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Reverse saturable absorption (RSA) in fluorinated iridium derivatives

Michael J. Ferry, Ryan M. O'Donnell, Neal Bambha, Trenton R. Ensley, William M. Shensky III,
Jianmin Shi

Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD, USA 20783-1197

ABSTRACT

The photophysical properties of cyclometallated iridium compounds are beneficial for nonlinear optical (NLO) applications, such as the design of reverse saturable absorption (RSA) materials. We report on the NLO characterization of a family of compounds of the form $[\text{Ir}(\text{pbt})_2(\text{LX})]$, where pbt is 2-phenylbenzothiazole and LX is a beta-diketonate ligand. In particular, we investigate the effects of trifluoromethylation on compound solubility and photophysics compared to the parent acetylacetonate (acac) version. The NLO properties, such as the singlet and triplet excited-state cross sections, of these compounds were measured using the Z-scan technique. The excited-state lifetimes were determined from visible transient absorption spectroscopy.

Keywords: RSA, iridium, nonlinear, Z-scan

1. INTRODUCTION

Heavy transition metals exhibit large spin-orbit coupling (SOC) constants which enable rapid intersystem crossing from excited state singlets to triplet states. These triplet states are typically long lived, hundreds of ns and longer, which render them as useful candidates for Reverse Saturable Absorption (RSA) applications. Previously, our group has studied RSA materials containing platinum^{1, 2} and iridium^{3, 4} metal centers. We continue the exploration of iridium complexes here in the context of RSA materials development.

Two iridium compounds were synthesized with the same core structure, $[\text{Ir}(\text{pbt})_2(\text{LX})]$ where pbt is the cyclometallating 2-phenylbenzothiazole ligand and LX represents an anionic ancillary ligand. “Ancillary” ligands are referred to as such in the literature because the metal-to-ligand charge transfer (MLCT) transitions that govern the absorption and excited state properties of cyclometallated iridium compounds are predominantly ascribed to the “ $\text{Ir}(\text{pbt})_2$ ” core.^{5, 6} However, recent work by Yersin and Thompson demonstrated that these ancillary ligands may not be entirely innocent and can affect SOC between excited states.⁷ In order to determine the control that ancillary ligands exert on RSA properties, we varied the LX ligand using β -diketonate moieties of either electron donating or withdrawing character. $[\text{Ir}(\text{pbt})_2(\text{dpm})]$, where dpm is dipivaloylmethane, was chosen due to the electron donating character of the tert-butyl groups when compared to the parent acetylacetonate, acac, compound. $[\text{Ir}(\text{pbt})_2(\text{hfacac})]$, where hfacac is 1,1,1,5,5,5-hexafluoroacetylacetonate, was designed to contrast with $[\text{Ir}(\text{pbt})_2(\text{dpm})]$ due to the electron withdrawing nature of the trifluoromethyl groups on the β -diketonate ligand. The chemical structures for the compounds studied are given in Figure 1. In this work, we demonstrate that the β -diketonate ligand choice drastically affects the excited state lifetime of the compounds which results in significantly different RSA properties.

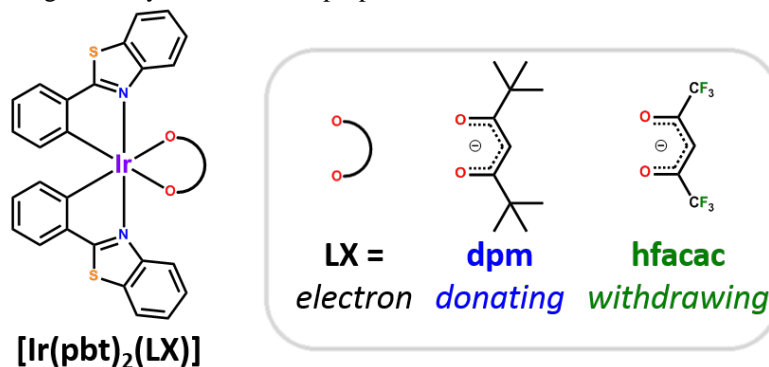


Figure 1. Chemical structures of $[\text{Ir}(\text{pbt})_2(\text{dpm})]$ and $[\text{Ir}(\text{pbt})_2(\text{hfacac})]$.

2. EXPERIMENT/METHODOLOGY

2.1 Chemistry

All solvents and reagents were purchased from Sigma-Aldrich and used as received. ^1H NMR spectra were measured on a Bruker 400 or 600 MHz Avance NMR spectrometer, referenced to the internal residual solvent peak, and processed using Mnova software.

The compounds were synthesized using previously reported procedures.^{6,8} The appropriate β -diketonate derivative (3 equivalent) was added to a suspension of $[\text{Ir}(\text{pbt})_2\text{Cl}]_2$ dimer (1 equivalent) in dichloromethane. Tetrabutylammonium hydroxide (1.0 M in MeOH, 3-5 equivalent) was added to the mixture which was subsequently refluxed for 16 h under nitrogen. After cooling to room temperature, the crude reaction mixture was filtered through a silica plug using dichloromethane as the eluent. The solution volume was reduced under reduced pressure via rotary evaporator and ethanol was added to induce precipitation. The suspension was cooled in a refrigerator (3 °C) for one hour to yield orange or red microcrystalline powders. The solids were collected by vacuum filtration on a Buchner funnel, washed with cold ethanol, diethyl ether, and hexanes, and dried in a vacuum oven (55 °C). Yields: 50 – 80%.

$[\text{Ir}(\text{pbt})_2(\text{dpm})]$ where the free ligand dpm is dipivaloylmethane, or 2,2',6,6'-tetramethyl-3,5-heptanedione:

^1H NMR ($(\text{CD}_3)_2\text{CO}$, 600 MHz): 8.16 (dd, 2H, $J = 7.8, 0.6$ Hz), 8.02 (d, 2H, $J = 7.8$ Hz), 7.75 (dd, 2H, $J = 7.2, 0.6$ Hz), 7.52 (td, 2H, $J = 7.8, 1.2$ Hz), 7.45 (td, 2H, $J = 7.8, 1.2$ Hz), 6.86 (td, 2H, $J = 7.2, 1.2$ Hz), 6.62 (td, 2H, $J = 7.2, 1.8$ Hz), 6.50 (d, 2H, $J = 7.8$ Hz), 5.49 (s, 1H), 0.82 (s, 18H).

$[\text{Ir}(\text{pbt})_2(\text{hfacac})]$ where the free ligand hfacac is 1,1,1,5,5,5-hexafluoroacetylacetone:

^1H NMR ($(\text{CD}_3)_2\text{CO}$, 600 MHz): δ 8.29 (d, 2H, $J = 8.4$ Hz), 7.82 (d, 2H, $J = 7.8$ Hz), 7.79 (d, 2H, $J = 8.4$ Hz), 7.62 (td, 2H, $J = 7.8, 1.2$ Hz), 7.58 (td, 2H, $J = 7.8, 1.2$ Hz), 6.95 (td, 2H, $J = 7.8, 1.2$ Hz), 6.71 (td, 2H, $J = 7.8, 1.2$ Hz), 6.39 (d, 2H, $J = 7.8$ Hz), 6.00 (s, 1H).

2.2 Absorption spectroscopies

UV-Vis absorption spectra were recorded using a Shimadzu UV-2700 spectrophotometer using 1 mm borosilicate glass cuvettes (Spectrocell). The transient absorption setup (HELIOS/EOS, Ultrafast Systems) was described in a previous work⁹ and was pumped by an amplified Ti:Sapphire laser system (Solstice, Spectra-Physics) producing 800 nm, 3.5 mJ, 100 fs (FWHM) pulses at a 1 kHz repetition rate.

2.3 Z-scans

To determine singlet and triplet cross sections, σ_S and σ_T , we performed Z-scans¹⁰ of the two iridium compounds along with the reference standard C60.

A single longitudinal, single transverse mode Gaussian laser (NL-101SH, EKSPLA) producing 8 ns (FWHM), 532 nm pulses at a 10 Hz repetition rate was focused by a $f=150$ mm lens to a $22\mu\text{m}$ waist for the open aperture ns Z-scan. The Rayleigh Range for the Z-scan was 2.9 mm, longer than the 1 mm path length of the cell. The sample was scanned over a ± 50 mm range about focus, with a gradient in the step interval from a maximum of 2 mm at the wings, to 0.25 mm near focus, generating greater point density in the region of interest, and maintaining an accurate baseline measurement in the wings. Each data point is a 5 shot average within a 2% energy window about each energy reading.

For the picosecond Gaussian Z-scans, the frequency doubled output from a single longitudinal mode laser (PL2230, EKSPLA) produced 30 ps (FWHM), 532 nm pulses at a 10 Hz repetition rate. The beam was not diffraction limited, with $M^2 = 1.46$. We focused this beam 4.4 mm beam with a 250 mm lens to achieve a $22\mu\text{m}$ waist and Rayleigh range of 2 mm.¹¹ We scanned with the same point density and energy windows on the ps and ns Z-scans.

Focal spot size was determined via imaging with magnification.¹² With a magnification of 14, we had 85 pixels across the beam, and accurately determined the beam waist to be $22.0\mu\text{m}$ for the ns and ps Z-scans. Using this beam waist, we confirm the reported values for C_{60} of $16 \times 10^{-18} \text{ cm}^2$ for the singlet excited state cross section, σ_S , and $13 \times 10^{-18} \text{ cm}^2$ for the triplet cross section, σ_T .¹³⁻¹⁵

2.4 Theory

The data files were analyzed by the ARL software application called Scanalyzer, developed with MATLAB. The application includes a graphical user interface and implements a five-level intensity-based model. This model was first described by Guiliano and Hess.¹⁶ In this model, the propagation of the laser beam is expressed in terms of intensity, and is coupled to the rate equations of the five-level system. An energy level diagram is shown in Figure 2 below.

The time evolution of the population density of the five levels are modeled through a coupling of the rate equations with the optical absorption from the laser. In the software application, the temporal profile was chosen to be Gaussian. The spatial profile of the laser was characterized and modeled using a beam quality factor M^2 . Each level has an absorption cross section. RSA occurs when the cross section of one or more of the excited states is greater than the cross section of the ground state.

The Z-scan data was modeled by calculating the spatial profile of the beam at each location in z , and then propagating this beam through the sample. For the e-scan data, the spatial profile of the beam at focus was calculated, and the energy was varied across the range of energies used in the experiment. The Z-scan data and e-scan data were fit to the five-level model in these samples by varying the triplet cross section (σ_T in Figure 2) and minimizing the root mean square difference between the data points and the model.

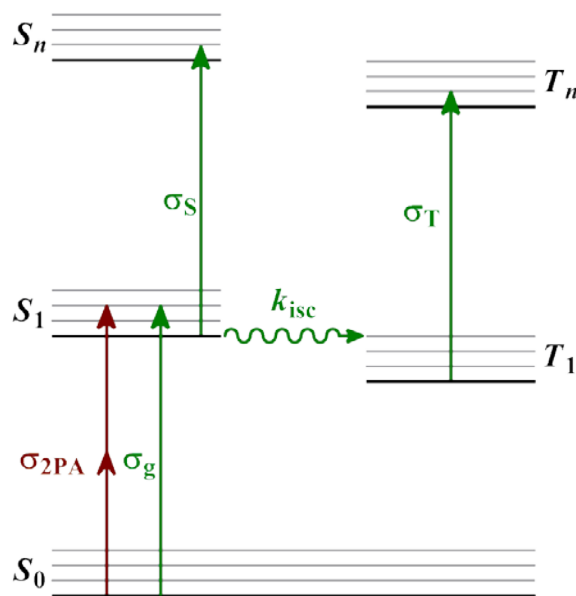


Figure 2. Five-level model

3. DATA AND MODELING

3.1 Molar Absorptivity

The molar absorption spectra for $[\text{Ir}(\text{pbt})_2(\text{dpm})]$ and $[\text{Ir}(\text{pbt})_2(\text{hfacac})]$ dissolved in toluene are presented in Figure 3. Both compounds exhibited broad absorption bands in the visible with molar absorption coefficients, ϵ , on the order of $5,000 - 10,000 \text{ M}^{-1}\text{cm}^{-1}$ which were attributed to a mixture of metal-to-ligand charge transfer (MLCT) and ligand-localized charge transfer (LLCT) transitions by analogy to previously reported assignments, *i.e.* $[\text{Ir}^{\text{III}}(\text{pbt})_2(\text{acac})]^0 \rightarrow [\text{Ir}^{\text{IV}}(\text{pbt})(\text{pbt}^-)(\text{acac})]^0$.^{8, 17} Compared to $[\text{Ir}(\text{pbt})_2(\text{dpm})]$, the absorption spectra for the fluorinated derivative $[\text{Ir}(\text{pbt})_2(\text{hfacac})]$ was hypsochromically shifted by $\sim 25 \text{ nm}$. This could result from the electron withdrawing nature of the trifluoromethyl groups and lead to a more positive $\text{Ir}^{\text{III/IV}}$ redox potential which would manifest as an increased HOMO-LUMO gap compared to the $[\text{Ir}(\text{pbt})_2(\text{dpm})]$ compound.

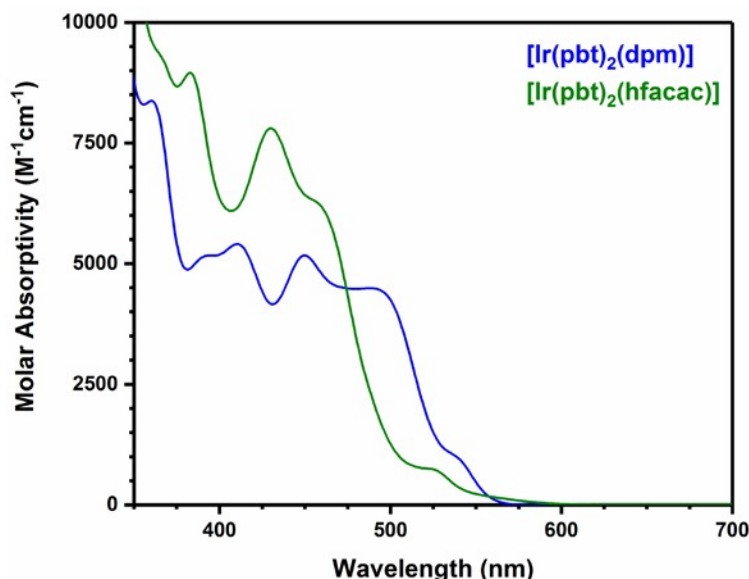


Figure 3. Molar absorptivity spectra for $[\text{Ir}(\text{pbt})_2(\text{dpm})]$ and $[\text{Ir}(\text{pbt})_2(\text{hfacac})]$ in toluene.

3.2 Transient absorption spectroscopy and excited state kinetics

Ultrafast transient absorption spectra of the compounds were obtained in toluene solutions using 400 nm femtosecond pulses for the pump and white light continuum generated in a sapphire crystal for the probe, and are shown in Figure 4. The ultrafast transient absorption data for $[\text{Ir}(\text{pbt})_2(\text{dpm})]$ in toluene did not display any ultrafast kinetics and agreed well with nanosecond data (shown as a 5 ns overlaid on the 5 ps delay data in Figure 4). The triplet excited state exhibited single exponential decay kinetics with a lifetime of 1.32 μs . The excited state lifetime for $[\text{Ir}(\text{pbt})_2(\text{hfacac})]$ in toluene was found to be four orders of magnitude shorter, 240 ps. The lifetimes are collected in Table 2.

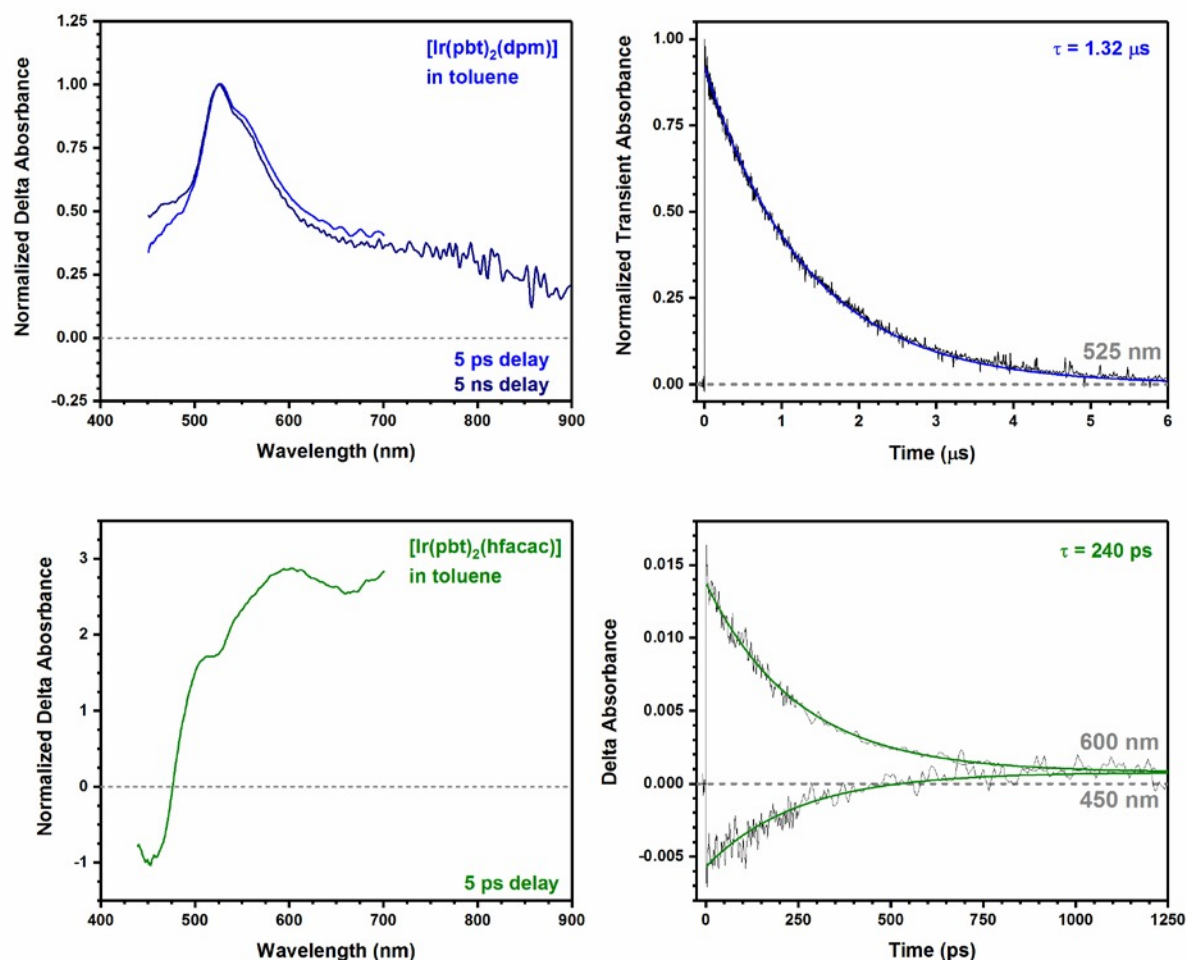


Figure 4. Transient absorption spectra and single-wavelength kinetics of $[\text{Ir}(\text{pbt})_2(\text{dpm})]$ (blue, top) and $[\text{Ir}(\text{pbt})_2(\text{hfacac})]$ (green, bottom) in toluene with overlaid fits to experimental data.

3.3 Z-scans

Picosecond Z-scans are in Figure 5, with the nanosecond Z-scans given in Figure 6. The results are tabulated in Table 1.

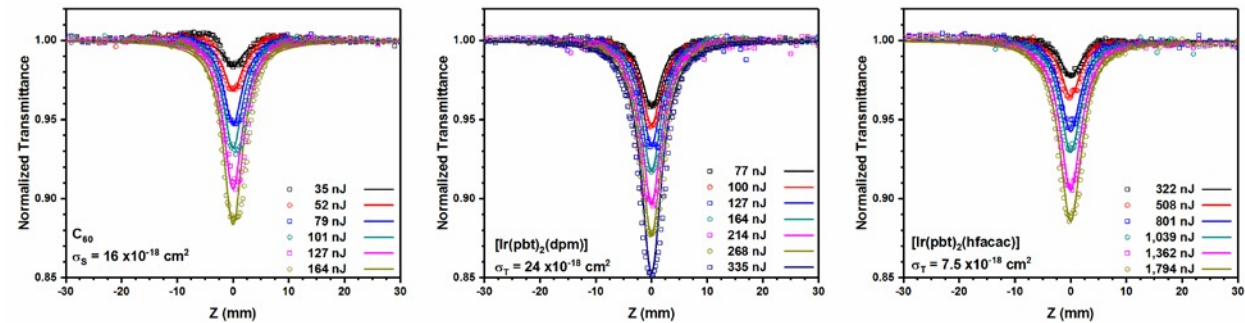


Figure 5. ps Z-scans with fits (solid lines) overlaid on experimental data (open symbols).

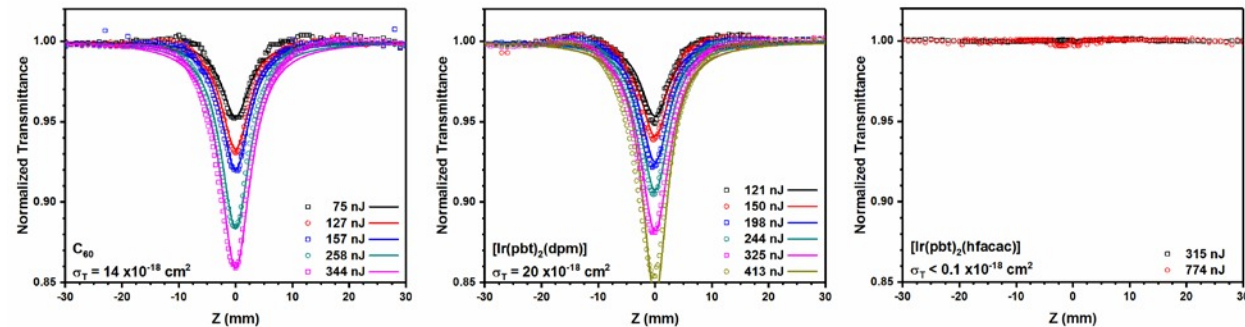


Figure 6. ns Z-scans with fits (solid lines) overlaid on experimental data (open symbols).

Table 1. Table of cross sections.

Cross Section	Literature	This Work
C ₆₀ σ _S (532 nm)	16 x 10 ⁻¹⁸ cm ² [13]	16 x 10 ⁻¹⁸ cm ²
C ₆₀ σ _T (532 nm)	13 x 10 ⁻¹⁸ cm ² [14]	14 x 10 ⁻¹⁸ cm ²
C ₆₀ σ _T (534 nm)	14 x 10 ⁻¹⁸ cm ² [15]	
[Ir(pbt) ₂ (dpm)] σ _T (532 nm)		24 x 10 ⁻¹⁸ cm ² (ps) 20 x 10 ⁻¹⁸ cm ² (ns)
[Ir(pbt) ₂ (hfacac)] σ _T (532 nm)		7.5 x 10 ⁻¹⁸ cm ² (ps) <0.1 x 10 ⁻¹⁸ cm ² (ns)

Table 2. Table of excited state parameters.

Parameter	Value
C ₆₀ τ _S	1.18 ns [13]
C ₆₀ τ _T	250 μs [14,15]
[Ir(pbt) ₂ (dpm)] τ _T	1.32 μs
[Ir(pbt) ₂ (hfacac)] τ _T	240 ps

For the iridium compounds, the triplet yield was assumed to be unity based on literature precedence and the interpretation of the ultrafast transient absorption spectroscopy.^{5,7,18} Because of the unity triplet quantum yield and triplet lifetime of 1.32 μ s for [Ir(pbt)₂(dpm)], there is significant triplet populations for both ps and ns pulses meaning that both the ps and ns Z-scans interrogate the triplet excited state with σ_T (ps) = 24×10^{-18} cm² or σ_T (ns) = 20×10^{-18} cm², which agree within experimental error. However for [Ir(pbt)₂(hfacac)], the extremely short triplet excited state lifetime of 240 ps means that no triplet population is present on the nanosecond time scale. However, the value of $\sigma_T = 7.5 \times 10^{-18}$ cm² was determined via ps Z-scans measurements.

4. CONCLUSIONS

The NLO properties of the cyclometallated iridium compounds [Ir(pbt)₂(dpm)] and [Ir(pbt)₂(hfacac)] were characterized via transient absorption spectroscopy and both ps and ns Z-scan measurements. It was determined that the electron withdrawing trifluoromethyl groups on the ancillary ligand of [Ir(pbt)₂(hfacac)] drastically diminished the excited state lifetime of the compound compared to the electron donating *tert*-butyl groups contained in [Ir(pbt)₂(dpm)].

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