Phosphorescent Platinum(II) Complexes with C^C* Cyclometalated NHC Ligands

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CONSPECTUS: This Account describes our achievements toward the development of a new class of platinum(II) complexes with interesting photophysical properties. The general motif of a strongly donating N-heterocyclic carbene with a cyclometalating phenyl group attached to the nitrogen atom together with β-diketone based counterligands enabled us to synthesize a new class of phosphorescent emitters for use in organic light-emitting diodes (OLEDs). This Account is divided into sections and introduces imidazolium based as well as triazolium based structures and discusses the effects of structural changes on the photophysical properties. Starting from the basic methylated (substituted) phenylimidalium precursors, we initially extended the π-system of the phenyl ring to the dibenzofuran ligand, its regioisomer, and thio-derivative. As the substituents of the β-diketone ligands turned out to have a strong influence on the photophysical properties (higher quantum yields as well as shorter decay times) a series of dibenzofuranyl-3-methylimidazol as well as diphenylbenzimidazol platinum complexes were synthesized to investigate the different steric and electronic effects, which are described in a separate section. The next section of the Account then describes other extensions of the π-system. Exchange of the methyl group against a phenyl ring, as well as the extension of the π-system in the backbone of the NHC-ligand lead to a significant improvement of the photophysical properties, which reached a maximum for the diphenylbenzimidazole (DPBIC) system. Further extension of the π-system to the diphenynaphthylimidazol then lead to an unfavorable long decay time.

The effect of substitution is discussed for cyano groups, which change the electronic situation and lead to highly emissive complexes. We are currently working on studying the effect of other substituents on the photophysical properties, as well as the introduction of additional heteroatoms into the general motif.

Our initial work in that area had been on 1,2,4-triazole complexes. For the basic phenyl/methyl substituted system, two different isomers are accessible, the 4-phenyl-4H-1,2,4-triazoles as well as the 1-phenyl-1H-1,2,4-triazoles. It was interesting to note that the photophysical properties of the corresponding complexes are strongly dependent on the substituent R of the β-diketone ligand. For R = methyl, the properties are significantly different, while we found almost identical photophysical results for R = mesityl for both 1,2,4-triazole isomers. The last section describes the synthesis of bimetallic complexes. To investigate whether it is possible to cyclometalate twice into the same phenyl ring, we synthesized dicationic NHC precursors from para- and meta-disubstituted bis(imidazole)benzenes. The bimetallic complexes show interesting photophysical properties with quantum yields of up to 93%.

All experimental work was accompanied by quantum chemical calculations, which turned out to be very useful for the prediction of the emission wavelengths as well as the interpretation of the emissive states of the platinum complexes.

INTRODUCTION

The development of more energy efficient lighting is one of the important tasks to reduce the worldwide energy consumption, which just for lighting is close to 20% of the total energy demand. By improving the efficiency of the light sources, a significant reduction of the global energy demand can be envisioned. During the past decade, extremely energy efficient light-emitting diodes (LEDs) have been developed, which has recently been honored by the 2014 Nobel Prize in physics. But contrary to the incandescent light from light bulbs, the directional light of LEDs is limited when it comes to lighting applications. One concept that is currently seen as the next generation lighting is the development of organic light-emitting diodes (OLEDs). They also allow for new designs of lighting in the form of wallpapers as they can be produced in larger areas. In 1998, it was recognized that the incorporation of transition metal complexes allows for quantum yields beyond the fluorescence limit of 25%. These phosphorescent emitters play a key role for the design of these new lighting materials. OLEDs are built from different thin layers as shown in Figure 1. The formation of excitons by recombination of electrons and holes in the recombination layer leads to phosphorescent emission if suitable transition metal complexes are doped into this layer.

After the initial report of the green phosphorescent tris(2-phenylpyridine)iridium complex, Ir(ppy)_3, cyclometalated 2-phenylpyridines and derived motifs have been investigated in detail in the past decade. One example, the bidentate 2-(4,6-difluorophenyl)pyridyl (N^C) ligand, is shown in Figure 2, together with an acetylacetonate (acac) ligand at a platinum center. Variations of the general motif include more rigid terdentate, N^C^N^N^N, and tetratentate, N^C^C^N^N^N^N, ligands.

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Based on an efficient spin–orbit coupling they show good quantum yields, short decay times, and high stability, but the majority emit in the green to red part of the spectrum, and the need for a phosphorescent blue emitter has become obvious. To shift the color coordinates of the N-coordinated complexes, stronger donating ligands have been developed. Maintaining the concept of cyclometalation, the nitrogen atoms were replaced by stronger donating N-heterocyclic carbene carbon atoms (C\textsuperscript{C*C*}).

**CYCLOMETALATED C\textsuperscript{C*C*} PLATINUM COMPLEXES**

The first published example of a platinum(II) complex with a cyclometalated N-heterocyclic carbene (NHC) ligand\textsuperscript{15,16} and acac ligand is shown in Figure 3. We\textsuperscript{17} and others\textsuperscript{17,18} started to study this new class of complexes in 2009 and investigated the effect of different substituents in the para-position.

![Figure 3. C\textsuperscript{C*C*}-cyclometalated platinum complex.](image)

We observed green-blue phosphorescence with emission wavelengths of 416–546 nm and moderate quantum yields of 5–32\% (Table 1). These cyclometalated (NHC)Pt(acac)\textsuperscript{17} complexes can be synthesized by reaction of the corresponding imidazolium salts with silver(I) oxide. Without isolation, the resulting intermediate is transmetalated onto dichloro(1,5-cyclooctadiene)-platinum(II). After changing the solvent (from dioxane/butanone to DMF), an excess of 2,4-pentanedione and potassium-tert-butanolate is added (Scheme 1).

These complexes with electron-donating and -withdrawing substituents could be synthesized in yields between 19\% and 57\% and have been characterized by standard techniques including \textsuperscript{195}Pt NMR and two-dimensional NMR methods\textsuperscript{17}.

![Scheme 1. Synthesis of Different para-Substituted C\textsuperscript{C*C*}-Cyclometalated Platinum(II) Complexes\textsuperscript{17}.](image)

Frequently we could also get crystals suitable for solid state structure determination\textsuperscript{20} and studied their photoluminescence (PL) data.

With the exception of the nitro-substituted complex, all complexes show very similar absorption spectra. The emission spectra show structured emission bands in the blue-green part of the spectrum with maxima around 450–460 nm, again with the exception of the nitro-substituted complex, which shows a pronounced bathochromic shift of the emission with an unstructured band at around 550 nm. As examples, the very different emission spectra of the methyl- and the nitro-substituted compound are given in Figure 4. We believe that this is due to aggregate formation and a MMLCT (metal-metal-to-ligand charge transfer) and used concentration-dependent measurements, but the origin of the shift could not be determined without a doubt.

To investigate their photophysical properties, the absorption and emission spectra were generally measured in amorphous poly(methyl methacrylate) (PMMA) films at room temperature with 2\% emitter concentration. We found that, with the exception of the electron-withdrawing nitro group, all complexes showed emissions in the deep blue part of the spectrum. Changing the substituent in the 4-position had a significant effect on the observed quantum yield as well as on the decay lifetime (Table 1). Compared to the unsubstituted complex (QY = 7\%), one methoxy group changed the observed quantum yield to 32\%.

**DIBENZOFURAN AND -THIOPHENE LIGANDS**

When we used a ligand with a different skeleton and extended \(\pi\)-system, the quantum yield improved to 90\% for the \([1-(dibenzo[\text{b,d}]furan-4-yl)-3-methylimidazolin-2-ylidene \text{acetylacenato} \text{platinum(II)}\) complex shown in Figure 5. The dibenzofuran (DBF) NHC complex showed a strong emission at 463 and 497 nm with a decay time of 23 \(\mu\)s, which turned out to be independent of the temperature of the measurement. The emission spectra measured at 5, 77, 100, 200, and 300 K are given in Figure 5.

![Figure 5. Emission spectra of a dibenzofuran (DBF) NHC complex.](image)
The standard device built for this emitter (DBF-NHC)-Pt II(acac) is described in detail in the literature. Different measurements have been carried out which can be summarized in the following way: the electroluminescence spectra are showing their maxima at 480 nm and a pronounced progression of the emission band independent of the dopant concentration, while the maximum luminance is strongly concentration dependent and can be found between 4900 cd m \(^{-2}\) (13 V, 6\% doping) and 6750 cd m \(^{-2}\) (13.2 V, 12\% doping). At the highest doping concentration of 12\% also the maximum external quantum efficiency (EQE) of 6.2\% is reached. The corresponding dibenzothiophene (DBT) complex (Figure 6) was synthesized in an analogous way but showed inferior photophysical properties (QY = 63\%, \(\tau = 31\ \mu s\)).

Depending on the halogenation procedure of the dibenzofuran, two different isomers can be synthesized (Scheme 2).

Bromination in 4-position is the result of a deprotonation/lithiation at \(-40^\circ C\) followed by metal–halogen exchange at \(-78^\circ C\) using 1,2-dibromoethane. The use of benzyltrimethylammonium dichloroiodate (BTMA·ICl\(_2\)) and zinc chloride results in the iodination in 2-position of the dibenzofuran. The halogenated dibenzofurans can be coupled in a copper(I) catalyzed Ullmann-type reaction to generate the corresponding (benz)imidazoles, which can be methylated using an excess of iodomethane in tetrahydrofuran (THF) at elevated temperatures (Scheme 2). The platinum complexes shown in Figure 7 were synthesized following our previously reported general route. The photophysical properties of the two isomeric complexes turned out to be very different. Especially

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**Figure 4.** Absorption spectra of cyclometalated (NHC)Pt II(acac) complexes together with the emission spectra of the methyl (Me) and nitro (NO\(_2\)) substituted complexes.

**Figure 5.** C\(^4\)-C\(^\#\)-cyclometalated (DBF-NHC)Pt II(acac) complex and its emission spectra at different temperatures.

**Figure 6.** ORTEP representation of the [1-(dibenzo[b,d]-thiophen-4-yl)-3-methyl-1H-imidazolin-2-yldene-κC,κC’] (2,4-pentanedionato-κO,κO’)-platinum(II) complex. Thermal ellipsoids are drawn at the 50\% probability level. Selected bond lengths (Å) and angles and dihedral angles (deg): Pt(1)–C(1) 1.954(4); Pt(1)–C(5) 1.975(4); Pt(1)–O(1) 2.091(3); Pt(1)–O(2) 2.056(3); O(1)–Pt(1)–O(2) 89.60(13); C(1)–Pt(1)–C(5) 80.47(18); C(4)–N(1)–C(1)–Pt(1) 1.3(5); N(1)–C(1)–Pt(1)–O(1) 176.3(3).

**Scheme 2. Synthesis of Different DBF Isomers**

\[\begin{align*}
\text{(i)} & \quad \text{BrLi, } C_6H_5Br_2; \\
\text{(ii)} & \quad \text{BTMA·ICl} \_2, \text{ZnCl}_2; \\
\text{(iii)} & \quad \text{Cu}_2O, \text{KOH, DMSO, (benz)imidazole;} \\
\text{(iv)} & \quad \text{CH}_3\text{I, THF, reflux.}
\end{align*}\]

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**Figure 7.** (DBF_BIM) and iso-(DBF_BIM) platinum(II) complexes with sterically demanding mesacac ligands.
in combination with a variation of the substituents at the β-diketonate, which will be described in the next paragraph in detail, emitters with high quantum yields and comparatively short decay times could be synthesized (Figure 7).

The isomers differ significantly in the decay time, which is lower by more than 50% for the iso-(DBF_BIM)PtII(mesacac) complex, while emission wavelengths and quantum yields are comparable (Table 2).

### Table 2. PL Data (2% in PMMA) of the Cyclometalated Benzimidazole Mesacac Platinum Complexes

<table>
<thead>
<tr>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>DBF_BIM</td>
<td>370</td>
<td>475</td>
<td>84</td>
<td>1.926(7)</td>
</tr>
<tr>
<td>iso-DBF_BIM</td>
<td>340</td>
<td>479</td>
<td>80</td>
<td>1.970(7)</td>
</tr>
</tbody>
</table>


d and CIE coordinates at rt. *Emission wavelength [nm]. **Quantum yield in %, excited with λ exc, N2 atm. **Decay lifetimes [μs] (excited by laser pulses (355 nm, 1 ns)) given as τ0 = τ/Φ.

Both isomers (Figure 7) could be characterized by solid state structures.23 Figure 8 shows the solid state structure of the iso-(DBF_BIM) complex.

![Figure 8. ORTEP representation of the iso-DBF complex. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles and dihedral angles (deg): C(1)−Pt(1), 1.926(8); C(9)−Pt(1), 1.970(7); O(2)−Pt(1), 2.082(5); O(3)−Pt(1), 2.059(5); C(1)−Pt(1)−C(9), 80.4(3); O(2)−Pt(1)−O(3), 89.5(2); C(8)−N(1)−C(1)−Pt(1), −0.8(8).](image)

As can be seen from the emission spectra in Figure 9, the maximum emission wavelength is very similar for both isomers, but the profile is significantly different. The different electronic structure of both isomers also had an influence on the decay time of the emission (Table 2).

### VARIATION OF THE COUNTERLIGAND MOTIF

The [1-(dibenzo[b,d]furan-4-yl)-3-methylimidazolin-2-ylidene] platinum complex (Figure 5) was then used to investigate the effect of different β-diketonates (Scheme 3).24 Depending on the auxiliary ligand, the complexes emit either in the deep-blue or the orange-red part of the spectrum (Table 3). We found that by changing the CH3 groups (QY 90%) to CF3 groups (QY 0%), the emission was completely shut off. Obviously the CF3 groups deactivate the complex by shifting the electronic levels so thoroughly that no emission could be observed any more.

While the sterically demanding tert-butyl groups did not significantly change the emission data and the structured emission profile with three distinct peaks, the phenyl groups (Ph) led to a significant red shift of the emission with a single broad band. According to our DFT calculations, the phenyl ring rotates into the plane of the acac core in the triplet state, thereby extending the π-system. This allows for an increased delocalization and a red shift of the emission. The emission profile of the complex with mesacac ligand also changed to one broad band, reduced the decay time to 19 μs, and kept the wavelength of the emission and the quantum yield (Table 3).

We therefore studied the influence of the β-diketonate ligands with aromatic groups also for other ligand motifs and could see an overall improvement of the photophysical properties when methyl-substituted aromatic β-diketonates were used.

DFT calculations (B3LYP/6-31G*) confirm that substituents in the ortho-positions force the aryl group in an orthogonal position, while the unsubstituted phenyl ring shows a dihedral angle of 30° between the acetylacetonate plane and the phenyl ring. The calculated singlet state geometries of the (DBF-NHC)PtII(phacac) and (DBF-NHC)-PtII(mesacac) are given in Figure 10.

Another example is the series of complexes we synthesized using the 1,3-diphenylbenzo[d]imidazolin-2-ylidene (DPBIC) ligand with five different β-diketonates (Scheme 4, Figure...
Next to the regular acetylacetonate (R = Me), we used the 2,2,6,6-tetramethylheptane-3,5-dione (R = tBu), 1,3-diphenylpropane 1,3-dione (R = Ph), 1,3-dimesitylpropane-1,3-dione (R = Mes), and 1,3-bis(2,3,5,6-tetramethylphenyl)-propane-1,3-dione (R = Duryl) in the synthesis of the corresponding platinum DPBIC complexes. The mesacac ligand was synthesized by a Friedel−Crafts-reaction using malonyl dichloride, AlCl₃, and 1,3,5-trimethylbenzene following a reported procedure. The Duryl ligand was synthesized in a similar reaction with 1,2,4,5-tetramethylbenzene.

Figure 12 shows the resulting emission spectra of the DPBIC complexes, which clearly demonstrate the influence of the β-diketonate ligand on the emission process. Also in this case, the emission profile changes from a structured emission for the alkyl substituted β-diketonates to a single broad emission band for the aromatic auxiliary ligands.

As can be seen from the data in Table 4, the aromatic β-diketonate ligands together with the DPBIC ligand significantly reduce the decay lifetimes to 4 μs, while the measured quantum yields are only slightly lower than in the DBF case and emit in the same region around 470 nm.

### EXTENSION OF THE π-SYSTEM

Obviously there are various extensions of the π-systems possible, starting with using benzimidazole instead of imidazole or a naphthyl ligand instead of the phenyl system (Figure 13).

The synthesis of the precursor salts could be accomplished by different synthetic strategies described in Scheme 5. For the benzimidazole and naphthyl ligands with two phenyl rings in 1,3-position (DPBIC, DPNIM), we used the amines as starting material and closed the ring using triethylorthoformiate and ammonium tetrafluoroborate. For the MPBIM ligand, Cu(I) catalyzed coupling chemistry was followed by methylation using iodomethane, while for the MNBIM ligand, Pd(0) catalysis followed by the above-described ring closure reaction with HC(OCH₂CH₃)₃ were successful (Scheme 5).

Using the established synthesis, the corresponding platinum complexes (Figures 13 and 14) could be synthesized in good yields. But not only this extension of these π-systems is possible: a delocalized system could also be added in the 3-position of the imidazole core, examples are given in Figure 14.
As expected, the change of the $\pi$-system was reflected in the absorption and emission spectra. The complexes shown in Figures 13 and 14 have been measured in 2% PMMA films and exhibit at least three distinct maxima (Figure 15).

For the complexes with the smallest $\pi$ extension, DPIM and MPBIM, the first observed emission peak lies in the deep blue region at around 450 nm, with vibronic progressions toward the green region of the spectrum. When the $\pi$-systems become larger, the corresponding emission maxima are red-shifted with the exception of DPBIC, which remains a true blue emitter (CIE 0.158, 0.147). With increasing size of the $\pi$ system the color changes to higher wavelengths can be explained by the resulting stabilization of the LUMO and thus a smaller energy gap between the singlet ground state and the first excited emissive state.

Table 5 summarizes the photophysical results for the measurements in PMMA films. The highest quantum yield was found for DPNIM with the largest $\pi$ system accessible, but the emission maximum is shifted to 515 nm and exhibits an extremely long decay time of more than 400 $\mu$s. But even the addition of only one phenyl ring (DPIM) compared to the methyl substituted complex increases the quantum yield from 7% to nearly 17%. The addition of a phenyl ring in the backbone of the N-heterocyclic carbene (MPBIM) leads to an even stronger effect by increasing the quantum yield to 40%.

### SUBSTITUTION BY CYANO GROUPS

There are many aromatic systems with electron-donating and -withdrawing groups accessible via different synthetic routes. We initially started with electron-withdrawing cyano groups; the first $C^\wedge C*$-cyclometalated complex with good photophysical properties carried a cyano group in 4-position (Figure 3). Phenylimidazolium salts with cyano substituents, the 1-(4-cyanophenyl)-3-isopropyl-1H-benzodimidazolium tetrafluoroborate (IPrBICN) and the 1-(4-cyanophenyl)-3-methyl-4-(1-methylprop-2-yl)-1H-imidazolium iodide (TBuICN) were synthesized; the synthetic pathways are given in Scheme 6.

For the synthesis of the IPrBICN ligand, we started from the 2-nitroaniline and introduced the isopropyl group by reduction of the imine, while for the benzonitrile, Pd(0) coupling chemistry was used followed by standard ring closure conditions. In the case of TBuICN, the benzonitrile was introduced via substitution of the fluoro derivative and quaternization by...
methyl iodide, which allowed for the synthesis of the ligand in two steps.

To investigate the effect of the aromatic β-diketones on this class of compounds, we synthesized two complexes for each of the ligand systems, one with the regular acetylacetonate and one with the mesityl derivative. Three of the complexes could also be characterized by solid state structures (Figure 16). The photophysical data given in Table 6 again confirm the beneficial effect of the mesityl groups as the quantum efficiency improved by 20% and also the decay time was significantly shorter while the emission wavelengths and emission profile (Figure 17) did not change.

Table 6. PL Data (2% in PMMA) of Cyano Substituted Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>λ_{exc} (nm)</th>
<th>CIE x</th>
<th>y</th>
<th>λ_{em} (nm)</th>
<th>Φ</th>
<th>τ_{e} (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(IPrBICN)Pt(acac)</td>
<td>330</td>
<td>0.158</td>
<td>0.161</td>
<td>444, 473</td>
<td>63</td>
<td>15.5</td>
</tr>
<tr>
<td>(TBuICN)Pt(acac)</td>
<td>355</td>
<td>0.164</td>
<td>0.216</td>
<td>443, 474</td>
<td>57</td>
<td>17.0</td>
</tr>
<tr>
<td>(IPrBICN)Pt(mesacac)</td>
<td>370</td>
<td>0.164</td>
<td>0.212</td>
<td>442, 471</td>
<td>80</td>
<td>8.9</td>
</tr>
<tr>
<td>(TBuICN)Pt(mesacac)</td>
<td>370</td>
<td>0.166</td>
<td>0.229</td>
<td>443, 471</td>
<td>85</td>
<td>8.4</td>
</tr>
</tbody>
</table>

“Excitation wavelength [nm].” CIE coordinates at room temperature. “Quantum yield in %, excited with λ_{exc}. N_{2} atmosphere; ‘Decay lifetimes [μs] (excited by laser pulses (355 nm, 1 ns)) given as τ_{e} = τ_{o}/Φ.”

Figure 17. Emission spectra of cyano substituted platinum β-diketonate complexes.

Scheme 7. Synthesis of 1-Phenyl-1H-1,2,4-triazole (i) and 4-Phenyl-1H-1,2,4-triazole (ii)

“Conditions: (i) Cu_{2}O, K_{2}CO_{3}, phen, DMF, Ar, 100 °C, 48 h; (ii) 180 °C, 3 h.”

Quaternization, for example, with methyl iodide then gives the corresponding 1,2,4-triazolium salts in high yields followed by the synthesis of the platinum(II) complexes, which were accessible via a similar route as described for the imidazolin-2-ylidene complexes. Two different series of complexes based on the two different motifs were reported in the literature.

The additional nitrogen atom caused significant changes in the photophysical properties of the two different triazole complexes compared to the imidazole based complexes shown before (Scheme 1). For the unsubstituted 1-phenyl-3-methylimidazolin-2-ylidene platinum(II) acetylacetonate a very low quantum yield of 7% (λ_{max} = 441 nm) was measured (Table 1), while for the 4-phenyl-1-methyl-1,2,4-triazol-5-ylidene platinum(II) acetylacetonate (Figure 18, R_{2} = CH_{3}, R_{3} = H), a quantum yield of 11% (λ_{max} = 431/456 nm) was observed. For the asymmetric 1-phenyl-4-methyl-1,2,4-triazol-5-ylidene platinum(II) acetylacetonate (Figure 18, R_{1} = H, R_{2} =...
CH₃, we even observed a QY of 30% (λ_max = 428/455/483 nm) and a comparable decay time (Table 7).

For the acetylacetonate (Figure 18, R₂ = CH₃) complexes, it was obvious that the asymmetric (red colored) triazole ligand led to significantly better results. Independent of the substitution (Figure 18, R₃ = Cl, OCH₃, CH₃) quantum yields between 30% and 40% were measured, more than twice the quantum yield found for the complexes with 4-phenyl triazole ligands. The emission spectra of the acetylacetonate complexes show a well-structured emission with three maxima (Table 7), which indicates strong contributions of ligand centered states to the emission process.

When we extended our research program to triazole complexes with mesityl substituted acetylacetonates (Figure 18, R₂ = Mes) the differences disappeared. As expected the photophysical properties improved significantly, quantum yields more than doubled to 82%, and the decay time was reduced by a factor of 3 to 4 μs. But to our surprise the difference between the two triazole motifs disappeared. Both complexes gave almost identical results with emission wavelengths of 477 and 478 nm.

The emission spectra of the mesacac complexes reveal a different emission behavior. In contrast to the vibronic structure observed for the acac complexes, we now see an unstructured emission with only one maximum. According to our DFT calculations another transition contributes to the emission process in the case of the mesacac ligand. The charge-transfer transition involves the metal center, which explains the improved quantum yields and reduced decay times. We also looked at different substituents in the 4-position of the aromatic ring, but they showed only minor effects on the emission wavelengths (H 478 nm; OCH₃ 477 nm; CH₃ 475 nm) with 82% quantum yield and decay times between 3 and 5 μs. This confirms the change of the emission process to a transition with reduced contributions of ligand centered states.

**Table 7. PL Data (2% in PMMA) of Triazole Based Complexes**

<table>
<thead>
<tr>
<th>R₁</th>
<th>R₃</th>
<th>λ_exc[^a]</th>
<th>CIE x, y[^b]</th>
<th>λ_em[^c]</th>
<th>Φ[^d]</th>
<th>τ_0[^e]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>330</td>
<td>0.169, 0.194</td>
<td>405, 431, 456</td>
<td>11</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>325</td>
<td>0.192, 0.272</td>
<td>411, 436, 465, 493</td>
<td>12</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>OMe</td>
<td>340</td>
<td>0.174, 0.200</td>
<td>421, 445, 468</td>
<td>14</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>335</td>
<td>0.166, 0.180</td>
<td>428, 455, 483</td>
<td>30</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>325</td>
<td>0.193, 0.261</td>
<td>432, 459, 488</td>
<td>41</td>
<td>11</td>
<td></td>
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<tr>
<td>Me</td>
<td>330</td>
<td>0.169, 0.227</td>
<td>470</td>
<td>38</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>OMe</td>
<td>330</td>
<td>0.165, 0.201</td>
<td>435, 462, 489</td>
<td>38</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

[^a]: Excitation wavelength [nm].  
[^b]: CIE coordinates at room temperature.  
[^c]: Emission wavelength [nm].  
[^d]: Quantum yield in %, excited with λ_exc, N₂ atmosphere.  
[^e]: Decay lifetimes [μs] (excited by laser pulses (355 nm, 1 ns)) given as τ₀ = τ/Φ..

**Scheme 8. Synthesis of Dicationic NHC Precursors**[^a]

**Scheme 9. Bimetallic Complexes**

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**BIMETALLIC COMPLEXES**

To evaluate the influence of a second platinum atom in the same system, a series of bimetallic complexes with the general formula [Pt(NHC)(L)]₂Ph, which are composed of two [Pt(NHC)/β-diketonate] fragments, were synthesized[^2]. These fragments are cyclometalated to a central phenyl ring either in *meta-* or *para*-position. The synthesis of the dicationic precursors could be accomplished by standard copper coupling conditions in DMSO using the 1,3- or 1,4-diiodobenzene followed by quaternization with methyl iodide or benzylation bromide. Scheme 8 describes the synthesis of the para-substituted 1,4-bis(imidazol)benzene (p-BIB) as well as the dicationic NHC precursors 1,4-bis(3-methylimidazol)benzene (BMIB) iodide and 1,4-bis(3-benzylimidazol)benzene (BBZIB) bromide.

The established route of the reaction with Ag₂O and subsequent transmetalation with Pt(COD)Cl₂ followed by treatment with an excess of the β-diketonate ligand and potassium tert-butanolate lead to the formation of the corresponding platinum(II) complexes in relatively low yields.
between 6% and 21%, but the complexes shown in Scheme 9 showed very good photophysical data given in Table 8.

The emission spectra of these complexes are given in Figure 19. It is interesting to note that in these cases we see neither different emission profiles for the alkyl- and the mesityl-acetylacetonates nor large differences in the photophysical data. Due to the low solubility of the bimetallic complexes, it was very difficult to get crystals suitable for solid state structure determination, but in case of the Bu2BMIM_Pt2 complex, we succeeded in growing single crystals and could unequivocally confirm the structure of the bimetallic compound (Figure 20).

### QUANTUM CHEMICAL CALCULATIONS

The experimental work was accompanied by density functional theory calculations, which have been extremely useful to identify potentially interesting ligand motifs. We developed a methodology to predict the emission wavelengths of the metal–organic complexes. Standard density functional theory calculations (B3LYP/6-31G(d), BP86/6-31G(d) together with a Hay–Wadt-ECP for platinum, Gaussian09) allowed us to screen in silico for promising structures. We then synthesized only those complexes that were predicted to emit in the blue/green part of the spectrum, which was of interest to us. This screening is based on the calibrated vertical energy differences between the fully optimized singlet and triplet states and the singlet state energy of the optimized triplet structure (ΔE = HF(T1) − S0(T1)). We also calculated the various transitions to analyze the contribution of the various states and to characterize the emission.

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### ABBREVIATIONS

- p-BIB, 1,4-bis(imidazole)benzene; BMIB, 1,4-bis(3-methylimidazol-2-ylidene)-benzene; BbzIB, 1,4-bis(3-benzylimidazol-2-ylidene)-benzene; COD, 1,5-cyclooctadiene; DBF, dibenzofuran; DMF, dimethylformamide; DMSO, dimethyl sulfoxide; DPBIC, 1,3-diphenylbenzol[d]imidazol-2-ylidene; DPIM, 1,3-diphenylimidazol-2-ylidene; DPBIM, 1,3-diphenylimidazol-2-ylidene; Duryl, 1,3-bis(2,3,5,6-tetramethylphenyl)propane-1,3-dione; EQE, external quantum efficiency; IPrBICN, 1-(4-cyanophenyl)-3-isopropyl-1H-benzol[d]imidazol-2-ylidene; Mesacac, 1,3-dimesitylpropane-1,3-dione; MNBIM, 3-methyl-1-naphthylbenzo[d]imidazol-2-ylidene; MPBIM, 3-methyl-1-phenylbenzo[d]imidazol-2-ylidene;
dene; OLED, organic light-emitting diode; phacac, 1,3-diphenyl-propane-1,3-dione; Phen, phenanthroline; PL, photoluminescence; PMMA, poly(methyl methacrylate); Pt(COD)-Cl, dichloro(1,5-cyclooctadiene)-platinum(II); TButICN, 1-(4-cyanophenyl)-3-methyl-4-(1-methylprop-2-yl)-imidazolin-2-ylidene; TLC, thin layer chromatography; QY, quantum yield

**REFERENCES**


(21) Measured at room temperature.


