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Computational prediction for emission energy of iridium (III) complexes based on TDDFT calculations using exchange-correlation functionals containing various HF exchange percentages

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Abstract The accurate prediction for the emission energies of the phosphorescent Ir (III) complexes is very useful for the realizing of full-color displays and large-area solid-state lighting in OLED fields. Quantum chemistry calculations based on TDDFT methods are most widely used to directly compute the triplet vertical excitation energies, yet sometimes the universality of these calculations can be limited because of the lack of experimental data for the relative family of structural analogues. In this letter, 16 literature emission energies at low temperature are linearly correlated with their theoretical values computed by TDDFT using exchange-correlation functionals containing various HF exchange percentage with the relation of $E_{exp}^{em} = 1.2 \bar{E}_{calc}^{em}$. The relation is proven to be robust across a wide range of structures for Ir (III) complexes. These theoretical studies should be expected to provide some guides for the design and synthesis of efficient emitting materials.

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Introduction

Iridium (III) complexes possessing good thermal stabilities, microsecond excited-state lifetimes, and high luminescence efficiencies have been extensively used as the emitting layers in organic light-emitting diodes (OLEDs) [1–5]. Rationally tuning the emission energy of Ir (III) complexes from blue to red light over the entire visible range is a key step for the realizing of full-color displays and large-area solid-state lighting in OLED fields. Experimentally, considerable effort has been devoted to the design and synthesis of novel Ir complexes that give efficient blue [6–11], green [12–17], and red emissions [18–22]. The chemical modification of the coordinating ligands either through the incorporation of electron donating/withdrawing groups or extension of the π-conjugation represents the most preferred strategy. However, the general design rules to modify the emission energy remain only partially filled and the determination of the desired emission wavelength is often a process of trial and error, companying with time-consuming synthetic procedure. Ideally one would like to predict with accuracy the emission energy of a new compound before synthesis, so that the time and cost can be greatly reduced.

There have been a number of recent studies where time-dependent density functional theory (TDDFT) was used to predict the emission energies or emission wavelengths of Ir (III) complexes based on the transition of the ground state $S_0 \rightarrow$ the lowest excited triplet state T_1 ($S_0 \rightarrow T_1$ vertical excitation energies) [23–28]. Generally, Ir (III) complexes with metal-to-ligand charge-transfer character of the emissive state

are typically charge-transfer (CT) compounds. It is well-known that TDDFT method often yields errors in the excitation energies of charge-transfer states [29, 30], and the better calculated results may be reached by using exchange-correlation (XC) functionals which include a mixture of exact Hartree-Fock exchange [31]. However, there are no rules for how much exact exchange should be included for a particular system. Indeed, the HF exchange fraction is known to have a significant role in the prediction of the emission energies with TDDFT calculations [32–35]. For most cases, the selection of XC functionals in TDDFT calculations on the emission energies is often based on the known experimental data. For example, fac-tris (2-phenylpyridine) iridium fac-Ir (ppy) $_3$ with strong emission occurring in the range of 508–519 nm [36, 37] in experiments has been extensively used in OLEDs [38–43]. The predicted emission energies using TDDFT method are highly dependent on the amount of HF exchange incorporated in the XC functionals. As shown in Fig. 1, the calculated values using TD-BMK functional are in good agreement with the experimental data. Thus, TDDFT calculations with BMK functional are appreciated for predicting emission energies of Ir (ppy) $_3$ and its derivatives. However, on the other hand, it is difficult to choose the suitable XC functionals if one wishes to predict a compound within the related family of structural analogues for which no experimental data is available in the literature.

In this paper, based on the published experimental data for 16 Ir complexes with reported emission wavelengths from 388 to 688 nm (Fig. 2 and Table 1), the relationship between the calculated emission energies and the experimental ones is established with a relation of $E_{exp}^{em} = 1.2 \bar{E}_{calc}^{em}$. Employing this simple and efficient relation, we found that the agreement between calculated and experimental energies was excellent. Furthermore, a novel feature of our method is that we only need to calculate emission energies ($S_0 \rightarrow T_1$ vertical excitation energies) using XC functionals containing various HF exchange percentage at the optimized T_1 geometries, instead
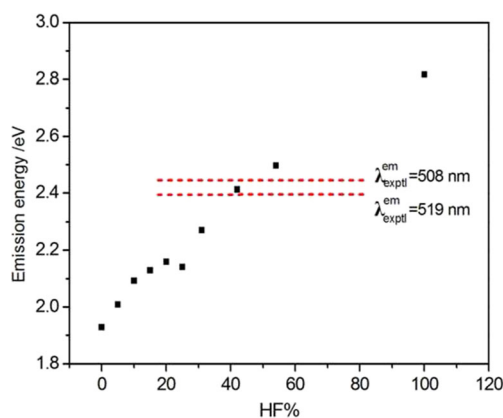

Fig. 1 Dependence of calculated emission energies of Ir (III) complex on the HF% in TDDFT functionals, together with the experimental values

of choosing the suitable XC functional based on the known experimental data.

Computational methods

The lowest excited-state triplet geometry optimization of all the Ir complexes was carried out using the B3LYP exchange-correlation functional [51, 52]. A double-ξ quality LANL2DZ basis set [53, 54] was employed for the Ir atom and a 6–31G* type basis set [55] for the remaining atoms. The influence of the basis set has been evaluated. For compounds investigated herein, the calculated results generally decrease by 0.02–0.07 eV when the basis set has been extended from 6-31G* to 6–311++G**, indicating that the influence of the basis set is limited (Table 1S, Supporting information). The TDDFT calculations using the BLYP (0%HF) [56, 57], MPWLYP1M (5%HF) [58], TPSSh (10%HF) [59], B3LYP* (15%HF) [60], B3LYP (20%HF) [51, 52], PBE1PBE (25%HF) [61, 62], MPW1B95 (31%HF) [63], BMK (42%HF) [64], M06-2X (54%HF) [65], and M06-HF (100%HF) [66] functionals based on the optimized T_1 geometries were performed to obtain emission energies E_{calc}^{em}. All calculations were performed with the Gaussian 09 software package [67].

It is known that the environment parameters, such as solvents, temperatures, and relaxation of geometry, can affect the emission energies. To minimize the number of response variables, the reference experimental values were taken in this paper from literature at low temperature (77 K and 90 K) because in rigid matrix the confined conformation is better mirrored to that of the optimized geometry in the gas phase.

Results

The nature of the lowest triplet state of all the complexes was checked by the spin density surface. The corresponding results have shown that the nature of the lowest triplet state is the same with all the functionals. TDDFT calculations with different functionals were performed to obtain the vertical emission energies E_{calc}^{em} of all the complexes in the gas phase and the corresponding data are collected in Table 2, together with the available experimental data. Here, solvent effects are not taken into account since the reference data were taken from the low temperatures where the geometry is frozen and the solvent effect is limited; however, we have determined for test cases that the differences are small (Table 2S, Supporting information).

It is evident from Table 2 that the values of E_{calc}^{em} for each complex strongly depend on the HF exchange amount. A general trend of all the complexes exhibits the increased variations with the increase of the HF exchange amount in emission energies. The poor

Fig. 2 Molecular structures of the Ir (III) complexes studied in this study
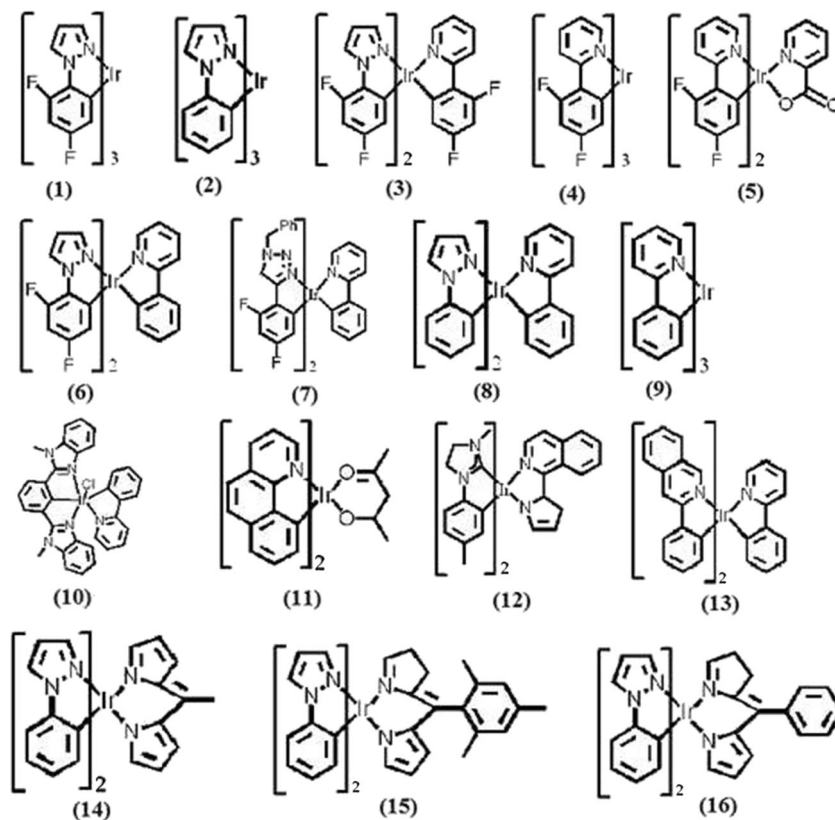
correlations with experiment were observed at the first glance. However, after further analysis of the data, a very strong correlation between $\bar{E}_{calc}^{em}$ and E_{exp}^{em} can be observed. $\bar{E}_{calc}^{em}$ denotes the average value of theoretically predicted emission energy obtained from ten XC functionals for each complex. A plot of $\bar{E}_{calc}^{em}$ versus E_{exp}^{em} displays the trend of increasing $\bar{E}_{calc}^{em}$ with increasing emission energy, as shown in Fig. 3. A good fitting line can be deduced in the plot in the following:

$$E_{exp}^{em} = 1.2\bar{E}_{calc}^{em} \tag{1}$$

Employing this relation, we recalculated the emission energies of all studied Ir (III) complexes and found that the calculated E_{calc}^{em} is in good agreement with experimental ones since the relative error is very small (< 7 %), as shown in Table 3. In addition, it is worthwhile to notice that the ΔSCF approach [68–70] is also one of the most popular methods to calculate emission energy. For comparison, ΔSCF results have been provided in Table 2, and the detailed data are listed in Table 3S, Supporting information. In our cases, it is can be seen that ΔSCF method also successfully predicts the experimental results in general. However, TDDFT gives the better linear correlation than ΔSCF method (Fig. 1S, Supporting information).

Our methodology is able to reproduce the experimental E_{exp}^{em} order for all the complexes studied, expect for complexes 6 and 7, for which the emission energy difference between them in experiment is very small.

Table 1 Experimental emission energies at low temperature for the complexes studies

Complex	Exptl	
	λ_{em}/nm	Ref
1	388[a]	[36]
2	412[a]	[36]
3	445[a]	[36]
4	454[a]	[36]
5	459[a]	[44]
6	465[a]	[36]
7	467[b]	[45]
8	479[a]	[36]
9	491[a]	[36]
10	535[c]	[46]
11	548[d]	[47]
12	579[d]	[48]
13	610[e]	[49]
14	644[a]	[50]
15	664[a]	[50]
16	668[a]	[50]

[a] In 2-MeTHF. [b] In butyronitrile glass. [c] In CH$_2$Cl$_2$-toluene (1:1 v/v). [d] In CH$_2$Cl$_2$. [e] In PMMA at 90 K

Table 2 Calculated E_{calc}^{em} using various XC functionals and LANL2DZ/6-31G* basis set in the gas phase based on the optimized T_1 geometries for all the complexes (in eV)

Complex	BLYP 0%HF	MPWLYP1M 5%HF	TPSSH 10%HF	B3LYP* 15%HF	B3LYP 20%HF	PBE0 25%HF	MPW1B95 31%HF	BMK 42%HF	M06-2X 54%HF	M06-HF 100%HF	Average[a]	ΔSCF Energy[b]	Exptl
1	2.4652	2.4891	2.4782	2.5293	2.515	2.475	2.617	2.7639	2.8672	3.1789	2.6379	2.9596	3.1959
2	2.2983	2.3373	2.3557	2.3987	2.3961	2.3654	2.5127	2.6562	2.7901	3.1615	2.5272	2.8088	3.0097
3	2.1772	2.2339	2.2591	2.3083	2.3052	2.2572	2.3932	2.5282	2.6007	2.8428	2.3906	2.6459	2.7865
4	2.1067	2.1816	2.2379	2.2844	2.2939	2.2562	2.3904	2.5306	2.6023	2.8526	2.3737	2.6083	2.7313
5	1.9934	2.0751	2.1914	2.2315	2.2766	2.2671	2.3981	2.5577	2.6454	2.9547	2.3591	2.4631	2.7015
6	2.0469	2.1035	2.1451	2.1886	2.1969	2.1554	2.2933	2.4238	2.512	2.8068	2.2872	2.4029	2.6667
7	2.0707	2.1326	2.1623	2.213	2.2119	2.156	2.301	2.423	2.5202	2.8016	2.2992	2.4398	2.6552
8	1.9910	2.0570	2.1190	2.1586	2.1785	2.1502	2.2831	2.4198	2.506	2.8179	2.2681	2.3763	2.5887
9	1.9285	2.0079	2.0917	2.1293	2.1592	2.141	2.2709	2.4124	2.4968	2.8165	2.2454)	2.3434	2.4125
10	1.5401	1.6335	1.736	1.8003	1.8652	1.8754	2.0525	2.3062	2.4669	3.0003	2.0276	2.1211	2.3178
11	1.5620	1.6587	1.7544	1.8255	1.8722	1.8382	2.0388	2.1692	2.4036	2.8434	1.9966	2.2742	2.2628
12	1.6751	1.6765	1.6367	1.6778	1.6552	1.5990	1.6887	1.7679	1.8131	1.9150	1.7105	1.8515	2.1416
13	1.4685	1.5374	1.5595	1.6244	1.6226	1.5557	1.7073	1.8217	1.9295	2.1856	1.7012	1.8346	2.0328
14	1.7027	1.679	1.6011	1.6279	1.5807	1.5064	1.5632	1.9009	1.5629	1.3935	1.6118	1.7426	1.9255
15	1.7078	1.6825	1.5884	1.6237	1.5715	1.4818	1.5499	1.918	1.5458	1.3523	1.6022	1.7349	1.8675
16	1.6787	1.6559	1.5651	1.5998	1.5483	1.4592	1.5291	1.5688	1.5362	1.3596	1.5501	1.7378	1.8563

[a] "Average" is the average of that columns for all XC functionals in the table. [b] The calculated emission energies are based on ΔSCF method.

These predicted results are very excellent from a computational standpoint considering the approximate nature in the calculations, such as basis set and solvent model. In order to further validate the application of our model, more neutral Ir (III) complexes have been examined, and satisfactory results were obtained (Table 4S, Supporting information). Compared to TDDFT method wherein the suitable XC functional must be carefully selected based on the known experimental data, the correlation obtained in this paper has the advantage that it only needs TDDFT calculations using these ten XC functionals to obtain the average emission energies. The correlation should be independent of molecule structures since these complexes are obtained from various

compounds. We believe that our method would give confidence to reliably predict emission energy for the unknown Ir (III) complexes across a wide range of structures with acceptable accuracy prior to the preparation of these materials.

Table 3 Comparison of calculated emission wavelengths and experimental ones for all the complexes (in nm)

Complex	Calc[a]/Nm	Exptl/Nm	Relative error (%)[b]
1	392	388	1.0
2	409	412	0.7
3	432	445	2.9
4	435	454	4.2
5	438	459	4.6
6	452	465	2.8
7	449	467	3.9
8	456	479	4.8
9	460	490	6.1
10	510	535	4.7
11	518	548	5.5
12	604	579	4.3
13	607	610	0.5
14	641	644	0.5
15	645	664	2.9
16	667	668	0.1

[a] Calculated by $1.2\bar{E}_{calc}^{em}$. [b] Relative error between the calculated and experimental emission.
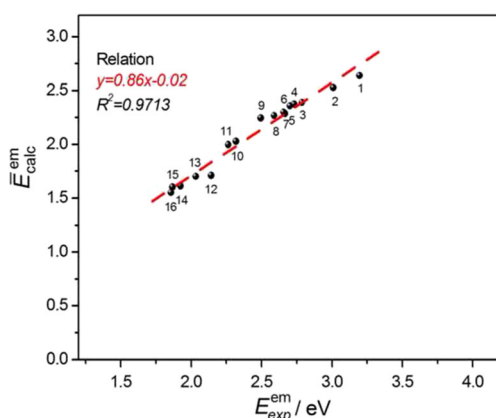
Fig. 3 Plot of $\bar{E}_{calc}^{em}$ versus E_{exp}^{em} for complexes **1–16**

Conclusions

In short, a method for accurately predicting the emission energies of neutral Ir (III) complexes on the basis of the correlation of computed average emission energies using TDDFT calculations with experimental emission energies has been established. The obtained relation can be used to predict emission energies for the unknown Ir (III) complexes across a wide range of structures with acceptable accuracy. These preliminary studies pave the way for designing and tuning of promising emitting materials before beginning a lengthy synthesis.

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