the charge transfer as desired for a potential TPA material. The energy of this transition is calculated to be 2.41 eV (515 nm), which is within the band assigned ^{3}MLCT in the UV-visible spectrum.

Two-photon absorption spectroscopy

The TPA spectrum of the cyclometalated iridium compounds outlined in Fig. 1 were measured to understand the effect of structural change on the magnitude of σ_2. The TPA spectrum of the compound Ir(4-pe-2-ppy)$_2$(acac), which was designed to imitate the A-π-D-π-A organic chromophores, *vide supra*, was recorded to confirm whether similar design principles for the increase of σ_2 for organic two-photon absorbers were applicable to these organometallic systems. Fig. 4 depicts the TPA spectra of the 4 known complexes of various structural types (IrL$_3$, IrL$_2$L′ and IrL$_2$(acac)) and the novel compound Ir(4-pe-2-ppy)$_2$(acac), overlain with the OPA spectra. A comparison of the one-photon and two-photon emission profiles, Fig. 5, indicates that emission is from the same state independent of the excitation method. The use of a 670 nm short-pass filter in the detection optics to eliminate stray laser light reaching the detector results in the spectrum being cut off at this point. A correction was applied to the integrated emission intensity to account for this. A two-photon process could be confirmed by a quadratic dependence of the integrated emission, $F(\lambda)$, on the incident laser intensity, P. By plotting $\ln(F(\lambda))$ against $\ln(P)$ a linear fit was found, the gradient of which gave the argument of the power dependence, see Table 2 and representative fit in Fig. 6. In all cases a gradient of 2, within experimental error, confirmed that TPA was being observed. These data were recorded at 800 nm, the optimum operating wavelength of the system, which is also the wavelength chosen for comparison of cross-sections, σ_2, and TPA action cross-sections, the product of Φ_P and σ_2.

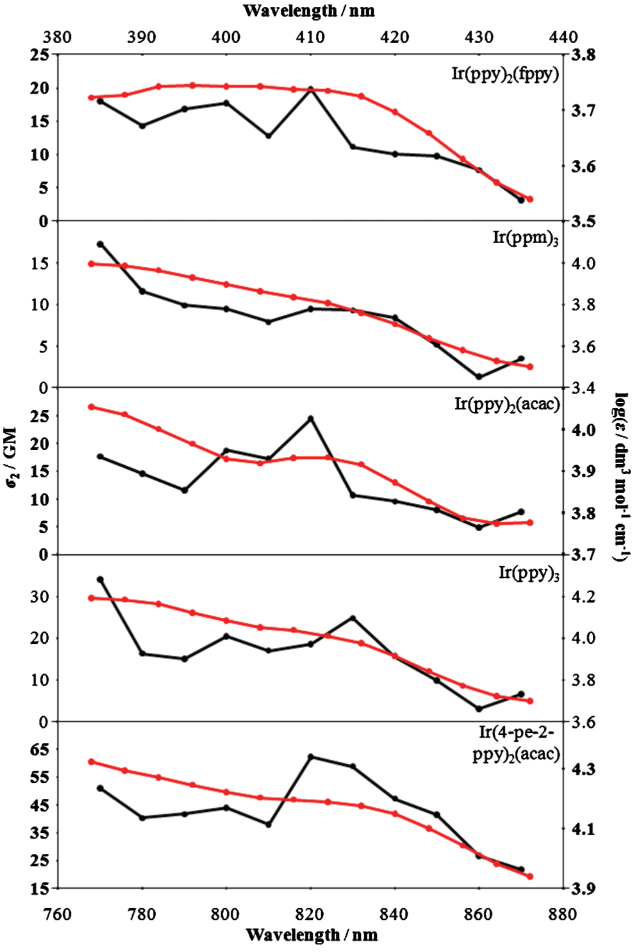


Fig. 4 TPA spectra (black, bottom abscissa, left ordinate) and OPA (UV-vis) spectra (red, top abscissa, right ordinate) for a series of iridium cyclometalated complexes (ppm = 2-phenylpyrimidine). Estimated error ± 20%.

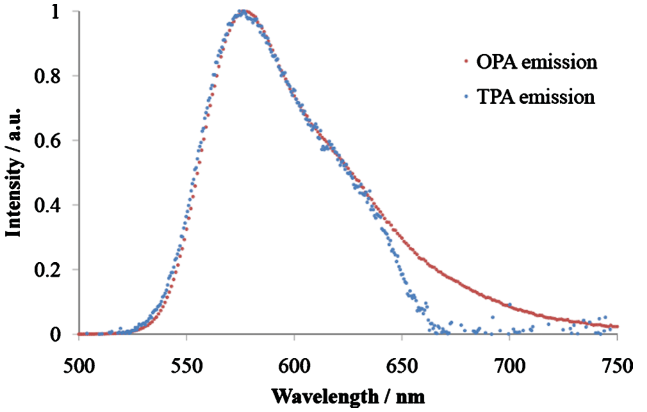


Fig. 5 Emission spectrum of Ir(4-pe-2-ppy)$_2$(acac) under one-photon (400 nm) and two-photon (800 nm) excitation.

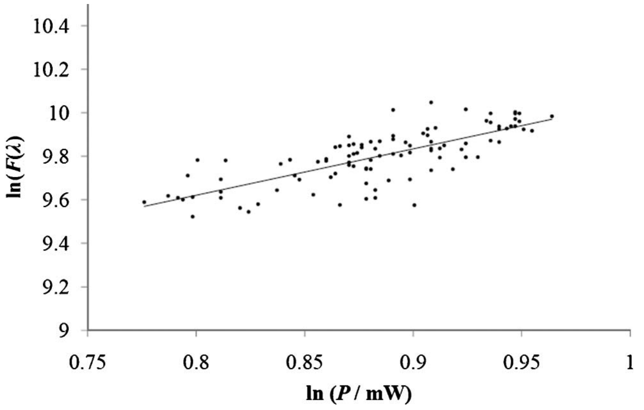


Fig. 6 A representative example of integrated luminescence intensity as a function of laser power for Ir(4-pe-2-ppy)$_2$(acac) at 800 nm. Gradient is 2.1 ± 0.2 ($R = 0.96$).

The fit of the OPA to the TPA excitation spectra is crude, which in part will be due to the inherent uncertainty in measuring TPA spectra. The region of spectrum measured covers several transitions of LC and MLCT character and these have will different cross sections for OPA and TPA, due to the different selection rules of the two processes, and hence different intensities in the two spectra. A similar explanation has been employed previously in the case of Eu complexes which show differences

Table 2 Two-photon absorption spectroscopic data and phosphorescence quantum yields (Φ_P) in degassed toluene

Compound	$Ir(ppy)_3$	$Ir(ppm)_3$	$Ir(ppy)_2(acac)$	$Ir(ppy)_2(fppy)$	$Ir(4\text{-pe-2-ppy})_2(acac)$
Gradient[a]	1.9 ± 0.1 (R = 0.99)	2.2 ± 0.1 (R = 0.96)	2.0 ± 0.1 (R = 0.96)	2.0 ± 0.1 (R = 0.95)	2.1 ± 0.2 (R = 0.96)
Φ_P[b]	0.64[c]	0.47	0.46	0.29	0.28
σ_2/GM[d]	20	9.5	17	18	44
$\Phi_2.\sigma_2$/GM[e]	13	4.5	8	6	12

[a] Gradient of plot of log(P/mW) against log($F(\lambda)$) at 800 nm measured over 100 data points, where P is laser power in mW and $F(\lambda)$ is the integrated emission spectrum. [b] Estimated error ± 0.1. [c] Literature values range from 0.40 (ref. 32) to 0.90 (ref. 33). [d] TPA cross section at 800 nm. 1 GM = 10^{-50} cm^4 s photon^{-1}. Estimated error ± 20%. [e] TPA action cross section at 800 nm.

between their OPA and TPA spectra.[9] Comparing the magnitude of the TPA cross-sections at 800 nm, it can be seen that all the complexes show relatively low values compared to some of the best organic chromophores,[2,3] however they are still appreciable when compared to other coordination and organometallic compounds measured with femtosecond excitation pulses. For instance $Ru(bpy)_3^{2+}$ has been reported to have a σ_2 value of only 4 GM,[34] while platinum N^C^N complexes that could be successfully used in time-resovled two-photon cell imaging have values that range between 4 and 20 GM.[35,36] The three complexes $Ir(ppy)_2(fppy)$, $Ir(ppy)_2(acac)$ and $Ir(ppy)_3$ show little variation in their σ_2 values. It appears the exchange of the ligand 2-phenylpyridine for 2-phenylpyrimidine has a strong negative effect on the TPA, with $Ir(ppm)_3$ having half the value of σ_2 of $Ir(ppy)_3$, although the reason for this is not known. The most noteworthy measurement is for $Ir(4\text{-pe-2-ppy})_2(acac)$ which has a σ_2 value more than double that of than $Ir(ppy)_2(acac)$ simply with the introduction of phenylethynyl appendages. This ability to improve the TPA properties by rational design is important if these species are to fulfil their potential applications. This also suggests the same design principles seen for large TPA susceptibilities in organic chromophores are relevant here and it can be expected that greater σ_2 values would be obtained with further increase in the conjugation and/or donor/acceptor strength. The magnitude of σ_2 is maximal at 820 nm, with a value of 62 GM (estimated error ± 20%).

It is however the *action cross-section* that is arguably the important parameter when evaluating species for imaging applications. Any potential TPA imaging agent would ideally have a large cross-section to excite a high proportion of the molecules that will be in a low concentration environment in any particular part of a sample, but would also have a large quantum yield to aide detection. The action cross-sections of $Ir(ppy)_3$ and $Ir(4\text{-pe-2-ppy})_2(acac)$ are of comparable magnitude (Table 2) and therefore exemplify why it must be borne in mind that while improving the two-photon cross-section is highly desirable, it cannot be at the expense of a diminished quantum yield. It is worth comparing these compounds therefore to the recently reported terpyridine iridium complexes which have comparable two-photon cross-sections but emission quantum yields two orders of magnitude smaller (Φ = 0.0026–0.0056). Thus, the cyclometalated complexes presented here are potentially more useful for certain applications and are arguably synthetically less challenging.

Conclusions

The two-photon cross-sections of a range of iridium complexes with various derivatives of the cyclometalating ligand 2-phenylpyridine and ancillary ligands have been measured. In all cases TPA was observed and a value of σ_2 of 20 GM was measured for the parent complex $Ir(ppy)_3$ at 800 nm which compares favourably with materials of a similar structural nature. In general it was found that there was little difference between complexes of the form $IrL_2(acac)$ and IrL_3 for the same ligand, L and thus the synthetically simpler $IrL_2(acac)$ sub-class should be developed further. In light of the structural features leading to large TPA cross sections in organic molecules and by considering the electronic structure of iridium complexes, the extended compound $Ir(4\text{-pe-2-ppy})_2(acac)$ was synthesised and found to have a cross-section more than twice that of $Ir(ppy)_2(acac)$ at 800 nm. This implies the extent of charge separation upon excitation must be increased in order to enhance the ability of these molecules to undergo TPA. It has therefore been shown that the design principles commonly employed for organic chromophores are applicable to these materials and thus large cross-section materials should be possible with tunable emission properties for a wide range of applications.

Acknowledgements

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