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DFT vs. TDDFT vs. TDA to simulate phosphorescence spectra of Pt- and Ir-based complexes

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This paper presents a thorough quantum investigation of the optical properties of twelve transition metal complexes using state of the art (TD)DFT computations. The studied molecules are two Pt-based and ten Ir-based complexes. Geometrical parameters, absorption and emission spectra are directly compared to available experimental data. Phosphorescence spectra have been computed within the Adiabatic Hessian (AH) method which takes into account mode mixing and a proper description of both ground and excited states potential energy surfaces (frequency calculations). For each compound, three methods have been considered to obtain the relaxed triplet excited state supposedly involved in the phosphorescence unrestricted DFT, TDDFT and its Tamm-Dancoff approximation (TDA). In overall, unrestricted DFT and TDA overperform TDDFT for the investigated complexes especially when an Ir centre is present. The AH model demonstrates its good capability to reproduce accurately phosphorescence spectra. Finally, simulation and experimental data are represented over a CIE chromaticity horseshoe.

1 Introduction

Luminescent transition metal complexes have received much attention in the two last decades since they can be used in crucial technical applications such as bio-sensing or organic light emitting diodes (OLED).^{1–7} In particular, it has been shown that some planar platinum(II) and octahedral iridium(III) complexes possess adequate properties to be used as phosphorescent emitters in OLED.^{8–10} Among others, these complexes may offer a high photoluminescence quantum efficiency and an interesting radiative rate constant.^{11–13} In addition, Pt(II) and Ir(III) complexes can emit in a large part of the visible range as their emission energies can be tuned by several means.^{14–16} Indeed, the frontier orbitals' energies can be adjusted by changing terminal moieties,^{17,18} by modifying intra- or interligand conjugation^{19,20} or by adding a metallic centre.^{21–23}

The huge amount of luminescent transition metal complexes that can be designed emphasizes the relevance to have robust theoretical tools to simulate molecular emission spectra. Density Functional Theory (DFT) offers the possibility to compute the energy of the transition responsible for phosphorescence. Recently, it has been demonstrated that the inclusion of the vibrational contributions in addition to the electronic transitions is accurate and cost-affordable.^{24,25} Different studies based on DFT succeeded

to reproduce the emission spectra of Ir(III) and Pt(II) complexes with a good agreement with experimental data.^{26–29} The solvent and temperature effects onto the phosphorescence spectra can also be taken into account in DFT.^{26,30} Despite the success of DFT to simulate emission spectra of molecular systems, the impact of the calculation method used to obtain a correct description of the triplet excited state involved in the phosphorescence process has not been extensively discussed yet. For instance, excited triplet states can be obtained from unrestricted DFT or from TDDFT calculations.^{31,32} Comparing simulated phosphorescence spectra obtained from unrestricted DFT and TDDFT calculations with respect to experimental data allows to identify the type of calculations that should be used.

To fill this gap, we started a systematic study on the optical (absorption and emission) properties of different complexes that contain a Pt(II)³³ or an Ir(III) metallic centres.^{34,35} Phosphorescence spectra were simulated within the framework of the Adiabatic Hessian (AH) approach from unrestricted DFT, TDDFT and TDA (Tamm-Dancoff approximation) triplet excited state geometries. The present article is organized as follows : in section 2 we give the computational approaches herein used, and in section 3 we present our results obtained on the computed molecular and electronic structures, together with absorption and emission spectra.

2 Computational details

The calculations presented in this study were conducted using DFT, the TDDFT and the TDA methods. All the computations were

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performed with the Gaussian16 suite of programs.³⁶ We used the hybrid exchange-correlation functional B3PW91^{37–39} since previous studies demonstrated that this functional provides satisfying results in modelling the optical properties of transition metal complexes.^{27,40,41} We employed the LANL2DZ basis set that includes relativistic effective core potentials for inner electrons of Pt and Ir,^{42–44} and augmented this basis set with polarization functions added on C(d; 0.587), N(d;0.736), O(d; 0.961), F(d; 1.577), P(d; 0.364), Cl(d; 0.648), Ir(f; 0.938) and Pt(f; 0.8018) atoms. Solvent effects (CH₂Cl₂) have been taken into account through the Polarizable Continuum Model (PCM).^{45,46} In order to facilitate numerical convergence, slight structural modifications have been applied with respect to the experimentally studied systems.^{33–35} For the Pt based complexes, methoxy and hexyl groups have been modified by hydroxy and methyl groups, respectively. All butyl moieties present on Ir based complex have been replaced by hydrogen atoms. All the geometries have been relaxed and associated Hessian matrices were diagonalized to be sure that the optimization procedures lead to true minima on the Potential Energy Surface (PES).

Absorption spectra have been calculated on ground state geometries using TDDFT.⁴⁷ Excited triplet states used to simulate phosphorescence spectra were obtained using either unrestricted DFT, TDDFT, and TDA.^{48–50} Our simulations of luminescence properties took into account the vibrational contributions to the electronic transitions. Phosphorescence spectra have been modelled using the Franck-Condon approximation together with the AH approach as implemented in the used version of Gaussian.^{24,25} AH model includes mode mixing and a proper description of both ground and excited states PES. We chose to perform AH calculations as different works emphasized the relevance of this model to simulate phosphorescence spectra of Ir(III) and Pt(II) metal complexes.^{26,27,30,51} The lowest normal modes in the vibronic treatment were neglected in order to obtain sufficient spectrum progression. We employed the class-based pre screening to limit the number of terms involved in the vibronic calculation with the following settings : $C_1^{max} = 70$, $C_2^{max} = 70$, $N_1^{max} = 100 \times 10^8$.^{52–54} For complex **1a**, analytical gradients of excited state energies have been computed at the ground state geometry to allow evaluation of vibronic effects by the general time dependent implementation employing the Vertical Gradient (VG) approximation to simulate an accurate absorption spectrum. In this model, the frequencies and normal modes of the excited state are taken to be equal to those of the ground state, and the shift between the minima of the two states is estimated by the gradient of the excited state at the geometry of the ground state.⁵⁵ The VMS software was used for data post-treatments.⁵⁶ The CIE 1931 coordinates were obtained using the software ColorCalculator and the horseshoes were plotted using an in-house python code.⁵⁷

3 Results and discussion

3.1 Ground states geometries and properties

Prior to the investigation of the excited states it is mandatory to retrieve with a decent accuracy the properties issuing from the

ground state. Those include geometrical parameters, electronic structures and electronic transitions (absorption). For the sake of clarity we kept the same compound's names with respect to their respective experimental articles.^{33–35} The molecular structures of the studied complexes are depicted in Figure 1.

3.1.1 Geometries and electronic structures

Systems **10** and **13** are square planar Pt(II) complexes.³³ Platinum atoms are bonded to two linked 2,3'-bipyridine-based C[^]N chelating ligands with F or OH terminal moieties. Complexes **11** and **13** are two Ir(III) isomers.³⁴ Ir atoms are bis-cyclometalated with pyrazolo[1,5-f]phenanthridine (*pzp*) and linked to a picolate moiety. The other complexes (named **1a**, **2a**, **2c**, **3a**, **3b**, **4a**, **4b**, and **5c**) contain an Ir center chelated by a tridentate 2-pyrazolyl-6-phenylpyridine-based ligand (*pzpyph*).³⁵ Ir atoms are also bonded with two P atoms linked to different radicals, such as Ph₃ or Ph₂CH₂Ph (Ph = phenyl). The sixth bond of the iridium atom is either un hydrogen or a chlorine atom (**4a** and **4b**), or a benzyl moiety (**5c**).

Fig. 1 Structures of the Pt based **10**, **13**,³³ and the Ir based **11**, **13**,³⁴ **1a**, **2a**, **2c**, **3a**, **3b**, **4a**, **4b**, and **5c**.³⁵ molecular compounds.

In overall, the computed geometrical parameters (relaxed geometry) of the ground states are in good agreement with respect to experiment. One should notice that the Ir-H and Ir-Cl bond lengths are slightly overestimated in our simulations by $\simeq 0.1$ and

0.2 Å, respectively. This trend is confirmed when we enforced a triple- ζ basis set, namely the DEF2TZVP (distances provided in SI). On these grounds, we started the investigation of the electronic structures of all complexes.

All frontier orbitals are provided in SI. They all clearly show that the Highest Occupied Molecular Orbitals (HOMO) are built upon the metallic centre with a strong metallic d character whereas the Lowest Unoccupied Molecular Orbitals (LUMO) are localized on the ligand's π^* . Our results are similar to the ones of previous ground state's studies using DFT.^{34,35} All the electronic HOMO-LUMO gaps remain in the same energetic range (between 3.65 and 4.10 eV) and describe a strong thermodynamics stability.

3.1.2 Electronic vertical absorption

Figure 2 exhibits the experimental and simulated (TDDFT) absorption spectra of the different compounds in CH_2Cl_2 . Table 1 gives the energy and the intensity of the main absorption bands together with the electronic theory vs. experiment shift of the first band position. The computed position of the first band of complex **10** lies 0.25 eV higher than the measured one while the other bands are in fair agreement with respect to the experimental data. Absorption of **13** is well reproduced, band energies being overestimated by ~ 0.15 eV. Simulated absorption spectra of **11** and **13** fit nicely the experimental ones. Spectra of others complex are also reproduced in a satisfying manner. We emphasize that only the measured energy and intensity of the three main bands of **3b** and **4b** are reported in the experimental article (see Table 1).³⁵ **1a**, **2a**, and **2c** calculations slightly underestimate the high energy band located around 4.5 eV by ~ 0.2 -0.3 eV. For **3a**, **3b**, **4a** and **5c**, calculations predict a band of high intensity, located between 3.73 and 3.91 eV, which correspond to band close in energy but less intense. For **4b** we predict an intense band at 3.72 eV which is not reported experimentally. The humps computed at around 4.5 eV for **3b**, **4a**, **4b** and **5c**, which can be seen in experimental spectra, are due to many transitions of low intensity and close in energy, and are therefore not reported in Table 1. The fact that simulated absorption spectra are globally in good agreement with respect to experimental ones shows the relevance of the functional and basis set used in this study. The contribution of the different orbitals to the main absorption transitions of low energy are provided in SI. As expected, departure orbital involved in the transitions around ~ 3 eV have a pronounced metallic character, leading to the so called Metal-to-Ligand Charge-Transfer (MLCT). Vibrational modes were included using the VG approach for the complex **1a** as a test case (see SI). As expected, inclusion of the vibrational contributions to the electronic transitions improves the agreement between experimental and simulated spectra. All these results gave us confidence to further investigate the triplet excited states.

3.2 Excited states geometries and properties

Three different methodologies have been considered to relax the triplet state involved in the emission process, unrestricted DFT, TDDFT and TDA. To simulate phosphorescence spectra, the vibrational contributions were added to the electronic transitions within the AH approximation. The experimental and computed

Fig. 2 Experimental (grey) and simulated (green) absorption spectra.^{33–35} HWHM= 0.12 eV for **10** and **13**, 0.20 eV for **11** and **13**, and 0.15 eV for the others complexes.

emission spectra and their relevant data are given in Figure 3 and Table 2, respectively.

All emission spectra measurements have been realized at room temperature on complexes in CH_2Cl_2 excepted for **11** and **13** where the solvent was 2-methyltetrahydrofuran (2-MeTHF). A classical LR-PCM approach was used to take into account solvent effects. Since the dielectric constant of CH_2Cl_2 (6.97) is close to the 2-MeTHF one (8.93) we considered CH_2Cl_2 for the whole

Table 1 Experimental, computed transitions (eV) together with computed oscillator strengths (f) and electronic shifts on the first absorption band (ΔE) for all complexes.^{33–35} Average and mean absolute error (MAE) of the electronic shifts are also provided.

[†] Approximately attributed from experimental spectrum.

Complex	Exp.	TDDFT (f)	ΔE
10	3.29, 3.73, 4.05, 4.54	3.54 (0.084), 3.86 (0.102), 3.93 (0.125), 4.47 (0.304)	0.25
13	2.93, 3.49, 4.23	3.07 (0.036), 3.56 (0.145), 4.42 (0.314)	0.14
I1	3.58, 4.47	3.39 (0.102), 4.29 (0.247)	-0.19
I3	3.56, 4.58	3.46 (0.104), 4.58 (0.176)	-0.10
1a	3.15, 3.63, 4.46	3.32 (0.030), 3.67 (0.060), 4.20 (0.167)	0.17
2a	3.05, 3.66, 4.54	3.25 (0.037), 3.76 (0.100), 4.26 (0.141)	0.20
2c	[†] 3.10, 3.64, 4.61	3.24 (0.029), 3.75 (0.096), 4.40 (0.301)	0.14
3a	3.12, 3.80, 4.61	3.17 (0.023), 3.90 (0.158), 4.56 (0.112)	0.05
3b	3.09, 3.81, 4.63	3.17 (0.022), 3.91 (0.150)	0.08
4a	3.06, 3.80, 4.48	3.15 (0.018), 3.75 (0.078)	0.09
4b	3.07, 4.16, 4.49	3.12 (0.014), 3.72 (0.068)	0.05
5c	2.95, 3.67, 4.59	2.96 (0.012), 3.73 (0.070)	0.01
Avg.	-	-	0.07
MAE	-	-	0.12

study.^{36,58}

3.2.1 DFT vs. TDDFT geometries

The relaxed relevant geometrical parameters are given in SI. DFT and TDDFT structures are quite similar, although small deviations appear. Pt-N and Pt-C bonds tend to shorten for complexes **10** and **13** going from the ground to the triplet excited state. For **I1** and **I3**, Ir-O and most of the Ir-C distances are shortened when complexes are in their triplet excited states whereas Ir-N distances are not significantly modified. For the other systems, Ir-N, and Ir-C distances tend to be shortened, and, on the opposite, Ir-P distances increased for those complexes when going from ground to excited states. As shown in SI, distances obtained in TDA are very similar to those obtained in TD-DFT.

3.2.2 Luminescence using unrestricted DFT

We now discuss the phosphorescence process computed by the unrestricted ansatz. Table 2 shows that the electronic energy obtained from these excited triplet states are in good agreement with respect to experiment. On these grounds, the AH approximation was used to simulate the luminescence spectra of all complexes. Figure 3 shows that the simulated spectra of complexes **10** and **13** are very well reproduced. For instance, one should mention that both the energies and the intensities of the band+shoulder of complex **10** are outstandingly reproduced in our simulation. The simulated spectra of **I1** and **I3** complexes are also satisfactorily reproduced with a slight energy deviation from experiment by 0.02 and -0.07 eV for complexes **I1** and **I3**, respectively. For the sake of clarity, other spectra will not be detailed but it is important to mention that the other luminescence simulated spectra reproduce nicely with the experimental ones.

It should be emphasized that the mean absolute error (MAE), calculated between the main experimental and simulated emission bands is rather small, around 0.1 eV (deviations ranging from -0.18 to 0.13 eV). Consequently, one may say that using unrestricted DFT together with AH ansatz is a powerful method

to simulate the phosphorescence spectrum of a transition metal complex.

3.2.3 Luminescence using TDDFT

We now focus our attention on the results from computations of the excited states using TDDFT. First, one should mention that the electronic emission may be far from experimental data. Despite a good accuracy for complexes **10**, **13**, **I1**, **I3**, **1a** and **2a** (a deviation smaller than 0.10 eV), the results for other complexes are in lesser agreement with respect to experiment with a systematic deviation around 0.5 eV. For instance, the complex's **4b** luminescence is around 2.58 eV ($\approx$ 480 nm) but is computed at 2.06 eV ($\approx$ 600 nm), which is quite far from experiment. For the comparison, the electronic emission is computed at 2.58 eV within the unrestricted paradigm.

As for unrestricted method, the spectra's shapes are nicely reproduced using AH on top of the TDDFT relaxation. However, the electronic emission MAE using TDDFT is 0.29 eV with deviations ranging from 0.08 to -0.54 eV which is far from the data obtained using the unrestricted method (MAE = 0.08) (see Table 2). Even if going from purely electronic to vibronic by inclusion of the vibrational contributions adds in most cases a strong correction, the spectra are often strongly shifted with respect to experiment. Those shifts in energy can be either positive or negative.

3.2.4 Luminescence using TDA

Triplet states were also obtained using the Tamm-Dancoff approximation for all the studied complexes. The electronic and vibronic (AH) luminescence energies are given in SI. As a first comment, one may say that even in this approximation (with respect to TDDFT) strongly affects the electronic energy, in average, it does not improve significantly the trend with respect to experiment. However, when one includes the vibrational contributions to the electronic transitions, the agreement becomes very good comparatively to experimental results. For instance, AH(TDA) gives in an average error of -0.08 eV which is very close to Unr. DFT one. Finally, the MAE is now a decent value and $\approx$ 50% lesser than TDDFT indicating that the TDA approach seems more suitable

than TDDFT to reproduce the luminescence spectra of transition metal complexes. This improvement when one enforces TDA instead of TDDFT on triplet states has already been underlined by Tozer and coworkers concerning vertical excitations.⁵⁹

3.2.5 CIE horseshoes

To fully assess the accuracy of both simulation methods, the experimental and simulated colours over a CIE 1931 chromaticity diagram have been generated of all complexes (see SI and Table 3) using the software ColorCalculator and an in-house python code.⁵⁷ The cases of complexes **I1** and **1a** are illustrated (arbitrary chosen, see Figure 4).

Colors predicted by the unrestricted method are often more accurate than TDDFT, except for complexes **10**, **13** and **I3** which are the less structured luminescence spectra. Furthermore, the colors predicted by TDA are less accurate than the Unr. DFT ones for the Pt-based complexes and for **I1** and **I3**. However TDA becomes marginally better than Unr. DFT for others complexes. In general, even if the luminescence energy (wavelength) is well reproduced in our simulations it remains insufficient to predict the exact color obtained on a CIE 1931 chromaticity diagram but remains a good tool to get a trend.

4 Conclusion

First, we need to recall the aim of this study. Is TDDFT over performing DFT when one wants to compute the phosphorescence wavelength of Ir- and Pt-based complexes? To answer this question we focused our attention on several transition metal complexes. For Pt-based complexes, as for Vazart et al.,²⁶ i.e. the deviation between TDDFT and unrestricted is small. On the contrary, the TDDFT method is erratic concerning the Ir-based complexes with electronic emission ranging from 0.08 to -0.54 eV and an MAE of almost 0.30 eV.

Excepting complexes **13**, **I1** and **I3**, the unrestricted method provides very reliable results for the electronic emission of Ir-based complexes. If one removes the aforementioned complexes, the electronic emission deviation is between 0.05 and -0.07 eV

Table 3 CIE (x,y) coordinates extracted from the measured and simulated spectra.^{33–35}

Complex	Exp.	Unrest. DFT	TDDFT	TDA
10	0.14, 0.24	0.18, 0.30	0.16, 0.23	0.15, 0.08
13	0.15, 0.54	0.15, 0.29	0.16, 0.41	0.14, 0.18
I1	0.28, 0.56	0.31, 0.53	0.43, 0.55	0.36, 0.55
I3	0.38, 0.56	0.45, 0.52	0.42, 0.55	0.48, 0.51
1a	0.24, 0.51	0.37, 0.55	0.15, 0.14	0.33, 0.57
2a	0.29, 0.57	0.42, 0.55	0.15, 0.17	0.40, 0.57
2c	0.29, 0.56	0.43, 0.54	0.57, 0.43	0.40, 0.57
3a	0.23, 0.51	0.38, 0.57	0.53, 0.47	0.36, 0.58
3b	0.24, 0.53	0.42, 0.54	0.52, 0.47	0.36, 0.59
4a	0.19, 0.49	0.39, 0.57	0.54, 0.46	0.37, 0.58
4b	0.25, 0.52	0.39, 0.57	0.54, 0.46	0.37, 0.58
5c	0.32, 0.59	0.51, 0.48	0.61, 0.39	0.46, 0.53

giving very good results.

The addition of the vibrational contributions to the electronic transitions permits us to simulate the luminescence spectra. In overall, TDA, TDDFT and unrestricted methods are able to reproduce the phosphorescence spectra of all studied complexes. However, since the electronic error with respect to experiment is very important in TDDFT for some cases, the related spectra can be strongly shifted. When one enforces unrestricted DFT, the largest absolute deviation is less than 0.20 and the mean absolute error remains around 0.10 eV in the AH ansatz. This statement is in agreement with a recent article dedicated to a large Cu₄I₄-based cluster, where the metal is formally *d*¹⁰, exhibiting two phosphorescence signatures.⁶⁰ All these results confirm that using unrestricted DFT to compute the phosphorescence wavelength is a good starting procedure to simulate the luminescence spectra. Furthermore, the Tamm-Dancoff approximation tends to strongly correct the band positions comparatively to the TDDFT when the vibrational contributions are included. This result matches a previously reported trend on fluorescence spectra.⁶¹ Since the spectra are better reproduced using the unrestricted method than TDDFT it is logical that we found a better

Table 2 Experimental, simulated (electronic and vibronic using unrestricted and TDDFT methods) emission bands in eV together with the average and the mean absolute error (MAE) with respect to the highest energy band.^{33–35}

† Approximately attributed from experimental spectra.

Complex	Exp.	Unr. DFT				TDDFT			
		Elec.	$\Delta_{\text{Elec.}}$	AH	Δ_{AH}	Elec.	$\Delta_{\text{Elec.}}$	AH	Δ_{AH}
10	2.66, 2.51	2.71	0.05	2.66, 2.51	0.00, 0.00	2.58	-0.08	2.71, 2.55	0.05, 0.04
13	2.53, 2.41	2.76	0.23	2.66, 2.51	0.13, 0.10	2.48	-0.05	2.58, 2.41	0.05, 0.00
I1	2.37	2.64	0.27	2.39	0.02	2.31	-0.06	2.29	-0.08
I3	2.28	2.49	0.21	2.21	-0.07	2.33	0.05	2.31	0.03
1a	2.60, 2.42, 2.26	2.64	0.04	2.53, 2.35, 2.20	-0.07, -0.07, -0.06	2.65	0.05	2.80, 2.64, 2.47	0.20, 0.22, 0.21
2a	2.54, 2.37, 2.22	2.53	-0.01	2.41, 2.23, 2.08	-0.13, -0.14, -0.14	2.62	0.08	2.76, 2.59, 2.43	0.22, 0.22, 0.21
2c	2.55, 2.37, 2.21	2.53	-0.02	2.43, 2.25, 2.10	-0.12, -0.12, -0.11	2.01	-0.54	2.20, 2.02, 1.87	-0.35, -0.35, -0.34
3a	2.59, 2.41, 2.27	2.58	-0.01	2.45, 2.27, 2.11	-0.14, -0.14, -0.16	2.08	-0.51	2.24, 2.06, 1.90	-0.35, -0.35, -0.37
3b	2.58, 2.41, 2.25	2.58	0.00	2.47, 2.30, 2.16	-0.11, -0.11, -0.09	2.09	-0.49	2.24, 2.07, 1.91	-0.34, -0.34, -0.34
4a	2.59, 2.42, 2.27	2.58	-0.01	2.44, 2.27, 2.11	-0.15, -0.15, -0.16	2.05	-0.54	2.23, 2.05, 1.89	-0.36, -0.37, -0.38
4b	2.58, 2.41, 2.27 [†]	2.58	0.00	2.45, 2.27, 2.11	-0.13, -0.14, -0.16	2.06	-0.52	2.23, 2.05, 1.89	-0.35, -0.36, -0.38
5c	2.50, 2.33, 2.14	2.43	-0.07	2.32, 2.14, 2.04	-0.18, -0.19, -0.10	1.96	-0.54	2.13, 1.96, 1.77	-0.37, -0.37, -0.37
Avg.	-	-	0.06	-	-0.08	-	-0.18	-	-0.14
MAE	-	-	0.08	-	0.10	-	0.29	-	0.23

Fig. 3 Experimental (grey) and simulated (blue= DFT, green= TDDFT, red= TDA) emission spectra using the AH model.^{33–35}

colour on the CIE plot for unrestricted than TDDFT.

Limitations are still present in the used approach. Especially, non negligible spin-orbit coupling is expected on organo-transition metal complex and a proper description of this coupling would be relevant.^{62–65} This would allow to compute absolute (instead of relative) intensities, the decay rate constant, and to include the Herzberg-Teller effects in the vibronic treatment. It will be interesting that future works focused onto the inclusion

Fig. 4 Experimental (circle) and simulated (triangle= DFT, square= TDDFT and diamond= TDA) rendering over a CIE 1931 chromaticity horseshoe diagrams of complexes **11** and **1a** (arbitrary chosen).

spin-orbit coupling and its effect onto the phosphorescence properties of transition metal-based complex.

Conflicts of interest

There are no conflicts to declare.

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