



Synthesis, structure, and solid-state phosphorescence of heteroleptic platinum(II) complexes bearing iminophenyl and iminophenoxy ligands

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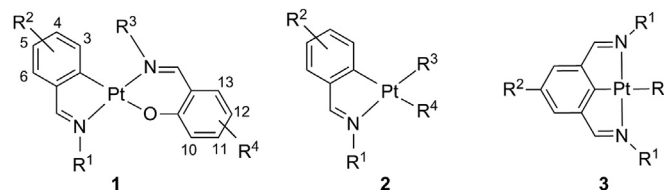
ABSTRACT

A series of heteroleptic platinum(II) complexes **1** bearing iminophenyl and iminophenoxy ligands have been synthesized and characterized using NMR, IR, and emission spectroscopies, mass spectrometry, and single crystal X-ray diffraction. The complexes exhibit intense phosphorescent emission with an absolute quantum efficiency (Φ_{298K}) up to 0.29 in the crystalline state. Chromogenic control of solid-state emission over a range of 99 nm can be performed simply by introducing methoxy (MeO) groups at different positions on the aromatic rings. Hypsochromic and bathochromic shifts from the orange **1a** crystal are observed with 4-/11-MeO (*para*-position of the imine moieties on the phenyl and phenoxy ligands; yellow emission) and 5-/12-MeO (*para*-position of the phenyl and phenoxy moieties; reddish orange and red emission) substitution, respectively. Time-dependent density functional theory (TD-DFT) calculations (B3LYP/6-31G*, LanL2DZ) indicated that the chromatic variation can be ascribed to the position-specific influence of the substituents on the HOMO and LUMO levels. The solid-state emission and heat-resistance are discussed based on the molecular packing of the crystals.

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1. Introduction

Metal complexes with cyclometallating ligands have attracted much interest, due to their characteristic emission properties, and have undergone extensive study in regard to both fundamentals and applications [1]. Typical examples are iridium [2,5–7] and platinum [3,4,8–10] complexes bearing pyridine [2,3], imidazole [4], pyrazole [5], triazole [6], *N*-heterocyclic carbene [7,8], amino-methyl [9], and imine [10] moieties as bidentate [2,3a–c,4–7,8a,b,10d–g] and tridentate [3d–h,8c,9,10e–i] ligands. During the course of our study on the molecular aggregation and emission properties of *trans*-bis(iminophenoxy)metal complexes [11–13], novel heteroleptic platinum(II) complexes **1** bearing iminophenyl and iminophenoxy ligands were synthesized. 2-Iminophenyl platinum(II) complexes **2** with chloro [10a–d], alkyl [10d–f], and acetylacetonato [10g] ligands and NCN-pincer complexes **3** [10h,i] have been prepared and studied with respect to their reactivity for chemical transformation [10a–h] and optical properties [10i].



Complex **1** exhibits intense phosphorescent emission in the crystalline state. Although solid-state lighting has been extensively studied using a variety of phosphorescent composite materials [1b], the solid-state phosphorescence of transition metal complex crystals remains unascertained, despite their potential for high-density integration to realize intense emission. Enhancement of solid-state emission has been performed mainly using two contrasting strategies in molecular design and crystal engineering; the avoidance of significant molecular contacts such as π – π stacking [12–14], and the construction of metal–metal contacts [12,13,15]. Further information is required to comprehensively understand the correlation between solid-state emission and molecular arrangement. X-ray diffraction of emissive crystal **1** revealed that the *N*-alkyl group R^3 on the iminophenoxy ligand blocks intermolecular π -stacking interactions, forming a face-to-edge molecular array that minimizes energy dispersion for solid-state phosphorescence.

The present platform **1** also exhibits an extraordinarily wide chromogenic change for solid-state emission, simply by changing the substitution position of the methoxy (MeO) group on the

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iminophenyl and iminophenoxy moieties. Chromogenic control in phosphorescent Ir and Pt complexes has been studied extensively by the introduction of various substituents on the cyclometallated ligands. However, no significant change in the emission color by simply introducing the same substituents at different positions on the ligands has been reported. Typically, chromatic shifts over 30, 45, 58 and 65 nm have been observed in the emission of Ir(ppy) analogs upon the introduction of F [16], CF₃ [16b], MeO [17], and C₆F₅ [18] substituents at different positions. The variation range observed for crystals **1** is 99 nm, which is much wider than that achieved in previous cases.

This paper describes the synthesis, structure, and solid-state emission of a series of heteroleptic platinum(II) complexes bearing iminophenyl and iminophenoxy ligands, with focus on the mechanistic rationale for the dynamic photophysical behavior with respect to the molecular arrays and electronic configuration in the crystals. The recent report of solid-state emission from a phenylpyridine platinum(II) complex [3c] has prompted us to report emission properties of the present novel complexes.

2. Experimental section

2.1. General methods

Melting points were measured in a glass capillary with a melting point apparatus (Büchi B-545). IR spectra were measured using a Bruker EQ UINOX55 spectrometer. ¹H and ¹³C NMR spectra were recorded on Varian Unity-Inova 500 and Jeol JNM-GSX-270 spectrometers. Diffuse reflectance UV–vis spectra of crystals were obtained with a Jasco V-570 spectrometer equipped with an integrating sphere (Jasco ISN-470). Emission spectra were measured with a Jasco FP-6500 spectrometer. Quantum yields were measured with the absolute method using a Jasco FP-6500 spectrometer equipped with an integrating sphere under UV excitation at 420 nm. Emission lifetime measurements were conducted with an Optical Building Blocks EasyLife V instrument using a 415 nm LED for excitation. Mass spectra were measured using a Jeol JMS-DX 303 spectrometer.

2.2. Synthesis of *ab*-(1-(alkyliminomethyl-κN)-2-phenoxy-κO)-*cd*-(1-(alkyliminomethyl-κN)-2-phenyl-κC²)-platinum(II) complexes (**1**)

A series of heteroleptic platinum complexes **1** was prepared by stirring a mixture of **5** [10c,20] and the sodium salt of the corresponding 2-(*N*-pentyliminomethyl)phenol (2.4 equiv) in dry tetrahydrofuran (THF) at room temperature. The crude mixture was purified by chromatographic separation (SiO₂, toluene). Complexes **1a–n** were characterized using ¹H, ¹³C NMR and FT-IR spectroscopy, in addition to high-resolution mass spectrometry. ¹H and ¹³C NMR signals were assigned based on COSY, NOESY, HMQC, and HMBC experiments.

2.2.1. *ab*-(1-(Pentyliminomethyl-κN)-2-phenoxy-κO)-*cd*-(1-(pentyliminomethyl-κN)-2-phenyl-κC²)-platinum(II) (**1a**)

Orange solid (24%). mp 144 °C; IR (KBr) 3051, 2952, 2926, 2862, 1606, 1537, 1472, 1450, 1435, 1362, 1343, 917, 751, 728 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 0.85 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 1.24–1.35 (m, 4H), 1.35–1.43 (m, 4H), 1.83–1.94 (m, 4H), 3.82 (tm, *J* = 7.2 Hz, 2H), 4.27 (tm, *J* = 7.2 Hz, 2H), 6.52 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H), 6.88 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.00 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H), 7.09 (ddd, *J* = 7.4, 7.4, 1.6 Hz, 1H), 7.19 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.27 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.34 (ddd, *J* = 8.6, 6.9, 1.9 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.90 (s, 0.67H; d, ³*J*_{H–Pt} = 71.4 Hz, 0.33H), 8.13 (s, 0.67H; d, ³*J*_{H–Pt} = 113 Hz, 0.33H); ¹³C NMR (CDCl₃, 125 MHz) δ 13.9,

14.1, 22.3, 22.4, 28.6, 29.1, 30.4, 33.8, 57.0, 65.6, 114.7, 121.7, 122.1, 122.6, 127.5, 130.5, 133.4, 133.8, 134.6, 141.8, 147.7, 161.7, 166.0, 176.3; HRMS (FAB⁺): *m/z* calcd for C₂₄H₃₃N₂O¹⁹⁵Pt, [M + H]⁺ 560.2235, found 560.2244. Anal. Calcd for C₂₄H₃₂N₂O: C, 51.51; H, 5.76; N, 5.01. Found. C, 51.40; H, 5.74; N, 5.08.

2.2.2. *ab*-(4-Methoxy-1-(pentyliminomethyl-κN)-2-phenoxy-κO)-*cd*-(1-(pentyliminomethyl-κN)-2-phenyl-κC²)-platinum(II) (**1b**)

Yellow solid (26%). mp 141 °C; IR (KBr) 2951, 2926, 2860, 1611, 1534, 1450, 1434, 1224, 829, 726 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 0.84 (t, *J* = 7.2 Hz, 3H), 0.91 (tm, *J* = 7.2 Hz, 3H), 1.25–1.36 (m, 4H), 1.36–1.46 (m, 4H), 1.84 (tt, *J* = 7.3, 7.3 Hz, 2H), 1.91 (tt, *J* = 7.3, 7.3 Hz, 2H), 3.79 (s, 3H), 3.83 (t, *J* = 7.2 Hz, 2H), 4.22 (t, *J* = 7.2 Hz, 2H), 6.17 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.35 (d, *J* = 2.4 Hz, 1H), 6.99 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 7.09 (ddd, *J* = 7.4, 7.4, 1.7 Hz, 1H), 7.27 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.77 (s, 0.67H; d, ³*J*_{H–Pt} = 72.3 Hz, 0.33H), 8.14 (s, 0.67H; d, ³*J*_{H–Pt} = 112 Hz, 0.33H); ¹³C NMR (CDCl₃, 125 MHz) δ 13.9, 14.1, 22.4, 22.5, 28.6, 29.2, 30.5, 33.9, 55.0, 57.0, 65.1, 102.6, 105.6, 116.5, 122.5, 127.4, 130.5, 133.9, 134.8, 141.7, 147.7, 160.8, 165.3, 167.9, 176.1; HRMS (FAB⁺): *m/z* calcd for C₂₅H₃₅N₂O₂¹⁹⁵Pt, [M + H]⁺ 590.2341, found 590.2371.

2.2.3. *ab*-(5-Methoxy-1-(pentyliminomethyl-κN)-2-phenoxy-κO)-*cd*-(1-(pentyliminomethyl-κN)-2-phenyl-κC²)-platinum(II) (**1c**)

Red solid (16%). mp 112 °C; IR (KBr) 3748, 3737, 2951, 2928, 1619, 1593, 1474, 1435, 1376, 1324, 1219, 1167, 946, 826, 727 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 0.85 (tm, *J* = 7.2 Hz, 3H), 0.90 (tm, *J* = 7.2 Hz, 3H), 1.26–1.36 (m, 4H), 1.36–1.44 (m, 4H), 1.84–1.95 (m, 4H), 3.74 (s, 3H), 3.81 (t, *J* = 7.2 Hz, 2H), 4.28 (t, *J* = 7.2 Hz, 2H), 6.65 (d, *J* = 3.2 Hz, 1H), 6.83 (d, *J* = 9.2 Hz, 1H), 6.99 (ddd, *J* = 7.5, 7.5, 0.9 Hz, 1H), 7.05 (dd, *J* = 9.2, 3.2 Hz, 1H), 7.08 (ddd, *J* = 7.5, 7.5, 1.6 Hz, 1H), 7.27 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.86 (s, 0.67H; d, ³*J*_{H–Pt} = 75.5 Hz, 0.33H), 8.13 (s, 0.67H; d, ³*J*_{H–Pt} = 116 Hz, 0.33H); ¹³C NMR (CDCl₃, 125 MHz) δ 13.9, 14.1, 22.3, 22.4, 28.6, 29.1, 30.5, 33.9, 56.1, 56.9, 65.7, 113.6, 120.5, 122.4, 122.6, 124.7, 127.6, 130.5, 133.7, 142.1, 147.8, 149.2, 161.0, 161.4, 176.2; HRMS (FAB⁺): *m/z* calcd for C₂₅H₃₄N₂O₂¹⁹⁵Pt, [M]⁺ 589.2268, found 589.2270.

2.2.4. *ab*-(1-(Pentyliminomethyl-κN)-2-phenoxy-κO)-*cd*-(4-methoxy-1-(pentyliminomethyl-κN)-2-phenyl-κC²)-platinum(II) (**1d**)

Yellow solid (17%). mp 155 °C; IR (KBr) 2951, 2926, 2859, 1606, 1547, 1473, 1451, 1417, 1342, 1215, 1041, 763 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 0.85 (t, *J* = 7.2 Hz, 3H), 0.90 (tm, *J* = 7.2 Hz, 3H), 1.28–1.35 (m, 4H), 1.35–1.41 (m, 4H), 1.82–1.93 (m, 4H), 3.74 (t, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 4.27 (t, *J* = 7.2 Hz, 2H), 6.51 (ddd, *J* = 7.8, 6.9, 1.1 Hz, 1H), 6.54 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.87 (dm, *J* = 8.6 Hz, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 7.19 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.33 (ddd, *J* = 8.6, 6.9, 1.8 Hz, 1H), 7.89 (s, 0.67H; d, ³*J*_{H–Pt} = 69.3 Hz, 0.33H), 8.01 (s, 0.67H; d, ³*J*_{H–Pt} = 104 Hz, 0.33H); ¹³C NMR (CDCl₃, 125 MHz) δ 13.9, 14.1, 22.4, 22.5, 28.7, 29.1, 30.5, 33.8, 55.1, 56.6, 65.5, 107.1, 114.7, 120.1, 121.7, 122.3, 129.1, 133.5, 134.5, 140.9, 143.7, 161.3, 161.7, 166.0, 175.0; HRMS (FAB⁺): *m/z* calcd for C₂₅H₃₅N₂O₂¹⁹⁵Pt, [M + H]⁺ 590.2341, found 590.2371.

2.2.5. *ab*-(1-(Pentyliminomethyl-κN)-2-phenoxy-κO)-*cd*-(5-methoxy-1-(pentyliminomethyl-κN)-2-phenyl-κC²)-platinum(II) (**1e**)

Orange solid (21%). mp 134 °C; IR (KBr) 3448, 2935, 2863, 1607, 1471, 1454, 1295, 756 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 0.85 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.27–1.35 (m, 4H), 1.35–1.41 (m, 4H), 1.83–1.92 (m, 4H), 3.77 (s, 3H), 3.81 (t, *J* = 7.2 Hz, 2H), 4.24 (t, *J* = 7.2 Hz, 2H), 6.51 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 1H), 6.78 (dd, *J* = 8.6, 3.0 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.88 (d, *J* = 3.0 Hz, 1H), 7.18 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.29 (d, *J* = 8.6 Hz, 1H), 7.34 (ddd, *J* = 8.5, 6.9, 1.8 Hz, 1H), 7.88 (s, 0.67H; d, ³*J*_{H–Pt} = 69.3 Hz, 0.33H), 8.11 (s, 0.67H;

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