



Design, synthesis, luminescence and non-linear optical properties of 1,3,5-triethynylbenzene-based alkynylplatinum(II) terpyridine complexes

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Dedicated to Professor Richard D. Puddephatt on the occasion of his 75th birthday

ABSTRACT

A series of 1,3,5-triethynylbenzene-based alkynylplatinum(II) terpyridine complexes has been designed and synthesized. The photophysical properties including UV-vis absorption and emission properties, as well as electrochemical properties of the complexes have been systematically evaluated. Interesting two-photon absorption and two-photon induced luminescence behaviors are also observed for these platinum(II) complexes.

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1. Introduction

Two-photon absorption processes have attracted enormous attention in the past few decades since its theoretical prediction [1] and subsequent experimental observations in the 1960s [2–4]. Although little is known on the structure-property relationship of the two-photon absorbing chromophores initially, the development of high power lasers has stimulated extensive scientific research by various groups which revealed a strong correlation between two-photon absorptivity and intramolecular charge transfer processes [5,6]. In general, some essential features in the design of molecules with large two-photon absorptivity include the presence of electron-rich and electron-withdrawing groups [3,7–13], a π -conjugated system to achieve extended charge separation [6,14,15] and coplanarity to enhance intramolecular charge transfer processes [6,16]. More interestingly, the increased two-photon absorptivity by branched conjugated systems has stimulated subsequent research in the various dendrimers [17,18], hyperbranched polymers [19,20], coordination and organometallic compounds [21–29] that display two-photon absorption behaviors. To date, two-photon absorption properties have found practical

applications in the area of materials science such as in frequency upconversion lasing [30,31], three-dimensional fluorescence imaging [32,33], optical data storage [34,35], photodynamic therapy [36,37] and so-on [6,38].

Among various organometallic compounds, the platinum(II) systems represent excellent candidates for the construction of two-photon absorbing materials due to the relatively large strong spin-orbit coupling and efficient excited state absorptions introduced by the platinum centers [39–42]. In particular, since the report on the preparation of soluble platinum(II) polyynyl complexes [43,44], the alkynylplatinum(II) complexes have received considerable attention in the area due to their extended π -conjugation which could facilitate the intramolecular charge transfer processes [45–48]. The high versatility of the alkynylplatinum(II) systems also allows the incorporation of various π -donors or π -acceptors, leading to strong photon absorption cross-sections that give rise to promising optical limiting, two-photon absorption and two-photon induced luminescence properties [39,49–53]. Some of the classical examples, for instance, are given by the alkynylplatinum(II) phosphine complexes [43–48,53–58] and the platinum(II)-containing organo-dendrimers [59–62], and the corresponding investigations on their two-photon absorption properties [47,48,53–58]. On the contrary, relatively limited examples on alkynylplatinum(II) terpyridine complexes with two-photon absorption properties have been

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reported [54,57], in spite of their high versatility in the molecular design and tunable photophysical properties[63–70]. Inspired by these, we report the design and synthesis of a series of alkynylplatinum(II) terpyridine complexes of 1,3,5-triethynylbenzene-based ligands (Scheme 1). In particular, the 1,3,5-triethynylphenyl core is employed due to its attention for the exploration of materials with non-linear optical properties [47,48,55,71–75]. The X-ray crystal structure of one of the complexes has been determined. Their interesting photophysical properties including their UV-vis absorption, emission as well as their electrochemical properties have been determined. In addition, their two-photon absorption and two-photon induced luminescence behaviors have also been carefully explored.

2. Syntheses

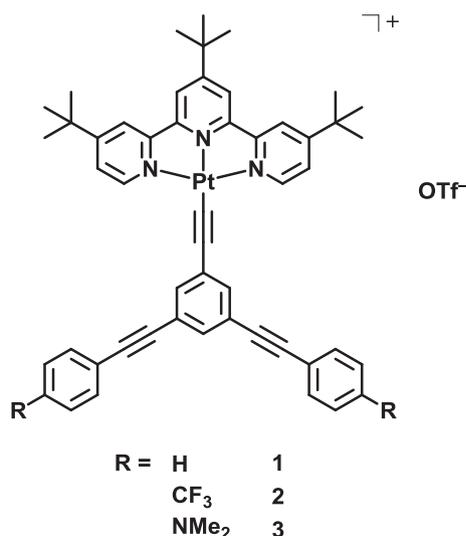
1–3 were synthesized by treating the corresponding chloroplatinum(II) terpyridine complexes with 1,3,5-triethynylbenzene-based alkynyl ligands through copper(I)-catalyzed dehydrohalogenation reactions in degassed dichloromethane solutions. **1–3** were purified by column chromatography followed by recrystallization from appropriate solvents. All the complexes have been characterized by ^1H NMR spectroscopy, positive FAB mass spectrometry, IR spectroscopy and gave satisfactory elemental analyses.

3. Results and discussions

3.1. X-ray crystallographic determination

Red single crystals of **3** suitable for X-ray diffraction studies have been obtained by recrystallization via slow diffusion of diethyl ether vapor into a dichloromethane solution of the complex. The perspective drawing and crystal packing motifs of the complex cation of **3** are shown in Figs. 1 and 2 respectively. The crystal structural determination data and selected bond lengths and angles are listed in Tables S1 and S2 respectively.

The platinum(II) metal center is found to adopt essentially a distorted square-planar geometry. The distance between the central phenyl ring carbon on the alkynyl ligand and the adjacent terpyridine is determined to be 3.41 Å (Fig. 3). In addition, the mean



Scheme 1. Molecular structures of 1,3,5-triethynylbenzene-containing alkynylplatinum(II) terpyridine complexes **1–3**.

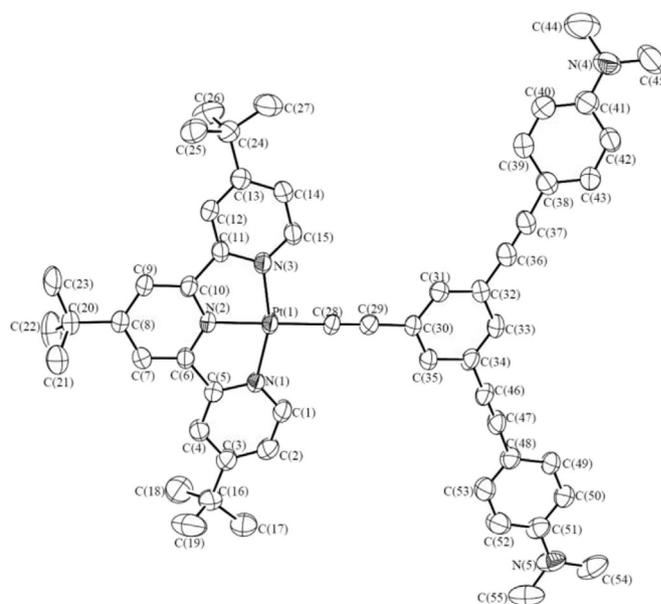


Fig. 1. Perspective drawing of the complex cation of **3** with atomic numbering. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

distance between the peripheral phenyl rings and the terpyridine plane of the adjacent complex molecule is determined to be 3.55 Å. These short π – π distances are suggestive of the involvement of π – π stacking interactions in the solid state [76], giving rise to the extensive network as observed in the crystal packing diagram.

3.2. Photophysical studies

3.2.1. UV-vis absorption studies

All the complexes dissolve in acetonitrile to give orange solutions. The UV-vis absorption spectra of **1–3** in acetonitrile at room temperature (Fig. 4) give intense absorption bands at 260–338 nm ($\epsilon \approx 10^4$ – $10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$) and moderately intense low-energy absorption bands at about 414–418 nm ($\epsilon \approx 10^3$ – $10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). With reference to the previous literature [77–84], the high-energy absorption bands are assigned as intraligand (IL) [$\pi \rightarrow \pi^*$] transitions of the terpyridine and 1,3,5-triethynylbenzene-based alkynyl ligands, while the low-energy absorption bands are assigned as predominately [$d\pi(\text{Pt}) \rightarrow \pi^*(\text{Bu}_3\text{tpy})$] metal-to-ligand charge transfer (MLCT) transitions. The photophysical data of **1–3** are summarized in Table 1.

3.2.2. Luminescence studies

The luminescence properties of **1–3** are evaluated and are summarized in Table 2. Upon excitation at $\lambda \geq 400 \text{ nm}$, **1** and **2** in acetonitrile solutions give broad and structureless emission bands at about 570 nm (Fig. 5). With reference to the previous literature [77–84], the emissions are assigned as derived predominantly from [$d\pi(\text{Pt}) \rightarrow \pi^*(\text{Bu}_3\text{tpy})$] $^3\text{MLCT}$ states with probable mixing of some [$\pi(\text{C}\equiv\text{C}) \rightarrow \pi^*(\text{Bu}_3\text{tpy})$] $^3\text{LLCT}$ character. All the complexes are found to be emissive in butyronitrile glass at 77 K and give similar emission spectra (Fig. 6). **1–3** in butyronitrile glass give vibronic-structured emission bands with vibrational progression spacings of 1300 cm^{-1} , which are typical of the aromatic deformation modes of the terpyridine ligands. These high-energy emission bands are therefore assigned as originated from metal-perturbed ^3IL [$\pi \rightarrow \pi^*$] excited states. An additional lower-energy emission band at 650 nm is observed for **3**, which might be assigned as

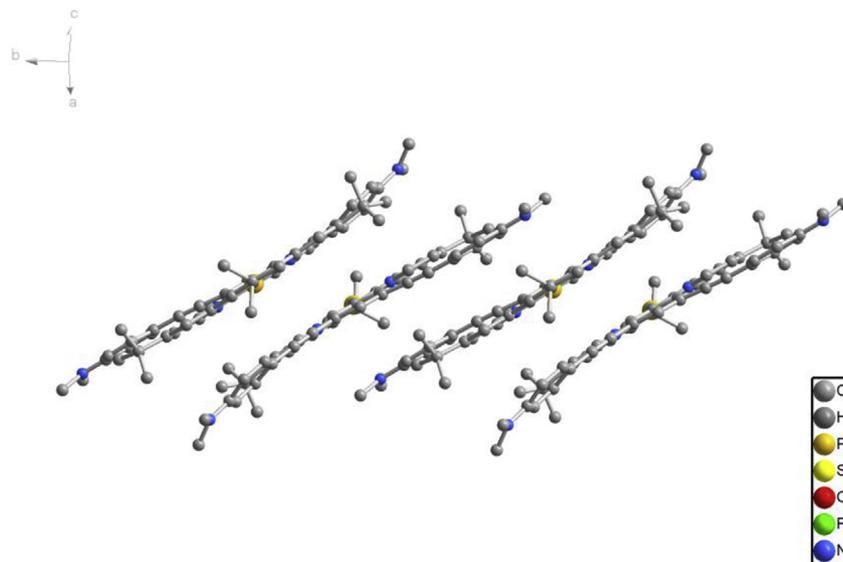


Fig. 2. Crystal packing diagram of the complex cation of **3**. Hydrogen atoms are omitted for clarity.

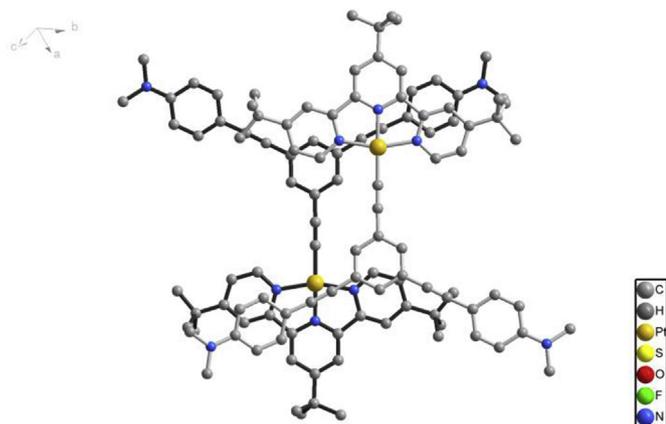


Fig. 3. Crystal packing diagram of the complex cation of **3** showing π - π stacking interactions between the central phenyl ring and the terpyridine moiety of the adjacent complex cation. Hydrogen atoms are omitted for clarity.

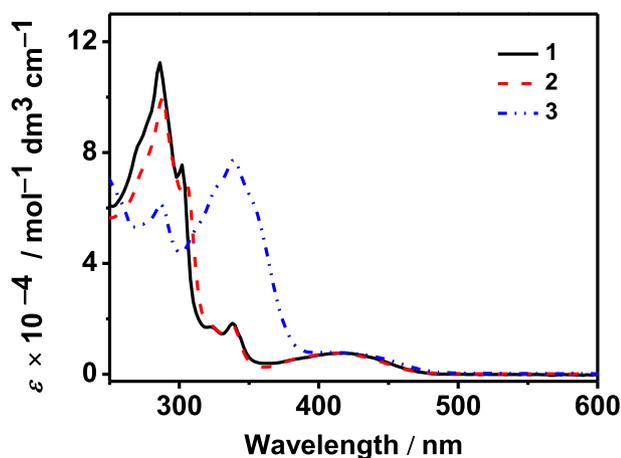


Fig. 4. UV-Vis absorption spectra of **1–3** in acetonitrile solutions at 298 K.

Table 1

UV-Vis absorption data of **1–3** in acetonitrile at 298 K.

Complex	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$)
1	270 sh (82300), 286 (113000), 302 (75500), 322 sh (17100), 338 (18400), 414 (7620)
2	272 sh (72600), 288 (103000), 306 (69800), 322 sh (18000), 336 (17300), 414 (7400)
3	278 sh (55100), 286 (61700), 316 sh (55600), 328 sh (68400), 338 (77700), 354 sh (60600), 418 (7800)

Table 2

Luminescence data of **1–3**.

Complex	Medium (T/K)	$\lambda_{\text{em}}/\text{nm}$ ($\tau_o/\mu\text{s}$)	Φ_{lum}^a
1	CH ₃ CN (298)	570 (0.2)	1.1×10^{-2}
	Glass (77) ^b	504 (12.1)	
	Solid (298)	517 (<0.1)	
	Solid (77)	516 (6.8)	
2	CH ₃ CN (298)	568 (<0.1)	2.5×10^{-3}
	Glass (77) ^b	502 (11.7)	
	Solid (298)	532 (1.4)	
	Solid (77)	535 (8.8)	
3	CH ₃ CN (298)	— ^c	— ^d
	Glass (77) ^b	506 (11.5)	
	Solid (298)	— ^c	
	Solid (77)	673 (0.2)	

^a Measured using a degassed aqueous solution of [Ru(bpy)₃]Cl₂ (excitation wavelength = 436 nm, $\Phi = 0.042$) as reference.

^b Measured in butyronitrile glass.

^c Non-emissive.

^d Not measured.

originated from the ³MLCT/LLCT excited states. In the solid state, **1** and **2** give vibronic-structured metal-perturbed ³IL [$\pi \rightarrow \pi^*$] emission bands with peak maxima at around 512–535 nm at both 298 and 77 K. The lack of emissive properties of **3** in both solution and solid state at room temperature could be ascribed to the quenching of the emissive ³MLCT excited state by photoinduced electron transfer, which has been commonly observed in the alkynylplatinum(II) terpyridine systems with amino groups in the literature [77–84]. Upon lowering the temperature to 77 K in the solid state, **3**

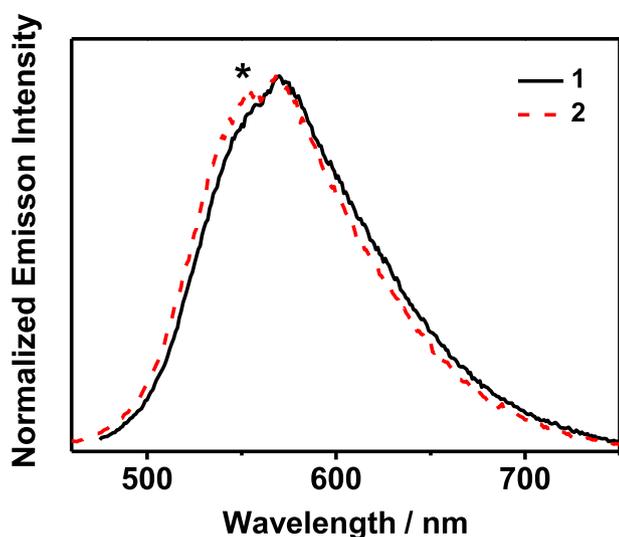


Fig. 5. Normalized emission spectra of 1 and 2 in degassed acetonitrile solutions at 298 K. Asterisk denotes instrumental artefact.

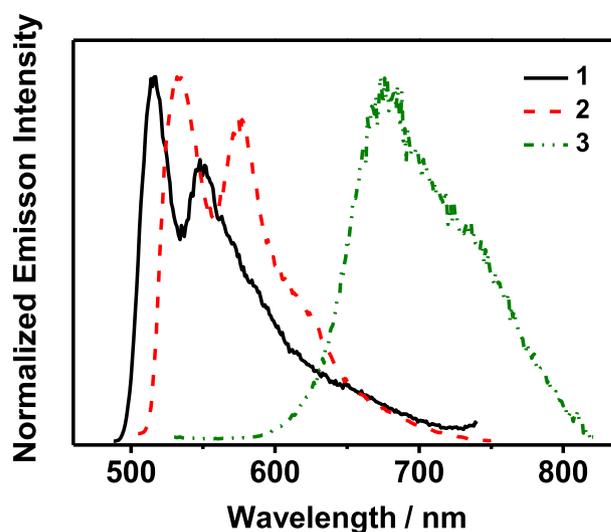


Fig. 7. Normalized emission intensity of 1–3 in the solid state at 77 K.

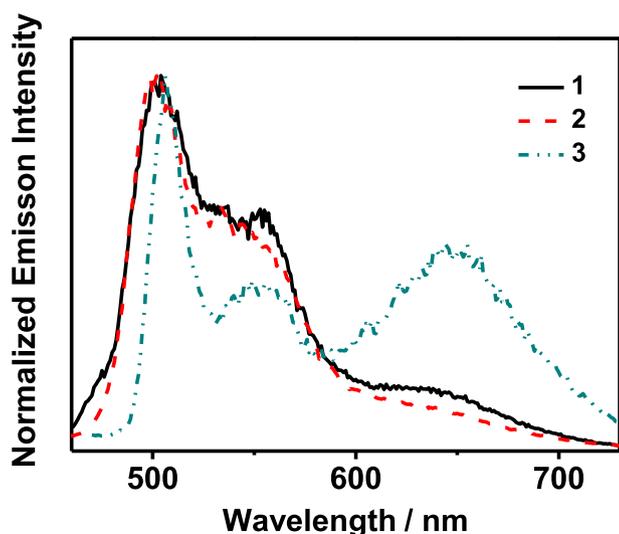


Fig. 6. Normalized emission spectra of 1–3 in butyronitrile glass at 77 K.

gives a weak lower-energy emission band at 673 nm (Fig. 7). Such a red shift in emission in 3 when compared to 1 and 2 in the solid state at 77 K could be ascribed to the involvement of π – π stacking interactions that is evident in the X-ray crystal structure of 3. The fine-tuning of the photophysical properties through variations in the substituent groups on the acetylene would provide guidelines and principles for the future design of metal complexes with desirable properties.

3.2.3. Electrochemical properties

The electrochemical properties of 1–3 are investigated in acetonitrile (0.1 M $^n\text{Bu}_4\text{NPF}_6$) by cyclic voltammetry and the data are summarized in Table 3. Two quasi-reversible reduction couples at around -1.00 and -1.49 V (vs. saturated calomel electrode, SCE) are observed for 1–3. The two reduction couples are insensitive to changes in the substituents of the alkynyl ligands. With reference to previous studies on related platinum(II) complexes [64,66], they are assigned as the successive one-electron reduction of the terpyridine ligand. In addition, the first oxidation wave at $+0.80$ V

Table 3

Electrochemical data for 1–3 in acetonitrile solution (0.1 M $^n\text{Bu}_4\text{NPF}_6$) at 298 K.

Complex	Oxidation E_{pa}^b [V vs. S.C.E.]	Reduction $E_{1/2}^c$ [V vs. S.C.E.]
1	+1.33	$-1.00, -1.49$
2	+1.40	$-0.98, -1.46$
3	+0.80	$-0.98, -1.46$

^a Working electrode, glassy carbon; scan; scan rate = 100 mV s^{-1} .

^b E_{pa} is the peak anodic potential for the irreversible oxidation waves.

^c $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$; E_{pa} and E_{pc} are peak anodic and peak cathodic potentials, respectively.

to $+1.33$ V vs. SCE for 1–3 is found to be less positive upon increasing the electron-donating ability of the substituents ($\text{NMe}_2 > \text{H} > \text{CF}_3$), indicative of the contribution from ligand centers. With reference to the previous literature [64,66], the irreversible anodic waves are assigned as the metal-centered oxidation from alkynyl ligand centered oxidation with mixing of platinum(II) to platinum(III) oxidation.

3.2.4. Two-photon induced luminescence

Upon excitation at 720 nm by a mode-locked femtosecond Ti:Sapphire laser, 1 and 2 in acetonitrile solutions are found to exhibit yellow emissions (Fig. 8 and S1). A summary of the non-linear photophysical data of complexes is tabulated in Table 4. The two-photon luminescence spectra of 1 and 2 show close resemblance to their corresponding single-photon induced emissions, as indicated by the similar emission energies of the two-photon and single-photon induced emissions. No linear absorptions are observed for 1 and 2 at $\lambda > 600$ nm in the UV-vis absorption spectra, suggesting that the emission induced by 720 nm excitation could not be attributed to a linear process but rather a nonlinear process. To further confirm the two-photon absorption behavior, the dependence of the upconverted luminescence intensity on the incident laser power for 1 and 2 is measured. A plot of $\log(\text{emission intensity})$ against $\log(\text{laser power})$ for both complexes gives a straight line with a slope of about 2, which is in line with the theoretical prediction of two-photon induced luminescence properties (Fig. 9 and S2) [85]. Furthermore, the two-photon absorption cross-sections (σ_2) of 1 and 2 are determined and found (Table 4). A comparison between the σ_2 values of 1 and 2 shows that 2 shows a 4-fold increase in the two-photon absorption cross-section, possibly due to the incorporation of the electron-

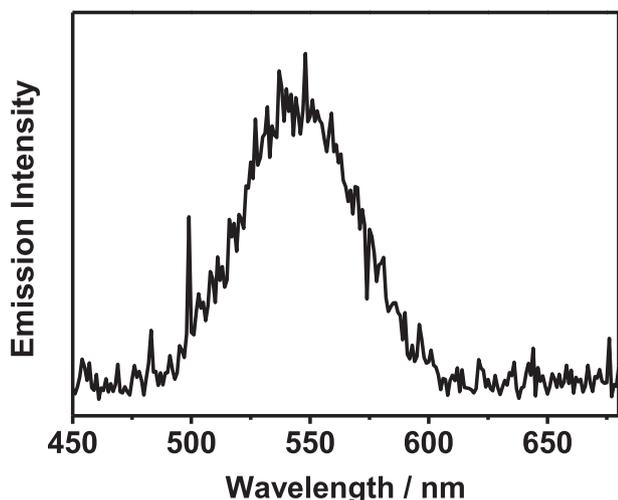


Fig. 8. Two-photon induced luminescence spectrum of **2** in acetonitrile at room temperature upon excitation with a mode-locked femtosecond Ti:Sapphire laser at 720 nm.

Table 4
Non-linear photophysical data for **1** and **2**.

Complex	$\lambda_{\text{ex}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	σ_2/GM	Power Dependence
1	720	549	2	1.91
2	720	544	8	1.76

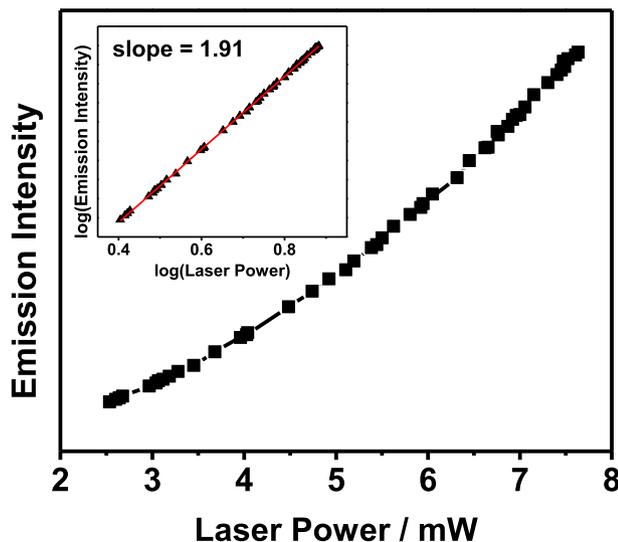


Fig. 9. Power dependence of the up-converted luminescence intensity (■) of **1** in acetonitrile at room temperature. The black line shows the theoretical curve for the quadratic function. The inset shows the log(emission intensity) (▲) vs log(laser power) and its linear regression (red solid line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

withdrawing $-\text{CF}_3$ groups which enhanced the dipole moment and the use of an octupolar molecular design which has been known to increase two-photon absorption cross-sections as a result of the increased intramolecular charge distribution [14,28,86].

4. Conclusion

To conclude, a series of 1,3,5-triethynylbenzene-based

alkynylplatinum(II) terpyridine complexes has been designed and synthesized. Their photophysical behaviors including UV-vis absorption and luminescence data and their electrochemical properties have been systematically evaluated. Their two-photon absorption and two-photon induced luminescence properties have also been determined. Such results not only have provided a more in-depth understanding into the structure-property relationship of the complexes, but also have offered further insights into the future design of metal complexes with desired non-linear optical properties. With the growing interests in the search for non-linear optical materials and continuous efforts from various research groups, platinum(II) complexes with rational molecular design are expected to show promising applications in the area of materials science such as in novel optoelectronics, photonics, fluorescence imaging and so-on.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jorganchem.2018.11.035>.

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