Accurate Prediction of Emission Energies with TD-DFT Methods for Platinum and Iridium OLED Materials

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Abstract

Accurate prediction of triplet excitation energies for transition metal complexes has proven to be a difficult task when confronted with a variety of metal centers and ligand types. Specifically, phosphorescent transition metal light emitters, typically based on iridium or platinum, often give calculated results of varying accuracy when compared to experimentally determined T1 emission values. Developing a computational protocol for reliably calculating OLED emission energies will allow for the prediction of a complexes color prior to synthesis, saving time and resources in the laboratory. A comprehensive investigation into the dependence of the DFT functional, basis set, and solvent model is presented here, with the aim of identifying an accurate method while remaining computationally cost-effective. A protocol that uses TD-DFT excitation energies on ground-state geometries was used to predict triplet emission values of 34 experimentally characterized complexes, using a combination of gas phase B3LYP/LANL2dz for optimization and B3LYP/CEP-31G/PCM(THF) for excitation energies. Results show excellent correlation with experimental emission values of iridium and platinum complexes for a wide range of emission energies. The set of complexes tested includes neutral and charged complexes as well as a variety of different ligand types.

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Introduction

Since the introduction of the first phosphorescent materials and devices proven to work as triplet emitters[1-3], Fig. 1, numerous groups have synthesized novel TM complexes for use in organic light emitting diode (OLED) devices. Iridium(III) and platinum(II) complexes make up the majority of emissive complexes studied due to their thermal stability, emission energies that can be tuned by modification of the ligands, and good quantum efficiencies in devices. For example, Yasukawa et al. have patented novel iridium- and platinum-based complexes consisting of trivalent linking groups for light emission of various wavelengths.[4] Kimyonok et al. showed that a series of synthesized iridium-copolymer dopant/host devices can be tuned to emit from 474 nm to 600 nm and exhibit quantum efficiencies similar to the well known Ir(ppy)$_3$ dopant.[5,3] Rausch et al. have improved the rigidity in platinum(II) complexes by using a tridentate ligand, resulting in much higher photoluminescent quantum efficiencies compared to a bidentate analogue.[6] Solomatina et al. have explored Pt(II) complexes with N-heterocyclic carbene (NHC) ligands that emit in the blue/green region of the spectrum.[7] Tuning of the quantum efficiencies can be achieved by augmenting the ligand sphere around the metal.[7]

Computational methods are often employed to predict a complex's lowest triplet emission energy (T1), determine the ground and excited state geometries, or visualize the location of electron density contributing to the emission. As with most applications of computational methods, knowing *a priori* what method provides the most accurate results is often a subject of debate. Shang et al. reported TD-DFT calculated emission values for an iridium complex that differ by 13 nm and 69 nm (M062X and B3LYP, respectively) from experimental values.[8] Their work used optimized triplet geometries as the input for the TD-DFT calculation, requiring a larger computational effort. Recent work by Xu et al., used TD-DFT methods towards prediction of T1 emission for a number of iridium complexes.[9] This approach required triplet state geometry optimizations with numerous functionals, using an average of all the results multiplied by 1.2 as the final predicted value T1 value. The use of gas phase calculations to compare to frozen solutions (77 K) may miss important interactions between host (solvent) and dopant (TM complex).[10-12] These interactions will become even more important when charged complexes are being used as dopants. Previous unpublished results from our lab determined that while gas phase time-dependent density functional theory calculations (TD-DFT, vertical excitations) work well for predicting T1 energies of iridium(III) complexes, the same method often leads to large errors in T1 when Pt(II) complexes are studied. Niehaus et al. have recently shown good agreement between calculated emission energies, using TD-DFT vertical excitations, and experimental emission values for iridium and platinum complexes. Specifically, calculated mean average percent deviations (MAPD) using B3LYP (1.8 %) or the modified LC-PBE (4.6 %) functionals, with a solvent model, within the TD-DFT framework provided a vast improvement over the original PBE (14.3 %) functional.[13]

An efficient computational method must be able to quickly, as well as accurately, predict ground state geometries and T1 emission energies of complexes with varying ligand sets. Methods such as ΔSCF, which requires triplet optimization, time consuming configuration interaction (CI) calculations, and the use of very large basis sets should be avoided if possible. Additionally, methods like Herein we report the identification of linear-response TD-DFT based method for the accurate prediction of emission energies for phosphorescent platinum(II) and iridium(III) complexes. Accuracy was maintained across the visible spectrum from deep blue to red emission. Application of this method towards different metals and different ligand sets shows its versatility and is expected to be accurate in its prediction of emission energies of novel complexes prior to synthesis.

Computational Methods

All calculations were performed with the Gaussian 09 package.[14] Optimization of ground state singlet geometries were carried out with the density functional theory[15,16] (DFT) framework using various functional/basis set/solvation combinations. Basis sets ranged from full relativistic effective core potentials (RECPs) to split-basis methods (metal treated with RECPs and main group atoms with an all-electron basis).

Optimized ground state geometries were treated with time-dependent DFT (TD-DFT)[17-19] calculations to obtain vertical excitation energies for the first 3 singlet and 3 triplet states. Comparison of computed vertical *excitations* to experimental *emission* energies of OLED materials is justified since OLED transient lifetimes are typically on the order of a few microseconds[20], thus emission can be considered as instantaneous (before nuclei can reorder) making the vertical electronic transition a good approximation of the emission energy. Additionally, the rigid structure of the complexes through the use of bidentate ligands, and their fairly locked geometry in the organic host material dramatically reduces the vibrational relaxation and reorganization energies. This can be seen by an OLEDs relatively small Stokes shift.[21]

The obtained results are categorized into three major sets:

(**1**) variation of the density functional
(**2**) variation of the basis set
(**3**) variation of the solvation model.

The first set of calculations (**1**) explored the effect of varying the density functional. The functionals B3LYP[22], PBE0[23,24], M06, M06-L, M06-HF[25-28] and BP86[29,30] were employed to determine how the amount and form of exchange-correlation influences the calculated excitation values. Additionally, the CAM-B3LYP[31] and M11[32] functionals were used to test if varying the exchange (at short range and long range) impacts the calculated T1. The ωB97X-D[33] functional was also tested to see the effect dispersion has on the calculations. The functionals were used for both the geometry optimization and the TD-DFT calculations. Functionals that gave the best agreement with experimental data were then passed on to the next set of calculations.

The second set of calculations (**2**) examined the calculated excitation energies dependence on the basis set. Relativistic effective core potential (RECP) basis sets are used to avoid time consuming all electron basis sets for transition metal atoms, as well as to include relativistic effects of heavy atoms. The basis sets selected comprise of the double and triple zeta basis sets developed by Stephens et al[34], CEP-31G and CEP-121G, respectively, and the Los Alamos double zeta LANL2dz[35-38] basis set. Additional calculations were performed using split-basis sets that employ a RECP on metal atoms and an all-electron basis set on all non-metal atoms. The 6-31g(d)[39,40] and 6-311g(d,p)[41,42] basis sets were both tested to treat main group atoms. Additional *d*-orbital polarization functions were added to phosphorus and chlorine atoms when present.

Lastly, set (**3**) consists of various solvation models to further improve the accuracy of calculated results. While the CPCM was used in sets (**1**) and (**2**) alongside gas phase calculations to determine the best functional/basis set method, IEFPCM[43,44], and SMD[45] solvation models were later evaluated on the best method to ensure the best solvation model is used. All but two complexes were experimentally tested in tetrahydrofuran (THF) or 2-methyl-THF at 77 K, while 298 K data was obtained in dichloromethane (CH_2Cl_2). Comparison of the dielectric constants for THF (7.42) and CH_2Cl_2 (8.93) suggest that calculations will not deviate much between the two, therefore THF was selected as the solvent for all calculations that employ a solvation model.

The general nomenclature used in this paper for the combinations of functionals and basis sets used for DFT optimization and TD-DFT excitation calculations is as follows; F/O/P, where F is the functional of choice, O is the basis set used for geometry optimization, and P is the phase (gas or THF) used for the excitation energy calculation. For example; a calculation denoted B3LYP/LANL2dz/THF used the B3LYP functional and the LANL2dz basis set for both geometry optimization and excited state calculation, with THF used only in the TD-DFT calculation. If the basis set and/or functional used in the excitation energy calculation was different than the basis set used for optimization, it is denoted explicitly, for example: B3LYP/LANL2dz/CEP-31G_THF.

Results and Discussion

A total of 34 TM complexes were screened through various functional/basis set/solvation methodologies, Table 1 and Fig. 2. This set comprised of OLEDs that span a variety of ligand types and emission wavelengths, which is critical due to the nature of the electromagnetic spectrum. Specifically, small differences in the blue region amount to a larger difference in energy compared to small differences in the red region of the visible spectrum. Therefore, a best method must be able to accurately differentiate small changes in emission energies for complexes with similar or different ligands.

Table 1. Experimental T1 emission values of the transition metal OLED complexes investigated in this work.

Complex	Experimental λ_{em}, nm (77 K)	 λ_{em}, nm (298 K)	Reference #
Ir1	491	508	[46]
Ir2	-	475	[47]
Ir3	-	480	[1]
Ir4	-	456	[48]
Ir5	-	455	[48]
Ir6	-	458	[48]
Ir7	-	431	[48]
Ir8	-	438	[49]
Ir9	443	466	[8]
Ir10	463	555	[50]
Ir11	464	555	[50]
Ir12	456	554	[50]
Ir13	458	474	[51]
Ir14	465	480	[51]
Pt1	480	486	[52]
Pt2	477	-	[52]
Pt3	480	-	[52]
Pt4	480	485	[52]
Pt5	468	476	[52]
Pt6	487	-	[52]
Pt7	476	484	[52]
Pt8	458	466	[52]
Pt9	438	456	[52]
Pt10	440	447	[52]
Pt11	555	-	[52]
Pt12	488	495	[53]
Pt13	489	495	[53]
Pt14	473	480	[53]
Pt15	493	506	[54]
Pt16	432	467	[54]

Pt17	570	595	[54]
Pt18	525	569	[54]
Pt19	440	478	[55]
Pt20	515	527	[56]

Functional Dependence. Work by Xu and coworkers has provided insight into the functional dependence of calculated T1 emissions.[9] They have previously shown that functionals containing a certain amount of exact Hartree-Fock exchange (HF) perform better than functionals without this exchange. Therefore a critical first step was to calibrate our results against functionals selected by Xu, include a larger set of the Minnesota functionals, and explore functionals with range-separated exchange formalism and dispersion corrections. Initial calculations employed the CEP-31G basis set in gas and solvated phases. The CPCM solvation model was used using tetrahydrofuran, THF, as the solvent (selection of solvent is discussed in detail below). The calculated emission energies were compared to both 298 K and frozen 77 K OLED experimental emission data.

Table 2. Comparison of the mean average percent deviations (MAPD) for calculated T1 vertical emission energies for iridium(III) OLED complexes against the experimentally reported values (Table 1) in gas phase and THF (CPCM solvation model).

		Iridium(III) Complexes			
Functional[a]	**% HF Exchange**	**MAPD Gas (298 K)**	**MAPD**[b] **Gas (77 K)**	**MAPD**[c] **THF (298 K)**	**MAPD**[b] **THF (77K)**
B3LYP	20	2.8	7.5	4.4	1.7
CAM-B3LYP	19/65[d]	5.2	3.3	5.2	3.2
M06	27	3.8	6.2	7.2	3.1
M06-L	0	10.7	25.5	5.1	16.4
M06-HF	100	31.8	29.7	33.4	31.5
M06-2X	54	20.6	16.7	21.2	16.5
M11	42.8/100[d]	16.6	13.7	17.7	15.0
PBE0	25	21.7	37.1	13.1	25.9
BP86	0	21.6	37.0	13.0	25.9
ωB97X-D	22/100	6.1	10.0	6.0	9.8

[a] Only the functional varied in calculations. CEP-31G basis set for all atoms.
[b] 7 of the 14 iridium complexes had 77 K data.
[c] 14 of the 14 iridium complexes had 298 K data.
[d] range separated functionals listed with *short*/*long* percentages of HF exchange.

Results in Table 2 show that the amount of HF exchange in the functionals influences the calculated vertical excitation energies, based on optimized singlet geometries, quite differently than Xu reports for triplet geometry TD-DFT calculations.[9] Specifically, Table 2 shows there is less dependence on the amount of HF exchange when calculating the TD-DFT emission of iridium complexes from the optimized ground state singlet geometry. The functionals with the best correlation to experimental data are B3LYP and M06, consisting of 20 % and 27 % HF, respectively. It can be extracted from Table 2 that the best correlation is found between calculated THF values and 77 K experimental values, and will therefore be the focus of this discussion. At the individual level, only 3 complexes have a calculated Δ_{nm} ($\mathrm{T1}_{\mathrm{CalcTHF}}$-$\mathrm{T1}_{\mathrm{Exp77K}}$) greater than 10 nm in the B3LYP/CEP-31G/THF (77 K) data set; **Ir9** (11 nm), **Ir11** (15 nm), and **Ir12** (14 nm). These values compute to small mean average percent deviations (MAPD) of 2.5 %, 3.2 %, and 3.1 %, respectively.

Results for the platinum complexes exhibit the same trend as iridium, with B3LYP and M06 proving to be the best functionals with the CEP-31G basis set, Table 3. Here M06 shows a slightly better performance for platinum complexes having a calculated MAPD of 2.0 % compared to 3.7 % with B3LYP in the 77 K data set.

Table 3. Comparison of the calculated mean average percent deviations (MAPD) for platinum(II) OLED complexes against the experimentally reported values (Table 1) in gas phase and THF (CPCM solvation model).

		Platinum(II) Complexes			
Functional[a]	**% HF Exchange**	**MAPD Gas (298 K)**	**MAPD**[b] **Gas (77 K)**	**MAPD**[c] **THF (298 K)**	**MAPD**[b] **THF (77K)**
B3LYP	20	4.7	7.2	2.3	3.7
CAM-B3LYP	19/65	4.3	5.9	3.3	4.9
M06	27	2.2	2.7	4.6	2.0
M06-L	0	15.7	17.5	8.4	10.9
M06-HF	100	20.6	17.7	20.2	17.2
M06-2X	54	13.6	11.1	15.2	12.7
M11	42.8/100	10.1	7.9	11.2	9.0
PBE0	25	22.6	29.5	18.2	20.3
BP86	0	27.3	28.6	17.4	21.3
ωB97X-D	22/100	9.1	13.1	9.1	13.2

[a] Only the functional varied in calculations. CEP-31G basis set for all atoms.
[b] 20 of the 20 platinum complexes had 77 K data.

[c] 16 of the 20 platinum complexes had 298 K data.
[d] range separated functionals listed with *short*/*long* percentages of HF exchange.

The platinum group consists of 19 complexes having a Δ_{nm} greater than 10 nm with the B3LYP/CEP-31G/THF method. Moreover, 4 of these (**Pt4**, **Pt8**, **Pt9**, **Pt21**) have calculated values red-shifted by more than 20 nm, while 2 complexes (**Pt18**, **Pt29**) are red-shifted by 30 nm or more. Comparison of Table 2 and Table 3 clearly shows that selection of the functional is extremely important when using TD-DFT excitation values for the prediction of the emission energies of iridium and platinum OLED complexes.

Basis Set Dependence. After determining the best functional(s), we examined the basis set dependence of the TD-DFT calculations. The two best functionals, B3LYP and M06, were used to geometry optimize the complexes and calculate the excitation energies using several basis sets, Fig. 3 (see Fig. ESM1 in Supporting Information for complete representation of basis sets). As previously mentioned, the main focus was on the correlation between the experimental 77 K data and the results from solvated calculations. The relationship between 298 K and gas phase calculated results is of lesser importance, but may provide insight into the shift of the complexes emission maxima at room temperature. This point will be further investigated in future work.

The top graph in Fig. 3 plots the calculated T1 values versus experimental emission maxima at 77 K for iridium complexes using different basis sets. Changing the basis set to the LANL2dz had only a small effect on the calculated T1 values for iridium when employing the B3LYP functional. The MADP was reduced to 1.4 % (**A**, Table 4) from 1.7 % with CEP-31G (Table 2). Using M06/LANL2dz for both optimization and excitation calculations has a MAPD value of 2.6 %, which is lower than the original value of 3.1 %, but remains less accurate than the results from B3LYP in Table 4. Because of its overall better performance, further basis set changes were only tested with B3LYP.

Analysis of Fig. 3 data shows the best functional/basis set combination for the calculation of the T1 emission is B3LYP/LANL2dz/CEP-31G_THF (orange in Fig. 3, method **F** in Table 4). This method uses B3LYP/LANL2dz for geometry optimization followed by B3LYP/CEP-31G for calculation of excited states using the CPCM solvation model with THF as the solvent. The calculated MAPD with this method is reduced to 1.1 %. Furthermore, method **F** reduces the number of iridium complexes with a calculated Δ_{nm} greater than 10 nm to two; **Ir1** and **Ir13**, which are calculated to be blue shifted by 10 and 11 nm respectively.

More interesting are the results calculated for the 20 platinum complexes. Although inherently more challenging to accurately calculate T1 values, Table 3, platinum complexes performed well with changes to the basis set. Similar to iridium, B3LYP, method **A**, outperforms M06, method **B**, with calculated MAPDs of 1.5 % and 2.7 %, respectively. A more dramatic decrease in the calculated MAPD is seen when method **F** is used for platinum. The calculated MAPD is reduced to 0.9 %, which is about half the magnitude of the other basis sets and almost 4 times lower than its original value of 3.7 %. Only 3 platinum complexes, using method **F**, have a calculated Δ_{nm} greater than 5 nm; **Pt4**, **Pt14**, and **Pt19**, and none of these three are greater than 15 nm.

Table 4. Calculated MAPD values for OLED complexes using various basis sets. Comparison of data is performed with the 77 K experimental data.[a]

	Method	Iridium MAPD (77 K)	Platinum MAPD (77 K)
(A)	B3LYP/LANL2dz/THF	1.4	1.5
(B)	M06/LANL2dz/THF	2.6	2.7
(C)	B3LYP/CEP-121G/THF	1.3	2.2
(D)	B3LYP/LANL2dz/CEP-121G_THF	1.2	0.9
(E)	B3LYP/CEP-31G/LANL2dz_THF	1.4	1.8
(F)	B3LYP/LANL2dz/CEP-31G_THF	1.1	0.9
(G)[b]	B3LYP/CEP-121G_6-311G(d,p)/THF	4.4	4.0
(H)[c]	B3LYP/CEP-31G_6-31G(d,p)/THF	3.9	4.1
(I)[d]	B3LYP/LANL2dz_6-311G(d,p)/THF	3.4	4.0

[a] THF written directly after the second forward slash indicates the same basis set was used for optimization and excited state calculations.
[b] Split basis set: CEP-121G on metal, 6-311G(d,p) on all other atoms.
[c] Split basis set: CEP31G on metal, 6-31G(d,p) on all other atoms.
[d] Split basis set: LANL2dz on metal, 6-311G(d,p) on all other atoms.

It is worth noting here that only subtle differences were seen between the CEP-31G and CEP-121G basis sets, methods **F** and **D**. Platinum shows no difference in value while there is a small 0.1 % difference in calculated MAPD, favoring the double zeta, CEP-31G basis set in the case of iridium. Therefore, the computational cost can be reduced by using the smaller basis set without loss of accuracy for iridium and platinum complexes. Comparison of methods **E** and **F** also show that it is important which basis set is used for the optimization and which basis set is used for the calculation of excitations. Method **E** is simply the reverse of method **F**, however, calculated excitation values of iridium and platinum are more accurate with method **F**. Lastly, calculated MADP values from Table 4 are larger by a factor of about three for iridium and about four for platinum when using split basis sets in methods **G**, **H** and **I**.

Solvent Model Dependence. Lastly, selection of the optimal solvent model was investigated by testing three popular solvent models: CPCM (which has been used up to this point), IEFPCM, and SMD. Calculations used method **F** from Table 3 to test all iridium and platinum complexes. While the inclusion of solvent is very important for an accurate description of emission energy for comparison against experimental 77 K data, as previously discussed, the actual solvation model used is not as important.

For iridium, the calculated MAPD values are 1.1 %, 1.8 %, and 1.3 % for CPCM, IEFPCM and SMD, respectively. Concomitantly, the MAPD for platinum complexes are 0.9 % (CPCM), 0.9 % (IEFPCM), and 1.0 % (SMD). Since most of these complexes are neutral, we would not expect a large difference between solvation models. However, complexes **Ir11**, **Ir12**, and **Ir13** are cationic complexes and therefore may be more dependent on the solvation model selected. The MAPD values for just these three complexes shows that CPCM (0.5 %) and SMD (0.5 %) are slightly favored compared to IEFPCM (0.9 %), which accounts for the smaller MAPD for CPCM and SMD in the iridium group. While the selection of solvation model does not greatly affect the calculated excitation values, the initial employment of the CPCM solvation model is now retrospectively verified by these results.

Conclusions

In this work we set out to present and justify a reliable TD-DFT *excitation* based method for the prediction of the triplet *emission* (T1) energy values for iridium and platinum complexes used in organic light emitting diodes. Accurate prediction of T1 values through a relatively inexpensive computational procedure is key to providing researchers with a starting point towards the development of novel OLED phosphorescent emitters. In order to prove accuracy, robustness, and cost efficiency of a TD-DFT based method, we calculated excitation values of 14 iridium and 20 platinum complexes, previously reported in the literature, that span the entire visible spectrum and consist of different ligand constructs.

As an initial test for accuracy we employed 10 density functionals, B3LYP, CAM-B3LYP, M06, M06-L, M06-HF, M06-2X, M11, PBE0, BP86, and ωB97X-D to test the influence exact exchange, range-separated exchange, and dispersion has on calculated TD-DFT excitation values. Results show that B3LYP and M06 outperformed all other functionals within the TD-DFT framework for predicting T1 values. B3LYP and M06 functionals were then used to test the T1 values dependence on the basis set selected, Table 4. Calculated MAPD values indicate the best method as method **F**, where the optimization is performed with B3LYP/LANL2dz followed by a TD-DFT calculation with B3LYP/CEP-31G_THF to obtain triplet excitation energies. The final parameter tested was the choice of solvation model used in the calculations. The inclusion of a solvent model is extremely important for accuracy (see Tables 2 and 3). The largest impact the solvation model had on the data was on cationic complexes **Ir11**, **Ir12**, and **Ir13**. In all results, the CPCM model exhibited slight improvements over IEFPCM and SMD.

We have identified a computational method with the ability to quickly and accurately predict triplet emission energies of phosphorescent transition metal complexes used in OLED devices, requiring only ground state singlet optimizations and vertical TD-DFT calculations. While the focus in this manuscript was on the correlation of 77 K experimental data and the solvated calculations, there is also a nice agreement between 298 K data and the calculated gas phase results (Tables 2 and 3). This unexpected result will be further explored to determine how well gas phase calculations, based on the identified best method, might be able to predict the room temperature Stokes shift derived from OLED complexes with more flexible ligand types.

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Electronic Supplementary Material (ESM) available: Experimentally derived emission maxima and B3LYP/LANL2dz/gas optimized Cartesian coordinates for all complexes.

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