

## Effect of n-propyl substituents on the emission properties of blue phosphorescent iridium(III) complexes

, Paul L. Burn, and Benjamin J. Powell

Citation: *The Journal of Chemical Physics* **146**, 174305 (2017); doi: 10.1063/1.4981797

View online: <http://dx.doi.org/10.1063/1.4981797>

View Table of Contents: <http://aip.scitation.org/toc/jcp/146/17>

Published by the [American Institute of Physics](#)

---

### Articles you may be interested in

[Probing the conformational behavior of the doubly substituted methyl-ethyl Criegee intermediate by FTMW spectroscopy](#)

*The Journal of Chemical Physics* **146**, 174304174304 (2017); 10.1063/1.4982682

[Two-photon absorption spectroscopy of stilbene and phenanthrene: Excited-state analysis and comparison with ethylene and toluene](#)

*The Journal of Chemical Physics* **146**, 174102174102 (2017); 10.1063/1.4982045

[Hierarchy of stochastic Schrödinger equation towards the calculation of absorption and circular dichroism spectra](#)

*The Journal of Chemical Physics* **146**, 174105174105 (2017); 10.1063/1.4982230

[Vibronic exciton theory of singlet fission. I. Linear absorption and the anatomy of the correlated triplet pair state](#)

*The Journal of Chemical Physics* **146**, 174703174703 (2017); 10.1063/1.4982362

[A direct-compatible formulation of the coupled perturbed complete active space self-consistent field equations on graphical processing units](#)

*The Journal of Chemical Physics* **146**, 174113174113 (2017); 10.1063/1.4979844

[A combined theoretical and experimental study of the valence and Rydberg states of iodopentafluorobenzene](#)

*The Journal of Chemical Physics* **146**, 174301174301 (2017); 10.1063/1.4981919

---



**COMPLETELY  
REDESIGNED!**

**PHYSICS  
TODAY**

*Physics Today* Buyer's Guide  
Search with a purpose.

# Effect of *n*-propyl substituents on the emission properties of blue phosphorescent iridium(III) complexes

Xiuwen Zhou (周秀文),<sup>1</sup> Paul L. Burn,<sup>2,a)</sup> and Benjamin J. Powell<sup>1,a)</sup>

<sup>1</sup>*School of Mathematics and Physics, The University of Queensland, Brisbane, Queensland 4072, Australia*

<sup>2</sup>*Centre for Organic Photonics and Electronics, School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, Queensland 4072, Australia*

(Received 8 February 2017; accepted 7 April 2017; published online 4 May 2017)

Ligand substitution is often used for tuning the emission color of phosphorescent iridium(III) complexes that are used in organic light-emitting diodes. However, in addition to tuning the emission color, the substituents can also affect the radiative and non-radiative decay rates of the excited state and hence the photoluminescence quantum yield. Understanding the substituent effect is therefore important for the design of new iridium(III) complexes with specific emission properties. Using (time dependent) density functional methods, we investigate the substituent effect of *n*-propyl groups on the structure, emission color, and emission efficiency of *fac*-tris(1-methyl-5-phenyl-[1,2,4]triazolyl)iridium(III) based phosphorescent complexes by comparing the calculated results for structural models with and without the *n*-propyl substituents. We find that attachment of the *n*-propyl groups increases the length of three Ir–N bonds, and although the emission color does not change significantly, the radiative and non-radiative rates do, leading to a prediction of enhanced blue phosphorescence emission efficiency. Furthermore, the calculations show that the attachment of the *n*-propyl groups leads to a larger activation energy to degradation and the formation of dark states. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4981797>]

## INTRODUCTION

Phosphorescent iridium(III) [Ir(III)] complexes have attracted significant attention due to their use as emissive materials in organic light-emitting diodes (OLEDs). The well-known green emitter, *fac*-tris(2-phenylpyridyl)iridium(III) [Ir(ppy)<sub>3</sub>], has been reported to have a near-unity photoluminescence quantum yield (PLQY), and highly efficient OLEDs based on it have been demonstrated.<sup>1</sup> Efficient red OLEDs based on Ir(III) complexes have also been reported.<sup>2</sup> However, there is still a limited range of blue and deep-blue phosphorescent Ir(III) complexes suitable for OLEDs both in terms of color and stability. Ligand substitution with strong electron withdrawing groups has often been used to tune the emission color of sky blue emissive materials to a deeper or more saturated blue, but the changes often result in a dramatic drop in the PLQY.<sup>3–6</sup> For example, *fac*-tris(1-methyl-5-phenyl-3-*n*-propyl-[1,2,4]triazolyl)iridium(III) [Ir(ptz)<sub>3</sub>] (**1**) (complex **1** in Figure 1) displays sky blue phosphorescence with a good ambient temperature PLQY (66%). Fluorination of Ir(ptz)<sub>3</sub> (complexes **2–4** in Figure 1) not only blue shifts the emission but also dramatically lowers the PLQY at room temperature.<sup>3,7</sup>

To understand why subtle structural variations can lead to dramatic changes in the PLQY and even the quenching of the photoluminescence,<sup>8</sup> we have conducted a series of experimental and theoretical studies for the four blue emissive complexes shown in Figure 1.<sup>3,7,9</sup> The measured PLQY ( $\Phi_{PL}$ )

is dependent on the radiative ( $k_r$ ) and non-radiative ( $k_{nr}$ ) decay rates, with  $\Phi_{PL} = k_r/(k_r + k_{nr})$ . We have previously reported that for all four complexes the radiative rates are of similar magnitude, but the non-radiative rates vary significantly.<sup>3,7</sup> Therefore, the decrease in the PLQY ( $\Phi_{PL}$ ) as the complexes are tuned to achieve deeper blue emission is primarily due to an increase in the non-radiative decay. Our previous theoretical work focused on understanding the mechanism of the excited state decay processes and predicting the radiative and non-radiative rates of Ir(III) complexes.<sup>7,9–12</sup> We have shown that it is possible to theoretically predict the radiative rate using relativistic time dependent density functional theory (TDDFT) calculations that include spin-orbit coupling perturbatively.<sup>10</sup> We have also identified a key non-radiative pathway for these complexes at room temperature, namely, a thermal population to non-emissive (dark) states which arises from a significant structural distortion—the breaking of an Ir–N bond.<sup>9</sup> The non-radiative rate was qualitatively predicted through the calculation of the activation energy barrier from the emissive to dark states. We also characterized the differences between the emissive and dark states through the calculation of their radiative rates and the analysis of the nature of their frontier molecular orbitals.<sup>9</sup>

However, many theoretical studies and our previous work use simplified structural models to reduce the computational difficulties. For example, for the Ir(ptz)<sub>3</sub> based complexes of the previous study hydrogen was used in place of the *n*-propyl groups attached to the triazolyl group of the practically used complexes (see right panel of Figure 1) to make the calculations simpler. Such simplifications are generally used when the substituent is expected to have a small effect on the emission

<sup>a)</sup>Electronic addresses: p.burn2@uq.edu.au and bjpowell@gmail.com

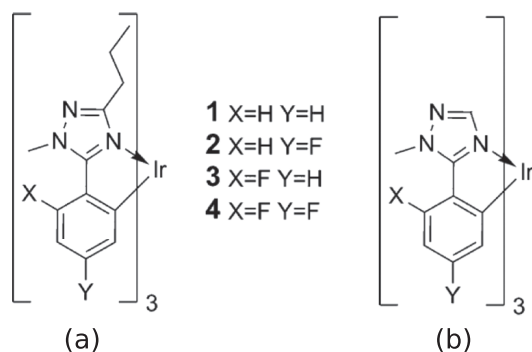


FIG. 1. (a) Structures of complexes **1–4** based on the parent *fac*-tris(1-methyl-5-phenyl-3-*n*-propyl-[1,2,4]triazolyl)iridium(III) (**1**).<sup>3,7</sup> The computational structural models used in this work are the complete models without simplification. (b) Simplified computational structural models used in our previous work<sup>7,9</sup> with the *n*-propyl groups replaced by hydrogen.

color. In the case of the Ir(PTZ)<sub>3</sub> complexes, the *n*-propyl groups are expected to have only weak inductive effect towards the ligand and not change the color of the emission dramatically.<sup>9</sup> However, how the *n*-propyl groups may affect the trend and shape of the triplet potential-energy curves and the radiative and non-radiative rates is not clear. Moreover, experimental studies have indicated that the solubilizing alkyl chains and aryl groups attached to the cyclometallating ligands of the Ir(III) complexes either cause little change in the PLQY or in some cases may cause an increase in the luminescence.<sup>13–15</sup> Therefore, it is important to know whether the *n*-propyl groups change the PLQY of the blue emissive complexes, and if they do, what is the mechanism giving rise to the change. More generally, to be able to design new blue phosphors based on Ir(III) complexes, it is of fundamental importance to understand the effect of all substituents on the emission properties, particularly the emission color and efficiency. To this end, in this paper we investigate the effect of *n*-propyl substituents on the structure, emission color, and PLQY of four blue emissive Ir(III) complexes based on Ir(PTZ)<sub>3</sub> and discuss the impact of the results on the design principles for new blue emissive Ir(III) complexes.

## THEORETICAL CALCULATIONS

### Geometry and electronic excitation

The structure of complex **1** was optimized taking the measured crystal structure<sup>3</sup> as the starting point. The structures of complexes **2–4** were then optimized with the initial structures based on the optimized structure of complex **1**. The geometry optimization was performed with density functional theory (DFT)<sup>16,17</sup> using the B3LYP<sup>18–20</sup> functional. The 6-31G\* basis set<sup>21</sup> was used for hydrogen, carbon, nitrogen, and fluorine, and the LANL2DZ basis set<sup>22</sup> with an effective core was used for iridium. Low-lying excited states were studied with TDDFT.<sup>23–25</sup> Again the B3LYP functional was used since many of the low-energy excitations of the complexes studied here have a metal-to-ligand charge transfer character. It is well known<sup>26–29</sup> that the inclusion of Hartree-Fock exact exchange significantly improves the physical description of charge-transfer excited states of small molecules in the TDDFT calculations. In addition, extensive benchmarking<sup>30</sup>

has shown that B3LYP accurately reproduces the energetics of these Ir(III) complexes.<sup>10</sup> All calculations in this work were performed using the Gaussian 09 set of programs<sup>31</sup> unless specified, with the functional and basis set described above used throughout.

### Triplet potential-energy surface

In our previous work,<sup>9</sup> we examined the possible reaction paths of thermal population to dark states<sup>6,32–37</sup> for blue emissive Ir(III) complexes and found that the elongation of an Ir–N bond was the most likely route for non-radiative decay. We therefore performed a relaxed potential-energy surface (PES) scan for the emissive state, that is, the lowest energy triplet (T<sub>1</sub>) state, along the reaction path of the elongation of an Ir–N bond. In the relaxed PES scan, the starting structure had the Ir–N bond length equal to that found in the optimized ground-state structure, and then a lengthening series of 0.1 Å increments were made in its length. The geometry at each scan point was optimized, subject to the constraint of this single extended bond length. The initial geometry for each optimization after increasing the Ir–N bond length took the position of the remaining atoms to be those found in the optimized structure for the previous Ir–N bond length. The energy of the T<sub>1</sub> state was then calculated. Unrestricted DFT was used for treating the T<sub>1</sub> states since they contain unpaired electrons. Unrestricted DFT is known to be quite good at modelling the properties of open-shell molecular systems including spin polarization (in contrast the unrestricted Hartree-Fock approximation overestimates polarization) and energetics.<sup>38</sup> To optimize the triplet states and calculate the triplet energies, a quadratically convergent self-consistent field (SCF) procedure<sup>39</sup> was used which is slower than regular SCF but more reliable.

It is worthwhile noting that the used relaxed PES scan is an approximated method for looking for the transition state and activation energy barrier, with the assumption that the reaction pathway can be described by the elongation of an Ir–N bond.<sup>9</sup> To verify whether a true transition state can be found near the energy maximum on the PES and how accurate the energy barrier is, we performed a transition state optimization calculation using the Bery algorithm with the initial structure as the energy maximum structure, for complex **1** in the simplified model. We obtained a true transition state with energy just 0.052 eV lower than that of the energy maximum. This indicates that the energy maximum on the PES indeed corresponds to a true transition state. Furthermore, the result is in agreement with the expectation that the values calculated with the approximated method represent an upper bound on the activation energy.<sup>9</sup>

### Radiative rate

Relativistic calculations were performed for selected structures to obtain the radiative rate and more accurate information on electron excitations. In these calculations, spin-orbit coupling (SOC) was included perturbatively to one-component TDDFT<sup>40</sup> utilizing the one-component zeroth order regular approximation (ZORA).<sup>41–43</sup> A total of 40 spin-mixed excitations were calculated. The calculations were carried out with ADF (2013.01 version),<sup>44</sup> using the B3LYP<sup>18–20</sup> functional and Slater type TZP basis sets<sup>45,46</sup> with a frozen

core approximation for the iridium [1s 2s 2p 3s 3p 3d 4s 4p 4d 4f], fluorine [1s], nitrogen [1s] and carbon [1s] shells.

## RESULTS AND DISCUSSION

### Structure

The first step in understanding the effect of the *n*-propyl substituents on the emissive properties was to determine whether the *n*-propyl groups caused a dramatic change to the structure of the blue emissive Ir(ptz)<sub>3</sub> complexes. The key geometric parameters of the complexes that would affect the emissive properties, that is, the interaction of the ligand with the Ir(III) cation, were compared. The comparison of the ground-state geometry calculated with complete (with *n*-propyl groups) and simplified (without *n*-propyl groups) structural models for all four complexes is summarised in Table I. We find that the Ir–N bonds are slightly longer for the *n*-propyl substituted complexes with the lengths of the three Ir–N bonds increased by around 0.04 Å compared to the simplified complexes. In contrast, the Ir–C bonds either undergo no change or a very small decrease (within 0.01 Å) in length. Thus, there are only subtle and small changes to the geometry of the structure on addition of the *n*-propyl groups.

### Emission color

In the next phase of the analysis we focused on the effect of the *n*-propyl substituents on the emission color, both qualitatively and quantitatively. It has previously been shown that for the Ir(ptz)<sub>3</sub> family of complexes, the lowest electronic excitation is predominately comprised of an electron transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).<sup>7,9,11</sup> The HOMO is a mixture of the *t*<sub>2g</sub> orbital of the metal and the  $\pi$  orbitals of the ligands, and thus has a strong mixed metal-ligand character. The LUMO is mainly comprised of the  $\pi^*$  orbitals of the ligands. Thus the inductive effect of the *n*-propyl substituents and the slight structural changes observed for the complexes would be expected to have an effect on the transition, although the significance of these affects requires quantification. We therefore studied the lowest electronic excitations to obtain a quantitative view on the effect of the *n*-propyl groups using complex **1** as the exemplar. The excitation energies of the three substates of the lowest energy triplet ( $T_1$ ) calculated for both the complete and simplified structural models are tabulated in Table II. We find that the presence of the *n*-propyl groups only has a very small effect on the excitation energies of the three substates of  $T_1$ , with changes of less than 1% in these energies.

TABLE I. Bond lengths of six Ir–ligand bonds (three Ir–N bonds and three Ir–C bonds) of complexes **1–4** at geometries optimized for the ground state in the complete and simplified structural models.

Complex	Complete model (Å)		Simplified model (Å) <sup>9</sup>	
	Ir–N <sub>1-3</sub>	Ir–C <sub>1-3</sub>	Ir–N <sub>1-3</sub>	Ir–C <sub>1-3</sub>
<b>1</b>	2.19	2.04	2.15	2.05
<b>2</b>	2.22	2.03	2.18	2.03
<b>3</b>	2.21	2.03	2.16	2.04
<b>4</b>	2.20	2.03	2.16	2.03

TABLE II. Excitation energies to the three lowest electronic excited states (i.e., the three substates of  $T_1$ :  $T_{1-1}$ ,  $T_{1-2}$ , and  $T_{1-3}$ ) of complex **1** calculated at the ground state equilibrium geometry in the complete model ( $\epsilon_{\text{comp}}$ ) and simplified model<sup>9</sup> ( $\epsilon_{\text{simp}}$ ). The absolute difference ( $d_{\text{abs}}$ ) and relative difference ( $d_{\text{relative}}$ ) are given to show differences between the excitation energies calculated from two structural models, with  $d_{\text{abs}} = |\epsilon_{\text{comp}} - \epsilon_{\text{simp}}|$  and  $d_{\text{relative}} = 2d_{\text{abs}}/(\epsilon_{\text{comp}} + \epsilon_{\text{simp}})$ . Note that the differences between the excitation energies calculated from two structural models are very small.

state	$\epsilon_{\text{comp}}$ (eV)	$\epsilon_{\text{simp}}$ (eV)	$d_{\text{abs}}$ (eV)	$d_{\text{relative}}$ (%)
$T_{1-1}$	2.8725	2.8764	0.0039	0.1
$T_{1-2}$	2.9034	2.9110	0.0076	0.3
$T_{1-3}$	2.9267	2.9110	0.0157	0.5

We also investigated the frontier molecular orbitals (HOMO and LUMO) involved in the predominant transition of these excitations. Figure 2 shows the isosurface of the HOMO and LUMO for the complete and simplified structural models of complex **1**. We found that neither the HOMO nor the LUMO has significant density on the *n*-propyl groups, as expected. This also implies that the *n*-propyl groups do not significantly affect the  $\pi$  and  $\pi^*$  orbitals of the ligands and thus the excitation energies of the lowest energy excitations. The same analysis on the excitation energies and frontier molecular orbitals has been carried out for complexes **2–4**, with a similar conclusion to that of complex **1**, that is, the *n*-propyl groups do not significantly affect the excitation energies of the lowest energy excitations. The  $T_1$  excitation energies and the frontier molecular orbitals for complexes **2–4** are provided in the [supplementary material](#). We therefore conclude that the *n*-propyl groups have a

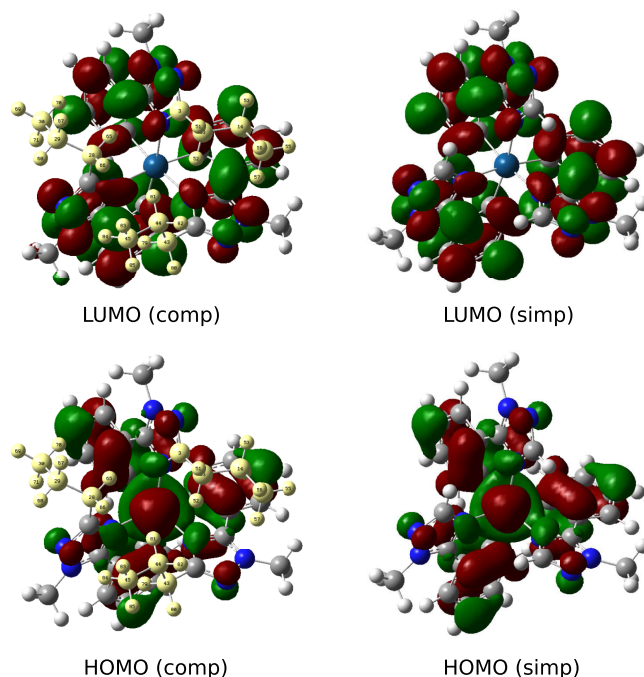


FIG. 2. Frontier molecular orbitals (HOMO and LUMO) of complex **1** at the geometry optimized for the ground state in the complete (with *n*-propyl groups, marked with “comp”) and simplified<sup>9</sup> (without *n*-propyl groups, marked with “simp”) models. For the complete model, neither the HOMO nor the LUMO has significant density on the *n*-propyl groups, the atoms of which are highlighted in light yellow.



TABLE III. Calculated radiative rates ( $k_r$ ) and activation energies ( $\Delta E_{\text{activation}}$ ) to the  $^3\text{MC}$  states for the complete and simplified models. The measured room temperature radiative rates ( $k_r$ ), non-radiative rates ( $k_{nr}$ ), and PLQYs ( $\Phi_{PL}$ ) for complexes **1-4** are also given.

Complex	Calculated (complete model)		Calculated (simplified model)		Experimental <sup>3,7</sup>		
	$k_r$ ( $\text{s}^{-1}$ )	$\Delta E_{\text{activation}}$ (eV)	$k_r$ ( $\text{s}^{-1}$ ) <sup>7</sup>	$\Delta E_{\text{activation}}$ (eV) <sup>9</sup>	$k_r$ ( $\text{s}^{-1}$ )	$k_{nr}$ ( $\text{s}^{-1}$ )	$\Phi_{PL}$
<b>1</b>	$3.5 \times 10^5$	0.728	$4.3 \times 10^5$	0.375	$(6.1 \pm 0.8) \times 10^5$	$(3.1 \pm 1.0) \times 10^5$	$0.66 \pm 0.07$
<b>2</b>	$2.5 \times 10^5$	0.935	$3.8 \times 10^5$	0.384	$(2.2 \pm 0.9) \times 10^5$	$(5.8 \pm 2.8) \times 10^5$	$0.27 \pm 0.05$
<b>3</b>	$3.0 \times 10^5$	0.580	$4.4 \times 10^5$	0.066	$4.0 \times 10^5$	$6.3 \times 10^6$	0.06
<b>4</b>	$2.5 \times 10^5$	0.132	$3.7 \times 10^5$	0.065	$(2.0 \pm 1.6) \times 10^5$	$(6.5 \pm 3.3) \times 10^6$	$0.03 \pm 0.01$

negligible effect on the lowest excited states and thus the emission color of the complexes.

### Emission efficiency (radiative rate, non-radiative rate, and PLQY)

The theoretically predicted radiative properties of the complete and simplified structural models were compared to study the effect of the *n*-propyl substituents on the emission efficiency by determining the rates of the radiative and non-radiative decay processes of the lowest excited state ( $T_1$ ) of the  $\text{Ir}(\text{ptz})_3$  complexes. The calculated radiative rate (averaged from that of the three substates of  $T_1$  state) by TDDFT with spin-orbit coupling perturbatively included is collated in Table III. We find that the radiative rates are decreased ( $\sim 35\%$ ) by the presence of the *n*-propyl groups for all four complexes although the relative magnitude of the radiative decay rates remains the same. The radiative rates of complex **1** and **3** are found to be slightly greater than that of complex **2** and **4**, which is consistent with experimental results.<sup>7</sup>

The prediction of the non-radiative decay rate is more complicated than the radiative rate since there are several

possible non-radiative paths, e.g., vibrational coupling, thermal population from emissive states to dark states, and intermolecular quenching processes. Our previous work has shown that a key non-radiative decay path is the thermal population to metal-centered triplet ( $^3\text{MC}$ ) states concomitant with the elongation and eventually breaking of an Ir–N bond. The  $^3\text{MC}$  states can be identified through the analysis of the nature of frontier orbitals, radiative rate, and the excitation energy and oscillator strength of the lowest electronic excitations. The rate of this non-radiative process can be qualitatively predicted from the activation energy barrier to the  $^3\text{MC}$  states via an Arrhenius equation,<sup>33</sup>

$$k_{nr}(T) = k_a e^{-\Delta E/k_B T}, \quad (1)$$

where  $k_a$  is the rate constant,  $\Delta E$  is the activation energy to the upper level, and  $k_B$  is the Boltzmann constant.  $k_{nr}(T)$  depends on  $\Delta E$  exponentially in contrast to its linear dependence of  $k_a$ . This suggests that the differences in the  $k_{nr}(T)$  among the four complexes are dominated by the differences in the activation energies.

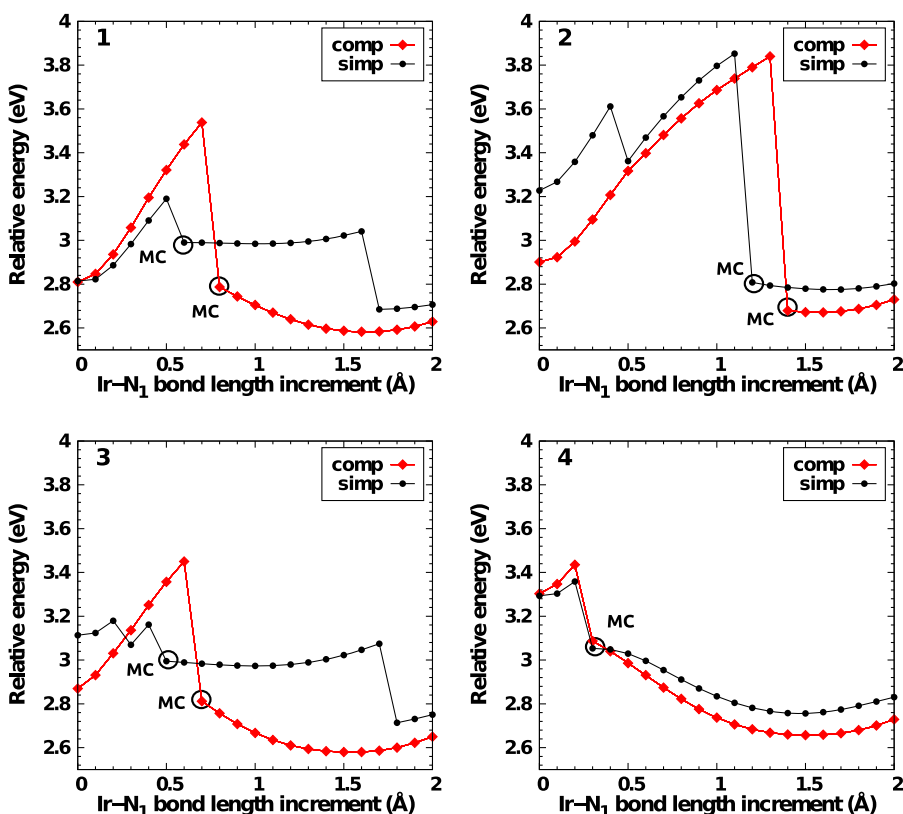


FIG. 3. Potential-energy surfaces (PESs) for complexes **1-4** as the Ir–N<sub>1</sub> bonds are lengthened (starting from the bond length in the equilibrium ground state geometry), with the remaining atomic positions optimized self-consistently. All energies are measured relative to that of the ground state. The curves labelled “comp” [red diamonds] show the energy of the lowest triplet ( $T_1$ ) state when the geometry is optimized for the  $T_1$  state for the complete structural models, and the curves labelled “simp” [black dots] show those for the simplified structural models.<sup>9</sup> The labels “MC” and the circles on the curves indicate where the character of the  $T_1$  state changes (discontinuously) from predominately metal-to-ligand charge transfer ( $^3\text{MLCT}$ ) to metal-centered ( $^3\text{MC}$ ).

TABLE IV. Calculated excitation energies ( $\epsilon$ ), oscillator strengths ( $f$ ), and radiative rates ( $k_r$ ) of the three lowest energy electronic excitations (i.e., the three substates of  $T_1$ ) of the  $^3MC$  states found for complexes **1-4** for the complete model.

Complex	Excitation 1			Excitation 2			Excitation 3		
	$\epsilon$ (eV)	$f$	$k_r$ ( $s^{-1}$ )	$\epsilon$ (eV)	$f$	$k_r$ ( $s^{-1}$ )	$\epsilon$ (eV)	$f$	$k_r$ ( $s^{-1}$ )
<b>1</b>	0.75	$2 \times 10^{-5}$	$5.2 \times 10^2$	0.76	$7 \times 10^{-5}$	$1.7 \times 10^3$	0.78	$7 \times 10^{-5}$	$1.9 \times 10^3$
<b>2</b>	0.45	$2 \times 10^{-4}$	$1.3 \times 10^3$	1.24	$4 \times 10^{-6}$	$2.4 \times 10^2$	1.24	$6 \times 10^{-6}$	$4.0 \times 10^2$
<b>3</b>	0.94	$3 \times 10^{-5}$	$1.1 \times 10^3$	0.94	$8 \times 10^{-5}$	$3.2 \times 10^3$	0.97	$7 \times 10^{-5}$	$2.7 \times 10^3$
<b>4</b>	1.18	$1 \times 10^{-5}$	$5.8 \times 10^2$	1.18	$3 \times 10^{-5}$	$1.5 \times 10^3$	1.23	$6 \times 10^{-5}$	$3.8 \times 10^3$

The activation energy barrier to the  $^3MC$  states can be calculated using the potential energy surface (PES) for the lowest triplet ( $T_1$ -PES) along the reaction path, which relates to the elongation of an Ir–N bond. We have therefore investigated how the *n*-propyl groups change the  $T_1$ -PES and the activation energy to the  $^3MC$  states. The  $T_1$ -PESs calculated for both the complete and simplified structural models are shown in Figure 3. The trend of the  $T_1$ -PESs calculated from the complete structures (with the *n*-propyl groups) remains similar to that calculated from simplified structural model. For all four complexes, the  $T_1$  state energy starts with an approximately quadratic rise reaching a local maximum, which is then followed by a sudden drop to a relatively flat region. However, the presence of the *n*-propyl groups has a significant effect on the shape of the  $T_1$ -PESs of complexes **1-3**, which become less structured—only one local maximum is found (whereas two local maxima were found on the  $T_1$ -PESs of complexes **1-3** calculated for the simplified models). It is interesting to note that the changes are much less pronounced in complex **4**, with the PESs calculated for both the complete and simplified models having only one local maximum with a similar Ir–N bond length and only slightly larger energy pathway for the former.

The activation energy for excitation to the  $^3MC$  dark states is the key quantity for the analysis of the non-radiative rate. It is thus of particular interest to see how the *n*-propyl substituents affect the activation energy and hence the non-radiative rate. The first step in the analysis was to identify the state on the PES where the  $T_1$  state changes from predominantly metal-to-ligand charge transfer ( $^3MLCT$ ) to  $^3MC$ .<sup>9</sup> We find that for all four complexes the transition between the  $^3MLCT$  and  $^3MC$  states occurs after the first energy maximum, and after this radiative decay is turned off. For all four  $^3MC$  states the frontier MOs have metal centered character, and the radiative rates of these states are two orders of magnitude smaller than that of the  $^3MLCT$  states (see Table IV). Thus the radiative decay is not competitive with the non-radiative decay processes, with the found  $^3MC$  states being dark.

The height of the activation barriers to  $^3MC$  states for the *n*-propyl substituted complexes is summarized in Table III and is compared with those calculated for the simplified structure models. We found that the activation energy barrier was higher when the *n*-propyl groups were present for all four complexes, that is, the attachment of the *n*-propyl groups makes the structural distortions leading to Ir–N bond breaking more difficult. As the *n*-propyl groups are electron donating inductively,

the N-atom involved in the dative bond to the Ir(III) would be more nucleophilic, which would lead to a stronger coulombic interaction and an enhanced ability to undergo structural distortions without irreversible breaking. Given that the non-radiative decay rate decreases exponentially with the activation energy, this increase of activation energy should result in a significant decrease in the non-radiative rate. Since the radiative rates are changed only slightly, the overall effect of the *n*-propyl substituents is that they should lead to these complexes having a higher PLQY. Interestingly, the *n*-propyl groups do not change the order of the activation energy for the four complexes, that is,  $\Delta E_{activation}(\mathbf{2}) > \Delta E_{activation}(\mathbf{1}) > \Delta E_{activation}(\mathbf{3}) > \Delta E_{activation}(\mathbf{4})$ .

## CONCLUSIONS

We have shown that the addition of *n*-propyl groups to the triazolyl rings of Ir(III) complexes increases the length of the Ir–N bond. Although the emission color is not changed significantly, the presence of the *n*-propyl groups does affect the emission efficiency by changing the radiative and non-radiative rates of decay. The radiative rates are all reduced by  $\sim 30\%$  but the non-radiative rates decrease exponentially due to a significantly increased activation energy barrier to the formation of  $^3MC$  dark states. Thus, the addition of *n*-propyl substituents is predicted to lead to an increase in the PLQY. The study has provided a theoretical basis for the design of new phosphorescent Ir(III) complexes using bulky substituents attached to the ligand. Furthermore, it provides an explanation as to why the addition of large substituents on both the triazolyl and phenyl rings of complex **2** increased the PLQY dramatically from 27% to 94%.<sup>47</sup>

## SUPPLEMENTARY MATERIAL

See [supplementary material](#) for frontier molecular orbitals and excitation energies to the lowest triplet for complexes **2-4** and listings of the Cartesian coordinates of the optimized ground-state geometry of complexes **1-4** in the complete structural model.

## ACKNOWLEDGMENTS

We thank Shih-Chun Lo for helpful discussions. X.Z. is a University of Queensland Development Fellow (No. UQFEL1717733) and was supported by a Swiss National Science Foundation Early Postdoc.Mobility Fellowship (No.

P2GEP2\_155709) and an Australia-APEC Woman in Research Fellowship (2016). P.L.B. was supported by a University of Queensland Vice-Chancellor's Research Focused Fellowship and is an Australian Research Council (ARC) Laureate Fellow (No. FL160100067). B.J.P. was supported by an ARC Future Fellowship (No. FT130100161). This research was undertaken with the assistance of resources provided at the NCI National Facility systems at the Australian National University through the National Computational Merit Allocation Scheme supported by the Australian Government, including Grant No. LE120100181.

- <sup>1</sup>C. Adachi, M. A. Baldo, S. R. Forrest, and M. E. Thompson, *Appl. Phys. Lett.* **77**, 904 (2000).
- <sup>2</sup>H. Yersin, A. F. Rausch, R. Czerwiec, T. Hofbeck, and T. Fischer, *Coord. Chem. Rev.* **255**, 2622 (2011).
- <sup>3</sup>S.-C. Lo, C. P. Shipley, R. N. Bera, R. E. Harding, A. R. Cowley, P. L. Burn, and I. D. W. Samuel, *Chem. Mater.* **18**, 5119 (2006).
- <sup>4</sup>Y.-S. Yeh, Y.-M. Cheng, P.-T. Chou, G.-H. Lee, C.-H. Yang, Y. Chi, C.-F. Shu, and C.-H. Wang, *ChemPhysChem* **7**, 2294 (2006).
- <sup>5</sup>T. Karatsu, E. Ito, S. Yagai, and A. Kitamura, *Chem. Phys. Lett.* **424**, 353 (2006).
- <sup>6</sup>T. Sajoto, P. I. Djurovich, A. B. Tamayo, J. Oxgaard, W. A. Goddard III, and M. E. Thompson, *J. Am. Chem. Soc.* **131**, 9813 (2009).
- <sup>7</sup>A. R. G. Smith, M. J. Riley, P. L. Burn, I. R. Gentle, S.-C. Lo, and B. J. Powell, *Inorg. Chem.* **51**, 2821 (2012).
- <sup>8</sup>A. C. Jacko, B. J. Powell, and R. H. McKenzie, *J. Chem. Phys.* **133**, 124314 (2010).
- <sup>9</sup>X. Zhou, P. L. Burn, and B. J. Powell, *Inorg. Chem.* **55**, 5266 (2016).
- <sup>10</sup>B. J. Powell, *Coord. Chem. Rev.* **295**, 46 (2015).
- <sup>11</sup>B. J. Powell, *Sci. Rep.* **5**, 10815 (2015).
- <sup>12</sup>A. C. Jacko, R. H. McKenzie, and B. J. Powell, *J. Mater. Chem.* **20**, 10301 (2010).
- <sup>13</sup>C.-H. Yang, M. Mauro, F. Polo, S. Watanabe, I. Muenster, R. Fröhlich, and L. De Cola, *Chem. Mater.* **24**, 3684 (2012).
- <sup>14</sup>D. Rota Martir, A. K. Bansal, V. Di Mascio, D. B. Cordes, A. F. Henwood, A. M. Z. Slawin, P. C. J. Kamer, L. Martinez-Sarti, A. Pertegas, H. J. Bolink, I. D. W. Samuel, and E. Zysman-Colman, *Inorg. Chem. Front.* **3**, 218 (2016).
- <sup>15</sup>V. N. Kozhevnikov, Y. Zheng, M. Clough, H. A. Al-Attar, G. C. Griffiths, K. Abdullah, S. Raisys, V. Jankus, M. R. Bryce, and A. P. Monkman, *Chem. Mater.* **25**, 2352 (2013).
- <sup>16</sup>P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- <sup>17</sup>W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- <sup>18</sup>P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.* **98**, 11623 (1994).
- <sup>19</sup>A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- <sup>20</sup>C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- <sup>21</sup>P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* **28**, 213 (1973).
- <sup>22</sup>P. J. Hay and W. R. Wadt, *J. Chem. Phys.* **82**, 299 (1985).
- <sup>23</sup>M. E. Casida, "Time-dependent density functional response theory for molecules," in *Recent Advances in Density Functional Methods*, edited by D. P. Chong (World Scientific, 1995), Vol. 1, p. 155.
- <sup>24</sup>M. E. Casida, *J. Mol. Struct.: THEOCHEM* **914**, 3 (2009).
- <sup>25</sup>E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984).
- <sup>26</sup>A. Dreuw, J. L. Weisman, and M. Head-Gordon, *J. Chem. Phys.* **119**, 2943 (2003).
- <sup>27</sup>A. Dreuw and M. Head-Gordon, *J. Am. Chem. Soc.* **126**, 4007 (2004).
- <sup>28</sup>D. J. Tozer, *J. Chem. Phys.* **119**, 12697 (2003).
- <sup>29</sup>D. J. Tozer, R. D. Amos, N. C. Handy, B. O. Roos, and L. Serrano-Andres, *Mol. Phys.* **97**, 859 (1999).
- <sup>30</sup>A. R. G. Smith, P. L. Burn, and B. J. Powell, *Org. Electron.* **33**, 110 (2016).
- <sup>31</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *GAUSSIAN 09*, Revision E.01, Gaussian, Inc., Wallingford CT, 2009.
- <sup>32</sup>J. Van Houten and R. J. Watts, *Inorg. Chem.* **17**, 3381 (1978).
- <sup>33</sup>T. J. Meyer, *Pure & Appl. Chem.* **58**, 1193 (1986).
- <sup>34</sup>J. A. G. Williams, "Photochemistry and photophysics of coordination compounds: Platinum," in *Photochemistry and Photophysics of Coordination Compounds II*, edited by V. Balzani and C. Sebastiano (Springer, 2007), p. 205.
- <sup>35</sup>*Highly Efficient OLEDs with Phosphorescent Materials*, edited by H. Yersin (John Wiley & Sons, 2008).
- <sup>36</sup>G. Treboux, J. Mizukami, M. Yabe, and S. Nakamura, *Chem. Lett.* **36**, 1344 (2007).
- <sup>37</sup>L. Yang, F. Okuda, K. Kobayashi, K. Nozaki, Y. Tanabe, Y. Ishii, and M.-a. Haga, *Inorg. Chem.* **47**, 7154 (2008).
- <sup>38</sup>A. S. Menon and L. Radom, *J. Phys. Chem. A* **112**, 13225 (2008).
- <sup>39</sup>G. B. Bacskay, *Chem. Phys.* **61**, 385 (1981).
- <sup>40</sup>F. Wang and T. Ziegler, *J. Chem. Phys.* **123**, 154102 (2005).
- <sup>41</sup>C. Chang, M. Pelissier, and P. Durand, *Phys. Scr.* **34**, 394 (1986).
- <sup>42</sup>E. Van Lenthe, E. J. Baerends, and J. G. Snijders, *J. Chem. Phys.* **99**, 4597 (1993).
- <sup>43</sup>E. Van Lenthe, E. J. Baerends, and J. G. Snijders, *J. Chem. Phys.* **101**, 9783 (1994).
- <sup>44</sup>E. J. Baerends, T. Ziegler, J. Autschbach, D. Bashford, A. Bérces, F. M. Bickelhaupt, C. Bo, P. M. Boerrigter, L. Cavallo, D. P. Chong, L. Deng, R. M. Dickson, D. E. Ellis, M. van Faassen, L. Fan, T. H. Fischer, C. Fonseca Guerra, M. Franchini, A. Ghysels, A. Giammona, S. J. A. van Gisbergen, A. W. Götz, J. A. Groeneveld, O. V. Gritsenko, M. Grüning, S. Gusarov, F. E. Harris, P. van den Hoek, C. R. Jacob, H. Jacobsen, L. Jensen, J. W. Kaminski, G. van Kessel, F. Kootstra, A. Kovalenko, M. V. Krykunov, E. van Lenthe, D. A. McCormack, A. Michalak, M. Mitoraj, S. M. Morton, J. Neugebauer, V. P. Nicu, L. Noodleman, V. P. Osinga, S. Patchkovskii, M. Pavanello, P. H. T. Philipsen, D. Post, C. C. Pye, W. Ravenek, J. I. Rodríguez, P. Ros, P. R. T. Schipper, G. Schreckenbach, J. S. Seldenthuis, M. Seth, J. G. Snijders, M. Solà, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T. A. Wesolowski, E. M. van Wezenbeek, G. Wiesenecker, S. K. Wolff, T. K. Woo, A. L. Yakovlev, *ADF/SCM, Theoretical Chemistry (Vrije Universiteit, Amsterdam, The Netherlands, 2013)*, <http://www.scm.com>.
- <sup>45</sup>E. Van Lenthe and E. J. Baerends, *J. Comput. Chem.* **24**, 1142 (2003).
- <sup>46</sup>D. P. Chong, *Mol. Phys.* **103**, 749 (2005).
- <sup>47</sup>S.-C. Lo, R. E. Harding, C. P. Shipley, S. G. Stevenson, P. L. Burn, and I. D. W. Samuel, *J. Am. Chem. Soc.* **131**, 16681 (2009).