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Four new binuclear platinum (II) complexes with 2-(1H)-quinolinone as bridging ligands: Synthesis, crystal structure and photophysical properties

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ABSTRACT

Four new binuclear platinum (II) complexes were successfully synthesized named $[Pt(bzq)(\mu\text{-}C_9H_7NO)]_2$ (**1**), $[Pt(dpp)(\mu\text{-}C_9H_7NO)]_2$ (**2**), $[Pt(dpq)(\mu\text{-}C_9H_7NO)]_2$ (**3**), $[Pt(ppy)(\mu\text{-}C_9H_7NO)]_2$ (**4**), where 7,8-benzoquinoline (hbzq), 2,3-diphenylpyrazine (hdpp), 2,3-diphenylquinoxaline (hdpq) and 2-phenylpyridine (hppy), were used as cyclometalated ligands and 2-(1H)-quinolinone ($\mu\text{-}C_9H_8NO$) firstly served as a bridging ligand, respectively. Their crystal structure, photophysical and time-dependent density functional theory calculations characteristics were investigated. The X-ray structure for four compounds showed that Pt(II)-Pt(II) distances were 2.8485 Å, 2.8325 Å, 2.8833 Å, 2.8707 Å respectively, which testified absorption and emission of the complexes benefited from metal-metal-to-ligand charge transfer (MMLCT) transitions. A near-infrared emissive peak of **2** is 762 nm in the neat film.

1. Introduction

The most important oxidation is the + 2 for the third row transition element platinum(Pt), with electronic configuration d^8. Pt(II) complexes are square planar almost stemming from sufficiently large ligand field of Pt(II) [1]. The square planar conformation is the main reason for properties of platinum(II) complexes such as absorption, luminescence and other excited state properties. These platinum(II) complexes have developed research interest for their numerous potential applications as optoelectronic devices [2,3], organic light-emitting diodes (OLEDs) [4,5], vapor-sensing [6], as well as oxygen-Sensing [7]. Most applications are based on mononuclear cyclometalated Pt(II) complexes, whose emission results from mixed charge transfer excited states, such as ligand-centered (^{3}LC), ligand-to-ligand charge-transfer (^{3}LLCT), and metal-to-ligand charge transfer (MLCT) excited states. For instance, Thompson and his coworkers developed a series of mononuclear platinum (II) complexes with emissive peaks in a range from 456 to 600 nm [8]. Thilagar's group presented mononuclear platinum complexes, which displayed emissive peaks between 482 and 606 nm [9].

Binuclear platinum complexes have characters of photophysical properties generating broad interest. Via metal-metal-to-ligand charge transfer (MMLCT) transitions involving charge transfer between a filled Pt-Pt antibonding orbital and a vacant [10], ligand-based π*orbital, marked red-shifted emission spectra can be observed relative to the mononuclear emission spectra [8–9,11–12]. But, this phenomenon could take place when the intramolecular distance of Pt(II)-Pt(II) is less than 3.5 Å. The MMLCT transition energy decreases following decreasing Pt-Pt separation. Red-shifted spectra could be obtained by intermolecular interaction (π-π, Pt(II)-Pt(II) interaction) accompanying low quantum efficiency. So merit of binuclear platinum complexes can avoid decreasing energy gap by intermolecular interaction bringing about radiationless relaxation and low quantum efficiency. It has been reported that Thompson and co-workers previously reported a series of binuclear platinum(II) complexes based on bridging pyrazolate ligands with intramolecular distance of Pt(II)-Pt(II) between 3.3763(7) and 2.8343(6) Å [13]. Weiguo Zhu et al. displayed a red emission at 690 nm in solution due to its intramolecular Pt-Pt interaction [14]. An emission peak of the complex anti-$[\{Pt(d\text{-}t\text{-}bpy)(NS_2)\}_2]ClO_4$ is 548 nm with Pt-Pt distance 2.973 Å while the emission peak of anti-$[\{Pt(d\text{-}t\text{-}bpy)(N_2S)\}_2]ClO_4$ is 562 nm with Pt-Pt distance 2.979 Å [15].

Enlightened by intramolecular Pt-Pt interaction, a method for realizing red-shifted spectra is to develop binuclear platinum complexes. In this contribution, we report four binuclear cyclometalated platinum(II) complexes, namely $[Pt(bzq)(\mu\text{-}C_9H_7NO)]_2$ (**1**), $[Pt(dpp)(\mu\text{-}C_9H_7N\ O)]_2$ (**2**), $[Pt(dpq)(\mu\text{-}C_9H_7NO)]_2$ (**3**), $[Pt(ppy)(\mu\text{-}C_9H_7NO)]_2$ (**4**), in which 7,8-benzoquinoline (hbzq), 2,3-diphenylpyrazine (hdpp), 2,3-diphenylquinoxaline (hdpq), 2-phenylpyridine (hppy), were used as cyclometalated ligands, and 2-(1H)-quinolinone ($\mu\text{-}C_9H_8NO$) was firstly adopted as an auxiliary ligand. We get four very short intramolecular distance of Pt(II)-Pt(II), which is 2.8485 Å, 2.8325 Å, 2.8833 Å,

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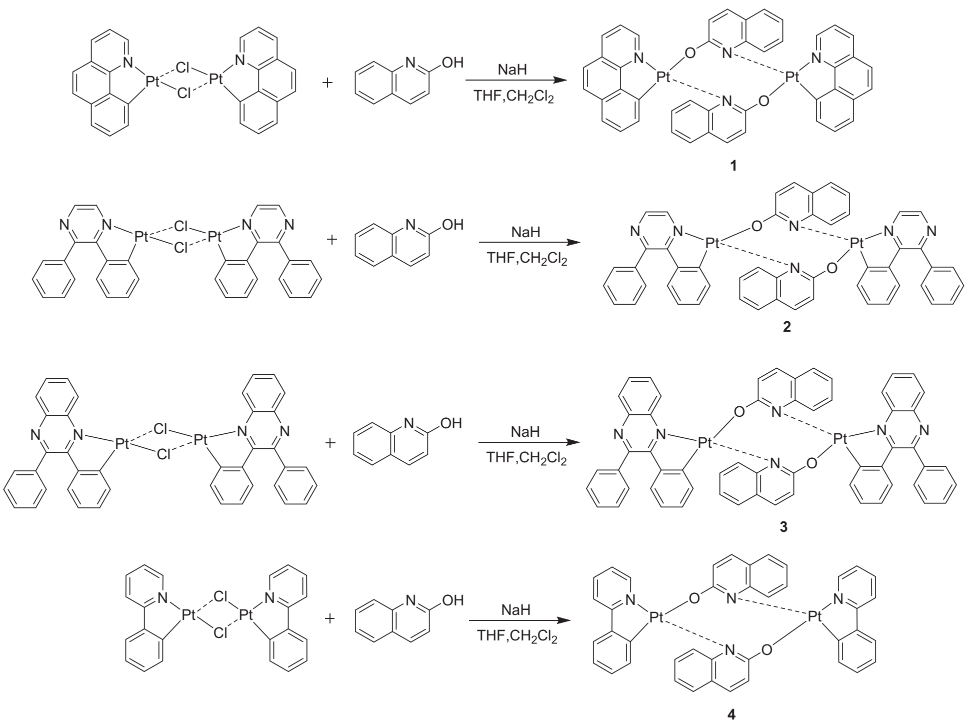

Scheme 1. Procedure for sythesis of ligands.

2.8707 Å, respectively. They contribute to form MMLCT transitions to impact on their luminescence.

2. Experimental section

2.1. Materials and methods

All commercially available starting materials were used directly without further purification. The solvents were carefully dried prior to use. ^{1}HNMR spectra were measured on Varian INOVA-400 MHz. Mass spectra were recorded on Finnigan-LCQDECA Mass spectrometer. Element analyses were performed with a Finnigan-LCQDECA microanalyzer. UV–Vis absorption spectra were carried out at room temperature on Perkin Elmer Lambda 950 spectrophotometer. The preparation of neat films were fabricated by placing solid samples between two layers of quartz plate and poly(methyl methacrylate) films (PMMA) were obtained by spin coating a mixture of PMMA, samples and tetrahydrofuran THF on quartz plate. The phosphorescence (PL) spectra were record on Horiba Fluorolog-4 spectrophotometer at 298 K and 77 K respectively. Samples were degassed by more than three freeze-pump-thaw cycles prior to measurement. Quantum efficiency measurements were carried out at room temperature in a solution of THF, $[Ru(bpy)_3]Cl_2$ (excitation wavelength = 436 nm, Φ_{lum} = 0.042) was applied in degassed aqueous solution as reference [16]. The equation $\Phi_s = \Phi_r(A_r/A_s)(n_s/n_r)_2(I_s/I_r)$ was used to calculate the quantum yields where s is the quantum yield of the sample, r is the quantum yield of the reference, n is the refractive index of the solvent, As and Ar are the absorbance of the sample and the reference at the wavelength of excitation and Is and Ir are the integrated are as of emission bands [17]. Phosphorescence lifetime measurements were recorded on Horiba-Fluorolog-4 spectrophotometer. The excitation source is NANOLED 370 (λ 370 nm) and the photo collection adopts TCSPC method (time-correlated single photocounts). The single crystal X-ray diffraction data of **1**–**4** were gathered on the Bruker SMART 1000 CCD detector equipped when compounds **1**–**2** were adopted by a graphite monochromated Mo Ká radiation (λ = 0.71073 Å) and **3**–**4** were used by a graphite monochromated Cu Ká radiation (λ = 1.54184 Å). (CCDC: 1557992–1557995)

2.2. General procedure for synthesis of ligands (Scheme S1.)

2,3-diphenylquinoxaline (hdpq): A hdpq ligand is synthesized by following our previous work [18].

2,3-diphenylpyrazine (hdpp): To a mixture of 1,2-diphenylethanedione (8.411 g, 37.54 mmol) in anhydrous ethanol (30 mL), ethidene diamine (2.403 g, 40.01 mmol) was added. The mixture was heated at 75 °C for 8 h. After cooled to room temperature, the mixture was sealed in the fridge overnight, filtered, and washed with anhydrous ethanol. The residue was purified by column chromatography using silica gel and petroleum ether/ethyl acetate = 3:1 as an eluent to give a yellow solid (5,6-diphenyl-2,3-dihydropyrazine, dpdhp). Yield (1.108 g, 76%). ^{1}HNMR ($CDCl_3$, 400 MHz) δ: 7.50–7.48(d, J = 7.2 Hz, 4H), 7.40–7.39(d, J = 4 Hz, 2H), 7.35–7.32(t, J = 7.6 Hz, 4H), 3.80 (s, 4H).

To a suspension of dpdhp (0.212 g, 0.906 mmol) in anhydrous ethanol (15 mL), ferricchloride (0.179 g, 1.104 mmol) was added. The mixture was heated and stirred for 8 h at. It was immediately extracted with dichloromethane (DCM) and water. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was evaporated to remove the solvent and the residue was purified by column chromatography using silica gel and petroleum ether/ethyl acetate = 5:1 as an eluent to give a pale green solid. Yield (0.0715 g, 34%).^{1}HNMR ($CDCl_3$, 400 MHz); δ: 7.99(s, 1H), 7.97(d, J = 1.4 Hz, 1H), 7.67(t, J = = 7.4 Hz, 1H), 7.52(t, J = 7.8 Hz, 3H).

2.3. General procedure for synthesis of ì-chloro-bridged dimmer platinum (II) (Scheme S2.)

$[(bzq)\ PtCl]_2$: A solution of hdpq (0.141 g, 0.499 mmol) in 2-ethoxyethanol (4.5 mL) was added to a solution of K_2PtCl_4 (0.104 g, 0.251 mmol) in water (1.5 mL). The mixture was heated at 100 °C under nitrogen atmosphere for 24 h. The solvent was removed under reduced pressure distillation. The precipitate was treated with ethanol to give a dark red solid which was filtered off and washed with ethanol (2 × 10 mL). Yield (0.583 g, 63%).