Thiazol-2-thiolate-Bridged Binuclear Platinum(II) Complexes with High Photoluminescence Quantum Efficiencies of Up to Near Unity

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ABSTRACT: Binuclear platinum(II) complexes with strong Pt-Pt interactions are an interesting class of luminescent materials, of which photophysical properties could be controlled via multiple ways through organic ligands and Pt-Pt distance. While a number of binuclear platinum(II) complexes have been developed with tunable emissions, achieving high photoluminescence quantum efficiency (PLQE) remains challenging and of great interest. Here we report the synthesis

and characterization of a series of binuclear 2,4-difluorophenylpyridine platinum(II) complexes bridged by thiazol-2-thiolate ligands with different bulkiness. The three complexes were found to have short Pt-Pt distances ranging from 2.916 to 2.945 Å. The strong Pt-Pt interactions lead to pronounced metal-metal-to-ligand charge transfer (MMLCT) absorptions between 450-500 nm, and strong ³MMLCT emission in the orange/red region. The PLQEs of the new complexes range between 2 and 20 % in solution, and 26 to 100 % in solid state. These complexes also exhibit excellent stability in halogenated solvents.

INTRODUCTION

Binuclear platinum(II) complexes have received great research attention for their remarkable and unique photophysical properties that allow their applications in various areas, such as sensing and organic light emitting diodes (OLEDs).¹⁻⁶ One of the intriguing features of these complexes is the property turnability via multiple ways of synthetic control, e.g. the bulkiness of the bridging and cyclometallating ligands, as well as their electronic structures.⁷⁻¹¹ For instance, by simply increasing the bulkiness of the bridging ligands in a series of pyrazolate-bridged binuclear platinum complexes, the Pt-Pt distance can be well controlled.⁷ Depending on the different degrees of Pt-Pt interactions, these complexes could exhibit either monomer-like emissions from ligand center/metal-to-ligand center transitions (³LC/MLCT), or dimer-like emissions from ³MMLCT that involve electronic transitions from the filled antibonding σ^* Pt-Pt orbital to the vacant ligand based π^* orbital.⁷ Dual emissions from both ³LC/MLCT and ³MMLCT could be achieved in several pyrazolate-bridged binuclear platinum complexes, when there is an equilibrium between two excited states.¹¹ On the other hand, binuclear platinum(II) complexes with half-lantern structures could be obtained when a four-bond bridging group like pyridine-2-thiolate ligands (Hpyt) was used.¹²⁻¹⁶ These complexes have short Pt-Pt distances and small dihedral angles between the two platinum squares. The rigid geometry of these complexes enhances the Pt-Pt interactions, making them stable ³MMLCT emitters.¹⁵⁻¹⁸ Moreover, most of these complexes could undergo two electron oxidative addition of halogens forming non-emissive Pt(III) binuclear complexes.^{12, 15-16, 19} Recently, research interest has been drawn to this type of binuclear complexes and their use in red and near infrared OLEDs.^{17, 20-21} However, the high sensitivity of some of these complexes towards halogenated solvents and their low solubilities limited their potential applications.¹³ Also the PLQEs of these complexes are not yet on an ideal level, which could be further improved. Therefore, searching for alternative bridging ligands that can preserve the half-lantern structure for the binuclear platinum complexes with improved stability in halogenated solvents and higher quantum efficiencies is of great interest.

Herein, we report three binuclear platinum(II) complexes bridged by thiazol-2-thiolate ligands with different bulkiness, BFPtTht (1), BFPtMeTht (2), and BFPtPhTht (3) (F=Hdfppy = 2-(2,4-difluorophenyl)pyridine, Tht = thiazole-2-thiolate, MeTht = 4-methylthiazole-2-thiolate, PhTht = 4-phenylthiazole-2-thiolate). These new binuclear platinum complexes are stable and not vulnerable to halogen oxidative addition in halogenated solvents. The emission of these complexes was slightly tuned by increasing the bulkiness of the bridging ligands. All these complexes exhibited strong ³MMLCT luminescence in solid and in solution with high PLQEs of up to near unity.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization. The new platinum complexes were synthesized following the straightforward synthetic procedure shown in scheme 1. The dichlorobridged platinum complexes were obtained following previously reported procedure and were used without any further purification and characterization.²² The three new binuclear platinum complexes were isolated in the anti-configuration as confirmed by single crystal structure and ¹H NMR spectroscopy. The purity of these complexes was further confirmed by the elemental analysis and mass spectrometry. (See experimental section for details)

Scheme 1. Synthetic scheme for thiazol-2-thiolate-bridged binuclear platinum(II) complexes.



R=H(1), Me(2), Ph(3)







The single crystal structures of all three binuclear platinum(II) complexes were determined using single X-ray diffraction, as described in the experimental section. Selected crystallographic data are presented in Table S1. All three complexes exhibit half-lantern structures, as shown in Figure 1A. Each platinum atom is coordinated in a square planar geometry to the donating atoms N and C of the cyclometallating ligands and the S and N of the bridging ligands. Both the bridging and cyclometallating ligands possess a head to tail anti configuration like the previously reported platinum complexes bridged by 2-pyridinethiolate ligands.^{13, 19} The cyclometallating ligands are planar and slightly slanted from each other. The dihedral angles between them are small and range between 4.83 and 19.63°. The intramolecular distances between the centroids of the cyclometallating ligands range between 3.675 and 4.552 Å, and the shortest distance was recorded in complex 2 (3.675 Å). The intermolecular distances between the centroids were found to be between 3.693 and 5.567 Å for the three complexes, suggesting little-to-no π - π intermolecular interactions (Figure 1B-C, Figure S1). The Pt-Pt distances are 2.9158(4) Å for complex 1, 2.9432(4) Å for complex 2, and 2.9226(5) Å and 2.9447(5) Å for complex 3, slightly larger than the Pt-Pt distance in dfppyPtPyt (2.8660(3) Å).² These short Pt-Pt distances suggest that strong electronic Pt-Pt interactions could exist. However, unlike the case of pyrazolatebridged binuclear platinum complexes where the Pt-Pt distance was controlled by the bulkiness of the pyrazolate ligands, no similar correlation between the bulkiness of the thiazol-2-thiolate ligands and the Pt-Pt distance was observed in these binuclear platinum complexes. This is not surprising as the half-lantern structures are able to deliver short Pt-Pt distances. A list of selected bond lengths and angles are summarized in Table S2.



Figure 1. A) Molecular structures for **1**, **2**, and **3**. (Ellipsoids are drawn at their 50% probability level and the hydrogen atoms are omitted for clarity. C, S, N, Pt, and F atoms are grey, yellow, blue, dark blue, and green, respectively.) Inter- and intramolecular interactions found in B) complex **1** C) complex **2**.

Electronic Absorption Spectroscopy and Computational Studies. The absorption spectra of complexes 1-3 in dichloromethane (DCM) at a concentration of 10^{-5} M are shown in Figure 2. The peaks below 350 nm can be assigned to π - π * transitions (LC). The lowest energy peaks for these complexes are attributed to MMLCT transitions, as a result of strong Pt-Pt interactions. These broad MMLCT peaks exhibit a small redshift upon the increase in the bulkiness of the bridging group. The maxima of these peaks range from 470 nm for complex 1, 476 nm for complex 2, and 487 nm for complex 3. To better understand the nature of the electronic

transitions, linear-response time-dependent density functional theory (LR-TDDFT)²³⁻³⁰ calculations were performed on complexes 1-3 using Becke, 3-parameter, Lee-Yang-Parr (B3LYP) exchange-correlation (XC) functional.³¹ The frontier molecular orbitals of these complexes along with their first two electronic transitions are displayed in Figure 3. The electronic structure of these complexes does not change much across the series. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), HOMO-1, and LUMO+1 of the three complexes look similar. Note that the energy of HOMO increases slightly upon the increasing of the bulkiness of the bridging ligand. This increase of the energy level is consistent with the redshift of the absorption spectra of these complexes. On the other hand, LUMO and LUMO+1 reside on the in phase and out of phase π^* of the cyclometallating ligands, respectively. For all molecules, we show the first two transitions that predominantly correspond to HOMO \rightarrow LUMO (S₁), HOMO \rightarrow LUMO+1 (S₂). The comparison between the simulated and the experimental electronic absorption spectra (Figure S2) shows that the electronic transitions of these complexes are well modeled by LR-TDDFT and confirms the MMLCT and LC assignments. Additional theoretical calculations for complexes 1-3, including i) the frontier molecular orbitals, ii) the descriptions of their main contributions, and iii) the main compositions of the lowest excitations, can be found in the Supporting Information (Figure S3-S5 and Table S3-S5).



Figure 2. Experimental electronic absorption spectra of complexes 1-3 in DCM.



Figure 3. Energy diagrams illustrating the frontier molecular orbitals (HOMO, HOMO-1, LUMO, and LUMO+1). Orbital energies are in eV. The excitation energies are calculated using LR-TDDFT, and only dominant transitions are shown.

Photoluminescent Properties. The emission spectra of these complexes measured in both the solid state and solution are displayed in Figure 4. All these complexes exhibited strong, broad, and featureless ³MMLCT emission in the solid state and solution. The emissions in DCM solution at room temperature are broader and more redshifted, as compared to those in the solid

state. In addition, the emissions of these complexes at glassy 2-methyltetrahydrofuran (2-MeTHF) at 77 K are similar to those of single crystals. This suggests that the rigidity of the media has a significant impact on the emissions. The rigidity can restrict the reorganization of the molecules in the excited state, which is responsible for bringing the two platinum atoms closer. This restriction leads to a smaller stokes shift and narrower emission. Similar trends have been seen in other binuclear platinum(II) complexes bridged by hydroxypiridine ligands.¹⁴ Moreover, The emissions of these complexes exhibit a small redshift upon the increase in the bulkiness of the bridging ligand, consistent with the shift of absorption spectra. The Commission Internationale de I'Eclairage (CIE) chromaticity coordinates of the crystals of the complexes were (0.5899, 0.3811) for **1**, (0.6194, 0.3786) for **2**, and (0.6399, 0.3440) for **3**.



Figure 4. A) Images of the single crystals of complexes **1-3** under ambient light and UV irradiation (365 nm). B) Steady state emission spectra of **1-3** for single crystals. C) Steady state emission spectra of **1-3** in DCM (solid lines) and in glassy 2-MeTHF at 77K (dashed lines).

Table 1 summarizes the photophysical properties of complexes 1-3. The excited-state decay lifetimes of these complexes were fit using monoexponential decay function (Figure S6). All these complexes were highly emissive and exhibited long excited-state lifetimes in the microsecond regime. The PLQEs of these materials are extremely high and could reach remarkable near unity for complex 2 in the solid state. These PLQEs are among the highest ever reported for platinum binuclear complexes.^{16, 19} A selection of thiolate-bridged binuclear complexes and their photophysical properties are summarized in Table S6. The quantum efficiencies and lifetimes of complexes 1-3 show strong dependence on the environment. The lowest PLQEs were recorded in DCM, especially for complex 1 that exhibit a value of 2 %. The radiative and nonradiative decays for complexes 1-3 in DCM vary between $0.6-1.9 \times 10^5 \,\text{s}^{-1}$ and $3.3-29 \times 10^5$ s⁻¹, respectively. The most significant difference was seen in the nonradiative decay of complex 1, which is almost nine times larger than those in other complexes. In order to find out the reason for the different PLQEs of the three complexes in DCM, the chemical and photochemical stabilities of complexes 1-3 were investigated. ¹H NMR spectra of these complexes in DCM were monitored in the presence and absence of UV irradiation (Figure S11-S15). No changes were observed in the ¹H NMR spectra of complexes **1-3** in DCM without UV irradiation, suggesting the high chemical stability of these complexes towards halogenated solvents. These results are in contrast to what have been observed in other platinum complexes bridged by ligands like 2-pyridinethiolate, which can undergo oxidative addition of halogen in halogenated solvents producing non-emissive Pt(III) complexes within few minutes to few hours.¹⁹ However, the ¹H NMR measurements under UV irradiation shows that complex **1** is not as photostable as complex 2 and 3. The low photochemical stability of complex 1 in DCM explains its low PLQE in DCM.

The PLQEs of these complexes improve significantly in more rigid environments, for instance, doping them in polystyrene (PS) and in single crystal forms. Reduced non-radiative decays and little-to-no reabsorption due to no overlaps between absorption and emission are believed to be the two main reasons for the remarkable PLQEs of these complexes in solid state. The patterns of the change of PLQEs in different environments are consistent for all the complexes, with complex **2** having the highest PLQEs in all environments, i.e. solution, dispersed in PS, and single crystals. The high solubility and stability of these complexes in solvents and their extremely high PLQEs make them of great interest for various applications.

Absorption, λ_{abs} , nm (ϵ , M ⁻¹ cm ⁻¹) ^a					
1	281 (30500), 308 (26000), 454 (3600), 470(3200)				
2	309 (24700), 353 (17100), 411 (6100), 458 (5200), 476 (5300)				
3	279 (40300), 362 (18200), 462 (4500), 487 (5600)				
	Emission, λ_{max} (nm)	lifetime	$arPsi_{ ext{PL}}$	$k_r (\times 10^5 \text{ s}^{-1})$	k_{nr} (× 10 ⁵ s ⁻¹)
		(µs)	(%)		
DCM					
1	646 (590) ^b	0.33 (4.7) ^b	2	0.6	29
2	656 (595) ^b	2.1 (4.8) ^b	31	1.5	3.3
3	683 (618) ^b	1.6 (4.3) ^b	20	1.9	4.4
Crystals					
1	604 (611) ^c	2.0 (3.9) ^c	26	1.3	3.7
2	610 (595) ^c	2.6 (3.3) ^c	100	3.8	-
3	626 (626) ^c	1.9 (3.4) ^c	68	3.6	1.7
1% in PS					
1	593	2.1	51	2.4	2.3
2	600	2.2	73	3.3	1.2
3	625	20	62	3.1	19

 Table 1. Photophysical properties of complexes 1-3.

^a measured in DCM. ^b measured in 2-MeTHF at 77k. ^c measured at 77K. The radiative and non-radiative decays were calculated using these equations: $k_r = \Phi/\tau$, $k_{nr} = (1 - \Phi)/\tau$.

Electrochemical Properties.

Cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) were used to investigate the electrochemical properties of the new complexes. To ensure suitable solubility and electrochemical potential windows, the anodic and cathodic sweeps were conducted in DCM and tetrahydrofuran (THF), respectively. The peak potential values were determined using DPV, while the electrochemical reversibility of the binuclear platinum(II) complexes was studied using CV. The CV traces and redox potentials are presented in Figure 5 and Table 2. All values are reported in reference to ferrocenium/ferrocene (Fc⁺/Fc). All three complexes display single reversible oxidation waves between 0.24 and 0.36 V, as well as single reversible or quasireversible reduction waves between -2.32 and -2.42 V. The reduction potentials of these complexes are associated with the cyclometallating ligands and display a good correlation with both the location and relative energies of the calculated LUMOs. Oxidative CV studies in DCM revealed reversible oxidation potentials, which could be assigned to the oxidation of Pt(II) to Pt(III). The reversible oxidation processes of binuclear platinum complexes with strong Pt-Pt interactions in non-coordinating solvents, such as DCM, is common.^{8, 32} In general, the irreversibility of oxidation potentials is caused by the high susceptibility of the platinum centers to nucleophilic reactions with coordinating solvents.⁸ The oxidation potentials of these complexes are higher than that of $[Pt(\mu-pyt)(ppy)]_2$ (Hppy= 2-phenylpyridine) (-0.1V vs. Fc⁺/Fc) that undergoes oxidative addition of halogen in halogenated solvents.¹²⁻¹³ These higher oxidation potentials might explain the lack of reactivity of the new complexes with halogenated solvents.

	$E_{1/2}(0x)^{a}$	E _{1/2} (red) ^b
1	0.26°	-2.32 ^d
2	0.36°	-2.38°
3	0.24°	-2.42°

 Table 2. Electrochemical data of complexes 1-3.

^a measured in DCM. ^b measured in THF. ^c reversible. ^d quasi-reversible.



Figure 5. Cyclic voltammograms (A) for oxidation in DCM and (B) for reduction in THF of complexes **1-3**.

CONCLUSION

In summary, the structural, photophysical, and electrochemical properties of three binuclear platinum(II) complexes bridged by a series of thiazol-2-thiolate ligands with different bulkiness are investigated. The three complexes with a half-lantern structure have short Pt-Pt distances between 2.916 and 2.945 Å, which result in strong interactions between the d_z^2 orbitals of the two platinum units. They are found to be stable and highly efficient ³MMLCT emitters with quantum efficiency reaching unity, these emissions could be slightly tuned by the bulkiness of the bridging ligand. LR-TDDFT calculations were performed to gain better understanding of the photophysical processes in these complexes. LR-TDDFT results match with the experimental results nicely, which confirm that the MMLCT transitions are responsible for the emissions. The high stability and the outstanding quantum efficiencies of these complexes make them valuable for various applications, which would be reported in due course.

EXPERIMENTAL SECTION

General. 2-(2,4-difluorophenyl)pyridine, 4-phenyl-1,3-thiazole-2-thiol, and potassium tetrachloroplatinate(II) were purchased from Aldrich Chemical Co., 4-methyl-1,3-thiazole-2thiol and 1,3-thiazole-2-thiol were purchased from Enamine. All the chemicals were used as received without further purification. The mass was determined using 6200 Q-TOF-MS (Agilent) coupled to a DART SVP (IonSense) ambient ionization source. The elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA.¹H NMR spectroscopy was used to characterize the synthesized products.

Synthesis of complexes 1-3. The platinum complexes 1-3 were synthesized by reacting $[Pt(\mu-Cl)(dfppy)]_2$ (Hdfppy= 2-(2,4-difluorophenyl)pyridine) with 2.5 equivalent of the respective thiazol-2-thiolate ligand and 2.5 equivalent of K₂CO₃ in 1,2-dichloroethane. The reaction mixture was heated at 83 °C for 1 day under N₂ atmosphere. The resulting solution was evaporated to near dryness. The final products were purified using flash column chromatography with DCM as the eluent and recrystallized from methanol/dichloromethane mixture.

BFPtHTht (1). [Pt(μ -Cl)(dfppy)]₂ (0.2 g, 0.238 mmol) was added to 30 ml of 1,2-dichloroethane followed by the addition of 2.5 equivalent of 1,3-thiazole-2-thiol (0.069 g, 0.595 mmol), and 2.5 equivalent of K₂CO₃ (0.138g, 0.595 mmol). The reaction mixture was at 83 °C under N₂ atmosphere for 1 day. The resulting orange solution was evaporated to dryness. The orange solid obtained was dissolved in small amount of DCM and purified using flash silica chromatography with DCM as eluent. The product constituted the first fragment. The orange solid was recrystallized from methanol/dichloromethane mixture (ratio 1:1). The dimer was isolated as trans isomer with a yield of 13 % (31 mg). ¹H NMR (500 MHz, Chloroform-d) δ 8.46 (d, J = 3.9 Hz,

2H), 8.15 – 8.00 (m, 2H), 7.87 – 7.68 (m, 4H), 7.32 – 7.27 (m, 2H), 7.09 (d, J = 3.8 Hz, 2H), 6.63 – 6.38 (m, 4H). Elemental analysis For C₂₈H₁₆F₄N₄Pt₂S₄ calc C, 33.53; H, 1.61; N, 5.59; S, 12.79 found C, 33.77; H, 1.49; N, 5.53; S, 12.52. TOF-MS: calculated m/z: 1001.95 found m/z: 1002.95.

BFPtMeTht (**2**). Yield 31 % (75 mg). ¹H NMR (500 MHz, Chloroform-d) δ 7.83 (d, J = 6.5 Hz, 2H), 7.76 – 7.57 (m, 4H), 7.03 (ddd, J = 7.3, 5.7, 1.7 Hz, 2H), 6.84 (dd, J = 9.5, 2.5 Hz, 2H), 6.54 (s, 2H), 6.31 (ddd, J = 12.6, 8.8, 2.5 Hz, 2H), 2.62 (s, 6H). Elemental analysis For C₃₀H₂₀F₄N₄Pt₂S₄ calc C, 34.95; H, 1.96; N, 5.43; S, 12.44 found C, 35.11; H, 1.98; N, 5.32; S, 12.17. TOF-MS: calculated m/z: 1030.99 found m/z: 1030.99.

BFPtPhTht (**3**) Yield 36% (99 mg). ¹H NMR (500 MHz, Methylene Chloride-d2) δ 8.30 (dd, J = 5.6, 1.7 Hz, 2H), 7.85 – 7.63 (m, 8H), 7.36 – 7.24 (m, 6H), 7.15 – 7.03 (m, 2H), 6.89 (s, 2H), 6.61 (dd, J = 9.7, 2.5 Hz, 2H), 6.30 (ddd, J = 12.8, 8.9, 2.5 Hz, 2H). Elemental analysis For C₄₀H₂₄F₄N₄Pt₂S₄ cale C, 41.59; H, 2.09; N, 4.85; S, 11.10 found C, 41.29; H, 2.19; N, 4.59; S, 10.80. TOF-MS: calculated m/z: 1154.02 found m/z: 1155.02.

Sample preparation. Low concentration solution samples (10⁻⁵ M) were prepared by dissolving complexes **1-3** in dichloromethane to obtain absorption, steady state phosphorescence, and time-resolved emission spectra in solutions. The single crystals were placed in quartz tubes to measure their steady state phosphorescence and time-resolved emission spectra. The 1% PS films were prepared by dissolving the complexes and polystyrene in DCM and spin coating the solutions on clean glass substrates.

Photophysical characterization. The absorption spectra were measured using a Cary 5000 UV-Vis-NIR spectrometer. The emission spectra were recorded using an Edinburgh 298 FS5 steady state spectrometer. The samples were excited at a wavelength of 450 nm using a 150 W xenon lamp. The emission lifetime was determined using Time Correlated Single Photon Counting (TCSPC) measurements. Edinburgh EPL-450 picosecond pulsed diode laser was used as an excitation source. The PLQE measurements were done using Hamamatsu Quantaurus-QY Spectrometer (Model C11347-11) equipped with an integrating sphere sample chamber. The PLQEs were determined by the equation: $\eta_{QE} = I_S / (E_R - E_S)$ where Is corresponds to the luminescence emission spectrum of the sample, E_R and E_S represent the excitation spectrum for the reference and the sample respectively.

Computational details. All density functional theory (DFT) and linear response time-dependent (LR-TD) DFT calculations are performed using the NWChem program (version 6.8)³³. The geometry optimization and LR-TDDFT calculations are performed using the Becke, 3-parameter, Lee–Yang–Parr (B3LYP) exchange-correlation (XC) functional³¹. The 6-311G basis set is used for the hydrogen. For the other elements, the effective core potentials from references³⁴⁻³⁵ are used and the corresponding valence-double zeta basis from references³⁴⁻³⁵ are employed. The structure optimizations of complexes were performed in vacuum. The singlet-to-singlet excitations are calculated by solving the LR-TDDFT equation. The 35 lowest excitations are used to generate the absorption spectra. The vertical excitation model (VEM)³⁶ is used to consider the effect from solvent dichloromethane on the excitation of the complexes. The frontier molecular orbital figures were prepared using the Chemissian, version 4.60 program.³⁷

X-ray Crystallography. Single crystals of 1-3 were grown from methanol/dichloromethane solution using a slow evaporation method at room temperature. A suitable crystal was selected and mounted in a cryoloop under Paratone-N oil. Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector and dual Mo and Cu microfocus sealed X-ray sources was used to collect the single crystal X-ray data. The data were

collected at 100.00(10) K. Olex235 software was utilized in solving the structure. The XT³⁸ structure solution program using Intrinsic Phasing and the XL³⁹ refinement package using Least Squares minimization were employed in solving and refining the structure respectively. Table S1 in the Supporting Information summarizes the refinement details and the resulting factors.

Electrochemistry. Cyclic voltammetry and differential pulsed voltammetry were done using Epsilon E2 electrochemical analyzer with C3 cell stand. Measurements were conducted in anhydrous DCM and THF under nitrogen for the anodic and cathodic sweeps, respectively. 0.1 M tetra(n-butyl)ammonium hexafluorophosphate was used as the supporting electrolyte. A Pt wire, an Ag wire, and a glassy carbon electrode acted as the counter, the pseudo-reference, and the working electrodes respectively. The redox potentials are determined using DPV and are reported relative to an internal ferrocenium/ferrocene (Fc⁺/Fc, 0.45 V vs. SCE)⁴⁰ reference. The electrochemical reversibility was determined using CV.

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Supporting Information

The ¹H NMR spectra, crystallographic data for complexes **1-3**, the PL spectra of complexes **1-3** measured in 1% polystyrene and in the single crystals, the excited state decay curves of

complexes **1-3** in different media, and additional DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

CCDC 1982194-1982196 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data request/cif, or by emailing

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Notes

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A series of binuclear platinum(II) complexes bridged by thiazol-2-thiolate ligands with different bulkiness are reported. The three complexes have half-lantern structures with short Pt-Pt distances. The strong Pt-Pt interactions in these complexes lead to strong ³MMLCT emissions in the orange/red region with photoluminescence quantum efficiencies of up to near unity.