Branched Luminescent Multinuclear Platinum(II) Alkynyl Complexes: Candidates for Efficient Two-Photon Induced Luminescence

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Three luminescent multinuclear platinum(II) alkynyl complexes with readily tunable emission characteristics are found to show two-photon absorption (TPA) and two-photon induced luminescence (TPIL) properties, and their two-photon absorption cross-sections have been determined.

Introduction

Two-photon absorption (TPA) takes place when a molecule is excited from the ground state to an excited state by simultaneous absorption of two photons, while two-photon induced luminescence (TPIL) is the emission of light with energy higher than that of the absorbed light via two-photon absorption processes. Practical applications based on TPA have been rather limited in the past. It has only been since the mid 1990s, when advances in high-power lasers and the availability of materials with large TPA become more apparent, that there has been increasing attention devoted to TPA-based applications in photonic and biophotonic areas, such as optical data storage,[1−3] power limiting,[4,5] upconversion lasing,[6,7] three-dimensional fluorescence imaging,[8,9] three-dimensional microfabrication,[10,11] pulse reshaping and stabilization,[12] and photodynamic therapy.[13,14] Extensive efforts have been concentrated on the synthesis of organic chromophores with large two-photon absorption cross-section (σ_2) values.[15−18] It has been reported that π-conjugated molecules that undergo large changes in quadrupole moment upon excitation can show large two-photon absorption cross-sections.[17] In particular, compounds with donor−π−donor, donor−acceptor−donor, and acceptor−donor−acceptor structural motifs could exhibit large σ_2 values.[17] In addition, multibranched and dendritic systems with various structural motifs, such as 4,4′,4″-trisubstituted triphenylamine,[15,19] 1,3,5-tricyanobenzene,[20] 1,3,5-trisubstituted benzene,[21] truxene,[22] and others,[23] are also reported to show exceptionally large σ_2 values. These molecular design strategies have been proven to be useful in the preparation of novel materials with large two-photon absorption cross-sections.

In contrast, upconversion of light using d-block transition-metal complexes is relatively uncommon and most of the species used are coordination compounds.[4,24−26] In fact, the incorporation of electron-donor or -acceptor moieties through the formation of relatively strong M−C bonds appears to be an attractive and promising strategy toward molecular materials with nonlinear optical properties. For instance, a number of ferrocenyl,

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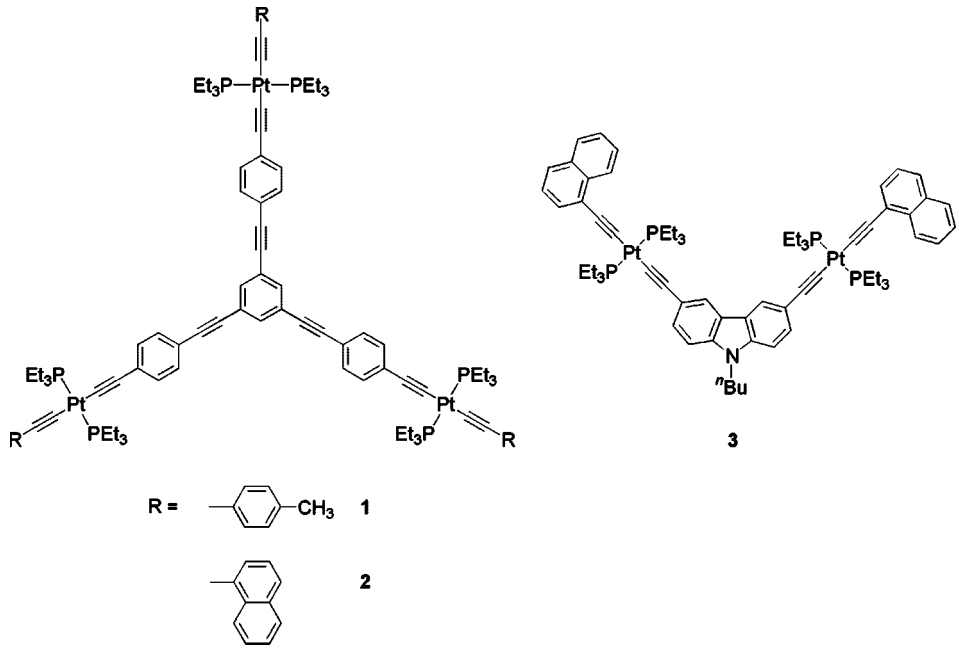
Chart 1. Structures of the Platinum Complexes



manganese(I), ruthenium(II), and gold(I) organotransition-metal complexes have been studied by various groups and are found to have interesting nonlinear optical responses.[27−34] The platinum(II) alkynyl polymers and molecular materials represent one of the recent foci for the study of metal-containing NLO materials due to their strong excited-state absorptions in the visible range and relatively large spin−orbit coupling.[35−42] Their negligible absorption in the visible region have rendered them as promising optical limiters in the visible region.[39,41,43,44] Most of these materials are mononuclear platinum(II) complexes that are structurally related to bis((4-(phenylethynyl)phenyl)ethynyl)bis(tributylphosphine)platinum(II), with reported σ_2 values in the range of ∼5−10 GM, and their luminescence is reported as originating from the singlet or triplet excited state of the (4-(phenylethynyl)phenyl)ethynyl backbone.[36−38,40] Incorporation of electron-donating or -accepting functionalities into this class of complexes for the enhancement of σ_2 values has been recently demonstrated.[38−40] Although dendrimer-encapsulated derivatives of bis((4-(phenylethynyl)phenyl)ethynyl)bis(tributylphosphine)platinum(II) have also been reported,[37] the use of multinuclear platinum(II) alkynyls with dendritic or branched phenyleneethynylene backbones in the field of NLO studies has been largely neglected,[40,44] in spite of the potential advantages of branched molecules and dendrimers, which is in contrast to the extensive studies of dendritic or branched compounds in organic NLO materials.[23] With our recent work and ongoing interest in the synthesis of luminescent branched alkynyls with various metal centers,[45−49] we became interested in the exploration of these branched metal complexes as molecular materials with relatively efficient TPA and TPIL capabilities. These branched materials also possess better solubilities and processabilities in comparison to those of their linear counterparts, which may be advantageous for future applications. We are also interested in the effect on NLO properties of these metal-containing carbon-rich materials by changing the emission origin from the 4-(phenylethynyl)phenylethynyl backbone to a more low-lying moiety. In this regards, three multinuclear branched platinum(II) alkynyl complexes with two-photon induced luminescence properties are reported and their structures are shown in Chart 1.

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Experimental Section

Materials and Reagents. [{RC≡C(PEt$_3$)$_2$PtC≡CC$_6$H$_4$C≡C}$_3$-C$_6$H$_3$-1,3,5] (R = C$_6$H$_4$CH$_3$ (**1**), Np (**2**))[46] and the precursor complex [{ClPt(PEt$_3$)$_2$C≡C}$_2$-3,6-^{n}BuCarb-9][50] were synthesized according to literature procedures. 1-Ethynylnapthalene (Aldrich, 97%) was purchased and used as received. All amines were distilled over potassium hydroxide and stored in the presence of potassium hydroxide prior to use. All other solvents and reagents were of analytical grade and were used as received.

Physical Measurements and Instrumentation. UV−visible spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, IR spectra as KBr disks on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer (4000−400 cm^{-1}), and steady-state excitation and emission spectra on a Spex Fluorolog-2 Model F 111 fluorescence spectrophotometer equipped with a Hamamatsu R-928 photomultiplier tube. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. ^{1}H NMR spectra were recorded on a Bruker DPX-300 Fourier transform NMR spectrometer, while ^{31}P{^{1}H} NMR spectra were recorded on either a Bruker DPX-300 or a Bruker DPX-500 Fourier transform NMR spectrometer. Chemical shifts (δ, ppm) of ^{1}H NMR spectra were recorded relative to tetramethylsilane (Me$_4$Si), while those of ^{31}P NMR spectra were recorded relative to 85% H$_3$PO$_4$. Positive ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the new complexes were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

The two-photon induced luminescence measurements were performed with a mode-locked femtosecond Tsunami Ti:Sapphire laser (Spectra-Physics, 100 fs, 82 MHz) as a pump source. The tunable wavelength range of the pulses was 700−900 nm. The luminescence signals from both the solution and solid-state samples were collected at right angles to the samples with a pair of lenses and were dispersed with an Acton SP300 monochromator equipped with a photomultiplier (Hamamatsu R928) detector. A blue band color filter was used to block the laser line. A standard lock-in amplification technique was employed for the photoluminescence measurements. In the experiment, the two-photon absorption cross-section at 740 nm and the luminescence quantum yield of rhodamine 6G in methanol were assumed to be 20 GM (Gøppert-Mayer, 1 GM = 1 × 10^{-50} cm^4 s photon^{-1} molecule^{-1}) and 0.98,[51] respectively. The time-averaged laser power at 740 nm was kept constant for the sample and the reference. For power-dependent measurements, the intensity of the incident laser was controlled with a neutral-density metallic filter.

All solutions for photophysical and two-photon induced luminescence studies were degassed on a high-vacuum line in a two-compartment cell consisting of a 10 mL Pyrex bulb and a 1 cm path length quartz cuvette and sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. The solutions were subjected to at least four freeze−pump−thaw cycles. Thin-film solid-state two-photon induced luminescence measurements were carried out with solid samples dissolved in dichloromethane and casted onto a quartz plate.

Crystal Structure Determination. Single crystals of **3** were grown by the slow evaporation of a dichloromethane−methanol solution containing the complex. Crystal data for **3**: [C$_{68}$H$_{89}$NP$_4$Pt$_2$], formula weight 1434.46, monoclinic, space group $P2_1/c$, a = 22.582(4) Å, b = 10.013(2) Å, c = 28.585(6) Å, β = 91.91(3)°, V = 6460(2) Å^3, Z = 4, D_c = 1.475 g cm^{-3}, μ(Mo Kα) = 4.464 mm^{-1}, F(000) = 2880, T = 253 K. A crystal of dimensions 0.40 mm × 0.20 mm × 0.15 mm mounted in a glass capillary was used for data collection at 253 K on a MAR diffractometer with a 300 mm image plate detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection was made with 2° oscillation steps of φ, 10 min exposure time, and a scanner distance at 120 mm. A total of 100 images was collected. The images were interpreted and intensities integrated using the DENZO program.[52] The structure was solved by direct methods employing the SHELXS-97 program[53] on a PC. Pt, P, and most non-hydrogen atoms were located according to direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least squares using the SHELXL-97 program[54] on a PC. Restraints were applied to the ^{n}Bu group, assuming similar C−C bond lengths. According to the SHELXL-97 program,[54] all 8716 independent reflections (R_{int} equal to 0.0617, 4350 reflections larger than 4σ(F_o), where $R_{int} = \sum|F_o^2 - F_o^2(\text{mean})|/\sum[F_o^2]$) from a total of 27 496 reflections participated in the full-matrix least-squares refinement against F^2. These reflections were in the ranges $-25 \le h \le 24$, $-11 \le k \le 10$, and $-33 \le l \le 32$ with $2\theta_{max}$ equal to 50.56°. One crystallographic asymmetric unit consists of one formula unit. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated by the SHELXL-97 program.[54] The positions of hydrogen atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms and participated in the calculation of final R indices. Since the structure refinements are against F^2, R indices based on F^2 are larger than (more than double) those based on F. For comparison with older refinements based on F and an OMIT threshold, a conventional index R1 based on observed F values larger than 4σ(F_o) is also given (corresponding to (intensity)2σ(I)). wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. The goodness of fit is based on F^2: GOF = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined. The weighting scheme is $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where P is $[2F_c^2 + \text{Max}(F_o^2,0)]/3$. Convergence ($(\Delta/\sigma)_{max}$ = 0.001, average 0.001) for 676 variable parameters by full-matrix least-squares refinement on F^2 reaches to R1 = 0.0340 and wR2 = 0.0745 with a goodness of fit of 0.803; the parameters a and b for the weighting scheme are 0.0369 and 0.0, respectively. The final difference Fourier map shows maximum rest peaks and holes of 0.918 and −0.638 e Å^{-3}, respectively.

Synthesis of Complex 3. All reactions were performed under anaerobic and anhydrous conditions using standard Schlenk techniques under an inert atmosphere of nitrogen. [{ClPt(PEt$_3$)$_2$C≡C}$_2$-3,6-^{n}BuCarb-9] (200 mg, 0.166 mmol) and 1-ethynylnapthalene (76 mg, 0.5 mmol) were dissolved in a mixture of THF (20 mL) and diethylamine (10 mL). To this reaction mixture was added CuCl (5 mg) as a catalyst. The yellow mixture was then stirred overnight at room temperature. The white organic ammonium salt that formed during the course of the reaction was filtered out and the solvent removed under reduced pressure. The resulting greenish yellow gummy residue was then redissolved in dichloromethane, and this solution was washed successively with brine and deionized water and dried over anhydrous Na$_2$SO$_4$. The solvent was then removed under reduced pressure. The yellow residue was subjected to column chromatography on basic aluminum oxide (50−200 μm) using dichloromethane as the eluent. Yield: 131 mg, 55%. ^{1}H NMR

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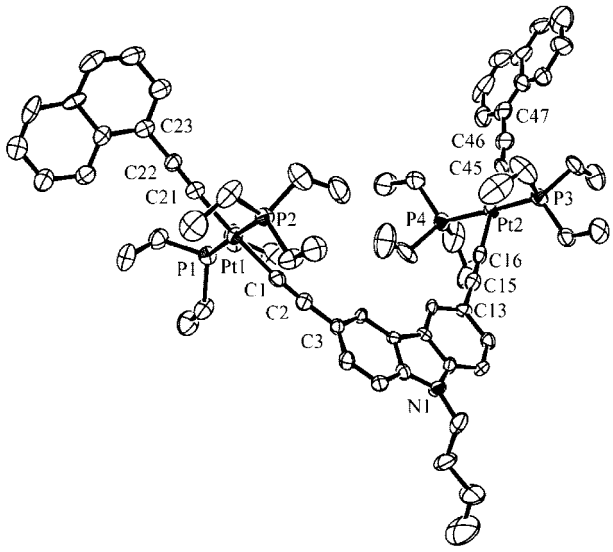

Figure 1. Perspective drawing of complex **3** with atomic numbering. Hydrogen atoms have been omitted for clarity. The thermal ellipsoids are shown at the 30% probability level.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations (Esd's) in Parentheses for Complex 3

Bond Distances			
Pt(1)−C(21)	2.012(11)	Pt(2)−P(4)	2.299(3)
Pt(1)−C(1)	2.024(11)	Pt(2)−P(3)	2.308(3)
Pt(1)−P(1)	2.302(3)	C(1)−C(2)	1.208(13)
Pt(1)−P(2)	2.303(3)	C(15)−C(16)	1.239(14)
Pt(2)−C(16)	2.016(13)	C(21)−C(22)	1.177(12)
Pt(2)−C(45)	2.027(13)	C(45)−C(46)	1.218(17)
Bond Angles			
C(21)−Pt(1)−C(1)	176.4(4)	C(45)−Pt(2)−P(3)	92.8(3)
C(21)−Pt(1)−P(1)	92.2(3)	P(4)−Pt(2)−P(3)	175.36(11)
C(1)−Pt(1)−P(1)	88.9(3)	C(2)−C(1)−Pt(1)	175.5(10)
C(21)−Pt(1)−P(2)	89.3(3)	C(1)−C(2)−C(3)	175.9(12)
C(1)−Pt(1)−P(2)	89.6(3)	C(16)−C(15)−C(13)	172.9(11)
P(1)−Pt(1)−P(2)	178.30(11)	C(15)−C(16)−Pt(2)	177.3(10)
C(16)−Pt(2)−C(45)	179.0(4)	C(22)−C(21)−Pt(1)	176.9(10)
C(16)−Pt(2)−P(4)	90.5(3)	C(21)−C(22)−C(23)	175.8(12)
C(45)−Pt(2)−P(4)	88.7(3)	C(46)−C(45)−Pt(2)	174.9(12)
C(16)−Pt(2)−P(3)	87.9(3)	C(45)−C(46)−C(47)	170.6(17)

($CDCl_3$, 298 K, 400 MHz): δ 0.93 (t, J_{HH} = 6.8 Hz, 3H, $-NCH_2CH_2CH_2CH_3$), 1.2−1.4 (m, 38H, $-PCH_2CH_3$ and $-NCH_2CH_2CH_2-$), 1.81 (quintet, J_{HH} = 6.8 Hz, 2H, $-NCH_2CH_2-$), 2.2−2.3 (m, 24H, $-CH_2P$), 4.22 (t, J_{HH} = 6.8 Hz, 2H, NCH_2-), 7.22 (d, J_{HH} = 8.6 Hz, 2H, H's at 1-position of carbazole), 7.3−7.5 (m, 10H, H's on Np moieties and H's at 2-position of carbazole), 7.63 (d, J_{HH} = 8.1 Hz, 2H, H's on Np moieties), 7.99 (d, J_{HH} = 1.7 Hz, 2H, H's at 4-position of carbazole), 8.54 (d, J_{HH} = 8.1 Hz, H's on Np moieties). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 298 K, 162 MHz): δ 11.6 (J_{Pt-P} = 2380 Hz). IR (KBr disk, cm^{-1}): 2085 s ν(C≡C). Positive ion FAB-MS: *m/z* 1433 $[M]^+$, 1316 $[M - PEt_3]^+$. Anal. Found: C, 56.7; H, 6.34; N, 1.00. Calcd for **3**: C, 56.9; H, 6.25; N, 0.98.

Results and Discussion

Similar to the synthesis of complexes **1** and **2**, reaction of the chloroplatinum(II) precursor complex [{ClPt(PEt_3)$_2$C≡C}$_2$-3,6-^{n}BuCarb-9][50] with 1-ethynylnaphthalene in the presence of a catalytic amount of CuCl in $HNEt_2$ and THF afforded complex **3** as a pale orange-yellow solid.[46] The X-ray crystal structure of complex **3** has been determined. Figure 1 shows the perspective drawing of complex **3**. The structural features of complex **3** are comparable to those in the chloroplatinum(II) precursor complex [{ClPt(PEt_3)$_2$C≡C}$_2$-3,6-^{n}BuCarb-9].[50] The bond angles between the alkynyl ligand and the platinum metal centers are in the range of 174.9(12)−177.3(10)° and are close to the ideal of 180° for sp-hybridized carbon, further confirming the σ-bonded nature of the alkynyl groups in these complexes. The slightly longer Pt−C bond distances found in complex **3** (2.012(11)−2.027(13) Å) compared to those in the precursor complex (1.87(3) and 1.97(3) Å) are ascribed to the stronger *trans* influence as a consequence of the presence of the second set of alkynyl groups in the bis(alkynyl) complexes in comparison to that of the chloroplatinum(II) precursor complex. The coordination geometry of complex **3** at the platinum center is essentially square planar with slight distortions, with the P−Pt−C bond angles in the range of 87.9(3)−92.8(3)°, probably due to relief of steric hindrance from the presence of bulky ligands about the platinum(II) metal centers. The coordination planes about each platinum atom in complex **3** are not coplanar with the carbazole backbone, with interplanar angles of 69.1−70.4°, which are similar to those found in the crystal structure of the chloroplatinum precursor.[50] All the bond distances and angles were found to be normal and are comparable to that found in other related platinum(II) alkynyl complexes.[46] Selected bond distances and angles are given in Table 1.

The electronic absorption spectra of the complexes are dominated by intense absorption bands at ca. 354−370 nm with extinction coefficients on the order of 10^4 dm^3 mol^{-1} cm^{-1}. Similar absorption bands with comparable extinction coefficients have been observed for the organic alkynes and the corresponding chloroplatinum(II) precursor complexes, which are suggestive of the largely intraligand (IL) character of these absorption bands. The linear electronic absorption and emission spectra of complexes **1** and **3** are shown in Figure 2, and the corresponding spectral data of complexes **1**−**3** are summarized in Table 2. In view of the observation of slight red shifts of absorption and emission energies on going from the chloropalladium(II) alkynyl complex to its chloroplatinum(II) analogues, the lowest energy absorption bands of these complexes are best described as the $\pi \rightarrow \pi^*$ IL/dπ(Pt) π^*(C≡C) MLCT transitions with predominantly IL character.[47] Upon photoexcitation at λ >350 nm, vibronically structured emission bands were observed for complexes **1** (532 nm), **2** (548 nm), and **3** (546 nm) in degassed benzene solutions. The large Stokes shifts and the luminescence lifetimes in the microsecond range are typical of emission origins with triplet parentage. In view of the close resemblance of

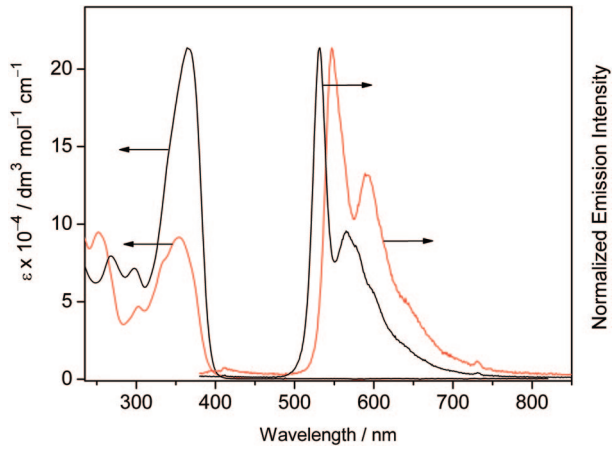

Figure 2. Electronic absorption spectra in dichloromethane (left) and normalized emission spectra in the solid state (right) of complexes **1** (black lines) and **3** (red lines) at room temperature.

Table 2. Linear and Nonlinear Photophysical Data for Complexes 1−3

complex	abs[a] λ/nm (ε/dm^3 mol^{-1} cm^{-1})	λ_{em}[b]/ nm (τ_o/μs) λ_{ex} = 355 nm	λ_{em}[b]/ nm (τ_o/μs) λ_{ex} = 740 nm	Φ_{em}[b,c]	σ_2[b]/GM
1	268 (79 610), 298 (71 610), 338 sh (134 590), 364 (213 650)	532 (41.4)	533	0.30	32
2	308 (78 380), 370 (244 950)	546 (68.0)	547	0.31	13
3	252 (94 920), 302 (46 990), 332 sh (74 260), 354 (91 540), 372 sh (66 640), 412 sh (2110)	548 (<0.1)	548	0.19	14

[a] In CH_2Cl_2 at 298 K. [b] In benzene at 298 K. [c] Using quinine sulfate in 1.0 N H_2SO_4 as the reference (excitation wavelength 365 nm, Φ = 0.55).[55]

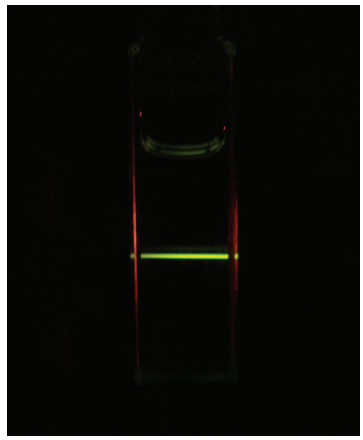

Figure 3. TPIL observed from complex **1** in benzene at a concentration of 1.80 × 10^{-4} mol dm^{-3} upon excitation with a mode-locked femtosecond Ti:Sapphire laser at 740 nm. The horizontal green line is the TPIL observed from complex **1**, while the red vertical lines are scattered light of the 740 nm excitation laser by the 1 cm quartz cell.

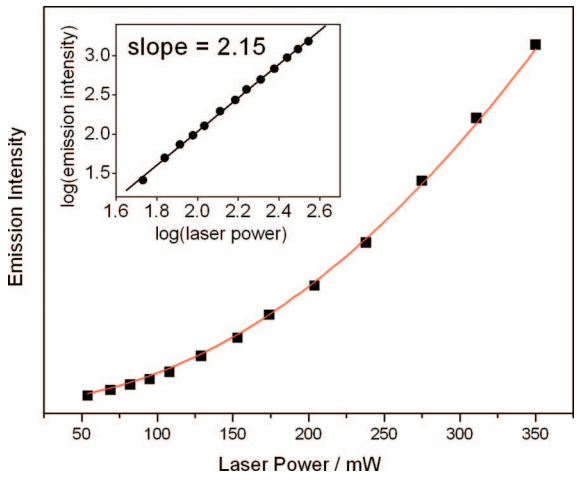

Figure 4. Power dependence of the upconverted luminescence intensity (■) of complex **3** in the thin-film solid state at room temperature. The red line shows the theoretical curve for the quadratic function. The inset shows the log(emission intensity) (●) vs log(laser power) and its linear regression (—).

vibronic structures and emission energies for complexes **2** and **3**, which are different from those of complex **1**, the emissions of complexes **2** and **3** are likely to emanate from similar intraligand triplet excited states that are associated with the naphthyl moieties. Such spin-forbidden transitions are "switched on" due to the strong spin−orbit coupling exhibited by the heavy $Pt(PEt_3)_2$ moieties. However, a red shift in emission energies was observed on going from the palladium alkynyl complexes to their platinum analogues,[47] which is indicative of some mixing of dπ(M) → π*(C≡C) ^{3}MLCT character in the emissive states. Thus, the nearly identical yellow-orange emission bands observed for complexes **2** and **3** are likely to originate predominantly from the ^{3}IL states of the naphthyl alkynyl moieties with some mixing of dπ(Pt) → π*(C≡CNp) ^{3}MLCT character. On the other hand, the yellowish green emission of complex **1** was assigned to be derived from triplet states of the $(C{\equiv}CC_6H_4C{\equiv}C)_3C_6H_3$-1,3,5 central core with some mixing of MLCT[dπ(M) → π*(C≡CR)] character, as the mononuclear complex *trans*-$[Pt(PEt_3)_2(C{\equiv}CC_6H_4CH_3)_2]$ has been found to emit at shorter wavelength with an emission maximum at ca. 450 nm. The absence of ^{3}IL emissions derived from the central $(C{\equiv}CC_6H_4C{\equiv}C)_3C_6H_3$-1,3,5 and $(C{\equiv}C)_2$-3,6-^{n}BuCarb-9 moieties in complexes **2** and **3**, respectively, was attributed to the facile energy transfer from the central core to the lower lying excited states associated with the peripheral naphthyl moieties in these multinuclear platinum(II) systems.[46]

Upon excitation by a mode-locked femtosecond Ti:Sapphire laser at 740 nm, complexes **1**−**3** emit in the green to yellow region both in degassed benzene solutions (concentration ~10^{-5} M) and as a thin film in the solid state at room temperature. Figure 3 shows an image of the TPIL observed for complex **1** excited by a mode-locked femtosecond Ti:Sapphire laser at 740 nm. No linear absorption in the wavelength range from 500 to 820 nm was observed for the platinum(II) complexes. The lack of linear absorption in this region implies that the emission induced by 740 nm excitation could not be attributed to a linear process but rather to a nonlinear process. The upconverted emissions of these complexes are nearly identical with those observed in their corresponding single-photon excited emission spectra. The dependence of the upconverted luminescence intensities on the incident laser power was measured, and the power dependence curve for complex **3** in the thin-film solid state is shown in Figure 4. The inset shows the plot of log(emission intensity) vs log(laser power), which gave a straight line with a slope of 2.15. The nearly perfect quadratic dependence and the slope of ca. 2 in the log(emission intensity) vs log(laser power) plot both in degassed benzene solutions in the concentration range 3 × 10^{-5}−1 × 10^{-6} mol dm^{-3} and in the thin-film solid state further confirm the two-photon nature of the process.

The two-photon absorption cross-sections of the complexes could be determined by comparing their two-photon induced luminescence intensity with the two-photon fluorescence excitation cross-section of rhodamine 6G at a concentration of 2.65 × 10^{-5} mol dm^{-3} as the reference, according to eq 1:

$$\sigma_{2(s)} = \frac{C_r n_r \Phi_r S_s}{C_s n_s \Phi_s S_r} \sigma_{2(r)} \quad (1)$$

where σ_2 is the two-photon absorption cross-section, C is the concentration, n is the refractive index, Φ is the luminescence quantum yield, and S is the integrated luminescence signal. The subscripts r and s refer to the reference and the sample material, respectively. The luminescence quantum yields and two-photon absorption cross-sections of complexes **1**−**3** are summarized in Table 2. The obtained σ_2 values of these branched multi-

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nuclear platinum(II) complexes are about 2−3 times larger than for most other mononuclear platinum(II) complexes that are structurally related to bis((4-(phenylethynyl)phenyl)ethynyl)-bis(tributylphosphine)platinum(II), with reported σ_2 values generally in the range of ∼5−10 GM,[36−38,40] probably due to the increased number of chromophoric units in the branched complexes. An enhancement in TPA cross-section was noted upon incorporation of the relatively more electron-rich tolyl moieties at the periphery in complex **1** in comparison to the naphthyl moieties in complex **2**. This provides a convenient handle for the enhancement of TPA cross-section by a simple modification of the peripheral substituents. In view of the readily tunable directional energy transfer within different moieties of the molecule, these complexes represent a new class of versatile materials for the preparation of TPIL materials with different emission characteristics.

In summary, multinuclear platinum(II) alkynyl complexes are found to show two-photon absorption and two-photon induced luminescence properties. The substituents of these complexes could be readily modified with electron-donating or -withdrawing substituents, which provides a handle for the perturbation of both the emission energies and TPA cross-sections. Work is in progress to study the structure−property relationship of the substituents on the two-photon absorption cross-sections and two-photon induced luminescence properties of the platinum(II) alkynyl complexes.

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Supporting Information Available: Tables giving crystal data, atomic coordinates, thermal parameters, and all bond distances and angles for complex **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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