

Contents lists available at ScienceDirect

### Journal of Organometallic Chemistry



journal homepage: www.elsevier.com/locate/jorganchem

# Synthesis, characterization, luminescence and nonlinear optical (NLO) properties of truxene-containing platinum(II) alkynyl complexes

Carmen Ka Man Chan<sup>a</sup>, Chi-Hang Tao<sup>a</sup>, King-Fai Li<sup>b</sup>, Keith Man-Chung Wong<sup>a</sup>, Nianyong Zhu<sup>a</sup>, Kok-Wai Cheah<sup>b,\*\*</sup>, Vivian Wing-Wah Yam<sup>a,\*</sup>

<sup>a</sup> Institute of Molecular Functional Materials<sup>1</sup>, Department of Chemistry and HKU-CAS Joint Laboratory of New Materials, The University of Hong Kong, Pokfulam Road, Hong Kong, PR China

<sup>b</sup> Centre for Advanced Luminescence Materials, Hong Kong Baptist University and Department of Physics, Hong Kong Baptist University, Kowloon, Hong Kong, PR China

#### ARTICLE INFO

Article history: Received 15 July 2010 Received in revised form 14 September 2010 Accepted 17 September 2010

Keywords: Luminescence Platinum(II) complexes Truxene Metal alkynyls Two-photon induced luminescence Transient absorption

#### 1. Introduction

#### ABSTRACT

A series of luminescent trinuclear platinum(II) alkynyl complexes containing dihydro-5*H*-diindeno[1,2-a;1',2'-c]fluorene (truxene) as the core and aryl alkynyl ligands with different electronic properties at the periphery has been successfully synthesized and characterized. The electronic absorption, emission, nanosecond transient absorption and electrochemical properties of these complexes have been reported. These complexes showed long-lived emissions in degassed benzene solution at room temperature, and their emissions have been assigned to originate from triplet states of intraligand (IL) character with some mixing of metal-to-ligand charge-transfer (MLCT) character. The luminescent platinum(II) alkynyl complexes are found to show two-photon absorption (2PA) and two-photon induced luminescence (TPIL) properties, and their two-photon absorption cross-sections have been determined to be 6–51 GM upon excitation at 720 nm.

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There has been a growing interest in the development of organic  $\pi$ -conjugated molecules in material chemistry due to their potential application in a wide range of electronic and optical devices [1–8]. One of the most challenging goals in material chemistry is to develop new classes of  $\pi$ -conjugated materials with new branches and cores, in order to investigate their physical and chemical properties, as well as their structure–property relationship within the molecules. Star-shaped molecules are branched macromolecules that consist of linear conjugated chains, which are joined together by a central core [9,10]. In contrast to polymers and small molecules, rigid star-shaped molecules and extended  $\pi$ -conjugated dendrimers possess interesting properties, such as electrical, optical, nonlinear optical and electroluminescent properties, and optoelectronic devices including organic light-emitting diodes (OLEDs) based on these materials have been reported [9–14].

Moreover,  $\pi$ -conjugated dendrimers with large building blocks can exhibit two or three-dimensional architecture, which may overcome luminescence quenching and improve the film formation capability [15,16].

10,15-Dihydro-5*H*-diindeno[1,2-*a*;1',2'-*c*]fluorene (truxene) appears to be a promising building block for the construction of functional materials due to its rigid structures, good thermal and chemical stabilities and high quantum yields [9–13,17]. Truxene is a heptacyclic aromatic system with C<sub>3</sub> symmetry, which has been recognized as a potential starting material for the construction of larger polyarenes, bowl-shaped fragments of fullerenes, liquid crystalline compounds and C<sub>3</sub> tripodal compounds in asymmetric catalysis and chiral recognition [9-13]. The structure of truxene consists of three fluorene moieties sharing a central benzene ring, which represents an excellent choice as a core for the construction of star-shaped molecules [9-13]. It is believed that the truxene  $\pi$ -system would have similar properties as the fluorene  $\pi$ -system, which has been demonstrated to be an efficient building block for chromophores with high two-photon absorptivities [17]. Unlike the one-dimensional quadrupolar fluorene chromophore, this attractive dendritic truxene building block can be readily functionalized at C-2. C-7 and C-12 positions and C-5. C-10 and C-15 positions. respectively, by virtue of its three-dimensional topology, to build

<sup>\*</sup> Corresponding author. Tel.: +852 2859 2153; fax: +852 2857 1586.

<sup>\*\*</sup> Corresponding author. Tel.: +852 3411 7029.

*E-mail addresses:* kwcheah@hkbu.edu.hk (K.-W. Cheah), wwyam@hku.hk (V.W.-W. Yam).

<sup>&</sup>lt;sup>1</sup> Areas of Excellence Scheme, University Grants Committee (Hong Kong).

<sup>0022-328</sup>X/\$ – see front matter @ 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.jorganchem.2010.09.044

octupolar or dendritic chromophores [9,10,17,18]. Since unsubstituted truxene is sparingly soluble in common organic solvents [18], introducing alkyl groups around the rim can enhance the solubility of the compound, which might increase the yield and facilitate the isolation of the desired products. This star-shaped truxene molecule has received much attention in the field of liquid crystals and self-association in solution [18–26]. Continuation of the development of these organic  $\pi$ -conjugated molecules or dendrimers has been pursued by several research groups, who have reported the synthesis of a number of truxene-containing compounds and the study of their optical properties [9–11,14,17,27–36].

Although different metal centres could be incorporated into the conjugated system, platinum atoms are preferred due to their strong excited state absorptions in the visible region and their relatively large spin-orbit coupling [37–44]. Because of their longlived <sup>3</sup>IL and <sup>3</sup>MLCT emissions, platinum(II) alkynyl-based conjugated polymers and oligomers have received much interest [45]. Various platinum complexes, oligomers and metallopolymers with different spacers and chain lengths have been reported by Lewis et al. [46,47], Raithby et al. [48–51], Schanze et al. [52–54], Gladysz et al. [55-57], Wong et al. [58-61] and others [62-64], and some of them have proven to be versatile and promising building blocks for the development of multinuclear luminescent complexes [52,64-68]. The incorporation of platinum(II) alkynyl complexes and polymers has attracted attention in the fields of nonlinear optics, such as optical limiting, two-photon absorption and twophoton induced luminescence [37,39,42,58,69,70]. Therefore, the study of nonlinear optical platinum(II) alkynyl polymers and molecular materials has received much attention, but most of these complexes are mononuclear and are structurally related to the (4phenylethynyl)phenylethynyl backbone [38,39,42,43].

Although organic chromophores with truxene have been synthesized, their two-photon absorption properties have not been much explored [14,17,71]. In contrast to truxene-containing organic chromophores, the construction of truxene-core coordination compounds was also relatively unexplored [72–74]. Recent works in the construction of linear and branched luminescent platinum(II) alkynyl complexes by Yam and coworkers [69,70,75–80] have also provided the motivations for the design and construction of bimetallic and polymetallic alkynyl complexes with different central cores. Herein, we report the design, synthesis, characterization and luminescence properties of a series of branched platinum (II) complexes with truxene as the core and aryl alkynyl ligands containing groups with different electronic properties, such as methoxybenzene, 2,5-diphenyl-[1,3,4]oxadiazole and naphthalene, as the peripheral units. The nanosecond transient absorption spectra of these complexes have been studied. The X-ray crystal structure of  $[{(MeOC_6H_4C \equiv C)(PPh_3)_2PtC \equiv C}_3truxene]$  (4) has also been determined.

#### 2. Experimental

#### 2.1. Materials and reagents

2-(4-Ethynylphenyl)-5-phenyl-1,3,4-oxadiazole[81] and [{Cl (PEt<sub>3</sub>)<sub>2</sub>PtC $\equiv$ C}<sub>3</sub>-truxene[70] were synthesized according to literature procedures. Triethynylhexabutyltruxene[82] and *trans*-[MeOC<sub>6</sub>H<sub>4</sub>C $\equiv$ C(PPh<sub>3</sub>)<sub>2</sub>PtCl][83] were prepared according to slight modification of reported procedures. *Trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (Aldrich, 98%), 1-ethynyl-4-methoxybenzene (Maybridge, 97%), 1-ethynylnaphthalene (Aldrich, 97%), and fluorescein (Acros, 99% pure, laser grade) were purchased and used as received. All solvents were purified and distilled using standard procedures before use. All other reagents were of analytical grade and were used as

received. All amines were distilled over potassium hydroxide and stored in the presence of potassium hydroxide prior to use.

#### 2.2. Physical measurements and instrumentation

<sup>1</sup>H NMR spectra were recorded on a Bruker DPX 300 (300 MHz) or a Bruker DPX 400 (400 MHz) Fourier-transform NMR spectrometer with chemical shifts in ppm ( $\delta$ ) reported relative to tetramethylsilane, Me<sub>4</sub>Si, while <sup>31</sup>P{<sup>1</sup>H} spectra were recorded either on a Bruker DPX 400 or a Bruker DPX 500 MHz Fourier-transform NMR spectrometer with chemical shifts relative to 85% H<sub>3</sub>PO<sub>4</sub>. IR spectra were obtained as KBr disks on a Bio-Rad FTS-7 Fouriertransform infrared spectrophotometer (4000–400 cm<sup>-1</sup>). Positiveion fast-atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT95 mass spectrometer or a Thermo Scientific DFS High Resolution Magnetic Sector mass spectrometer. Elemental analyses were performed on a Flash EA 1112 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences in Beijing.

UV-Vis absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state excitation and emission spectra obtained at room temperature and at 77 K were recorded on a Spex Fluorolog-2 Model F111 fluorescence spectrofluorometer with a Hamamatsu R928 photomultipler tube (PMT) detector. The solutions were rigorously degassed with at least four successive freeze-pump-thaw cycles. Solid-state photophysical studies were carried out with solid-samples contained in a quartz tube inside a quartz-walled Dewar flask. Measurements of the ethanol-methanol (4:1, v/v) glass or solidsamples at 77 K were conducted by using liquid nitrogen filled in the optical Dewar flask. Emission lifetime measurements were performed by using a conventional nanosecond pulsed laser system. The excitation source used was with a 355-nm output (third harmonic, 8 ns) from a Spectra-Physics Quanta-Ray Qswitched GCR-150 pulsed Nd-YAG laser (10 Hz). Luminescence decay signals were detected by a Hamamatsu R928 photomultiplier tube, recorded on a Tektronix Model TDS-620A (500 MHz, 2 GS  $s^{-1}$ ) digital oscilloscope, and analyzed by using a program for exponential fits.

Photoluminescence quantum yields were measured by the optical dilute method reported by Demas and Crosby [84]. An aqueous solution of quinine sulfate in  $1.0 \text{ N H}_2\text{SO}_4$  has been used as the reference and all samples were irradiated at 365 nm since all the complexes absorb strongly in this region. The refractive index of the samples and the reference solution were 1.501 and 1.333, respectively. The luminescence quantum yield of the reference was 0.55 with excitation wavelength at 365 nm [84].

The two-photon absorption (2PA) cross-section ( $\sigma_2$ ) could be determined by two main methods [85,86]. Two-photon induced luminescence (TPIL) is one of the methods to determine  $\sigma_2$ , in which the luminescence intensity generated by 2PA is measured and used to estimate the  $\sigma_2$  values according to equation (1). An unknown sample is compared to a reference with known  $\sigma_2$  values. Fluorescein (1 × 10<sup>-4</sup> M in 0.1 M NaOH aqueous solution) was used as the reference in the present study [87].

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

where  $\sigma_2$  is the two-photon absorption cross-section, *C* is the concentration, *n* is refractive index,  $\Phi$  is the luminescence quantum yield and *S* is the integrated luminescence signal. The subscripts *r* and *s* represent the reference and the sample material respectively. The  $\sigma_2$  and luminescence quantum yield of fluorescein in 0.1 M NaOH solution (pH ~ 11) at 720 nm were taken to be 19 GM (Gøppert-Mayer, 1 GM =  $1 \times 10^{-50}$  cm<sup>4</sup> s photon<sup>-1</sup> molecule<sup>-1</sup>) and

0.90, respectively [87]. The time-averaged laser power at 720 nm was kept constant for the sample and the reference. The laser pulses were generated by a mode-locked Ti:Sapphire laser (Spectra-Physics, Tsunami) operating at a repetition rate of 85 MHz. The pulses were amplified up to 1 mJ per pulse by the Ti:Sapphire regenerative amplifier (Spectra-Physics, Spitfire) with pulse duration of ~120 fs and repetition rate of 1 kHz. The 720-nm laser output from the OPA (Coherent, TOPAS-C light conversion) was used as the excitation source. The laser output was passed through the sample cell and the luminescence intensity was monitored by the spectrometer system with monochromator (ACTON Research Corporation, SpectraPro 2300i) and photomultiplier tube (Hamamatsu, R636-10). For the power dependence measurements, the laser beam power was altered by using two polarizers, which was partially reflected to a photodiode for the monitoring of the excitation power. The schematic diagram for the experimental setup has been described elsewhere [70].

Transient absorption measurements were performed on an LP920-KS Laser Flash Photolysis Spectrometer (Edinburgh Instruments Ltd, Livingston, UK) at room temperature. The excitation source was the 355 nm output (third harmonic) of a Nd:YAG laser (Spectra-Physics Quanta-Ray Lab-130 Pulsed Nd:YAG Laser) and the probe light source was an Xe900 450 W xenon arc lamp. The transient absorption spectra were detected by an image intensified CCD camera (Andor) with PC plug-in controller, operated by L900 spectrometer software. The absorption kinetics were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix Model TDS3012B (100 MHz, 1.25 GS/s) digital oscilloscope and analyzed using the same software for exponential fit (tail-fit data analysis). Samples were freshly prepared and degassed with at least four freeze-pump-thaw cycles 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.

Cyclic voltammetric measurements were performed using a CH Instruments, Inc., model CHI 750A electrochemical analyzer. Electrochemical measurements were performed in dichloromethane solutions with 0.1 M<sup>*n*</sup>Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte at room temperature. The reference electrode was an Ag/AgNO<sub>3</sub> (0.1 M in acetonitrile) electrode and the working electrode was a glassy carbon electrode (CH Instruments, Inc.) with a platinum wire as the counter electrode. The working electrode surface with first polished with 1 µm alumina slurry (CH Instruments, Inc.) and then with 0.3 µm alumina slurry (CH Instruments, Inc.) on a microcloth (Buehler Co.). It was rinsed with ultrapure deionized water and sonicated in a beaker containing ultrapure deionized water for 5 min. The polishing and sonicating steps were repeated twice and then the working electrode was rinsed under a stream of ultrapure deionized water. The ferrocenium/ferrocene couple (FeCp $_2^{+/0}$ ) was used as the internal reference [88]. All solutions for electrochemical studies were deaerated with prepurified argon gas prior to measurements.

#### 2.3. Synthesis of truxene-containing platinum(II) alkynyl complexes

#### 2.3.1. $[{(MeOC_6H_4C \equiv C)(PEt_3)_2PtC \equiv C}_3truxene]$ (1)

This was synthesized according to modification of a literature procedure for the related platinum(II) phosphine alkynyl complexes [70,77]. [ $\{Cl(PEt_3)_2PtC \equiv C\}_3$ truxene] (0.12 g, 0.10 mmol) and 1-ethynyl-4-methoxybenzene (0.05 g, 0.40 mmol) were dissolved in a mixture of THF (20 mL) and triethylamine (10 mL). Cul (5 mg, 0.03 mmol) was added to this reaction mixture as a catalyst. The yellow mixture was then stirred under nitrogen overnight at room temperature, after which the solvent was removed under reduced pressure. The yellow residue was then dissolved in dichloromethane, washed successively with brine and deionized

water, and dried over anhydrous MgSO<sub>4</sub>. The solution was then filtered, and the solvent was removed under reduced pressure. The vellow residue was subjected to column chromatography on basic alumina oxide (50–200  $\mu$ m) with dichloromethane as the eluent. Subsequent recrystallization of the crude product with dichloromethane-methanol afforded 1 as a yellow solid. Yield: 0.09 g, 37%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si):  $\delta$  0.46 (t, 30H, I = 7.3 Hz;  $-CH_2CH_2CH_3$ ), 0.84-0.93 (m, 12H; -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.24-1.31 (vq, 54H, *J* = 8.0 Hz; -CH<sub>3</sub>), 1.98-2.04 (m, 6H; -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.24-2.27 (m, 36H; -CH<sub>2</sub>P), 2.84-2.91 (m, 6H; -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.79 (s, 9H; -C<sub>6</sub>H<sub>4</sub>OMe), 6.78 (d, 6H, I = 8.7 Hz;  $-C_6H_4-$ ), 7.23 (d, 6H, I = 8.7 Hz;  $-C_6H_4-$ ), 7.29 (d, 3H, J = 8.3 Hz; protons at C-3, C-8, C-13), 7.33 (s, 3H; protons at C-1, C-6, C-11), 8.16 (d, 3H, J = 8.3 Hz; protons at C-4, C-9, C-14). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>, 298 K, relative to 85% H<sub>3</sub>PO<sub>4</sub>): δ 11.00 (s,  $I_{Pt-P} = 2381$  Hz). IR (KBr disk,  $\nu/cm^{-1}$ ): 2099 (m)  $\nu(C \equiv C)$ . Positive-ion FAB-MS: m/z: 2438  $[M + 2]^+$ . Elemental analysis calcd (%) for 1: C 59.17, H 7.20; found: C 58.91, H 7.00.

#### 2.3.2. $[{(C_6H_5 - 0xa - C_6H_4C \equiv C)(PEt_3)_2PtC \equiv C}_3truxene](2)$

The procedure was similar to that for **1** except that 2-(4-ethynylphenyl)-5-phenyl-1,3,4-oxadiazole (0.10 g, 0.40 mmol) was used instead of 1-ethynyl-4-methoxybenzene. Subsequent recrystallization of the crude product with dichloromethane-methanol afforded **2** as a yellow solid. Yield: 0.22 g, 79%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si):  $\delta$  0.47 (t, 30H, J = 7.3 Hz; -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.85-0.94 (m, 12H; -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.26-1.34  $(vq, 54H, I = 8.0 Hz; -CH_3), 1.99-2.04 (m, 6H; -CH_2CH_2CH_3),$ 2.25–2.29 (m, 36H; -CH<sub>2</sub>P), 2.86–2.91 (m, 6H; -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 7.30 (d, 3H, *J* = 8.1 Hz; protons at C-3, C-8, C-13), 7.35 (s, 3H; protons at C-1, C-6, C-11), 7.41 (d, 6H, J = 8.4 Hz;  $-C_6H_4-$ ), 7.52–7.55 (m, 9H;  $-C_{6}H_{5}-$ ), 7.99 (d, 6H, I = 8.4 Hz;  $-C_{6}H_{4}-$ ), 8.13-8.15 (m, 6H;  $-C_6H_4-$ ), 8.18 (d, 3H, J = 8.4 Hz; protons at C-4, C-9, C-13). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>, 298 K, relative to 85% H<sub>3</sub>PO<sub>4</sub>): δ 11.24 (s,  $J_{Pt-P} = 2362$  Hz). IR (KBr disk,  $\nu/cm^{-1}$ ): 2097 (m)  $\nu(C \equiv C)$ . Positive-ion FAB-MS: m/z: 2510  $[M]^+$ . Elemental analysis calcd (%) for 2: C 60.96, H 6.53, N 3.03; found: C 60.88, H 6.42, N 3.46.

#### 2.3.3. $[{(NpC \equiv C)(PEt_3)_2PtC \equiv C}_3truxene](3)$

The procedure was similar to that for 1 except that 1-ethynylnaphthalene (0.06 g, 0.40 mmol) was used instead of 1-ethynyl-4-methoxybenzene. Subsequent recrystallization of the crude product with dichloromethane-methanol afforded 3 as a pale orange solid. Yield: 0.10 g, 40%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si):  $\delta$  0.47 (t, 30H, J = 7.2 Hz;  $-CH_2CH_2CH_2CH_3$ ), 0.84-0.95 (m, 12H; -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.25-1.34 (vq, 54H, *J* = 8.0 Hz; -CH<sub>3</sub>), 1.99–2.04 (m, 6H; -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.25–2.32 (m, 36H; -CH<sub>2</sub>P), 2.86-2.92 (m, 6H; -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 7.31 (d, 3H, *J* = 8.1 Hz; protons at C-3, C-8, C-13), 7.33 (s, 3H; protons at C-1, C-6, C-11), 7.34–7.37 (m, 3H; Np), 7.42–7.49 (m, 9H; Np), 7.62 (d, 3H, I = 8.2 Hz; Np); 7.79 (d, 3H, I = 9.0 Hz; Np), 8.18 (d, 3H, I = 8.1 Hz; protons at C-4, C-9, C-14), 8.51 (d, 3H, J = 9.0 Hz; Np). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>, 298 K, relative to 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  11.55 (s,  $J_{Pt-P} = 2365$  Hz). IR (KBr disk,  $\nu/cm^{-1}$ ): 2089 (m)  $\nu(C \equiv C)$ . Positive-ion FAB-MS: m/z: 2496  $[M]^+$ . Elemental analysis calcd (%) for **3**: C 62.08, H 7.03; found: C 62.33, H 7.24.

#### 2.3.4. $[{(MeOC_6H_4C \equiv C)(PPh_3)_2PtC \equiv C}_3 truxene (4)$

*Trans*-[(MeOC<sub>6</sub>H<sub>4</sub>C $\equiv$ C)(PPh<sub>3</sub>)<sub>2</sub>PtCl] (0.16 g, 0.22 mmol) and triethynylhexabutyltruxene (0.78 g, 0.88 mmol) were dissolved in a mixture of THF (40 mL) and triethylamine (10 mL). Cul (5 mg, 0.03 mmol) was added to this reaction mixture as a catalyst. The yellow suspension was then refluxed under nitrogen overnight, after which the solvent was removed under reduced pressure. The yellow residue was then dissolved in dichloromethane, washed

successively with brine and deionized water, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solution was then filtered, and the solvent was removed under reduced pressure. Further purification was accomplished by column chromatography on basic aluminum oxide (50–200  $\mu$ m), in which the excess trans-[(MeOC<sub>6</sub>H<sub>4</sub>C $\equiv$ C)  $(PPh_3)_2$ PtCl] was first eluted with dichloromethane-*n*-hexane (1:1. v/v) followed by the elution of **4** with dichloromethane. Subsequent recrystallization of the crude product with dichloromethane-methanol afforded **4** as a light yellow crystal. Yield: 0.62 g, 85%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K, relative to Me<sub>4</sub>Si):  $\delta$  0.38 (t, 30H, I = 7.3 Hz;  $-CH_2CH_2CH_2CH_3$ ), 0.74–0.88 (m, 12H; -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.67-1.74 (m, 6H; -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.64-2.72 (m, 6H; -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.67 (s, 9H; -C<sub>6</sub>H<sub>4</sub>OMe), 6.18 (d, 6H, J = 8.8 Hz;  $-C_6H_4-$ ), 6.35 (s, 3H; protons at C-1, C-6, C-11), 6.36 (d, 3H, J = 7.4 Hz; protons at C-3, C-8, C-13), 6.46 (d, 6H, J = 8.8 Hz; $-C_6H_4-$ ), 7.35–7.44 (m, 54H; -PPh<sub>3</sub>), 7.81 (d, 3H, J = 7.4 Hz; protons at C-4, C-9, C-14), 7.82–7.88 (m, 36H; –PPh<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CDCl<sub>3</sub>, 298 K, relative to 85% H<sub>3</sub>PO<sub>4</sub>): δ 18.59 (s,  $J_{Pt-P} = 2639$  Hz). IR (KBr disk,  $\nu/cm^{-1}$ ): 2109 (w)  $\nu(C \equiv C)$ . Positive-ion FAB-MS: m/z: 3301  $[M]^+$ . Elemental analysis calcd (%) for **4**·H<sub>2</sub>O: C 69.49, H 5.35; found: C 69.18, H 5.40.

#### 2.4. Crystal structure determination

Single crystals of [{ $(MeOC_6H_4C\equiv C)(PPh_3)_2PtC\equiv C\}_3$ truxene] (**4**) suitable for X-ray diffraction studies were grown by layering methanol onto a concentrated dichloromethane solution of the complex.

Crystal data for  $[{(MeOC_6H_4C \equiv C)(PPh_3)_2PtC \equiv C}_3truxene]$  (4):  $[C_{192}H_{174}O_3P_6Pt_3]$ ; formula weight = 3300.40, trigonal, space group P321 (No. 150), *a* = 26.425(6) Å, *b* = 26.425(6) Å, *c* = 14.535(3) Å,  $\alpha = 120^{\circ}, \beta = 90^{\circ}, \gamma = 90^{\circ}, V = 8790(3) \text{ Å}^3, Z = 2, D_c = 1.247 \text{ mg m}^{-3},$  $\mu$ (Mo-K<sub> $\alpha$ </sub>) = 2.486 mm<sup>-1</sup>, *F*(000) = 3348, *T* = 173 K. A light yellow crystal of dimensions 0.20 mm  $\times$  0.30 mm  $\times$  0.60 mm was used for data collection at 173 K on an Oxford Diffraction Gemini S Ultra X-Ray single crystal diffractometer using graphite monochromatized Mo-K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods by employing the SHELXS-97 [89] program on PC. Pt, P and many non-H atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97 [90] on PC. There was one third of formula unit in the asymmetric unit. Restraints were applied to the benzene rings, assuming them to be regular hexagon rings with edges of 1.39 Å. Restraints were also applied to the *n*-butyl groups, assuming bond lengths of C–C to be around 1.55(2) Å. The O-C bond lengths were also assumed to be around 1.50(2) Å. The absolute structure was assisted by the calculated Flack absolute structure parameter, which was equal to 0.09(2). According to the SHELXL-97 program [90], all 9198 independent reflections (Rint equal to 0.0578, 6321 reflections larger than  $4\sigma(F_0)$ , where  $R_{\text{int}} = \sum |F_0^2 - F_0^2(\text{mean})| / \sum |F_0^2|$  from a total 22393 reflections were participated in the full-matrix least-squares refinement against  $F^2$ . These reflections were in the range  $-32 \le h \le 31$ ,  $-31 \le k \le 28$ ,  $-17 \le l \le 14$  with  $2\theta_{max}$  equal to 51.36°. In the final stage of least-squares refinement, only Pt and P atoms were refined anisotropically, other non-H atoms were refined isotropically. H atoms were generated by program SHELXL-97 [90]. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms were refined isotropically, and participated in the calculation of final R-indices. Since the structure refinements were against  $F^2$ , Rindices based on  $F^2$  were larger than (more than double) those based on F. For comparison with older refinements based on F and an OMIT threshold, a conventional index  $R_1$  based on observed F values larger than  $4\sigma(F_0)$  was also given (corresponding to Intensity  $\geq 2\sigma(I)$ ).  $wR_2 = \{\sum [w(F_0^2 - F_0^2)^2] / \sum [w(F_0^2)^2]\}^{1/2}$ ,  $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$ . The goodness of fit (GoF) was always based on  $F^2$ : GoF = S =  $\{\sum [w(F_0^2 - F_c^2)^2] / (n - p)\}^{1/2}$ , where *n* was the number of reflections and *p* was the total number of parameters refined. The weighting scheme was:  $w = 1/[\sigma(F_0^2) + (aP)^2 + bP]$ , where *P* was  $[2F_c^2 + Max(F_0^2, 0)]/3$ . Convergence  $((\Delta/\sigma)_{max} = 0.001, av. 0.001)$  for 182 variable parameters by full-matrix least-squares refinement on  $F^2$  reached to  $R_1 = 0.0852$  and  $wR_2 = 0.2272$  with a goodness-of-fit of 1.033; the parameters *a* and *b* for weighting scheme were 0.1522 and 0.00. The final difference Fourier map showed maximum rest peaks and holes of 2.056 (near Pt) and -1.111 eÅ<sup>-3</sup> respectively.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization of the metal complexes

The synthetic routes for the trinuclear truxene-containing platinum(II) complexes were outlined in Scheme 1. The branched platinum(II) bis-alkynyl complexes 1-3 were synthesized using a copper-catalyzed dehydrohalogenation approach with the corresponding precursor complex, [{Cl(PEt<sub>3</sub>)<sub>2</sub>PtC≡C}<sub>3</sub>truxene]. It has been demonstrated that addition of a catalytic amount of copper(I) halide in the preparation of these platinum(II) alkynyl complexes could increase the rate of reaction through transmetallation processes [91]. Triphenylphosphine-containing platinum(II) complex **4** was prepared in a different way from that of its triethylphosphine analogues, in which triethynylhexabutyltruxene and trans-[(MeOC<sub>6</sub>H<sub>4</sub>C $\equiv$ C)(PPh<sub>3</sub>)<sub>2</sub>PtCl] were heated to reflux at elevated temperature so as to enhance the solubility of the starting materials. Complexes 1-4 were obtained in reasonable yields with different alkynyl ligands, which demonstrated that the precursor complex, [{Cl(PEt<sub>3</sub>)<sub>2</sub>PtC=C}<sub>3</sub>truxene], is a versatile starting material for the synthesis of luminescent branched carbon-rich platinum-containing materials.

All the complexes have been characterized by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy, IR spectroscopy, positive FAB mass spectrometry, and gave satisfactory elemental analyses. The IR spectra of these trinuclear truxene-containing platinum(II) alkynyl complexes showed a moderate band at *ca*. 2100 cm<sup>-1</sup>, which is assigned as the  $\nu$ (C=C) stretch due to the alkynyl group attached to the platinum (II) centre. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of complexes **1–4** all showed a singlet signal, which is indicative of the highly symmetrical structure of the molecules, in the range of  $\delta$  11.0–11.6 ppm for the triethylphosphine-containing complexes **1–3** and  $\delta$  18.6 ppm for the triphenylphosphine-containing complex **4**. Platinum satellites with  $J_{Pt-P} \sim 2360$  Hz were observed for complexes **1–3**, which are characteristic of a *trans*-P–Pt–P configuration [92].

#### 3.2. Crystal structure analysis of complex 4

Fig. 1 shows the perspective drawing of complex **4**. The crystal structure determination data is summarized in Table 1, and the selected bond lengths and angles are given in Table 2. Only the *ipso* carbons on the butyl chains and the phenyl rings in the triphe-nylphosphines are shown in the figure. The platinum atoms in complex **4** adopted essentially a *trans*-square planar arrangement with P–Pt–C angles in the range of 84.7(5) and 95.0(5)°. Such slight distortion around the coordination plane was likely due to the coordination constraints imposed by the bulky triphenylphosphine ligands [93,94]. The Pt–C bond distances (1.958(19)–2.049(19) Å), as well as the C=C bond lengths (1.16(3)–1.29(3) Å) are found to be within the expected ranges for platinum(II) alkynyl complexes [62,64,66,76–80]. The distances of the Pt–P bond in **4** were in the



Scheme 1. Synthesis of truxene-containing trinuclear platinum(II) complexes 1-4.

range of 2.268(6) and 2.298(4) Å, which were slightly shorter than those reported previously [83,95]. The bond angles about the alkynyl ligand and the platinum metal centres were in the range of 168.8(15)–170.9(18)°, which were close to the ideal sp-hybridized carbon bond angle and further confirmed the  $\sigma$ -bonded nature of the alkynyl groups in the complex. Out-of-plane twisting of the coordination planes around the platinum atoms in complex **4** has also been observed, similar to that previously reported in other platinum(II) complexes [62,64,66,76–80]. The coordination planes about the platinum atoms were not coplanar with the aromatic rings and gave interplanar angles of around 26.3°. This feature was characteristic of platinum  $\sigma$ -aryl alkynyl complexes [62,64,66,76–80]. The truxene backbone was nearly coplanar with six butyl chains lying out of the aromatic plane, as was expected for the sp<sup>3</sup>-hybridized carbons. No  $\pi$ ··· $\pi$  stacking was found due to the presence of these butyl chains sticking out of the planes from the backbone.

#### 3.3. Electronic absorption spectra of the metal complexes

The electronic absorption spectra of these trinuclear platinum (II) complexes showed intense absorption bands at *ca*.



**Fig. 1.** Perspective drawing of complex **4** with atomic numbering scheme. Only the *ipso*-carbons of the butyl chains and the phenyl groups in triphenylphosphine were shown. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 30% probability level.

354–382 nm with extinction coefficients in the order of  $10^4-10^5$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>. Fig. 2 shows the electronic absorption spectra of [{Cl(PEt\_3)\_2PtC=C}\_3truxene], and complexes **2** and **3** in benzene at room temperature. The photophysical data of complexes **1–4** are summarized in Table 3.

In the view of rich vibronic structure and the very large extinction coefficient observed for the chloroplatinum(II) precursor complex, [{Cl(PEt<sub>3</sub>)<sub>2</sub>PtC=C}<sub>3</sub>truxene], that are comparable to the corresponding truxene alkynyl ligand, a substantial mixing of an intraligand (IL) [ $\pi \rightarrow \pi^*(C=C)_3$ truxene] character of the central alkynyl core unit is likely. In addition, the electronic absorption

Table	1
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Crystal and data collection parameters for	or complex <b>4</b>
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Empirical formula	$C_{192}H_{174}O_3P_6Pt_3$
Formula weight	3300.40
Crystal system	Trigonal
Space group	P 321(No. 150)
a (Å)	26.425(6)
b (Å)	26.425(6)
<i>c</i> (Å)	14.535(3)
α (°)	90.00
β(°)	90.00
γ(°)	120.00
V (Å <sup>3</sup> )	8790(3)
Z	2
$D_{cal} (gcm^{-3})$	1.217
$\mu$ (mm <sup>-1</sup> )	2.486
$F(0\ 0\ 0)$	3348
T (K)	173(2)
Crystal colour	Light yellow
Crystal size	0.30 mm $\times$ 0.20 mm $\times$ 0.15 mm
$\theta$ range for data collection	3.20–25.68°
Index ranges	$-32 \le h \le 31, -31 \le k \le 28, -17 \le l \le 14$
Total reflections collected	22393
Independent reflections	9198 [ $R_{int} = 0.0578$ ]
Completeness to $\theta = 25.68^{\circ}$	98.1%
Data/restraints/parameters	9198/10/182
Goodness-of-fit on F <sup>2</sup>	1.033
Final R-indices $[I > 2\sigma(I)]$	$R_1 = 0.0852, wR_2 = 0.2272^a$
R indices (all data)	$R_1 = 0.1142, wR_2 = 0.2399^a$
Largest diff. peak and hole	2.056 and -1.111 eÅ <sup>-3</sup>

<sup>a</sup>  $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ , where *P* is  $[2F_c^2 + Max(F_0^2, 0)]/3$ .

Table 2

Selected bond distances (Å) and bond angles (°) with estimated standard deviations
(e.s.d.s.) in parentheses for complex <b>4</b> .

Selected bond di	stances (Å)	Selected bond angles ( $^{\circ}$ )	
Pt(1)-C(1)	1.958(19)	C(1)-Pt(1)-C(20)	176.5(7)
Pt(1)-C(20)	2.049(19)	C(20) - Pt(1) - P(1)	178.5(3)
Pt(1)-P(1)	2.298(4)	C(1) - Pt(1) - P(2)	92.2(6)
Pt(1)-P(2)	2.268(6)	C(20) - Pt(1) - P(2)	84.7(5)
C(1) - C(2)	1.29(3)	C(1) - Pt(1) - P(1)	88.2(6)
C(20)-C(21)	1.16(3)	C(20) - Pt(1) - P(1)	95.0(5)
C(25)-O(1)	1.513(18)	C(2) - C(1) - Pt(1)	168.8(15)
C(28)-O(1)	1.542(19)	C(20)-C(21)-Pt(1)	170.9(18)
		C(1)-C(2)-C(3)	161.9(17)
		C(20)-C(21)-C(22)	175(2)
		C(7)-C(11)-C(16)	106.2(15)
		C(10)-C(11)-C(12)	117.2(15)
		C(7)-C(11)-C(12)	109.6(14)
		C(12)-C(11)-C(16)	108.1(15)
		C(10)-C(11)-C(16)	113.0(16)
		C(12)-C(11)-C(6)	108.1(15)

spectra of these complexes in dichloromethane and benzene were found to be nearly identical. These absorption bands were found to be relatively insensitive towards the polarity of the solvents, in accordance with the largely intraligand  $\pi \rightarrow \pi^*$  character of these transitions. A red shift in the absorption energy of triethynylhexabutyltruxene (314–328 nm) to [{Cl(PEt<sub>3</sub>)<sub>2</sub>PtC=C}<sub>3-</sub> truxene] (316-352 nm) to complexes 1-4 (354-382 nm) is observed, which suggests an involvement of the platinum(II) metal centre in such transition. With reference to previous spectroscopic studies on trans-[Pt(PEt<sub>3</sub>)<sub>2</sub>(C $\equiv$ CR)<sub>2</sub>] [96–100], in which the absorption bands at ca. 300-360 nm were assigned to contain a platinum-to-alkynyl metal-to-ligand charge transfer (MLCT) transitions, the low-energy transitions in these branched complexes might also involve a platinum-to-alkynyl MLCT character. Although absorptions due to the IL  $[\pi \rightarrow \pi^*]$  transitions of the peripheral alkynyl ligands may also occur at similar energies in the related systems [96-100], the insensitive nature of the absorption energies in 1-3 to the peripheral alkynyl ligands suggests a minor contribution of the peripheral aryl alkynyl ligands in these low-energy absorptions. Therefore, the lowenergy absorptions in these branched complexes are described as an admixture of IL  $[\pi \rightarrow \pi^*(C \equiv C)_3$ truxene] and MLCT  $[d\pi(Pt) \rightarrow T$  $\pi^*(C \equiv C)_3$  truxene] transitions with predominantly IL character.





Table 3				
Electronic absorption	and emission	data of	complexes	1–4.

Complex	$\lambda_{abs} [nm]$ ( $\epsilon [dm^3 mol^{-1} cm^{-1}]$ ) <sup>a</sup>	Medium (T [K])	λ <sub>em</sub> [nm] (τ <sub>o</sub> [μs])	$\Phi_{ m lum}{}^{ m b}$
1	320 (68200, sh),	C <sub>6</sub> H <sub>6</sub> (298)	515 (21)	0.05
	354 (188900),	solid (298)	517 (4.9)	
	366 (187400)	solid (77)	520 (29)	
		glass (77) <sup>c</sup>	509 (584)	
2	308 (103400),	C <sub>6</sub> H <sub>6</sub> (298)	516 (42)	0.07
	366 (305700)	solid (298)	_d	
		solid (77)	535 (80)	
		glass (77) <sup>c</sup>	516 (243)	
3	308 (60500),	C <sub>6</sub> H <sub>6</sub> (298)	547 (60)	0.06
	356 (203700, sh),	solid (298)	_d	
	364 (208500)	solid (77)	553 (53)	
		glass (77) <sup>c</sup>	540 (513)	
4	342 (80000, sh),	C <sub>6</sub> H <sub>6</sub> (298)	517	_e
	356 (101400, sh),	solid (298)	_d	
	382 (207900)	solid (77)	514 (166)	
		glass (77) <sup>c</sup>	506 (930)	

<sup>a</sup> Measured in C<sub>6</sub>H<sub>6</sub> at 298 K.

 $^b$  The luminescence quantum yield, measured at room temperature using quinine sulfate in 1.0 N  $H_2SO_4$  as the reference (excitation wavelength =365 nm,  $\Phi_{lum}=0.55$ ).

<sup>c</sup> Measured in EtOH-MeOH (4:1, v/v) glass.

<sup>d</sup> Non-emissive.

<sup>e</sup> Not determined.

#### 3.4. Emission properties of the metal complexes

Upon excitation at  $\lambda > 365$  nm. vibronically structured emission bands were observed for complexes 1 (515 nm), 2 (516 nm), and 3 (547 nm) in degassed benzene solutions while the triphenylphosphine-containing complex 4 was weakly emissive (517 nm) at room temperature. All complexes exhibited luminescence at 77 K and showed large Stokes shift and lifetimes in the microsecond range, which are indicative of their triplet parentage. The strong spin-orbit coupling introduced by the heavy platinum(II) centre would enhance the accessibility of the <sup>3</sup>IL  $[\pi \rightarrow \pi^*]$  excited states. The emission data of the complexes are summarized in Table 3. In contrast to the non-emissive behaviour of the precursor complex, [{Cl(PEt<sub>3</sub>)<sub>2</sub>PtC=C}<sub>3</sub>truxene], at room temperature, the bis-alkynyl complexes 1-3 showed intense yellowish green to yellowishorange vibronically structured emission bands at room temperature, with emission maxima at about 515-547 nm. The emission of 1 and 4 were found to occur at nearly identical wavelengths with similar vibronic structures as the emission bands of their corresponding chloroplatinum(II) complexes at 77 K, either in the solid state or in alcoholic glass. The emission energy of 1 and 4 appeared to be insensitive to the peripheral aryl alkynyl ligands. This finding is supportive of a triplet IL emission derived mainly from the central triethynylhexabutyltruxene moiety. However, the emission energies observed for the branched complexes were found to show a red shift on going from palladium complexes to platinum analogues, which suggested the involvement of some triplet MLCT character in the emissive state [76,77,79]. Therefore, the emission of these complexes was assigned as derived from a mixed <sup>3</sup>IL  $[\pi \rightarrow \pi^*(C \equiv C)_3 \text{truxene}]/^3 \text{MLCT} [d\pi(Pt) \rightarrow \pi^*(C \equiv C)_3 \text{truxene}]$  state with predominantly IL character. The emission from the <sup>3</sup>IL state of the peripheral alkynyl ligands was not observed since they are higher-lying in energy. The energy absorbed by the peripheral ligands would be transferred to the central truxene emitting core through directional energy transfer. Similar findings have also been observed in other related branched platinum(II) alkynyl complexes [70,77].

Degassed benzene solution of the branched platinum(II) alkynyl complex **2** with oxadiazole ligand showed intense yellowish green



1220 cm 1609 cm 2134 cm

1230 cm 1596 cm 2133 cm

Fig. 3. Emission spectra of 1 (top), 2 (middle) and 3 (bottom) in ethanol-methanol (4:1, v/v) glass at 77 K. Excitation wavelength at 370 nm.

Wavelength / nm

emission that displayed vibronically structured emission bands at room temperature, with the emission maximum at 516 nm. Its emission maximum was found to be similar to that of complexes 1 and 4. However, the band shapes of this complex either in benzene solution at room temperature or in alcoholic glass at 77 K were different from those observed for **1** and the other analogues (Fig. 3) [70]. With reference to previous spectroscopic studies on [{ClPt  $(PEt_3)_2(C \equiv CC_6H_4)_2$ -oxa-2,5] in alcoholic glass at 77 K (518 nm) [70], the emission of **2** is likely to be originated from similar intraligand triplet excited states that are originated from the peripheral oxadiazole moieties of lower-lying energy, with some mixing of  $d\pi(Pt) \rightarrow \pi^*(C \equiv C-oxa-2,5)^{-3}MLCT$  character. Similarly, complex 3 with polyaromatic peripheral naphthalene-containing ligands was found to emit in the yellowish-orange region at 547 nm, which is red-shifted from its analogues. With reference to previous spectroscopic studies on cis-[Pt(dppe)(C=CNp)<sub>2</sub>] [101], in which the <sup>3</sup>IL emissions of these platinum complexes with polyaromatic naphthyl alkynyl ligands have been observed at similar energies with comparable vibronic structures, the emission of **3** has been assigned as derived from states of <sup>3</sup>IL  $[\pi \rightarrow \pi^*(C \equiv CNp)]$  character. The lack of <sup>3</sup>IL emission from the truxene core could be ascribed to the presence of the lower-lying <sup>3</sup>IL excited state associated with the peripheral NpC $\equiv$ C units, i.e. the energy absorbed by the central truxene core would be

lable 4				
Nonlinear photophysical	data	for complexes	1-3 at	t 298 K

Complex	$\lambda_{em}{}^a/nm$ at $\lambda_{ex}=720~nm$	$\sigma_2/GM$	Power dependence
1	516	12	2.04
2	517	51	1.96
3	549	6	1.73

<sup>a</sup> Measured in C<sub>6</sub>H<sub>6</sub>.

transferred to the lowest energy emissive state of the peripheral ligands. Therefore, the emission of **3** is assigned as derived predominantly from the <sup>3</sup>IL states of the naphthyl alkynyl moieties with some mixing of  $d\pi(Pt) \rightarrow \pi^*(C \equiv CNp)^3$ MLCT character [70,77].

The emission spectrum of the complexes **1** and **4** in 77 K glass showed rich vibronic structures with vibrational progressional spacings of *ca*. 1220 and 2100 cm<sup>-1</sup>, typical of the aromatic ring deformation and the  $\nu$ (C $\equiv$ C) vibrational modes, respectively. Additional vibronic structures with progressional spacings of *ca*. 1098 and 1555 cm<sup>-1</sup> from the highest energy emission band in complex **2** were also observed, with the former corresponding to the  $\nu$ (C=O) stretch and the latter to the  $\nu$ (C=C) and  $\nu$ (C=N) vibrational modes. Vibrational progressional spacings of *ca*. 1380 cm<sup>-1</sup> were observed in the emission spectrum of complex **3**, indicative of the  $\nu$ (C=C) stretching mode of aromatic rings. The emission lifetimes in the solid state at room temperature are considerably shorter than that observed in dilute solutions, which may be ascribed to originate from triplet–triplet annihilation or self-quenching in the solid state.

## 3.5. Two-photon induced luminescence (TPIL) properties of the metal complexes

Complexes **1–3** are found to emit in the yellowish green and yellowish orange regions in benzene solutions upon excitation with a mode-locked femtosecond Ti:Sapphire laser at 720 nm. Table 4 shows the emission maxima and two-photon absorption cross-section  $\sigma_2$  at 720 nm determined using TPIL study. Fig. 4 shows the TPIL spectrum of complex **2** in benzene at room temperature. No linear absorption in the wavelength range of 500–820 nm was observed for these platinum(II) complexes, indicating that the



**Fig. 4.** Two-photon induced luminescence spectrum of complex **2** in benzene at room temperature upon excitation with a mode-locked femtosecond Ti:Sapphire laser at 720 nm.

emission induced by 720-nm excitation could not be attributed to a linear process but rather to a nonlinear process. The upconverted emissions of these complexes were nearly identical to that observed in their corresponding single-photon excited emission.

The dependence of the upconverted luminescence intensities on the incident laser power was measured and a typical power dependence curve of complex 2 in benzene solution at room temperature is shown in Fig. 5 as an example. The inset shows the plot of log(emission intensity) vs. log(laser power) that gave a straight line with a slope of 1.96. Since the 2PA has a quadratic dependence on intensity and the TPIL would be expected to show intensity dependence on the excitation power, theoretically, the log (emission intensity) vs. log(laser power) should give a straight line with a slope of 2 [43]. Therefore, the observed quadratic dependence of the emission intensity on the incident laser power further confirmed the two-photon nature of the process. The  $\sigma_2$ values of these branched complexes with excitation wavelength at 720 nm have been determined using the TPIL method and were found to be in the range of 6–51 GM, which are comparable to the values of 5–10 GM observed in other platinum(II) alkynyl complexes [38,40,43]. Through a systematic comparison study of these complexes, the  $\sigma_2$  values were found to be slightly dependent on the electronic properties of the peripheral substituents. In general, higher  $\sigma_2$  values could be observed for complexes with relatively more electron-rich or electron-deficient peripheral substituents. Complex **2** gave the greatest  $\sigma_2$  values among these truxene-containing complexes. It was interesting to note that incorporation of oxadiazole, which is a well-known electron-deficient moiety, would create a large change in the dipole moment within the molecules, which led to larger  $\sigma_2$  values. However, complex **3** did not give rise to an increase in  $\sigma_2$  values as compared to its analogues [70], because the naphthyl moieties are less electron-rich than the tolyl groups, which has been reported previously by our group [69]. These findings have demonstrated that truxene serves as a promising building block for the construction of two-photon induced luminescent materials. Through the incorporation of  $[{Cl(PEt_3)_2PtC \equiv C}_3truxene]$  and alkynyl ligands with different electronic properties, a versatile handle for the tuning of the  $\sigma_2$  values and the emission energies of this class of complexes could be readily achieved.



**Fig. 5.** Power dependence of the upconverted luminescence intensity of complex 2 in benzene at 298 K. The line ( $\blacksquare$ ) shows the theoretical curve for the quadratic function. The inset shows the log(emission intensity) ( $\blacktriangle$ ) vs. log(laser power) and its linear regression.



**Fig. 6.** Transient absorption difference spectra of **1** (top), **2** (middle) and **3** (bottom) in degassed benzene solution at 298 K following 355 nm pulsed excitation. The inset shows the transient absorption decays.

#### 3.6. Transient absorption properties of complexes 1-3

In order to provide additional information on the properties of the triplet state of the platinum(II) phosphine complexes produced by photoexcitation, nanosecond transient absorption spectra were measured at room temperature in degassed benzene solution.

#### Table 5

Electrochemical data for truxene-containing trinuclear branched platinum(II) alkynyl complexes at 298 K.<sup>a,b</sup>

Complex	Oxidation $E_{pa}^{c}$ [V versus S.C.E.]
1	+0.99, +1.29, +1.49
2	+0.96, +1.19, +1.65
3	+0.94, +1.09, +1.45
4	+0.99, +1.30

<sup>a</sup> Working electrode, glassy carbon; scan; scan rate = 100 mV s<sup>-1</sup>.

<sup>b</sup> Measured in dichloromethane (0.1 M <sup>*n*</sup>Bu<sub>4</sub>NPF<sub>6</sub>).

 $E_{pa}$  is the peak anodic potential.

These experiments were conducted with 355 nm pulses from a Nd:YAG laser. All the complexes exhibited strong bleaching bands at *ca*. 350–400 nm in the near-UV to blue region, with a broad and moderately intense excited state absorption feature extending throughout the whole visible region with a maximum between 400 and 700 nm. These findings are comparable to those observed in other related platinum(II) diphosphine alkynyl monomers and polymers [42,44,53,102–109]. The transient absorption spectra for complexes **1–3** are shown in Fig. 6.

The negative difference absorption bands found at ca. 370 nm for complexes **1–3** are characteristic of the  $\pi,\pi^*$  (S<sub>0</sub> $\rightarrow$ S<sub>1</sub>) absorption [44,103,106,109]. The bands of the ground-state bleaching represented the ground-state absorption of the central triethynylhexabutyltruxene and the peripheral alkynyl moieties. The positive bands that occurred at 400–700 nm for these complexes could be assigned as derived from the  ${}^{3}\pi,\pi^{*}$  absorption of the triplet excited state. The transient absorption decay lifetimes in each case are found to be comparable to that of their emission decay lifetimes, which supported the assignment of a transient absorption due to the triplet-triplet transition from the lowest energy triplet excited state [109]. The transient absorption spectrum of **3** showed a broad excited state absorption at  $\lambda_{max} \sim 550$  nm with a lifetime of 62 µs. This absorption is believed to arise from the  ${}^{3}\pi,\pi^{*}$  excited-state localized on the peripheral naphthalenecontaining ligands. Similar findings have been observed for a mononuclear platinum(II) bis(pyrenylethynyl) complex reported by Ziessel and Castellano [102,104].

#### 3.7. Cyclic voltammetry of the metal complexes

The electrochemical properties of the trinuclear platinum(II) alkynyl complexes containing truxene as the core have been investigated in dichloromethane (0.1 M  $^{n}$ Bu<sub>4</sub>PF<sub>6</sub>) by cyclic voltammetry and the data are summarized in Table 5. No observable reductive wave for all the complexes upon scanning up to -2.0 V vs. S.C.E. was found, which is similar to that reported in other structurally related platinum(II) alkynyl complexes [70,77,79,80,110,111].

The oxidative scans of complexes **1**–**4** show two to three irreversible waves at +0.94 to +0.99, +1.09 to +1.30 and +1.45 to +1.65 vs. S.C.E. In the view of the observation of a similar first oxidation of its chloroplatinum(II) precursor complex [{Cl(PEt\_3)\_2PtC=C}\_3-] truxene] (+1.06 V vs. S.C.E.) [70], the first irreversible oxidation waves of complexes **1**–**4** are probably due to the central triethy-nylhexabutyltruxene moiety. The irreversible oxidation waves of these complexes might also involve a certain degree of metal-centred character. Therefore, the irreversible oxidation waves of this class of complexes could best be described as ligand-centred oxidation with some mixing of a metal-centred character.

#### 4. Conclusions

Several trinuclear luminescent platinum(II) alkynyl complexes of truxene were successfully synthesized and characterized. The

electronic absorption spectra of these complexes are dominated by intraligand  $[\pi \rightarrow \pi^*(C \equiv C)_3$  truxene] transitions, mixed with some  $[d\pi(Pt) \rightarrow \pi^*(C \equiv C)_3 \text{truxene or } C \equiv CR] \text{ MLCT and IL } [\pi \rightarrow \pi^*(C \equiv CR)]$ character. These complexes were found to be emissive at room temperature with rich vibronic structures. These complexes were also found to show 2PA, and their 2PA cross-sections at excitation wavelength at 720 nm have been determined. The emissions of these complexes could be readily tuned by incorporation of alkynyl ligands with different electronic properties.

#### Acknowledgements

V.W.-W.Y. acknowledges support from The University of Hong Kong under the Distinguished Research Achievement Award Scheme, and the UGC Strategic Research Theme on Molecular Materials. The work described in this paper has been supported by the University Grants Committee Areas of Excellence Scheme (AoE/ P-03/08) and the Special Equipment Grant (SEG\_HKU07). C.K.M.C. acknowledges support from The University of Hong Kong and the receipt of a University Postgraduate Studentship. C.-H.T. acknowledges support from The University of Hong Kong and the receipt of a University Postdoctoral Fellowship. Dr. C.C. Ko is gratefully acknowledged for his kind assistance in the crystallographic data collection.

#### Appendix. Supplementary data

CCDC 784318 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge via http://www. ccdc.cam.ac.uk/conts/retreving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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