Vietnam Journal of Catalysis and Adsorption
Tạp chí xúc tác và hấp phụ Việt Nam

http://chemeng.hust.edu.vn/jca/

Syntheses and Characterizations of Platinum Complexes with New Pyrene-based Salicylaldiminato-type Ligand Substituted at 7-Position of Pyrene

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ARTICLE INFO

Received: 14/2/2021
Accepted: 30/3/2021

Keywords:

Coordination Chemistry; Platinum Complex; Pyrene; π-expanded Ligand; Salicylaldimine

ABSTRACT

Many experimental data show that bulky substituents on the molecules enhance solubility, catalytic activity, and photophysical properties due to the prevention of π-π stacking in metal salicylaldimines. In order to understand the effect of bulkiness of substituents on the properties of the obtained molecules, the author researched and synthesized two new pyrene-based salicylaldiminato-type ligands that were substituted at 7-position and functionalized on imine group with bulky substituents. After the introduction of the tert-butyl group at 7-position of pyrene by Friedel-Crafts reaction, the syntheses of new ligands 1-hydroxy-2-[((2,6-dimethylphenyl)-imino)methyl]-7-(tert-butyl)-pyrene **3**, 2-hydroxy-1- [((2,6-dimethylphenyl)imino)methyl]-7-(tert-butyl)-pyrene **4** and corresponding platinum complexes **3(Pt)**, **4(Pt)** were performed in the different ways with the synthetic processes of the complexes **1(Pt)** and **2(Pt)**. The new ligands and complexes were characterized by ^{1}H NMR, IR spectroscopy, mass spectroscopy, elemental analysis and X-ray diffraction, only for **3(Pt)**. In addition to measurements of the absorption and emission spectra, TDDFT calculations using the B3LYP functions were also performed. The complexes **3(Pt)** and **4(Pt)** exhibit good solubility and red-shift in absorption and emission spectra because of tert-butyl group at 7-position of pyrene and extension of the delocalized π-orbitals to the 2,6-dimethylphenyl on imine group. The change of functional groups also induces the upfield shift of the protons affected by ring currents of phenyl groups Ar-3, Ar-4 on imine groups. Introduction of t-butyl groups in pyrene moieties can stabilize radical forms in oxidation processes.

Introduction

Phosphorescent platinum(II) complexes have gained increasing attention over the last few decades owing to their employment in chemosensors[1,2], biomedical applications[3-6], photovoltaics and, electrophosphorescent devices[7-12]. Phosphorescent transition metal complexes are suitable for application in light-emitting devices due to the strong spin–orbit coupling induced by the heavy metal ion.[13,14] Most of the common phosphorescence emitters are based on octahedral iridium(III) or square planar platinum(II)

https://doi.org/10.51316/jca.2021.024

complexes. The latter often tends to form complex photophysical processes such as energy migration/transfer, charge separation, self-absorption, and excimer formation, which often give rise to low phosphorescence quantum yields. Therefore, rational molecular designs are essential, and inevitably, the intermolecular interactions in the condensed phases that govern these nonradiative decay processes need to be taken into consideration.[15]

Pyrene derivatives are an interesting class of conjugated organic compound because they are widely applicable in devices such as organic light-emitting devices, organic field-effect transistors, and photovoltaic cells.[16,17] Up to date, many studies to tune their properties by introduction of substituents have been reported.[16,17] Therefore, the incorporation of platinum into π-conjugated frameworks of pyrene allows their photophysical and electrochemical properties to be tuned. Previously, the author found that pyrene-based salicylaldiminato-type platinum complexes can be potential for chemosensors and organic devices such as OLEDs or DSSCs but they are still not suitable for those commercial applications where solubility, color purity, and strong emission are needed.[18,19]

In the present investigation, the author discusses the structural and photophysical properties of two isomeric platinum(II) complexes and the syntheses of two new isomeric pyrene-based salicylaldimine-type ligands substituted by tert-butyl group at 7-position of pyrene and substituted by the bulky group, 2,6-dimethylphenyl, on the imine group, leading to the redshift in both absorption and emission spectra compared to our reported platinum complexes. Moreover, interesting properties were also exhibited such as upfield signals in NMR spectra due to the effect of ring currents of benzene rings and stabilized radicals in electrochemical study.

Experimental

General Procedures

General experimental details have already been reported in elsewhere.[18,19,31-34]

Synthesis

Preparation of the ligands **1**, **2** and the corresponding platinum complexes **1(Pt)**, **2(Pt)** was presented in subsequent sections.

Preparation of 1-bromo-7-tert-butylpyrene was carried out following the reference.[20]

Preparation of 1-methoxy-7-tert-butylpyrene (**18**) was performed similar to the synthetic method of 1-methoxypyrene.[18]

Preparation of 1-hydroxy-7-tert-butylpyrene (**17**): A solution of 1-methoxy-7-tert-butylpyrene **18** (254 mg, 0.88 mmol) in 30 mL of CH_2Cl_2 was stirred at 0 °C. Next, 0.9 mL of BBr_3 was added into above solution. After being stirred at room temperature for 3 hours, the reaction mixture was quenched to excess amount of mixture of ice and water. The product was diluted with water and extracted with $CHCl_2$. The combined organic phases were washed with water and brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The product was purified by chromatography (AcOEt as eluent) to give 230 g of slight black powder (84%). To get an analytical sample, the product was recrystallized with a mixture of hexane and AcOEt to obtain a slight yellow powder. R_f = 0.71 (AcOEt). MS (APCI) found: 274.36, calcd for $C_{20}H_{18}O$: 274.88, ^1H NMR (500 MHz, Aceton-d6) δ 9.39 (s, 1 H), 8.39 (d, J = 9.2 Hz, 1 H), 8.23 (s, 1 H), 8.22 (s, 1 H), 8.07 (d, J = 5.0 Hz, 2 H), 8.04 (d, J = 5.9 Hz, 1 H), 7.97 (d, J = 9.0 Hz, 1 H), 7.90 (d, J = 9.0 Hz, 1 H), 7.58 (d, J = 8.2 Hz, 1 H), 1.57 (s, 9 H); Anal. Calcd for $C_{18}H_{14}O_2$: C 87.56, H 6.61; found: C 87.27, H 6.67.

Preparation of 1-methoxymethoxy-7-tert-butylpyrene (**16**) : To a stirring solution of 1-hydroxy-7-tert-butyl-pyrene **17** (130 mg, 0.47 mmol) and K_2CO_3 (349 mg, 2.53 mmol) in acetone (5 mL) at 0 °C under nitrogen was added chloromethyl methyl ether (110 μL, 1.44 mmol) and the reaction was stirred at room temperature. After being stirred for 3 hours, the reaction mixture was diluted with water and extracted with $CHCl_3$. The combined organic phases were washed with water and brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by chromatography over silica gel eluting with 1:1 hexane:CH_2Cl_2 and toluene to yield the pure product **16** as a colorless gel (keep it for a few weeks in air or vacuum to get solid-state). R_f = 0.54 (hexane:CH_2Cl_2 = 1:1), MS (APCI): Calcd. for $C_{22}H_{22}O_2$ ($[M+H]^+$): 318.42; Found: 318.89; ^1H NMR (500 MHz, $CDCl_3$): δ 8.42 (d, J = 9.1 Hz, 2 H), 8.16 (s, 1 H), 8.15 (s, 1 H), 8.06 (d, J = 8.4 Hz, 1 H), 8.03 (d, J = 9.1 Hz, 1 H), 7.95 (d, J = 9.0 Hz, 1 H), 7.90 (d, J = 9.0 Hz, 1 H), 7.74 (d, J = 8.4 Hz, 1 H), 5.54 (s, 2 H), 3.62 (s, 3 H); 1.57 (s, 9 H).

Preparation of 1-methoxymethoxy-7-tert-butylpyrene-2-

carbaldehyde (**15**): To a stirring solution of **16** (324 mg, 1.018 mmol) and distilled N,N,N′,N′-tetramethylethylenediamine (1mL, 6.69 mmol) in dry cyclopentyl methyl ether (5 mL) cooled to 0 °C under nitrogen was added n-butyllithium (6.3 mL of 1.6 M in hexane solution, 10 mmol) and the reaction was stirred for 2 hours. Dry DMF (2 mL, 25.68 mmol) was added and the reaction was allowed to warm to room temperature with stirring over 14 hours before being quenched with a dilute NH_4Cl aqueous solution. The mixture was diluted with EtOAc, washed with water and brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude material was purified by chromatography over silica gel eluting with 1:1 hexane:CH_2Cl_2 to afford the pure product **15** as a slight yellow solid (120 mg, 34%). To get purer sample, the product was recrystallized with ethyl acetate. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.78 (s, 1 H), 8.60 (s, 1 H), 8.36 (d, J = 9.2 Hz, 1 H), 8.23 (s, 1 H), 8.22 (s, 1 H), 8.14 (d, J = 9.2 Hz, 1 H), 8.05 (d, J = 9.0 Hz, 1 H), 8.01 (t, J = 9.0 Hz, 1 H), 5.41 (s, 2 H), 3.69 (s, 3 H), 1.58 (s, 9 H); MS(APCI): Calcd. for $C_{23}H_{22}O_3$ ([M+H]$^+$): 347.43; Found: 347.17; Anal. Calcd for $C_{23}H_{22}O_3$: C 79.74, H: 6.40; found: C: 79.47, H: 6.43.

Preparation of 1-hydroxy-7-tert-butylpyrene-2-carbaldehyde (**14**): To a stirring solution of **15** (91 mg, 0.263 mmol) in THF (10 mL) at room temperature was added hydrochloride solution (1.0 mL, 5 M) and the reaction was heated to 65 °C for 7 h. The solution was then cooled to room temperature and the solvent was removed and the residue was purified by flash chromatography over silica gel eluting with $CHCl_3$ to afford 77 mg of pure product as a yellow solid (97%). To get purer product, the obtained sample was recrystallized with ethyl acetate. ^{1}H-NMR (500 MHz, $CDCl_3$) δ = 11.92 (s, 1H), 10.26 (s, 1H), 8.46 (d, J = 9.1 Hz, 1H), 8.17 (s, 1 H), 8.14 (s, 1H), 8.11 (s, 1H), 8.03 (d, J = 9.1 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.82 (d, J = 9.0 Hz, 1H), 1.57 (s, 9 H); MS(APCI): Calcd. for $C_{21}H_{18}O_2$ ([M+H]$^+$): 303.37; Found: 303.15; Anal. Calcd for $C_{21}H_{18}O_2$: C 83.42, H: 6.00; found: C: 83.14, H: 6.03.

Preparation of 7-(tert-butyl)-2-(((2,6-dimethylphenyl)imino)methyl)pyren-1-ol (**3**): To a stirring solution of **14** (77 mg, 0.255 mmol) and glacial acetic acid (30 µl) in toluene (3 mL) at 100 °C was added 2,6-dimethyl-aniline (95 µl, 0.771 mmol) and the reaction was carried out for 24 hours. The solvent was then removed and the residue was purified by flash chromatography over silica gel eluting with $CHCl_3$ to afford 102 mg of the pure product **3** as a yellow solid. (quantitative). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 14.16 (s, 1 H), 8.74 (s, 1 H), 8.55 (d, J = 9.1 Hz, 1 H), 8.14 (s, 1 H), 8.10 (s, 1 H), 8.05(d, J =9.1 Hz, 1H), 8.04 (s, 1H), 7.89 (d, J = 9.0 Hz, 1H), 7.82 (t, J = 9.0 Hz, 1H), 7.16 (d, J = 7.5 Hz, 2H), 7.07 (t, J = 7.5 Hz, 1H), 2.30 (s, 6H), 1.58 (s, 9H), MS (APCI): Calcd. for $C_{25}H_{27}NO$ ([M+H]$^+$): 406.54; Found: 406.22. Anal. Calcd for $C_{29}H_{27}NO$: C 85.89, H: 6.71, N: 3.45 found: C: 85.62, H: 6.65, N: 3.32.

Preparation of bis(7-(tert-butyl)-2-(((2,6-dimethylphenyl)imino)methyl)pyreno-lato) platinum(II) complex (**3(Pt)**): A mixture of **3** (30.36 mg, 0.075 mmol), anhydrous EtCOONa (16.77 mg, 0.175 mmol) in 1.5 mL of PhCl was added $PtCl_2(PhCN)_2$ (16.07 mg, 0.034 mmol) at 140 °C. The mixture was stirred for 7 days. After being cooled to room temperature, the solvent was removed and the residue was purified by silica gel chromatorgraphy (toluene or chloroform as eluent) to give 29.94 mg of **3(Pt)** as a red solid. Yield: 88%. In order to obtain purer product, the above sample was purified by recrystallization using a mixture of chloroform, hexane and methanol as solvent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 2H), 7.93 (s, 2H), 7.85 (s, 4H), 7.61 (d, J = 9.1 Hz, 2H), 7.56(d, J=9.1 Hz, 2H), 7.54(t, J = 7.7 Hz, 2H), 7.50 (d, J = 9.0 Hz, 2H), 7.37 (d, J = 7.7 Hz, 4H), 6.61 (d, J = 9.0 Hz, 2H), 2.54 (s, 12H), 1.52 (s, 18H); MS(APCI): Calcd. for $C_{58}H_{52}N_2O_2Pt$ ([M+H]$^+$): 1004.15; Found: 1004.42. Anal. Calcd for $C_{58}H_{52}N_2O_2Pt$: C, 69.38; H, 5.22; N, 2.79. Found: C, 69.12; H, 5.22; N, 2.70. The single crystals suitable for X-ray crystallography analysis were obtained by slow diffusion of a solvent system of PhCl/EtOH.

Preparation of 2-hydroxy-7-tert-butylpyrene (**22**) was carried out following the reference.[21]

Preparation of 1-formyl-2-hydroxy-7-tert-butylpyrene (**21**): To a suspension of 2-hydroxy-7-tert-butylpyrene (101.22 mg, 0.37 mmol, 1 eq.) and AgOTf (284.7 mg, 1.11 mmol, 3.0 eq.) in dry CH_2Cl_2 (2 mL) was added a solution of Cl_2CHOMe (110 µL, 3.0 eq.) in dry CH_2Cl_2 (1 mL) at 0 °C under an nitrogen atmosphere. After being stirred at 0 °C for 3 hours, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. After being stirred at room temperature for 1 hour, the reaction mixture was filtered through a pad of Celite®. The organic layer was separated and the aqueous layer was extracted twice with dichloromethane. The combined organic layers were washed with brine, dried with $MgSO_4$ and filtered. The filtrate was concentrated in vacuo and the resulting residue was purified by flash column chromatography on silica gel (eluted with hexane/EtOAc = 4/1) to afford 89 mg of the desired product **21** as a yellow solid. Yield: 80%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.53 (s, 1H), 11.15 (s, 1H), 8.70 (d, J = 9.3

https://doi.org/10.51316/jca.2021.024

Hz, 1H), 8.29 (s, 1H), 8.28 (d, J = 8.9 Hz, 1H), 8.26 (s, 1H), 8.12 (d, J = 8.9 Hz, 1H), 7.86 (d, J = 8.9 Hz, 1H), 7.60 (s, 1H), 1.58 (s, 9H); MS (APCI): Calcd. for $C_{21}H_{18}O_2$ ($[M+H]^+$): 303.14; Found: 303.14.

Preparation of 7-(tert-butyl)-1-(((2,6-dimethylphenyl)imino)methyl)pyren-2-ol (**4**): To a stirring solution of 1-formyl-2-hydroxy-7-tert-butylpyrene (21.76 mg, 0.072 mmol) and glacial acetic acid (20 µL) in toluene (2 mL) at 100 ^oC was added 2,6-dimethyl-aniline (80 µL, 0.650 mmol) and the reaction was carried out for 21 hours. The solvent was then removed and the residue was purified by flash chromatography over silica gel eluting with $CHCl_3$ to give 29.12 mg of pure product as an orange solid. (quantitative). ^1H-NMR (500 MHz, $CDCl_3$) δ = 14.49 (s, 1 H), 9.57 (s, 1H), 8.38 (d, J = 9.3 Hz, 1H), 8.22 (s, 2H), 8.16 (d, J = 9.3 Hz, 1H), 8.07 (d, J = 9.1 Hz, 1H), 7.91 (d, J = 9.1 Hz, 1H), 7.75 (s, 1H), 7.18 (d, J = 7.6 Hz, 2H), 7.09 (t, J = 7.6 Hz, 1H), 2.33 (s, 6 H), 1.58 (s, 9H), MS (APCI): Calcd. for $C_{29}H_{27}NO$ ($[M+H]^+$): 406.21; Found: 406.22. Anal. Calcd for $C_{29}H_{27}NO$: C, 85.89; H, 6.71; N, 3.45. Found: C, 85.75; H, 6.81; N, 3.47.

Table 1: Crystal Data and Structure Refinement for Platinum Complexes **3(Pt)** and **1(Pt)**

	3(Pt)	1(Pt)
Formula	$C_{58}H_{52}N_2O_2Pt$	$C_{50}\ H_{52}N_2O_2Pt$
M	1004.15	908.03
Crystal Size/ mm	0.13 x 0.13 x 0.02	0.13 x 0.08 x 0.05
Crystal Color	Red	Red
λ/ Å	0.71075	0.71075
T/K	173	123
Crystal System	Monoclinic	Triclinic
Space Group	$P2_1/c$	P-1
a/ Å	19.246 (3)	11.146 (4)
b/ Å	12.0028 (17)	11.495 (4)
c/ Å	9.6019 (16)	17.015 (6)
α/ deg	90	85.512 (7)
β/ deg	97.028 (4)	85.047 (6)
γ/ deg	90	64.606 (5)
V/ $Å^3$	2201.4 (6)	1960.0 (11)
Z	2	2
ρ/ g cm^{-1}	1.515	1.539
µ(MoKα)/ mm^{-1}	3.222	3.624
$2θ_{max}$/ deg	55.1	55.1
R_1	0.0463	0.0544
wR_2	0.1153	0.1170

Preparation of bis[7-(tert-butyl)-1-(((2,6-dimethylphenyl)imino)methyl)pyreno- lato] platinum(II) complex: A mixture of **4** (29.1 mg, 0.072 mmol), anhydrous EtCOONa (15.7 mg, 0.163 mmol) in 1.5 mL of PhCl was added $PtCl_2(PhCN)_2$ (15.4 mg, 0.033 mmol) at 140 ^oC. The mixture was stirred for 26 hours. After being cooled to room temperature, the solvent was removed and the residue was passed through flash chromatography (toluene as eluent) and then purified by GPC (toluene as eluent) to give **4(Pt)** as a red solid. Yield: ≈ 4 mg (12%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.99 (s, 2H), 8.12 (d, J = 9.4 Hz, 2H), 8.12 (s, 2H), 8.07 (d, J = 9.4 Hz, 2H), 8.07(s, 2H), 7.89 (d, J = 9.1 Hz, 2H), 7.52 (d, J = 9.1 Hz, 2H), 7.4-7.3 (m, 6 H), 6.71 (s, 2H), 2.55(s, 12H), 1.52 (s, 18H); MS(APCI): Calcd. for $C_{58}H_{52}N_2O_2Pt$ (M^+): 1004; Found: 1004.

Results and discussion

Synthesis

Both new isomeric pyrene-based salicylaldiminato-type platinum complexes prepared in this work are depicted in Chart 1. Introduction of t-butyl substituents in pyrene moieties was proposed to further improve the solubility, reduce the aggregation of the obtained compounds for not only ease of purification and characterization but also the synthesis, especially for the syntheses of the complex **4(Pt)**. The author used 2,6-dimethyl-phenyl group as a bulky substituent on imine group to prevent π-π stacking and also expected the π-conjugation of this group and the pyrene moieties.

The syntheses of the ligand **3** and the complex **3(Pt)** are outlined in Scheme 1 while the syntheses of the ligand **4** and the complex **4(Pt)** are presented in Scheme 2. At the beginning of this research, the author has planned to synthesize directly new isomeric formyl-pyrene derivatives **14** and **21** from corresponding hydroxy-pyrene via ortho-formylation reactions such as a combination of Mannich reaction and Duff reaction or a combination of ortho-lithiation and quenching with DMF reactions because of the convenient solid-state of hydroxy-pyrene and the short synthetic process. Currently, the application of the combination of Mannich reaction and Duff reaction is successful, however, the yield of this reaction is quite low (about 10-20%). Thus, the author decided to use ortho-lithiation way for the synthesis of **3(Pt)**.[18]

To introduce formyl group on pyrene moiety, Prof. Yamato of Saga University has usually used a combination of a very strong Lewis acid, such as $TiCl_4$,

$SnCl_4$ and $AlCl_3$, and Cl_2CHOMe.[22,23] Very recently, Prof. Doi of Tohoku University found that the combination of Lewis acid AgOTf and Cl_2CHOMe in dichloromethane is a wonderful way for the formylation of benzene and naphthalene derivatives.[24] Through considering the molecular orbitals of pyrene, the author has used this method for the formylation of 2-hydroxy-7-tert-butylpyrene **22**.

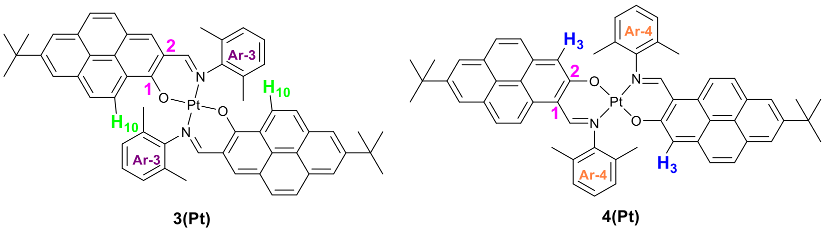
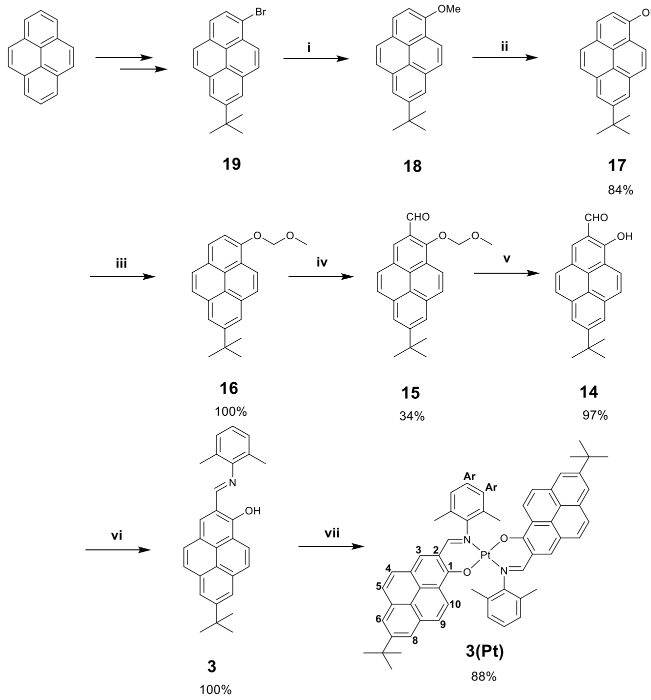


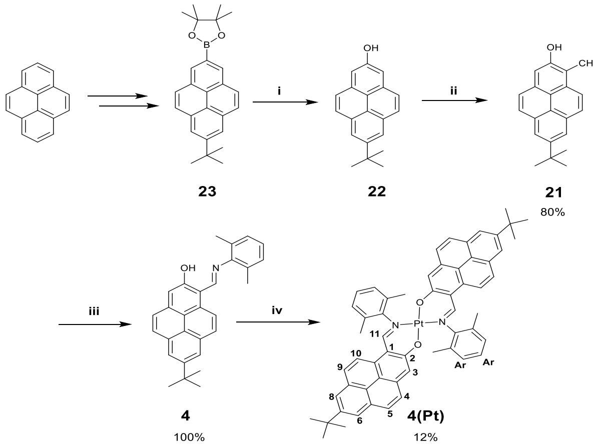
Chart 1: Chemical structures of two isomeric platinum complexes **3(Pt)** and **4(Pt)**



Scheme 1: Synthesis of Compound **3** and **3(Pt)**[a].

[a] (i) NaOMe, CuI, DMF, MeOH, N_2, 100 °C; (ii) BBr_3, CH_2Cl_2, r.t.; (iii) MOMCl, K_2CO_3, Acetone, N_2, r.t.; (iv) n-BuLi, TMEDA, CPME, DMF, 0 °C – r.t.; (v) HCl, THF, reflux; (vi) 2,6-dimethylaniline, AcOH, PhMe, 100 °C; (vii) $PtCl_2(PhCN)_2$, EtCOONa, PhCl, 140 °C

Wonderfully, the author got the aldehyde compound **21** in 65% yield after 30 min. Consequently, the ligands **3**, **4**, and the complexes were prepared following usual manner in previous reports.[18,19] It should be mentioned that the compound **16** has a solid-state at room temperature if the author dries it enough and the interactions between the bulky group on imine group of the ligands and confront pyrene moieties require a long reaction time for the metalation reaction.



Scheme 2: Synthesis of Compound **4** and **4(Pt)**[a]

[a] (i) NaOH, H_2O_2, $^nC_3H_7CN$, H_2O, r.t.; (ii) AgOTf, Cl_2CHOMe, CH_2Cl_2, 0 °C; (iii) 2,6-dimethylaniline, AcOH, PhMe, 100 °C; (iv) $PtCl_2(PhCN)_2$, EtCOONa, PhCl, 140 °C.

X-ray Crystallography

The molecular structure of the complex **3(Pt)** was determined along with the molecular structure of the complex **1(Pt)** by single-crystal X-ray diffraction.[18] The structures of these complexes are shown in Figure 2. Details of the crystallization procedure and the important crystallographic parameters can be found in the experimental section.

Both complexes were determined to be anti-form straightforwardly by single crystal diffraction study. The crystal of **3(Pt)** is made of one crystallographically independent complex while the crystal of **1(Pt)** is made up of two crystallographically independent complexes, Complex #1 and Complex #2 and the structure of

Complex #1 is represented in Figure 2.[18] The comparison of geometric parameters selected from X-ray diffraction analysis and DFT calculations for the Complexes **3(Pt)** and **1(Pt)** was shown in Table 2.

As expected for a d^8 complex, both complexes adopt a square-planar geometry around the metal center. Interestingly, both complexes exhibit different stair-stepped structures due to the different bulkiness of functional groups on imine group (the distances between two pyrene rings: 1.33 and 0.60 Å for **3(Pt)** and **1(Pt)**, respectively). The Pt-N and Pt-O bond lengths (for **3(Pt)**: Pt-N = 2.017(4), Pt-O = 1.974(3) and for **1(Pt)**: Pt-N = 2.008(8)-2.014(8), Pt-O = 1.991(7)-1.996(6)) (Table 2) correspond well with those reported for salicylaldiminato platinum complexes.[25,26]

Table 2: Comparison of selected geometric parameters coming from X-ray diffraction analysis and DFT calculations for the Complexes **3(Pt)** and **1(Pt)**

3(Pt) (R = 2,6-diMe-Ph)			**1(Pt)** (R = CH_3)			
Parameters	X-ray	Optimized geometry	Parameters	X-ray		Optimized geometry
				#1	#2	
N1-Pt1	2.017 (4)	2.043	N1-Pt1	2.008 (8)	2.014 (8)	2.036
N1*-Pt1	2.017 (4)	2.043	N1^{i}-Pt1	2.008 (8)	2.014 (8)	2.036
O1-Pt1	1.974 (3)	2.019	O1-Pt1	1.996 (6)	1.991 (7)	2.020
O1^{i}-Pt1	1.974 (3)	2.019	O1^{i}-Pt1	1.996 (6)	1.991 (7)	2.020
O1-C1	1.312 (5)	1.304	O1-C1	1.291 (10)	1.292 (10)	1.306
N1-C18	1.464 (6)	1.447	N1-C18	1.479 (11)	1.479 (11)	1.466
N1-C17	1.301 (6)	1.306	N1-C17	1.295 (11)	1.295 (11)	1.299
N1-O1*	2.750	2.818	N1-O1*	2.772	2.787	2.812
O1*-Pt1-N1*	92.90 (15)	92.13	O1*-Pt1-N1*	92.4 (3)	91.8 (3)	92.20
O1-Pt1-N1	92.90 (15)	92.13	O1-Pt1-N1	92.4 (3)	91.8 (3)	92.20
O1*-Pt1-N1	87.10 (15)	87.87	O1*-Pt1-N1	87.6 (3)	88.2 (3)	87.80
O1-Pt1-N1*	87.10 (15)	87.87	O1-Pt1-N1*	87.6 (3)	88.2 (3)	87.80

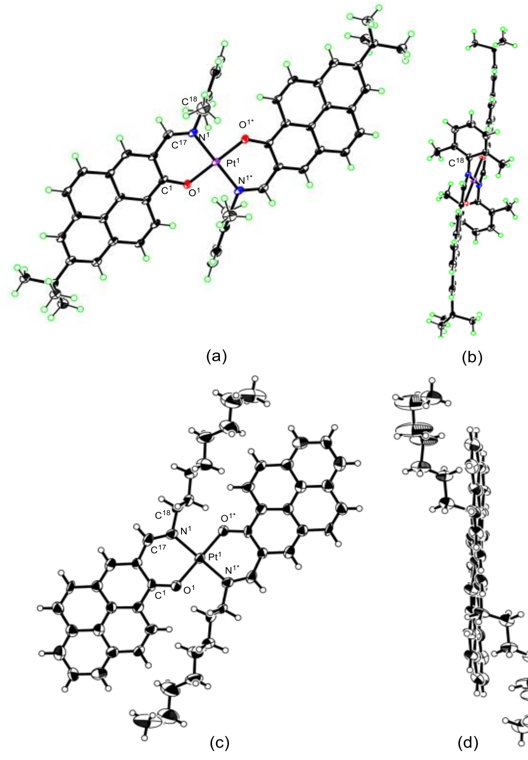


Figure 2: X-ray crystal structure of **3(Pt)** (top) and **1(Pt)** (bottom): (left) top view; (right) side view. The thermal ellipsoids are scaled to the 50% probability level

^{1}H NMR study

The ^1H NMR data for the ligands **3**, **4,** and the complexes **3(Pt)**, **4(Pt)** are listed in the Experimental. The assignment of the signals was carried out with the help of 2D ^1H COSY and NOESY spectra (See Figure 3). Both complexes **3(Pt)** and **4(Pt)** were diamagnetic d^8 low-spin metal(II) species since sharp ^1H NMR signals were observed in the diamagnetic region in $CDCl_3$. The aromatic proton signals of the two phenol moieties in **3(Pt)** and **4(Pt)** could not be distinguished from each other (see Appendix).

Most interestingly, a relationship between the structure and electronic spectra, the chemical shifts of two proton signals H_{10} (a doublet signal) for **3(Pt)** and H_3 (a singlet signal) for **4(Pt)** shifted to the upfield region compared to the corresponding ligands. These can be explained by the shielding effect of the aromatic ring currents of benzene ring of 2,6-dimethylphenyl group that close to the protons H_{10} (for **3(Pt)**) and H_3 for **4(Pt)**).[27]

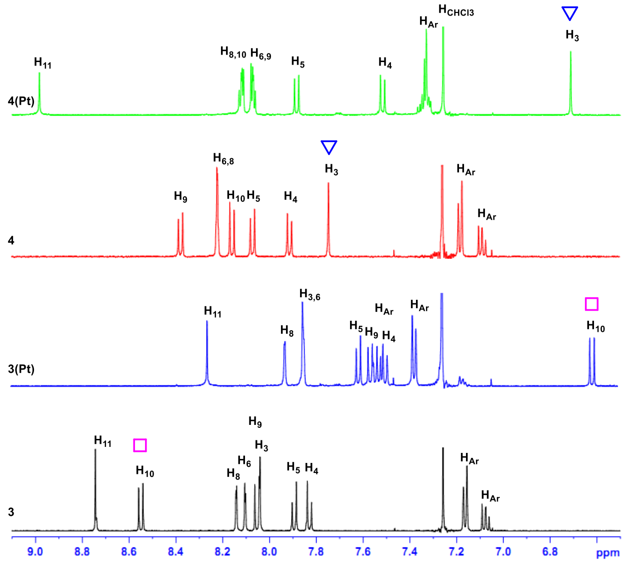


Figure 3: ^1H NMR spectra of the ligands **3**, **4** and the corresponding platinum complexes **3(Pt)** and **4(Pt)** in $CDCl_3$ at 25 °C

Photophysical study

The UV-vis absorption and emission data of the ligands **1**, **2**, **3**, **4** and the corresponding complexes **1(Pt)**, **2(Pt)**, **3(Pt)**, **4(Pt)** in dichloromethane are summarized in Table 3, Figure 4, and Figure 5. From these data, these complexes are red emitters and suitable for optical applications such as OLEDs or DSSCs. Although extinction coefficients of new complexes **3(Pt)** and **4(Pt)** are similar to the behaviors of the reported complexes **1(Pt)** and **2(Pt)**, the maximum wavelengths of absorption and emission spectra of both complexes **3(Pt)** and **4(Pt)** are red-shifted compared to those of reported complexes **1(Pt)** and **2(Pt)** due to the π-conjugation of benzene rings on imine group and pyrene moieties.[28] With the introduction of the bulky groups on **3(Pt)** and **4(Pt)**, they are being expected high photoluminescence quantum yield that the author is investigating.

Electrochemical study

The cyclic voltammogram (CVs) of **3(Pt)** along with that of **1(Pt)** and **2(Pt)**, recorded in benzonitrile under anaerobic conditions in the range 0.0 – 0.7 V vs Fc/Fc^+ (Figure 6), showed two reversible redox waves corresponding to the transfer of two electrons at 0.21 V and 0.43 V for the complex **3(Pt)** while both complexes **1(Pt)** and **2(Pt)**, all without bulky substituents, were found to give only one irreversible oxidation peak. These results indicate that **3(Pt)** could stabilize radical forms via two processes of the one-electron oxidation.

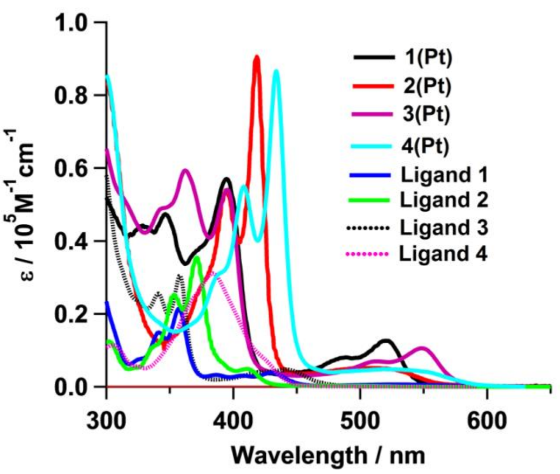


Figure 4: Absorption spectra of the ligands **4**, **3**, **2**, **1** and the corresponding platinum complexes **4(Pt)**, **3(Pt)**, **2(Pt)**, **1(Pt)** in CH_2Cl_2, at 25 °C (qualitative values for **4(Pt)**)

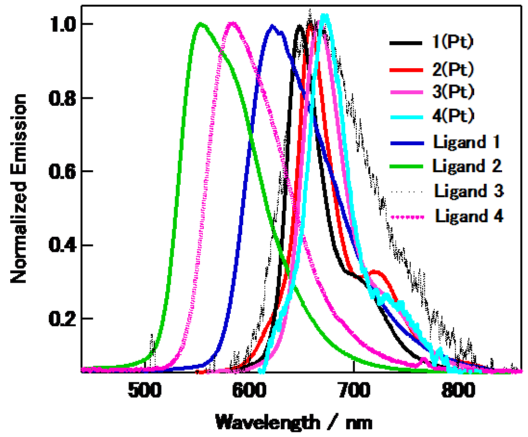


Figure 5: Emission spectra of the ligands **4**, **3**, **2**, **1**, and the corresponding platinum complexes **4(Pt)**, **3(Pt)**, **2(Pt)**, **1(Pt)** in CH_2Cl_2, at 25 °C (for each compound, obtained by exciting at its absorption maximum wavelength)

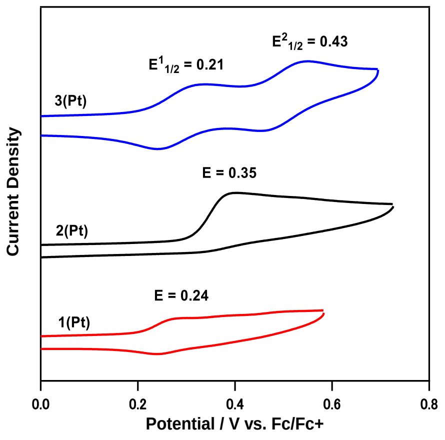


Figure 6. Cyclic voltammograms of **3(Pt)**, **2(Pt)** and **1(Pt)** in benzonitrile at a scan rate of 0.1 V/s

Table 3. Several Photophysical Parameters of Platinum Complexes **4(Pt)**, **3(Pt)**, **2(Pt)**, and **1(Pt)** and of Their Corresponding Ligands **4**, **3**, **2**, and **1** in CH_2Cl_2, at 25 °C

Compounds	λ_{abs} (nm)	ε_{max} x 10^{-4} (M^{-1} cm^{-1})	Δ λ_{abs} (nm)	λ_{em} (nm)	Δ λ_{em} (nm)	Φ (%)	τ (μs)
4	384	3.1	-46	582	-40	-	-
3	441	0.5	+11	658	+36	-	-
2	411	0.5	-19	553	-69	6.4	0.00066
1	430	0.4	-	622	-	8.2	0.00021
4(Pt)	524	-	+4	674	+29	1.0	-
3(Pt)	549	1.1	+29	667	+19	1.3	-
2(Pt)	514	0.5	-6	659	+11	1.3	0.53
1(Pt)	520	1.2	-	648	-	1.0	0.13

These results are similar to those of group 10 metal(II)-(disalicylidene)diamine complexes and related compounds.[29,30]

Computational study

Theoretical studies were performed for the further understandings of **3(Pt)** and **4(Pt)**. The DFT calculations using Gaussian 09 were performed with density functional theory, B3LYP, using the basic set 6-31G(d) for N, O, H, and C atoms and the basic set LanL2DZ for Pt atom.[18,31-34] The geometries were fully optimized, and the agreement between the calculated distance (see below) and angles for the complexes **4(Pt)**, **3(Pt)**, **2(Pt)**, and **1(Pt)** with the corresponding values obtained from single crystal X-ray diffraction study (only for **3(Pt)** and **1(Pt)**, see Table 2) is excellent.

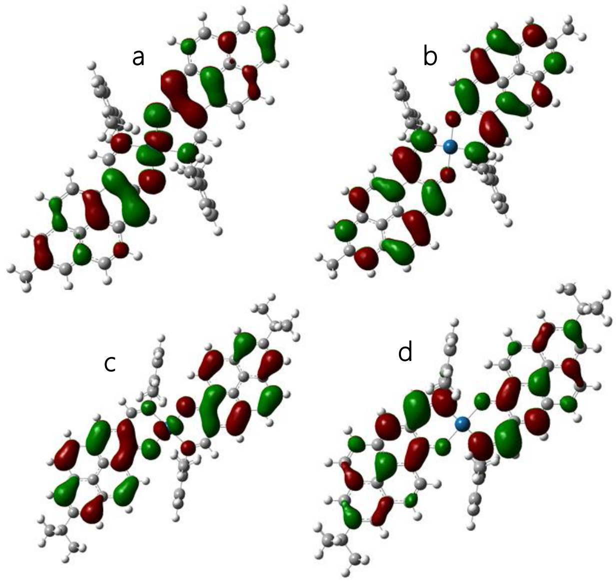


Figure 7: Plots of the (a) HOMO of **4(Pt)**, (b) LUMO of **4(Pt)**; (c) HOMO of **3(Pt)**, (d) LUMO of **3(Pt)** obtained from the RB3LYP/6-31g(d) level for C, H, O, N elements and LanL2DZ for Pt element . All the MO surfaces correspond to an isocontour value (0.02 a.u.)

As seen in Figure 7, the frontier molecular orbitals of these platinum complexes are mainly dominated by atomic orbitals originating from ligands in both cases and the contribution of platinum ions is small. The effect of nodal plane of pyrene in **3(Pt)** and **4(Pt)** is similar to that of **1(Pt)** and **2(Pt)**. The significant difference was observed for HOMO, -4.59, -4.82, -4.69 and -4.89 eV for **3(Pt)**, **4(Pt)**, **1(Pt)**, and **2(Pt)**, respectively. This supports to explanation of higher first oxidation potential in cyclic voltammogram and red-shift in absorption and emission spectra of **3(Pt)** compared to those of **1(Pt)**. The lowest excitations found in both complexes **3(Pt)** and **4(Pt)** were assigned to be the HOMO to LUMO transition. The detailed assignments of absorption spectrum obtained by time-dependent density functional theory (PCM/TDDFT) are summarized in Table 4.

Conclusions

Two new isomeric pyrene-based salicylaldiminato-type platinum complexes have been synthesized to investigate the impact of bulky substituents on pyrene moieties and imine group on the solubility, structural, photophysical, and electrochemical properties. It is found that both complexes have high solubility and red-shift in both absorption and emission spectra. The effects of the bulky substituents induce more distorted stair-stepped structure compared to the reported compounds, without bulky substituents, upfield shifts by the shielding effect were created by ring currents of benzene rings on imine groups. Most interestingly, stable radical forms were observed in the electrochemical study because of the bulky group, tert-butyl, on pyrene rings. The author is also performing the measurements of photoluminescence quantum yield for these complexes and studying several metal complexes of these new ligands.

Table 4: Composition, Energy (eV), Calculated and Experimental Absorption Wavelengths (nm), and Oscillator Strength (OS) if the Relevant Electronic Transitions of Platinum complexes **3(Pt)** and **4(Pt)** in CH_2Cl_2 (only transitions with: OS > 0.01 and Composition > 10% were considered, H = HOMO, L = LUMO)

No	Main Compositions	Energy (eV)	Wavelength (nm)	λ_{exp} (nm)^a	OS
Complex **4(Pt)**					
1	H→L (97%)	2.25	551	524	0.05
3	H-1→L (96%)	2.78	446		1.23
6	H-2→L+1(93%)	3.09	401		0.20
10	H-3→L+1(87%)	3.35	370		0.38
13	H→L+2 (79%)	3.62	343		0.03
Complex **3(Pt)**					
1	H→L (97%)	2.31	536	549	0.13
4	H-1→L+1(95%)	2.94	422		0.12
5	H→L+2 (95%)	3.08	403		0.61
8	H-2→L (87%)	3.38	367		0.87
10	H-1→L+3(82%)	3.48	357		0.07

Acknowledgments

This work was supported in part by the Priority Research Program sponsored by the Asian Human Resources Fund from Tokyo Metropolitan Government (TMG), Nippon Glass Sheet Foundation, a research grant funded by Hanoi University of Science and Technology (Grant No. T2017-PC-022), and a research grant funded by Vietnam Electricity Power Generation Corporation 1 (Grant No. 84/HĐ-KHCN-EVNGENCO1-BKHN). L.X.D. appreciates Tokyo Metropolitan University (TMU) for a pre-doctoral fellowship. The author appreciates the scientific and supervision support of Ken-ichi Sugiura and Ken-ichi Yamashita (TMU), the quantum yield and lifetime measurements of Yoshitane Imai and Kazuki Nakabayashi, the technical assistance of Toshihiko Sakurai (TMU).

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