Synthesis, Air Stability, Photobleaching, and DFT Modeling of Blue Light Emitting Platinum CCC-N-Heterocyclic Carbene Pincer Complexes

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Supporting Information

ABSTRACT: The recently reported metalation/transmetalation route for the synthesis of CCC-bis(NHC) pincer ligand supported transition-metal complexes was extended to Pt. 2-(1,3-Bis(N-butylimidazol-2-ylidene)phenylene)(chloro)platinum(II) (1) and its bromo analogue 2 were synthesized and characterized. X-ray crystal structure determinations revealed complexes 1 and 2 to have distorted-square-planar configurations around the metal. Photophysical and thermal properties of these complexes are reported, and their extended photostability in air is discussed and contrasted. Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) computations of the ground state and various low-lying excited states have revealed admixing of Pt 5d orbitals and the ligand π* orbitals for both the ground state and the low-lying excited states of complex 1, indicating the low-lying states to be a mixture of metal-to-ligand charge-transfer and ligand-centered transition (MLCT-LC). Somewhat surprisingly, the computed gas-phase geometry of the excited state of complex 1 had a significant distortion, mostly about the Caryl−Pt−Cl angle. These complexes were congeners of materials for organic light emitting diodes (OLEDs).

INTRODUCTION

The development of new molecular architectures to impart desired physical and chemical properties has been an area of highly active research. Specifically, stable carbenes have drawn intense attention, in spite of their relatively short history.1 The special stability of N-heterocyclic carbenes (NHCs) was established with the first report of the X-ray crystallographically determined molecular structure by Arduengo and co-workers.1b,2 The dramatic importance of the nitrogen substituents determined molecular structure by Arduengo and co-workers established with the first report of the X-ray crystal structure of an acyclic diamido carbene.3 was further demonstrated when Alder and co-workers reported the X-ray crystal structure of an acyclic diamido carbene.3 The applications of NHCs have blossomed since the 1991 report, and these compounds have been widely established as strong ligands for transition metals.3c,4 Numerous applications to catalytic organic transformations have been demonstrated, including olefin metathesis,7 Pd cross-coupling reactions such as the Heck,6 Suzuki−Miyaura,7 Negishi,8 Sonogashira,9 Buchwald−Hartwig,7c,10 and many more.11 In addition, they have been demonstrated to catalyze C−heteroatom bond forming reactions such as C−N,10,12 C−Si,13 and C−O.14 Furthermore, their photophysical properties have been explored for materials applications.15 Besides serving as excellent ligands to transition metals, NHCs have been demonstrated to be organocatalysts for the benzoin condensation,16 Stetter reaction,17 and more.18

Pincer ligands have been one of the most widely investigated and applied architectures in modern organometallic chemistry.7 The confluence of NHCs and pincer ligand chemistry has seen much activity in recent years.20 The aryl-bridged bis(NHC)-pincer ligands consist of four major classes, depending on the atoms making the bonds to the metal and the linker between the aryl and NHC groups (Scheme 1). The xylylene-bridged C=C=C-NHC (type A)21 and 2,6-lutidinyl bridged C≡N-C-NHC (type C)22,21c,22 pincer complexes are usually found to have C2 symmetry due to the CH3 spacer. The phenylene-bridged CCC-NHC (type B)23 and pyridylene-bridged CNC-NHC (type D)23b,c,24 pincer complexes normally have higher symmetry and adopt a C∞v geometry. We introduced the class of phenylene-bridged CCC-bis(NHC) pincer ligand systems,23 and others have also begun exploring this architecture.25 The impact of molecular inorganic and organometallic compounds in photonic applications has been growing rapidly. Recent reports have illustrated their importance in developments for artificial photosynthesis,26 photocatalytic splitting of water,27 solar cell applications,28 organic light-emitting diodes (OLEDs),29 and photoluminescence.29a,h,30 A recent paper detailed the pyridylene CNC-bis(NHC) pincer ligand Pt system...
and its photoluminescence.\textsuperscript{31} We report herein the development and characterization of square-planar Pt\textsuperscript{II} CCC-NHC phenylene-bridged pincer complexes \textsuperscript{1} and \textsuperscript{2} and their properties. To understand the nature of the observed transitions, we describe the application of theoretical methods (DFT) to explore the geometric and electronic properties of the ground state and excited state (both vertical and adiabatic transitions).

\section*{RESULT AND DISCUSSION}

\textbf{Synthesis and Characterization.} The CCC-NHC pincer ligand precursors were synthesized according to the literature.\textsuperscript{23,32} Simultaneous activation of the three C–H bonds of the tridentate ligand was achieved through the well-established basicity and electrophilicity of Zr(NMe\textsubscript{2})\textsubscript{4}.\textsuperscript{23,33} A Pt(II) source was added to the in situ prepared Zr reagent to achieve transmetalation (Scheme 2). All reactions were carried out at room temperature under an inert atmosphere. When transmetalation was complete, water was added, and excess Zr reagent was decomposed and precipitated. The identity of each complex was established by $^1$H and $^{13}$C NMR spectroscopy, ESI-MS, and elemental analysis (see the Experimental Section).

Two of the primary observations in the $^1$H NMR spectra were the disappearance of the imidazolium protons (11.27 ppm, 2H) and an aryl H (8.96 ppm). The $^1$H NMR data of chloro complex \textsuperscript{1} and bromo complex \textsuperscript{2} also indicated characteristic long-range $^{195}$Pt–$^1$H coupling. The NHC carbon signal of chloro complex \textsuperscript{1} was observed at 171.7 ppm with $^{1}J_{\text{Pt}-\text{C}} = 1168$ Hz. The Pt-bound aryl carbon signal was observed at 133.8 ppm with $^{1}J_{\text{Pt}-\text{C}} = 937$ Hz. The NHC carbon signal of bromo complex \textsuperscript{2} was observed at 170.5 ppm with $^{1}J_{\text{Pt}-\text{C}} = 1166$ Hz. The Pt-bound aryl carbon signal of \textsuperscript{2} was observed at 134.0 ppm with $^{1}J_{\text{Pt}-\text{C}} = 953$ Hz. All chemical shifts and coupling constants were similar to those previously reported for Pt-NHC complexes.\textsuperscript{31,34} The ESI-MS of the Pt-Cl complex \textsuperscript{1} revealed the molecular ion plus Na (575 Da). The molecular ion was observed for the Pt-Br complex \textsuperscript{2} (595 Da). The experimental values for the CHN analyses of both complexes were within an acceptable range.

X-ray-quality crystals of chloro complex \textsuperscript{1} were obtained by slow diffusion of Et\textsubscript{2}O into a CH\textsubscript{2}Cl\textsubscript{2} solution. X-ray-quality crystals of bromo complex \textsuperscript{2} were observed after transmetalation and were collected from the reaction mixture. ORTEP representations of the molecular structures of \textsuperscript{1} and \textsuperscript{2} are depicted in Figure 1.\textsuperscript{35} Selected bond distances and angles for complexes \textsuperscript{1} and \textsuperscript{2} are given in Table 1 and are consistent with those for previously reported Pt(II) complexes.\textsuperscript{31,34a,36} The structural data for the pyridylene-bridged CNC analogue have been listed for comparison.\textsuperscript{31} The structures of complexes \textsuperscript{1} and \textsuperscript{2} are similar. The Pt–C\textsubscript{aryl} bond lengths in chloro complex \textsuperscript{1} (2.030(3) and 2.035(3) Å) and in bromo complex \textsuperscript{2} (2.037(6) and 2.036(6) Å) fall into the range observed for neutral and cationic Pt(II) pincer complexes.\textsuperscript{31,34a,36} Both complexes display distorted-square-planar configurations at the metal center, which has been commonly seen for four-coordinate Pt(II) pincer complexes.\textsuperscript{31,34a,36} The C7–Pt\textsuperscript{II}–C\textsubscript{aryl} angles were bent (\textsuperscript{1}157.44(11)°; \textsuperscript{2}157.3(2)°) due to ligand constraints.

It was possible to compare the metric data for Pt–Cl complex \textsuperscript{1} to those for its pyridylene-bridged CNC analogue. The Pt–C\textsubscript{aryl} bond length of complex \textsuperscript{1} (2.030(3) and 2.035(3) Å) was slightly shorter (∼0.025 Å) than the Pt–N bond length of the pyridylene-bridged CNC complex, while the Pt–C\textsubscript{NHC} bonds of complex \textsuperscript{1} were about 0.06 Å longer.\textsuperscript{31} On comparison of the Pt–Cl bond distances, a greater trans influence of the Caryl anionic ligand was for complexes \textsuperscript{1} and \textsuperscript{2} are given in Table 1 and are consistent with those for previously reported Pt(II) complexes.\textsuperscript{31,34a,36} The structural data for the pyridylene-bridged CNC analogue have been listed for comparison.\textsuperscript{31} The structures of complexes \textsuperscript{1} and \textsuperscript{2} are similar. The Pt–C\textsubscript{aryl} bond distances in chloro complex \textsuperscript{1} (2.030(3) and 2.035(3) Å) and in bromo complex \textsuperscript{2} (2.037(6) and 2.036(6) Å) fall into the range observed for neutral and cationic Pt(II) pincer complexes.\textsuperscript{31,34a,36} Both complexes display distorted-square-planar configurations at the metal center, which has been commonly seen for four-coordinate Pt(II) complexes.\textsuperscript{34a,36} The C7–Pt\textsuperscript{II}–X atoms are linear (\textsuperscript{1}179.40(8)°; \textsuperscript{2}178.66(18)°). However, the C2–Pt\textsuperscript{II}–C13 angles were bent (\textsuperscript{1}157.44(11)°; \textsuperscript{2}157.3(2)°) due to ligand constraints.

Figure 1. ORTEP diagram (50% thermal ellipsoids) of CCCBu-NHC-Pt\textsuperscript{II}-Cl (1) and CCCBu-NHC-Pt\textsuperscript{II}-Br (2). Hydrogen atoms are omitted for clarity.
Table 1. Selected Bond Lengths and Angles of CCCBu-NHC-PtII-X Complexes 1 (X = Cl) and 2 (X = Br) and the CNCBu-NHC-PtII-Cl Complex

<table>
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<tr>
<th></th>
<th>bond lengths (Å)</th>
<th>bond angles (deg)</th>
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<tr>
<td></td>
<td>Pt−C2</td>
<td>Pt−C7</td>
</tr>
<tr>
<td>1</td>
<td>2.030(3)</td>
<td>1.941(3)</td>
</tr>
<tr>
<td>2</td>
<td>2.037(6)</td>
<td>1.955(6)</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>bond lengths (Å)</th>
<th>bond angles (deg)</th>
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<tbody>
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<td></td>
<td>Pt−C1</td>
<td>Pt−N1</td>
</tr>
<tr>
<td>CNC</td>
<td>1.972(8)</td>
<td>1.968(5)</td>
</tr>
</tbody>
</table>

“Pyridylene-bridged CNC analogue with X = Cl. Data from ref 31.

notable in the longer bond length (2.397(7) Å vs 2.278(2) Å, Table 1). Other metric data for the two compounds were very similar.

**Photophysical Studies.** Complexes 1 and 2 were found to emit blue light with UV stimulation. Their absorption and emission data in MeOH solution have been included in Table 2 and Figure 2a. In MeOH solution, the UV absorption spectra of complexes 1 and 2 in (a) MeOH solution (the inset shows d−d transitions) and (b) solid state at 298 K (irradiated at 355 nm), and differential scanning calorimetry (DSC). It was found that the compounds melted at approximately 280 °C and remained as supercooled liquids over a large temperature range. The 10% weight loss temperatures (T_{loss}) were about 380 °C (see the Supporting Information). Notably, complexes 1 and 2 evaporated and deposited on the glass wall of the furnace. Spectroscopic analysis of the residues (fluorescent, NMR, and ESI-MS) indicated the compounds remained unchanged.

**Photostability in Air.** Previous studies on Pt NHC complexes suggested that their emissions could be stable under an inert atmosphere over an extended period of time.15a,40 Interestingly, the emissions of complexes 1 and 2 were found to be stable even under an ambient atmosphere (room temperature and 30–50% humidity). Time-resolved emission spectra of 1 and 2 were presented in Figure 3. The authentic blue λ_{max} (472 nm) of complexes 1 and 2 retained >97% intensity over 6 h of continuous irradiation. The shape of the spectra remained unvaried during the irradiation.
more than half of its initial emission strength and a visible darkening on the irradiated surface after only 1 h (Table 3). When significant photobleaching (>10%) was observed under any conditions, a control experiment was carried out to calibrate the contribution to decomposition from other pathways. In the control experiment, the initial emission spectrum A was collected and the analyte was then kept under the same conditions with the radiation beam blocked. After 1 h the irradiation was resumed and another emission spectrum B was taken. The loss of emission intensity between spectra A and B was ascribed to the sum of decompositions through all other pathways. Since each spectrum took ~2 min to accumulate, a significant measurement-induced photobleaching was observed for the less photostable analytes (Figures S1 and S2, Supporting Information). An exponential fitting based on the decay curve was applied to retrieve the photobleaching during the initial 2 min irradiation. After 1 h in the dark all compounds were found to undergo <1% decomposition, which confirms a direct correlation between photobleaching and loss of emission strength. On comparison of the pincer Pt(II) complexes 1 and 2 and the four commercially available emitters, these observations indicated that the Pt complexes were much more photostable under an ambient atmosphere.

**Computational Studies.** The pincer Pt(II) complexes were modeled by DFT and TD-DFT methods to better understand the observed photophysical properties. Previously, Halls and Schlegel employed a somewhat similar approach to study the first excited states of tris(8-hydroxyquinoline)aluminum(III) (Alq3). Schlegel employed a somewhat similar approach to study the first excited states of tris(8-hydroxyquinoline)aluminum(III) (Alq3).46 Additionally, Rocha, Martin, Batista, and co-workers successfully used DFT/TD-DFT theoretical methods and experimental approaches to study the electronic structure and spectroscopic properties of ruthenium polypyridyl complexes. In our calculations the structure of Pt-Cl complex 1 was simplified to structure 3 by replacing the two butyl groups with methyl groups. The computationally predicted ground-state geometry of 3 was in very good agreement with the geometric results from the experimental X-ray crystallography of 1. The rms deviation of the 20 heavy atoms was 0.047 Å.

The absorbance and fluorescence spectra for CCCMe,NHC-PtCl (3) were computed using the optimized molecular structure (Figure 4). The simulated absorption of structure 3 matched the experimental data of complex 1 in the energy range (230–380 nm). However, the calculated emission spectrum of the optimized planar excited-state geometry was very different from the experimental result (compare Figure 2a vs Figure 4 (×)), indicating that the planar excited state of the molecule was not the major radiative state.

Further TD-DFT calculations revealed that although CCCMe,NHC-PtCl (3) adopts a distorted-square-planar configuration at the ground state, constraining the first singlet excited electronic state to the C3v point group symmetry actually leads to a transition state. The imaginary vibrational mode (ωe = 8.71) corresponded to the Cl atom and the sides of the two pincer ligand asymmetrically bending out of the C3v plane. When performing a TD-DFT geometry optimization of the first excited state in C3v symmetry, the Cl atom bent out of

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**Table 3. Solid-State Emission and Lifetime Data of CCCBu-NHC-PtII-X Complexes 1 and 2 and Four Commercially Available Emitters**

<table>
<thead>
<tr>
<th>Compound</th>
<th>λmax/nm (rel intens/%)a</th>
<th>remaining intens/%b</th>
<th>τexc/µs</th>
</tr>
</thead>
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<tr>
<td></td>
<td>in N2</td>
<td>in air</td>
<td>in air</td>
</tr>
<tr>
<td>1</td>
<td>445 (39)</td>
<td>99 (0.4)</td>
<td>0.19/1.7</td>
</tr>
<tr>
<td>2</td>
<td>455 (66)</td>
<td>97 (0.3)</td>
<td>0.19/1.9</td>
</tr>
<tr>
<td>Alq3</td>
<td>506 (100)</td>
<td>99 (0.2)</td>
<td>51 (3.8)</td>
</tr>
<tr>
<td>Ir(dfppy)3</td>
<td>499 (100)</td>
<td>71 (4.6)</td>
<td>46 (3.0)d</td>
</tr>
<tr>
<td>Znq2</td>
<td>536 (100)</td>
<td>99 (1.8)</td>
<td>78 (1.8)</td>
</tr>
<tr>
<td>LBMQ</td>
<td>463 (100)</td>
<td>99 (0.3)</td>
<td>84 (5.6)</td>
</tr>
</tbody>
</table>

aIrradiated at 355 nm (1.67 mW/cm²). bλmax after 6 h of continuous excitation. Data presented are an average of three measurements; σ (standard deviation) values are included in parentheses. cSee ref 41, data collected under nitrogen. dAfter 1 h. eSee ref 43, data collected under nitrogen.

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**Scheme 3. Four Commercially Available Emitters**

![Scheme 3](image-url)

The rms deviation of the 20 heavy atoms was 0.047 Å.
plane significantly ($C_{xy}$−Pt−Cl = 93$^\circ$). HOMO and LUMO diagrams (Kohn−Sham orbitals) of the planar ground state and the optimized Cs-symmetric excited state are included in Figure 5. In the ground state, significant admixture among the d orbitals of Pt, the 3p orbital of Cl, and the ligand $\pi$ orbital was observed in both the HOMO and LUMO (Figure 5a,b). In the excited state, the Cl atom bends out of the molecular plane along the $C_{xy}$−Pt−Cl axis, leading to Cs symmetry (Figure 5c−f). The molecular orbitals are highly localized around the Pt and Cl atoms.

An emission spectrum was calculated on the basis of the optimized Cs geometry for the bent singlet excited state ($S_1$). The $S_1$ emission spectrum (Figure 6 (×)) was much closer to the observed one (Figure 2). $S_1$ and the optimized Cs geometry for the bent triplet excited state ($T_1$) are quite similar.48 The simulated spectrum suggested an emission from 380 to 510 nm with three major peaks at 390, 445, and 490 nm. This result matched the experimental data very well in the energy range and in having three maxima. The simulated absorbance spectrum is included in Figure 6. Compare the computed emission spectra of the planar $C_2v$ and bent Cs structures—the computed emission spectrum of the planar structure has only a small red shift, while the computed emission spectrum of the distorted structure has a much larger red shift. In the bent Cs excited state, the HOMO−LUMO transition loses almost all of its intensity and moves to around 1200 nm (see the Supporting Information). Also, in the bent Cs excited state, the first transition with appreciable intensity in the visible region was the third computed singlet electronic excitation.

Closers examination of molecular orbitals of CCCMe-NHC-PtII-Cl (3) revealed a decrease in the HOMO−LUMO gap when the Cl atom was distorted out of the molecular plane. A Walsh-like diagram of the ground-state orbital energies versus constrained $C_{xy}$−Pt−Cl angle at the TD-DFT $S_1$ excited-state geometries is included in Figure 7. This diagram demonstrates that the HOMO is more destabilized than the LUMO is stabilized as the geometry changes from the planar $C_{2v}$ structure to the bent Cs structure.49
The energies in the Walsh-like diagram demonstrate the large red shift in the emission spectrum; the geometric distortion contributed to this red shift. In the C\(_1\) structure, there is a drastic change in the HOMO shape, as ligand \(\pi\) character is removed when the C\(_{\text{Ar}}\)-Pt-Cl angle is bent away from 180°. The p orbital of the chlorine, which has lone pair character (slightly antibonding) in the planar structure, becomes strongly Pt-Cl antibonding (\(\sigma^*\)) in the C\(_1\) bent structure. In the LUMO, as the C\(_{\text{Ar}}\)-Pt-Cl angle is bent away from 180°, the bent chlorine retains much of the p lone pair character but creates a small “divot” in the Pt-Cl \(\pi\) character.

In the bent structure, both the HOMO and the LUMO have a significant amount of nonbonding metal d orbital character. This unique geometric change during the electronic transition may contribute to the air stability and photostability of the complex.

### CONCLUSION

The synthesis and characterization of the two novel CCC-NHC pincer Pt(II) complexes 1 and 2 have been reported. They display distorted-square-planar configurations, as expected for \(d^8\) four-coordinated transition-metal compounds. Complexes 1 and 2 were found to emit bright blue light in the solid state under UV irradiation with emissions that are stable under an N\(_2\) atmosphere upon evaporation, which suggests that they would be suitable for thermodeposition processing. Computational studies of the complexes illustrated the details of the molecular orbitals and the electronic transitions involved in the photophysical processes. Somewhat surprisingly, the computed gas-phase geometry of the excited state of model 3 displays a significant amount of geometric distortion, mostly about the C\(_{\text{Ar}}\)-Pt-Cl angle.

### EXPERIMENTAL SECTION

General Procedures. All starting materials were purchased from Sigma-Aldrich, Fisher Scientific, or Strem. The reagents were used as received unless otherwise mentioned. All solvents were dried and were degassed by passing through a basic alumina column under Ar protection. All reactions involving organometallic reagents were carried out under a N\(_2\) or Ar atmosphere using standard glovebox and Schlenk line techniques. NMR spectra were collected using a Bruker Avance 300 or 500 spectrometer and were referenced to the residual solvent peak (\(\delta\) in ppm, \(J\) in Hz). Electrospray ionization mass spectra were collected using a Waters Micromass ZQ mass spectrometer. Elemental analyses were carried out by Columbia Analytical Service or on a PerkinElmer 2400 Series II CHNS/O analyzer. UV-visible absorption spectra were collected using a HP 8453 UV-visible system. Emission spectra were collected using a PerkinElmer LS 55 fluorescence spectrometer. Photostability studies were carried out by exposing the solid sample to 355 nm radiation. The light source was a xenon lamp, and the detector was a photodiode array placed behind a filter next to the sample chamber. Lifetime measurements were carried out using 10 Hz pulsed 355 nm Nd:YAG laser output as the pumping source and a photomultiplier tube as the detector. TGA/DSC data were collected on a PerkinElmer Pyris 1 TGA/DSC 4000, with nitrogen flow at 20 mL/min and temperature gradient set at 20 °C/min.

2-(1,3-Bis(N-butylimidazol-2-ylidene)phenylene)(chloro)platinum(II) (1), 1,3-Bis(1,3-bis(butylimidazol-3-yl)benzene dichloride (0.20 g, 0.50 mmol), tetrakis(dimethylamino)zirconium (0.17 g, 0.63 mmol), and CH\(_2\)Cl\(_2\) (\~4.0 mL) were combined. The mixture was stirred for 1 h at room temperature to afford a red solution. [Pt(COD)Cl\(_2\)] (0.19 g, 0.50 mmol) was added, and the mixture was stirred vigorously at room temperature for 6 h. The reaction mixture was transferred to a round-bottom flask that contained 1 mL of distilled water, and the precipitate was removed by filtration. The filtrate was concentrated under vacuum to afford a yellow solid.
per d function. In all computations, the n-butyl group of the ligand was trimmed to methyl. All structures were fully optimized, and frequency calculations (analytical for DFT and numerical for TD-DFT) were performed on all ground and select excited-state structures to ensure that either a zeroth-order saddle point (a local minimum) or a first-order saddle point was achieved. To analyze the electronic structure of the TD-DFT excited states on roots with high oscillator strength, a natural transition orbital (NTO) analysis was performed. The NTO analysis diagonalized the transition density matrix and gave a representation of the electronic excitation in terms of a single excited particle and empty hole. While the ordering of the natural transition orbitals was slightly different from that of the ground state molecular orbitals, the NTOs and MOs appeared to be qualitatively similar. All molecular orbital plots presented in the article are ground-state Kohn–Sham orbitals at either the ground-state or excited-state geometries. The computed absorption spectrum was calculated from the vertical transitions obtained from TD-DFT single-point calculations on the optimized ground-state geometry. The geometry optimization from the vertical excitation from the ground state produced a transition state (verified by a numerical frequency calculation) that perturbed the Caryl−Cl angle away from 180°. The computed emission spectrum was calculated using the fully optimized, minimum-energy geometry of the S1 excited state. The computationally derived absorption and emission spectra were simulated with an in-house Fortran program by convoluting the computed excitation energies and computed oscillator strengths with a Gaussian line shape and a broadening of 20 nm.

In order to investigate the possibility that the observed emission spectrum comes from the planar triplet excited state, we computed spectra including spin-orbit coupling. PBE0 (the PBE exchange correction and Perdew–Burke–Ernzerhof (PBE) correlation function) calculations were performed with the Amsterdam Density Functional program (ADF, version 2008.01). ADF uses Slater-type orbital (STO) basis sets instead of Gaussian-type orbitals (GTO) and contains a density fitting (DFT-D) correction. In all computations, the Caryl−Pt−Cl−butyl group of the ligand was visualized with JIMP 2.68

■ ASSOCIATED CONTENT

Supporting Information

Figures, tables, text, and CIF files giving TGA, DSC spectra, and detailed crystallographic data for CCCC8H13NHC-PtH8-X complexes 1 and 2, as well as Cartesian coordinates for optimized geometries and detailed computed TD-DFT emission/absorption spectra for CCCC17H25NHC-PtH11Cl (3). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES