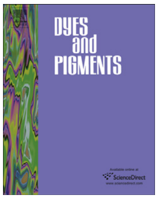
Dyes and Pigments xxx (2016) 1–6

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



Efficient red organic light-emitting diode based on simple Pt(II) O^N-complex

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ARTICLE INFO

Article history:
Received 31 March 2016
Received in revised form
6 June 2016
Accepted 10 June 2016
Available online xxx

Keywords:
Platinum(II) complexes
8-hydroxyquinoline
Electroluminescence
OLEDs

ABSTRACT

A first observation of red-orange electroluminescence (CIE chromacity coordinates $X = 0.5389$, $Y = 0.3842$) of platinum(II) bis-(8-hydroxyquinolinate) incorporated in multilayer OLED structure as a dopant component of the emission layer was made. It was estimated, that high chemical purity of abovementioned complex is vital for good electroluminescence properties. Besides, new reliable synthetic pathways to PtQ_2 have been developed, and its photophysical properties have been investigated.

1. Introduction

To date, cyclometalated complexes of iridium(III) and platinum(II) are the most important phosphorescent emitters for organic light-emitting devices [1,2] due to their unique properties – short lifetime of triplet exited states, high quantum yields of luminescence, broad range of possible colors of emission.

Emission of Pt(II) complexes is attributed to exited ^{3}MLCT states as well as possible intraligand π-π^* states. One can assume, that for efficient electroluminescence an energy of LUMO should match the energy level of cathode, while an energy of highest HOMO should be closed to the potential of hole-transport layer or to the ionization potential of anode in the case of a simple device [3]. This led to a large diversity of ligands and even types of complexes. Among all, C^N, N^N, N^C^N chelate complexes are the most studied and, simultaneously, are the most efficient [4,5]. Nevertheless, for practical applications not only a maximum quantum efficiency is important, but synthetic accessibility of complexes is also play a significant role.

Oxine (8-hydroxyquinoline, quinolin-8-ol) is a unique monoprotic bidentate chelating ligand widely used in analytical chemistry [6]. It can form complexes with the most of elements, and some of these complexes (e.g. AlQ_3, ScQ_3, GaQ_3) are well known as superior electroluminescent compounds as well as electron-transport materials (ETC) [7]. Surprisingly, much less attention has been paid to complexes of oxine with platinum group metals, in spite of their evident structural similarity to well-known highly efficient luminescent complexes with other O^N ligands [8]. According to the literature IrQ_3 or PtO_2 have not been tested before as emission materials in OLED's [9].

Taking into account the continuous interest for application of simple complexes of 8-hydroxyquinoline (HQ) for preparation of OLED's emission layers in the present paper we wish to report results of synthesis, properties and application for electro-optical devices of platinum(II) bis-(8-hydroxyquinolinate) (PtQ_2) as an effective red-emitting phosphor.

Synthesis of this complex was first described by Ballardini [10] in 1978, but the yield of the target complex was dispiritingly low. This method furthermore was slightly improved by the same group of authors [11]. Both approaches were based on an interaction of HQ with K_2PtCl_4 at different pH and stoichiometric relationships between reagents. But even by the improved method the PtQ_2 yield was not exceed 15%. Very recently another approach has been

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http://dx.doi.org/10.1016/j.dyepig.2016.06.018
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Please cite this article in press as: Taydakov I, et al., Efficient red organic light-emitting diode based on simple Pt(II) O^N- complex, Dyes and Pigments (2016), http://dx.doi.org/10.1016/j.dyepig.2016.06.018

published [12]. Platinum complexes of highly substituted 8-hydroxyquinolines were obtained by prolonged heating of Pt(hfacac)$_2$ (Hhfacac – hexafluoroacetylacetone) with corresponding ligands in toluene. The reported yields were about 80%. In the present research we adopted this method for the preparation of unsubstituted PtQ$_2$.

2. Experimental

2.1. General remarks and instrumentation

Platinum(II) hexafluoroacetilacetonate and 8-hydroxyquinoline were purchased from Aldrich. All other solvents and reagents were synthetic grade and purchased form Aldrich and Acros Organics. For spectroscopic measurements solvents were degassed by purging of He for 30 min before preparation of solutions. OLED-grade materials were purchased from Lumtec Corp. (Taiwan).

Impurity concentrations were measured by a NexION 300D (Perkim Elmer) inductively coupled plasma mass-spectrometer. Elemental analysis was performed on an Elementar Vario MicroCube CHNO(S) analyzer. NMR spectra were recorded at 298 K on a Bruker AC-300 instrument operated at 300.13 MHz for ^{1}H nucleus, in DMSO-d_6 as a solvent. TMS ($\delta = 0.00$ ppm) was used for ^{1}H NMR measurements as a standard.

IR spectra were recorded on a Tensor 27 (Bruker) FTIR spectrometer in KBr discs. UV-VIS absorption spectra were recorded on a Varian Cary-100 Scan instrument. Raman spectra were recorded in geometry of photon backscattering using an Ocean Optics QE65000 spectrometer supported by 785 nm excitation laser and optical fiber cable for input/output of a light signal. Integration time was 30 s for the every run in the range 200–2000 cm^{-1}. It was enough to collect Raman photons at 500–1000 mW laser pumping power and to avoid the Raman probe overheating.

Luminescent spectra were obtained on a Fluorolog FL3-22 (Horiba–Jobin–Yvon) spectrofluorimeter equipped by 450 W xenon lamp and standard Hamamatsu R-928 PMT. Quantum yields of solid samples were measured by an absolute method with a G8 integration sphere (GMP SA, Switzerland) on the same instrument. All spectra were corrected for instrumental responses.

Kinetics measurements were performed on the custom build setup equipped with Nd:YAG pulse laser (pulse width of 10 ns) equipped with a frequency tripler (355 nm). The emission was collected at a right angle to the excitation beam and wavelengths were selected with an iHR320 monochromator (Horiba–Jobin–Yvon). The signal was measured by Hamamatsu R928 PMT connected to a SR570 low noise current preamplifier (Stanford Research Systems) and 500 MHz band pass digital oscilloscope (Tektronix TDS 724C). Solutions of PtQ$_2$ in spectroscopic grade DMF or CH$_2$Cl$_2$ were degassed by purging of steam of He for 10 min.

2.2. Single crystal X-ray analysis

Single crystals of PtQ$_2$ were obtained by slow cooling of a hot saturated solution of complex in MeCN/MeOH mixture in a sealed tube under Ar. PtQ$_2$ crystals (black-red blocks, C$_{18}$H$_{12}$N$_2$O$_2$Pt, M = 483.39) are monoclinic, space group $P2_1/c$, at 120 K: a = 9.1958(5) Å, b = 10.3556(5) Å, c = 14.7597(8) Å, $\beta = 100.2355(11)°$, $V = 1383.17(13)$ Å^3, Z = 4 (Z′ = 1), d$_{calc}$ = 2.321 g/cm^3, μ(MoKα) = 101.56 cm^{-1}, F(000) = 912. The intensities of 13,291 reflections were measured with a Smart APEX II CCD diffractometer [μ (MoK$_\alpha$) = 0.71072 Å, ω-scans, 2θ < 58°] and 3673 independent reflections (R$_{int}$ = 0.0399) were used in the further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in an anisotropic-isotropic approximation. The refinement converged to wR2 = 0.0588 and GOF = 1.007 for all independent reflections (RI = 0.0255 was calculated against F for 2828 observed reflections with I > 2σ(I)). All calculations were performed using SHELXTL PLUS [13]. CCDC 1470748 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data *via* www.ccdc.cam.ac.uk/data_request/cif.

2.3. OLED fabrication and characterization

Multilayers OLED devices were fabricated by layer-by-layer vacuum thermal sputtering (<10^{-5} Pa) on a glass substrate (20 × 30 × 3 mm, RMS = 2.5 nm) with ITO conducting layer. The deposition rates of each layer were no more than 0.03 nm × s^{-1}. The OLED structure was ITO/MoO$_3$ (1 nm)/NPB (40 nm)/CBP:Ptq$_2$-complex (10%) (20 nm)/Alq$_3$ (40 nm)/LiF (1.2 nm)/Al (100 nm). MoO$_3$ was used as a hole blocking material [14] which we specially prepared as an extra pure (99.9995 wt% free of W impurity) material with a controlled nonstoichiometry [15]. NPD was used as one of the most efficient hole-transport materials [14,16] and it provided the necessary hole mobility. CBP is an up-to-date standard host matrix for phosphorescent dopants [17]. Alq$_3$ (specially purified to 99.9998 wt%) was used as an electron-transport host material [14,16], which controlled electron and hole carriers mobility's inside the emitting layer.

The electroluminescence (EL) of OLED structures were activated by a direct current which determined by an applied voltage and structure resistivity. Brightness and chromaticity coordinates of OLED structures were measured by a LumiCAM 1300 photometer-colorimeter (Instrument Systems Optische Messtechnik, GmbH). EL spectra of the devices were measured by a QE65000 spectrometer (Ocean Optics, Inc.).

2.4. Synthesis and characterization of PtQ$_2$

Toluene was distilled over sodium metal in Ar atmosphere just prior use. 8-Hydroxyquinoline was sublimated under dynamic vacuum (1 Torr). A pyrex tube was charged with a mixture of 0.36 g of Pt(hfacac)$_2$ (0.6 mmol), 0.186 g of HQ (1.3 mmol) and 8 ml of toluene, and the resulted suspension was degassed by three freeze-pump-thaw cycles. Then the tube was evacuated, flame sealed and heated in a furnace (in protective stainless steel tube) at 100 °C during 20 h. After cooling a dark precipitate was filtered off, washed with 2 ml of toluene, dried at 40 °C and 1 Torr and purified by recrystallization from DMF afforded 0.19 g of title compound (yield – 67%) as a dark orange crystalline powder.

^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.80 (dd, J = 1.4 Hz, 2H), 7.72 (q, J = 5 Hz, 2H), 7.50 (t, J = 3.1 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.01 (q, J = 2.9 Hz, 2H). IR (KBr, cm^{-1}): 3446, 1574, 1500, 1461, 1380, 1318, 1281, 810, 729, 662. Anal. found: C 44.80, H 2.52, N, 5.86. Anal. Calcld. for C$_{18}$H$_{12}$N$_2$O$_2$Pt: C 44.73, H 2.50, N, 5.80. mp > 300 °C (decomp. on air).

3. Results and discussion

3.1. Synthesis and structural characterization

Scheme 1 shows the synthesis of target complex **1**. This new approach, based on a ligand exchange between Pt(hfacac)$_2$ and HQ [12] gave much more satisfactory results than all previously reported methods in which K$_2$PtCl$_4$ was used as a starting material [10,11]. We optimized reaction conditions for relatively large amounts of starting materials and used a sealed tube for better protection of the reaction media from the air atmosphere.

A crystalline compound **1** is stable in air, and can be handled

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