Phosphorescence

The Chameleonic Nature of Platinum(II) Imidazopyridine Complexes

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Abstract: The synthesis and characterization of cyclometalated C^C* platinum(II) complexes with unique photophysical properties, aggregation induced enhancement of the quantum yields with a simultaneous decrease of phosphorescence lifetimes, is reported. Additionally, a change of emission color is induced by variation of the excitation wavelength. The aggregation behavior of these complexes is controlled by the steric demand of the substituents. The photophysical properties of these complexes are investigated through emission-excitation matrix analysis (EEM). The monomeric complexes are excellent room temperature phosphorescent blue emitters with emission maxima below 470 nm and quantum yields of up to 93%.

The energy problem has prompted extensive research into more efficient sources of illumination. In particular, organic light emitting diodes (OLEDs) have been found to be a promising alternative to conventional lighting. The most widely used phosphorescent dopants today are iridium organometallic compounds, although platinum compounds have been proven to be an alternative.^[1] Additionally, the square planar geometry of platinum(II) compounds has attracted a large interest in the field of inorganic photochemistry as it allows for intermolecular interactions that are not possible in octahedral and tetrahedral complexes.^[2] The tendency of platinum(II) to aggregate has been known for a long time but was only recently explained.^[3] The photophysical properties of platinum complexes strongly vary upon intermolecular interactions. Interestingly, the properties of an aggregated system largely differ from those of the monomers.^[4] The unique photophysical properties of platinum aggregates have been employed for molecular sensing applications: efficient vapochromism^[5] and solvatochromism effects^[6] have been observed. The intermolecular interactions of platinum(II) emitters are based on two possible scenarios: by self-assembly or accurate molecular design of rigid scaffolds. While the design of rigid scaffolds has intensively been investigated by Thompson and co-workers^[7] and other groups,^[8] the self-assembly has simply been classified as a phenomenological effect. Recently, self-assembled platinum(II) complexes have

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attracted interest as white OLED (WOLED) dopants.^[9] Unfortunately, the aggregation process is often associated with a setback of the photophysical properties, in particular, lower quantum yields. Examples for an enhanced quantum yield by aggregation are rare.^[10] Here, we present an aggregation induced enhancement of quantum yields with simultaneous shortening of the phosphorescence decay time, modulation of the emissive color through selective excitation, and control of the aggregation process through rational molecular design.

The imidazolium salts **4** (R_1 =methyl) and **8** (R_1 =mesityl) were prepared following a four-step procedure (Scheme 1). *N*- R_1 -3-nitropyridin-2-amines (**1**, **5**) were obtained by reaction of 2-chloro-3-nitropyridine and aqueous methylamine in isopropanol (i) and by reaction of 2-chloro-3-nitropyridine with 2,4,6-trimethylphenylamine (Mes-NH₂) in the presence of po-



Scheme 1. Preparation of the imidazolium salts **4** and **8**: (i) *i*PrOH, CH_3NH_{2r} (ii) Mes-NH₂, KF; (iii) Pd/C (10% Pd), MeOH, H₂; (iv) TEOF, acid; (v) Ph₂IOTf, DMF, 10 mol % Cu(OAc)₂.

tassium fluoride at elevated temperatures (ii), followed by reduction of the nitro groups over Pd/C (iii). Ring closure of compounds **2** and **6** was achieved by reaction with triethylorthoformate (TEOF, iv). The imidazolium salts **4** and **8** were obtained through a copper catalyzed reaction of **3** and **7** with diphenyliodonium triflate (Ph₂IOTf, v), respectively.

The platinum(II) complexes (**9–14**) were prepared in a onepot multistep reaction, following our recently reported procedure (Scheme 2):^[11] synthesis of the silver(I) *N*-heterocyclic carbene (NHC) complex in DMF through deprotonation of the imidazolium salts and formation of the carbene complex with silver(I) oxide (vi), transmetalation of the silver(I) carbene to dichloro(1,5-cyclooctadiene)platinum(II) [Pt(COD)Cl₂] (vii), cyclometalation at elevated temperature followed by reaction with acetylacetone ligand (HR₂acac) in the presence of potassium *tert*-butanolate as a base (viii). The complexes were isolated after column chromatography in yields of 11–62%.

All complexes were fully characterized by ¹H, ¹³C, and ¹⁹⁵Pt NMR spectroscopy, as well as elemental analysis and, in the case of **14**, by a solid-state structure. The formation of the carbene complex was verified by the disappearance of the



Scheme 2. Synthetic route for the preparation of the platinum(II) complexes: (vi) DMF, Ag_2O ; (vii) [Pt(COD)Cl₂]; (viii) HR_2acac , KO'Bu.

characteristic NCHN proton signal of the imidazolium salt in the ¹H NMR experiment and the appearance of the characteristic *ipso* carbon signal of the carbene at 163–164 ppm in the ¹³C NMR experiment. The ¹⁹⁵Pt NMR spectra for all complexes show chemical shifts from -3350 (9) to -3325 ppm (11), which is typical for cyclometalated C^C* platinum(II) complexes. Thermal stability of all complexes was analyzed by determining their melting point, which are in the range of 234°C (11) to more than 350°C (12). No decomposition was detected during the measurements.

Single crystals of **14**, suitable for X-ray diffraction, were obtained by slow evaporation of a solution of the compound in acetone. The complex crystallizes in the triclinic space group $P\bar{1}$ with the unit cell containing two molecules. The two bidentate ligands form a slightly distorted square-planar coordination sphere around the metal center (Figure 1a).



Figure 1. Solid state structure representations of **14**. Ellipsoids are drawn at 50% probability. a) ORTEP3 representation of the molecular structure. Selected bond lengths [Å] and angles [$^{\circ}$]: Pt(1)–C(1) 1.924(2), Pt(1)–C(8) 1.983(2), Pt(1)–O(1) 2.0884(16), Pt(1)–O(2) 2.0471(15), C(1)-Pt(1)-C(8) 80.42(9), O(1)-Pt(1)-O(2) 90.62(6). b) Mercury plot of the packing in the solid state. H atoms omitted for clarity.

The carbene–metal bond (1.924(2) Å) is noticeably shorter than the Pt(1)–C(8) bond of 1.983(2) Å. Due to the formation of a five-membered metallacycle, the bite angle of the cyclometalating ligand is contracted to 80.42(9)°, while the O(1)-Pt(1)-O(2) angle is close to the ideal value of 90°. The molecules form slightly offset stacks in the single crystal, where the planar *N*-heterocyclic fragments face one another and the sterically highly demanding β-diketonates point outwards, orthogonal to the coordination plane (Figure 1 b). The UV/Vis absorption spectra of complexes **9–14** were measured at 298 K in 0.1 mM CH₂Cl₂ solution (Figure S4 in Supporting Information). All complexes show a strong absorption at 280 nm and a second band centered at 330 nm. The very weak low energy ³MLCT absorption is observed at 430 nm (Figure S5). All complexes show strong phosphorescence at room temperature in the blue region of the spectrum with excellent quantum yields and relatively short phosphorescence decay times (Table 1).

Complexes **10–14** show a structured emission profile (Figure 2), characteristic for a metal perturbed ³ILCT emissive state.^[11] In the emission spectrum of complex **9** two bands are observed: a structured band centered at 460 nm, assigned to a metal perturbed ³ILCT emissive state, and a broad structureless band centered at 543 nm.

Table 1. Photophysical data for complexes 9-14 measured after excitation at 290 nm, at 298 K, film 2.0 wt.% emitter in PMMA (λ_{exc} =290 nm)					
Comp.	$\lambda_{ m em}^{[a]}$ [nm]	$arPsi^{ ext{[b]}}$ [%]	τ ^[c] [μs]	$k_{\rm r}^{\rm [d]}$ [10 ³ s ⁻¹]	k _{nr} ^[e] [10 ³ s ⁻¹]
9	462	76	3.6	280.2	67.3
10	464	77	6.0	165.3	38.0
11	467	90	3.5	287.4	28.7
12	464	87	3.6	275.6	35.8
13	467	65	6.6	150.8	52.8
14	467	93	3.8	262.7	18.4

[a] maximum emission wavelength, [b] absolute quantum yield ± 5 %, [c] decay lifetimes (excited by laser pulses 360 nm, 20 kHz) given as $\tau = \tau_{exp}/\Phi$, ^[d] $k_r = (\Phi/\tau_{exp})$, [e] $k_{nr} = (1-\Phi)/\tau_{exp}$. CIE coordinates are given in the Supporting Information.

The photophysical properties of complex **9** are found to be concentration dependent (Table 2). The formation of the lower energetic band is concomitant with the increase of the concentration (Figure 3). In accordance with the concentration de-



Figure 2. Normalized emission spectra of complexes 9-14 at 298 K (2.0 wt.% in PMMA); excitation at 290 nm.

pendency, associated with a red shift of the emission and a structureless band shape, we suggest that the emission centered at 550 nm could be assigned to an excimeric emissive species. This assignment is confirmed by concentration dependent measurements at 77 K in a glassy 2Me-THF matrix (Figure S7). By lowering the temperature to 77 K, the emission centered in the blue region of the spectrum becomes vibronically resolved (as expected for a metal perturbed ³LC emissive state). However, the emission at lower energies maintains an unstructured profile.

Table 2. Photophysical data for complex 9 measured at different concentrations (0.1–10.0 wt.%), at 298 K (λ_{exc} =290 nm).					
Conc.	λ _{em} ^[a] [nm]	$arPsi^{ ext{b]}}$ [%]	τ ^[c] [μs]	$k_{\rm r}^{\rm [d]}$ [10 ³ s ⁻¹]	k _{nr} ^[e] [10 ³ s ⁻¹]
0.1%	464	67	6.2	160.8	53.1
0.2%	462	61	6.9	144.4	56.3
0.5%	461	63	6.3	158.1	58.5
1.0%	464	71	5.7	176.9	51.3
2.0%	462	76	3.6	280.2	67.3
10.0%	566	78	1.6	630.9	138.8
1					

[a] maximum emission wavelength, [b] absolute quantum yield $\pm 5\%$ [c] decay lifetimes (excited by laser pulses 360 nm, 20 kHz) given as $\tau = \tau_{exp}/\Phi$, [d] $k_r = (\Phi/\tau_{exp})$, [e] $k_{nr} = (1-\Phi)/\tau_{exp}$.



Figure 3. Normalized emission spectra of complex 9 at 298 K at different concentrations in PMMA; excitation at 290 nm.

Therefore, we studied the self-aggregation of complex **9**. The photophysical properties as a function of concentration (from 0.1 to 10.0 wt.% in PMMA film) are shown in detail in Figure 3. In the range from 0.1 to 0.2 wt.%, only the emission from the monomer is observed. The formation of the excimer starts at 0.5 wt.%, and at 10.0 wt.%, only emission from the excimer is detectable. The aggregation process has a profound effect on the photophysical properties. We observe a shorter decay time of the excited state and, remarkably, an increase of the phosphorescent quantum yield (see Table 2). The aggregation enhanced photophysical process seems to be characteristic of the imidazopyridine system.^[10c] Strikingly, this phenomenon is not observed in the case of the analogous benzimidazole platinum(II) complex¹² (Figure S13 and Table S3).

We also observed a change in the aggregation behavior: the imidazopyridine complex **9** begins to aggregate at lower concentrations compared to the analogous benzimidazole complex. A possible explanation could be the lower electron density in the pyridine ring due to the electron withdrawing nitrogen atom. In the case of an electrostatically induced aggregation process, the reduced electron density on the system favors the π - π stacking process.^[13] As a result, the formation of aggregates is preferred in the case of the imidazopyridine with respect to the analogous benzimidazole complex.

The two emissive species of complex **9**, namely the monomer and the aggregate, possess different photophysical properties. To understand the photophysical self-aggregation behavior of complex **9**, an emission-excitation matrix analysis (EEM) was performed. The previously investigated concentrations (0.1 to 10.0 wt.%) of complex **9**, were excited at wavelengths ranging from 250 to 400 nm in increments of 5 nm while the resulting emission spectra were recorded. The concentration dependent EEM spectrum of complex **9** is shown in Figure 4. As previously discussed, the beginning of the self-aggregation is now clearly observed at 0.5 wt.%. At a concentration of 2.0 wt.%, nearly equal emission intensities of the monomer and excimer are detected. The EEM analysis comprehensibly shows the unique aggregation dependent photophys-



Figure 4. EEM analysis of complex 9; an enlarged version is given in the Supporting Information.

ical behavior of complex **9**. In addition, the two emissive species possess different excitation spectra. It is thus possible to selectively excite one or the other of the two emissive species. This aspect is clearly shown in a concentration-dependent EEM experiment at 77 K (Figure S11). We further observe modulation of the dominant emissive color, from blue to orange, whilst only changing the excitation wavelength from 320 to 390 nm as shown in Figure 5 (measurements at 77 K are reported in Figure S7 b).

The tendency to form aggregates can be prevented by rational molecular design. The introduction of bulkier substituents in the acetylacetonate fragment (complexes 10– 12) or in the NHC moiety (complexes 13–14) efficiently prevents the aggregation process. To confirm our theory, we designed complex 13 where the methyl group in the NHC frag-

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Figure 5. Normalized emission spectra of complex 9 at 298 K (2.0 wt.% in PMMA); excitation at different wavelengths.

ment is replaced by a bulky mesitylene substituent. The steric hindrance of the mesitylene moiety does not allow a planar structure (see DFT calculations in the Supporting Information). Therefore, the aggregation process should be inhibited, and we expect complex **13** to photophysically behave as a very diluted system of complex **9**. In agreement with our expectations, complex **13** shows remarkably similar photophysical properties compared to complex **9** at very low concentration: emission wavelength, decay time, and quantum yield are all within the range of experimental error and no particular differences could be observed (Figure S14).

In conclusion, the synthesis of new cyclometalated C^C* Pt^{II} complexes and their unique excimeric enhanced photophysical properties have been reported. All complexes are found to be excellent candidates for blue emitting phosphorescent OLED (PhOLEDs) with very high quantum yields (up to 93%) and very short phosphorescent lifetimes (down to 3.5 µs). In addition to the monomeric species, we observed an emissive species formed by self-aggregation. The formation of the aggregate leads to a red shift of approx. 100 nm, an enhanced guantum yield, and a shortening of the decay time by a factor of four with respect to the monomer emission. The dual emissive behavior of the new complex was characterized through emission-excitation matrix analysis (EEM). Herein we present the possibility to tune the emissive wavelength upon variation of the concentration and, even more remarkably, the possibility to obtain different emission colors from a single complex at a constant concentration only by selective excitation of the emissive species.

Experimental Section

Experimental Details are reported in the supporting information. CCDC 1560929 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Conflict of interest

The authors declare no conflict of interest.

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