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New Pt(II) complex with extra pure green emission for OLED application: synthesis, crystal structure and spectral properties

Dedicated to Prof. Irina P. Beletskaya at the occasion of the 85-th birthday.

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Abstract: New (2-(4-methylpyrazol-1-yl)phenyl) platinum(II) (dibenzoylmethane) Pt(mpp)(dbm) complex based on 4-methylpyrazole was synthesized using a simple scheme. Its crystal structure, spectral and electrochemical properties were studied. The extra pure green (CIE chromacity coordinates X=0.1419, Y=0.7444) electroluminescence for OLED structures was obtained.

Keywords: pyrazole; dibenzoylmethane; organic light-emitting diode; platinum (II) complex; metallocycles

1. Introduction

Cyclometalated complexes of platinum (II) and iridium(III) are the most important phosphorescent phosphors for organic light-emitting devices [1,2]. Besides, they are extensively use for various luminescent applications [3,4], in sensors [5,6] and for biomedical purposes [7,8]. They have a number of unique properties such as a wide range of emission colors, high quantum yields of luminescence, a short lifetime of triplet excited states. The emission of Pt (II) complexes is attributed to MLCT (metal-to-ligand charge transfer) excited states as well as possible intraligand π - π^* states. We can assume, that for efficient electroluminescence the LUMO energy

should match the cathode work function level, while the energy of the highest HOMO should be close to those of hole-transport layer commonly made from NPB or CBP [9,10]. This leads to a large variety of ligands, as well as to the types of complexes. To nowadays among all complexes the C[^]N, N[^]N, N[^]C[^]N chelate complexes are the most studied and the most efficient [11,12].

In general, for the OLED technology a synthetic accessibility of electroluminescent complexes may be not less important than the high quantum efficiency. Another significant challenge is a creation of emitters with fine RGB colors. Theoretically, color of luminescence of Pt(II) complexes can be precisely adjusted by a proper choice of ligands, but up to now the most effective way to find such an emitters is screening of complexes libraries [9,10].

Heteroleptic C[^]NPtL complexes (where L is noncyclometalating ancillary ligand) offer some advantages over symmetrical bis-C[^]N complexes. Their physical (such as volatility, solubility, etc.) and photophysical properties can be independently adjusted by variation of both C[^]N and L compositions. An ancillary ligand can also have a significant influence on the electron density at the metal center. Subsequently, the amount of ground state electron density at Pt-center will affect to the emission color, due to alterations in nature of the lowest energy transition [13]. An immense number of combinations of C[^]NPt blocks and ancillary ligands (L) have been investigated to nowadays. They have included, but not limited mainly by derivatives of 2-phenylpyridine, 2-(2-thienyl)pyridine [13,14], 2-phenylisoquinoline [15], functionally substituted 2-phenylpyridines [16,17], 2-phenylbenzothiazole [18] and other arylated heterocycles. Simple 1,3-diketones have been used as monoanionic ancillary ligands in the most of abovementioned complexes, but examples of C[^]NPt blocks coordinated by diimine (1,10-phenanthroline, 2,2'-bipyridyl) [19], chlorine atoms or CO groups [20] have been also known. A lot of reviews, devoted to different aspects of Pt(II) organometallic chemistry and applications of complexes have been published to the date [21,22].

Much less attention have been paid to C[^]N platinum complexes with arylated azoles and 1,3-diketones as O[^]O ancillary ligands. Most of the known compounds can be attributed to carbene complexes with arylimidazole [23, 24] or benzimidazole [25] ligands. Only a few complexes based on 1-phenylpyrazole as a C[^]N –ligand and 1,3-diketones were described by Batagoda [26] and Wu [27], and no other examples of such compounds bearing pyrazole fragment have been reported up to date. Unfortunately, no attempts to study their electroluminescence were performed.

In the present research we have succeed to make Pt(II) complex with extra pure green electroluminescence based on 4-phenyl-4-methylpyrazole as a cyclometalated ligand and diphenylpropanedione-1.3 as an ancillary ligand.

2. Experimental Section

2.1 General Information

K₂PtCl₄ was purchased from Aldrich. All other solvents and reagents were synthetic grade and purchased from 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). 4-Methyl-1-phenyl-1H-pyrazole was obtained in 72 % yield by procedure, described by Pavlik [28].

Impurity concentrations were measured by a NexION 300D (Perkin Elmer) inductively coupled plasma mass-spectrometer. Elemental analysis was performed on an Elementar Vario Micro-Cube CHNO(S) analyzer. NMR spectra were recorded at 298 K on a Bruker DRX-500 instrument operated at 500.13 MHz for ¹H nucleus, in CDCl₃ as solvents. TMS (δ = 0.00 ppm) was used for ¹H and ¹³C NMR measurements as a standard.

Electrochemical measurements were performed on a BASiEpsilonE2P electrochemical analyzer (USA) managed by Epsilon-EC-USB-V200 software.

UV-VIS absorption spectra were recorded on a Varian Cary-100 Scan instrument.

Photoluminescent (PL) spectra and decay kinetics of powdered complex and solutions were obtained using a Fluorolog FL3-22 (Horiba-Jobin-Yvon) spectrofluorimeter equipped by 450 W Xenon lamp and standard Hamamatsu R-928 PMT. PL quantum yields were measured on the same setup in the integration sphere (absolute method). The measurements were performed at least three times and the results were averaged.

The synthesized complexes were purified by vacuum sublimation at dynamic pressure 5×10^{-6} Pa and temperature of the complex about 270°C.

Electroluminescent spectra (EL) spectra of OLED devices were recorded by a QE65000 spectrometer. The electroluminescent (EL) characteristics were measured with computer controlled Keithley 2400 source meter in combination with a QE65000 spectrometer (Ocean Optics, Inc.) supported by optical fiber cable. Integration time was 30 s for the every run in the 300-800 nm wavelength range. A LumiCAM 1300 photometer-colorimeter (Instrument Systems

Optische Messtechnik, GmbH) was used for measurements of brightness and chromaticity coordinates of OLED structures. All measurements have been conducted in air without device encapsulation.

2.2 Synthesis of (2-(4-Methylpyrazol-1-yl)phenyl)platinum(II) (dibenzoylmethane) (*Pt(mpp)(dbm)*).

A cyclometallated product was prepared in one step according to the modified procedure of Wu [27]. In a Schlenk tube under Ar atmosphere 158 mg (1 mmol) of 4-methyl-1-phenyl-1H-pyrazole and 208 mg (0.5 mmol) of K_2PtCl_4 in 5 ml of water-2-etoxyethanol mixture (1:3 v/v) were heated with stirring for 12 h at 100°C. After the cooling, 15 ml of water was added, precipitate of dimer complex was separated, washed with water and dried at 80°C at 0.1 Torr to a constant weight. To the resulted solid 5 ml of 2-etoxyethanol was added followed by an addition of 340 mg (1.51 mmol) of 1,3-diphenylpropane-1,3-dione and 1 g (9.5 mmol) of Na_2CO_3 . The resulted suspension was stirred at 100°C for 15 h, cooled and decomposed by dropwise addition of deionized water (15 ml). The dark solid was separated, washed with deionized water, dried at 80°C at 0.1 Torr and purified by column chromatography (silica gel/ CH_2Cl_2). Yield - 104 mg (39 %) of yellow solid. 1H NMR (500 MHz, $CDCl_3$) δ : 8.07 (m, 4H), 7.70 (m, 3H), 7.55 (m, 3H), 7.47 (m, 4H), 7.10 (m, 3H), 6.78 (s, 1H), 2.19 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ : 178.36, 144.62, 139.93, 137.56, 131.81, 130.89, 130.69, 128.53, 127.07, 124.53, 123.93, 122.03, 116.94, 109.70, 97.14, 9.47. ^{195}Pt NMR (500 MHz, $CDCl_3$) δ : -2715. Elemental analysis (%) for $C_{25}H_{21}N_2O_2Pt$ (M = 576.52): calc.: C, 52.08; H, 3.67; N, 4.86; found: C, 52.12; H, 3.69; N, 4.83.

2.3 X-ray crystallography of *Pt(mpp)(dbm)* complex

The single crystals of *Pt(mpp)(dbm)* complex suitable for X-ray analysis, were obtained by slow diffusion of hexane to the saturated solution of complex in CH_2Cl_2 under Ar at RT.

At 110K crystals are monoclinic, $a = 12.3019(7)$ Å, $b = 11.4797(7)$ Å, $c = 14.4514(9)$ Å, $\beta = 103.5574(13)^\circ$, $V = 1984.0(2)$ Å³, $P2_1/c$ space group, $Z = 4$ ($Z' = 1$). $F(000) = 1112$, GOF = 1.000, a total of 40185 reflections ($2\theta_{max} > 58^\circ$) were measured with a Smart APEX II CCD diffractometer [$\lambda(MoK\alpha) = 0.71072$ Å, ω -scans, $2\theta < 58^\circ$], and 5274 independent reflections ($R_{int} = 0.0338$) were used in further refinement. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The positions of hydrogen atoms were calculated. Hydrogen atoms were refined in riding model with $U_{iso}(H)$ equal to 1.5 $U_{eq}(C)$ and 1.2 $U_{eq}(C)$ of the connected methyl and

other carbon atoms. The refinement converged to $wR2 = 0.0621$ and $GOF = 1.009$ for all independent reflections ($R1 = 0.0266$ for 4394 observed reflections with $I > 2\sigma(I)$). CCDC 1511807 contains the supplementary crystallographic data for this paper.

2.4 Computational studies.

The calculations were performed with the Gaussian 09 program package using the PBE1PBE functional. A mixed basis set is used where a cc-pVTZ basis set was used for carbon, hydrogen, nitrogen, oxygen, fluorine atoms and the cc-pVTZ-PP basis set with relativistic effective core potentials was used for platinum [29]. The conductor-like polarization continuum model CPCM [30] of CH_2Cl_2 solvent were applied to all calculations. The obtained structures were confirmed as the true minima by the absence of imaginary frequencies. TD-DFT computations were carried out on the optimized ground state S_0 geometries.

2.5 Electrochemical measurements

The electrochemical measurements were performed by using a conventional three-electrode system. In the case of powdered samples a glassy carbon with carbon paste electrode (CPE) was used as a working electrode. An Ag/AgCl (0.01M) electrode was used as a reference electrode, and a Pt wire was used as a counter electrode. 0.1 M Et_4NBF_4 was used as a supporting electrolyte for the determination of current - voltage characteristics. Acetonitrile was distilled over P_2O_5 and $KMnO_4$, and then over molecular sieves After purification, the solvent was stored under dry Ar atmosphere. Et_4NBF_4 , which was used as a base salt, was recrystallized from ethanol and dried in a vacuum chamber at 100 °C for 2 days. The preparation of a modified CPE electrode was as follows. A mixture of graphite powder and phosphonium salt (dodecyl(tri-tert-butyl)phosphonium tetrafluoroborate) with 90/10 (w/w) ratio was milled in a mortar until the homogeneous mass of the paste was obtained. This paste then was uniformly distributed of the surface of a glassy carbon substrate. The detailed description of the technique is given in Ref.[31,32].

2.6 OLED fabrication

Multilayers OLED devices were fabricated by layer-by-layer vacuum thermal sputtering ($<10^{-5}$ Pa) on a glass substrate (20x30x3 mm) with ITO conducting layer. The deposition rates of each layer were no more than $0.03 \text{ nm}\times\text{s}^{-1}$. The emission layer consisted of CBP: Pt(mpp)(dbm)-complex (8%) was deposited with the rate $\sim 0.01 \text{ nm}\times\text{s}^{-1}$ due to low pressure of Pt(mpp)(dbm) vapor at 250 °C. The OLED structure ITO (anode)/ MoO_3 (1 nm) / NPB (N,N' -Di(1-naphthyl)- N,N' -diphenyl-(1,1'-biphenyl)-4,4'-diamine, 40 nm) / CBP (4,4'-Bis(N -carbazolyl)-1,1'-

biphenyl): Pt(mpp)(dbm) complex (8 wt. %) (30 nm) / BCP (2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline, 15 nm) / LiF (1.2 nm) / Al (100 nm) was fabricated. Extra pure MoO₃ (99.9995 wt% free of W impurity) with controlled oxygen nonstoichiometry [33] was used as a hole blocking material [9]. NPB was used as one of the most efficient hole-transport materials and it provided the necessary hole mobility [2,9]. CBP is an up-to-date standard host matrix for phosphorescent dopants [10]. BCP was used as an electron-transport material with good hole blocking properties [9].

3. Results and discussion

3.1 Synthesis and structural characterization

Among thousands of known cyclometallated Pt(II) complexes, only few examples of compounds with simultaneously coordination with 1,3-diketone and 1-phenylpyrazole ligands have been described [26,27] (Fig.1).

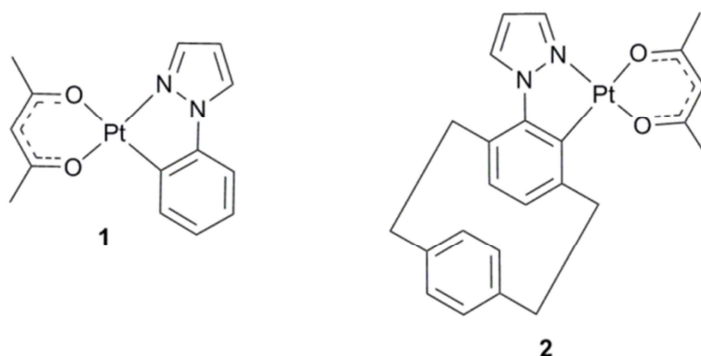


Fig. 1. The known examples of complexes based on 1-phenylpyrazole and 1,3-diketones.

In the both Ref. [16,22] the synthetic approach to cyclometallated complexes was based on two-step methodology: (i) formation of Pt(II) dimer in the reaction of Pt(II) precursor with phenylazole and (ii) subsequent cleavage of dimer by the interaction with the large excess of 1,3-diketone in the presence of the base. We used the same approach for the preparation of Pt(mpp)(dbm) complex (Fig.2).

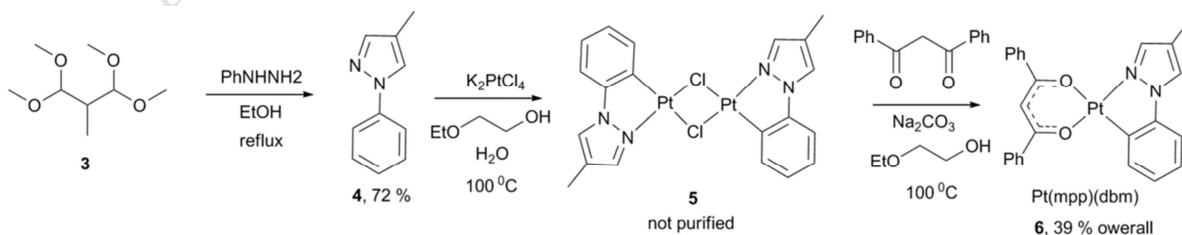


Fig. 2. Preparation of Pt(mpp)(dbm) complex

The Pt(mpp)(dbm) complex was obtained in 39 % overall yield by the convectional procedure started from very simple commercial precursors. No palladium-catalyzed cross-coupling reactions were used. As-synthesized Pt(mpp)(dbm) complex was as pure as 99.9905 wt% (trace metals) according to the ICP-MS measurements. Taking into account the influence of impurities on electroluminescence efficiency [34,35] we additionally purified the Pt(mpp)(dbm) complex by high-vacuum sublimation. The final purity of powdered preparation was 99.9987 wt% (See Table S1, Fig. S1). The obtained complex composition was proved by NMR, elemental analysis and its structure was confirmed by X-ray single crystal analysis.

The X-ray diffraction analysis has unambiguously revealed the formation of a desired product Pt(mpp)(dbm) (Fig. 3). The platinum is characterized by square-planar geometry with Pt-O, Pt-N and Pt-C bonds lengths equal to 1.996(3)-2.052(3), 1.961(3) and 1.979(4) Å, respectively. In crystal molecules are assembled into dimers by stacking interaction between the phenyl group of β -diketonate and methylpyrazol with the shortest C...C contact equal to 3.38 Å (Fig. S1).

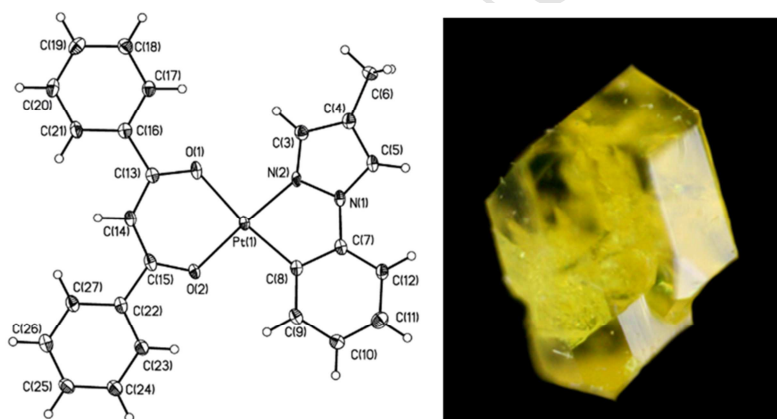


Fig. 3. The general view of molecular structure of Pt(mpp)(dbm) complex (left) in representation of atoms by thermal ellipsoids ($p=50\%$). Microphotograph of Pt(mpp)(dbm) single crystal (right)

3.2 Photophysical property

The absorption spectra of complex and free ligands were recorded in CH_2Cl_2 degassed solutions at 4.5×10^{-5} mol/L (Fig. 4). The intense band at 280-260 nm is attributed to spin-allowed ligand-centered transitions of **dbm** and **mpp** ligands ($\pi \rightarrow \pi^*$ transitions), while relatively weak bands at 320 - 440 nm region are commonly assigned to mixed $^3\text{MLCT}$ or LLCT (ligand-to-ligand charge transfer state) [2,22]. The reason of their origin is strong spin-orbit coupling of the Pt atom. A strong spin-orbit coupling leads to the mixing of lowest triplet and higher-lying singlet excited states and this, in turn, causes an increase of phosphorescent quantum efficiency.

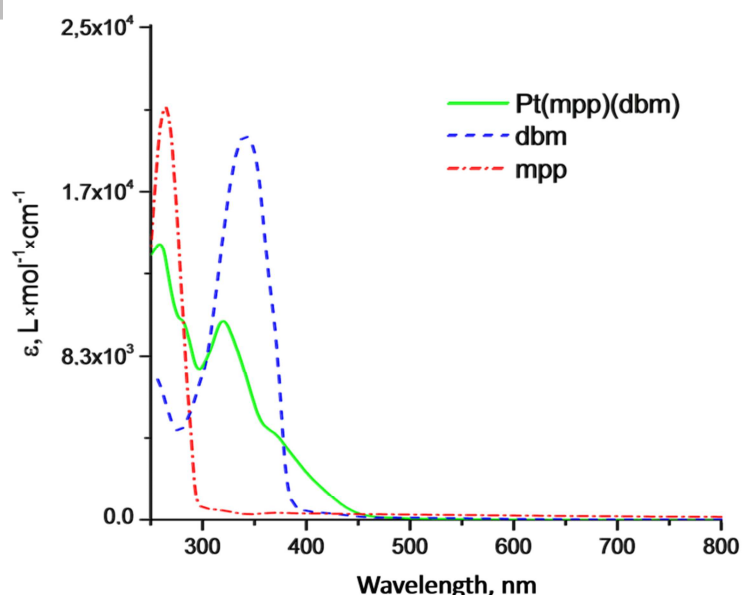


Fig.4. The absorption spectra of complex and free ligands in CH_2Cl_2 degassed solutions.

The PL spectrum of $\text{Pt}(\text{mpp})(\text{dbm})$ complex solution in CH_2Cl_2 had one band with 535 nm maximum (Fig.5) which corresponded to green emission (the CIE chromacity coordinates $X=0.3581$, $Y=0.5480$). Similar to the other $\text{Pt}(\text{II})$ complexes this band resulted from $^3\text{MLCT}$ states, as well as from LLCT [2,22]. The $^3\text{MLCT}$ nature of excited states can be confirmed by the Gaussian line shape and the relatively long lifetime of the state ($\tau = 1.8 \mu\text{s}$ at 535 nm for degassed 5×10^{-4} M solution in CH_2Cl_2). The absolute PL quantum yield (PLQY) was 8.70 ± 0.13 % ($\lambda_{\text{ext}} = 370$ nm) for the solution.

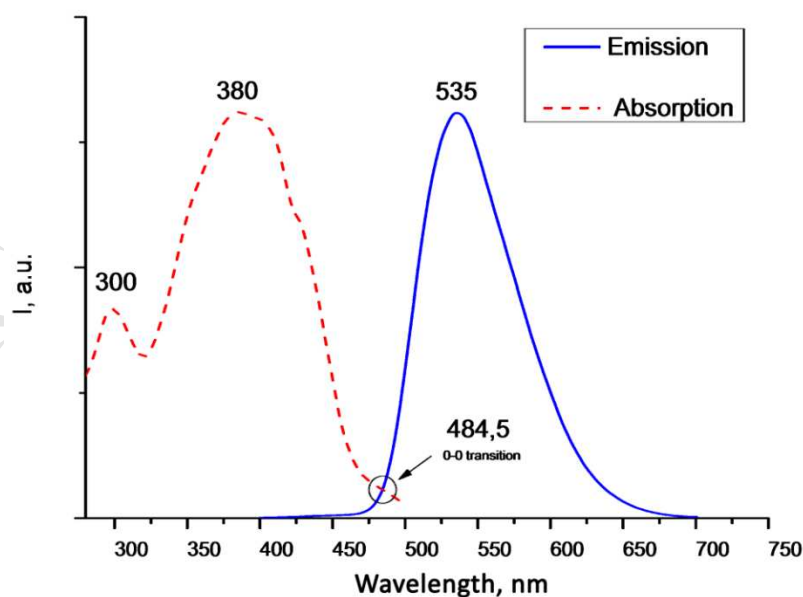


Fig. 5. The normalized absorption and emission spectra of $\text{Pt}(\text{mpp})(\text{dbm})$ complex in 5×10^{-5} mol/L degassed CH_2Cl_2 solution ($\lambda_{\text{ext.}} = 370$ nm).

The PL spectrum of the sublimed powdered complex had two small shoulders on the both sides on the band (Fig.6). The band maximum was shifted to the red wavelength region in comparison with the solution measurements. This phenomenon is well known [36] for Pt(II) complexes and usually attributed to formation of partially ordered structures (e.g. by π - π stacking and other weak interactions) in solid.

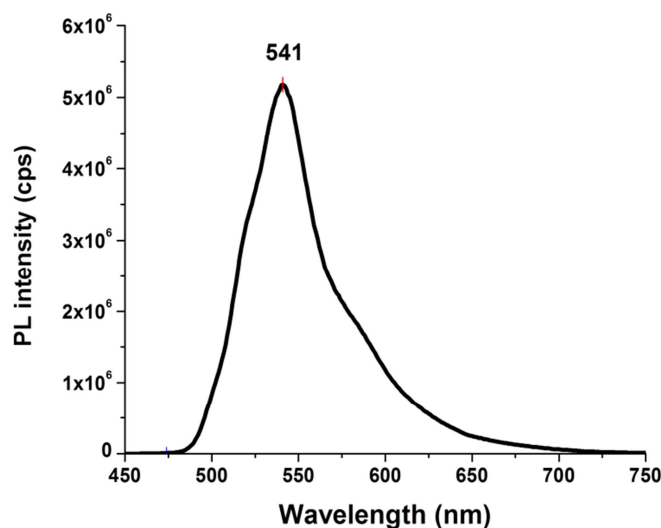


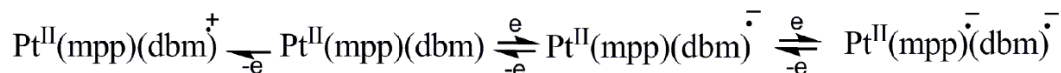
Fig. 6. The emission spectrum of sublimed solid Pt(mpp)(dbm) complex ($\lambda_{\text{ext}} = 370$ nm).

The nature of this emission band was estimated by means of TD-DFT calculation of the complex. The optimized geometry for Pt(mpp)(dbm) is rather close to the experimental one. In particular the Pt-O, Pt-N and Pt-C bonds lengths are 1.993-2.080 1.969 Pt-C 1.968 Å, correspondingly. TD DFT calculation have revealed the presence of T_1 - S_0 transition with the energy equal to 486.8 nm that is rather close to experimental value (484.5 nm) of 0-0 band i.e. intercrossing of the absorption and emission spectra (see Fig. 5). The lowest energy transitions (T_1 - S_0) is mainly HOMO to LUMO, which is the ligand-to-ligand transition (i.e. from phenylpyrazole to 1,3-diketone ligand). But, as the both frontier orbitals contain some Pt contributions, than the transition should be regarded as a mixed metal–ligand to metal–ligand charge transfer (see Table 2).

3.3 Electrochemical property

The Pt(mpp)(dbm) displays a reversible (ipa/ipc~0.4) Pt-based reduction at -1.53 V ($E_{1/2}$ an E_{semidif} vs. Ag/AgCl). (Fig. 7, Table 1). The Pt(mpp)(dbm) displays a reversible (ipa/ipc~0.08 and $DEp/2=Ea-Ec/2 = 80\text{mV}$) [37]. The oxidation process measured for Pt(mpp)(dbm) in CPE were not reversible and were ill-defined. Oxidation peak potential is +0.99 V ($E_{\text{ox. semidif}}$) vs Ag/AgCl (Fig. 8, Table 1). General electrochemical characteristics of Pt(mpp)(dbm) are given in Table 1. The energy levels of the HOMO and LUMO were calculated based on the electrochemical data

using previously proposed formulas ($E_{\text{LUMO}} = -(E_{[\text{semidif,red vs. Fc}^+/\text{Fc}]} + 4.8)$, $E_{\text{HOMO}} = -(E_{[\text{semidif,red vs. Fc}^+/\text{Fc}]} + 4.8)$ [38]. The estimated values for HOMO and LUMO were calculated as -5.34 and -2.82 eV, respectively. Complex [Pt(MPP)(DBM)] is able to reversibly accept two electrons and give back one electron (irrev.) according to the Scheme 1.



Scheme 1. Oxidation and reduction steps of the compound [Pt(MPP)(DBM)].

Table 1. Electrochemical properties of [Pt(mpp)(dbm)]

	Reduction	
	$^1E_p^c/E_p^a$, V	$^2E_p^c/E_p^a$, V
vs. Ag/AgCl	-1.57/-1.49	-2.22/-2.08
vs. Fc/Fc ⁺	-2.02/1.94	-2.67/-2.53
Semidif vs. Fc/Fc ⁺	-1.98	-2.62
	Oxidation	
	$^1E_p^a/E_p^c$, V	$^2E_p^a/E_p^c$, V
vs. Ag/AgCl	1.15(irrev)	1.66(irrev)
vs. Fc/Fc ⁺	0.70	1.21
Semidif vs. Fc/Fc ⁺	0.54	1.13

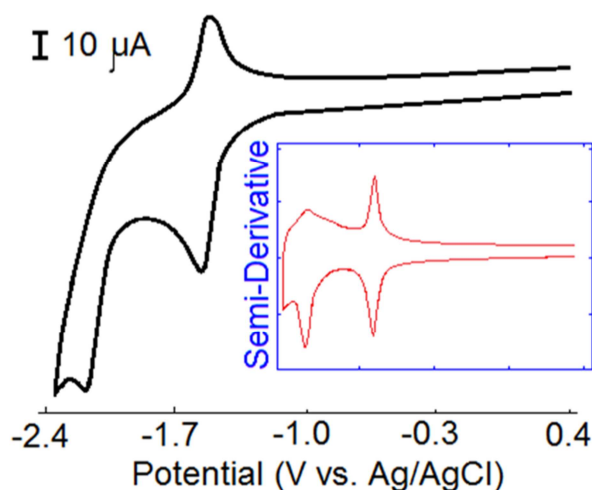


Fig. 7. Cyclic voltammograms (reduction) obtained with a modified CPE of [Pt(mpp)(dbm)] (graphite + ionic liquid + Pt complex) in 2 ml CH₃CN (0.1 M Et₄NBF₄).

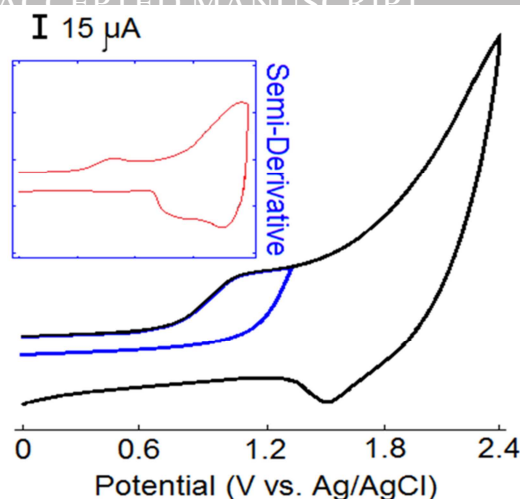
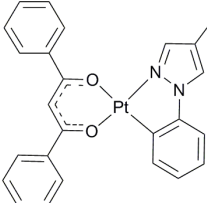
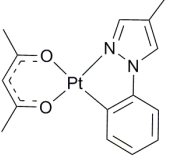
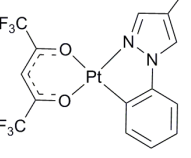
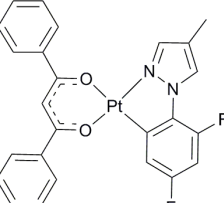
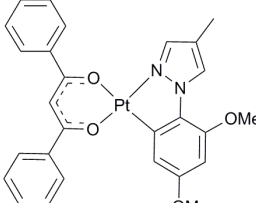
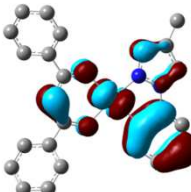
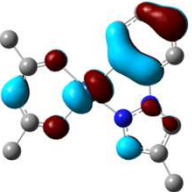
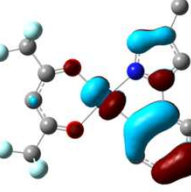
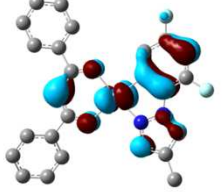
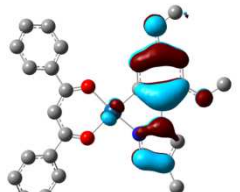
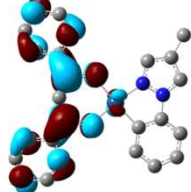
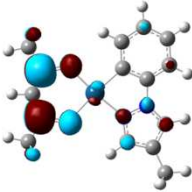
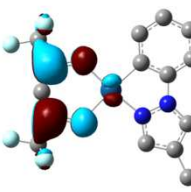
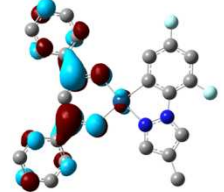
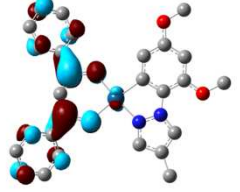


Fig. 8. Cyclic voltammograms (oxidation) obtained with a modified CPE of [Pt(mpp)(dbm)] (graphite + ionic liquid + Pt complex) in 2 ml CH₃CN (0.1 M Et₄NBF₄).

3.4 Theoretical calculations

To check how the modification of ligands in the complex studied affects the energy of T₁-S₀ transition we have performed the DFT calculations for the series of complexes in which we modified either 1,3-diketone (i.e. LUMO) or phenylpyrazole (i.e. HOMO) moieties. The general view of theoretically studied complexes, the frontier orbitals as well as energies of T₁-S₀ transition are shown in Table 2. As one can see, the rational choice of substituents in 1,3-diketones makes possible to vary the energy of triplet state within ~100 nm or HOMO-LUMO gap by *ca.* 1.0 eV, while the inclusion of electron withdrawing or π -donor substituents to the phenylpyrazole fragment doesn't perturb the triplet state. The examination of the energy of HOMO orbital clearly shows that in the whole series, the energy varies in the rather narrow range and replace of the fluorine in Pt-III with the methoxy group in Pt-IV costs only *ca.* 0.01 eV. While the replace of the methyl substituents in Pt-II with the CF₃ ones in Pt-III causes the increase of the LUMO energy by *ca.* 0.5 eV. Considering that various 1,3-diketones are in general much more available commercially, it seems that such a route of modification of platinum complexes with a phenylpyrazole fragment can be beneficial for fine tuning of optical properties of complexes and OLED structures.

Table 2. View of frontier orbitals (HOMO/LUMO) and calculated values of energy of 0-0 transition for series of complexes.

Complex				
				
Pt(mpp)(dbm)	Pt-I	Pt-II	Pt-III	Pt-IV
HOMO				
				
LUMO				
				
λ (T_1 - S_0 transition), nm				
486.9	410.2	519.9	481.3	487.2
484.5 experimental				

3.5 OLED performance.

To investigate the performance of new complex as a phosphorescent emitter the OLED with the structure described in the Section 2.6 was made. The energy level diagram and molecular structures of additional layers are presented in Fig. 9. One can see that the energy state of Pt(mpp)(dbm) molecules matches well to the CBP matrix.

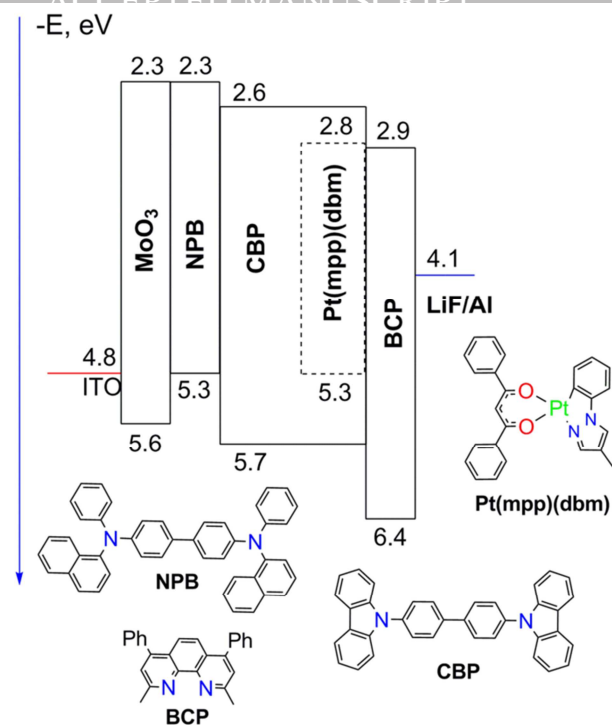


Fig. 9. Energy level diagram (relative to vacuum level) and topology of the fabricated OLED.

As a result the produced OLED structure had typical UC characteristic (Fig S6) with a comparatively high turn-on voltage of 6.7 V. The maximum values of current efficiency, power efficiency, and external quantum efficiency were obtained at 32 mA/cm² (see Fig. S9-S11). The EL spectrum has two maxima at the region of 510-540 nm most likely due to aggregation of complex in the matrix [39,40]. Emissive states are ³MLCT and ³LC (³ππ*) as it was stated for other platinum(II) complexes [2] (Fig.10). The most interesting property of the OLED structures based on Pt(mpp)(dbm) as an emitting agent is the obtained CIE color coordinates of X=0.1419, Y=0.7444 which are very close to the standard CIE green color 546.1 nm. The OLED structure had the uniform distribution of lighting intensity of 400 Cd/m² at 10 V.

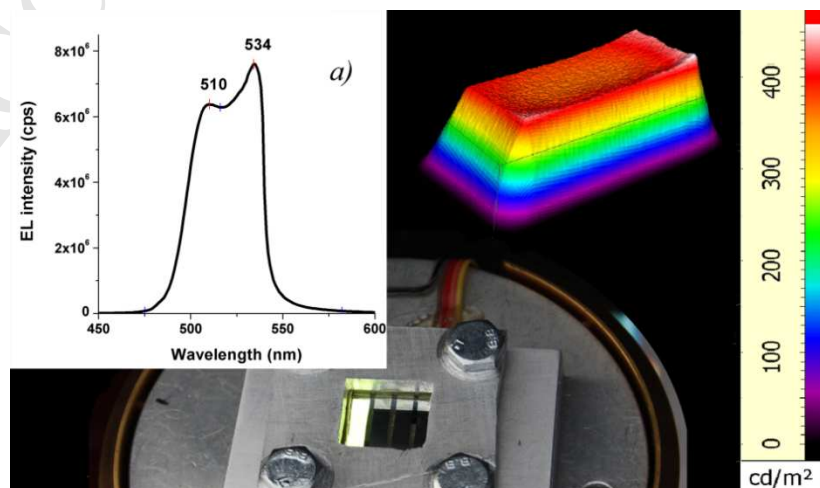


Fig. 10. Electroluminescence of OLED structure ITO/MoO₃ (1 nm)/NPB (35 nm)/CBP:Pt(MPP)(DBM) (8%) (30 nm)/BCP (15 nm)/LiF (1.2 nm)/Al (100 nm) at 8 V and 3D intensity brightness map at 10 V.

Conclusion

In conclusion the high pure (2-(4-methylpyrazol-1-yl) phenyl) platinum(II) (dibenzoylmethane) was synthesized using the simple scheme followed by the vacuum sublimation. The chemical purity of 99.9987 wt% determined by the ICP-MS and the fine matching let's achieved the extra pure green emission of the multilayer OLED structure (CIE chromacity coordinates X=0.1419, Y=0.7444).

Acknowledgements

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Figure captions

Fig. 1. The known examples of complexes based on 1-phenylpyrazole and 1.3-diketones.

Fig. 2. Preparation of Pt(mpp)(dbm) complex.

Fig. 3. The general view of molecular structure of Pt(mpp)(dbm) complex (left) in representation of atoms by thermal ellipsoids ($p=50\%$). Microphotograph of Pt(mpp)(dbm) single crystal (right).

Fig. 4. The absorption spectra of complex and free ligands in CH_2Cl_2 degassed solutions.

Fig. 5. The normalized absorption and emission spectra of Pt(mpp)(dbm) complex in 5×10^{-5} mol/L degassed CH_2Cl_2 solution ($\lambda_{\text{ext}} = 370$ nm).

Fig. 6. The emission spectrum of the sublimed solid Pt(mpp)(dbm) complex ($\lambda_{\text{ext}} = 370$ nm).

Fig. 7. Cyclic voltammograms (reduction) obtained with a modified CPE of [Pt(mpp)(dbm)] in CH_3CN (0.1 M Et_4NBF_4).

Fig. 8. Cyclic voltammograms (oxidation) obtained with a modified CPE of [Pt(mpp)(dbm)] in CH_3CN (0.1 M Et_4NBF_4).

Fig. 9. Energy level diagram (relative to vacuum level) and topology of the fabricated OLED.

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Scheme 1. Oxidation and reduction steps of the compound [Pt(mpp)(dbm)].

New Pt(II) complex with extra pure green emission for OLED application:
synthesis, crystal structure and spectral properties

Ilya Taidakov, Rasim Saifutyarov, Konstantin Lyssenko, Roman Avetisov, Elena Mozhevitina,
Andrew Khomyakov, Mikhail Khrizanforov, Yulia Budnikova and Igor Avetissov.

- New (2-(4-methylpyrazol-1-yl)phenyl) platinum(II) (dibenzoylmethane) was made
- crystal structure, spectral and electrochemical properties of Pt(MPP)(DBM) were studied
- Extra pure green electroluminescence for OLED structures was obtained