ORGANOMETALLICS

Highly Efficient Solid-State Phosphorescence of Platinum Dihalide Complexes with 9-Phenyl-9-arsafluorene Ligands

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S Supporting Information

ABSTRACT: Platinum dihalide (chloride, bromide, and iodide) complexes with 9-phenyl-9-arsafluorene, which can be safely prepared and are air stable, were synthesized. The dibromide and diiodide complexes showed highly efficient phosphorescence even at 298 K in the solid state, and their quantum yields were up to a value of 0.52. The structures of the complexes were analyzed by X-ray crystallography. Time-dependent density functional calculations support our understanding of the initial electron transition processes. The rigid and bulky structure of the arsafluorene backbone effectively induced solid-state phosphorescence unlike that of a triphenylarsine analogue, which has three unbridged phenyl groups.

INTRODUCTION

Platinum complexes have attracted much attention as phosphorescent materials.¹ They have many potential applications: for example, as photocatalysts,² sensitizers,³ organic light emitting diodes (OLED),⁴ and chemosensors.⁵ Room-temperature solid-state phosphorescence is a prerequisite for these applications. Thus, the chemical structures of emissive platinum complexes have been extensively investigated. For example, Naota and co-workers employed rigid salicylaldimine ligands incorporating oligoethylene and oligo(ethylene glycol) capsules, and the quantum yields of the complexes were ~ 0.38 in the solid state at 298 K.6 The ligands were designed to avoid nonradiative decay via concentration self-quenching and molecular motion around the luminophore. The ligand structure must be sophisticated to isolate a molecule and to restrict molecular motion, resulting in highly efficient solid-state phosphorescence. However, to fulfill these requirements, complicated ligand designs must be used.⁷ Consequently, a simpler ligand design is desirable to allow easy preparation of phosphorescent platinum complexes in the solid state.

From a structural viewpoint, 9-heterofluorene^{8,9} is a promising ligand backbone. It is easy to synthesize, the biphenylene moiety is highly rigid, and substitution at the 9position increases steric hindrance. Nevertheless, there have been no reports on the solid-state phosphorescence of transition-metal complexes containing 9-heterofluorene. To apply 9-heterofluorenes as a ligand, pnictogen-type 9-



heterofluorenes are preferred due to their coordination affinity for transition metals. Among them, 9-phosphafluorene has been the most widely researched,¹⁰ especially in the fields of catalysis¹¹ and optoelectronics.¹² However, practical application of 9-phosphafluorene complexes are limited because of their air sensitivity, which means that oxidized impurities are often present.^{11b}

Recently, we reported the synthesis of 9-arsafluorenes via nonvolatile intermediates.¹³ This safe and facile synthetic procedure is superior to conventional methods, which use volatile and toxic organoarsines.¹⁴ The synthetic route for 9-phenyl-9-arsafluorene (3) is shown in Scheme 1.¹³ The nonvolatile cyclic oligoarsine precursor hexaphenylcyclohexaarsine (1) was prepared from phenylarsonic acid.¹⁵ Iodine was added to 1, yielding diiodophenylarsine (2). The obtained





Received: November 11, 2015

solution of 2 was added to 2,2'-dilithiobiphenyl, and the product was purified by recrystallization, leading to 3. The prepared 9-arsafluorenes were more air-stable than phospha-fluorenes.¹⁶ They possessed intense emission in the solid state at 77 K, though no emission was observed at 298 K.

In this study, we investigated the synthesis of platinum dihalide complexes containing 9-phenyl-9-arsafluorene (3-PtX₂, X = Cl, Br, I). We also performed structural analysis of the synthesized complexes. The dibromide and diiodide complexes showed highly efficient phosphorescence in the solid state even at 298 K (the quantum yields were up to a value of 0.52).¹⁷ Furthermore, the effect of the rigid fluorene backbone on solid-state phosphorescence was investigated by comparison with triphenylarsine (4), whose three phenyl rings can freely rotate. Crystallographic studies and theoretical calculations support our understanding of the highly efficient phosphorescence and electron transitions.

RESULTS AND DISCUSSION

Synthesis. A schematic of the synthesis of platinum dihalide complexes with 3 is shown in Scheme 2. A chlorobenzene





(PhCl) solution of 3 and *cis*-bis(benzonitrile)dichloroplatinum (*cis*-PtCl₂(PhCN)₂) was refluxed under a nitrogen atmosphere. Recrystallization from CH₂Cl₂ and MeOH gave the platinum dichloride complex 3-PtCl₂ as yellow crystals in quantitative yield. Halogen exchange reactions with KBr and KI were carried out in a mixture of PhCl and methyl isobutyl ketone (MIBK) to give 3-PtBr₂ (orange crystals) and 3-PtI₂ (red crystals), respectively. The chemical structures of the obtained complexes were determined by NMR spectroscopy and single-crystal X-ray diffraction analysis. In the ¹H NMR spectra, each peak due to ligand protons in 3-PtX₂ shifted downfield from that of bare ligand 3. The electron density of the ligands decreased on coordination to the platinum center, indicating ligand complexation.

To compare the optical properties of the complexes, platinum dihalide complexes with triphenylarsine $(4-PtX_2, X = Cl, Br, I)$ were prepared from *cis*-PtCl₂(PhCN)₂ by the same procedure as those of **3**. The chemical structures were confirmed by NMR spectroscopy. The signals in the ¹H NMR spectra of 4-PtX₂ shifted downfield after the coordination.

Crystallographic Studies. Crystallographic studies on 3-PtX₂ were carried out to understand the solid-state structural features. Crystals for X-ray diffraction analysis were prepared by slow mixing of MeOH with the CH₂Cl₂ solutions. The chloride, bromide, and iodide complexes of 3-PtX₂ crystallized in the triclinic space group $P\overline{1}$ for the chloride and bromide and orthorhombic *Pna*2₁ for the iodide. The structures of 3-PtX₂ are asymmetrical. ORTEP drawings of the complexes are shown in Figure 1. The complexes adopt a trans square-planar geometry in the solid state.



Figure 1. ORTEP drawings of 3-PtX₂ (X = Cl, Br, I). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

Selected bond lengths are given in Table 1. The average Pt– X bond lengths in 3-PtX₂ are 2.3, 2.4, and 2.6 Å, respectively,

Table 1. Selected Bond Lengths in 3-PtX₂

Х	Pt–X (Å)	Pt–As (Å)
Cl	2.307(2), 2.299(2)	2.394(1), 2.393(1)
Br	2.4335(8), 2.4229(8)	2.3954(8), 2.3952(8)
Ι	2.607(1), 2.603(1)	2.398(1), 2.393(1)

reflecting the different radii of the coordinated halogen atoms. The average Pt-As bond length is approximately 2.4 Å in all complexes of 3-PtX₂. The Pt-As bond lengths are not influenced by the identity of the halide.

The X–Pt–X (X = Cl, Br, I) angles are 179.5, 179.2, and 179.5°, respectively, and the As–Pt–As angles in 3-PtX₂ (X = Cl, Br, I) are 179.2, 179.0, and 178.6°, respectively (Table 2).

Table 2. Selected Bond Angles in 3-PtX,

х	X-Pt-X (deg)	As-Pt-As (deg)	X-Pt-As (deg)
Cl	179.45(8)	179.21(4)	93.24(6), 92.86(6), 87.28(6), 86.62(6)
Br	179.16(3)	179.00(3)	93.39(3), 93.09(3), 87.28(3), 86.25(3)
Ι	179.54(3)	178.55(4)	93.28(3), 91.93(3), 87.63(3), 87.16(3)

Thus, the geometries around the metal in the obtained complexes were all planar in the solid state. The As–Pt–X angles are approximately 90°, and the sums of the As–Pt–X angles are 360° , consistent with square-planar coordination to the platinum center.

The symmetry of the obtained complexes was collapsed in the crystalline state. The 9-arsafluorene moieties were slightly bent in the complexes with Pt, as shown by the interplanar angles of the five-membered ring and the fused benzene rings. The average interplanar angles of 3-PtX₂ (X = Cl, Br, I) are 2.6, 3.0, and 4.0°, respectively. In addition, the twist of the phenyl ring to the fluorene moiety was estimated by the torsion angle given by C-C-As-centroid, as shown in Figure 2. All of the complexes have different torsion angles: 3-PtCl₂ (26.4 and 1.6°), 3-PtBr₂ (23.0 and 3.4°), and 3-PtI₂ (18.6 and 11.2°). In the case of 3-PtI₂, the difference in the torsion angles was much



Figure 2. Estimation of the twist of the phenyl ring with respect to the fluorene moiety in **3**-PtX₂.

smaller than in those of 3-PtCl₂ and 3-PtBr₂, suggesting that 3-PtI₂ has a more symmetrical structure.

Optical Properties. UV-vis absorption spectra of 3-PtX₂ were measured in chloroform (Figure 3a). The longest



Figure 3. (a) UV–vis absorption spectra of 3-PtX₂ in chloroform solutions ($c = 6.3 \times 10^{-5}$ M). (b) Diffuse reflection spectra (the Kubelka–Munk calibration) and photographs of 3-PtX₂ in the solid state.

absorption maxima of $3-PtX_2$ (X = Cl, Br, I) lie in the UV region (292, 317, and 367 nm, respectively), corresponding with the results of TD-DFT calculations using the B3LYP functional as implemented in Gaussian 09 (Table S5 in the Supporting Information).¹⁸ However, the solids of $3-PtX_2$ (X = Cl, Br, I) were yellow, orange, and red, respectively (Figure 3b). In the UV-vis absorption spectra measured under concentrated conditions (Figure S8 in the Supporting Information), no new peaks due to intermolecular interactions, i.e., $\pi - \pi$ or Pt-Pt interactions, were observed. On the other hand, in the solid state, low-lying absorption bands may be observed because, on symmetry lowering, the forbidden transitions become allowed.¹⁹ The calculated HOMO-LUMO transition energies of 3-PtX₂ (X = Cl, Br, I) are 470.5, 495.9, and 540.0 nm, respectively. These values correspond to the diffuse reflection spectra in Figure 3b. Thus, the electron transitions are responsible for the colors of the solid samples.

 3-PtX_2 showed intense emissions in the solid state at 298 K; in contrast, no emissions were observed in solution. Exciton deactivation, caused by molecular motion, was reduced in the solid state. The crystalline samples recrystallized from CH₂Cl₂ and MeOH showed bright luminescence. However, the dispersion samples, measured on the aggregates prepared by slow mixing of poor solvents (hexane or MeOH) with good solvents (CH₂Cl₂), were nonemissive. Thus, 3-PtX_2 showed crystallization-induced emission (CIE) activity.

For the measurement of solid-state emissions, all samples were prepared by recrystallization from CH_2Cl_2 and MeOH. The solid-state excitation and PL spectra of 3-PtX₂ at 298 K are

shown in Figure 4. In the excitation spectra (Figure 4a), the absorption maxima were observed at the approximately same



Figure 4. (a) Excitation spectra of 3-PtX₂ in the solid state (λ_{em} 680 nm). (b) PL spectra of 3-PtX₂ (X = Cl, Br, I) in the solid state (λ_{ex} 403, 370, and 400 nm, respectively). Both excitation and PL measurements were carried out at 298 K.

wavelength as those of the diffuse reflection spectra in Figure 3b. Thus, it is the HOMO–LUMO transitions, which are forbidden in solutions but allowed in the solid state, that are responsible for this emission.

The solid-state emission properties of 3- and 4-PtX₂ are summarized in Table 3. The quantum yields of 3-PtX₂ (X = Cl,

Table 3. Solid-State Emission Properties of $3-PtX_2$ and $4-PtX_2$

		298 K		77 K		
ligand	Х	λ_{\max}^{a} (nm)	Φ^b	λ_{\max}^{a}	(nm)	Φ^b
3	Cl	624	0.01	603		0.53
3	Br	626	0.26	618		0.88
3	Ι	640	0.52	624		0.73
4	Cl	n.d.	n.d.	581		0.82
4	Br	n.d.	n.d.	с		с
4	Ι	647	0.03	626		0.67
^a Emission	maxima.	^b Absolute	quantum	vields.	^c The	emission

"Emission maxima. "Absolute quantum yields. The emission properties of 4-PtBr₂ were not determined because it showed polymorphism; for further details, see ref 21.

Br, I) are 0.01, 0.26, and 0.52, respectively, and the quantum yield was higher for heavier halides. This is probably because the heaver and larger halogen atoms can move less in a crystalline matrix. In particular, the quantum yield of 3-PtI₂ was significantly high.¹⁷ In the crystalline state, 3-PtI₂ prevented π - π interactions, and the H–I interaction effectively fixed the molecular conformation (Figure 5).²⁰ Furthermore, the quantum yields of 3- and 4-PtX₂ (X = Cl, Br, I) were improved



Figure 5. (a) Packing structure of **3**-PtI₂. Hydrogen atoms are omitted for clarity. (b) Intermolecular H–I interaction.

by cooling to 77 K, which reduced molecular motion. The emission lifetimes were measured to examine the components of their emissions in the solid state at 298 K (Figure S9 in the Supporting Information). The emissions were composed of single-lifetime components, and the lifetimes of 3-PtX₂ (X = Cl, Br, I) are 3.2, 12.0, and 25.5 μ s, respectively, long enough to conclude that the emissions are due to phosphorescence.

Notably, 4-PtX₂ showed either no or very weak emissions at 298 K (Figure 6), despite the intense emission observed at 77



Figure 6. Photographs of 3- and 4-PtX₂ (X = Cl, Br, I) under UV irradiation (365 nm) at 298 K.

K.²¹ The molecular motions of the three phenyl rings in 4 were less restricted than in the fluorene moiety of 3 at 298 K; however, the motion of the phenyl rings was frozen at 77 K. This result suggests that the rigid fluorene backbone was responsible for the solid-state phosphorescence of 3-PtX₂ even at room temperature.

CONCLUSION

In conclusion, we synthesized the platinum dihalide complexes 3-PtX₂ (X = Cl, Br, I) using 9-phenyl-9-arsafluorene (3), which can be prepared by a safe and facile process. These complexes had CIE activity and showed highly efficient phosphorescence at 298 K in the solid state. In particular, the quantum yield of 3- PtI_2 ($\Phi = 0.52$) was significantly high. In the case of using triphenylarsine 4 as a ligand, the iodine complex 4-PtI₂ emitted weakly at 298 K. From the X-ray diffraction results, the complexes of 3-PtX₂ had asymmetrical structures without large distortions, enabling HOMO-LUMO transitions. Bulky and rigid 9-phenyl-9-arsafluorene ligands prevented intermolecular $\pi - \pi$ interactions and molecular motion, which would otherwise deactivate the excitons via a nonradiative pathway. This is the first study on the use of a 9-heterofluorene backbone to construct solid-state phosphorescent platinum complexes. As a general strategy to improve the emission properties, multidentate ligands have been used to enhance the structural rigidity of the complex, and bulky substituents have been incorporated to avoid close packing of adjacent molecules.^{6,7a-g} Furthermore, the design of the ligand is simpler than that for existing ligands.

Facile synthesis, air stability, and simple structure are great advantages in the molecular design of ligands for solid-state emissive complexes. This ligand will open a new route to luminescent materials. Further functions of these ligands and complexes with other metals are under investigation.

EXPERIMENTAL SECTION

Materials. *cis*-Bis(benzonitrile)dichloroplatinum (*cis*-PtCl₂(PhCN)₂) were purchased from Sigma-Aldrich Co., Ltd. Dichloromethane (CH₂Cl₂), methanol (MeOH), chlorobenzene (PhCl), methyl isobutyl ketone (MIBK), potassium bromide, and potassium iodide were purchased from Nacalai Tesque, Inc. Other chemicals were purchased from Wako Pure Chemical Industry, Ltd. All commercially available chemicals were used without further purification. Hexaphenylcyclohexaarsine (1) was prepared following a literature procedure.¹⁵

Measurements. ¹H NMR (400 MHz) spectra were recorded on a Bruker DPX-400 spectrometers, and samples were measured in CDCl₃ using Me₄Si as an internal standard. The following abbreviations are used; s, singlet; d, doublet; t, triplet; m, multiplet. The UV–vis spectra were recorded on a Jasco spectrophotometer (V-670 KKN). Emission spectra were obtained on an FP-8500 instrument (JASCO), and absolute PL quantum yields (Φ) were determined using a JASCO ILFC-847S instrument; the quantum yield of quinine sulfate reference was 0.52, which is in agreement with the literature value.²² Emission lifetimes were measured using Quantaurus-Tau (Hamamatsu Photonics).

X-ray Crystallographic Data for Single-Crystalline Products. The single crystals were mounted on glass fibers with epoxy resin. Intensity data were collected at room temperature on a Rigaku RAXIS RAPID II imaging plate area detector with graphite-monochromated Mo K α radiation. The crystal to detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. The data were collected at room temperature to a maximum 2θ value of 55.0°. Data were processed by the PROCESS-AUTO²³ program package. An empirical or numerical absorption correction²⁴ was applied. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction²⁵ was applied. The structures were solved by Patterson methods²⁶ and expanded using Fourier synthesis.²⁷ Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on observed reflections and variable parameters. In the case of the product recrystallized from acetone, the final cycle of full-matrix least-squares refinement on F was based on observed reflections and variable parameters. All calculations were performed using the CrystalStructure^{28,29} crystallographic software package. Crystal data and more information on X-ray data collection are summarized in Table S1 in the Supporting Information.

Syntheses. ¹³C NMR was not measured for complexes 3-PtX₂ and 4-PtX₂ because of the low solubility of the products.

Synthesis of 3-PtCl₂. A PhCl solution (10 mL) of 3 (0.160 g, 0.525 mmol) and *cis*-PtCl₂(PhCN)₂ (0.124 g, 0.262 mmol) was refluxed under N₂ overnight. The solvent was removed in vacuo and, subsequently, recrystallized from CH₂Cl₂ and MeOH, yielding 3-PtCl₂ as a yellow solid (0.218 g, 0.249 mmol, 95%). ¹H NMR (CDCl₃, 400 MHz): δ 8.21 (d, 1H, *J* = 7.2 Hz), 7.94 (d, 1H, *J* = 7.6 Hz), 7.73 (d, 1H, *J* = 8.4 Hz), 7.60 (d, 1H, *J* = 7.6 Hz), 7.56 (t, 2H, *J* = 8.2 Hz), 7.43 (t, 2H, *J* = 3.2 Hz), 7.33–7.38 (m, 5H) 7.18 (t, 1H, *J* = 7.4 Hz), 7.10 (t, 1H, *J* = 7.6 Hz) ppm.

Synthesis of 3-PtBr₂. A PhCl (5 mL) and MIBK (1 mL) solution of 3-PtCl₂ (23.5 mg, 0.027 mmol) and KBr (88.6 mg, 0.75 mmol) was refluxed overnight under N₂. The solvents were removed in vacuo, and CH₂Cl₂ was added to the residue. After filtration, the solvent was removed in vacuo. The residue was recrystallized from CH₂Cl₂ and MeOH to give 3-PtBr₂ as an orange solid (15 mg, 0.015 mmol, 57%). ¹H NMR (CDCl₃, 400 MHz): δ 8.27 (d, 2H, *J* = 7.6 Hz), 7.94 (d, 2H, *J* = 8.0 Hz), 7.54 (t, 2H, *J* = 6.6 Hz), 7.37 (t, 2H, *J* = 6.8 Hz), 7.21–7.34 (m, 5H) ppm.

Synthesis of 3-Ptl₂. A PhCl (4 mL) and MIBK (0.5 mL) solution of 3-PtCl₂ (46.1 mg, 0.053 mmol) and KI (177 mg, 1.07 mmol) was refluxed overnight under N₂. The distilled water (5 mL) was added to the reaction mixture, leading to a red precipitate in the organic layer. The precipitates were collected by filtration to give 3-PtI₂ as a red solid (43 mg, 0.041 mmol, 77%). ¹H NMR (CDCl₃, 400 MHz): δ 8.25 (d,

2H, *J* = 7.6 Hz), 7.93 (d, 2H, *J* = 8.4 Hz), 7.54 (t, 2H, *J* = 7.6 Hz), 7.39 (t, 2H, *J* = 7.0 Hz), 7.24–7.36 (m, 5H) ppm.

Synthesis of 4-PtCl₂. A PhCl solution (7 mL) of 4 (0.162 g, 0.529 mmol) and *cis*-PtCl₂(PhCN)₂ (0.125 g, 0.265 mmol) was refluxed under N₂ overnight. The solvent was removed in vacuo, and subsequent recrystallization from CH₂Cl₂ and MeOH gave 4-PtCl₂ as a pale yellow solid (223 mg, 0.254 mmol, 96%). ¹H NMR (CDCl₃, 400 MHz): δ 7.72 (dd, 6H, J = 6.8 Hz, 1.2 Hz), 7.45–7.38 (m, 9H) ppm.

Synthesis of 4-PtBr₂. A PhCl (5 mL) and MIBK (1 mL) solution of 4-PtCl₂ (23.9 mg, 0.027 mmol) and KBr (88.1 mg, 0.70 mmol) was refluxed overnight under N₂. The solvents were removed in vacuo, and CH₂Cl₂ was added to the residue. After filtration, the solvent was removed in vacuo. The residue was recrystallized from CH₂Cl₂ and MeOH to give 4-PtBr₂ as a yellow solid (15 mg, 0.015 mmol, 57%). ¹H NMR (CDCl₃, 400 MHz): δ 7.73 (dd, 6H, *J* = 6.0 Hz, 1.6 Hz), 7.43–7.40 (m, 9H) ppm.

Synthesis of 4-Ptl₂. A PhCl (4 mL) and MIBK (0.5 mL) solution of 4-PtCl₂ (46.3 mg, 0.053 mmol) and KI (177 mg, 1.07 mmol) was refluxed overnight under an N₂ atmosphere. The solvents were removed in vacuo, and CH₂Cl₂ was added to the residue. After filtration, the solvent was removed in vacuo. The residue was recrystallized from CH₂Cl₂ and MeOH to give 4-PtI₂ as a yellow solid (42 mg, 0.040 mmol, 75%). ¹H NMR (CDCl₃, 400 MHz): δ 7.72–7.70 (m, 6H), 7.41–7.40 (m, 9H) ppm.

Computational Details. Time-dependent density functional theory (TD-DFT) calculations using the B3LYP functional were used to investigate the origin of the electronic transitions of the platinum dihalide (chloride, bromide, and iodide) complexes with 9-phenyl-9-arsafluorene ligands (3-PtX₂). Geometry optimizations were performed using the crystal structure 3-PtX₂ geometries as the initial coordination. DFT calculations were carried out in Gaussian 09.¹⁸ The CEP-121G basis set was used for the Pt and I atoms, and the 6-311G* basis set was used for As, Br, C, Cl, and H atoms.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.5b00944.

NMR spectra, X-ray diffraction data, and theoretical calculations (PDF)

X-ray data for 3-PtCl₂ (CIF)

X-ray data for 3-PtBr₂ (CIF)

X-ray data for 3-PtI₂ (CIF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Prof. M. Shimizu and Mr. R. Shigitani of Kyoto Institute of Technology for emission lifetime measurements. This study is a part of a Grant-in-Aid for Scientific Research on Innovative Areas "New Polymeric Materials Based on Element-Blocks (No. 2401)" (No. 24102003) of The Ministry of Education, Culture, Sports, Science and Technology, Japan.

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