Photophysical Properties of Cyclometalated Platinum(II) Diphosphine Compounds in the Solid State and in PMMA Films

Belle Coffey, Lily Clough, Daphne D. Bartkus, Ian C. McClellan, Matthew W. Greenberg, Christopher N. LaFratta, Joseph M. Tanski, and Craig M. Anderson*

ABSTRACT: Platinum(II) compounds were synthesized with both chelate cyclometalated ligands and chelate diphosphine ligands. The cyclometalated ligands include phenylpyridine and a benzothiophene-containing ligand. The three new benzothiophene compounds were characterized by nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrometry (HR-MS), and photophysical measurements. In the case of one compound, L1-DPPM, the structure was determined by single crystal X-ray diffraction. The structural coherence of the noncrystalline emissive solid state was measured by X-ray total scattering real space pair distribution function analysis. Quantum yield values of all of the platinum compounds measured in the solid state and in PMMA films were much greater than in solution.

INTRODUCTION

Phosphorescent organometallic complexes have application potential in devices due to their tunable and efficient luminescent properties.1−3 Due to these complexes’ emissive properties, they are widely studied for their application in fields such as bioimaging, chemical sensors, organic light-emitting diodes, and light-emitting electrochemical cells.4−7 Specifically, the photoluminescent properties of organometallic Pt(II) complexes have been reported and widely studied.8−12 The luminescent properties of these complexes are likely due to the presence of strong carbon donors, the inclusion of aromatic rings, and the large spin-orbit coupling of the heavy metal platinum center.5,13,14 Additionally, the photophysical properties of Pt(II) complexes can be tuned by altering the ligand environment of the coordination compound,11 including changes to cyclometalated ligands and/or the auxiliary ligands.8,14,15

In this study, a class of benzothiophene-based (Figure 1, L1) cyclometalated Pt(II) complexes with chelating bis-(diphenylphosphino) ligands (Figures 1 and 2) was synthesized and characterized, and their photophysical properties were recorded in different states. The chelating C=N ligand L1 contains a strong sigma donor carbon atom formed by C−H activation cyclometalation. Recently, a report comparing platinum compounds with thiophene-containing ligands and phenylpyridine ligands, and a variety of auxiliary ligands has been published.15 We look to examine how a change to a benzothiophene and an imine-derived ligand would affect the...
photophysical properties of a set of platinum complexes. Additionally, benzothiophene derivatives are synthesized and studied for their pharmaceutical applications.\textsuperscript{16,17} The inclusion of strong sigma donors has been used to improve the population of MLCT states by increasing the energy of the d–d ligand field excited states, while varying excitation wavelength and electron-donor ability of the metal's ligands has changed the rates of intersystem crossing.\textsuperscript{2,5,16–21} Two C^N ligands, with sigma donor properties, \textit{L1} and \textit{PPY} (Figure 1), were utilized to synthesize six Pt(II) complexes with bis(diphenylphosphino) chelating ligands. This created two sets of monomeric Pt(II) complexes with either \textit{L1} or \textit{PPY} as the C^N chelate (Figure 2). The C^N ligands' effects on the tunability of the photophysical properties of each complex were analyzed in various states. The cations of \textit{PPY-DPPP}, \textit{PPY-DPPE}, and \textit{PPY-DPPP} (Figure 2) have been previously synthesized with different counterions, while the bis-(dicyclohexylphosphino)alkane derivatives have been reported as perchlorate salts.\textsuperscript{1,4,8,25–26}

Substantial differences in the photophysical properties of the \textit{PPY} and \textit{L1} analogs were observed. The structural differences between \textit{PPY} and \textit{L1} are important to understanding each ligand's effects on the photophysical properties of the complexes. The structure of \textit{L1} contains a thiophene moiety, while \textit{PPY} does not, thus resulting in complexes that were blue-shifted compared to the red-shifted \textit{L1} analogs (vide infra).

If a phosphorescent complex has the potential for application in a device, then it is invaluable to consider the photoluminescent quantum yield.\textsuperscript{27–29} Photophysical properties of complexes are often evaluated in solutions, but in devices, these complexes are usually immobilized in a solid matrix.\textsuperscript{1,30} Polymethyl methacrylate (PMMA) doped films are easy to prepare and have been reported to drastically increase emissive properties compared to the solution phase, specifically the photoluminescent quantum yield of various Pt and Ir complexes.\textsuperscript{8,9,11,27,31} The emissive properties of all cyclometalated Pt(II) complexes (Figure 2) in this study were measured in the solution, in the solid state, and in the doped polymer (PMMA) film. As mentioned, the cations of \textit{PPY-DPPP}, \textit{PPY-DPPE}, and \textit{PPY-DPPP} have been reported for their catalytic and photoluminescent properties;\textsuperscript{1,4,22–25} however, to the best of our knowledge, there is no literature to date for the three \textit{PPY} analogs presented here as perchlorate salts (Figure 2) in doped PMMA.

**RESULTS AND DISCUSSION**

**Synthesis and Characterization.** The complexes were synthesized and characterized by their \textit{H} and \textit{31P} NMR and UV–vis spectra. The spectra for the \textit{PPY} analogs with different counterions were consistent with previously published data.\textsuperscript{1,4} \textit{L1}, a benzothiophene-imine functionalized C^N ligand, was used in the chelate-assisted C–H activation reaction to yield the monodentate Pt(II) complex \textit{L1-Met} (see the Supporting Information). \textit{L1-Met} subsequently underwent a substitution reaction yielding the desired Pt(II) complexes: \textit{L1-DPPE}, \textit{L1-DPMM}, and \textit{L1-DPPP}. Complexes \textit{L1-DPPE}, \textit{L1-DPMM}, and \textit{L1-DPPP} were characterized by \textit{H} and \textit{31P} NMR spectroscopy; HR-MS; and, in the case of \textit{L1-DPMM}, single crystal X-ray diffraction (SCXRD). A complex ion is formed when the neutral bisphosphine ligand substitutes for an anionic chloride ligand. The use of LiClO\textsubscript{4} had the most success in precipitating the complexes compared to other ions such as chloride and hexafluorophosphate (PF\textsubscript{6}^−). The complexes were purified through a Pasteur pipette silica column providing pure crystalline yellow and orange products in good yields (77–91%). All three \textit{L1} complexes have low solubility in many common solvents but are soluble in somewhat polar solvents such as DCM, acetonitrile, acetone, THF, and DMSO. All three complexes exhibit appropriate \textit{195Pt} and \textit{31P} coupling in both the \textit{H} NMR and \textit{31P} NMR spectra, which aided in their characterization.

The \textit{H} NMR characterization relied heavily on the diagnostic methylene and imine peaks\textsuperscript{32} of the chelated \textit{L1} ligand\textsuperscript{10} and on the alkyl chain protons of the various bis(diphenylphosphino) ligands. For example, the \textit{H} NMR of \textit{L1-DPPP} clearly displayed the imine resonance as a doublet at 8.90 ppm (\(\textit{J}_{\text{Pt-H}} = 44 \text{ Hz}, \textit{J}_{\text{H-P}} = 9 \text{ Hz}\), the methylene of \textit{L1} as a singlet at 5.33 ppm (\(\textit{J}_{\text{Pt-H}} = 14 \text{ Hz}\), and the methylene of the bis(diphenylphosphino)methane as a triplet at 5.12 ppm (\(\textit{J}_{\text{Pt-H}} = 40 \text{ Hz}, \textit{J}_{\text{H-P}} = 21 \text{ Hz}\)). The \textit{31P} NMR spectra of all three compounds corroborate the proposed structures. Two resonances were observed each with \textit{195Pt} satellites, thus confirming one phosphorus trans to the nitrogen of the \textit{L1} ligand and the other phosphorus atom trans to the carbon donor of \textit{L1}. For example, in the \textit{31P} NMR spectrum of \textit{L1-DPMM}, the resonance of the phosphorus that is trans to the nitrogen of \textit{L1} appeared at –40.9 ppm and exhibited both \textit{31P} and \textit{195Pt} coupling (\(\textit{J}_{\text{P-P}} = 3000 \text{ Hz}, \textit{J}_{\text{P-P}} = 110 \text{ Hz}\), whereas the resonance of the phosphorus atom trans to the strong carbon donor appeared at –35.3 ppm and exhibited both phosphorus and platinum coupling (\(\textit{J}_{\text{P-P}} = 1800 \text{ Hz}, \textit{J}_{\text{P-P}} = 110 \text{ Hz}\)), with a significantly lower \textit{195Pt-P} coupling constant\textsuperscript{33,34}. The structure of \textit{L1-DPPP} was determined by an X-ray diffraction study. Bond lengths and angles were within the accepted range for platinum(II) compounds (Figure 3).\textsuperscript{35–38}

**Photophysical Measurements.** The absorbance spectra, lifetimes of excited states, emission spectra, and quantum yield values have been previously reported for the three \textit{PPY} analogs as chloride salts; however, it appears that values have not been measured or reported in doped PMMA thin films for perchlorate salts. Therefore, we have included values for these complexes to compare and contrast the \textit{L1} compounds.\textsuperscript{1,4,22,23} All luminescent properties were measured in the solution (Figure 4), in the solid state, and in a PMMA thin film (95% wt PMMA, 5% wt Pt complexes) (Figure 5 and Table 1). Observing a similar pattern to the \textit{PPY} analogs, each
Figure 3. ORTEP of compound L1-DPPM (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (°): Pt-C(1): 2.034 (2); Pt-N(1): 2.116 (2); Pt-P(1): 2.2309 (6); Pt-P(2): 2.3218 (6); C(1)-Pt-N(1): 78.27 (8); C(1)-Pt-P(1): 102.04 (7); N(1)-Pt-P(1): 107.70 (5); C(1)-Pt-P(2): 173.70 (6); N(1)-Pt-P(2): 107.70 (5); and P(1)-Pt-P(2): 71.80 (2).

Figure 4. Absorbance and normalized emission spectra of all L1 analogs in the CH2Cl2 solution.

Figure 5. Normalized emission spectra of all selected compounds (5% wt) in doped PMMA film (95% wt).

L1 compound became more emissive in the solid state and slightly more emissive still in the PMMA films. All L1 platinum complexes absorbed blue light ranging from 430 to 450 nm, with L1-DPPE absorbing the lowest energy wavelength at 450 nm. These peaks for all three complexes, L1-DPPE, L1-DPPM, and L1-DPPP, had molar extinction coefficients ranging from 1.3 × 10^3 to 2.3 × 10^3 (Table 1). Extinction coefficients on the order of 10^3 have been shown in the literature to represent MLCT bands for platinum species. The PPY analogs, however, absorbed higher energy wavelengths, ranging from 370 to 385 nm, similar to the cations previously reported.

The emissive properties of the two sets (L1 versus PPY) of analog complexes differed significantly. The solution spectra of all L1 analogs contained two emission peaks, one higher energy wavelength peak around 550 nm and an intense orange peak at around 630 nm, whereas the phenyl-pyridine analogs had emission peaks at higher energies between 400 and 500 nm. By comparing the dashed traces in Figures 4 and 5, it can be observed that, when immobilized in PMMA films, the higher energy peak of each L1 complex is greatly reduced but there is very little change in the lower energy emission wavelengths at 620–640 nm (Figure 5). This supports the idea that immobilization in PMMA films encourages predominately phosphorescence, as the higher energy bands may be due to fluorescence in solution. Luminescent lifetimes were recorded for all new L1 analogs. Lifetime values were recorded in the solution, solid state, and PMMA films (Table S1). The lifetime measurements for the emission peaks assigned to the higher energy bands with a bathochromic shift of approximately 100 nm were in the 6–14 ns range and thus suggest a fluorescence assignment. However, the lower energy bands with a bathochromic shift of approximately 200 nm all had longer lifetimes in the hundreds of nanoseconds, consistent with phosphorescence. The lifetime values of each L1 complex drastically increased when the lifetime measurements were recorded in the complexes’ aggregate states. For example, in the solution, L1-DPPP had an observed lifetime of 146 ns (Table S1), which increased approximately 600% in the solid state (905 ns) and by 700% in a PMMA film (1054 ns). The longer lifetimes support the idea of increased phosphorescence and luminescent properties of these complexes in aggregate forms, such as the solid state and PMMA films.

PPY-DPPE, PPY-DPPE, and PPY-DPPP were all weakly emissive in solution yet bright emitters in their solid state and PMMA films. This phenomenon has been previously reported and is referred to as aggregate-induced emission. A similar pattern was observed with the L1 analogs. An emission spectrum in solution could be observed for all L1 analogs; however, they were weak in intensity, similar to the PPY

Table 1. Absorption and Emission Data of Selected Complexes

| Compound    | Absorption peak (nm) | Extinction coefficient \(\times 10^3\) M⁻¹ cm⁻¹ | Emission peaks in solution (nm) | Emission peaks in solid state (nm) | Emission peaks in PMMA film (nm) |
|-------------|----------------------|----------------------------------------------|----------------------------------|-----------------------------------|----------------------------------|
| L1-DPPE     | 430                  | 2.3                                          | 550, 640                         | 520, 620                          | 540, 650                         |
| L1-DPPM     | 450                  | 1.8                                          | 550, 640                         | 550, 660                          | 550, 620                         |
| L1-DPPP     | 355                  | 2.2                                          | 431 (max)                        | 480, 550                          | 480, 520                         |
| PPY-DPPE    | 355                  | 2.8                                          | 431 (max)                        | 490, 520                          | 490, 520                         |
| PPY-DPPP    | 360                  | 2.1                                          | 431 (max)                        | 490, 520                          | 490, 520                         |

“Solution samples were recorded in DCM at 0.1 mM. Excited emission spectra was the lowest energy peak for each compound. These values compare reasonably to those previously reported for the PPY complex cations.”
analogs. In contrast, when the emission spectra were recorded in the solid state and PMMA films, the complexes became bright emitters. The increased luminescence of the doped films is quite evident when analyzing the quantum yield data of the compounds (Table 2). As mentioned, all PPY and L1-derived complexes were weak emitters in solution and had quantum yields of less than 1%. These values in the solution were recorded relative to [Ru(bipy)₃]Cl₂ as no signals were detectable using an integrating sphere.⁴⁷,⁴⁸ The solid-state and PMMA measurements were recorded with an integrating sphere, and quantum yield values in the solid state ranged from 2 to 18%. PPY-DPPM had the most efficient solid-state photoluminescent quantum yield at 18%, whereas the rest of the complexes had solid-state quantum efficiencies ranging from 2 to 7% (Table 2). In the solid state, with the exception of PPY-DPPM, there is no significant difference in quantum yields between the L1 and PPY analogs.

The quantum yield of each complex increases further when immobilized in a PMMA film. The quantum yield doubles and in some cases triples (Table 2) for the complexes. PPY-DPPM has the highest quantum yield at 30% in a PMMA film. The PMMA films of the L1 compounds range from 12 to 15%. The PPY films have higher quantum yields ranging from 15 to 30%; however, in both sets of analogs, there is a sharp increase in quantum yields when doped into a polymer film compared to the solid state.

Generally, the photoluminescent quantum yield of a complex is determined by the relative rates of different transitions throughout the relaxation process.⁶,²⁸,²⁹ The amount of intersystem crossing and the internal conversion are important nonradiative transitions that influence the quantum yields of the complexes. When a complex is immobilized as a dopant in a polymer film, there is restricted molecular motion. Since motion is restricted in the polymer matrix, the rate of nonradiative transitions decreases.³⁰

**Table 2. Photoluminescent Quantum Yield Values (%) for Studied Complexes**

| compound | solution | solid state | PMMA film |
|----------|----------|-------------|------------|
| L1-DPPP | 0.25     | 5.4         | 15         |
| L1-DPPE | 0.30     | 7.3         | 13         |
| L1-DPPM | 0.21     | 4.8         | 12         |
| PPY-DPP | 0.28     | 6.2         | 15         |
| PPY-DPP | 0.02     | 4.2         | 24         |
| PPY-DPPM| 0.04     | 18          | 30         |

**Table 3. TD-DFT-Calculated Vertical Excitations of High Oscillator Strength Transitions and Coefficients of Principal Contributing Orbital Transition**

| Sᵢ   | excitation energy (nm) | oscillator strength | principal contributing transitions | coefficient of principal contributing transition |
|------|------------------------|---------------------|-----------------------------------|-----------------------------------------------|
| S₁   | 428                    | 0.0380              | HOMO −2 to LUMO                    | 0.96165                                      |
| S₄   | 356                    | 0.1050              | HOMO −1 to LUMO +1                | 0.97513                                      |
| S₇   | 322                    | 0.0360              | HOMO to LUMO                       | 0.97937                                      |

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**TD-DFT and DFT Calculations.** DFT and TD-DFT calculations were run on the L1 complexes to help assign the observed electronic transitions in absorbance spectroscopy. All complexes were optimized at the B3LYP/LANL2DZ level of theory. The results of geometry optimization of L1-DPPM in either gas phase or with implicit solvation show reasonable agreement to the structure observed in the solid state by SCXRD (Table S2 and Figure 3).

TD-DFT calculations were compared to the electronic spectra of the three L1 analogs. The TD-DFT simulations of absorbance spectra successfully reproduce the major features experimentally observed in the absorbance spectra for the L1 complexes (Figure 6 and Figures S1 and S2). The TD-DFT (hole particle) natural transition orbitals of the high oscillator strength transitions can generally be described as primarily a band in the lower energy visible region can be described as a mixed metal to ligand charge transfer/intraligand charge transfer (MLCT/ILCT). For this transition, the hole NTO is concentrated on the electron-rich benzothiophene moiety and the filled platinum d orbital, and the particle NTO of clear π* character, largely in the L1 platinacycle π system. Higher energy intense transitions show a similar hole/particle character. An intense S4 transition appears to be localized on the naphthyl ligand fragment π system in the hole NTO and empty dₓ²₋ᵧ² orbital, both platinacycles, and one of the PPh₃ phenyl rings π systems in the particle NTO.

**Real Space X-ray Pair Distribution Function Analysis.** Aggregation-induced emission (AIE) in the solid state has been invoked previously in other similar transition metal complexes where photoluminescent quantum yield enhancement is observed in the solid state as compared to the solution state.¹⁴⁻¹⁶ To measure the structural coherence of the emissive solid state for our L1 complexes, we performed X-ray total scattering real space pair distribution function analysis (PDF). While many emissive molecular solids are not amenable to X-ray structural analysis by traditional Bragg diffraction, the use of X-ray PDF analysis can resolve atomic structural information in crystalline, disordered/nanocrystal-
line, amorphous, and molecular solids. The reduced X-ray pair distribution function \( G(r) \) represents the probability of finding two atoms separated at a pair distance \( r \) and is obtained by the Fourier transform of the properly normalized total scattering structure function \( F(Q) \).49

Reduced pair distribution functions, \( G(r) \), of \( \text{L1-DPPM} \), \( \text{L1-DPPE} \), and \( \text{L1-DPPP} \) were recorded in the solid state and showed a highly disordered molecular solid. As illustrated in Figure 8, which shows \( \text{L1-DPPM} \), the observed \( G(r) \) is consistent with prior measurements of molecular solids showing sharp well-defined intramolecular correlations at low \( r \) (below \( r \approx 3.7 \) Å), poorly defined broad density oscillations representing disordered intermolecular correlations at higher \( r \) (at above \( r \approx 8.0 \) Å), and an intermediate region containing both inter- and intramolecular correlations (Figures 8 and 9).50−53 Significantly, there is little evidence of a well-defined atomic order past 1 nm in these samples, suggesting a highly disordered emissive solid state.

Similar results are seen for \( \text{L1-DPPE} \) and \( \text{L1-DPPP} \), with one substantial difference being a notable shift of the most intense intramolecular correlation for \( \text{L1-DPPM} \), reflecting in part overlapping distances from the Pt–L coordination sphere and the relatively large \( Z \) of Pt, to higher \( r \) (Figure 9). This behavior is consistent with simulations of \( G(r) \) from Debye scattering equation calculations using DFT optimized structures and represents the elongation of the Pt–L bond lengths caused by geometrical distortion from the larger propyl linker (Figure S11 and Table S2). In general, the intramolecular \( G(r) \) is well modeled by refinements of the atomic structure of the molecular unit (Figure S12). The results from PDF analysis suggest that enhanced emissive properties arise from a highly disordered solid state in our complexes, as our observations are consistent with structural coherence not persisting more than a couple of molecular units. This is consistent with other prior literature reports of solid-state photoluminescence enhancement or aggregate-induced emission from both crystalline and amorphous samples, which show that long-range translational order is not a necessary condition for AIE effects.54−57

Figure 7. NTOs for high oscillator strength transitions. Hole (left) and particle (right) NTOs for \( S_1, S_0 \) and \( S_2 \) in Table 3.

Figure 8. Reduced X-ray pair distribution function, \( G(r) \), of \( \text{L1-DPPM} \) illustrating representative intramolecular, intra- + intermolecular, and intermolecular atom–atom distance regions observed for the solids.

Figure 9. Reduced X-ray pair distribution function, \( G(r) \), of \( \text{L1-DPPM} \) (green), \( \text{L1-DPPE} \) (blue), and \( \text{L1-DPPP} \) (red) over full-\( r \) and around Pt–L interatomic distances (inset). The \( G(r) \) for each sample is normalized to unity at the most intense correlation to aid in comparing the structure of each sample.
CONCLUDING REMARKS

Three Pt(II) complexes with the chelating benzothiophene-imine functionalized ligand L1 were synthesized and characterized, and their photophysical properties were measured and compared to PPY cations. Each complex and its phenyl-pyridine analog were used as dopants in PMMA films to study the photophysical effects of altering the ligand structure in thin films. All complexes were weakly emissive in solution but became bright emitters in their solid state and when immersed in a PMMA film. All L1 cyclometalated Pt(II) complexes showed evidence of being aggregate-induced emitters, similarly to their phenyl pyridine analogs, as quantum yield values significantly increased from the complexes’ solution state to its solid state and PMMA doped film. This emissive solid state was observed to be amorphous from total X-ray scattering PDF analysis, and the AIE effect likely arises from local structural rigidity rather than long-range rigid crystalline order.

EXPERIMENTAL SECTION

General. Solvents and reagents were purchased from Sigma Aldrich unless otherwise noted. K2PtCl4 was purchased from the Pressure Chemical Company. NMR spectra were recorded at Bard College using a Varian MR-400 MHz spectrometer (1H, 400 MHz; 13C, 100.6 MHz; 31P, 162 MHz and 7Li, 128.6 MHz) referenced to SiMe4 (1H, 13C). Shifts are given in ppm and coupling constant J values in Hz. Abbreviations used are as follows: s = singlet, d = doublet, t = triplet, and m = multiplet. Electrospary mass spectra were performed at Vassar College using an LC/MSD-TOF spectrometer.

Computational Details. Calculations were carried out using TD-DFT and DFT implemented in the Jaguar 9.1 suite of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP functional using a mixed basis set consisting of LANL2DZ with an effective core potential for the Pt atom and the 6-31G** for all other atoms. All final structures were confirmed to be energetic minima by harmonic vibrational analysis. In the case of the TD-DFT calculations, the UV–vis absorbance spectra were simulated by optimization of the first 25 excited states and the use of a CPCM implicit solvation model of dichloromethane to improve energetic agreement to the experimental UV–vis spectra. The resulting vertical excitation energies are convoluted with a Gaussian function of 34 nm half width for the purposes of visualization. The initial geometry guess was generated using crystallographic data molecular mechanics as implemented in Avogadro version 1.2.0 using the UFF force field.

Photophysical Measurements. Quantum yield (QY) measurements were taken using a PTI QM400 (Horiba) equipped with a petite integrating sphere and a 920C cooled PMT detector. The emission spectra were corrected using a SLS200 stabilized tungsten-halogen light (Thorlabs) as a calibration source. Measurements of solutions were done in 1 cm path length quartz cuvette (FireflySci, Inc.), while measurements of powders and films were taken using a Teflon powder holder. For powders, a quartz window was used with the holder, but this was removed for film measurements. PMMA thin films were fabricated through a drop casting method. Approximately 5 mg of the platinum species was dissolved in 2 mL of DCM. A ratio of 5 to 95% wt was used to calculate the correct weight of PMMA to add to the solution. PMMA was slowly added to the stirring solution. Once all PMMA had dissolved, the solution was slowly dropped onto optical-grade cover glass and allowed to dry overnight. Films could then be cut and placed in the powder holder for QY measurements or supported on glass for steady-state measurements. During QY measurements, slit sizes were adjusted and/or neutral density filters were used to keep the fluorescence signal in the linear range of the detector (<1 Mcps). Excitation and emission slits were typically set to ~1 nm passband. To confirm the instrument’s performance, a 5 μM solution of rhodamine 101 (Millipore Sigma, CAS 116450-56-7) in ethanol was measured using an excitation wavelength of 552 nm, and the emission was collected from 660 to 800 nm. The QY of the fluorescence was measured six times with an average value of 0.91. The manufacturer’s instruction manual states that the QY should be 0.92 ± 0.04. We also confirm the instrument’s performance using a weaker emitter, harmaline (Millipore Sigma, CAS 304-21-2), which has a literature QY of 0.32 ± 0.02. We measured a 10 μM solution of harmaline in a pH 2 solution acidified with H2SO4 four times at an excitation wavelength of 367 nm over an emission range of 380–700 nm with an average QY of 0.34. Additionally, we confirmed the instrument’s performance with a weakly emitting sample, tris(bipyridine)ruthenium(II)chloride, in an aqueous solution at 10 μM. The sample was measured three times with an excitation wavelength of 436 nm over an emission range of 460–760 nm with an average QY of 0.021 and compared to the literature value of 0.028. Steady-state emission spectra were recorded using a PTI QM-40 instrument with a PMT detector, which is sensitive up to 850 nm. The luminescence lifetimes of the complexes were measured by time-correlated single-photon counting following excitation with a 365 or 450 nm LED in methylene chloride solution or by placing solid samples in the sample holder.

X-ray Diffraction. L1-DPPM was crystallized by slow diffusion of pentane into an acetone solution. X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo Kα (λ = 0.71073 Å)) at 125 K with crystals mounted in a nylon loop with Paratone-N cryo-protectant oil. The structure of L1-DPPM was solved using direct methods (SHELXT 2014/5) and standard difference map techniques and was refined with full-matrix least-squares procedures on F2 (SHELXL 2017/1). All nonhydrogen atoms were refined anisotropically.

X-ray Total Scattering Measurements and Pair Distribution Function Analysis Data Reduction. Total scattering measurements were performed using the 28-ID-2 (XPD) high energy X-ray Powder Diffraction beamline at the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory. X-ray scattering data were collected using a large-area 2D PerkinElmer detector (2048 × 2048 pixels, 200 × 200 μm2 each) in rapid acquisition mode with a sample-to-detector distance of 232 mm. The incident energy of the X-rays was 67.29 keV (λ = 0.1842 Å). Samples were prepared in 1.5 mm Kapton polimide tubes and sealed with modeling clay. Beamline calibration was performed with a Ni powder standard. Raw 2D detector intensities were azimuthally integrated and converted to 1D I(Q), where $Q = \frac{4\pi\sin \theta}{\lambda}$ is the magnitude of the elastic scattering momentum transfer, using pyFAI. Background subtraction, polarization correction, and normalization to the total scattering structure function $F(Q)$ and Fourier transformation to obtain the pair...
distribution function (PDF) $G(r)$ were performed using the reduction methods of PDFgetX3 implemented in the xPDFsuite. The range of scattering vector used in the Fourier transform to obtain the $G(r)$ was chosen to optimize the tradeoff between real space resolution and statistical noise ($Q_{\text{max}} = 18 \AA^{-1}$, Figure S13). PDF simulations and refinement of $G(r)$ to experimental data were performed using a custom code written in Python utilizing PDF calculators and refinement tools from the Diffpy-CMI complex modeling framework. More information on refined parameters and output is contained in Figure S12.

**Preparation of Compounds.** See the Supporting Information for additional experimental details, including copies of NMR spectra, UV/vis spectra, and emission spectra. $\text{[Pt(dmsco)}_{2}\text{Cl]}$ was synthesized according to a previously published procedure. $\text{L1 and L1-Met}$ were synthesized according to a modification of known procedures and can be found in the Supporting Information.

$L1$-DPPE $\text{[Pt(C_{20}H_{15}SN)(Ph_{2}PCH_{2})_{2})ClO}_{4}$. $\text{L1-Met}$ (0.10 g, 0.16 mmol) and bis(diphenylphosphino)ethane (0.060 g, 0.16 mmol) were dissolved in acetonitrile (25 mL). The resulting mixture was stirred and heated at 80 $^\circ$C for 1 h. LiClO$_4$ (3 equiv) was added to the stirring mixture and was heated for 30 min. The solution was gravity filtered to remove solids, and the solvent was removed by rotary evaporation, yielding a yellow solid. The product was purified through a Pasteur pipette silicon column using 10:1 DCM/acetone as the eluent, and the solid obtained after removal of the solvent was characterized by $^1$H and $^{31}$P NMR spectroscopies. Yield: 80% (0.07 g, 0.07 mmol). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 2.47 (m, 4H, (CH$_2$)$_2$), 5.01, 6.96 (2H, (CH$_2$)$_2$), 7.13–7.90 (aromatics), 8.19 (d, 1H, CH), $^3$J$_{P-H} = 8.8$ Hz, $^3$J$_{P-H} = 85.8$ Hz). $^{31}$P NMR (161 MHz, CD$_2$Cl$_2$): $\delta$ 37.5 (d, $^3$J$_{P-P} = 3356$ Hz, $^3$J$_{P-P} = 4.6$ Hz), 48.9 (d, $^3$J$_{P-P} = 2249$ Hz, $^3$J$_{P-P} = 4.6$ Hz). ESI-HR-MS (m/z): found: m/z 893.1861, calcld for [C$_{47}$H$_{40}$NP$_2$Pt$_5$]: m/z 893.1848.

$L1$-DPPM $\text{[Pt(C_{20}H_{15}SN)(Ph$_2$PCH$_2$)$_2$)}ClO$_4$. $\text{L1-Met}$ (0.060 g, 0.10 mmol) and bis(diphenylphosphino)methane (0.040 g, 0.10 mmol) were dissolved in dichloromethane (15 mL). The resulting mixture was stirred and heated at 40 $^\circ$C under inert conditions for 1 h. LiClO$_4$ (3 equiv) was then added to the stirring mixture and was heated for 30 min. The solution was gravity filtered to remove solids, and then the solvent was removed using rotary evaporation. The resulting yellow oil was purified through a Pasteur pipette silicon column using 10:1 DCM/acetone as the eluent. The isolated solid product was characterized by $^1$H and $^{31}$P NMR spectroscopies. Yield: 80% (0.07 g, 0.07 mmol). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 4.67 (t, 2H, CH$_2$), 7.84 (aromatics), 8.33 (d, 1H, CH), $^3$J$_{P-H} = 88.0$ Hz, $^3$J$_{P-H} = 8.6$ Hz). $^{31}$P NMR (161 MHz, CD$_2$Cl$_2$): $\delta$ 37.5 (d, $^3$J$_{P-P} = 3356$ Hz, $^3$J$_{P-P} = 4.6$ Hz), 48.9 (d, $^3$J$_{P-P} = 2249$ Hz, $^3$J$_{P-P} = 4.6$ Hz). ESI-HR-MS (m/z): found: m/z 893.1861, calcld for [C$_{47}$H$_{40}$NP$_2$Pt$_5$]: m/z 893.1848.

$L1$-DPPP $\text{[Pt(C}_{20}H_{15}SN)(Ph$_2$P(CH$_2$)$_2$PPh$_2$)$_2$]}ClO$_4$. $\text{L1-Met}$ (0.030 g, 0.04 mmol) and bis(diphenylphosphino)propane (0.020 g, 0.04 mmol) were dissolved in dichloromethane (10 mL). The resulting mixture was stirred and heated at 40 $^\circ$C under inert conditions for 1 h. LiClO$_4$ (3 equiv) was then added to the stirring mixture and was heated for 30 min. The solution was gravity filtered to remove solids, and then the solvent was removed by rotary evaporation. The resulting yellow oil was purified through a Pasteur pipette silicon column using 10:1 DCM/acetone as the eluent. The isolated solid product was characterized by $^1$H and $^{31}$P NMR spectroscopies. Yield: 77% (0.02 g, 0.03 mmol). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 2.04 (s, 2H, CH$_2$), 2.46 (s, 2H, CH$_2$), 2.58 (2H, CH$_2$), 4.71 (s, 2H, CH$_2$), 6.96–8.00 (aromatics), 8.06 (d, 1H, CH, $^3$J$_{P-H} = 7$ Hz, $^3$J$_{P-H} = 82.4$ Hz). $^{31}$P NMR (161 MHz, CD$_2$Cl$_2$): $\delta$ $-4.9$ (d, $^3$J$_{P-P} = 3351$ Hz, $^3$J$_{P-P} = 29$ Hz), $-0.40$ (d, $^3$J$_{P-P} = 2146$ Hz, $^3$J$_{P-P} = 29$ Hz). ESI-HR-MS (m/z): found: m/z 907.2008, calcld for [C$_{92}$H$_{84}$NP$_2$Pt$_5$]: m/z 907.2004.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04509.

Additional figures and tables; DFT and TD-DFT calculation results; and experimental details and spectra (PDF)

Compound L1-DPPM (CIF)

**AUTHOR INFORMATION**

**Corresponding Author**

Craig M. Anderson – Department of Chemistry & Biochemistry, Bard College, Annandale-on-Hudson, New York 12504, United States; orcid.org/0000-0001-5875-4380; Phone: 845-752-2356; Email: canderso@bard.edu; Fax: 845-752-2339

**Authors**

Belle Coffey – Department of Chemistry & Biochemistry, Bard College, Annandale-on-Hudson, New York 12504, United States

Lily Clough – Department of Chemistry & Biochemistry, Bard College, Annandale-on-Hudson, New York 12504, United States

Daphne D. Bartkus – Department of Chemistry & Biochemistry, Bard College, Annandale-on-Hudson, New York 12504, United States

Ian C. McClellan – Department of Chemistry & Biochemistry, Bard College, Annandale-on-Hudson, New York 12504, United States

Matthew W. Greenberg – Department of Chemistry & Biochemistry, Bard College, Annandale-on-Hudson, New York 12504, United States

Christopher N. LaFratta – Department of Chemistry & Biochemistry, Bard College, Annandale-on-Hudson, New York 12504, United States

Joseph M. Tanski – Department of Chemistry, Vassar College, Poughkeepsie, New York 12604, United States

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsomega.1c04509

**Notes**

The authors declare no competing financial interest.

CCDC for compound L1-DPPM is available at www.ccdc.cam.ac.uk/data_request/cif.

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