

# Alternative preparation and characterization of platinum(II) organometallic dinuclear complexes and oligomers with 3,8-diethynylphenanthroline derivatives

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## Abstract

Novel platinum(II) organometallic dinuclear complexes and oligomers with two types of phenanthroline ligands, the 3,8-diethynylphenanthroline (**L1**) and 3,8-bis-(4-ethynyl-phenylethynyl)-1,10-phenanthroline (**L2**), were synthesized with *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>(1-ethynyl-4-methyl-benzene)Cl and *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> by transmetalation of copper ion. The alternative procedure targeted platinum oligomer termination selection of either chloride or respective phenanthrolines, and was successfully performed with different purifications of extraction and column chromatography. The terminal structure of present platinum complexes and oligomers was revealed with by analysis of both <sup>31</sup>P{<sup>1</sup>H}-NMR and <sup>1</sup>H-NMR spectral data. Alternative preparations of platinum oligomers with two types between chloride and respective phenanthroline termination are very useful for the selective synthesis for hybrid polymer with the coupling reaction with two different platinum oligomers with different diethynylaryl ligands. The platinum organometallic compounds showed similar absorption bands in the UV-Vis region. Those prepared with **L1** had a strong absorption band at around 400 nm, assignable to the lowest energy metal-perturbed <sup>1</sup>[ $\pi$ - $\pi^*$ ] transitions, while in compounds prepared with **L2**, the strong band appeared around 410 nm, because **L2** has an extended  $\pi$  conjugation relative to **L1**. No distinct differences were observed in the absorption spectra of these platinum oligomers between the different terminal structures, chloride or various phenanthrolines. The luminescence spectra of the platinum compounds prepared with either **L1** or **L2**, however, showed a distinct difference. Those with **L1** showed only a phosphorescence assignable to a typical metal-perturbed <sup>3</sup>[ $\pi$ - $\pi^*$ ] transition with vibronic progressions centered at around 530 nm in deoxygenated CH<sub>2</sub>Cl<sub>2</sub> at room temperature,

while those with **L2** showed weak dual emissions assignable to a mixture of typical metal-perturbed  $^1[\pi-\pi^*]$  and  $^3[\pi-\pi^*]$  transition in the visible region.

**Keywords:** Platinum; Organometallic oligomer; Phenanthroline; Phosphorescence; Dual emissions

## Introduction

Research regarding many kinds of metal-alkynyl organometallic complexes and oligomers continues to inspire structurally unique rigid-rod polymers with respect to their potential applications in the field of optical and electronic devices [1-8]. Extensive studies of platinum(II) bis-phosphine organometallic oligomers with many kinds of diethynylarene ligands have been carried out to determine the photophysical properties of two-photon chromophores, nonlinear optics, and solar cell applications over the past two decades [9-18]. In particular, photophysical studies of platinum(II) complexes and oligomers with diethynyl-substituted imine ligands, such as pyridine, bipyridine, and terpyridine derivatives, have been reported by several groups [19-22]. This is because multinuclear complex systems with platinum(II) organometallic units and other metal complex units coordinated to polypyridine derivatives are expected to open up a new area in supramolecular chemistry. As a part of this research trend, we have previously reported the photophysics of platinum(II) organometallics and ruthenium(II)-platinum(II) supramolecular complex with 3-ethynylphenanthroline [23]. Furthermore, the photophysical study of similar supramolecular complex polymer with iridium(II)-platinum(II) system has recently been reported by Harvey's group [24]. However, to the best of our knowledge, platinum(II) organometallic oligomers linked with diethynylphenanthroline derivatives have not yet been reported. The molecular framework of phenanthroline is rigid and flat compared to bipyridine, and the solubility of ruthenium and iridium complexes with phenanthroline for general organic solvents is different from their complexes with bipyridine. We therefore became interested in the preparation and photophysical properties of new platinum(II) organometallic complexes and oligomers linked with two phenanthroline ligands, including diethynyl-substituent at the 3- and 8- position, as shown in Fig. 1.

We report herein an alternative preparation and photophysical characterization of novel dinuclear platinum complexes, **D1** or **D2** with *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>(1-ethynyl-4-methyl-benzene)Cl and 3,8-diethynylphenanthroline (**L1**) or 3,8-bis-(4-ethynyl-phenylethynyl)-1,10-phenanthroline (**L2**), platinum(II) organometallic oligomers, **O1-Cl** and **O1-Phen**, with *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and **L1**, and similar platinum(II) oligomers, **O2-Cl** and **O2-Phen**, with *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and **L2** as a further extending  $\pi$  conjugated ligand (Fig. 1). Structural determinations of the platinum oligomers considered, including either chloride or respective phenanthroline ligands, **O-Cl** or **O-Phen**, at the oligomer terminations, were revealed by the analysis comparing the <sup>31</sup>P{<sup>1</sup>H}-NMR and <sup>1</sup>H-NMR spectral data of the compounds with those of **D1**, **D2**, and previously reported platinum oligomers, as shown in Fig. 2 [25-29]. Alternative preparations of platinum oligomers with two types between chloride and respective phenanthroline termination are very useful for the selective synthesis for hybrid polymer with the coupling reaction with two different platinum oligomers with different diethynylaryl ligands.

## Results and discussion

### Synthesis and characterization of dinuclear complexes, **D1** and **D2**

Two types of phenanthroline ligands including two terminal C≡C–H units, 3,8-diethynylphenanthroline (**L1**) and 3,8-bis-(4-ethynyl-phenylethynyl)-1,10-phenanthroline (**L2**), were synthesized by Sonogashira coupling reaction in good yields. Novel dinuclear platinum complexes, **D1** and **D2**, were synthesized for the structural characterization of the corresponding platinum oligomers **O1** and **O2**, as shown in Fig. 1. The complex *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>(1-ethynyl-4-methyl-benzene)Cl, **CIPt(PBu<sub>3</sub>)<sub>2</sub>(ETol)**, in Fig. 2 was prepared due to high-yield synthesis of **D1** and **D2** by a similar method in Schanze's group [30]. Complex **D1** or **D2** was prepared by reacting **CIPt(PBu<sub>3</sub>)<sub>2</sub>(ETol)** and the respective phenanthroline ligand **L1** or **L2** (2:1 ratio) with 5% copper iodide for transmetalation. Dinuclear complexes **D1** and **D2** were characterized by IR, <sup>1</sup>H-NMR, <sup>31</sup>P{<sup>1</sup>H}-NMR spectroscopy and elemental analysis.

The elemental analysis results of **D1** and **D2** are in accordance with the structures shown in Fig. 1. IR spectra of **D1** and **D2** indicated the η<sup>1</sup> coordination of metal-carbon bonds between the Pt atom and their ethynyl functional groups, **L1** and **L2**. The characteristic strong ν(C≡C) bands in **D1** and **D2** were observed at 2098 cm<sup>-1</sup>. The ν(CC–H) bands in **L1** and **L2** at around 3175 cm<sup>-1</sup> disappeared in the spectra of **D1** and **D2**. In addition, the ν(C≡C) band assigned to the ethynyl substituent between phenanthroline and the phenyl group in **L2** (2210 cm<sup>-1</sup>) remained almost intact in **D2** (2205 cm<sup>-1</sup>). Formation of the Pt–C≡C bond was further supported by the <sup>1</sup>H-NMR measurements. No assignable signal for the ethynyl proton (**L1** (3.39 ppm) or **L2** (3.22 ppm) in CDCl<sub>3</sub>) was detected in **D1** and **D2**, and all observed signals corresponded to the protons of their phenanthroline derivatives, ethynyltoluene and tributylphosphine in accurate proportions.

Table 1 lists the <sup>31</sup>P{<sup>1</sup>H}-NMR data of the compounds in Fig. 1, and the several platinum compounds with ethynylbenzene and/or diethynylbenzene reported by Schanze et al. [25] and Sterzo et al. [26] in Fig. 2. Only one signal set of pseudo triplets was observed in the CD<sub>2</sub>Cl<sub>2</sub> solution of **CIPt(PBu<sub>3</sub>)<sub>2</sub>(ETol)**, as shown in Fig. S1. This indicates that **CIPt(PBu<sub>3</sub>)<sub>2</sub>(ETol)** was the site of trans configuration for two ligands of tributylphosphine on the platinum center, because the orthogonalized configuration of this complex would show two signal sets of pseudo triplets for different trans influence of the two other ligands between chloride and ethynyltoluene. All compounds listed in Table 1 are also estimated as trans configuration because similar previously reported platinum complexes have mostly been assigned as trans configuration [25-29], and the chemical shift for the present compounds showed the same values regardless of whether a trans or cis isomer of Pt(PBu<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> was used for their preparation.

Furthermore, notable results between two types of platinum complexes, CIPt(PBu<sub>3</sub>)<sub>2</sub>(ethynyl ligand) as **1-3** and Pt(PBu<sub>3</sub>)<sub>2</sub>(ethynyl ligand)<sub>2</sub> as **5** and **6**, were distinguishable according to their values of chemical shift in Table 1, although the values of coupling constant J(<sup>31</sup>P-<sup>195</sup>Pt) were almost the same in these compounds. The chemical shifts

for **1-3** were observed at around 7 ppm, while those for **5** and **6** were observed at around 4 ppm [25, 26]. A similar signal set of pseudo triplets was observed in the CD<sub>2</sub>Cl<sub>2</sub> solution of **D1** and **D2**, as shown in Fig. S2. The chemical shifts of **ClPt(PBu<sub>3</sub>)<sub>2</sub>(ETol)** (6.83 ppm), **D1** (3.27 ppm), and **D2** (3.27 ppm) mostly corresponded with those of previous compounds **1-7** in Fig. 2, although the signals of these compounds were observed a little bit up-field of those of **1-7** [25, 26]. This result is clearly reflected in the differences between the two types of coordination structures, Cl–Pt(PBu<sub>3</sub>)<sub>2</sub>–C≡C and C≡C–Pt(PBu<sub>3</sub>)<sub>2</sub>–C≡C, through the chemical shift of <sup>31</sup>P-NMR in two tributylphosphine ligands coordinated to the platinum center in these complexes. The discriminant criterion between Cl–Pt(PBu<sub>3</sub>)<sub>2</sub>–C≡C and C≡C–Pt(PBu<sub>3</sub>)<sub>2</sub>–C≡C conformations revealed by the difference of <sup>31</sup>P-NMR chemical shifts in these platinum compounds is very useful for the discussion of the termination structure of the platinum oligomers between **O1-Cl** and **O1-Phen**, as well as between **O2-Cl** and **O2-Phen**, including the previously reported oligomers **4** and **7**, as described in the next section.

### Alternative procedure and characterization of platinum oligomers

Investigation of the reaction condition between **L1** (or **L2**) and *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> was performed for high-yield synthesis of the soluble platinum organometallic oligomer to the organic solvents because the amounts of the insoluble platinum-**L1** (or platinum-**L2**) polymers were easily changed under different reaction conditions such as temperature, solvents, time, etc. Many studies have reported searching for the reaction condition to obtain soluble platinum-diethynylaryl organometallic oligomers with *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and many types of aromatic compounds, including two ethynyl substituent groups [9-22, 25-29]. The present soluble platinum oligomers to CH<sub>2</sub>Cl<sub>2</sub>, **O1** and **O2**, were successfully obtained in moderate yields accompanied by insoluble polymers via the preparation described in the experimental section. The structural similarity between the insoluble and soluble compounds was confirmed with the IR spectra of these compounds.

We succeeded in developing an alternative procedure to achieve two terminations between chloride and phenanthroline for the oligomers **O1** and **O2** by different purification after the same reaction condition. The platinum oligomers with chloride termination as **O1-Cl** and **O2-Cl** illustrated in Fig. 1 were obtained under the present reaction condition regardless of whether a THF or CH<sub>2</sub>Cl<sub>2</sub> was used as a solvent, while platinum oligomers with phenanthroline termination as **O1-Phen** and **O2-Phen** (Fig. 1) were scarcely synthesized in the present reaction condition. The deduction was performed with the <sup>31</sup>P{<sup>1</sup>H}-NMR data of reaction mixtures before the purification. However, the oligomers with phenanthroline termination **O1-Phen** and **O2-Phen** were selectively obtained when the extract operation with CH<sub>2</sub>Cl<sub>2</sub> and KCN aqueous solution was performed for pulling out copper ions of the catalyst and diisopropylammonium chloride to the KCN solution.

On the other hand, platinum oligomers with chloride termination **O1-Cl** and **O2-Cl** were obtained when alumina column chromatography was used to separate them from other substances. We therefore deduced that changing the termination from **O-Cl** to **O-Phen** on platinum oligomers could be produced by extraction with KCN aqueous solution. Structural determination of the present platinum oligomers, including two different types of termination, was characterized by IR,  $^1\text{H-NMR}$ ,  $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$  spectroscopy, as detailed below. In present study, we found the selective preparation of platinum oligomers with chloride and phenanthroline termination by different purification was possible, and this selective preparation may be effective with the synthetic method of the many kinds of platinum compounds with diethynylarene ligands.

All observed peaks of IR spectra in the oligomers **O1** and **O2** corresponded to the peaks of their respective phenanthrolines and tributylphosphine, except that the  $\nu(\text{CC-H})$  bands in **L1** and **L2** around  $3175\text{ cm}^{-1}$  disappeared. The characteristic strong  $\nu(\text{C}\equiv\text{C})$  bands in **O1** and **O2** were observed at around  $2095\text{ cm}^{-1}$ , as well as in **D1** and **D2**. Additionally, the  $\nu(\text{C}\equiv\text{C})$  band assigned to the ethynyl substituent between phenanthroline and the phenyl group in **L2** ( $2210\text{ cm}^{-1}$ ) remained almost intact in **O2-Cl** ( $2203\text{ cm}^{-1}$ ) and **O2-Phen** ( $2204\text{ cm}^{-1}$ ).

Two signal sets of pseudo triplets were observed in the  $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$  spectra of four oligomers here, **O1-Cl** (Fig. S3), **O1-Phen** (Fig. S4), **O2-Cl**, and **O2-Phen**, as listed in Table 1. One strong set of pseudo triplets was shown at around 3.4 ppm in all oligomers, and was assigned to the phosphorus atoms of tributylphosphines on the internal repeating unit,  $\text{C}\equiv\text{C-Pt}(\text{PBU}_3)_2\text{-C}\equiv\text{C}$ . Another weak signal set of pseudo triplets appeared at around 7.0 ppm in the platinum oligomers with chloride termination, **O1-Cl** and **O2-Cl**, while it was observed at around 4.4 ppm in platinum oligomers with phenanthroline termination, **O1-Phen** and **O2-Phen**. This was because, as mentioned above, the coordination structures between  $\text{Cl-Pt}(\text{PBU}_3)_2\text{-C}\equiv\text{C}$  and  $\text{C}\equiv\text{C-Pt}(\text{PBU}_3)_2\text{-C}\equiv\text{C}$  conformation are distinguishable by the difference in the  $^{31}\text{P-NMR}$  chemical shifts of their tributylphosphines bonded to the platinum center at about 4 ppm and 7 ppm. Thus, the signals in platinum oligomers at 7.0 ppm were assigned to the phosphorus atoms of tributylphosphines with the chloride termination structure,  $\text{Cl-Pt}(\text{PBU}_3)_2\text{-C}\equiv\text{C}$ , and those at 4.4 ppm were assigned to the phenanthroline termination,  $\text{L1(or L2)-Pt}(\text{PBU}_3)_2\text{-C}\equiv\text{C}$ . In fact, not only our oligomers but also previously reported oligomers **4** (chloride termination structure type, 7.4 ppm) and **7** (ethynylbenzene termination structure type, 4.0 ppm) were consistent with the assignment of the coordination structures shown in Fig. 2 and Table 1 [25, 26].

The estimation of the coordination structures on the termination of the platinum oligomers considered here was further supported by  $^1\text{H-NMR}$  measurement. The signal data of the chemical shift for phenanthroline ligands on present compounds are collected in Table 2. The signal at 3.43 ppm, assignable to the ethynyl proton of terminal **L1** ligand in **O1-Phen**, was clearly observed, while no assignable signal was detected for the ethynyl proton in **O1-Cl**. Similar observation of the signal for the ethynyl proton between **O2-Cl** and **O2-Phen** were obtained. The assignable signals for **L1** and **L2** protons were detected among 7-10 ppm, while those for tributylphosphine protons

were detected among 0-3 ppm in all oligomers. The strong signals assignable to the phenanthroline protons on the internal repeating unit in **O1** oligomers clearly showed up-field shifts of more than 0.1 ppm, compared to the signals of free **L1**, and the values of the chemical shift for phenanthroline protons in **D1** were almost consistent with those in **O1** oligomers. In the case of **O2** oligomers, the values of strong signals assignable to the phenanthroline protons of **L2** on the internal repeating unit remained almost intact, and the signals assignable to the phenyl protons of **L2** were clearly shifted up-field by more than 0.1 ppm compared to the signals of free **L2**. These up-field shifts might have been due to the  $\pi$ -back donation effect through the formation of Pt–C $\equiv$ C bonding. In addition, the values of the chemical shift for phenanthroline protons in **D2** were almost consistent with those on the internal repeating unit in **O2** oligomers.

The repeated numbers (*n*) of the present oligomers in Fig. 1 were estimated from about 7 to 9 of the relative NMR integration with two signals between the internal repeating unit and the terminal unit in the  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of four oligomers, **O1-Cl** (*n* = 9), **O1-Phen** (*n* = 7), **O2-Cl** (*n* = 7), and **O2-Phen** (*n* = 7). This was because the estimation of the repeated number with  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectral data is a commonly used technique in many platinum phosphine organometallic oligomers [25-29]. Furthermore, there was a good correlation to the estimation for the molecular weight determination of platinum compounds **O1-Cl** and **O1-Phen** between the  $^{31}\text{P}$ -NMR data and the GPC analysis data, although the GPC estimates (**O1-Cl**: *n* = 8 and **O1-Phen**: *n* = 6) tended to be a slightly smaller molecular weight than the  $^{31}\text{P}$ -NMR data. The repeated numbers of the present four oligomers were estimated as small values between 7 and 9 compared to previously reported platinum organometallic oligomers with diethynylbipyridine ligands, which were estimated as *n* = 86 by the GPC technique [21]. This difference in polymerization between the present phenanthrolines and reported bipyridine ligands in similar platinum organometallic compounds might reflect the difference in solubility of the organic solvents between two ligands, because **L1** and **L2** were less soluble to the organic solvents than the bipyridine derivatives.

### Photophysical data of platinum complexes and oligomers

Figure 3 shows the absorption spectra of **L1**, **D1**, and **O1-Cl** in  $\text{CH}_2\text{Cl}_2$ . Both **D1** and **O1-Cl** have a strong absorption band at around 400 nm, which was primarily assigned to the metal-perturbed  $\pi$ - $\pi^*(\text{L1})$  transitions of **D1** and **O1** oligomers, while the band assignable to the lowest energy  $\pi$ - $\pi^*(\text{L1})$  transition of free **L1** appears at around 320 nm. The lower transition energy of metal-perturbed  $\pi$ - $\pi^*(\text{L1})$  in platinum compounds relative to that of free **L1** can be attributed to the delocalization among the molecular orbitals of several adjacent phenanthroline ligands interacting through the Pt  $d\pi$  orbitals as described in previous studies [23, 25]. Figure 4 shows the absorption spectra of **L2**, **D2**, and **O2-Cl** in  $\text{CH}_2\text{Cl}_2$ . Their lowest absorption bands were assigned to the metal-perturbed  $\pi$ - $\pi^*(\text{L2})$  transitions at around 410 nm in both **D2** and **O2-Cl**, and a lower energy transition relative to that of free **L2**

was also demonstrated at around 360 nm. A similar change of the energy for the metal-perturbed  $\pi$ - $\pi^*$  transition in the present platinum compounds with **L2** supported the interpretation of the delocalization effect among the phenanthroline ligand mentioned above. The absorption spectra of platinum oligomers **O1-Cl** and **O1-Phen** are shown in Fig. S5, while those of **O2-Cl** and **O2-Phen** are presented in Fig. S6. These spectra of platinum oligomers with two different terminal structures not only in **O1** but also in **O2** were almost the same. This result suggests that a strong lowest absorption band assigned to metal-perturbed  $\pi$ - $\pi^*$  transitions of platinum oligomers is mainly derived from the internal repeating unit in respective platinum oligomers, and the absorption band for terminal units of respective platinum oligomers overlaps in their strong absorption bands. This interpretation is consistent with previous experimental and theoretical studies of platinum diethynylbenzene polymers by Schanze et al [31].

Platinum complex **D1** and two types of oligomers, **O1-Cl** and **O1-Phen**, showed visible emission bands with vibronic progressions centered at around 530 nm in deoxygenated  $\text{CH}_2\text{Cl}_2$  at room temperature upon excitation at 325 nm, as shown in Fig. 5. These emissions were very similar and assigned to a typical metal-perturbed  $^3[\pi$ - $\pi^*]$  phosphorescence, which is well known in the emissions for platinum complexes and oligomers with many kinds of diethynylaryl ligands [9-17]. The similarity of the vibrated emission for the three compounds is supported by the idea that the triplet excited state is localized on a single  $-\text{Pt}(\text{PBu}_3)_2-\text{C}\equiv\text{C}-\text{Phen}-\text{C}\equiv\text{C}-\text{Pt}(\text{PBu}_3)_2-$  unit. This interpretation is furthermore consistent with a previous study of platinum oligomers of diethynylbenzene by Liu et al. [25].

Complex **D2** and two types of oligomers, **O2-Cl** and **O2-Phen**, including those with **L2**, showed weak emission bands between 440-800 nm at room temperature in deoxygenated  $\text{CH}_2\text{Cl}_2$ , as shown in Fig. 6. On the other hand, in atmospheric  $\text{CH}_2\text{Cl}_2$ , only a weak broad emission band of maximum peak at around 500 nm was observed in the high-energy area (440-550 nm) for these compounds, and this band could be assigned to a  $^1[\pi$ - $\pi^*]$  fluorescence. In deoxygenated  $\text{CH}_2\text{Cl}_2$ , the maximum peak emissions at 560 nm for these compounds were assignable to a metal-perturbed  $^3[\pi$ - $\pi^*]$  phosphorescence, and the emissions in Fig. 6 were dual emissions of fluorescence and phosphorescence from the  $[\pi$ - $\pi^*]$  state. Almost the same emission spectra were observed between the two oligomers with different terminations, **O2-Cl** and **O2-Phen**, as with the oligomers of **O1**. Dual emissions of platinum diethynylaryl organometallic polymers have been reported and expected to use for the white OLED material [13, 32]. The new compounds shown in Fig. 1 were unfortunately unstable for UV light irradiation under the deoxygenated condition, because the color of the deoxygenated  $\text{CH}_2\text{Cl}_2$  solution of these compounds gradually changed from pale yellow to orange-yellow under UV irradiation.

## Conclusions

Platinum(II) organometallic complexes and oligomers with two types of phenanthroline ligands, including two ethynyl terminal units, **L1** and **L2**, were synthesized by transmetalation with copper ion in moderate yields. That an alternative procedure was performed with platinum oligomers **O1** and **O2**, with two types between chloride and phenanthroline termination illustrated in Fig. 1 using different purifications between the extraction and the column chromatography, is worthy of special mention. The repeated numbers of the four new oligomers were estimated as small values compared to previously reported similar platinum organometallic polymers with 5,5'-diethynyl-2,2'-bipyridine. The difference in polymerization between the present phenanthroline and reported bipyridine might reflect the difference in solubility to the organic solvents, because **L1** and **L2** were less soluble to these solvents.

All present platinum compounds showed similar absorption spectra. The compounds prepared with **L1** had a strong absorption band at around 400 nm, assignable to the lowest energy metal-perturbed  $\pi$ - $\pi^*$  (**L1**) transitions, while the compounds created with **L2** had a strong absorption band at around 410 nm because **L2** has a more extended  $\pi$  conjugation than **L1**. The absorption spectra of platinum oligomers with two different terminal structures were almost the same. This result indicates that the lowest energy absorption band assigned to metal-perturbed  $\pi$ - $\pi^*$  transitions is mainly derived from the internal repeating unit in respective platinum oligomers.

We are currently extending our photophysical research to the solid state and film state of the present platinum oligomers, and of the photochemical reaction of their compounds in solution under the deoxygenated state.

## Experimental Section

### Material and measurements

All chemicals used for syntheses were purchased from Aldrich or TCI and used without further purification. All reactions were carried out under an argon atmosphere. Solvents were freshly distilled according to standard procedures. The 3,8-diethynylphenanthroline (**L1**) was synthesized by the similar method of Ziessel et al [33]. The **CIPt(PBu<sub>3</sub>)<sub>2</sub>(ETol)** was synthesized by the similar method of Liu et al. [30]. The characterization of the novel platinum complexes has been done by IR, <sup>1</sup>H NMR, <sup>31</sup>P NMR, UV-Vis spectroscopy, and elemental analyses. Elemental analyses for dinuclear platinum complexes were performed for C, H, and N elements on a Perkin-Elmer 2400II CHNS/O full-automatic analyzer. Molecular weights for platinum compounds were determined by Gel Permeation Chromatograph GPC-104/101 on a Shodex instrument equipped with a two-consolidated column of PL-404 and UV detector. Measurements were performed in THF, using monodisperse polystyrene standards at 40 °C, flow rate 1 ml/min. IR spectra were obtained on a JASCO FT/IR 460 spectrometer using the KBr-pellet method. The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded with a Bruker AVANCE NMR spectrometer (400MHz) at room temperature and the chemical shifts were referenced to CDCl<sub>3</sub>(7.260 ppm) or CD<sub>2</sub>Cl<sub>2</sub> (5.320 ppm), while the phosphorus chemical shifts were relative to external 85% H<sub>3</sub>PO<sub>4</sub>. UV-Vis spectra were recorded on a SHIMADZU UV-1800 spectrophotometer in CH<sub>2</sub>Cl<sub>2</sub> (emission spectroscopic grade) at room temperature. Excitation spectra were recorded on a HITACHI F-2500 fluorescence spectrophotometer and corrected emission spectra were measured with a HAMAMATSU C7473 photonic multi-channel analyzer. Emission spectra at room temperature were measured in a degassed CH<sub>2</sub>Cl<sub>2</sub> by argon bubbling (20min).

### Preparation of 3,8-bis-(4-trimethylsilylethynyl-phenylethynyl)-1,10-phenanthroline

A flask was charged with **L1** (343 mg, 1.5 mmol) and 1-iodo-4-trimethylsilylethynyl-benzene (991 mg, 3.3 mmol) and dissolved with THF (75 ml). Diisopropylamine (DIPA) (7.5 ml), Pd(PPh<sub>3</sub>)<sub>4</sub> (87 mg, 0.075 mmol), and CuI (14 mg, 0.075 mmol) was added to the flask. After the mixture was stirred at 40 °C for 22 h, THF and DIPA were removed by reduced pressure. The residue was dissolved with the mixture solution (88 ml) of CH<sub>2</sub>Cl<sub>2</sub>-MeOH (10:1). The solution was added the aqueous solution (80 ml) of KCN (560 mg) and sonicated to remove copper ion in organic layer for 1h. The organic layer was washed with H<sub>2</sub>O (50 ml × 3) and dried over anhydrous MgSO<sub>4</sub>. The solvents were removed by evaporation with evaporator, and the residue was purified on SiO<sub>2</sub> column chromatography with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (97:3) as eluent. Yellow powder was obtained and dried at 50 °C under vacuum for 3 h. Yield: 550 mg (64%).

Anal. Calcd for  $C_{38}H_{32}N_2Si_2 \cdot 1/2H_2O$ : C, 78.4; H, 5.7; N, 4.8. Found: C, 78.7; H, 5.5; N, 4.8. IR ( $cm^{-1}$ )  $\nu(C\equiv C)$ : 2210, 2099.  $^1H$  NMR ( $CDCl_3$ ): 9.26 (d,  $J = 2.0$  Hz, 2H, Phen-H2 and -H9), 8.35 (d,  $J = 2.0$  Hz, 2H, Phen-H4 and -H7), 7.79 (s, 2H, Phen-H5 and -H6), 7.55 (d,  $J = 8.8$  Hz, 4H, Phenyl-H2 and -H6), 7.48 (d,  $J = 8.8$  Hz, 4H, Phenyl-H3 and -H5), 0.27 (s, 18H, -Si(CH<sub>3</sub>)<sub>3</sub>).

### Preparation of 3,8-bis-(4-ethynyl-phenylethynyl)-1,10-phenanthroline (L2)

The 3,8-bis-(4-trimethylsilylethynyl-phenylethynyl)-1,10-phenanthroline (881 mg, 1.54 mmol) was dissolved in the mixture solution (100 ml) of THF-MeOH (1:1) and added 1.0 M KOH aq. (3.1 ml). After stirring for 1 h, a 1.0 M NH<sub>4</sub>Cl aq. (10 ml) and H<sub>2</sub>O (100 ml) were added in the mixture solution and extracted with CH<sub>2</sub>Cl<sub>2</sub> (150 ml  $\times$  2). Extracted organic layer was clouded and filtrated with a suction filter, and the target compound was obtained as pale yellow powder. The filtrate was dried over anhydrous MgSO<sub>4</sub>, and CH<sub>2</sub>Cl<sub>2</sub> was removed by evaporation with evaporator. The residue was washed with CH<sub>2</sub>Cl<sub>2</sub> (15 ml) and filtered with a suction filter. Totally, pale yellow powder was obtained and dried at 50 °C under vacuum for 3 h. Yield: 507 mg (77%).

Anal. Calcd for  $C_{32}H_{16}N_2 \cdot 5/3H_2O$ : C, 83.8; H, 4.3; N, 6.1. Found: C, 83.5; H, 4.3; N, 6.1. IR (KBr,  $cm^{-1}$ )  $\nu(C\equiv C)$ : 2210, 2099,  $\nu(C-H)$ : 3178. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{abs}$  nm ( $\epsilon \times 10^{-4}$ ) 372 (7.7), 352 (9.4), 294 (6.8), 286 (6.8).  $^1H$  NMR ( $CD_2Cl_2$ ): 9.23 (d,  $J = 2.0$  Hz, 2H, Phen-H2 and -H9), 8.41 (d,  $J = 2.0$  Hz, 2H, Phen-H4 and -H7), 7.84 (s, 2H, Phen-H5 and -H6), 7.60 (d,  $J = 8.4$  Hz, 4H, Phenyl-H2 and -H6), 7.53 (d,  $J = 8.4$  Hz, 4H, Phenyl-H3 and -H5), 3.28 (s, 2H, C $\equiv$ C-H).

### Preparation of platinum dimer (tol- $\equiv$ -){Pt(PBt<sub>3</sub>)<sub>2</sub>}{- $\equiv$ -phen- $\equiv$ -}{Pt(PBt<sub>3</sub>)<sub>2</sub>}{- $\equiv$ -tol} (D1)

The **L1** (35.6 mg, 0.16 mmol) and **ClPt(PBu<sub>3</sub>)<sub>2</sub>(ETol)** (293 mg, 0.39 mmol) were dissolved to a THF (20 ml) under Ar. After the solution was added DIPA (2 ml) and CuI (4 mg, 0.020 mmol), the mixture was stirred at 35 °C for 18 h under dark place. The solution was added MeOH (5 ml) and concentrated by evaporation with evaporator. The crude product was dissolved with the mixture solution (110 ml) of CH<sub>2</sub>Cl<sub>2</sub>-MeOH (10:1) and added a KCN aq. (150 mg in 100 ml) and extracted to remove copper ion. The organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated by evaporation with evaporator. The residue was purified on SiO<sub>2</sub> column chromatography with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (97:3) as eluent, and yellow compound was obtained. Yield: 175 mg (68%).

Anal. Calcd for  $C_{82}H_{128}N_2Pt_2P_4$ : C, 59.5; H, 7.8; N, 1.7. Found: C, 59.5; H, 7.8; N, 1.7%. FT-IR (KBr,  $cm^{-1}$ )  $\nu(C\equiv C)$ : 2098. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{abs}$  nm ( $\epsilon \times 10^{-4}$ ) 390 (10.4), 365 (7.3), 316 (3.9), 284 (6.4), 268 (6.7).  $^1H$ -NMR ( $CD_2Cl_2$ , 400MHz, 5.320ppm):  $\delta = 8.95$  (d,  $J = 2.0$  Hz, 2H, Phen-H2 and -H9), 7.98 (d,  $J = 2.0$  Hz, 2H, Phen-H4 and -H7), 7.63 (s, 2H, Phen-H5 and -H6), 7.15 (d,  $J = 8.0$  Hz, 4H, Toly-H2 and -H6), 7.03 (d,  $J = 8.0$  Hz, 4H,

Tolyl-H3 and -H5), 2.29 (s, 6H, Tolyl-CH<sub>3</sub>), 2.17 (m, 24H, P-CH<sub>2</sub> α), 1.65 (m, 24H, P-CH<sub>2</sub> β), 1.48 (m, 24H, P-CH<sub>2</sub> γ), 0.95 (t, J = 7.5 Hz, 36H, -CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm) = 3.27 (J(Pt-P) = 2340 Hz). GPC (THF): M<sub>n</sub> = 1260 g·mol<sup>-1</sup>, M<sub>w</sub> = 1350 g·mol<sup>-1</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.07.

### Preparation of platinum dimer (tol-≡-){Pt(PBt<sub>3</sub>)<sub>2</sub>}(≡-ph-≡-phen-≡-ph-≡-){Pt(PBt<sub>3</sub>)<sub>2</sub>}(≡-tol) (D2)

The **L2** (69.0 mg, 0.16 mmol) and **ClPt(PBu<sub>3</sub>)<sub>2</sub>(ETol)** (267 mg, 0.36 mmol) were dissolved to a THF (30 ml) under Ar. After the solution was added DIPA (3 ml) and CuI (4 mg, 0.020 mmol), the mixture was stirred at 60 °C for 20 h under dark place. The solution was added MeOH (5 ml) and concentrated by evaporation with evaporator. The crude product was dissolved with the mixture solution (110 ml) of CH<sub>2</sub>Cl<sub>2</sub>-MeOH (10:1) and added a KCN aq. (200 mg in 70 ml) and extracted to remove copper ion. The organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated by evaporation with evaporator. The residue was purified on SiO<sub>2</sub> column chromatography with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (97:3) as eluent, and yellow compound was obtained. Yield: 180 mg (61%).

Anal. Calcd for C<sub>98</sub>H<sub>136</sub>N<sub>2</sub>Pt<sub>2</sub>P<sub>4</sub>: C, 63.4; H, 7.4; N, 1.5. Found: C, 63.6; H, 7.4; N, 1.5%. FT-IR (KBr, cm<sup>-1</sup>) ν(C≡C): 2205, 2098. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>abs</sub> nm (ε × 10<sup>-4</sup>) 405 (11.7), 391 (11.6), 326 (7.0), 297 (6.9), 276 (6.8), 267 (6.9). <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400MHz, 5.320ppm): δ = 9.26 (broad s, 2H, Phen-H2 and -H9), 8.43 (broad s, 2H, Phen-H4 and -H7), 7.86 (broad s, 2H, Phen-H5 and -H6), 7.48 (d, J = 8.4 Hz, 4H, Phenyl-H2 and -H6), 7.27 (d, J = 8.4 Hz, 4H, tolyl-H3 and -H5), 7.14 (d, J = 8.1 Hz, 4H, Tolyl-H2 and -H6), 7.02 (d, J = 8.1 Hz, 4H, Tolyl-H3 and -H5), 2.29 (s, 6H, Tolyl-CH<sub>3</sub>), 2.14 (m, 24H, P-CH<sub>2</sub> α), 1.61 (m, 24H, P-CH<sub>2</sub> β), 1.46 (m, 24H, P-CH<sub>2</sub> γ), 0.94 (t, J = 7.3 Hz, 36H, -CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm) = 3.27 (J(Pt-P) = 2350 Hz). GPC (THF): M<sub>n</sub> = 1670 g·mol<sup>-1</sup>, M<sub>w</sub> = 1820 g·mol<sup>-1</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.09.

### Preparation of Pt-L1 oligomer with chloride termination (O1-Cl)

The **L1** (58.0 mg, 0.25 mmol) and *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (167 mg, 0.25 mmol) were dissolved to a CH<sub>2</sub>Cl<sub>2</sub> (60 ml) under Ar. After the solution was added DIPA (10 ml) and CuI (5 mg, 0.025 mmol), the mixture was stirred at 50 °C for 11 h under dark place. The color of the solution gradually changed from orange to dark red. The mixture solution was added MeOH (5 ml) and concentrated by evaporation with evaporator. The crude product was added CH<sub>2</sub>Cl<sub>2</sub> (5 ml) and an insoluble solid was collected by filtration with a suction filter and washed with CH<sub>2</sub>Cl<sub>2</sub> (5 ml). It was presumed that the insoluble solid was a long-chain Pt-**L1** polymer from the identification of IR and <sup>31</sup>P{<sup>1</sup>H} NMR spectra between this solid and present Pt-**L1** oligomer. The filtrate was purified on alumina column chromatography with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (97:3) as eluent. Yellow powder was collected by filtration with a suction filter, washed with ether (30 ml) and MeOH (10 ml), and dried at 30 °C under vacuum for 5 h. Yield: 60 mg (30%).

FT-IR (cm<sup>-1</sup>)  $\nu(\text{C}\equiv\text{C})$ : 2091. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 8.98 (broad s, Phen-H2 and -H9 center), 8.93 (d, J = 2.0 Hz, Phen-H2 and -H9 edge), 8.01 (broad s, Phen-H4 and -H7 center), 7.98 (d, J = 2.0 Hz, Phen-H4 and -H7 edge), 7.66 (s, Phen-H5 and -H6 center), 7.65 (s, Phen-H5 and -H6 edge), 2.23 (m, P-CH<sub>2</sub>  $\alpha$  center), 2.06 (m, P-CH<sub>2</sub>  $\alpha$  edge), 1.70 (m, P-CH<sub>2</sub>  $\beta$  center), 1.61 (m, P-CH<sub>2</sub>  $\beta$  edge), 1.53 (m, P-CH<sub>2</sub>  $\gamma$  center), 1.48 (m, P-CH<sub>2</sub>  $\gamma$  edge), 0.97 (m, -CH<sub>3</sub> center), 0.95 (m, -CH<sub>3</sub> edge). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) = 7.03 (J(Pt-P) = 2360 Hz, edge), 3.40 (J(Pt-P) = 2330 Hz, center). GPC (THF):  $M_n = 3660 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w = 6050 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w/M_n = 1.65$ .

### Preparation of Pt-L1 oligomer with phenanthroline derivative termination (O1-phen)

The **L1** (88.2 mg, 0.36 mmol) and *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (268 mg, 0.40 mmol) were dissolved to a THF (50 ml) under Ar. After the solution was added DIPA (10 ml) and CuI (7.6 mg, 0.036 mmol), the mixture was stirred at 60 °C for 29 h under dark place. The mixture solution was added EtOH (20 ml) and concentrated by evaporation with evaporator. The crude product was added the mixture solution (110 ml) of CH<sub>2</sub>Cl<sub>2</sub>-MeOH (10:1) and an insoluble solid was collected by filtration with a suction filter and washed with CH<sub>2</sub>Cl<sub>2</sub> (10 ml). It was presumed that the insoluble solid was a long-chain Pt-**L1** polymer from the identification of IR and <sup>31</sup>P{<sup>1</sup>H} NMR spectra between this solid and **O1-Cl**. The filtrate was added a KCN aq. (270 mg in 100 ml) and extracted to remove copper ion in the organic layer. The organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated until 2-3 ml by evaporation with evaporator. Brown powder was obtained to pour the solution to a MeOH (200ml), collected by centrifuge separation, and dried at 30 °C under vacuum for 5 h. Yield: 112 mg (37%).

FT-IR (cm<sup>-1</sup>)  $\nu(\text{C}\equiv\text{C})$ : 2093. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 9.13 (d, J = 2.0 Hz, Phen-H9 terminal), 9.02 (d, J = 2.0 Hz, Phen-H2 terminal), 8.98 (broad s, Phen-H2 and -H9 center), 8.95 (d, J = 2.0 Hz, Phen-H2 and -H9 edge), 8.34 (d, J = 2.0 Hz, Phen-H7 terminal), 8.04 (d, J = 2.0 Hz, Phen-H4 terminal), 8.01 (broad s, Phen-H4 and -H7 center), 7.99 (d, J = 2.0 Hz, Phen-H4 and -H7 edge), 7.73 (s, Phen-H5 and -H6 terminal), 7.65 (s, Phen-H5 and -H6 edge and center), 3.43 (s, C $\equiv$ C-H terminal), 2.22 (m, P-CH<sub>2</sub>  $\alpha$  center), 2.16 (m, P-CH<sub>2</sub>  $\alpha$  edge), 1.69 (m, P-CH<sub>2</sub>  $\beta$  center), 1.61 (m, P-CH<sub>2</sub>  $\beta$  edge), 1.51 (m, P-CH<sub>2</sub>  $\gamma$  center), 1.49 (m, P-CH<sub>2</sub>  $\gamma$  edge), 0.97 (m, -CH<sub>3</sub> center), 0.96 (m, -CH<sub>3</sub> edge). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) = 4.41 (J(Pt-P) = 2250 Hz, edge), 3.44 (J(Pt-P) = 2320 Hz, center). GPC (THF):  $M_n = 2530 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w = 4230 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w/M_n = 1.67$ .

### Preparation of Pt-L2 oligomer with chloride termination (O2-Cl)

The **L2** (107 mg, 0.25 mmol) and *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (184 mg, 0.275 mmol) were dissolved to a THF (40 ml) under Ar. After the solution was added DIPA (4 ml) and CuI (5 mg, 0.025 mmol), the mixture was stirred at 60 °C for 26 h under dark place. The color of the solution gradually changed from orange to dark brown. The mixture solution

was added MeOH (5 ml) and concentrated until 10 ml by evaporation with evaporator. Brown powder was obtained to pour the concentrated solution to hexane (150 ml) and purified on alumina column chromatography with CH<sub>2</sub>Cl<sub>2</sub>-MeOH (97:3) as eluent. Yellow powder was collected by filtration with a suction filter, washed with ether (30 ml), and dried at 30 °C under vacuum for 5 h. Yield: 97 mg (38%).

FT-IR (cm<sup>-1</sup>)  $\nu$ (C≡C): 2203, 2096. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 9.22 (broad s, Phen-H2 and -H9), 8.39 (broad s, Phen-H4 and -H7), 7.83 (broad s, Phen-H5 and -H6), 7.49 (d, J = 8.2 Hz, Phenyl-H2 and -H6 center), 7.48 (d, J = 8.2 Hz, 4H, Phenyl-H2 and -H6 edge), 7.29 (d, J = 8.2 Hz, Phenyl-H3 and -H5 center), 7.26 (d, J = 8.2 Hz, Phenyl-H3 and -H5 edge), 2.16 (m, P-CH<sub>2</sub> α center), 2.02 (m, P-CH<sub>2</sub> α edge), 1.63 (m, P-CH<sub>2</sub> β center), 1.56 (m, P-CH<sub>2</sub> β edge), 1.48 (m, P-CH<sub>2</sub> γ center), 1.46 (m, P-CH<sub>2</sub> γ edge), 0.96 (m, -CH<sub>3</sub> center), 0.94 (m, -CH<sub>3</sub> edge). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) = 7.02 (J(Pt-P) = 2360 Hz, edge), 3.40 (J(Pt-P) = 2340 Hz, center). GPC (THF): M<sub>n</sub> = 3530 g·mol<sup>-1</sup>, M<sub>w</sub> = 6770 g·mol<sup>-1</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.92.

### Preparation of Pt-L2 oligomer with phenanthroline derivative termination (O2-phen)

The **L2** (77 mg, 0.18 mmol) and *trans*-Pt(PBu<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (133 mg, 0.20 mmol) were dissolved to a THF (40 ml) under Ar. After the solution was added DIPA (4 ml) and CuI (4 mg, 0.018 mmol), the mixture was stirred at 60 °C for 26 h under dark place. The mixture solution was added EtOH (20 ml) and concentrated by evaporation with evaporator. The crude product was added the mixture solution (110 ml) of CH<sub>2</sub>Cl<sub>2</sub>-MeOH (10:1) and an insoluble solid was collected by filtration with a suction filter and washed with CH<sub>2</sub>Cl<sub>2</sub> (10 ml). It was presumed that the insoluble solid was a long-chain Pt-**L2** polymer from the identification of IR and <sup>31</sup>P{<sup>1</sup>H} NMR spectra between this solid and **O2-Cl**. The filtrate was added a KCN aq. (150 mg in 80 ml) and extracted to remove copper ion from organic layer. The organic layer was dried over anhydrous MgSO<sub>4</sub> and concentrated until 2-3 ml by evaporation with evaporator. Brown powder was obtained to pour the solution to a MeOH (100ml), collected by centrifuge separation, and dried at 30 °C under vacuum for 5 h. Yield: 115 mg (63%).

FT-IR (cm<sup>-1</sup>)  $\nu$ (C≡C): 2204, 2095. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 9.22 (broad s, Phen-H2 and -H9), 8.39 (broad s, Phen-H4 and -H7), 7.83 (broad s, Phen-H5 and -H6), 7.49 (d, J = 8.2 Hz, Phenyl-H2 and -H6 center), 7.48 (d, J = 8.2 Hz, 4H, Phenyl-H2 and -H6 edge), 7.29 (d, J = 8.2 Hz, Phenyl-H3 and -H5 center), 7.26 (d, J = 8.2 Hz, Phenyl-H3 and -H5 edge), 3.29 (s, C≡C-H terminal), 2.16 (m, P-CH<sub>2</sub> α center), 2.02 (m, P-CH<sub>2</sub> α edge), 1.63 (m, P-CH<sub>2</sub> β center), 1.56 (m, P-CH<sub>2</sub> β edge), 1.48 (m, P-CH<sub>2</sub> γ center), 1.46 (m, P-CH<sub>2</sub> γ edge), 0.96 (m, -CH<sub>3</sub> center), 0.94 (m, -CH<sub>3</sub> edge). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) = 4.40 (J(Pt-P) = 2260 Hz, edge), 3.40 (J(Pt-P) = 2360 Hz, center). GPC (THF): no data for low solubility.

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## Figure Captions

**Fig. 1** Molecular structures of ligands and platinum compounds examined.

**Fig. 2** Molecular structures of previously reported platinum oligomers.

**Fig. 3** UV-Vis absorption spectra of **D1** (solid line), **O1-Cl** (----), and **L1** (---) in  $\text{CH}_2\text{Cl}_2$  at room temperature.

**Fig. 4** UV-Vis absorption spectra of **D2** (solid line), **O2-Cl** (----), and **L2** (---) in  $\text{CH}_2\text{Cl}_2$  at room temperature.

**Fig. 5** Emission spectra of **D1** (solid line), **O1-Phen** (----), and **O1-Cl** (---) in  $\text{CH}_2\text{Cl}_2$  at room temperature upon excitation at 325 nm.

**Fig. 6** Emission spectra of **D2** (solid line), **O2-Phen** (----), and **O2-Cl** (---) in  $\text{CH}_2\text{Cl}_2$  at room temperature upon excitation at 325 nm.

Fig. 1

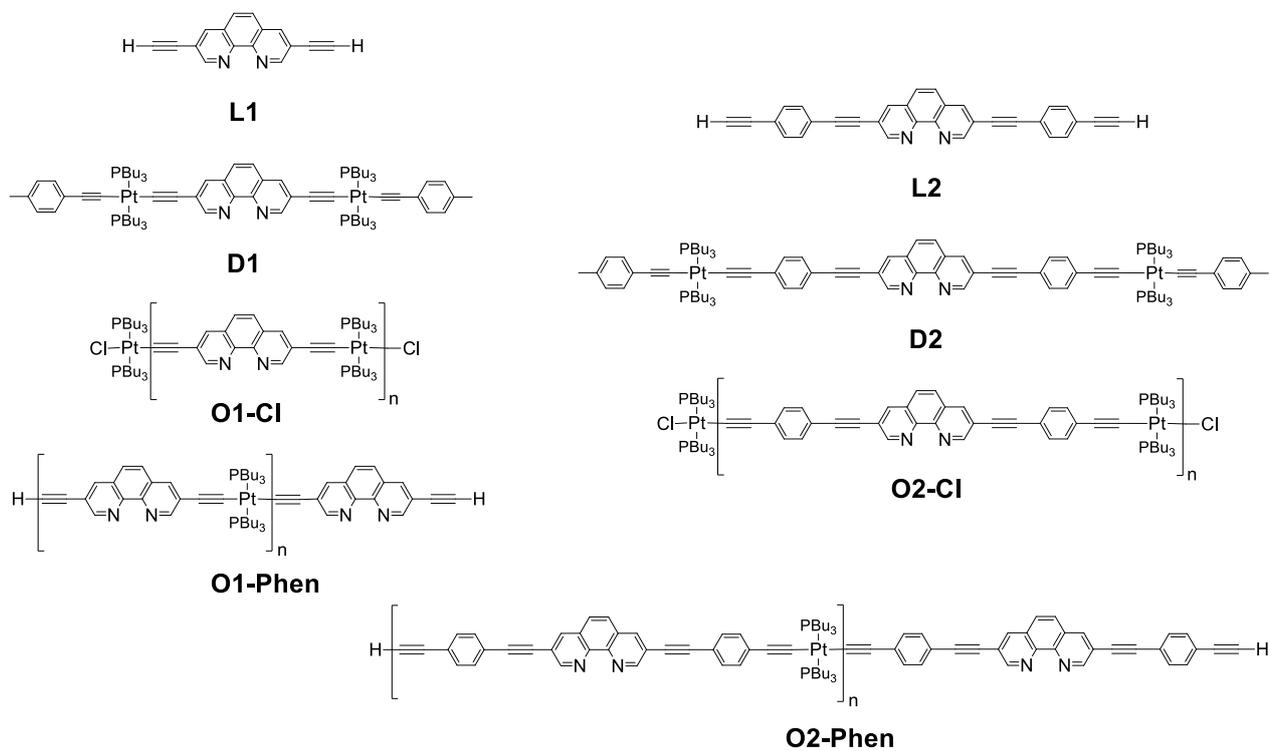


Fig. 2

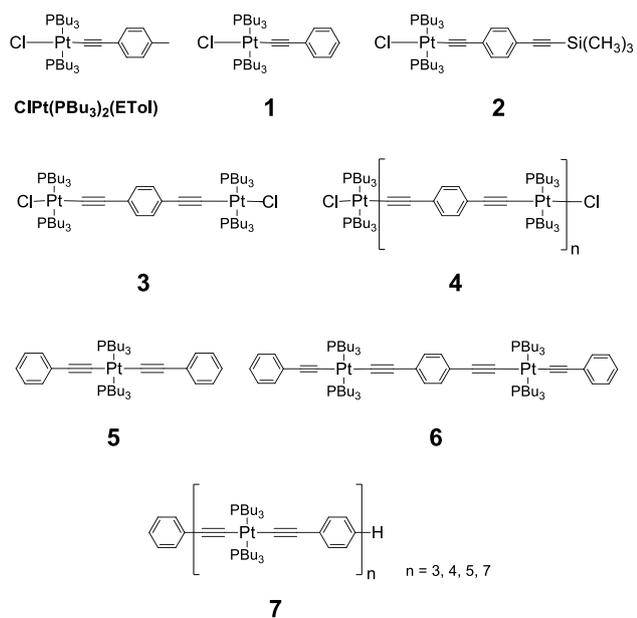


Fig. 3

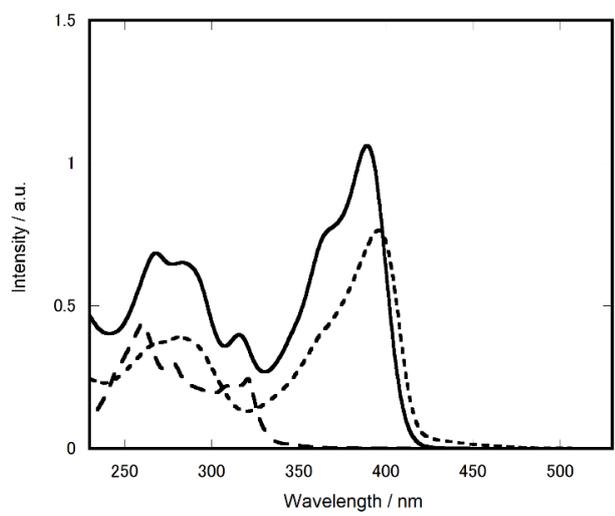


Fig. 4

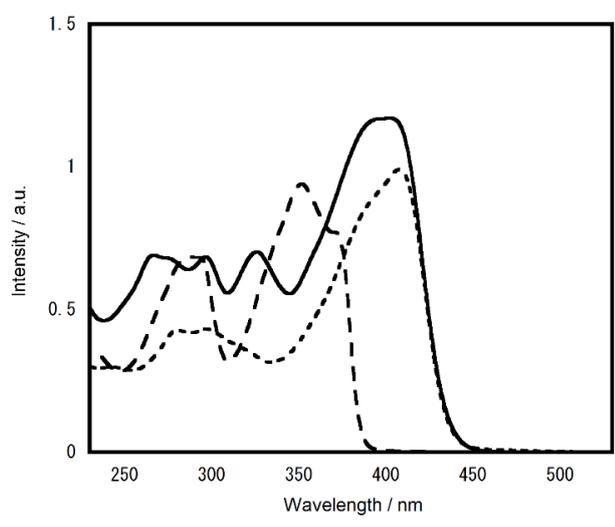


Fig. 5

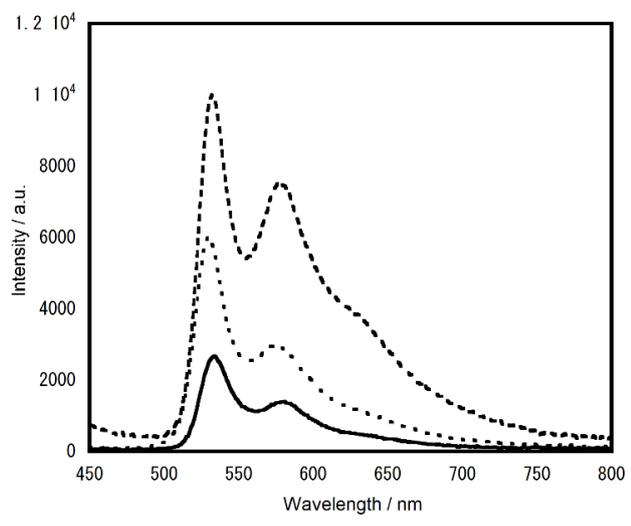


Fig. 6

